PNC ZJ1211 98-001(1/2)

限定資料

分置01

核種移行データベースの開発研究(Ⅱ)

(動力炉・核燃料開発事業団　委託研究報告書：本編)

１９９８年2月

三菱マテリアル株式会社

本資料についての問合せは下記に願います。

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核種移行データベースの開発研究（Ⅱ）

上田　真三*

要旨

動力炉・核燃料開発事業団では、2000年3月までに性能評価レポートを作成する予定である。本研究は、レポート作成にあたって必要とされる核種移行データベース及び評価用モデルを整備することを目的として平成8年度に引き続き実施したものである。主な実施内容を以下に示す。

1. 重要元素の核種移行データベースの整備

21元素に対し、OH^-、CO_3^{2-}、Cl^-、F^-、SO_4^{2-}、PO_4^{3-}を対象とした溶液中の化学種及び固相のデータ整備及びその国際的専門家のレビューを行った。また、岩石などへの17元素の収着データ及び7元素の拡散データ整備を行った。ベントナイトに関しては Pu の収着及び拡散データベースの整備を行った。

2. データベース整備に係わるデータ取得

ベントナイト、花崗閃緑岩、凝灰岩を対象に Th の収着試験を実施した。またベントナイトを対象に Ra、Np、Tc、U、ケイ砂混合ベントナイトを対象に Cs,Se,Ni の拡散試験を実施した。

3. ベントナイトの間隙水水質推定モデルの検討

イオン交換モデルにおける吸着化学種の活量補正について評価を行った。また空隙水組成に及ぼす不純物の影響に検討し、空隙水 pH に対して方解石、石膏、硫化鉄の存在が影響することを明らかにした。

4. コロイドの核種移行に与える影響の評価

Hwang らのモデルを確証するためのデータ取得試験を実施するとともに、コロイドの存在が核種移行に与える影響の評価を行った。

本報告書は、三菱マテリアル株式会社が動力炉・核燃料開発事業団の委託により実施した研究成果報告書である。

契約番号：090D0169

事業団担当課室及び担当者：東海事業所環境技術開発部地層処分開発室　柴田雅博

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LIMITED DISTRIBUTION

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February 1998

Development of Database System for Performance Assessment(Ⅱ)

Shinzo Ueta*

Abstract

PNC is planning to submit a Performance Assessment Report by March 2000. This research was carried out succeeding the research last year in order to prepare the database for nuclide migration analysis and its modeling. The main results are as follows.

1. Nuclide migration database preparation for important nuclides

Thermodynamic database of 21 elements was developed, focusing on the formation of complexes and/or compounds with the hydrate, carbonate, chloride, fluoride, sulfate, and phosphate. The database was reviewed by international researchers. Rock sorption database of 17 elements and diffusion database of 7 elements were prepared. Bentonite sorption and diffusion databases of Pu were prepared.

2. Data acquisition for database

Sorption experiments for Th and diffusion experiments for Cs,Se,Ni,Ra,Tc,Np, and U were carried out.

3. Modeling study for prediction of bentonite porewater chemistry

Different approaches commonly used for ion exchange modeling are evaluated. And sensitivity analyses for the effect of impurities in compacted bentonite were performed.

4. Estimation of colloid influence on nuclide migration

Colloid migration behavior was calculated by using Hwang's model.

Work performed by Mitsubishi Materials Corporation under with Power Reactor and Nuclear Fuel Development Corporation.

Contract No. : 090D0169

PNC Liaison : Mr. Masahiro Shibata , Geological Isolation Development Section.

*Naka Energy Research Center, Mitsubishi Materials Corporation

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1. 研究目的

高レベル放射性廃棄物地層処分研究の第２次とりまとめに向けて、核種移行解析の基礎データとして、より信頼性の高い、充実した核種移行に関するデータベースが求められている。本研究は、第２次とりまとめで必要となるこれらのデータベースを整備することを目的とする。

本研究は、平成７年度より開始され、これまでに核種移行データベースとして、性能評価上重要となる主要な元素に対し、熱力学データベース、ベントナイトおよび岩石への核種の収着／拡散現象に関する総合的データベースの開発および整備を行ってきた。本年度は、これまでのデータベースに関する調査検討を継続するとともに、本年度末までに予定されているデータベースの凍結に向け、総合的な取りまとめを行った。また、データベース開発の一環として、信頼性の高いデータが不足しているデータの取得、データの信頼性評価のための収着のモデル化、緩衝材間空隙水組成のモデル化の検討、およびコロイドの影響を考慮した岩体中の核種移行の評価を実施した。

2. 実施項目

(1)重要元素の核種移行データベースの整備

(2)データベース整備に係わるデータ取得

(3)ベントナイトの間隙水化学とそのモデル化に関する検討

(4)コロイドの核種移行に与える影響評価

3. 実施内容

3.1 重要元素の核種移行データベースの整備

重要元素に対する熱力学データベース並びにベントナイト及び岩石に対する収着／拡散データベースの整備を実施した。

3.1.1 熱力学データベースの整備

(1)目的

地層処分の性能評価において重要な 22 種の元素のうち、溶解度の評価が重要である 21 種の元素（Ni, Se, Zr, Nb, Tc, Pd, Sn, Sb, Sm, Pb, Bi, Po, Ra, Ac, Th, Pa, U, Am, Cm）に対し、

水酸化物、炭酸・重炭酸塩、塩化物、フッ化物、硝酸塩、リン酸塩等の溶液中の化学種および固相を考慮して、熱力学データベースの整備を行うことを目的とした。

(2)整備手法

データベースの整備にあたっては、国際的な専門家数名からなる委員会を設置し、委員会では、元素毎に担当を決め、担当元素の熱力学データの調査および評価を行った。なお、一部の重要元素については、担当を動燃事業団殿とし、専門家委員会によるレビューを行った。対象元素のうち、アクチニド元素に関しては、昨年度の３価に対するデータベース整備に引き続き、本年度は４価を中心に整備を行った。データベース整備においては、データベースの地球化学計算コードでの利用を念頭に置いた上で、活量補正の取扱いについても検討を行うこととし、さらに、溶解度計算で用いるべき計算コードの検討と提案を行った。

最終的に、各委員の最先端の知見に基づいた、核種移行解析の基礎データとして、専門家が集合する国際会議を２回実施し、より信頼性の高い、熱力学データベースを完成させた。

(3)実施内容

動燃事業団殿によって選定された地層処分の性能評価において重要な元素は次の通りである。

・第一優先度核種：Pu, U, Np, Th, Am, Ra, Sn, Zr, Ni, Pd, Tc, Se, Pa, Cm, Cs

・第二優先度核種：Sm, Ac, Po, Pb, Nb, Bi, Sb

また、それぞれの核種について、次の化学種が評価対象である。

・水酸化物、炭酸塩、塩化物、フッ化物、硫酸塩、リン酸塩

これらについてデータベースを整備し、かつ以下に示す国内外の専門家によってレビューを継続的に受けた。

Dr. H. Wanner (HSK, Switzerland), Dr. D. Rai (Battelle PNL, U. S. A.),
Prof. G. Choppin (Florida State Univ., U. S. A.), Dr. M. Ochs (BMG, Switzerland),
Prof. Tochiyama (Tohoku Univ, Japan), Prof. Moriyama (Kyoto Univ., Japan),
Dr. Nakayama, Dr. Yamaguchi (JAERI, Japan)

今年度までに行った本調査における成果の概要は次の通りである。

まず Sn, Sb, Pb, Bi, Nb 及び Pd については、既存の編集されたデータベースよりも実験値の報告データに主眼をおいてデータセットの開発を行った。データ量の多寡については核種ごとに差があり、異なるイオン強度のデータが使用可能な場合には SIT 法(Specific ion interaction theory)を用いてイオン強度０の平衡定数に外挿した。

３価のアクチニド元素については、まず Am は十分な文献値があり、これを元にして米国バテル研究所で開発した Pitzer モデルをベースに評価した。また、Pu, Cm, Sm についてはアナログが適用できるとしてデータ設定を行った。

４価のアクチニド元素については、Th は Pitzer モデルをベースに評価モデルを開発した。このモデルは種々のリガンドとの反応及び ThO_2 固相の形成に関するデータを含んでいる。また他のアクチニドについても同様のモデルを適用したが、NEA データベースにおける U の加水分解、U と Np の SO_4^{2-}錯体形成、全元素の酸化物固相形成についてはそれぞれ元素ごとに扱った。

５価及び６価のアクチニド元素については、それぞれ AnO_2^{+}、AnO_2^{2+}の反応を取り扱い、Pitzer モデルの適用性にも考慮しつつ、イオン強度０、25℃の平衡定数を整理した。

以上の結果はそれぞれデータベースとして整理して報告した。

3.1.2 ベントナイトおよび岩石への収着／拡散データベースの整備

(1) 文献調査によるデータの抽出と評価

(a) 目的

性能評価において重要な元素を対象に、ベントナイトおよび岩石への吸着／拡散データに関する文献調査を行い、処分環境での核種の収着／拡散の評価に有効となるデータを抽出し、固相の性質、溶液条件等の実験条件と共に、分配係数(Kd)、拡散係数（見かけの拡散係数 Da あるいは実効拡散係数 De）等のデータをデータベースとして取りまとめた。

また、データが必要とされている元素で、データが存在しないものについては、化学的アナログを考慮して、評価に用いるべきデータの提案を行った。

(b) 実施概要

本年度は、5 種の岩石（花崗岩、凝灰岩、玄武岩、泥岩、砂岩）および関連する鉱物を対象に、17 種類の元素(Zr, Nb, Pb, Sb, Sm, Pb, Bi, Po, Ra, Ac, Th, Pa, U, Np, Pu, Am, Cm)の収着データ、および 7 種の元素(Ra, Th, U, Np, Pu, Am, Cm)の拡散データについて、データベースの整備を行った。また、ベントナイトに関しては、動燃事業団殿の協力のもと、Pu の収着および拡散のデータベース整備を実施した。

(c) 実施内容

核種移行評価に関して、充填材（緩衝材）及び周辺岩盤は効果的なバリアであるとともに、評価の確実性の高いバリアでもあり、処分性能評価の観点から重要性の高い調査対象である。ベントナイトについては収着／拡散現象に関する総合的データベースシステムを既に提示している。このシステムではベントナイトと地下水特性の関連性、重要元素の熱力学データ、及び分配係数や基礎データを基にした見かけの拡散係数を計算するために必要な収着と拡散のモデルを定義した。また既に Ra、Sr、及び Pb の分配係数値の計算、及び Cs の見かけの拡散については報告している。しかしデータ不足のためにこのアプローチは限定された状況でのみ使用可能である。現時点では多くの元素について適用できる収着モデルはなく、またベントナイトに比べて岩石の表面化学特性は良く知られていないという制約がある。このため、周辺岩盤中の核種移行は、重要核種によってなされた収着と拡散の比較検討成果を基に評価していかざるを得ない。

このような状況の下で、収着及び拡散データベースの整備を実施した。まず文献調査では対象元素に関する多数の分配係数及び見かけの拡散係数データをとりまとめ、図及びデータ表とすることにより2件のExcelファイルを作成し提出した。これらのファイルは、ユーザー用の取扱説明、更新日等を明記したデータベースに関する情報、各元素のデータベース、参考文献などをそれぞれシートとして含んでいる。

(2)収着現象のモデル化とモデルの適応性の検討

(a)目的

データの信頼性能評価および現象理解に基づいた、処分環境条件での分配係数の設定を行う為に、メカニズムを考慮した収着のモデル化とそのモデルの適用性の検討を行った。

(b)実施概要

本年度は十分な実験値が報告されているNiについて、スメクタイトのイオン交換と表面錯体を取り扱うモデルを考慮した。

(c)実施内容

ベントナイトー地下水系におけるNiの収着挙動を、イオン交換と表面錯体反応で評価した。また必要に応じてNi固相の形成を考慮した。溶液組成とベントナイト表面のスペシエイションについては97年度に報告したベントナイトのモデルを基に、液固比の関数として計算した。ここでベントナイトの主要な構成粘土鉱物であるモンモリロナイトとNiのイオン交換定数には文献値を用いた。またNiの表面錯体定数は既存の実験値と整合するように再評価して使用した。以上により、構築したモデルは幅広い条件で取得された分配係数実験値に対応できるものとなった。

3.2 データベース整備に係わるデータ取得

3.2.1 目的

データベース整備において、性能評価あるいは現象解明の観点から不足しており取得することが必要と判断されるベントナイト／岩石への核種の分配係数並びにベントナイト中の核種の拡散係数を取得する為の試験を実施することを目的とする。

3.2.2 試験項目

本年度は、ベントナイト、花崗閃緑岩、凝灰岩を対象に、Th の収着試験を実施する。また、ベントナイト密度、間隙水条件等をパラメータとして、Ra, Np, Tc, U のベントナイト中での拡散試験を実施する。さらに、緩衝材材料の違いによる核種の収着・拡散を評価する為に、ケイ砂混合ベントナイト中での Cs 等の拡散試験を実施する。

以下に試験項目を示す。

①ベントナイト及び地質媒体に対する Th の収着試験

②ベントナイト中での核種の拡散試験

③ケイ砂混合ベントナイト中での核種の拡散試験

3.2.3 試験内容

(1) ベントナイト及び地質媒体に対する Th の収着試験

液性をパラメータに、ベントナイト及び地質媒体に対する Th の収着試験を実施した。

(a) 試験条件

表 3.2.3-1 に Th の収着試験の試験マトリクスを、表 3.2.3-2 に収着試験の条件を示した。

表 3.2.3-1 Th の収着試験マトリクス（○の部分を実施）

	試験液性		
	蒸留水との平衡水	人工海水との平衡水	炭酸添加平衡水
ベントナイト	○	○	○
花崗閃緑岩	○	○	——
凝灰岩	○	○	——

表 3.2.3-2 Th の収着試験条件

項目	内容
試験方法	バッチ式収着試験
液固比	ベントナイト：100ml/1g（クニゲルＶ１） 花崗閃緑岩：50ml/1g[群馬県沢入産(動燃殿より支給)] 凝灰岩　　：50ml/1g[岐阜県東濃産(動燃殿より支給)]
試験液性	３種類：①蒸留水との平衡水 ②人工海水との平衡水 (ASME 規格人工海水) ③炭酸添加平衡水($NaHCO_3$:0.1mol/l)
固液分離	２種類：メンブランフィルタ（0.45μm） ：限外濾過(MWCO10000)
試験雰囲気	大気雰囲気
試験温度	室温（25℃)
分析方法	ICP-MS 分析(Th-232)

(b) 試験手順

トリウムの溶解度は低いため、収着試験時の液相トリウム濃度が高ければ、試験実施中に沈殿を起こしてしまう可能性がある。そこで、本研究では。まず固相試料と液相試料接触時の平衡水液組成分析を実施し、その各平衡水中でのトリウムの溶解度測定を実施した。収着試験時の液相のトリウム濃度は各平衡液に対して測定された溶解度以下で実施することとした。試験フローを以下に示すとともに、図 3.2.3-1 にまとめた。

ア．ベントナイト・岩石試料－各試験液接触時の平衡液組成分析

分配係数測定試験を行う所定の液固比において、各試験条件（７条件）に対して１バッチづつ浸出試験を行い、平衡後の元素（イオン）組成分析を行った。浸出期間は１週間とした。固液分離はベントナイト試料については MWCO10000 の限

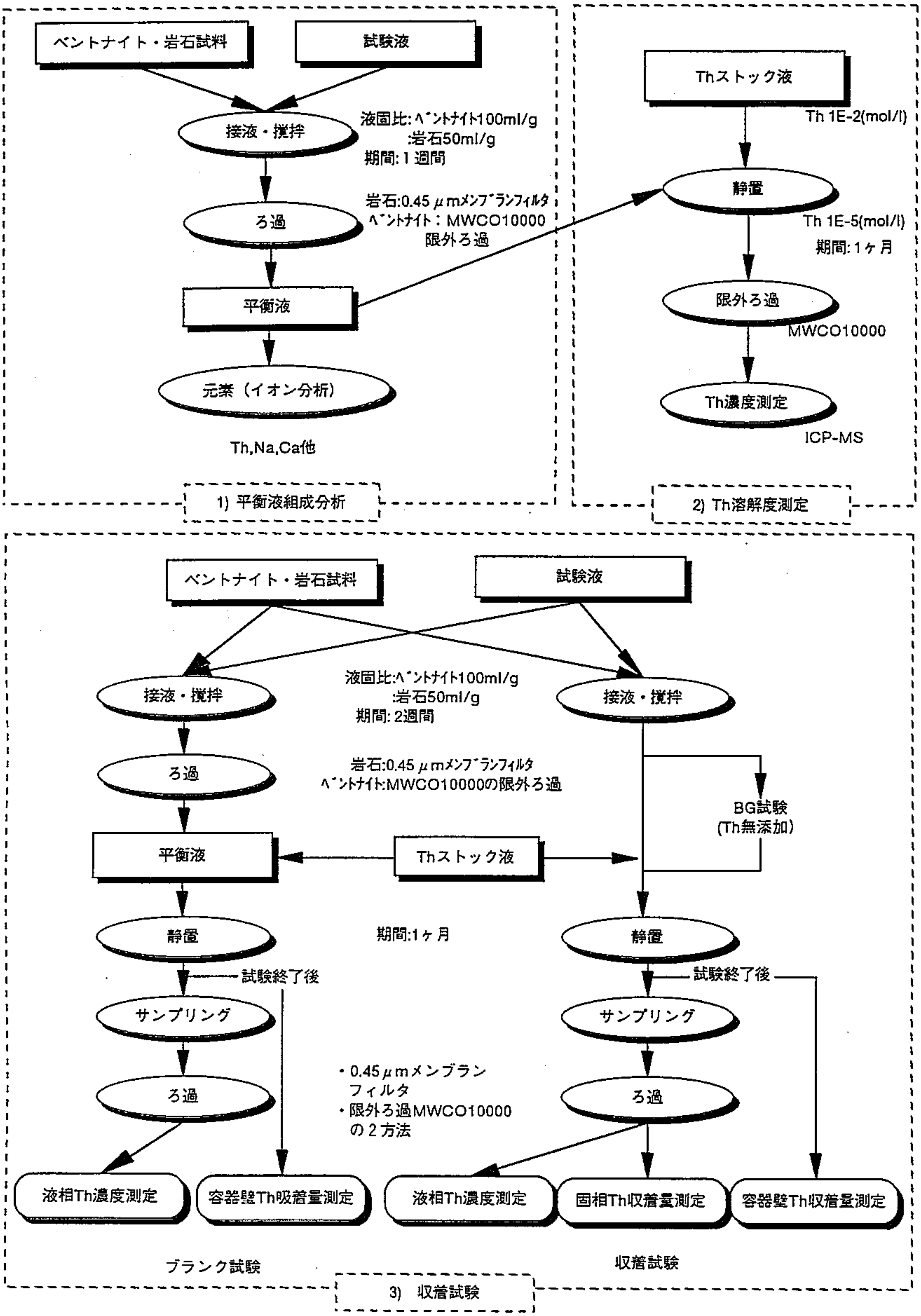


図3.2.3-1　Th収着試験フロー

外ろ過フィルタ(ミリポア社製型番 UFP-2TGKBK、ろ過膜を事前に蒸留水で洗浄)を、岩石試料については 0.45μm メンブランフィルタ（アドバンテック社製型番 A045A090C) とした。以降の一連の試験のおいて使用したろ過フィルタも上記フィルタと同じ規格のものを用いた。

分析項目は Th, Na, K, Ca, Mg, Al, Si, Fe, Cl^-, NO_3^-, SO_4^{2-}, CO_3^{2-}及び pH とした。

イ. Th の溶解度の確認試験

吸着試験の Th 初期濃度は、各試験条件における Th の溶解度以下である必要がある。ここでは、ア. で作製した平衡溶液と同じ溶液中での Th の溶解度を調べ、吸着試験における妥当な初期濃度を決定した。溶解度測定における試験期間は吸着試験期間と同様の 1 ヶ月を期間としした。

試験手順を以下に示した。

①Th ストック液の作製

ThO_2（Th:天然トリウム）0.264g を 6N-HNO_3に加熱・溶解させ Th:1E-2 M 溶液 100ml とし Th のストック溶液とした。

②各バッチの平衡液の作製

ア. と同様の試験を実施し、ベントナイト試料については MWCO10000 の限外ろ過、岩石試料については 0.45μm メンブランフィルタでろ過後、各バッチの平衡液を 40ml 回収する。pH を測定しておく。

③溶解度確認試験

②で回収した液 40ml に対して、Th:1E-2 M のストック液 0.04ml を添加する。(バッチ液中 Th 濃度 1E-5M) 添加後 pH が変動した場合には、pH を②で測定した pH に NaOH 溶液で戻す。この際、添加した NaOH の濃度及び量を記録する。

④サンプリング・分析

添加から 1 週間及び 1 ヶ月後、溶液を MWCO10000 のフィルタで限外ろ過する。濾液を ICP-MS で分析し、溶解度を確認する。

ウ. 分配係数測定試験

前述のイで取得された各バッチの Th の溶解度以下で、分配係数測定を行う。

溶解度測定試験の結果は後述するが、ここでは、その試験結果から、バッチ式

吸着試験を実施する各固相－平衡水中のTh初期濃度条件を表3.2.3-3に示すように決定した。

表3.2.3-3　収着試験におけるThの初期濃度条件

固相－液相条件	初期Th濃度条件 (mol/l)
花崗閃緑岩－蒸留水	1E-9
花崗閃緑岩－海水	5E-9
凝灰岩－蒸留水	1E-6
凝灰岩－海水	4E-8
ベントナイト－蒸留水	8E-10
ベントナイト－海水	4E-9
ベントナイト－炭酸添加水	1E-6

なお、初期濃度条件が低い条件の試験では、収着平衡時の液相Th濃度が低くなり検出下限値(4.3×10^{-10} mol/l)以下になることも予測されるため収着試験液相濃度変化だけでなく、固相へ吸着したTh量の分析も行い分配係数の算出を試みることとした。

さらに、収着試験において液相へ添加したTh量に対して、試験終了時に液相中、固相上、容器壁上に存在するTh濃度を確認することにより試験前後におけるThのマスバランスを確認することにより、容器壁収着分を分配係数へ反映させるために実施しているブランク試験の妥当性を検討した。

試験手順を以下に示す。

①ブランク試験液の作製

各液性条件に対して、ベントナイト試料については液固比200ml/2gで、岩石試料については液固比100ml/2gで２週間振とうさせたのち、液相をベントナイト試料についてはMWCO10000の限外ろ過、岩石試料については0.45μmメンブランフィルタでろ過し回収し、ブランク試験液とする。ブランク試験液のpHを測定する。

②ブランク試験の開始

表3.2.3-3に示す初期濃度になるように①で回収した溶液（ベントナイトのブランク試験は100ml,岩石試料のブランク試験は50ml）にThトレーサを添加

する。添加後pHが低下した場合はNaOHでpHを戻す。

この際、添加したNaOHの濃度及び量を記録しておく。

③吸着試験の開始

各液性条件に対して、ベントナイト試料については液固比100ml/1gで、岩石試料については液固比50ml/gで2週間振とうさせたのちpHを測定する。次に各バッチが②と同様の初期濃度となるようにThを添加する。添加後pHが低下した場合はNaOHでpHを戻す。この際、添加したNaOHの濃度及び量を記録しておく。

④液相のサンプリング

1ヶ月間放置後、ベントナイトに対する試験のうち、フィルタに目詰まりを起こし、ろ過が困難なものについては遠心分離により固液を分離する。その他の岩石試料については直接、上澄み液を20ml程度サンプリングし、0.45μmメンブランフィルタでろ過する。さらに、20mlサンプリングし、分画分子量10000の限外ろ過を行う。ろ過時におけるろ紙への吸着の影響を考慮し、ろ液の最初の1mlは捨てるものとする。各バッチの残液でpHを測定する。

⑤固相の回収

試験終了後の固相を回収し、蒸留水10mlで洗浄する。洗浄後105℃で24時間乾燥させ、固相試料の重量を測定する。

⑥固相に吸着したTh量の測定

⑤で回収した固相及び1N硝酸10mlをバイアル瓶に入れる。24時間振とうさせ、固相に吸着したThを浸出させる。MWCO10000限外ろ過を行い、ろ液中のTh濃度を測定し、固相中に吸着したThの量を算出する。

この際、固相マトリクスからのThの溶出量、並びに浸出に使用した硝酸に不純物として含有するThをバックグランドとして測定しておくために以下の2種類の試験を別途行っておく。

1)固相マトリクスからのThの溶出量(B.G.試験)

収着試験バッチとThトレーサを添加しないこと以外は、同条件に調整したバッチで①～⑤の手順を踏み、液相中のバックグラウンドTh濃度、固相収着バックグラウンドTh濃度ならびに容器壁収着バックグラウンドTh濃度を測定する。

2)硝酸に含有するTh

本試験で使用する1N硝酸中のThの濃度を測定する。

⑦容器液へ吸着したThの分析

試験溶液に接触していた容器壁を蒸留水10mlで３～５回洗浄し、固相の微粉末を十分取り除いたのち、1N硝酸5mlで洗い、その液中のTh濃度を測定し、容器壁へ吸着したThの濃度を測定する。

(c) 解析方法

分配係数の解析方法とマスバランスの計算手法を以下に示す。

ア．分配係数

本研究では、収着試験バッチとブランク試験との液相トレーサ濃度差を固相収着量とて決定される一般的な分配係数測定手法を基本として実施したものの、この方法ではブランク試験液相中のトレーサ濃度が検出限界以下となった場合に分配係数の決定が困難である。そのため、本研究では、収着試験バッチの固相に収着したトレーサを酸で浸積させることにより浸出させ分析することにより固相の収着量および分配係数を決定する方法も用いた。

1)ブランク試験液相トレーサ濃度との差からの分配係数の決定

収着試験バッチにおける容器壁への収着による影響をブランク試験を行うことにより補正する方法と、収着試験バッチの容器壁を洗浄し直接容器壁収着分を算出する方法との２種類の方法を用いて分配係数を決定した。

各方法における分配係数算出式を以下に示した。

① 容器壁への収着をブランク試験により補正

分配係数は液相中のTh濃度に対する固相中Th濃度の比で表されるので下式が成立する。

$$Kd=\frac{\left[\left\{C_o-(C_t-C_{BG})\right\}L/1000+C_{BG}Kd\,S/1000\right]/S}{C_t/1000}$$

上式を整理して

$$Kd=\frac{C_o-(C_t-C_{BG})}{C_t-C_{BG}}\times\frac{L}{S} \qquad \text{3.2.3-1(1)式}$$

ここで、　Kd：分配係数(ml/g)

C_o：ブランク試験平衡後の液相 Th の濃度(mol/l)

C_t：収着試験平衡後の液相 Th 濃度(mol/l)

C_{BG}：Th を添加しない固相のみを投入した試験(B.G.試験)における平衡後の液相 Th 濃度(mol/l)

L：バッチ中液量(ml)

S：バッチ中固相量(g)

解析の際、ブランク試験液相が検出限界の場合はデータの解析不可とした。

ブランク試験液相が検出限界以上でかつ、収着試験液相が検出限界以下の場合は検出限界値(4.3×10^{-10}mol/l)を、BG 試験平衡後液相濃度が検出限界以下の場合は0をデータとして設定することにより、本試験結果から推定される最低限の分配係数を取得し、～以上というデータの表記とした。

② 容器壁への収着を収着試験バッチの容器壁収着量分析値により補正

①と同様に初期 Th 濃度 C_{init} および容器壁洗浄液中 Th 濃度 C_v を用いて下式が成立する。

$$Kd = \frac{\left[\{C_{init} - (C_t - C_{BG})\}L/1000 - C_v V_v/1000 + C_{BG} Kd\, S/1000\right]/S}{C_t/1000}$$

上式を整理して

$$Kd = \frac{\{C_{init} - (C_t - C_{BG})\}L - C_v V_v}{C_t - C_{BG}} \times \frac{1}{S} \qquad \text{3.2.3-1(2)式}$$

ここで、C_{init} : 各バッチの初期液相中 Th 濃度 (mol/l)

C_v : 容器壁収着 Th を酸で浸出させたときの浸出液中 Th 濃度(mol/ l)

V_v : 容器壁収着 Th を酸で浸出させたときの浸出酸液量 (=5ml)

解析の際、収着試験液相が検出限界以下の場合は検出限界値(4.3×10^{-10}mo/l)を、BG 試験平衡後液相濃度が検出限界以下の場合は 0 を、容器壁酸浸出洗浄液中の濃度が検出限界以下の場合は検出限界値(4.3×10^{-10}mo/l)をデータとして設定することにより、本試験結果から推定される最低限の分配係数を取得し、～以上いうデータの表記とした。

2)酸浸出により直接固相への収着量を求めたときの分配係数

酸浸出により脱離した Th は、平衡液液性の収着試験時にはマトリクス中もしくは特性収着により分配平衡反応に寄与しない Th を含む場合があるため、ここでは酸浸出により脱離した Th が、平衡液液性での分配平衡反応に寄与しない Th であった場合と、すべて寄与する Th であった場合の２種類の場合を考慮して分配係数の解析を行った。

①酸浸出により脱離したThが分配平衡反応に寄与しないThを含む場合

BG試験の脱離試験（酸浸出）によって脱離したThを分配平衡反応に寄与していないと考えると分配係数は下式で表される。

$$Kd=\left(\frac{C_{i-s}}{M_{i-s}}-\frac{C_{BG-s}}{M_{BG-s}}\right)\cdot V_s\cdot\frac{1}{C_t} \qquad \text{3.2.3-2a 式}$$

ここで、

C_{i-s}：収着試験バッチの脱離試験における酸浸出液中のTh濃度(mol/l)

C_{BG-s}：BG試験バッチの脱離試験における酸浸出液中のTh濃度(mol/l)

M_{i-s}：収着試験バッチの脱離試験時の乾燥固相量(g)

M_{BG-s}：BG試験バッチの脱離試験時の乾燥固相量(g)

V_s：脱離試験における酸浸出量(= 10ml)

なお、BG試験平衡後液相濃度も検出限界以下の場合は0をデータとして設定することにより、本試験結果から推定される最低限の分配係数を取得し、～以上いうデータの表記とした。

②酸浸出により脱離したThが分配平衡反応に寄与するThである場合

BG試験の脱離試験（酸浸出）によって脱離したThが分配平衡反応に寄与するとすると分配係数は下式で表される。

この場合、Thトレーサを添加してないBG試験からも、酸脱離したThから分配係数を下式により決定できる。

$$Kd=\left(\frac{C_{i-s}}{M_{i-s}}\right)\cdot V_s\cdot\frac{1}{C_t} \qquad \text{3.2.3-2b 式}$$

ここで、

C_{i-s}：収着試験もしくはBG試験バッチの脱離試験における酸浸出液中のTh濃度(mol/l)

M_{i-s}：収着試験もしくはBG試験バッチの脱離試験時の乾燥固相量(g)

収着試験もしくはBG試験平衡後液相中Th濃度が検出限界以下の場合は検出限界値(4.3×10^{-10}mol/l)をデータとして設定することにより、本試験結果

から推定される最低限の分配係数を取得し、～以上いうデータの表記とした。

イ．マスバランス

バッチに添加した Th 量と、試験終了時の液相、固相（BG 量は除く）ならびに容器壁量の Th 量を比較することにより、バッチ試験前後のマスバランスを確認した。

ブランク試験もしくは収着試験バッチに添加した Th 量は、下式で表される。

$$Th\text{添加量}(mol) = C_{init} \times \frac{L}{1000} \qquad 3.2.3\text{-}3\text{式}$$

試験終了時の Th 量は下式で表される。

$$\begin{aligned}&\text{試験終了時の}Th\text{量}(mol)\\&= (\text{液相中}Th\text{量}) + (\text{固相中}Th\text{量}) + (\text{容器壁中}Th\text{量}) \qquad 3.2.3\text{-}4\text{式}\\&= C_{init} \times \frac{L}{1000} + \left(\frac{C_{i-s}}{M_{i-s}} - \frac{C_{i-BG}}{M_{i-BG}}\right) \times \frac{V_s}{1000} + C_v \times \frac{V_v}{1000}\end{aligned}$$

なお、試験終了時の Th 量については、平衡後液相中 Th 濃度もしくは容器壁から浸積させた液中の Th 濃度が検出限界となったものもある。このため、検出限界となった場合の Th 濃度は 0～4.3×10^{-10}mol/l の間であるので、ここでは検出限界となったデータを 0 とおくことにより、最低 Th 量を、検出限界となったデータを 4.3×10^{-10}mol/l とおくとにより最高 Th 量を算出することとした。

(d) 試験結果および考察

各試験の試験結果を以下にまとめて示した。

ア．ベントナイト・岩石試料ー各試験液接触時の平衡液組成分析

ベントナイト、花崗閃緑岩、凝灰岩試料と各試験液（蒸留水、海水、炭酸添加水）との接液後の平衡後イオン組成を、表3.2.3-4に示した。

各条件における平衡後、試験液中でのTh濃度は蒸留水に接触させた凝灰岩試料を除いて、平衡水分析での検出下限値(1ppb=4.3×10^{-9}[mol/l])以下であった。蒸留水に接触させた凝灰岩試料は、検出下限値に近い数ppb程度のThが検出された。この条件におけるSi, Al等のイオン成分が、他の条件のものと比較して高いことを考えると凝灰岩マトリクスコロイド成分（岩石試料は0.45μmのメンブランフィルタでろ過しているため、0.45μm以下のコロイド状微粒子が平衡液組成中に含有している可能性がある。）中に含まれるThが検出された可能性がある。このことは、コロイドが生じにくい海水系でイオン強度が高い条件で、コロイドと考えられる成分（Si,Al成分）が少なく、同時にThも検出下限以下になっていることからも解釈される。

表3.2.3-4　ベントナイト・岩石試料と各試験液接触時の平衡液組成分析結果（mg/l）

	試料	花崗閃緑岩		凝灰岩		ベントナイト		
	試験液	蒸留水	海水	蒸留水	海水	蒸留水	海水	炭酸添加水
元素 または イオン種等	Na	0.75	10400	27	9880	80.1	10500	2100
	K	2.51	404	<0.20	330	0.8	396	3.09
	Ca	7.75	429	3.64	550	0.44	435	2.33
	Mg	0.1	1350	2.32	1310	<0.10	1350	1.91
	Al	0.3	0.059	7.92	<0.05	0.1	<0.05	<0.05
	Si	2.08	1.09	24.7	6.26	2.7	2.23	2.33
	Fe	0.06	<0.05	4.25	0.3	<0.05	<0.05	<0.05
	P	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
	Cl^-	0.23	20300	0.18	19900	1.3	19400	14.7
	NO_3^-	<0.5	<0.5	<0.5	<0.5	0.53	<0.5	2.9
	SO_4^{2-}	<2.0	2670	19.7	2630	25.1	2650	27.8
	HCO_3^-	21.9	124	36.6	103	158	130	4340
	CO_3^{2-}	<0.1	0.6	<0.1	0.5	0.3	0.2	251
	Th	<0.001	<0.001	0.0044	<0.001	<0.001	<0.001	<0.001
	pH	6.8	8.0	7.2	8.0	7.6	7.6	9.1

イ．Th の溶解度の確認試験

各平衡液条件における Th の溶解度確認試験の結果を表 3.2.3-5 に示した。

28 日後の溶解度データをもとに、各岩石－平衡水系での Th の収着試験における初期溶液濃度を設定した。収着試験における液相の沈殿をさけるために、初期 Th 濃度は、28 日後溶解度より低い値に設定した。（表 3.2.3-5 参照）

溶解度確認試験の結果として、各バッチについても試験時間の違いによる溶解度の違いはあまりみられなかった。各固相－液相における Th の溶解度の比較としては、蒸留水系では、凝灰岩を除き溶解度が低く、約 1×10^{-9}[mol/l]程度であった。海水系では若干溶解度が高い傾向が見られるものの 28 日後のデータをみるとオーダは違わないことがわかる。

一方、凝灰岩－蒸留水系ならびにベントナイト－炭酸添加水系では溶解度が、他のバッチと比較して 2 オーダ程度高い結果となった。

炭酸添加水系での高溶解度は、炭酸錯体の形成によるものと考えることができる。以下に凝灰岩－蒸留水系の高溶解度について検討する。溶解度試験では、すべての固相－液相条件において、分画分子量 10000 の限外ろ過を行っているため、前記ア．で考察されたようなコロイドの影響はない。にもかかわらず溶解度が高いのは、なんらかの錯形成成分が液相に含まれている可能性も考えられるものの、平衡水分析の結果からは錯成分は同定できない。また、凝灰岩－海水系では溶解度がさほど高くないことを考えると、海水系で錯成分は存在しないもしくは、錯体を形成しないことになる。

凝灰岩－蒸留水系での Th の溶解度が高いことの現象解明は今後の課題である。

表3.2.3-5　各平衡水条件におけるThの溶解度測定結果

平衡水条件		Th濃度　(mol/l)		収着試験初期Th濃度設定値 (mol/l)
固相	液相	7日後	28日後	
花崗閃緑岩	蒸留水	1.2E-09	1.2E-09	1E-09
	海水	2.6E-08	9.8E-09	5E-09
凝灰岩	蒸留水	5.0E-06	6.3E-06	1E-06
	海水	2.1E-08	4.6E-08	4E-08
ベントナイト	蒸留水	1.1E-09	8.6E-10	8E-10
	海水	3.0E-08	4.1E-09	4E-09
	炭酸添加水	8.1E-06	8.7E-06	1E-06

ウ．Th の分配係数測定試験

各岩石－平衡水条件における Th の収着試験結果を表 3.2.3-6 に示した。

各条件ともブランク試験 n=1 件、収着試験 n=2 件、BG 試験 n=1 件づつデータを測定した。収着試験終了時の液相中 Th 濃度（メンブランろ過および限外ろ過）、固相を回収し 1N 硝酸で浸積させたあとの浸積液中の Th 濃度、容器壁へ収着している Th を 1N 硝酸で浸出させたあとの浸積液中の Th 濃度等をまとめて示した。

酸浸出に用いた 1N 硝酸中の Th は検出限界値以下であった。収着試験前後のマスバランスならびに分配係数算出においては、データ処理の煩雑性を避けるために、1N 硝酸中の Th 濃度は 0 として処理した。

1)マスバランスの確認

試験前後のマスバランスを計算した結果を表 3.2.3-7 に示す。試験終了時の Th 量については、液相がメンブランろ過の場合と限外ろ過の場合の２種類のデータを用い、さらに検出限界となった液相（酸浸出液も含む）の Th 濃度範囲として最小 0 と最大 4.3×10^{-10}mol/l（検出限界値）のデータを入力し最小値、最大値を得ることで、試験終了時 Th 量の範囲を取得することとした。

初期 Th 添加量と試験終了時 Th 量（範囲）をグラフ化して図 3.2.3-2 に示した。ブランク試験バッチは、いずれも良好にマスバランスが取れていることがわかる。

収着試験バッチについては、初期 Th 濃度がかなり低い花崗岩系ではばらつきが多い（収着した Th と比較して、BG として酸浸出した Th 量が大きいため）ものの、その他の条件のバッチでは良好にマスバランスが取れていることが分かる。

表3.2.3-6　Thの収着試験結果

固相	液相	バッチ種類	液固比 (ml/g)	初期液相濃度 目標値 (mol/l)	初期pH	Thトレーサ添加時			収着試験終了時					
						Th添加後pH	NaOH添加量 (mol)	調整後pH	液相中Th濃度 (mol/l)		液相pH	固相からの脱離試験		容器壁からの脱離試験
									メンブランろ過	限外ろ過		回収固相量(g)	浸出液Th濃度 (mol/l)	浸出液Th濃度 (mol/l)
花崗閃緑岩	蒸留水	ブランク試験	50	1E-09	7.80	3.32	2.5E-07	7.92	<4.3E-10	<4.3E-10	7.74	---	---	1.1E-08
		収着試験1	50	1E-09	7.89	3.45	2.5E-07	7.94	<4.3e-10	<4.3e-10	7.59	0.91	1.9E-06	<4.3e-10
		収着試験2	50	1E-09	8.13	3.64	2.5E-07	7.59	<4.3e-10	<4.3e-10	7.59	0.95	1.6E-06	<4.3e-10
		岩石浸出BG	50	0	8.42	---	---	---	<4.3e-10	<4.3e-10	7.82	0.97	1.5E-06	<4.3e-10
	海水	ブランク試験	50	5E-09	8.06	6.98	7.5E-08	7.83	<4.3E-10	<4.3E-10	7.79	---	---	8.4E-09
		収着試験1	50	5E-09	7.82	6.87	1.3E-07	7.97	<4.3e-10	<4.3e-10	7.95	0.92	1.5E-06	<4.3e-10
		収着試験2	50	5E-09	7.88	6.82	1.3E-07	8.10	<4.3e-10	<4.3e-10	7.97	0.97	1.5E-06	<4.3e-10
		岩石浸出BG	50	0	7.46	---	---	---	<4.3e-10	<4.3e-10	8.08	0.97	1.6E-06	<4.3e-10
凝灰岩	蒸留水	ブランク試験	50	1E-06	8.50	3.30	3.5E-07	8.46	4.7E-07	7.9E-08	7.74	---	---	3.8E-07
		収着試験1	50	1E-06	8.60	5.42	3.5E-07	8.20	2.4E-08	1.1E-09	7.92	0.90	3.7E-08	<4.3e-10
		収着試験2	50	1E-06	8.48	5.98	3.5E-07	8.06	2.4E-08	1.1E-09	7.78	0.92	3.8E-08	<4.3e-10
		岩石浸出BG	50	0	8.68	---	---	---	6.9E-09	<4.3e-10	7.93	0.90	1.2E-08	<4.3e-10
	海水	ブランク試験	50	4E-08	7.68	6.83	1.0E-07	7.81	2.8E-09	1.9E-09	7.69	---	---	7.3E-09
		収着試験1	50	4E-08	7.53	6.86	1.0E-07	7.55	<4.3e-10	<4.3e-10	7.67	0.96	5.7E-07	4.7E-10
		収着試験2	50	4E-08	7.58	6.94	1.0E-07	7.58	<4.3e-10	<4.3e-10	7.72	0.87	6.2E-07	5.2E-10
		岩石浸出BG	50	0	7.35	---	---	---	<4.3e-10	<4.3e-10	7.76	0.94	4.8E-07	1.0E-09
ベントナイト	蒸留水	ブランク試験	100	8E-10	9.50	7.23	3.8E-08	9.50	<4.3E-10	<4.3E-10	8.00	---	---	6.5E-10
		収着試験1	100	8E-10	9.97	9.38	4.3E-07	10.11	5.2E-10	<4.3e-10	9.67	0.73	1.4E-07	8.2E-10
		収着試験2	100	8E-10	10.03	9.40	5.0E-07	10.21	1.2E-09	<4.3e-10	10.00	0.74	1.3E-07	6.0E-10
		岩石浸出BG	100	0	10.24	---	---	---	5.2E-10	<4.3e-10	9.85	0.73	1.3E-07	4.7E-10
	海水	ブランク試験	100	4E-09	7.98	6.99	2.5E-07	8.03	<4.3E-10	<4.3E-10	7.37	---	---	4.4E-08
		収着試験1	100	4E-09	7.80	7.09	2.5E-07	7.97	<4.3e-10	<4.3e-10	7.97	0.95	5.3E-08	9.5E-10
		収着試験2	100	4E-09	7.75	7.06	2.5E-07	8.03	<4.3e-10	<4.3e-10	7.90	0.92	6.9E-08	9.5E-10
		岩石浸出BG	100	0	7.88	---	---	---	<4.3e-10	<4.3e-10	7.95	0.99	5.0E-08	1.1E-09
	炭酸添加水	ブランク試験	100	1E-06	8.84	8.73	1.8E-06	8.94	8.0E-07	8.1E-07	9.00	---	---	<4.3E-10
		収着試験1	100	1E-06	8.36	8.14	7.5E-07	8.26	7.5E-09	6.9E-09	8.63	0.74	2.9E-06	5.3E-09
		収着試験2	100	1E-06	8.36	8.14	7.5E-07	8.34	7.4E-09	5.9E-09	8.57	0.75	3.0E-06	4.8E-09
		岩石浸出BG	100	0	8.79	---	---	---	<4.3e-10	<4.3e-10	8.92	0.76	3.5E-08	5.6E-10
1N硝酸				---						<4.3e-10		---	---	---

＊メンブランろ過＝0.45 μmメンブランフィルタろ過
限外ろ過＝MWCO10000限外ろ過

表3.2.3-7　試験前後におけるThのマスバランス

固相	液相	バッチ種類	初期Th添加量	試験終了時Th量（BGから浸出するTh量を除いた量）			
				検出限界データ=0		検出限界データ=4.3e-10	
			(mol)	液相ﾒﾝﾌﾞﾗﾝ濾過値	液相限外濾過値	液相ﾒﾝﾌﾞﾗﾝ濾過値	液相限外濾過値
花崗閃緑岩	蒸留水	ブランク試験	5.0E-11	5.7E-11	5.7E-11	7.9E-11	7.9E-11
		収着試験1	5.0E-11	6.1E-09	6.1E-09	6.1E-09	6.1E-09
		収着試験2	5.0E-11	1.7E-09	1.7E-09	1.7E-09	1.7E-09
	海水	ブランク試験	2.5E-10	4.2E-11	4.2E-11	6.3E-11	6.3E-11
		収着試験1	2.5E-10	-1.5E-10	-1.5E-10	-1.3E-10	-1.3E-10
		収着試験2	2.5E-10	-4.4E-10	-4.4E-10	-4.2E-10	-4.2E-10
凝灰岩	蒸留水	ブランク試験	5.0E-08	2.6E-08	5.8E-09	2.6E-08	5.8E-09
		収着試験1	5.0E-08	1.5E-09	3.4E-10	1.5E-09	3.4E-10
		収着試験2	5.0E-08	1.5E-09	3.4E-10	1.5E-09	1.5E-09
	海水	ブランク試験	2.0E-09	1.7E-10	1.3E-10	1.7E-10	1.3E-10
		収着試験1	2.0E-09	7.7E-10	7.7E-10	7.9E-10	7.9E-10
		収着試験2	2.0E-09	2.0E-09	2.0E-09	2.0E-09	2.0E-09
ベントナイト	蒸留水	ブランク試験	8.0E-11	3.2E-12	3.2E-12	4.6E-11	4.6E-11
		収着試験1	8.0E-11	1.6E-10	1.0E-10	1.6E-10	1.5E-10
		収着試験2	8.0E-11	2.8E-11	-9.3E-11	2.8E-11	2.8E-11
	海水	ブランク試験	4.0E-10	2.2E-10	2.2E-10	2.6E-10	2.6E-10
		収着試験1	4.0E-10	5.5E-11	5.5E-11	9.8E-11	9.8E-11
		収着試験2	4.0E-10	2.4E-10	2.4E-10	2.9E-10	2.9E-10
	炭酸添加水	ブランク試験	1.0E-07	8.0E-08	8.1E-08	8.0E-08	8.1E-08
		収着試験1	1.0E-07	3.9E-08	3.9E-08	3.9E-08	3.9E-08
		収着試験2	1.0E-07	4.0E-08	4.0E-08	4.0E-08	4.0E-08

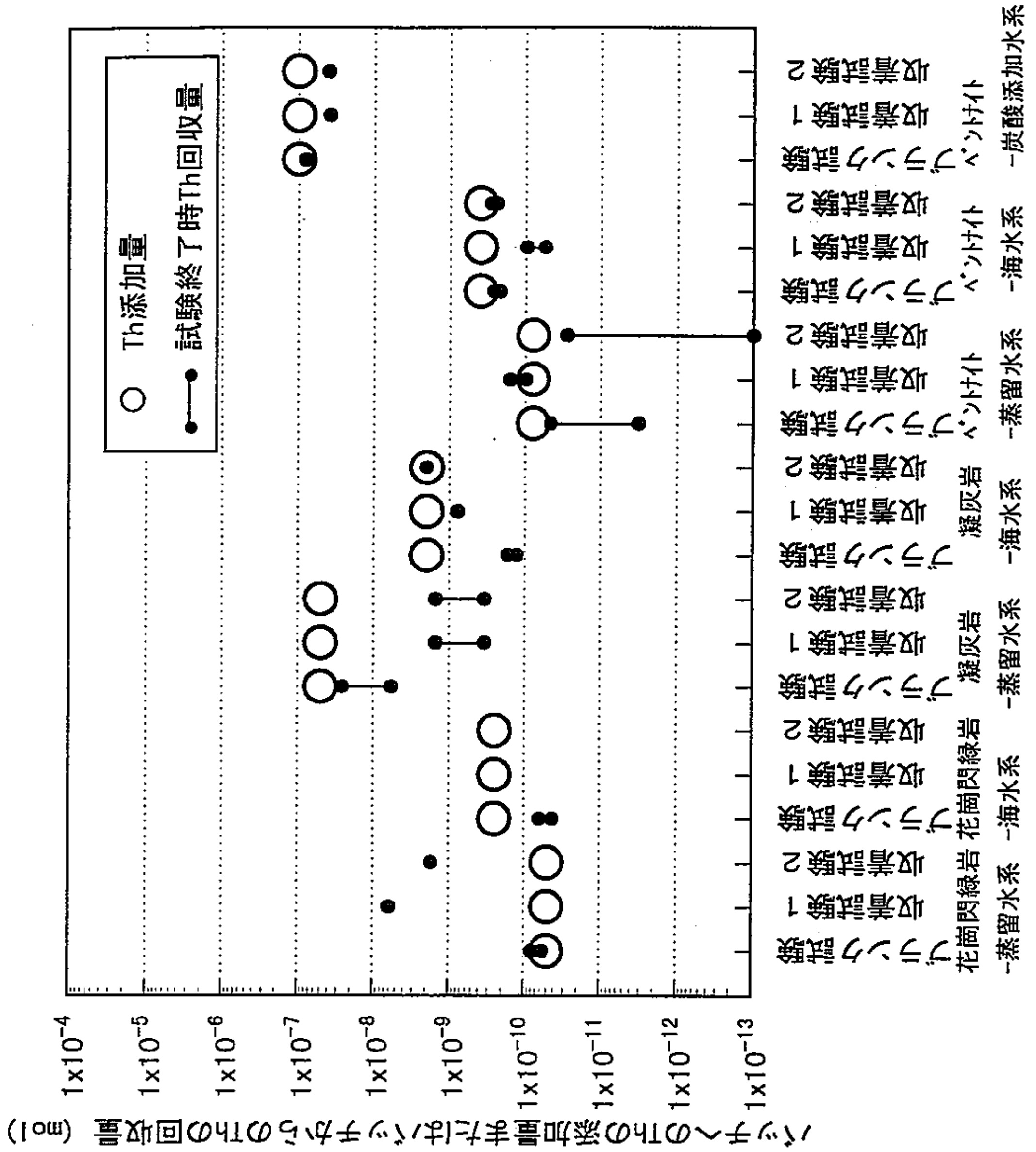


図3.2.3-2　バッチ式収着試験におけるThのマスバランス

2)分配係数の算出

平衡後液相濃度変化から算出した分配係数（容器壁への収着量の評価をブランク試験により解析した場合と、収着試験と同バッチの容器壁Th収着量分析値を用いて解析した場合の２ケース）を表3.2.3-8に示すとともに、グラフ化して図3.2.3-3に示した。

また、収着試験バッチの試験終了後固相のTh濃度から算出した分配係数を表3.2.3-8に示すとともに図3.2.3-4に示した。この際、液相中Th濃度は、保守性を考慮して限外ろ過したときの値を用いた。データは、B.G.試験バッチの酸浸出により脱離したThが、平衡液液性での分配平衡反応に寄与するThである場合（固相Th濃度=1N硝酸浸出Th全量）と寄与しないThの場合（固相Th濃度=1N硝酸浸出Th全量-BG試験浸出Th量）の２ケースで解析を行った。データの保守性を考慮すると、B.G.試験試料の酸浸出により脱離するThは分配平衡反応に寄与しないものとする方が保守的である。

ブランク試験バッチと収着試験バッチの液相中平衡後Th濃度から分配係数を解析できたのは、凝灰岩－蒸留水系、凝灰岩－海水系ならびにベントナイト－炭酸添加水系の３条件のみであった。また、収着試験終了後の容器壁収着量を用いて解析した結果は、ほとんどのバッチにおいて分配係数を取得することができた（～以上というデータも含めて）。傾向として、容器壁への収着量を決定する際、ブランク試験結果を用いるよりも容器壁収着Thを直接分析した方が高い分配係数が取得されている。また、初期液相Th濃度が検出下限値に近いバッチ（上記３条件以外のバッチ）は高い分配係数を取得できず、低い分配係数が取得され、～以上という形でしか値を評価できなかった。ベントナイト－蒸留水系における収着試験２バッチ目については、10ml/g程度の低い分配係数値が得られているものの、このデータは誤差の大きい検出下限に近い条件で取得されたデータであり信頼性は低い。実測されたデータ（～以上というデータは除いて）から判断すると、限外ろ過を行った方が、メンブランろ過を行った場合より分配係数は高いことが分かる。

なお、容器壁の収着量の測定データ（表3.2.3-6）を見ると、炭酸添加水系ではブランクバッチでの容器壁への収着はみられないものの、収着試験バッチでは容器壁への収着があり分配係数算出式の前提に則さない。このようなデー

表3.2.3-8　各固相に対するThの分配係数の算出

固相	液相	バッチ種類	液固比 (ml/g)	初期濃度目標値 (mol/l)	液相中の濃度変化からのKd算出				固相吸着量からのKdの算出	
					式3.2.3-1(1)による算出a)		式3.2.3-1(2)による算出b)			
					ﾒﾝﾌﾞﾗﾝ濾過 (ml/g)	限外濾過 (ml/g)	ﾒﾝﾌﾞﾗﾝ濾過 (ml/g)	限外濾過 (ml/g)	① (ml/g)	② (ml/g)
花崗閃緑岩	蒸留水	収着試験1	50	1E-09	解析不可	解析不可	> 6.1E+01	> 6.1E+01	> 4.9E+04	> 1.4E+04
		収着試験2	50	1E-09	解析不可	解析不可	> 6.1E+01	> 6.1E+01	> 3.9E+04	> 3.8E+03
		岩石浸出BG	50	0	---	---	---	---	> 3.5E+04	---
	海水	収着試験1	50	5E-09	解析不可	解析不可	> 5.3E+02	> 5.3E+02	> 3.7E+04	解析不可
		収着試験2	50	5E-09	解析不可	解析不可	> 5.3E+02	> 5.3E+02	> 3.7E+04	解析不可
		岩石浸出BG	50	0	---	---	---	---	> 3.8E+04	---
凝灰岩	蒸留水	収着試験1	50	1E-06	1.3E+03	3.6E+03	> 2.9E+03	> 4.6E+03	3.9E+02	2.7E+02
		収着試験2	50	1E-06	1.3E+03	3.6E+03	> 2.8E+03	> 4.6E+03	3.8E+02	2.7E+02
		岩石浸出BG	50	0	---	---	---	---	> 3.0E+02	---
	海水	収着試験1	50	4E-08	> 2.7E+02	> 1.8E+02	> 4.6E+03	> 4.6E+03	> 1.4E+04	> 1.8E+03
		収着試験2	50	4E-08	> 2.7E+02	> 1.8E+02	> 4.6E+03	> 4.6E+03	> 1.7E+04	> 4.6E+03
		岩石浸出BG	50	0	---	---	---	---	> 1.2E+04	---
ベントナイト	蒸留水	収着試験1	100	8E-10	解析不可	解析不可	解析不可	> 7.7E+01	> 4.5E+03	> 2.3E+02
		収着試験2	100	8E-10	解析不可	解析不可	1.2E+01	> 7.9E+01	> 4.0E+03	解析不可
		岩石浸出BG	100	0	---	---	---	---	> 4.2E+03	---
	海水	収着試験1	100	4E-09	解析不可	解析不可	> 8.2E+02	> 8.2E+02	> 1.3E+03	> 1.2E+02
		収着試験2	100	4E-09	解析不可	解析不可	> 8.2E+02	> 8.2E+02	> 1.7E+03	> 5.6E+02
		岩石浸出BG	100	0	---	---			> 1.2E+03	---
	炭酸添加水	収着試験1	100	1E-06	1.1E+04	1.2E+04	> 1.3E+04	> 1.4E+04	5.6E+03	5.6E+03
		収着試験2	100	1E-06	1.1E+04	1.4E+04	> 1.3E+04	> 1.7E+04	6.7E+03	6.7E+03
		岩石浸出BG	100	0	---	---	---	---	> 1.1E+03	---

a) 容器壁への収着をブランク試験結果から補正した分配係数
b) 容器壁への収着を同バッチの容器壁収着量分析結果から補正した分配係数
① 予め試料中に含まれるバックグラウンドThのうち1M硝酸で浸出したThが、液相との平衡反応に寄与する吸着形態である場合
② 予め試料中に含まれるバックグラウンドThのうち1M硝酸で浸出したThが、液相との平衡反応に寄与しない吸着形態である場合

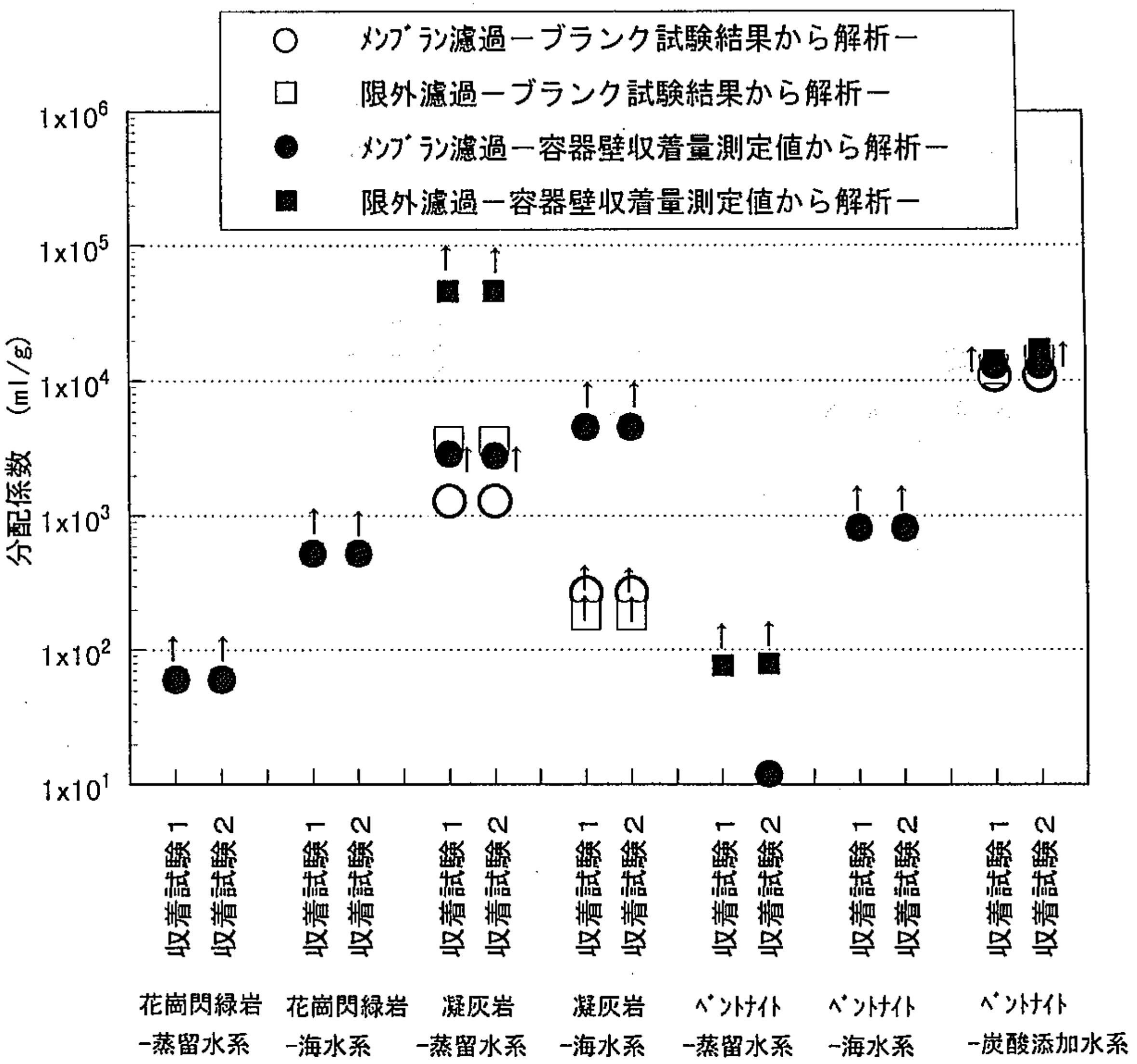


図3.2.3-3　収着試験バッチ液相の濃度変化から算出したThの分配係数

（↑は分配係数が～以上という意）

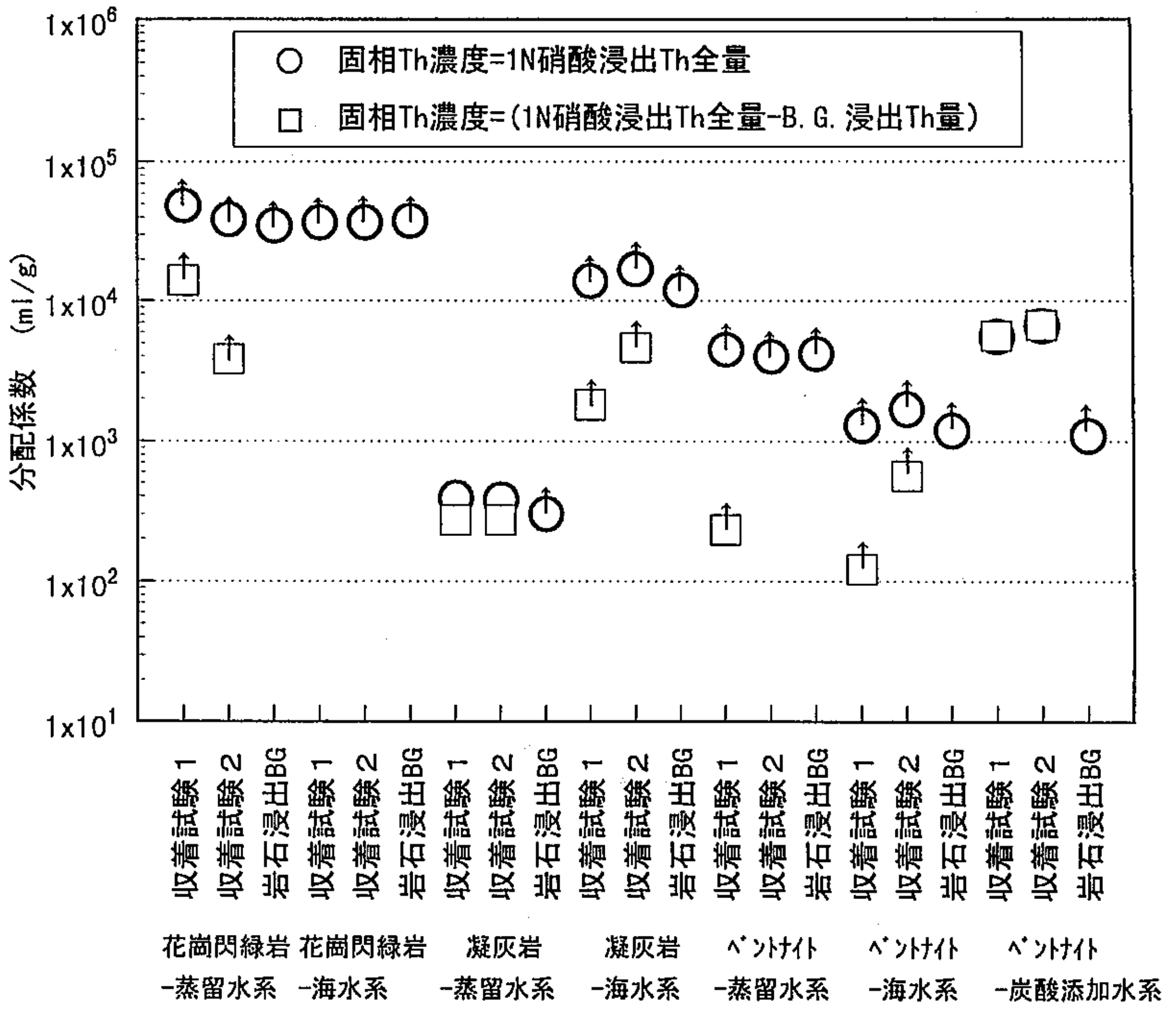


図3.2.3-4 収着試験バッチ固相のTh濃度から算出されたThの分配係数

（↑は収着試験平衡後の液相濃度が定量下限以下となった試験のデータで、
分配係数が～以上という意）

タは、真に収着試験バッチのみ Th が容器壁へ収着していたとすると保守性がないが、蒸留水で洗浄しきれなかったベントナイトの微粒子が容器壁に収着し、その微粒子にさらに Th が収着していた可能性もあるので、データの信頼性を一概に否定はできない。今後のさらに分配係数測定時の現象解析の把握を必要とするとことである。

固相中の Th 量からの分配係数データが取得できたのは、凝灰岩－蒸留水系とベントナイト－炭酸添加水系のみであり、他のデータはいずれも～以上というデータであるため、岩石間、平衡水液性に対する依存性を議論するのは困難である。

凝灰岩－蒸留水系ならびにベントナイト－炭酸添加水系のデータについては、平衡後の液相の濃度変化（ブランク試験との液相濃度差）から得られた分配係数と試験終了後の固相中の Th の酸浸出データから得られた、両分配係数が存在する。

両者を比較してみると、試験終了後の固相中の Th の酸浸出データから決定した分配係数データの方が若干低い値を示しており、この傾向から収着試験バッチ固相の酸浸出 Th 濃度から決定した分配係数の方の方が保守性があることがわかる。

(2)ベントナイト中での核種の拡散試験

放射性廃棄物処分における人工バリア候補材であるベントナイト中での核種の見かけの拡散係数測定を行った。核種は、安全評価上重要であり現状において拡散係数データの乏しい Ra、Np、Tc、U の 4 元素を対象とした。還元環境に原子価が敏感に影響する Np, Tc, U については地下処分施設周辺の還元環境下での地下水雰囲気を模擬して、雰囲気制御ボックスを用いて試験を還元条件で実施した。Ra は酸化還元電位に鋭敏でないことから、大気雰囲気で試験を行った。試験は、蒸留水及び海水系の 2 種類の試験液性でのデータを取得した。また、人工バリア施工時に考慮すべきパラメータとして、ベントナイトの密度を変化させてデータ取得を実施した。

(a)試験条件

Ra はアルカリ土類金属であり吸着メカニズムはイオン交換反応が支配的である。このような元素の分配係数は、ある程度大きいものの極端に高くはないのが一般的である。。本研究では、経験的に適当な拡散試験期間として1～3週間程度拡散試験期間を設定した。一方、Np(Ⅳ)、Tc(Ⅳ)および U(Ⅳ)については Ra と比較するとオーダーで分配係数が高い可能性がある。このため、本研究においては、まず、適当な時期に n=1 個目のカラムを Ra の試験と同程度である 0.5mm 間隔でセクショニングをし、ある程度拡散が進行していることを確認した。次にある程度拡散が進行した時期に n=2 個目のセクショニングを行った。n=2 個目のカラムのセクショニングは最長で試験期間を4ヶ月程度とし、セクショニング間隔は、作業的に薄くできる限度である 0.2mm とし、より詳細な拡散プロファイルの取得を試みた。見かけの拡散係数測定の試験条件を表 3.2.3-9 に、試験マトリクスを表 3.2.3-10 にそれぞれ示した。

表 3.2.3-9　ベントナイト中での核種の見かけの拡散係数測定条件

項目	内容
試験法	非定常拡散試験　In-diffusion 法
試料	ベントナイト(クニゲル V1)
乾燥密度	1.4 及び 1.8 g/cm^3
カラム寸法	ϕ20mm×20mm の円筒形カラム
温度	室温
試験雰囲気	大気雰囲気:Ra 還元雰囲気(Ar 雰囲気[O_2<1ppm])+$Na_2S_2O_4$:Np, Tc, U
試験液性	蒸留水または模擬海水 (3%-NaCl)を $Na_2S_2O_4$ 濃度 0.005mol/l に調製した溶液

表 3.2.3-10 見かけの拡散係数測定試験マトリクス

元素 (価数)	試験 雰囲気	セクショニング間隔 (mm)	試験期間(日)			備考
			蒸留水系		海水系	
			密度(g/cm^3)			
			1.4	1.8	1.8	
Ra(Ⅱ)	大気中	0.5	7.0	15.0	20.0	両側拡散試験
		0.5	7.0	15.0	20.0	
Np(Ⅳ)	還元条件	0.5	50.2	50.2	50.2	片側拡散試験
		0.2	76.2	76.2	76.2	
Tc(Ⅳ)	還元条件	0.5	82.8	83.0 *	83.0	片側拡散試験
		0.2	108.8	108.9 *	108.9	
U(Ⅳ)	還元条件	0.5	55.1	96.0 *	96.0	片側拡散試験
		0.2	123.1	123.1 *	123.1	

*平成8年度実施済み

(b)試験手順

試験手順のフロー（ストック溶液作製部分は代表例としてウランのフローを示した。）を図3.2.3-5に示す。

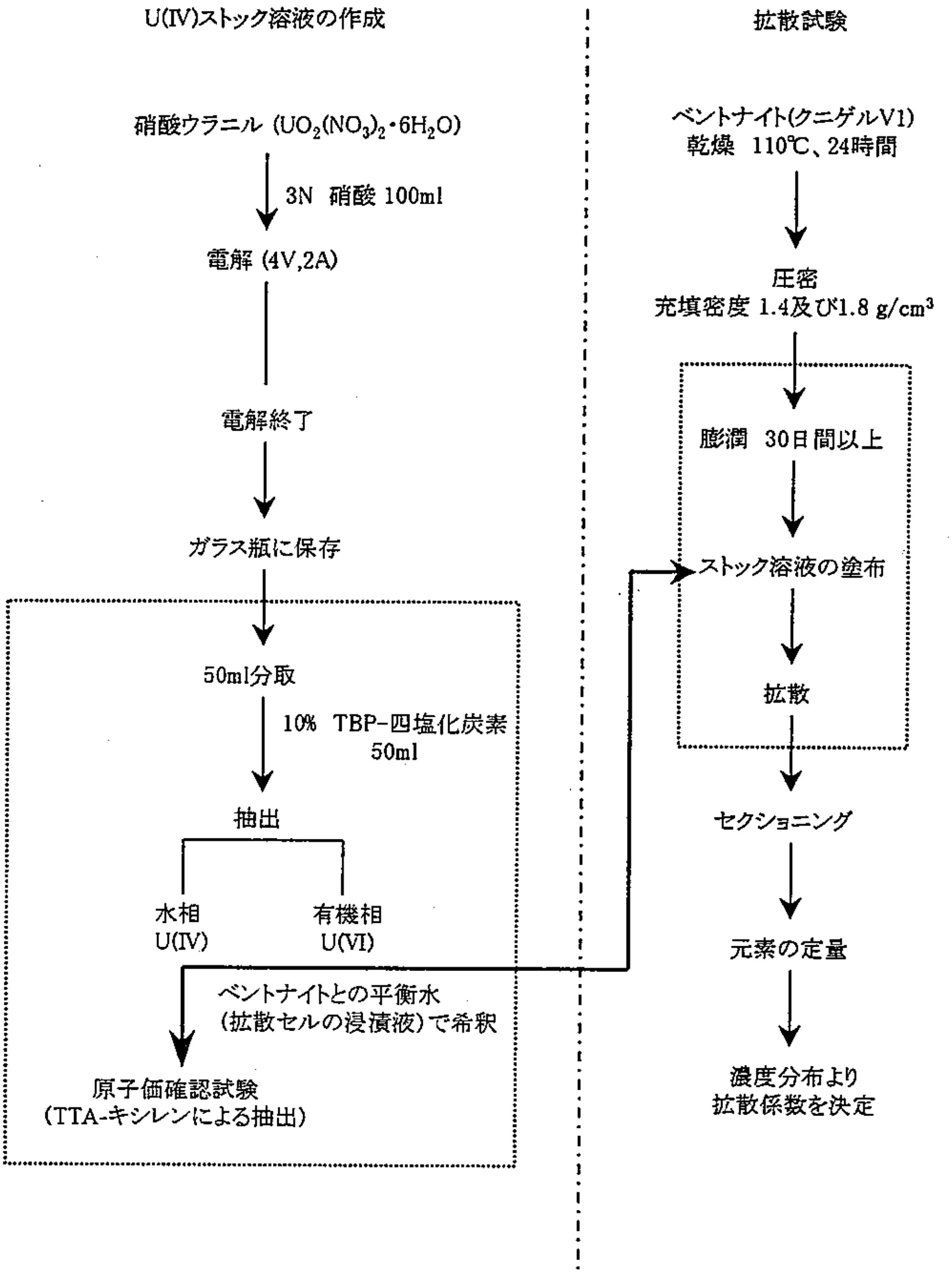


図3.2.3-5　ストック溶液の作製および拡散試験フロー　(例:U(IV))

▭ は雰囲気制御ボックス内

①ストック溶液の作製

Tc, Np, U は還元環境における原子価にストック液を調製して拡散試験に供した。以下に各元素に対する還元方法をまとめた。また、各元素の放射化学純度等を添付資料 I に示した。

ア. Tc(IV)のストック溶液

Tc-99 の NH_4TcO_4 を蒸留水を用いて 50(kBq/ml)に希釈した。希釈後の Tc-99 溶液を雰囲気制御ボックス内に搬入し、0.005(mol/l)の亜二チオン酸ナトリウム溶液($Na_2S_2O_4$, 和光純薬 化学用)を添加したベントナイト浸漬液(脱気水で調製)を加えて一週間放置し、ストック溶液とした。

イ. Np(IV)のストック溶液

Np-237 の原液を 0.5(mol/l)の塩酸を用いて 100(kBq/ml)に希釈した。希釈後の Np-237 溶液を雰囲気制御ボックス内に搬入し、0.005(mol/l)の亜二チオン酸ナトリウム溶液を添加したベントナイト浸漬液を加えて一週間放置し、NaOH で pH6～7 に調製し、ストック液とした。

ウ. U(IV)のストック溶液

U(IV)ストック溶液の調製フローを図 3.2.3-5 内に示した。

3N 硝酸溶液に硝酸ウラニル $UO_2(NO_3)_2 \cdot 6H_2O$ を溶解し、ウラン濃度 0.1(mol/l)の硝酸溶液を作製した。

陽イオン交換膜で仕切った電解槽の陰極側にウラン溶液を入れ、3N の硝酸溶液を陽極側に入れた。陰極側にチタン板を、陽極側に白金メッキしたチタン板を挿入し、4(V),2(A)の直流電流を 3 時間流してウランをIV価に還元した。

電解還元後、陰極側のウラン溶液を容器に回収し、酸素濃度を 1(ppm)以下とした雰囲気制御ボックス内で 10%TBP-四塩化炭素を用いて U(VI)の溶媒抽出を行った。抽出の繰り返しは 3 回行い、U(VI)が抽出された有機相は毎回廃棄し、最後の水相のみ回収した。これにヒドラジンを加え、さらに亜二チオン酸ナトリウムを添加したベントナイト浸漬液で 10 倍に希釈した。これを NaOH で pH6～7 に調製し、ストック液とした。

②ストック液中の原子価状態の確認

Tc, U および Np について、原子価状態の確認を行った。原子価が酸化還元電位に鋭敏でない Ra ついては、原子価状態の確認は行っていない。

Tc については、大気環境と還元環境におけるベントナイト平衡水での支配化学種が明確に異なるためベントナイト平衡水中における電気泳動試験を実施することにより原子価状態を確認した。U および Np については、還元環境で支配的となるⅣ価の化学種をストック溶液中から抽出することにより、原子価状態を確認した。

ア. Tc(Ⅳ)のストック溶液の電気泳動試験

Tc のストック溶液中での原子価状態を調べるために、電気泳動試験を行った。試験は雰囲気制御ボックス内で行った。泳動用ろ紙を泳動装置にセットし、ろ紙を $Na_2S_2O_4$ 溶液 0.005(mol/l)に浸漬させた。Tc(Ⅳ)のストック溶液を 0.45(μm)のメンブランフィルターでろ過した後、それぞれ 0.1(ml)をろ紙に滴下して電圧を 25(V)印可し泳動させた。泳動終了後、雰囲気制御ボックス内でろ紙を自然乾燥させ、1(cm)刻みに切断した。切断したろ紙をバイアル瓶に入れ、液体シンチレータ(PACKARD 社、PICO-FLOUR40、検出下限:7 cpm)を加えて液体シンチレーションカウンターを用いて放射能濃度を測定し、Tc の泳動状況を観察した。なお、電荷状態と泳動距離との関係について比較を行うため、電荷状態が+1 価として安定している Cs-137 および-1 価として安定している Cl-36 を用いて、同条件で測定を行った。試験結果を図 3.2.3-6 に示した。測定結果データは添付資料Ⅱに示した。

Tc は、ベントナイト平衡水中においては、大気環境では＋Ⅶ価の TcO_4^-の化学形を有するが、還元環境では＋Ⅳ価の $Tc(OH)_4^0$ イオンが支配的となると推定されるため、還元環境では電気泳動を行ってもあまり移動しない結果となることが推察される。試験結果では、わずかに陽極側に移動している傾向が見られた。この結果から作製したストック液中にはわずかに陰イオン形態の化学形の Tc は存在する可能性はあるものの、Cl の電気泳動結果と比較して Tc はほとんど移動していないことを考慮すると、概ね Tc(＋Ⅳ)の中性種が支配的であると考えられる。

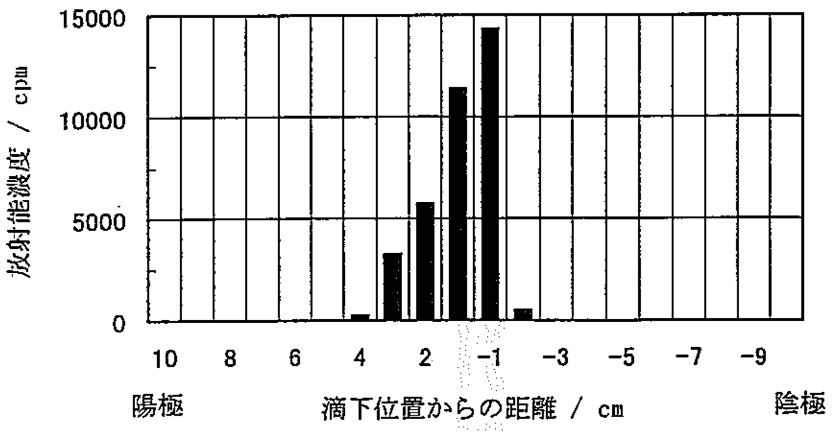


図3. 2. 3-6(1) Tc-99の電気泳動試験結果(充填密度1.4g/cm3)

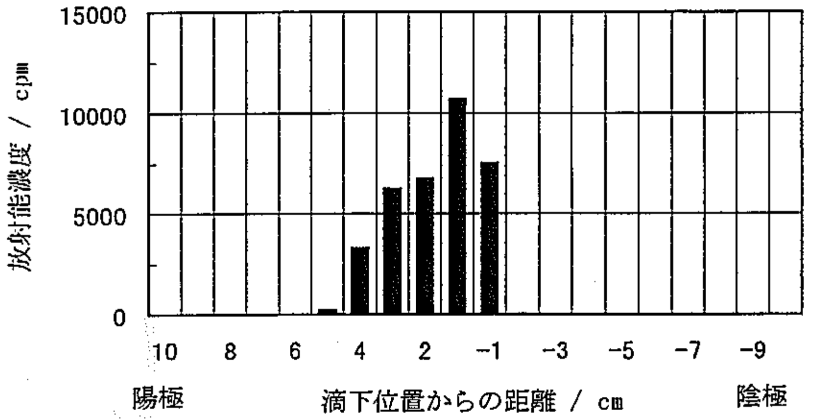


図3. 2. 3-6(2) Tc-99の電気泳動試験結果(充填密度1.8g/cm3)

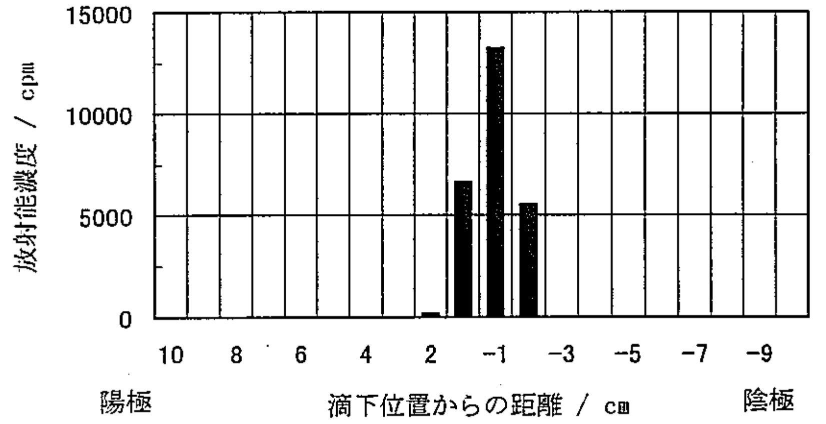


図3. 2. 3-6(3) Tc-99の電気泳動試験結果(充填密度1.8g/cm3、海水系)

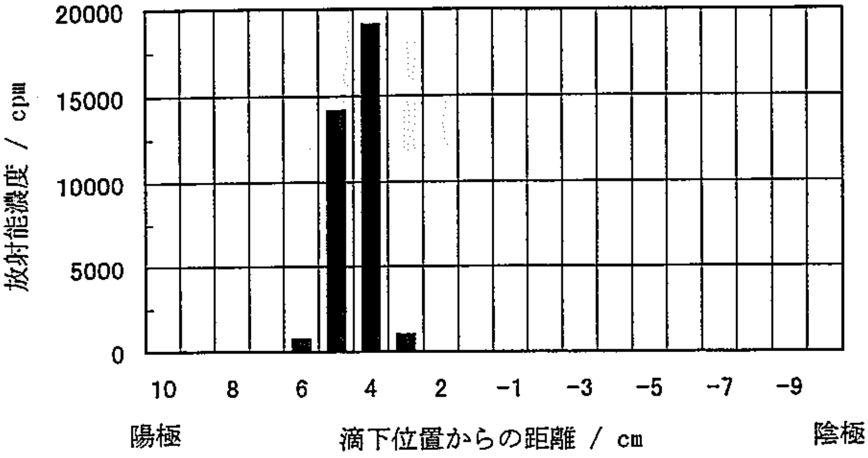


図3. 2. 3-6(4) Cl-36の電気泳動試験結果

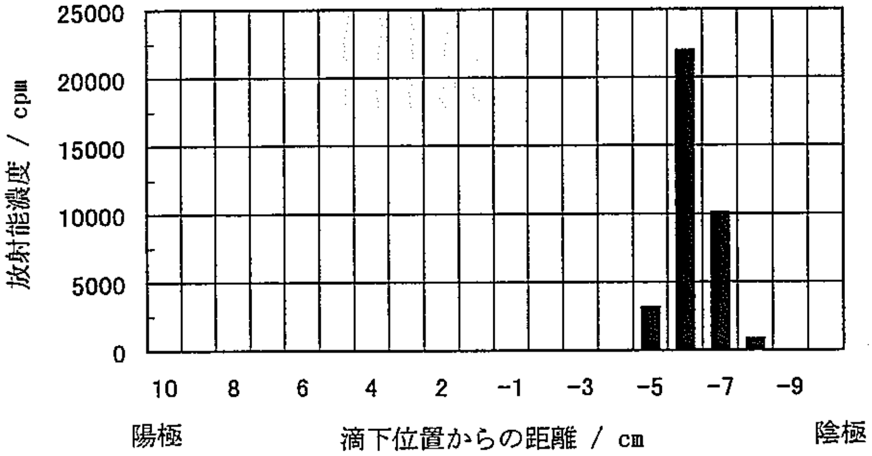


図3. 2. 3-6(5) Cs-137の電気泳動試験結果

イ. U(IV)およびNp(IV)の確認試験

ストック溶液を 0.5M TTA-キシレン溶液で抽出を行った。抽出終了後、水相中のU(VI)および Np(V)を液体シンチレーションカウンタ(PACKARD 社 TRI-CARB 2750TR/LL, シンチレータ PACKARD 社 PICO-FLOUR40)で測定し、U(IV)およびNp(IV)のストック溶液の純度を確認した。表3.2.3-11にその結果を示す。Uについては、ストック液中のほとんどが有機相中に抽出され U(+IV)の生成を確認した。Np については、75%程度しか有機相に抽出されなかった。Np はストック液のような酸性還元環境では+3価の化学形態も有するため、この分が水相に残存し抽出されなかったものと考えられる。

表 3.2.3-11 Np および U ストック溶液の溶媒抽出試験結果

元素	有機相(IV価) / cpm	水相 / cpm
Np	12709	3196
U	2154	16

以上の結果から、Tc, U, Np とも+4価の化学種が支配的であることが確認された。若干、各元素とも他原子価の化学形のものが混在する可能性があるものの、これらの原子価の元素を排除もしくは目的の価数にすべて調製することは現実的に困難である。(特に、ベントナイト平衡水中には U(VI)や Np(V)と錯形成を起こしやすい炭酸イオンが多量に含まれるため、これらの原子価のものはわずかに存在していても溶解度が高いため、結果的に空隙水中に多く存在する可能性があり、目的の原子価の拡散プロファイルを乱す可能性がある。)

本試験で取得された結果は、場合によっては目的とした原子価以外の複数の化学種が混在した系における拡散プロファイルが取得された可能性もある。しかし、それらを分割して、それぞれの化学種の見かけの拡散係数を評価することは困難であるため実施しない。取得されたプロファイルから拡散の解析式でフィッティングできる領域で拡散係数を取得するものとする。

③非定常拡散カラムへのベントナイトの充填

ベントナイト(クニゲル V1)を 110℃、24 時間以上乾燥させ、所定の乾燥密度になるよう秤量し、非定常拡散カラムに充填し、直径 20mm、高さ 20mm の円柱状に圧縮成形した。

④カラムの脱気・膨潤

ベントナイト試料を充填した非定常拡散カラムをグローブボックス内に搬入し、0.005(mol/l)の亜二チオン酸ナトリウムを加えた蒸留水及び海水中に浸した。その後、グローブボックスの前室に入れ、真空脱気を行い、常温常圧下で30～120日間含水させた。

⑤トレーサの塗布・拡散試験の開始

飽和したベントナイトカラムの端面にストック溶液を、25μl 塗布(沈殿を含むストックは沈殿ごと)し、試験開始とした。大気雰囲気で試験を行う Ra(II)については図 3.2.3-7(1)に示すような両側拡散の試験体系とした。雰囲気制御下で試験を行う Tc(IV), U(IV), Np(IV)については図 3.2.3-7(2)に示すような片側拡散の試験体系で、片側を亜二チオン酸ナトリウム溶液と接触させた状態でグローブボックス内にて保持した。定期的に pH および Eh(vs. SCH)をモニタリングし、Eh の上昇が見られた場合、亜二チオン酸ナトリウムを添加し、還元環境(pH7 で Eh：-0.5～-0.6[V]程度)を維持した。

⑥試料のスライス・スライス片の濃度測定

所定の期間拡散させた後、グローブボックスからカラムを取り出し、素早く試料を塗布面から 0.5(mm)間隔もしくは 0.2(mm)間隔でセクショニングし、スライス片の重量を速やかに秤量した。110℃で 24 時間乾燥させ、乾燥後のスライス片の重量を測定した。

Ra, Tc, Np については乾燥後のスライス片に、ヘキサメタリン酸ナトリウム(ベントナイトの分散剤)2(ml)もしくは 1N-硝酸 2(ml)を加え、3 時間程度浸透させた後、液体シンチレータ(PACKARD 社、PICO-FLOUR40)を 18(ml)加えてよく振り、液体シンチレーションカウンター(PACKARD 社 TRI-CARB 2750TR/LL)で放射能測定することにより、スライス片中のトレーサ濃度を求めた。

U については秤量後、1N 硝酸 4(ml)加えて U を浸出させ上澄み液 1(ml)を分取し、分画分子量 10000 のフィルターで固液分離した後、高周波誘導結合プラズマ質量分析法(セイコー電子工業 SPQ-8000A1 型 ICP 質量分析計)により U-238 濃度を測定することによりトレーサ濃度を求めた。

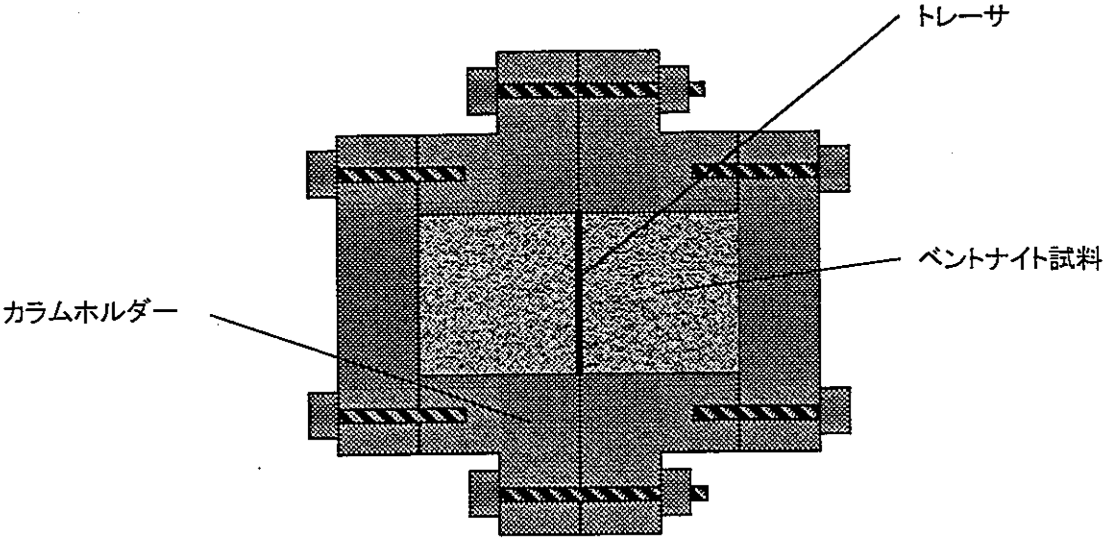


図3.2.3-7 (1) 非定常拡散カラム（両側拡散）

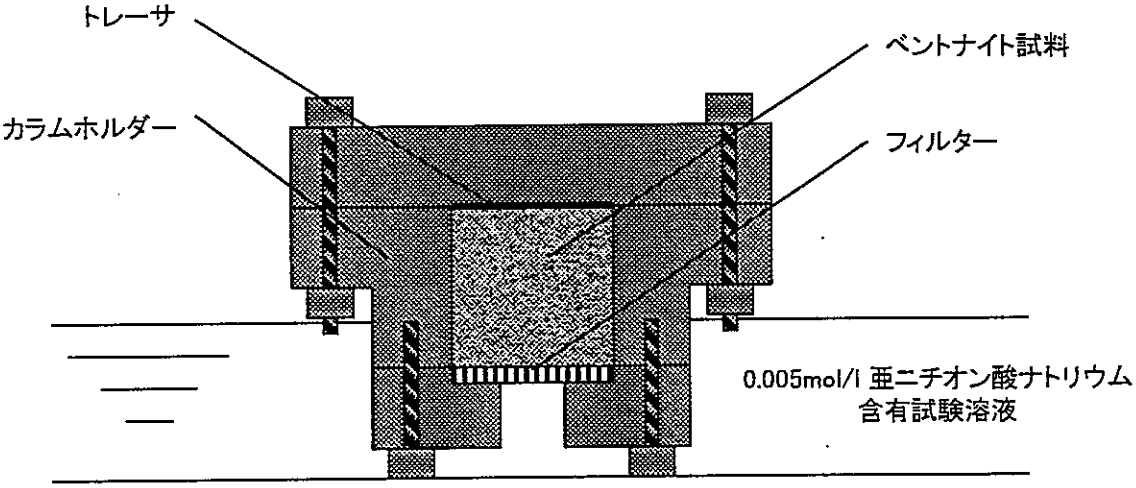


図3.2.3-7 (2) 非定常拡散カラム（片側拡散）

(c)見かけの拡散係数の解析方法

試験終了時の濃度プロファイルから見かけの拡散係数を算出するための解析解を示した。また、実測データから濃度プロファイルを算出した手法についても整理した。

ア. 本試験体系における解析解

本拡散試験体系おける拡散方程式の解析解を以下に示した。

一次元の Fick の第 2 法則は、

$$\frac{\partial C}{\partial t}=\frac{\partial}{\partial x}\left(D\frac{\partial C}{\partial x}\right) \qquad \cdots \ 3.2.3\text{-}5\text{式}$$

C：核種濃度[cpm/g, μg/g]

t：拡散時間[s]

x：拡散源からの距離[m]

D：拡散係数[m^2/s]

である。Dが濃度に依存せず一定であると仮定すると 3.2.3-5 式は次式で表される。

$$\frac{\partial C}{\partial t}=D\frac{\partial^2 C}{\partial x^2} \qquad \cdots \ 3.2.3\text{-}6\text{式}$$

i．薄膜拡散源に対する解析解

薄膜拡散源に対する初期条件および境界条件は、

初期条件として、$|x|>0 \quad t=0 \quad C=0$

境界条件として、$|x|\to\infty \quad t\geq 0 \quad C=0$である。

これらの条件下での解は、次式の様になる。

①両側拡散の場合

$$C(x,t)=\frac{M}{2\sqrt{\pi Dt}}\exp\left(-\frac{x^2}{4Dt}\right) \qquad \cdots \ 3.2.3\text{-}7a\text{式}$$

M：拡散源の総量

$$M = \int_{-\infty}^{+\infty} C dx$$

②片側拡散の場合

$$C(x,t) = \frac{M}{\sqrt{\pi D t}} \exp\left(-\frac{x^2}{4Dt}\right) \qquad \cdots 3.2.3\text{-}7b\ 式$$

ⅱ．境界濃度一定（コンスタントソース）に対する解

境界濃度一定の場合、初期条件および境界条件は

初期条件として、$C(t,X) = 0,\quad t = 0,\quad X > 0$

境界条件として、$C(t,X) = C_0,\quad t > 0,\quad X = 0$

解析解は以下の式となる。

$$\frac{C(t,X)}{C_0} = erfc\left(\frac{X}{2\sqrt{D_a \cdot t}}\right) \qquad \cdots 3.2.3\text{-}8\ 式$$

ここで、

$$erfc(Z) = 1 - \frac{2}{\sqrt{\pi}} \int_0^Z \exp(-\eta^2) d\eta$$

本研究では、Raについては両側拡散の拡散試験体系で拡散試験を実施し、塗布したトレーサも沈殿を起こさず全量、薄膜拡散として拡散した濃度プロファイルが後述の試験結果から得られたため、式3.2.3-7aの解析解でフィッテングを行い見かけの拡散係数を求めた。Tc, Np 及び U の試験については、トレーサを沈殿ごと塗布したためトレーサ源の空隙水中濃度は溶解度により濃度一定に保たれると考え、式 3.2.3-8 の解析解を用いてフィッテングを行い見かけの拡散係数を求めた。

イ. 濃度Cおよび位置xの算出方法

①濃度

i番目のスライス片中のトレーサ濃度Cは、圧密ベントナイトスライス片単位g当たりのトレーサ元素量として求めた。元素量の単位は、濃度測定方法が放射線測定であるRa, Tc, Npについてはcpmを、スライス片中での含有重量を測定したUについてはμgとした。

Uについてはスライス片を硝酸で浸出させることによりUを浸出させた後、固液分離し液相中に溶出したUの量を測定したが、酸浸出ではベントナイトに予めバックグラウンドとして浸出するUの量が無視できない。このため、予めベントナイト乾燥重量をパラメータ(スライス片重量はセクショニング厚さにより変化するためベントナイト乾燥重量をパラメータとした。)とした硝酸への浸出試験(図3.2.3-8に結果を示した。)を実施することにより、バックグランド影響によるデータの補正を行った。

以下に濃度の算出式を示す。

1)スライス片中のUの濃度

$$C_i = \frac{(T_i - T_{i\text{-}BG})\cdot V}{W_i} \qquad \cdots 3.2.3\text{-}9a式$$

C_I : i番目のスライス片中のUの濃度(μg/g)

T_I : i番目のスライス片を硝酸に浸出させたときの浸出液中のUの濃度(μg/1)

$T_{i\text{-}BG}$: i番目のスライス片と同乾燥重量のクニゲルV1を硝酸に浸出させたときの浸出液中のUの濃度(μg/1)

W_i : i番目のスライス片の乾燥前重量(g)

2)スライス片中のRa、Tc、Npの濃度

$$C_i = \frac{T_i}{W_i} \qquad \cdots 3.2.3\text{-}9b式$$

C_i : i番目のスライス片中のトレーサ濃度(cpm/g)

T_i : i番目のスライス片中のトレーサ量(cpm)

W_i : i番目のスライス片の乾燥前重量(g)

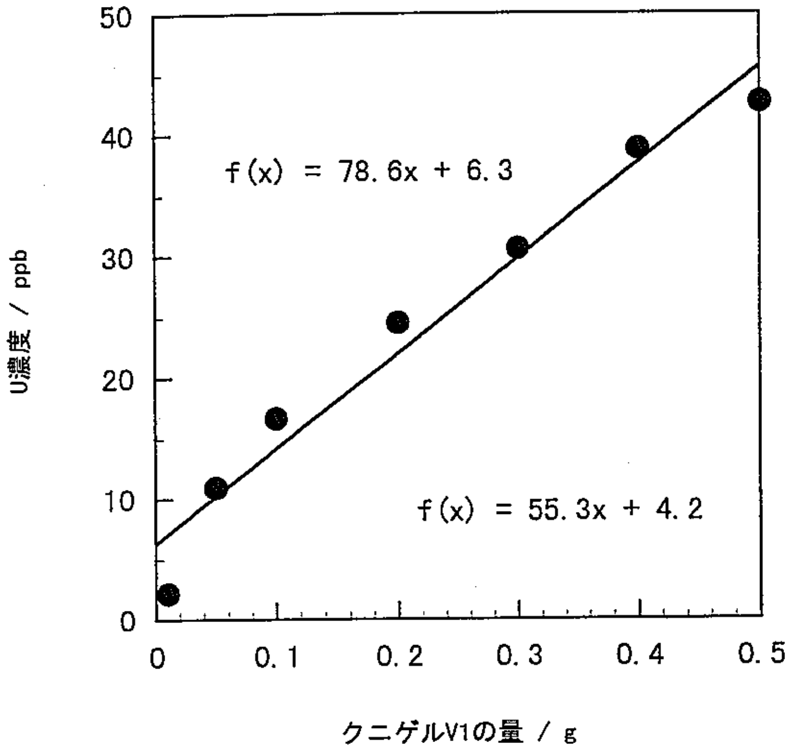


図3.2.3-8　クニゲルV1のバックグラウンド測定結果

②位置

各スライス片は所定の厚さ毎にスライスしているが、押し出し時の誤差により必ずしもスライス厚さは均等ではない。このため、各スライス片の位置は、スライス片の乾燥重量より補正した。高濃度側から押し出されたi番目のスライス片の乾燥前重量を W_i(g)とすると、スライス片 i のトレーサ塗布面からの距離 X_i は次式で表される。

$$X_i = \frac{W_i + W_{i-1}}{2} \times \frac{L}{\sum_{i=1}^{n} W_i} + X_{i-1} \qquad \cdots 3.2.3\text{-}10\ 式$$

X_i： スライス片 i のトレーサ塗布面からの距離(mm)

L ： カラム厚さ(cm)

n： スライス片の数

(d)試験結果

各試験の結果取得された各スライス片中のトレーサ濃度およびスライス片重量データを添付資料Ⅲに示した。

i．Ra

試験終了時における濃度プロファイルを図 3.2.3-9(1)～(6)にプロットするのと同時に、3.2.3-7a 式で求めた結果を図と共に示した。解析は、一次式で回帰するために、濃度及び距離データをそれぞれ ln(濃度)、(距離)^2 に変換して行った。解析範囲は、添付資料Ⅲ内に太字の*イタリック*で示したデータ範囲とした。

解析の結果取得された見かけの拡散係数を表 3.2.3-12 に示した。

ii．Tc、Np 及びU

試験終了時における濃度プロファイルを図 3.2.3-10～12 にプロットするのと同時に、3.2.3-4 式でフィッティングした結果を図中に実線で示した。フィッティングは、Co(拡散源における沈殿を含まないトレーサ濃度)及び Da(見かけの拡散係数)を、同時に変化させて最小二乗法によりフィッテングを行った。解析範囲は、添付資料Ⅲ内に太字の*イタリック*で示したデータ範囲とした。最初のスライス片(トレーサの塗布面のスライス片については、トレーサ元素の沈殿を含む可能性があるので解析データからは除外した。

解析の結果取得された見かけの拡散係数を表 3.2.3-12 に示した。

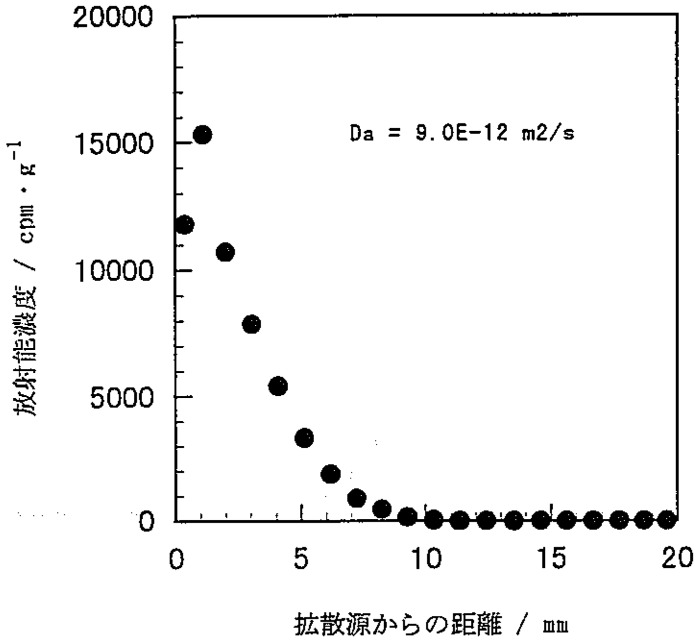
Tc, Np 及び U の見かけの拡散係数は、スライス片厚さに依存して変化しているものが多々見受けられ、傾向として細かくスライスしたときの方が解析で取得される拡散係数が小さくなる。これは拡散係数解析時のデータポイントの細かさが原因となっている。0.5mm のセクショニングの場合は、拡散プロファイルが取得される塗布面近傍でのデータ数が 0.2mm スライスの場合と比べ疎になっている。拡散係数解析時の表面近傍のデータの重みが異なるためフィッテイング結果が影響したものと考えられる。

このように、ほとんど拡散せず表面近傍に拡散プロファイルが限定されるときは、セクショニングの幅をより細かくとることにより、より小さな見かけの拡散係数の取得が可能であることが分かる。しかし、セクショニング片を細かくすることは、スライス片一枚当たりのトレーサ量も減少するため、溶解度低いU、Tcのような元素については分析下限の影響が問題となってくる。また、本試験における 0.2mm の幅のセクショニングは、膨潤した圧密ベ

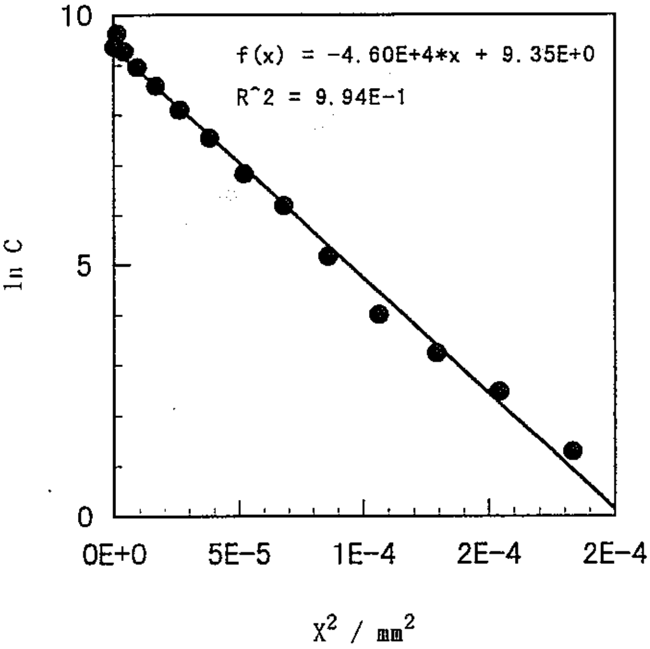
表 3.2.3-12　Ra,Tc,Np および U の見かけの拡散係数測定結果

元素（価数）	試験雰囲気	ｾｸｼｮﾆﾝｸﾞ間隔 (mm)	見かけの拡散係数 (m^2/s)		
			蒸留水系		海水系
			密度(g/cm^3)		
			1.4	1.8	1.8
Ra(Ⅱ)	大気中	0.5	9.0×10^{-12}	5.3×10^{-12}	1.7×10^{-12}
		0.5	8.5×10^{-12}	5.2×10^{-12}	2.0×10^{-12}
Np(Ⅳ)	還元条件	0.5	1.6×10^{-14}	4.9×10^{-14}	2.6×10^{-14}
		0.2	1.6×10^{-14}	3.2×10^{-14}	1.3×10^{-15}
Tc(Ⅳ)	還元条件	0.5	6.8×10^{-14}	1.0×10^{-13}＊	3.5×10^{-13}
		0.2	8.1×10^{-15}	7.5×10^{-14}＊	1.1×10^{-14}
U(Ⅳ)	還元条件	0.5	1.2×10^{-13}	1.2×10^{-13}＊	1.8×10^{-14}
		0.2	6.8×10^{-14}	1.1×10^{-14}＊	2.1×10^{-14}

＊平成8年度実施済み

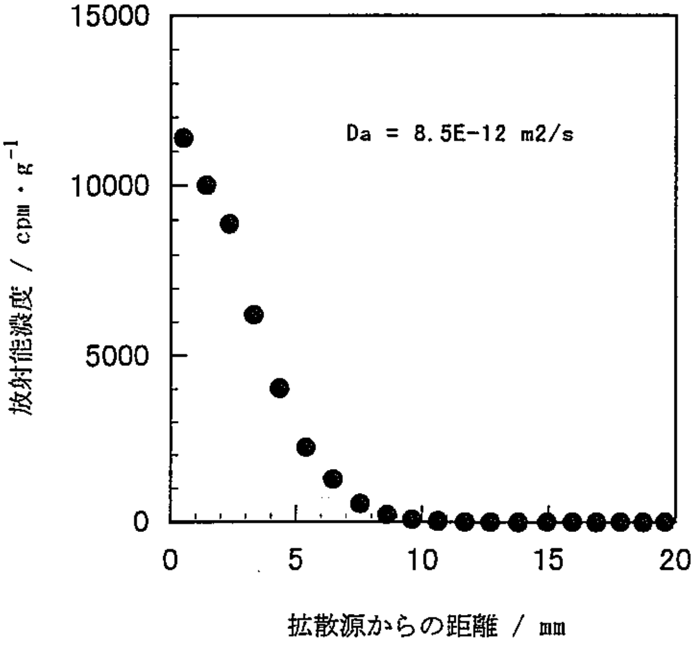


(a) Ra-226の濃度プロファイル（拡散期間7 日）

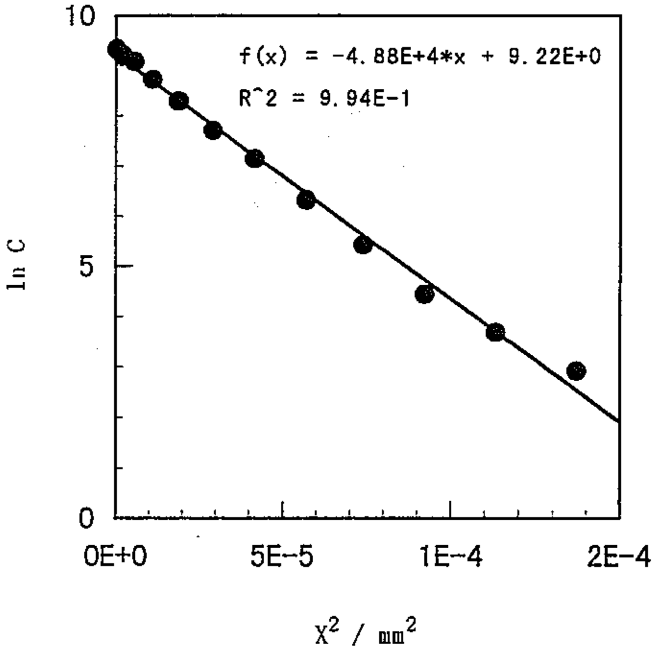


(b) 最小二乗法によるフィッティング

図3.2.3-9(1)　非定常拡散試験①（核種Ra-226，クニゲルV1，充填密度1.4g/cm^3）

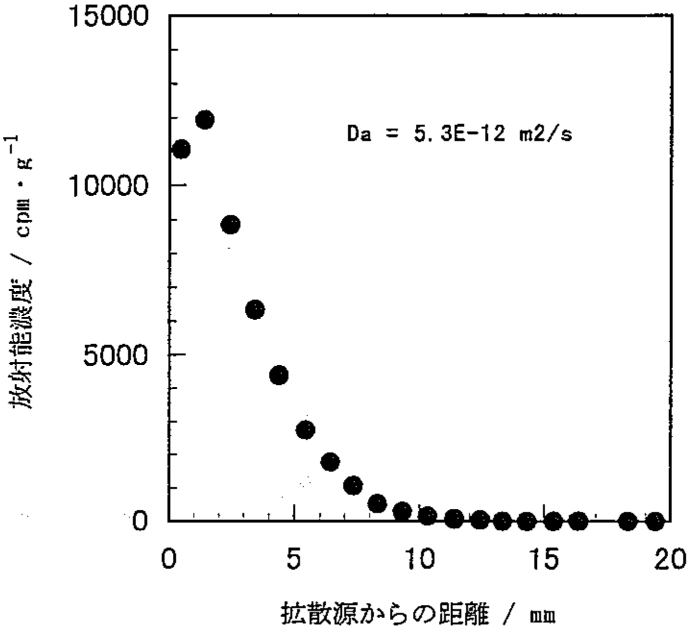


(a) Ra-226の濃度プロファイル（拡散期間7 日）

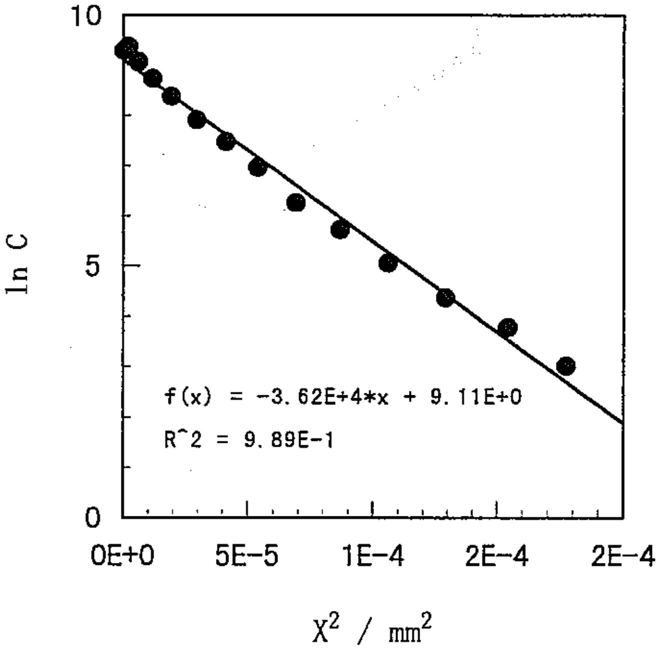


(b) 最小二乗法によるフィッティング

図3.2.3-9(2) 非定常拡散試験②（核種Ra-226, クニゲルV1, 充填密度1.4g/cm^3）

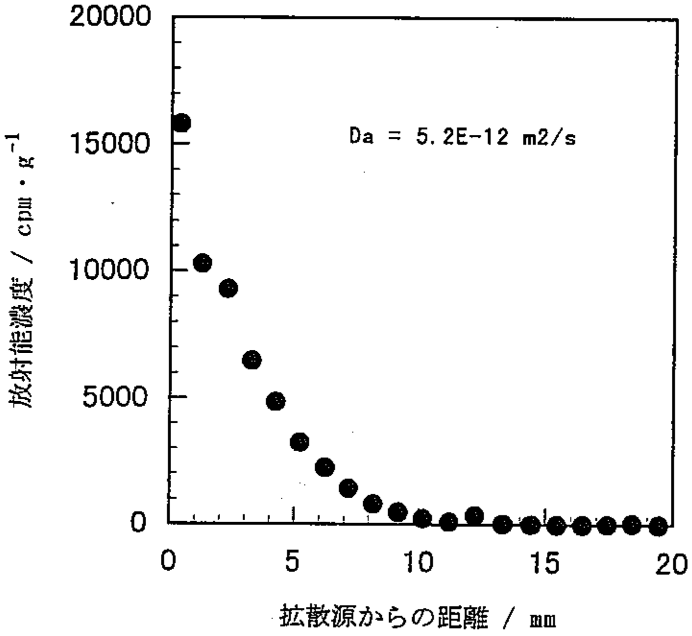


(a)Ra-226の濃度プロファイル（拡散期間15日）

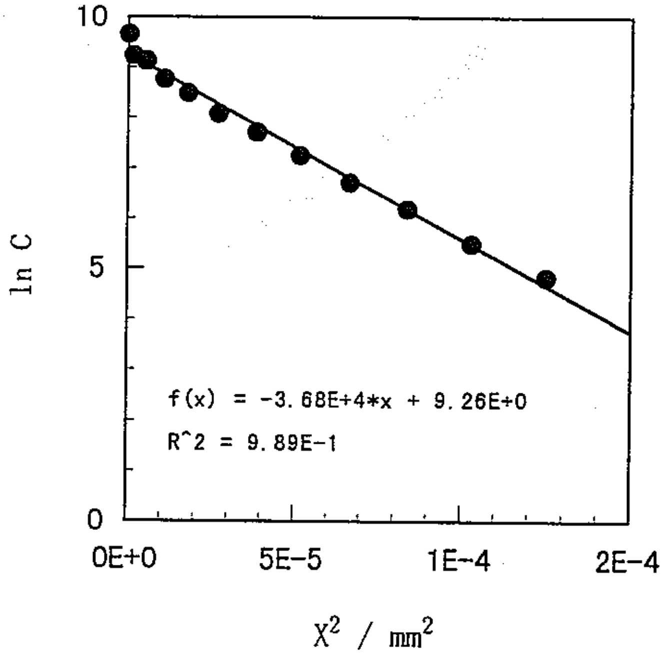


(b)最小二乗法によるフィッティング

図3.2.3-9(3)　非定常拡散試験①（核種Ra-226,クニゲルV1,充填密度1.8g/cm^3）

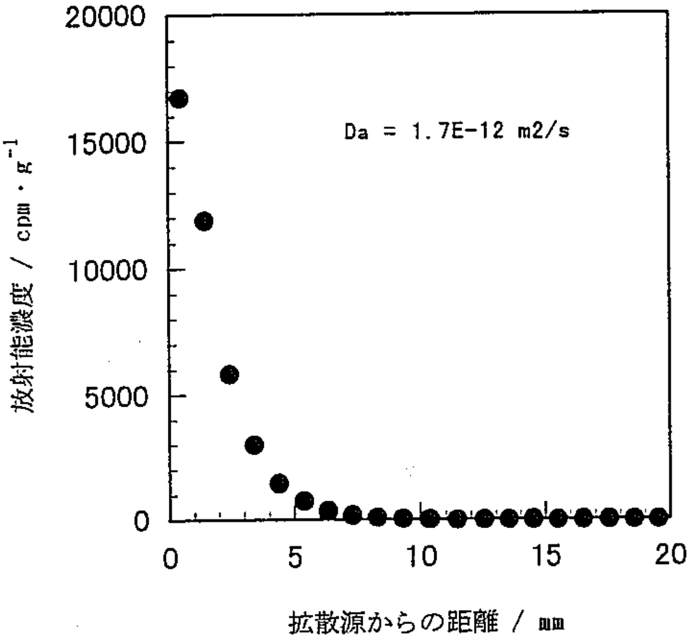


(a) Ra-226の濃度プロファイル（拡散期間15日）

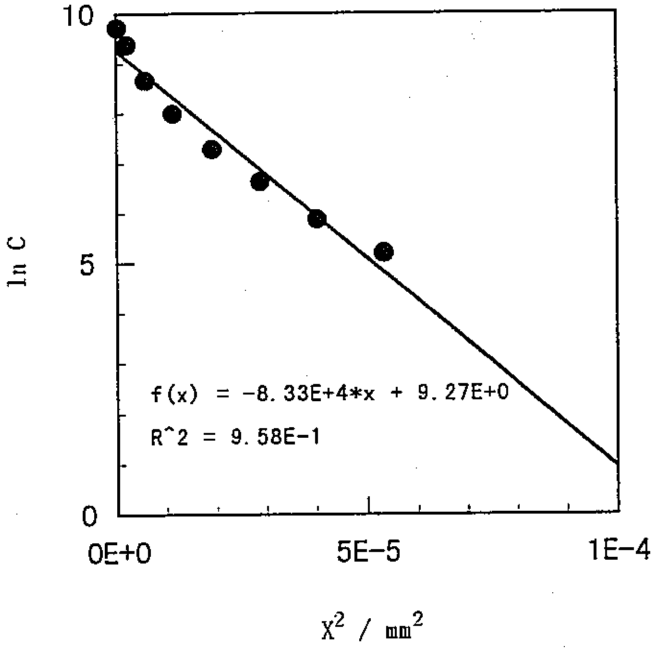


(b) 最小二乗法によるフィッティング

図3.2.3-9(4)　非定常拡散試験②（核種Ra-226, クニゲルV1, 充填密度1.8g/cm^3）

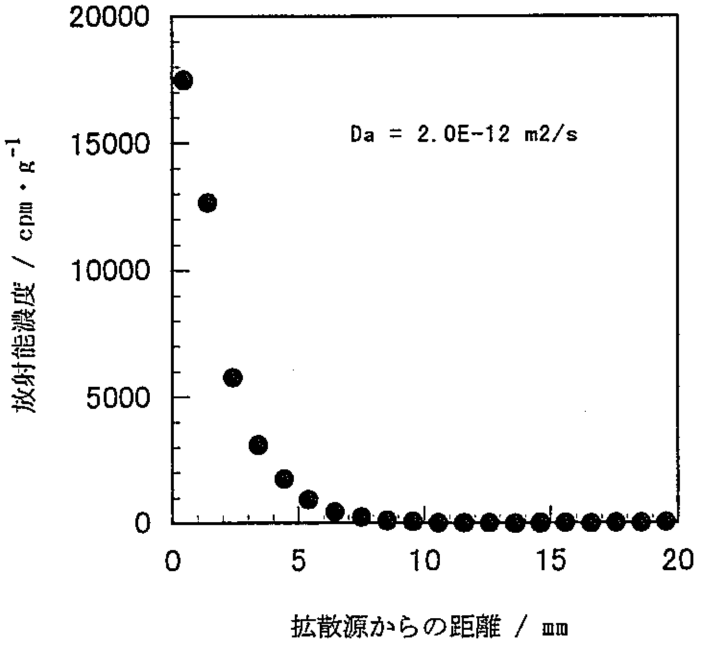


(a) Ra-226の濃度プロファイル（拡散期間20日）

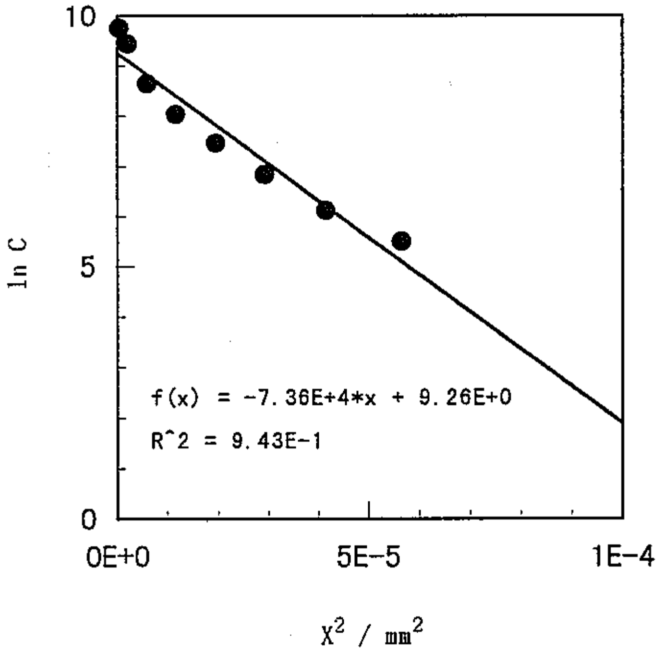


(b) 最小二乗法によるフィッティング

図3.2.3-9(5) 非定常拡散試験①（核種Ra-226, クニゲルV1, 充填密度1.8g/cm^3、海水系）



(a) Ra-226の濃度プロファイル（拡散期間20日）



(b) 最小二乗法によるフィッティング

図3.2.3-9(6) 非定常拡散試験②（核種Ra-226, クニゲルV1, 充填密度1.8g/cm^3、海水系）

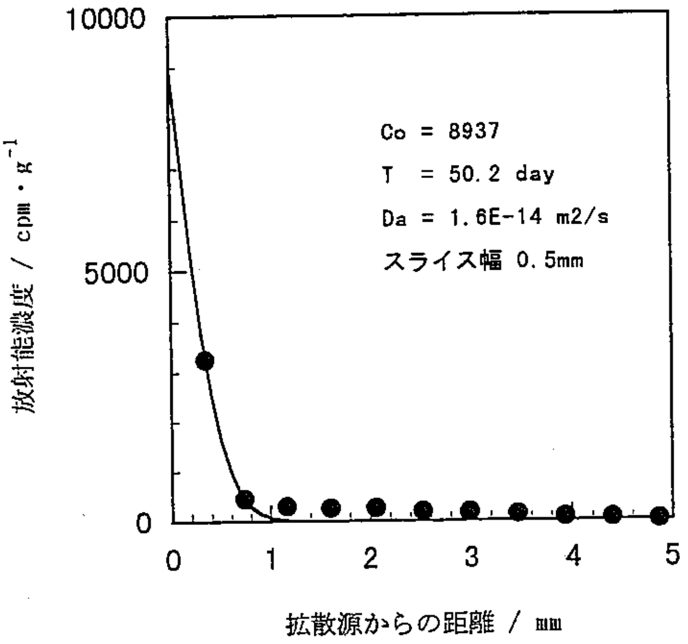


図3.2.3-10(1) 非定常拡散試験①（核種Np-237, クニゲルV1, 充填密度1.4g/cm^{3}）

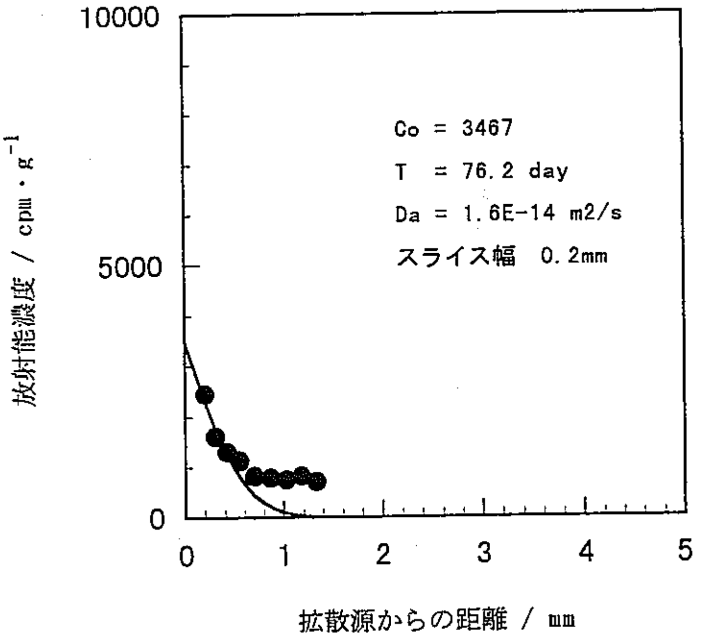


図3.2.3-10(2) 非定常拡散試験②（核種Np-237, クニゲルV1, 充填密度1.4g/cm^{3}）

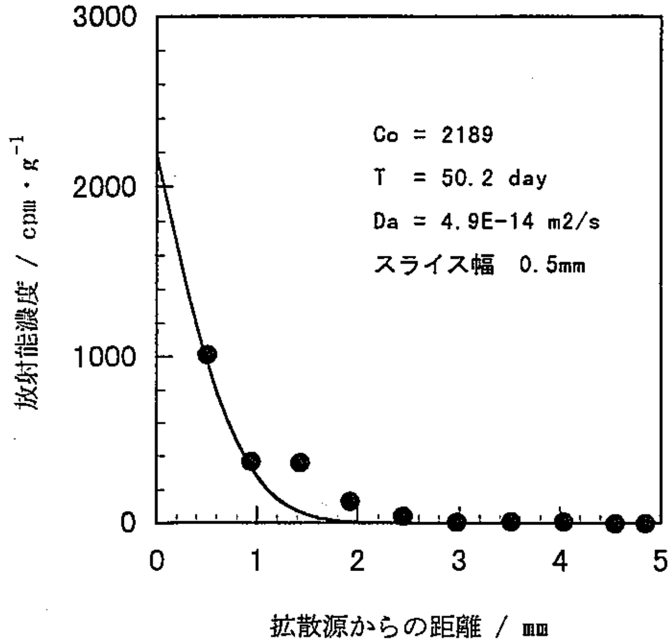


図3.2.3-10(3) 非定常拡散試験① (核種Np-237, クニゲルV1, 充填密度1.8g/cm^3)

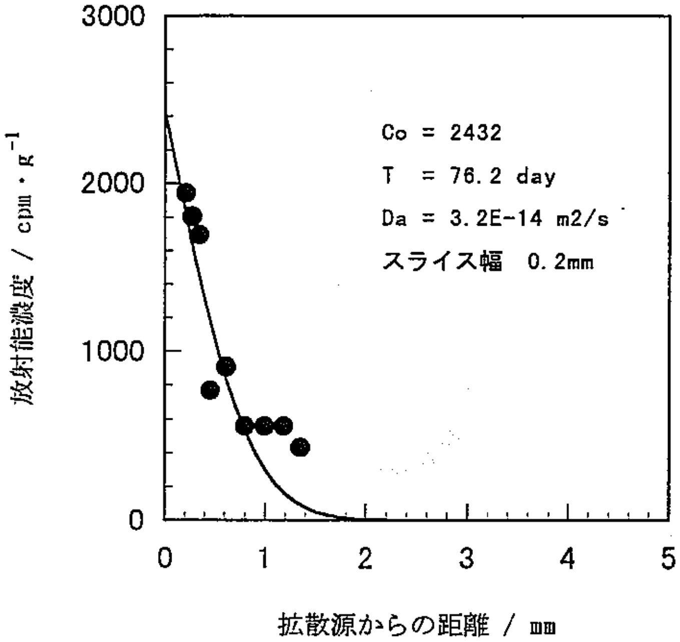


図3.2.3-10(4) 非定常拡散試験② (核種Np-237, クニゲルV1, 充填密度1.8g/cm^3)

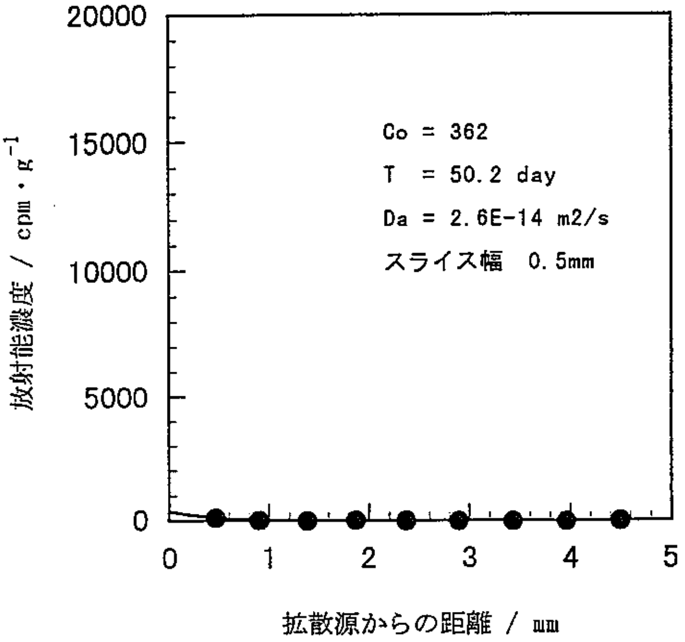


図3.2.3-10(5) 非定常拡散試験① (核種Np-237,クニゲルV1,充填密度1.8g/cm^3,海水系)

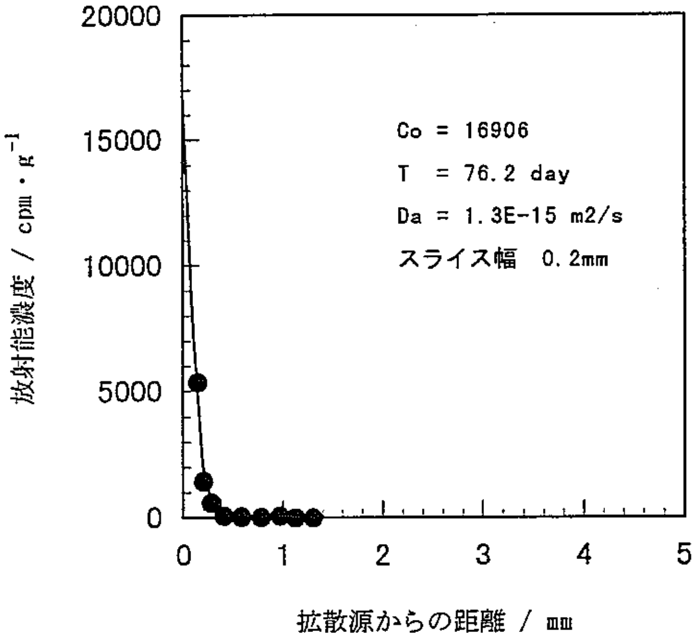


図3.2.3-10(6) 非定常拡散試験② (核種Np-237,クニゲルV1,充填密度1.8g/cm^3,海水系)

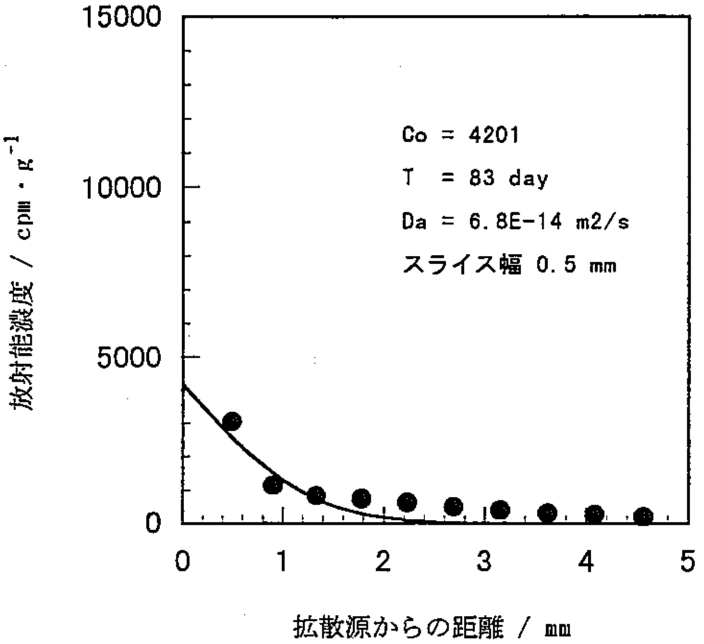


図3.2.3-11(1) 非定常拡散試験①（核種Tc-99, クニゲルV1, 充填密度1.4g/cm^3）

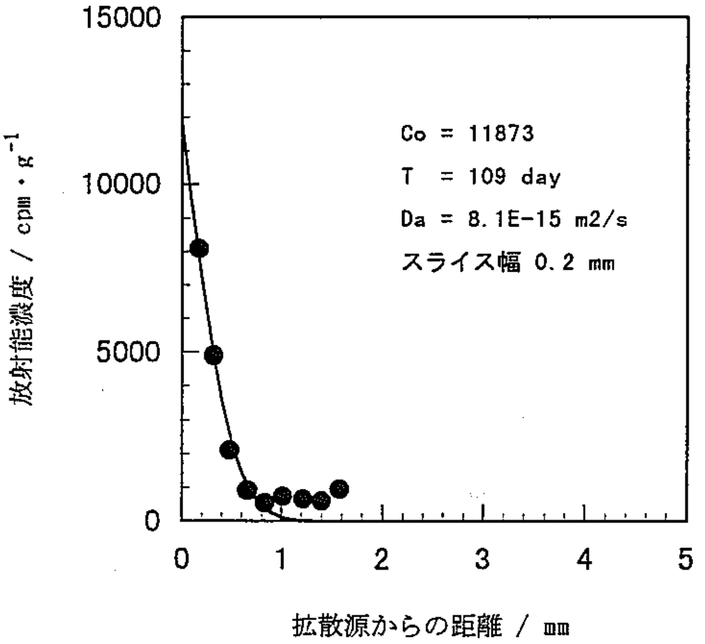


図3.2.3-11(2) 非定常拡散試験②（核種Tc-99, クニゲルV1, 充填密度1.4g/cm^3）

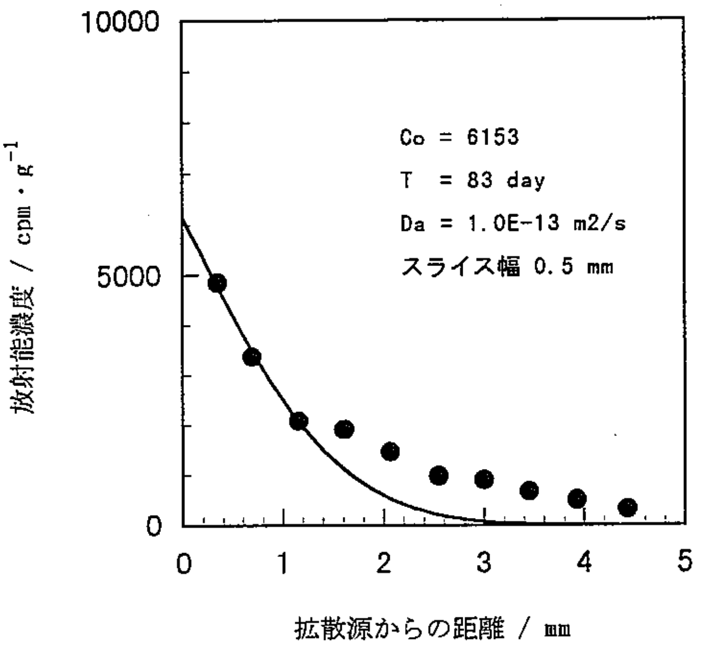


図3.2.3-11(3) 非定常拡散試験①（核種Tc-99, クニゲルV1, 充填密度1.8g/cm^3）

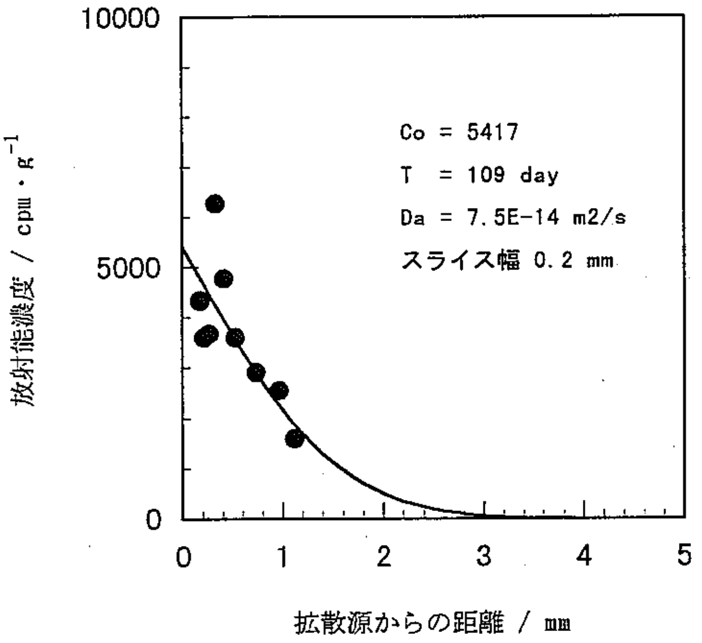


図3.2.3-11(4) 非定常拡散試験②（核種Tc-99, クニゲルV1, 充填密度1.8g/cm^3）

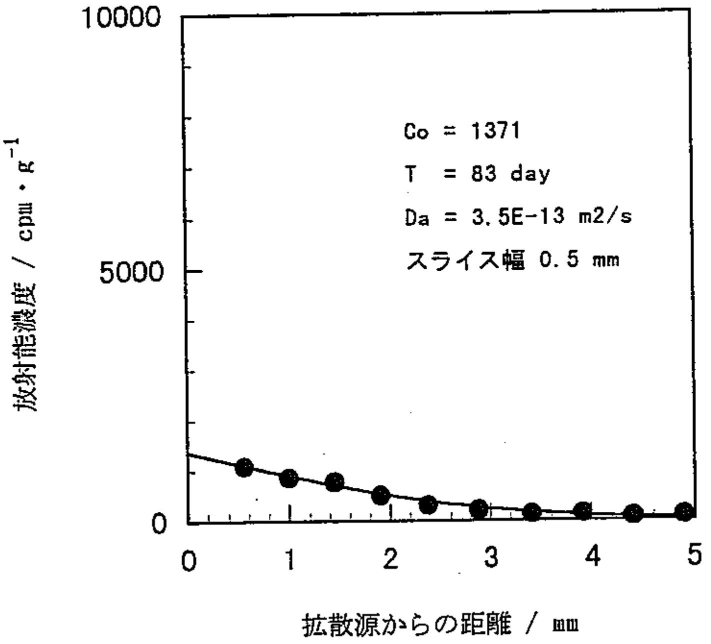


図3.2.3-11(5) 非定常拡散試験① (核種Tc-99,クニゲルV1,充填密度1.8g/cm^3,海水系)

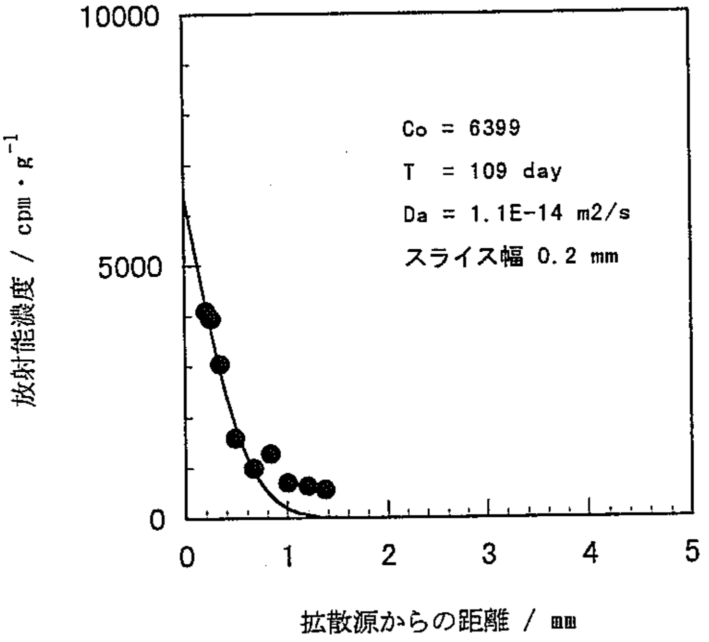


図3.2.3-11(6) 非定常拡散試験② (核種Tc-99,クニゲルV1,充填密度1.8g/cm^3,海水系)

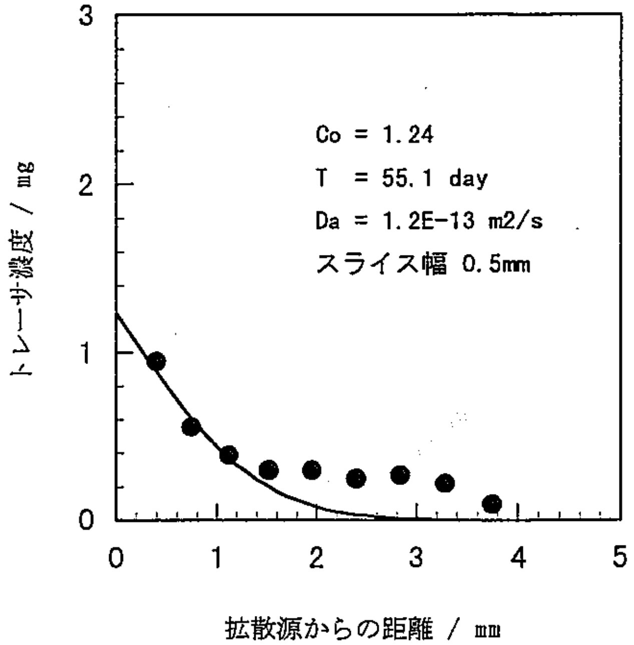


図3.2.3-12(1) 非定常拡散試験① (核種U, クニゲルV1, 充填密度1.4g/cm^3)

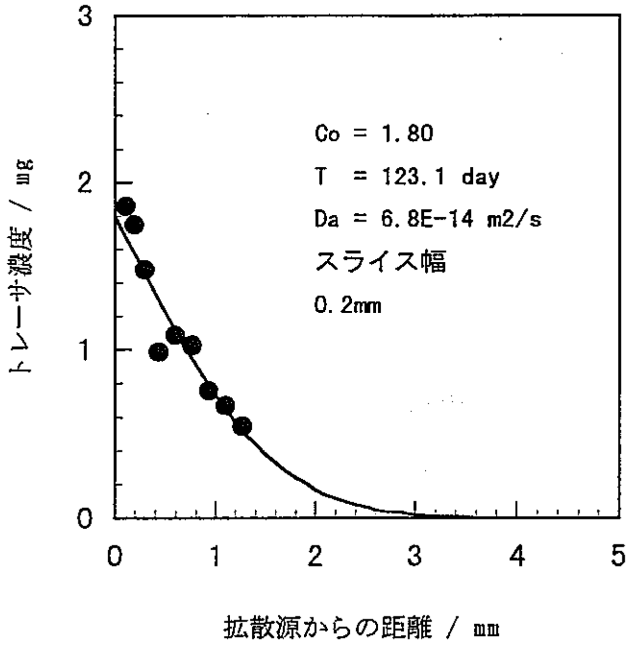


図3.2.3-12(2) 非定常拡散試験② (核種U, クニゲルV1, 充填密度1.4g/cm^3)

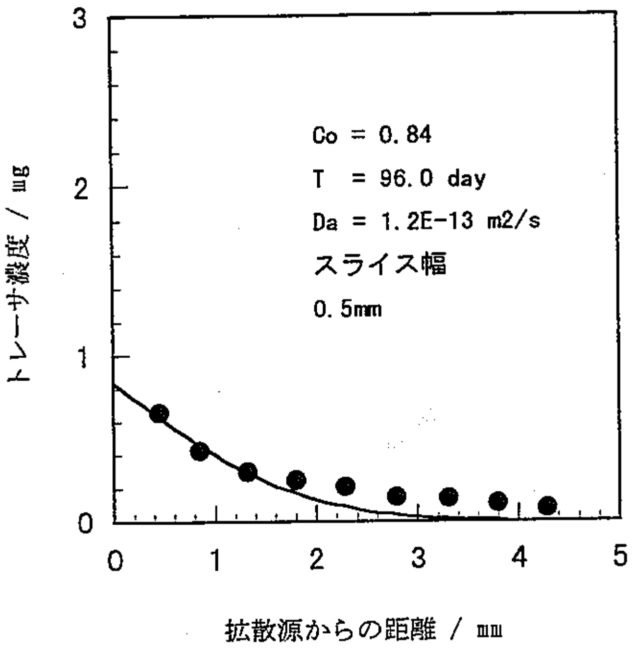


図3.2.3-12(3) 非定常拡散試験① (核種U, クニゲルV1 ,充填密度 1.8g/cm^3)

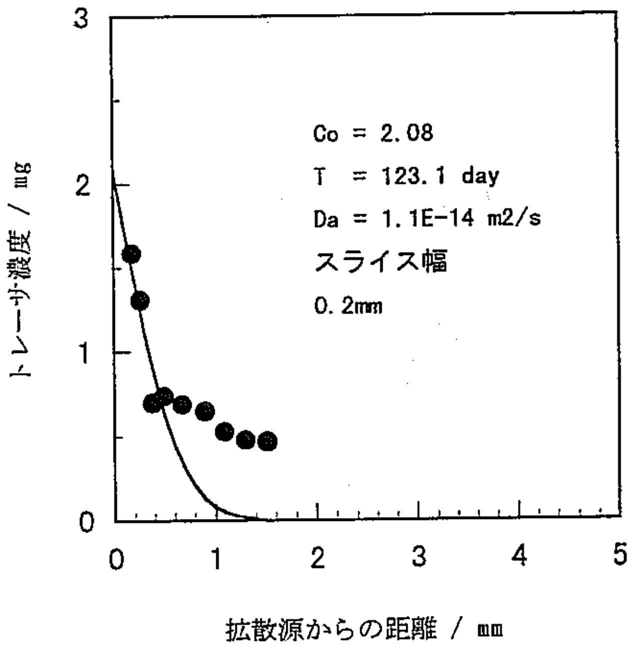


図3.2.3-12(4) 非定常拡散試験② (核種U, クニゲルV1 ,充填密度 1.8/cm^3)

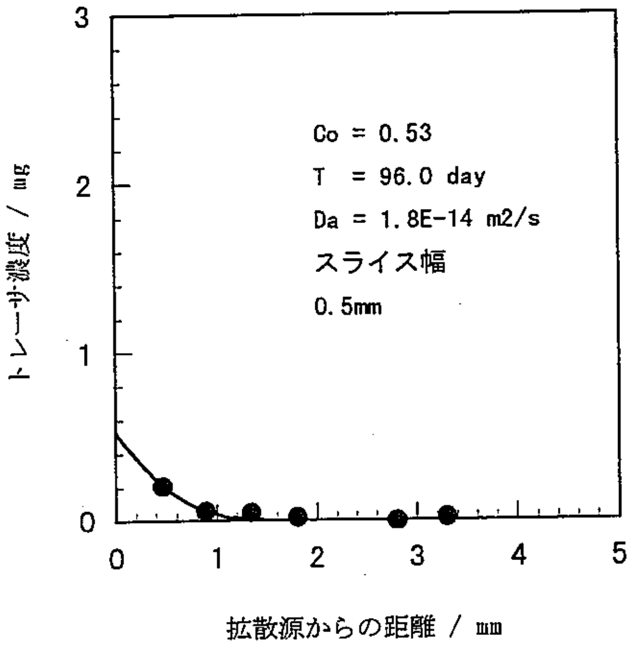


図3.2.3-12(5) 非定常拡散試験①（核種U, クニゲルV1 ,充填密度 1.8g/cm^3,海水系）

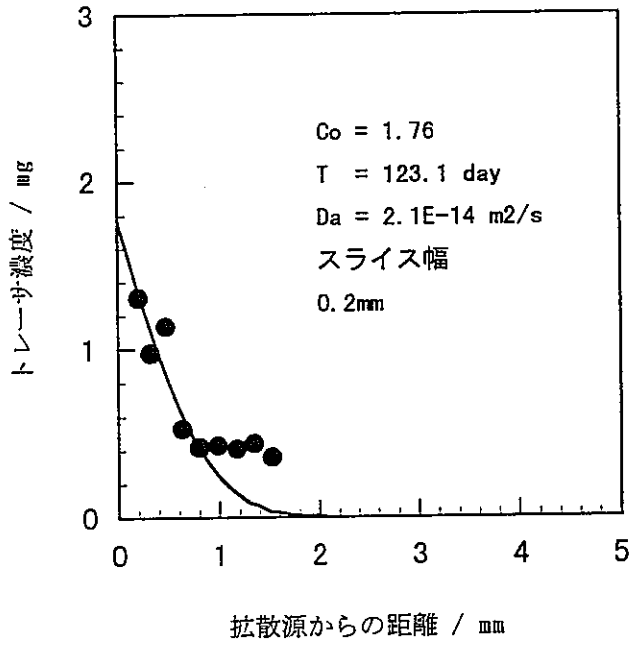


図3.2.3-12(6) 非定常拡散試験①（核種U, クニゲルV1 ,充填密度 1.8g/cm^3,海水系）

ントナイトをスライスする幅としては、作業的にほぼ限界に近い幅である。

以上のことから判断して、今回取得したデータは 0.2mm のデータの方がより現実的な値に近いことが判断されるが、実際の圧密ベントナイト中での見かけの拡散係数は、さらにより小さい値である可能性もある。

Tc, Np 及び U とも表面付近でのデータを解析に用いているが、カラム全体をセクショニングした 0.5mm のプロファイルを見ると僅かではあるがテイリングが見られ、比較的拡散の早い化学種もわずかに存在していることが示唆される。このことから、U, Np についてはU(VI), Np(V)の炭酸錯体、Tc についてはTc(VII)等のアニオン形を有し比較的拡散が早い化学種も塗布したトレーサ中にわずかに残存していた可能性がある。

図 3.2.3-13 に Ra, Tc, Np および U の見かけの拡散係数の密度依存性及び液性依存性をそれぞれ示した。

Ra の見かけの拡散係数は密度の増加とともに減少する傾向が見られた。また、同密度条件では海水系の方が見かけの拡散係数は小さくなる傾向にあった。

Tc, Np および U についてはより信頼性の高い 0.2mm セクショニング時の結果を参考に考察した。

Tc の見かけの拡散係数は密度の増加ともに増加する傾向が見られた。また、同密度条件では海水系の方が見かけの拡散係数は小さくなる傾向にあった。

Np の見かけの拡散係数は密度の増加ともに僅かに増加する傾向が見られた。また、同密度条件では海水系の方が見かけの拡散係数は小さくなる傾向にあった。

U の見かけの拡散係数は密度の増加ともに減少する傾向が見られた。また、同密度条件では海水系も蒸留水系も見かけの拡散係数はほぼ同程度であった。

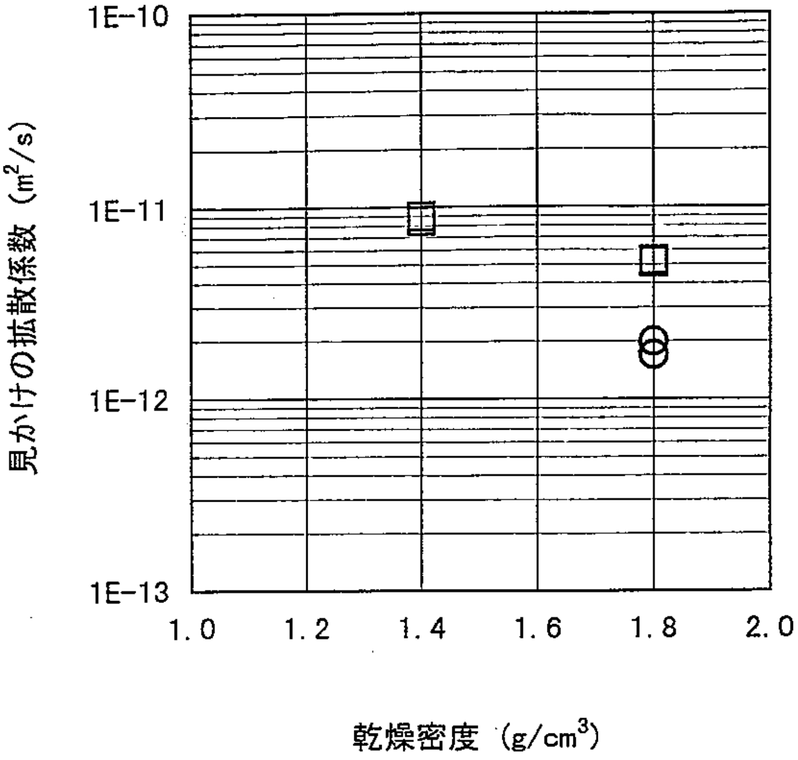


図3.2.3-13(1) Ra-226の見かけの拡散係数の乾燥密度依存性

□：蒸留水系、○：海水系（スライス幅　1.0mm）

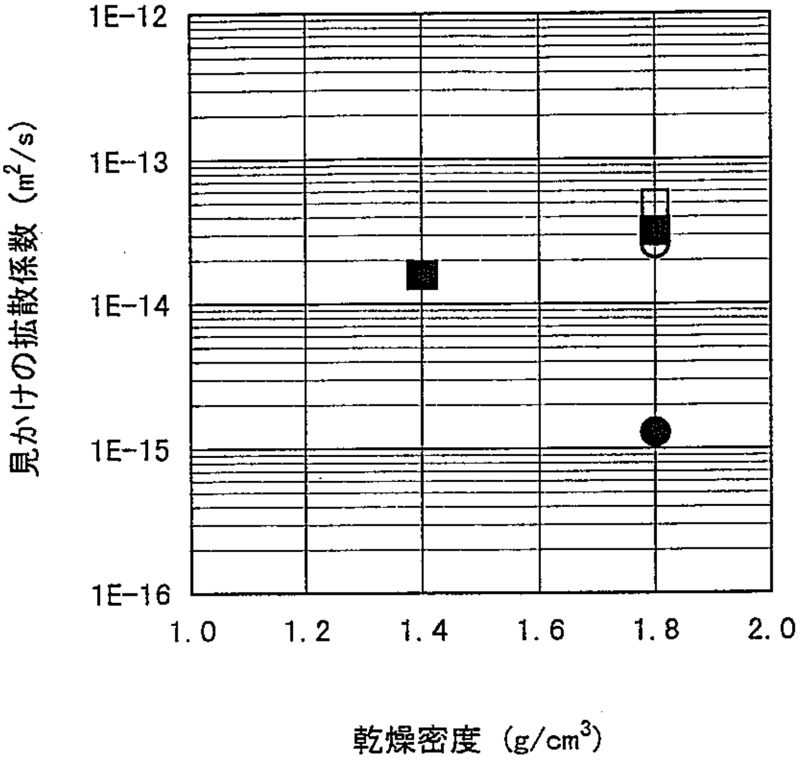


図3.2.3-13(2) Np-237の見かけの拡散係数の乾燥密度依存性

□：蒸留水系、○：海水系　（スライス幅　0.5mm）
■：蒸留水系、●：海水系　（スライス幅　0.2mm）

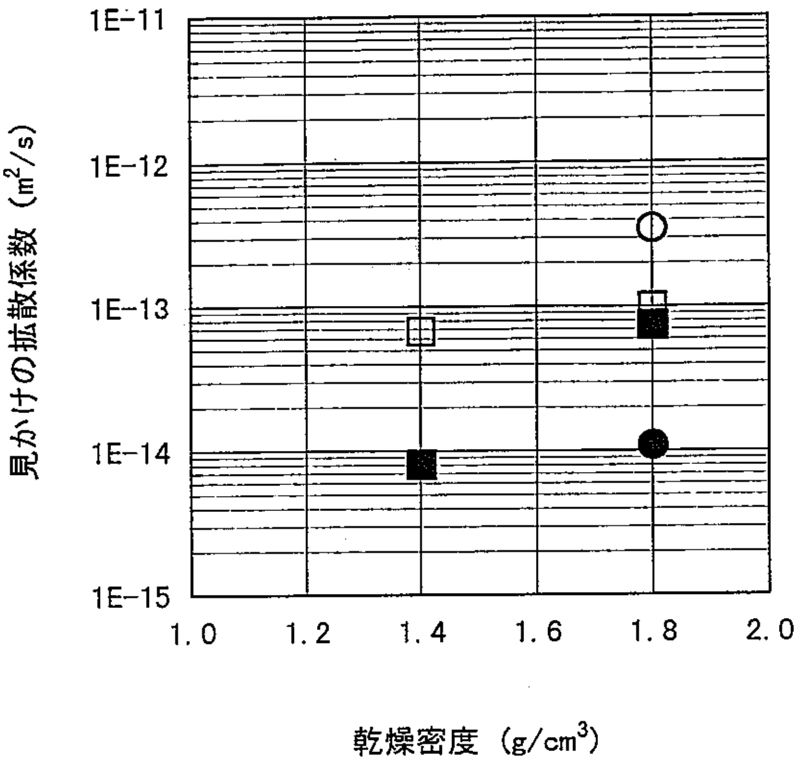


図3.2.3-13(3)　Tc-99の見かけの拡散係数の乾燥密度依存性

□：蒸留水系、○：海水系　（スライス幅　0.5mm）
■：蒸留水系、●：海水系　（スライス幅　0.2mm）

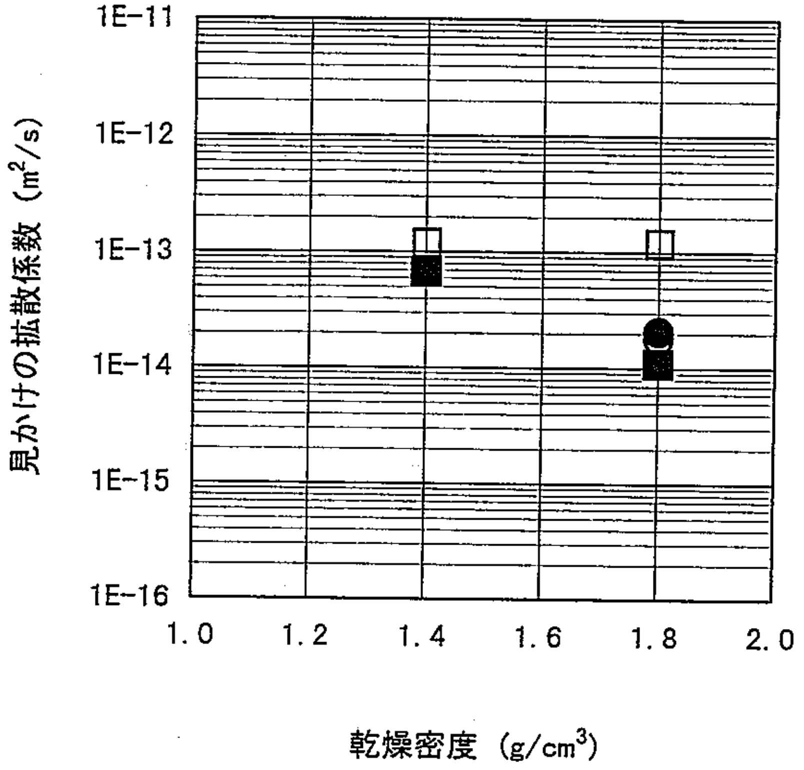


図3.2.3-13(4) Uの見かけの拡散係数の乾燥密度依存性

□：蒸留水系、○：海水系　（スライス幅　0.5mm）
■：蒸留水系、●：海水系　（スライス幅　0.2mm）

(3)ケイ砂混合ベントナイト中での核種の拡散試験

ケイ砂混合ベントナイト中での核種の見かけの拡散係数の測定を行った。拡散係数測定の対象は Cs, Ni, Se の3元素とした。

(a) 試験条件

試験条件を表 3.2.3-13 に示す。

表 3.2.3-13 ケイ砂混合ベントナイト中の核種の拡散試験条件

項目	測定条件
試験法	非定常拡散試験(In-diffusion 法)
試料	ベントナイト:クニゲルV1 珪砂:3号及び5号珪砂を等重量混合
乾燥密度	1.8 g/cm^3
ベントナイト配合率	30wt.%
温度	室温
試験トレーサ	Cs-137 / CsCl Ni-63 / $NiCl_2$ Se(cold) / Na_2SeO_3
雰囲気	大気雰囲気 :Cs-137, Ni-63 低酸素濃度雰囲気(気相 O_2<0.1ppm) :Se
繰り返し数	2

(b)試験手順

試験手順は、(2)のベントナイト中での核種の拡散試験に準じた。

全元素とも、セクショニング間隔は 1mm とした。

Se については酸化還元電位に敏感な元素であるため、溶液の酸化還元状態によっては異なる原子価をとる。本試験では、Se(IV)にそろえるため、雰囲気制御（低酸素雰囲気）下で試験を行った。グローブボックス内で 1M-Na_2SeO_3 溶液 25μl を試料の一端面に塗布し、片側を脱気水と接触させた状態でグローブボックス内にて保持した。所定に期間拡散させた後、試料を 1(mm)ずつスライスした。スライス片は蒸留水 80(ml)で 7 日間浸漬させ、分画分子量 10000 の限外ろ過フィルターで固液分離を行い、ろ液をフレームレス原子吸光分析法（日立 Z-5700 形 偏光ゼーマン原子吸光光度計、検出下限 1(μg/L))で濃度の定量を行った。

Cs-137、Ni-63 についてトレーサー元素を含む溶液を 25(μl)づつ塗布し、両側拡散で試験を行った。濃度分析は、前項(2)と同じく液体シンチレーションカウンタによる放射線分析とした。

(c)解析方法

前項(2)の(c)のベントナイト中での核種の拡散試験における解析方法に準じた。

Cs および Se については溶解度が高く塗布トレーサの全量が拡散すると考えられるので、薄膜拡散源からの拡散に対する解析解を用いた。

Ni については、試験終了後に取得された濃度プロファイルより、境界濃度一定からの拡散が起きているものと判断し、境界濃度一定条件の解析解を用いた。

Cs については、両側拡散試験であるため、3.2.3-7a 式を用いて解析した。

Se については、片側拡散試験であるため、3.2.3-7b 式を用いて解析した。

Ni については、境界濃度一定条件からの拡散であるため 3.2.3-8 式を用い解析した。

(d)結果

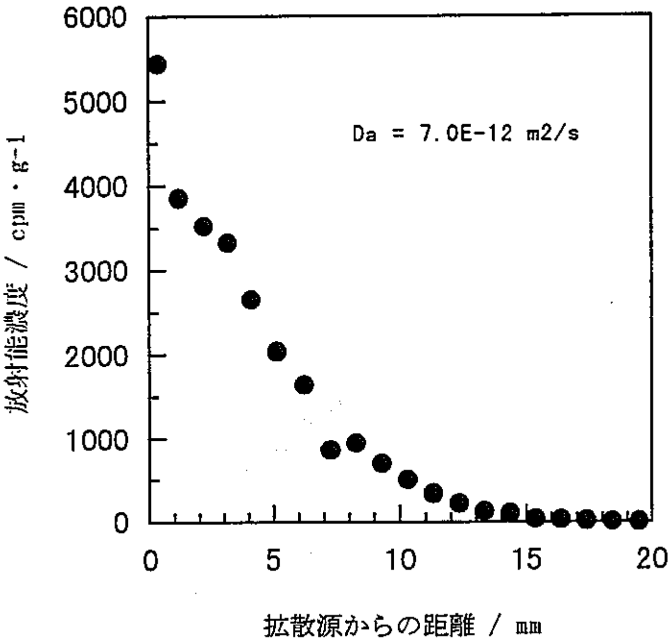
各試験の結果取得された各スライス片中のトレーサ濃度およびスライス片重量データを添付資料Ⅲに示した。

試験終了時における濃度プロファイルを図 3.2.3-14～16 にプロットするのと同時に、フィッティングした結果を図も示した。解析範囲は、添付資料内に太字の*イタリック*で示したデータ範囲とした。

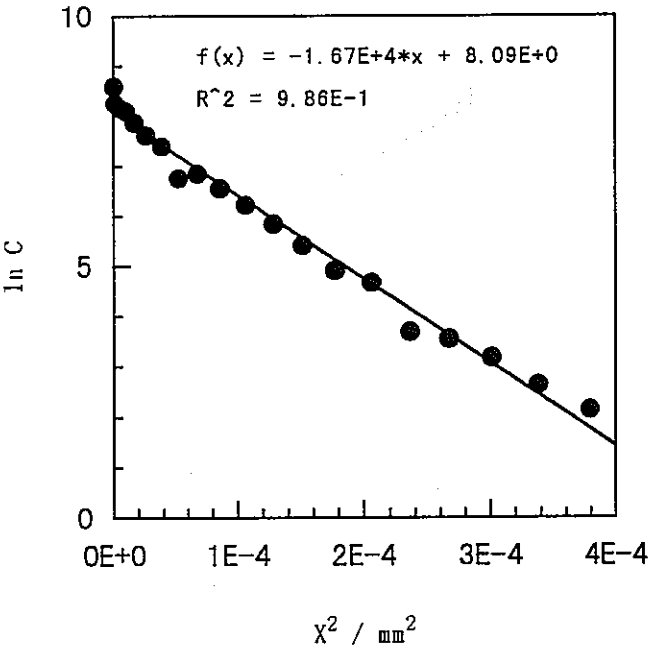
解析の結果取得された各元素の見かけの拡散係数を表 3.2.3-14 に示した。

表 3.2.3-14 ケイ砂混合ベントナイト中の見かけの拡散係数

元素	雰囲気	見かけの拡散係数 (m^2/s)
Cs	大気中	7.0×10^{-12} 6.6×10^{-12}
Ni	大気中	1.9×10^{-13} 1.3×10^{-13}
Se	低酸素雰囲気	1.1×10^{-11} 1.2×10^{-11}

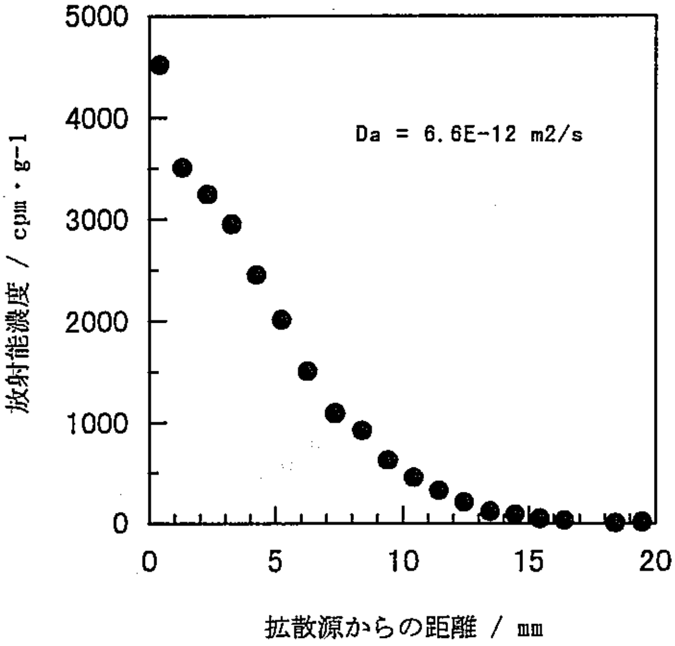


(a)Cs-137の濃度プロファイル（拡散期間25日）

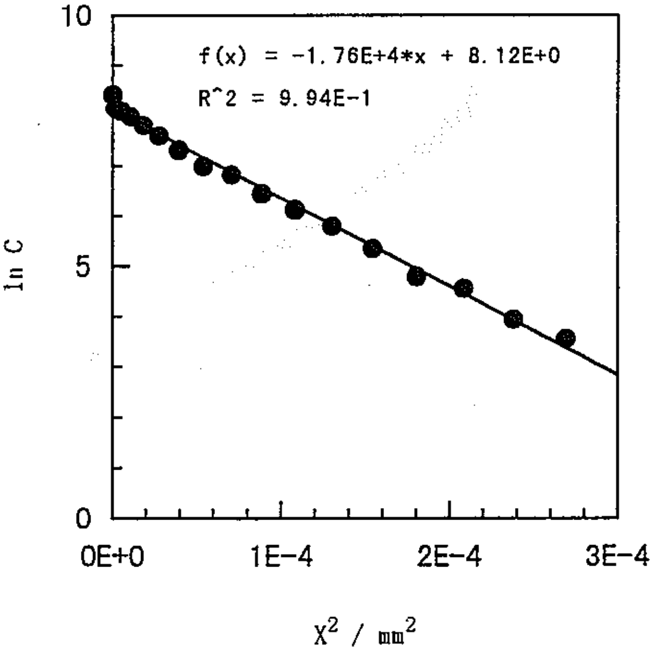


(b)最小二乗法によるフィッティング

図3.2.3-14(1) 非定常拡散試験①（核種Cs-137,ケイ砂混合ベントナイト,充填密度1.8g/cm^3）



(a) Cs-137の濃度プロファイル（拡散期間25日）



(b) 最小二乗法によるフィッティング

図3.2.3-14(2) 非定常拡散試験②（核種Cs-137, ケイ砂混合ベントナイト, 充填密度1.8g/cm^3）

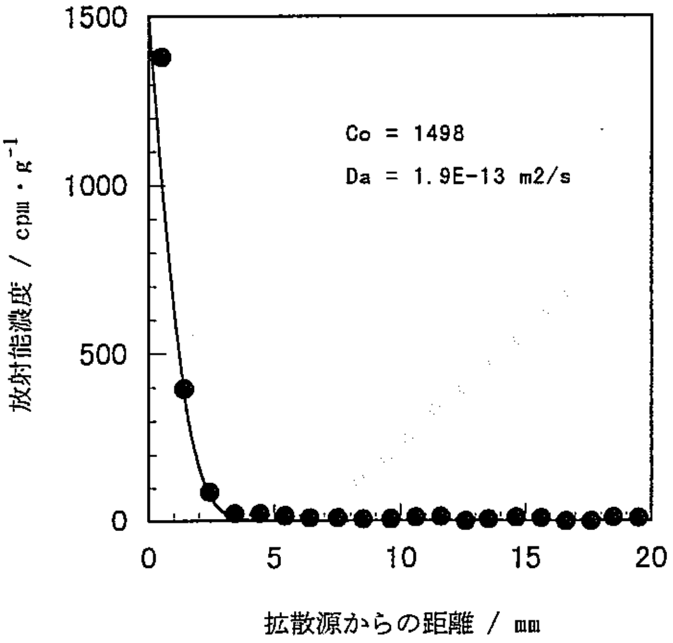


図3.2.3-15(1) 非定常拡散試験① (核種Ni-63, ケイ砂混合ベントナイト, 充填密度1.8 g/cm^3)

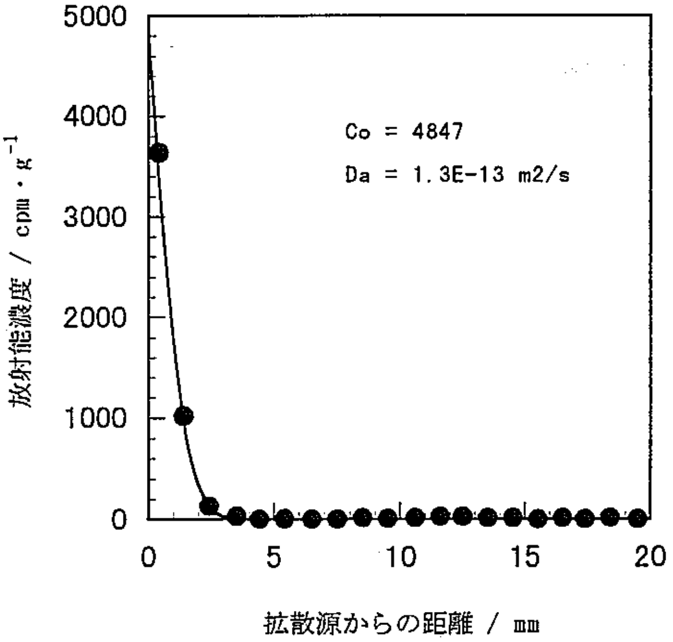
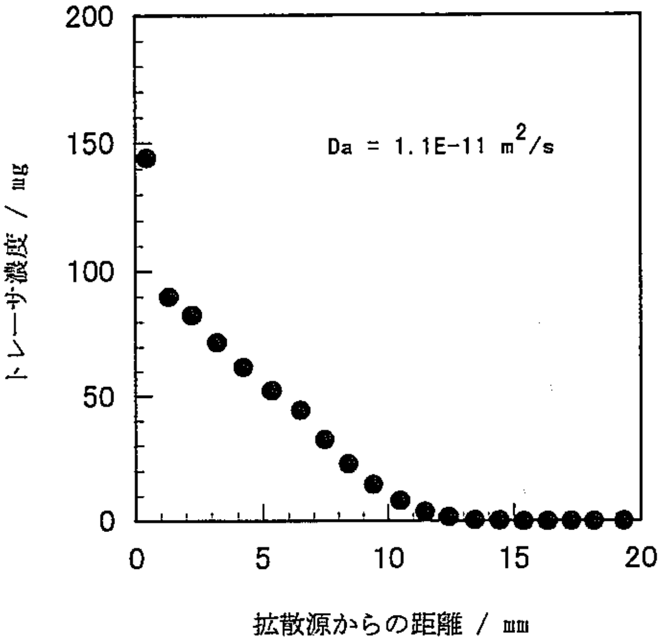
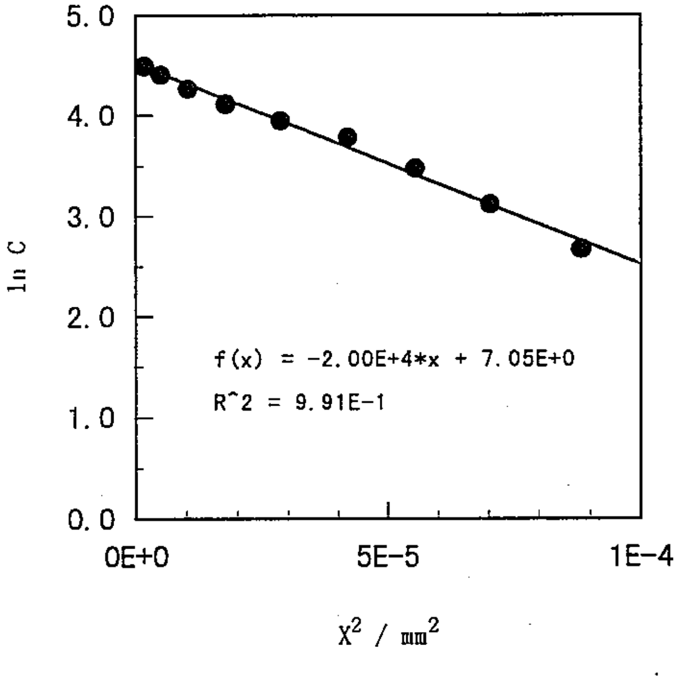


図3.2.3-15(2) 非定常拡散試験② (核種Ni-63, ケイ砂混合ベントナイト, 充填密度1.8 g/cm^3)

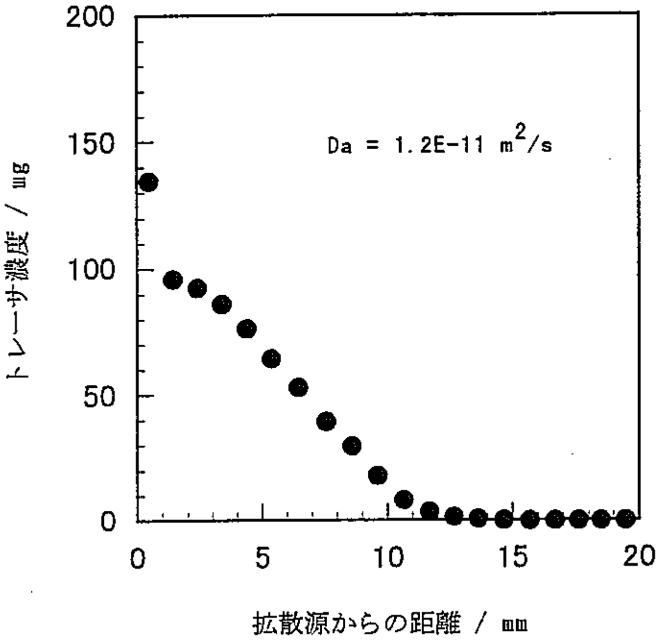


(a) Seの濃度プロファイル（拡散期間 13日）

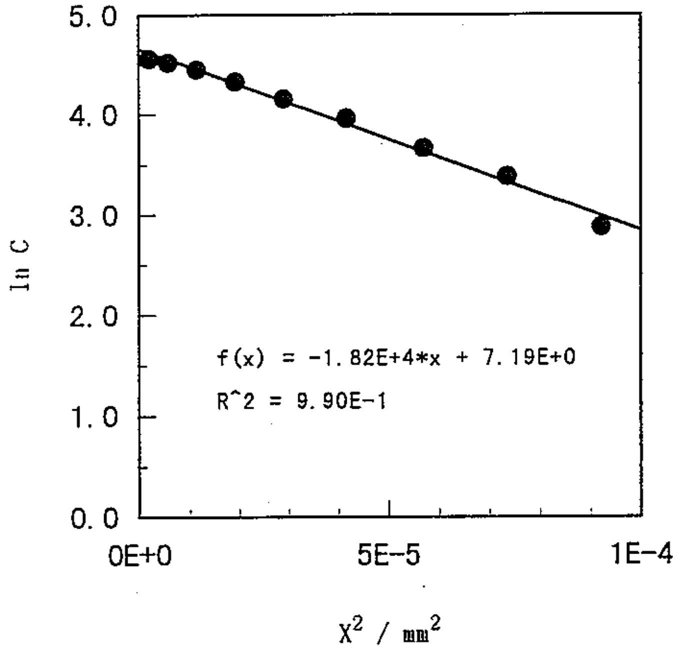


(b) 最小二乗法によるフィッティング

図3.2.3-16(1)　非定常拡散試験①（核種Se, ケイ砂混合ベントナイト, 充填密度1.8g/cm^3）



(a) Seの濃度プロファイル（拡散期間 13日）



(b) 最小二乗法によるフィッティング

図3.2.3-16(2)　非定常拡散試験②（核種Se, ケイ砂混合ベントナイト, 充填密度1.8g/cm^3）

3.3 ベントナイトの間隙水水質推定モデルの検討

(1) 目的

核種の溶解度を支配するベントナイト間隙水水質は、性能評価上重要な要素であるが、現状では実験による直接測定が容易ではないために、第２次取りまとめにおいては、現象理解に基づいたモデルによる推定が必要である。本研究では、ベントナイトの間隙水水質の推定を行うことを目的とし、そのモデルの検討を行った。

(2) 実施概要

計算コードにおける、イオン交換反応の吸着種の活量の与え方について、いくつかの方法での比較計算を行い、その取り扱い方法の検討を行った。また、モデルを用いた計算において、間隙水水質に影響を与える因子とその感度を明らかにし、ベントナイト―水反応試験から得られる情報と比較検討したうえで、処分環境での間隙水水質推定における入力条件の検討を行い、間隙水の計算を行った。

(3) 実施内容

まず、イオン交換モデルにおける吸着化学種の活量補正について評価を行った。また種々のモデルで使用されているモル分率、当量分率、錯体モデルについて比較評価した。その結果、多くのモデルは適切な定数を使用した場合にはほぼ同様の結果を導出することが明らかとなった。なお、調査初期には各モデル間の相違がみられていたが、これは化合物モデルにおける定数値の間違いや、モデル間で適用するパラメータの換算ミスが原因であることが判明した。調査結果を基に、当量分率モデルとその定数が適用されるべきであると推奨した。錯体モデルは、多くの専門家には受け入れられがたい。モル分率モデルと当量分率モデルは熱力学的に適正で定数も一般に適正である。このうち当量分率モデルの方がMINEQLやHYDRAQLのような多くの化学種変化計算コードでの適用がより容易である。

また、不純物の影響については、溶解して空隙水組成に影響を与えると考えられる。しかしその定量は困難なため、ここでは感度解析計算を実施した。その結果次の点が判明した。まず、圧密したクニゲルＶ１中のpHに関して、方解石、石膏、硫化鉄の存在は大きな影響を及ぼす。方解石の溶解平衡によりpHは増加する。石膏の溶解も

しくは多量のNaClの溶解はpHを低下させる。硫化鉄の酸化はpHを大きく下げる。しかし、圧密ベントナイト中のpHはシラノール基の酸塩基反応の平衡や炭酸塩によるバッファ効果により緩衝される。またCO_2に関して閉鎖系を仮定した場合、方解石の溶解によるCO_2分圧の増加が生じる。

ベントナイト空隙水組成に関しては、上記の各点を踏まえてモデル化を行い計算を実施し、種々の条件における空隙水素製を推定した。計算にあたっては、動燃事業団殿が提示している5種類の地下水組成を用いるとともに、併せて炭素鋼製のオーバパックを起源とするヘマタイトやゲーサイト等の腐食生成物の共存についても考慮した。

3.4 コロイドの核種移行に与える影響の評価

3.4.1 目的

本研究は、高レベル放射性廃棄物の地層処分研究の第 2 次取りまとめに向けて、より信頼性の高い、ニアフィールド周辺岩盤中での核種移行評価を行うため、地下水中に共存するコロイドの影響について評価を行うことを目的とする。

3.4.2 実施概要

岩盤中でコロイドが共存する場合の核種移行を評価する場合、コロイド－溶質－岩石間の3相間の相互作用を考慮する必要がある。本研究では、これら相互作用を取り扱う数学的モデルを用いて、コロイドが共存する場合の核種移行解析を行った。さらに、数値解法により崩壊連鎖の影響についても検討を行った。以下に実施した項目を示す。

(1) コロイド－溶質－岩石間の3相間の相互作用を考慮した解析モデルの確証
(2) 処分条件でのコロイド影響の予測評価
(3) コロイド共存下での崩壊連鎖を伴う核種移行

3.4.3 実施内容

(1) コロイド－溶質－岩石間の3相間の相互作用を考慮した解析モデルの確証

コロイドが核種移行に与える影響を評価するにあたり、本年度は、上述したようにコロイド－溶質－岩石間の3相間の相互作用を取り扱う Hwang らのモデル(Hwang et al.、1990)を用いることとした。図 3.4.3-1 には、Hwang らのモデルの概念を示す。Hwang らのモデルでは、移流、拡散の現象に加えて、上述したようにコロイド－イオン－岩盤間の3相間の相互作用が考慮されている。ここでは、Hwang らのモデルの検証を行うとともに、動燃事業団殿で実施する岩石中のコロイド共存系での核種移行試験(COLLOID 試験)の結果を、Hwang らのモデルを用いて予測を行った。また、予測解析では、コロイド－溶質およびコロイド－岩石間の相互作用に関するデータが必要であることから、これらデータ取得のため必要な実験を実施した。

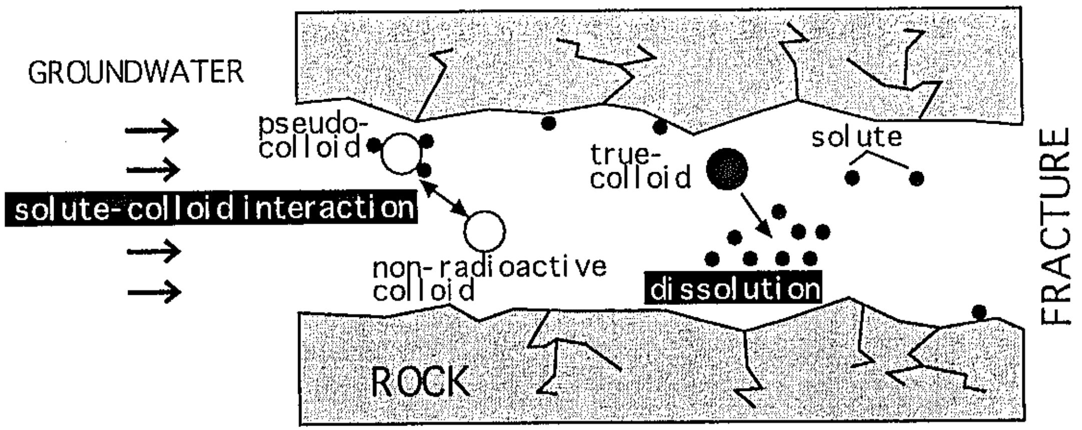


図3.4.3-1　Hwangらのモデルにおけるコロイドと核種の移行の概念
(Hwangら、1990参照)

(ｉ) Hwangらのモデルの検証

(a) Hwangらのモデルの解析解の検証

Hwang et al.(1990)の報告では、コロイドに吸着されたイオンの移行式として、以下の式が提案されている。

$$\varepsilon_1\xi_1\frac{\partial C_1(x,t)}{\partial t}-\varepsilon_1\xi_1 D_1\frac{\partial^2 C_1(x,t)}{\partial x^2}+\varepsilon_1\xi_1 v_1\frac{\partial C_1(x,t)}{\partial x}+\varepsilon_1 S_1(x,t)+\varepsilon_1 S_2(x,t)+\varepsilon_1\xi_1\lambda C_1=0$$

(3.4.3-1 式)

ここで、$C_1(x,t)$; コロイドに吸着されたイオンの濃度、x; 亀裂入口からの距離、t; 時間、ε_1; 亀裂中の地下水の体積分率、ξ_1; 地下水中のコロイドの体積分率、D_1; コロイドの分散係数、v_1; コロイドの流速、$\varepsilon_1 S_1(x,t)$; コロイドが岩盤へ吸着する割合、$\varepsilon_1 S_2(x,t)$; コロイドからイオンが脱離する割合、λ; 崩壊定数である。なお、Hwangらのモデルでは、コロイドが岩盤中を移行する過程で起こる可能性のある物理的なろ過効果は考慮されていない。

一方、コロイドには吸着されないで移行するイオンの移行式については、

$$\varepsilon_1\frac{\partial C_2(x,t)}{\partial t}-\varepsilon_1 D_2\frac{\partial^2 C_2(x,t)}{\partial x^2}+\varepsilon_1 v_2\frac{\partial C_2(x,t)}{\partial x}-\varepsilon_1 S_2(x,t)+\varepsilon_1 S_3(x,t)+\varepsilon_1\lambda C_2+\frac{q(x,t)}{b}=0$$

(3.4.3-2 式)

$$q(x,t)=-\varepsilon_p D_p\frac{\partial N(x,y,t)}{\partial y}\bigg|_{y=b}$$

(3.4.3-3 式)

の式が提案されている。ここで、$C_2(x,t)$; コロイドに吸着されないイオンの濃度、D_2; イオンの分散係数、v_2; イオンの流速、$\varepsilon_1 S_3(x,t)$; イオンが岩盤へ吸着される割合、q(x,t); 岩石マトリクス中へのイオンの拡散、ε_p; 岩石中の空隙率、D_p; 岩石マトリクス中のイオンの拡散係数、N(x,y,t); 岩石マトリクス中の放射性イオンの濃度、b; 亀裂の 1/2 幅である。

岩石に吸着するイオンの濃度 $C_3(x,t)$については、

$$(1-\varepsilon_1)\frac{\partial C_3(x,t)}{\partial t}-\varepsilon_1 S_1(x,t)+(1-\varepsilon_1)\lambda C_3(x,t)=0$$

(3.4.3-4 式)

コロイドに吸着したイオンについては、

$$(1-\varepsilon_1)\xi_2\frac{\partial C_1(x,t)}{\partial t}-\varepsilon_1 S_1(x,t)+(1-\varepsilon_1)\xi_2\lambda C_1(x,t)=0$$

(3.4.3-5 式)

で表されている。ここで、ξ_2; 岩盤に吸着したコロイドの体積比である。

また、岩石マトリクス中でのイオンの遅延係数 R_p は次のようである。

$$R_p\frac{\partial N(x,t)}{\partial t}-D_p\frac{\partial^2 N(x,t)}{\partial y^2}+R_p\lambda N(x,t)=0$$

(3.4.3-6 式)

ここで、各濃度 C_1、C_2、C_3 および体積率 ξ_1、ξ_2 については、次のような平衡定数を用いて表すと仮定している。

$$Kd_1=\frac{\xi_2}{\xi_1},\quad Kd_2=\frac{C_3(x,t)}{C_2(x,t)},\quad Kd_3=\frac{C_1(x,t)}{C_2(x,t)}$$

(3.4.3-7 式)

そして、Hwang らは(3.4.3-7 式)を用いて、(3.4.3-1 式)から(3.4.3-5 式)までを加え、遅延係数 R、分散係数 D および流速 v を導入した C_1 に対する次式を得ている。

$$R\frac{\partial C_1(x,t)}{\partial t}+v\frac{\partial C_1(x,t)}{\partial x}-D\frac{\partial_2 C_1(x,t)}{\partial x^2}+RaC_1(x,t)+\frac{q(x,t)}{\varepsilon_1 b}=0$$

(3.4.3-8 式)

ただし、

$$R=\xi_1\left(1+\frac{1-\varepsilon_1}{\varepsilon_1}Kd_1\right)+\left(1+\frac{1-\varepsilon_1}{\varepsilon_1}Kd_2\right)\frac{1}{Kd_3}$$

$$v = v_1\left(\xi_1 + \frac{v_2}{Kd_3 v_1}\right)$$

$$D = D_1\left(\xi_1 + \frac{D_2}{D_1 Kd_3}\right)$$

(3.4.3-9 式)

初期条件および境界条件は、

$$N(x,\infty,t) = 0,\quad x > 0,\quad t > 0$$

$$N(x,y,t) = \frac{1}{Kd_3}C_1(x,t)$$

$$N(x,y,t) = 0,\quad x > 0,\quad t > 0$$

$$C_1(0,t) = Kd_3 C_0,\quad t > 0$$

$$C_1(\infty,t) = 0,\quad t > 0$$

$$C_1(x,t) = 0,\quad t > 0$$

(3.4.3-10 式)

で表され、Hwang らは、C_1 について以下のような解析解を導いている。なお、 C_0 は入口でのイオン濃度である。

[Hwang らの解析解]

$$C_1 = \frac{2Kd_3 C_0}{\sqrt{\pi}} \int_{\frac{x}{2}\sqrt{R/Dt}}^{\infty} \exp\left(-\frac{\sqrt{v^2 + 4R\lambda D} - v}{2D}x\right)$$

$$\times erfc\left\{\frac{x^2 \varepsilon_p \sqrt{D_p R_p} Kd_3}{8D\varepsilon_1 \eta^2 b\sqrt{t - Rx^2/(4D\eta^2)}}\right\} \exp\left\{-\left(\eta - \frac{xv}{4D\eta}\right)^2\right\} d\eta$$

(3.4.3-11 式)

一方、(3.4.3-1 式)から(3.4.3-10 式)に基づき、本研究において導出した解析解は以下のようであった。

[MMTL で導いた解析解]

$$C_1 = \frac{Kd_3 C_0}{\sqrt{\pi}} \exp(x\nu) \int_{\frac{x}{2}\sqrt{R/Dt}}^{\infty} \exp\left(-\eta^2 - \frac{x^2\nu^2}{4\eta^2}\right) \exp\left(-\alpha x^2\right)$$

$$\times \left\{ \exp\left(-\sqrt{\lambda}Y\right) erfc\left(\frac{Y}{2T} - \sqrt{\lambda}T\right) + \exp\left(\sqrt{\lambda}Y\right) erfc\left(\frac{Y}{2T} + \sqrt{\lambda}T\right) \right\} d\eta$$

(3.4.3-12 式)

ここで、

$$\nu = \frac{v}{2D}, \quad \alpha = \frac{\lambda R}{4D\eta^2}, \quad Y = \frac{Rx^2}{4AD\eta^2}, \quad A = \frac{\varepsilon_1 bRKd_3}{\varepsilon_p\sqrt{R_p D_p}}, \quad T = \sqrt{t - \frac{Rx^2}{4D\eta^2}}$$

(3.4.3-13 式)

である。これらは、Kd$_3$ を無視すると、すなわちコロイドの影響について無視すると、Hwang らのモデルの元となっているコロイドが存在しない場合の核種移行モデル、Tang らのモデル(Tang et al.、1981)の解析解と一致する。そして、(3.4.3-12 式)は λ を無視して整理すると、

$$C_1 = \frac{2Kd_3 C_0}{\sqrt{\pi}} \int_{\frac{x}{2}\sqrt{R/Dt}}^{\infty} \exp\left(-\frac{R}{4D\eta^2}x^2\right)$$

$$\times erfc\left\{ \frac{x^2 \varepsilon_p \sqrt{D_p R_p}}{8D\varepsilon_1 \eta^2 b\sqrt{t - Rx^2/(4D\eta^2)}Kd_3} \right\} \exp\left\{ -\left(\eta - \frac{x\nu}{4D\eta}\right)^2 \right\} d\eta$$

(3.4.3-14 式)

と表され、(3.4.3-11 式)において、erfc 括弧内の Kd$_3$ が分子にあるのは誤りであると判断される。また、本来半減期 λ を扱う項についても、次のように(3.4.3-11 式)と(3.4.3-

14 式)の下線部を対照すると一致しないが、本研究では半減期の影響評価は主な対象ではないことから、取り敢えず Hwang らの文献中の記述に基づくこととした。

・(3.4.3−11式)

$$C_1 = \frac{2Kd_3C_0}{\sqrt{\pi}}\int_{\frac{x}{2}\sqrt{R/Dt}}^{\infty}\underline{\exp\left(-\frac{\sqrt{v^2+4R\lambda D}-v}{2D}x\right)}$$

$$\times erfc\left\{\frac{x^2\varepsilon_p\sqrt{D_pR_p}Kd_3}{8D\varepsilon_1\eta^2b\sqrt{t-Rx^2/(4D\eta^2)}}\right\}\exp\left\{-\left(\eta-\frac{xv}{4D\eta}\right)^2\right\}d\eta$$

・(3.4.3−14式)

$$C_1 = \frac{2Kd_3C_0}{\sqrt{\pi}}\int_{\frac{x}{2}\sqrt{R/Dt}}^{\infty}\underline{\exp\left(-\frac{R}{4D\eta^2}x^2\right)}$$

$$\times erfc\left\{\frac{x^2\varepsilon_p\sqrt{D_pR_p}}{8D\varepsilon_1\eta^2b\sqrt{t-Rx^2/(4D\eta^2)}Kd_3}\right\}\exp\left\{-\left(\eta-\frac{xv}{4D\eta}\right)^2\right\}d\eta$$

そこで、後述する COLLOID 試験の予測解析および処分条件でのコロイド影響の予測については、以下の解析解を計算するプログラムを作成して評価を行うこととした。

[本研究で用いた解析解]

$$C_1 = \frac{2Kd_3C_0}{\sqrt{\pi}}\int_{\frac{x}{2}\sqrt{R/Dt}}^{\infty}\exp\left(-\frac{\sqrt{v^2+4R\lambda D}-v}{2D}x\right)$$

$$\times erfc\left\{\frac{x^2\varepsilon_p\sqrt{D_pR_p}}{8D\varepsilon_1\eta^2b\sqrt{t-Rx^2/(4D\eta^2)}Kd_3}\right\}\exp\left\{-\left(\eta-\frac{xv}{4D\eta}\right)^2\right\}d\eta$$

(3.4.3-15 式)

なお、後述の各核種移行解析では、コロイドが存在しない場合の評価を上式より行う場合は、地下水中のコロイドの体積分率 ξ_1 を無視して解析を行うこととした。

[パラメーター一覧]

$C_1(x,t)$[－]; 疑似コロイド中の核種の濃度
$C_2(x,t)$[－]; 溶液中の核種の濃度
$C_3(x,t)$[－]; 岩石に吸着した核種濃度
x[m]; 移行距離
t[y]; 時間
ε_1[－]; 亀裂中を地下水の体積分率
ε_p[－]; 岩石の空隙率
ξ_1[－]; 地下水中のコロイドの体積比
ξ_2[－]; 岩盤に吸着した疑似コロイドの体積比
v_1[m/y]; コロイドの流速
v_2[m/y]; 地下水流速
D_1[m^2/y]; コロイドの分散係数
D_2[m^2/y]; 核種の分散係数
D_p[m^2/y]; マトリクスへの核種の拡散係数
$\varepsilon_1 S_1(x,t)$[－]; コロイドが岩盤へ吸着する割合
$\varepsilon_1 S_2(x,t)$[－]; コロイドからイオンが脱離する割合
$\varepsilon_1 S_3(x,t)$[－]; 核種が岩盤へ吸着する割合
$N(x,y,t)$[－]; 岩石マトリクス中の核種の濃度
B[m]; 亀裂の 1/2 幅
Kd_1[－]; 岩盤へのコロイドの吸着
Kd_2[－]; 岩盤へのイオンの吸着
Kd_3[－]; コロイドへのイオンの吸着
λ[1/y]; 崩壊定数

(b) 計算プログラムの検証

作成した上記(3.4.3-15 式)を計算するプログラムによる計算結果を、他の核種移行モデルに基づく計算結果と比較することにより、プログラムの検証を行った。表 3.4.3-1 には、(3.4.3-15 式)の計算に必要なパラメータを示すとともに、各パラメータについて設定した値を示す。作成したプログラムが正しければ、表 3.4.3-1 に示した

ように、コロイドの影響を無視し得るようパラメータの値を設定すれば、その計算結果は、既に認知されているイオンのみの移行モデルによる解析結果と良い一致を示すことが考えられる。そこで、ここでは以下に示すヘンリー型吸着の一次元核種移行の一般解による計算結果と比較を行った。

$$\frac{\partial C}{\partial t} = -V_n \frac{\partial C}{\partial x} + D_n \frac{\partial^2 C}{\partial x^2}$$

$$C(0,t) = C_0, \quad t \geq 0$$

$$C(\infty,t) = 0, \quad t \geq 0$$

$$C(x,t) = 0, \quad t = 0$$

(3.4.3-16 式)

$$\frac{C}{C_0} = \frac{1}{2} erfc\left\{\frac{x - V_n t}{2(D_n t)^{1/2}}\right\} + \frac{1}{2}\exp\left(\frac{V_n x}{D_n}\right) erfc\left\{\frac{x + V_n t}{2(D_n t)^{1/2}}\right\}$$

(3.4.3-17 式)

図 3.4.3-2 には、作成した(3.4.3-15 式)を解く計算プログラムによる結果と、(3.4.3-17 式)に基づいて計算した結果を示す。その結果、プログラムによりコロイドの影響を無視して計算したイオンの移行は、既往のイオンのみの移行を解くヘンリー型吸着の一次元核種移行の一般解での計算結果と良い一致を示した。このことから、本研究で作成した計算プログラムについては問題ないものと判断し、後述の種々の計算を行った。

表 3.4.3-1　計算に必要なパラメータとプログラム検証のための設定値

パラメータ	設定値
①Kd_1:岩盤へのコロイドの吸着	0.001[m^3/kg]$^{*)}$
②Kd_2:岩盤へのイオンの吸着	0.5[m^3/kg]$^{*)}$
③Kd_3:コロイドへのイオンの吸着	0.0[m^3/kg]$^{*)}$
④D_1:コロイドの分散係数	$4.4x10^{-1}$[m^2/y]
⑤D_2:核種の分散係数	$3.2x10^{-1}$[m^2/y]
⑥ε_1:亀裂中を地下水の体積分率	0.99[-]
⑦b:亀裂の 1/2 幅	$4x10^{-2}/2$[m]
⑧ε_p:岩石の空隙率	0.02[-]
⑨D_p:マトリクスへの核種の拡散係数	$5x10^{-15}$[m^2/y]
⑩R_p:遅延係数	$R_p=1+(1-\varepsilon_p)\rho Kd_2/\varepsilon_p$
⑪v_1:コロイドの流速	$4.4x10^{-2}$ [m/y]
⑫v_2:地下水流速	$3.2x10^{-2}$[m/y]
⑬ξ_1:地下水中のコロイドの体積比	$1x10^{-50}$[-]

*) Hwang らのモデルでは、各 Kd パラメータは[-]で与える必要があるため、計算を実施するにあたっては岩石およびコロイドの比重[kg/m^3]を乗じた。

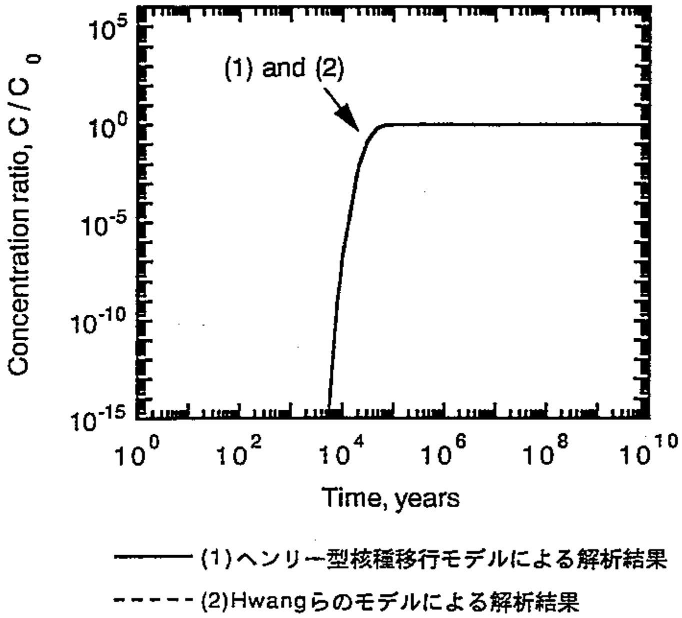


図3.4.3-2　コロイドが存在しない場合の核種移行解析結果の比較

(ⅱ) Hwangらのモデル確証試験のためのデータ取得

動燃事業団殿では、コロイドを共存する場合の岩盤中核種移行挙動の解明等を目的として、「COLLOID 試験」を進めている。ここでは、Hwangらのモデルの確証に資するため、動燃事業団殿で実施するCOLLOID試験のうち、花崗岩亀裂中でのベントナイトコロイドと$Sr^{2+}(SrI_2)$の移行試験の結果を、(3.4.3-15 式)に示した解析解より予測を行った。この際、予測解析に必要な各パラメータの値は試験条件に基づき設定したが、コロイド－岩石間(Kd_1)、イオン－岩石間(Kd_2)、コロイド－イオン間(Kd_3)の吸着性に関するデータについては取得されていないことから、

- ・ベントナイトコロイド－花崗岩
- ・$Sr^{2+}(SrI_2)$－花崗岩
- ・ベントナイトコロイド－$Sr^{2+}(SrI_2)$

の吸着試験を実施して、求めた分配係数を予測計算に資すこととした。

(a) 試験方法

ベントナイトコロイド－花崗岩、$Sr^{2+}(SrI_2)$－花崗岩およびベントナイトコロイド－$Sr^{2+}(SrI_2)$の分配係数を取得するため、バッチ式吸着試験を実施した。試験手順を以下に示すとともに、図3.4.3-3にはこの際の試験フローを示す。

①ベントナイトコロイド分散溶液の作製

試験に供するベントナイトコロイド分散液については、ベントナイトの粉末を蒸留水中に1g/500mlの割合で分散させ、24時間振とうさせたのち、ポアサイズ0.8μmのメンブランフィルタでろ過したものを用いた。この際、ベントナイトの粉末については、吸着試験においてベントナイト中の種々雑多な同伴鉱物から生成したコロイドの影響を無視できるよう、モンモリロナイトを99wt.%以上含有するクニピアF(クニミネ工業製)を使用した。

得られたモンモリロナイトコロイドの量は、次のようにして求めた。モンモリロナイトは、$(Na, Ca_{1/2})_{0.33}(Al_{1.67}Mg_{0.33})Si_4O_{10}(OH)_2$ F.W.=366.33の組成式で表され、Si:Al:Mg比は4:1.67:0.33である。そこで、モンモリロナイトの成分であるSi、AlおよびMgの液中での濃度を、限外ろ過処理(MWCO; 10,000)の有無に分けて測定し、そのSi、AlおよびMg比から液中に分散するモンモリロナイトコロイドの濃度を算出した。この際、Si、AlおよびMgの濃度測定は、ICP発光分光分析装置を用いて行った。

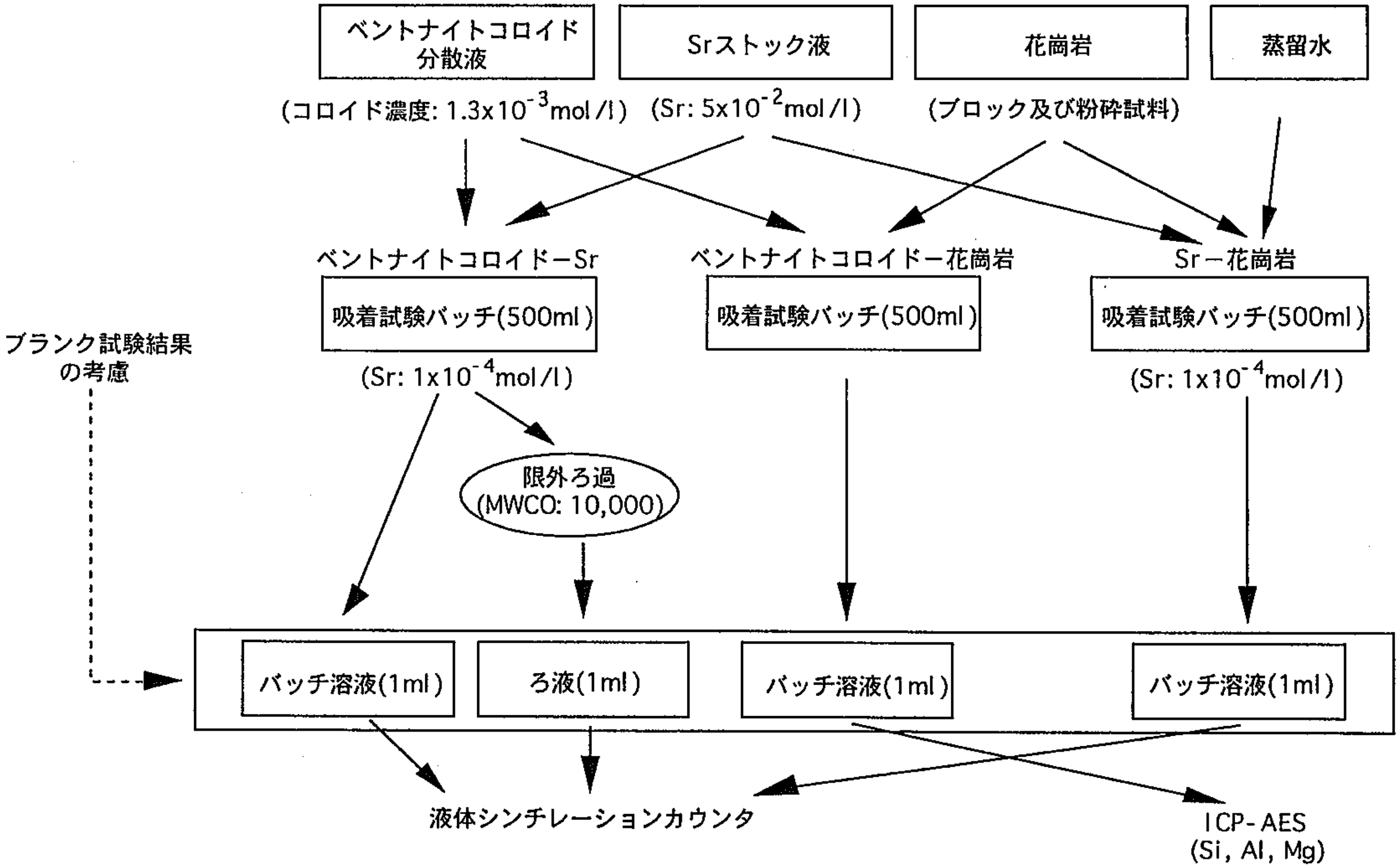


図3.4.3-3　吸着試験のフロー図

測定結果を表 3.4.3-2 に示す。それから分かるように、Si、Al および Mg の元素濃度比は、上述のモンモリロナイトの組成式における元素比とほぼ一致した。このことから、ここで生成したモンモリロナイトコロイドの濃度は、Al 比をベースに算出した。

モンモリロナイトコロイドの生成量(mol/l)
　＝ 分画したコロイド成分中の Al 濃度(mol/l)／1.67

その結果、吸着試験に供するモンモリロナイトコロイドの濃度は、1.3×10^{-3}mol/l の濃度であると推算された。

表 3.4.3-2　モンモリナイトを分散させた液中の Si、Al および Mg の分析結果

	ろ過処理後の濃度*[1] [mol/l]	イオン成分濃度*[2] [mol/l]	コロイド成分濃度*[3] [mol/l]
Si	5.0×10^{-3}	8.5×10^{-5}	4.9×10^{-3}
Al	2.1×10^{-3}	$< 3.7\times10^{-5}$	2.1×10^{-3}
Mg	4.6×10^{-4}	4.6×10^{-5}	4.1×10^{-4}

*1：メンブランフィルタ(0.8 μm)でろ過後の濃度
*2：限外ろ過(MWCO 10,000)後の濃度
*3：コロイド成分 ＝ (*1) − (*2)

②Sr ストック液の作製

市販のヨウ化ストロンチウム(SrI_2、特級)を蒸留水に溶解させ、5×10^{-2}mol/l の Sr のストック液を作製した。

③花崗岩試料の作製

花崗岩は、動燃事業団殿より支給された岩手県釜石鉱山産のものを使用した。支給された花崗岩については、動燃事業団殿の COLLOID 試験では亀裂面が平滑処理(バフ研磨)された花崗岩が扱われることから、本試験でもベントナイトコロイドおよび Sr のそれら花崗岩への吸着性能をより再現し得るよう、表面をバフ研磨したブロック状花崗岩(25mm 角)へと加工した。

また、後述の Hwang らのモデルによる処分環境下でのコロイドの影響の予測評価では、ベントナイトコロイド(モンモリロナイトコロイド)－粉砕花崗岩間の吸着性に関するデータも必要なことから、支給された花崗岩からは、粉砕して 38～42 μm に分級したものも用意した。粉砕した花崗岩試料の比表面積は、BET 法により測定した結果、

0.39m^2/g であった。

④吸着試験

・モンモリロナイトコロイド－花崗岩

作製したモンモリロナイトコロイド分散液(コロイド濃度 1.3×10^{-3}mol/l)500ml をポリ瓶に入れ、そこに花崗岩のブロック 1 個を入れたバッチを作製した。また、後述の Hwang らのモデルによる処分環境下でのコロイドの影響の予測評価では、モンモリロナイトコロイド－粉砕花崗岩間の吸着性に関するデータも必要なことから、ここではモンモリロナイトコロイド分散液 500ml に粉砕した花崗岩 2g を入れたバッチも作製し、これらは 24 時間振とうさせたのち静置した。

・Sr^{2+}(SrI_2)－花崗岩

Sr ストック液 1ml を蒸留水により希釈して、吸着試験用溶液 500ml(Sr 濃度 1×10^{-4}mol/l)を用意して、花崗岩ブロック 1 個を入れたバッチを作製した。これらは、上記同様 24 時間振とうさせたのち静置した。

・モンモリロナイトコロイド－ Sr^{2+} (SrI_2)

Sr ストック液 1ml を作製したモンモリロナイトコロイド分散液(コロイド濃度 1.3×10^{-3}mol/l)により希釈して 500ml(Sr 濃度 1×10^{-4}mol/l)とし、24 時間振とうさせたのち静置した。

なお、上記 Sr を用いた吸着試験では、トレーサ量の Sr-90 のスパイクを行った。

⑤ブランク試験

Sr ストック液を蒸留水により希釈した溶液(Sr 濃度 1×10^{-4}mol/l)、およびモンモリロナイトコロイド分散液で希釈した溶液(コロイド濃度 1.3×10^{-3}mol/l)をそれぞれポリ瓶に 500ml 入れて、ブランク試験用のバッチを作製した。また、花崗岩試料についても、蒸留水 500ml の入ったポリ瓶にブロック試料 1 個および粉砕試料 2g を各々入れたバッチを作製して、これらは 24 時間振とうさせたのち静置した。

なお、Sr を用いたブランク試験は、上記吸着試験と同様に、トレーサ量の Sr-90 をスパイクした。

⑥吸着量の測定

吸着試験における各々のバッチ試料の液相部を、静置後 1 日目、3日目、7 日目および 14 日目にサンプリングし、吸着量について測定を行った。以下に、吸着量の測定方法を示す。

・花崗岩に吸着したモンモリロナイトコロイド量の測定

サンプリングした液中でのSi、AlおよびMgの濃度をICP発光分光分析装置を用いて測定し、初期濃度と比較することにより、花崗岩に吸着したモンモリロナイトコロイドの量を求めた。この際、花崗岩から溶出した同種のイオン量およびモンモリロナイトコロイドの容器壁への吸着量については、モンモリロナイトコロイドおよび花崗岩のブランク試験の結果から評価、考慮した。

・Srの花崗岩への吸着量

サンプリングした液中のSr濃度を液体シンチレーションカウンタを用いて測定し、初期濃度と比較することにより花崗岩に吸着したSrの量を求めた。Srの容器壁への吸着量については、Sr^{2+} (SrI_2)のブランク試験の結果から評価、考慮した。

・Srのモンモリロナイトコロイドへの吸着量

サンプリングした液相は、限外ろ過(MWCO 10,000)を行ったものと行わないもに分けてSrの濃度を測定することにより、モンモリロナイトコロイドに吸着したSrの量を算出した。この際、Srの濃度は、上記同様に液体シンチレーションカウンタを用いて測定を行った。また、モンモリロナイトコロイドやSrの容器壁への吸着量については、上記同様、ブランク試験の結果から評価、考慮した。

なお、サンプリング時には、各吸着試験バッチの液相のpHについても測定を行ったが、いずれもpHも8～9であったことから、本試験ではとくに試薬を用いての厳密なpH調整は行わなかった。

(b) 試験結果

測定した吸着量を表 3.4.3-3 に示す。その結果から、以下の式に基づきそれぞれの分配係数 Ka または Kd を算出した。

$$Ka=\frac{C_0-C}{C}\frac{V}{S} \text{または} Kd=\frac{C_0-C}{C}\frac{V}{M}$$

(3.4.3-18 式)

ここで、C_0: ブランク試験バッチ中の物質 i の濃度、C: 吸着試験バッチ中の物質 i の濃度、V: 液量、S: 表面積および M: 固相重量である。算出した分配係数については、表 3.4.3-3 に併せて示した。

その結果、モンモリロナイトコロイドは、表面を平滑処理した花崗岩のブロックには吸着されず、$Ka=0m^3/m^2$ であった。これに対して、粉砕した花崗岩(38～42 μm)への分配係数は $Kd=2.1\times10^{-3}m^3/kg$ であった。

また、Sr と花崗岩ブロックの分配係数は、吸着試験 14 日目では $Ka=7.7\times10^{-2}m^3/m^2$ と算出された。しかしながら、表 3.4.3-3 からも分かるように、14 日目の値が、3 日目、7 日目の値と比較して定常に達した値であるとは考えにくい。そこで、ここでは結果の保守性を確保するため、Sr と花崗岩ブロック間の分配係数については 3 日目の吸着試験データに基づき、$Ka=6.2\times10^{-2}m^3/m^2$ を設定することとした。

Sr とモンモリロナイトコロイドの分配係数については、$Kd=1.5\times10^3m^3/kg$ と算出された。これに対し、動燃事業団殿で実施する COLLOID 試験では、亀裂表面を平滑処理した花崗岩を扱うことから、Hwang らのモデルにより試験結果を予測するにあたっては、入力パラメータであるコロイド－岩盤、イオン－岩盤およびコロイド－イオン間の各吸着量は表面分配係数で与えた方が良い考えられる。そこで、$Kd=1.5\times10^3m^3/kg$ の値は、モンモリロナイト粒子の比表面積が $800\times10^3m^2/kg$ 程度(日本粘土学会、1987)であることから、表面分配係数 $Ka=1.9\times10^{-3}m^3/m^2$ に換算して Hwang らのモデルの入力値とした。

表3.4.3-3　吸着試験の結果

(吸着試験)

	モンモリロナイトのブロック花崗岩への吸着量		モンモリロナイトの 粉砕花崗岩への吸着量		Srのブロック 花崗岩への吸着量		Srのモンモリロナイトへの吸着量	
	液相中コロイド濃度 (mol/l)	分配係数 (m3/m2)	液相中コロイド濃度 (mol/l)	分配係数 (m3/kg)	液相中Sr濃度 (cpm/ml)	分配係数Ka (m3/m2)	液相中Sr濃度 (cpm/ml)	分配係数Kd (m3/kg)
1日目	1.30E-03	0.00E+00	1.20E-03	2.10E-03	10100	0	20	1.00E+03
3日目	1.30E-03	0.00E+00	1.20E-03	2.10E-03	6840	6.10E-02	11	1.80E+03
7日目	1.30E-03	0.00E+00	1.20E-03	2.10E-03	6292	7.50E-02	14	1.50E+03
14日目	1.30E-03	0.00E+00	1.20E-03	2.10E-03	6228	7.70E-02	14	1.50E+03

(ブランク試験)

	液相中コロイド濃度 (mol/l)	液相中Sr(トレーサ)濃度 (cpm/ml)	ブロック花崗岩からの溶出 Si, Al, Mg濃度	粉砕花崗岩から溶出 Si, Al, Mg濃度
1日目	1.30E-03	10065	検出下限値以下	検出下限値以下
3日目	1.30E-03	9955	〃	〃
7日目	1.30E-03	9854	〃	〃
14日目	1.30E-03	9870	〃	〃

(c) Hwangらのモデルによる COLLOID 試験結果の予測

表 3.4.3-4 には、COLLOID 試験の結果を予測するにあたって設定した各解析パラメータの値を示す。図 3.4.3-4 には、その値から予測された COLLOID 試験におけるコロイド共存下でのイオンの移行、およびコロイドが存在しない場合のイオンのみの移行を示す。その結果、両者は約83時間(約300,000sec)でCOLLOID試験で扱う岩石亀裂カラム(カラム長さ 30cm)を破過することが予測された。また、動燃事業団殿から提示されたCOLLOID 試験の条件では、両者の破過に時間的ずれがないことが予測された。

表 3.4.3-4　COLLOID 試験の結果を予測するため与えた各パラメータ設定値

パラメータ	設定値
①Kd_1 (岩盤へのコロイドの吸着)	$Ka_1=0m^3/m^2$ *)
②Kd_2 (岩盤へのイオンの吸着)	$Ka_2=6.1\times10^{-2}\ m^3/m^2$ *)
③Kd_3 (コロイドへのイオンの吸着)	$Ka_3=1.9\times10^{-3}\ m^3/m^2$ *)
④D_1 (コロイドの分散係数)	$D_1= De_1+\alpha_1 v_1$ より算出 De_1: コロイドの拡散係数($3.2\times10^{-5}m^2/yr$) α_1: コロイドの分散長($0.1\times L$)
⑤D_2 (核種の分散係数)	$D_2= De_2+\alpha_2 v_2$ より算出 De_2: イオンの拡散係数($5.7\times10^{-3}m^2/yr$) α_2: 核種の分散長($0.1\times L$)
⑥ε_1 (亀裂中の地下水の体積分率)	$\varepsilon_1=0.89$
⑦b (亀裂の 1/2 幅)	$0.5\times10^{-3}/2m$ (COLLOID 試験で扱う花崗岩の亀裂幅)
⑧ε_p (岩石の空隙率)	$\varepsilon_p=0.02$ (釜石鉱山産花崗岩データ)
⑨D_p (岩石マトリクスへの核種の拡散係数)	D_p ; $0m^2/yr$ (v_2 の値から影響しないと判断)
⑩R_p (遅延係数)	$R_p=1+Ka_2/b$ より算出
⑪v_1 (コロイドの流速)	$v_1=1.4v_2$ (HDC 現象を考慮した際の最大値)
⑫v_2 (地下水流速)	$v_2=94.5m/yr$ (COLLOID 試験での試験条件)
⑬ξ_1 (地下水中のコロイドの体積比)	$\xi_1=1.8\times10^{-4}$ (COLLOID 試験での試験条件)

*) Hwang のモデルでは、各 Ka パラメータは[-]で与える必要があるため、計算を実施するにあたってはCOLLOID試験においてイオンおよびコロイドが岩石と反応する[S/V]を乗じた。

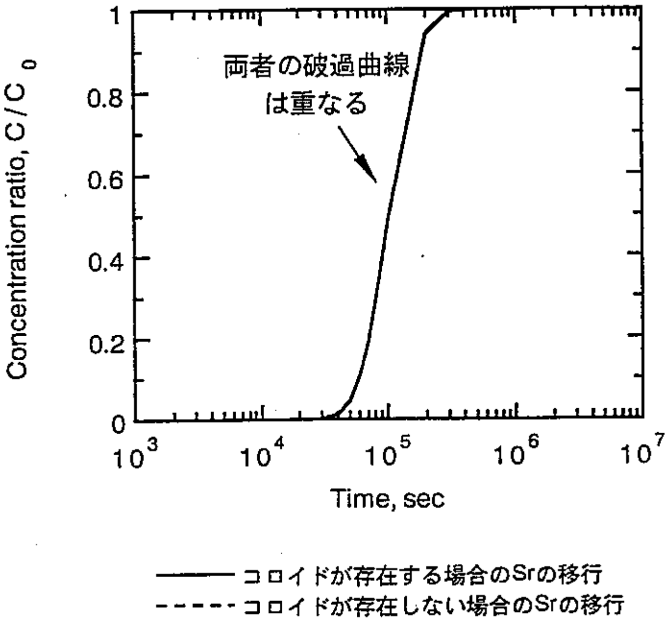


図3.4.3-4　Hwangらのモデルによる COLLOID試験の予測

(2) 処分条件でのコロイドの影響の予測評価

地層処分システムの性能評価を行う上で重要な核種については、①溶出開始時の核種のインベントリ、②放射線学的影響上の重要性、③半減期を考慮し、また諸外国の性能評価も参考にして、

Am-243 — Pu-239 — U-235
Am-241 — Np-237 — U-233
Pu-240 — U-236 — Th-232
U-238 — U-234 — Th-230
Cs-135, Sn-126, Pd-107, Tc-99, Zr-93, Se-79

の 11 元素 18 核種が評価対象核種として選定されている(動燃事業団、高レベル放射性廃棄物地層処分研究開発の技術報告書、1992)。ただし、ここでは Am、Pu、U および Th については、そのうちの代表核種として Am-243、Pu-239、U-235 および Th-230 を選定し、作成した(3.4.3-15 式)の計算プログラムを用いて、コロイドを共存する場合の核種移行について解析を行った。

(ⅰ) 半減期を考慮しない場合の解析

まず、本解析では、選定した 11 核種について、半減期を考慮しないで($\lambda=0$ として)コロイド・核種移行解析を実施した。計算に必要なパラメータは、保守的かつ処分地層の環境を考慮して設定した。表 3.4.3-5 および表 3.4.3-6 には、設定したパラメータの値を示すが、これらは動燃事業団殿がこれまでに取得した実験データ、および調査した深地層データに基づいた。ただし、表 3.4.3-5 に示した Kd_1 の値は、これまでにデータ取得がされた例がなかったことから、既述したように、本研究において取得した粉砕花崗岩に対するベントナイトコロイドの吸着データを基に設定した。評価地点は L=100m とした。なお、本解析において、ベントナイトコロイドの花崗岩への吸着量を粉砕試料に対するデータで設定したことについては、他の入力パラメータである核種と花崗岩間の分配係数についても、粉砕岩石に対するデータしか得られていないことに帰すものである。

解析結果を図 3.4.3-5～図 3.4.3-15 に示す。その結果、コロイドが共存する場合、

Kd_3の値が大きいほど、すなわち、コロイドへの吸着性能の高い核種ほど、移行が助長される傾向にあることが示された。表 3.4.3-7 には、(3.4.3-9 式)から導出されるコロイドを共存する場合の核種の v/R と、コロイドの影響を考慮しないで計算した核種の v_2/R_2 の値を示す。それからも分かるように、Kd_3の値が大きいほど $(v/R)/(v_2/R_2)$ の比は高く、得られた破過曲線はそれを反映する。

また、表 3.4.3-7 に示した $(v/R)/(v_2/R_2)$ 比に基づけば、コロイド(ここでは、ベントナイトコロイド)が共存することで、2倍以上顕著に移行が助長される核種としては Am-243、U-238 および Sn-126 が挙げられ、これらはいずれも Kd_3>1m³/kg であることが分かる。

表 3.4.3-5 主要 11 元素の移行解析に必要な各パラメータの設定値

パラメータ	設定値
①Kd_1 (岩盤へのコロイドの吸着)	$Kd_1=0.001m^3/kg$ *)
②Kd_2 (岩盤へのイオンの吸着)	表 3.4.3-6 参照 *)
③Kd_3 (コロイドへのイオンの吸着)	表 3.4.3-6 参照 *)
④D_1 (コロイドの分散係数)	$D_1= De_1+\alpha_1 v_1$ より算出 De_1: コロイドの拡散係数($3.2x10^{-5}m^2/yr$) α_1: コロイドの分散長(0.1xL)
⑤D_2 (核種の分散係数)	$D_2= De_2+\alpha_2 v_2$ より算出 De_2: イオンの拡散係数($5.7x10^{-3}m^2/yr$) α_2: 核種の分散長(0.1xL)
⑥ε_1 (亀裂中の地下水の体積分率)	$\varepsilon_1=0.99$ (飽和体を仮定)
⑦b (亀裂の 1/2 幅)	$4\times10^{-2}/2m$ (PNC 核種移行解析用データ参照)
⑧ε_p (岩石の空隙率)	$\varepsilon_p=0.02$ (釜石鉱山産花崗岩データ)
⑨D_p (岩石マトリクスへの核種の拡散係数)	$D_p=1.6\times10^{-7}m^2/yr$ (PNC 核種移行解析用データ参照)
⑩R_p (遅延係数)	$R_p=1+(1-\varepsilon_p)\rho Kd_2/\varepsilon_p$ より算出
⑪v_1 (コロイドの流速)	$v_1=1.4v_2$ (HDC 現象を考慮した際の最大値)
⑫v_2 (地下水流速)	$v_2=3.2\times10^{-2}m/yr$ (PNC 核種移行解析用データ参照)
⑬ξ_1 (地下水中のコロイドの体積比)	$\xi_1=1.0\times10^{-4}$ (PNC TN1100 96-010)

*) Hwang らのモデルでは、各 Kd パラメータは[-]で与える必要があるため、計算を実施するにあたっては岩石およびコロイドの比重[kg/m³]を乗じた。

表 3.4.3-6 評価対象 11 核種の Kd_2 および Kd_3 の設定値

元素	Kd_2[m^3/kg]	Kd_3[m^3/kg]
Am-243	0.5	5
Pu-239	0.5	1
U-238	1	10
Np-237	0.5	1
Th-230	0.5	1
Cs-135	0.01	0.01
Sn-126	1	5
Pd-107	0.1	0.01
Tc-99	0.1	0.5
Zr-93	0.1	1
Se-79	0.01	0

表 3.4.3-7 コロイドの影響の有無による核種の移行速度の比較

	v/R (m/yr)	v_2/R_2 (m/yr)	(v/R)/(v_2/R_2)	Kd_1 (m^3/kg)	Kd_2 (m^3/kg)	Kd_3 (m^3/kg)
Am-243	5.8E-3	2.2E-3	2.6	0.001	0.5	5
Pu-239	3.0E-3	2.2E-3	1.4		0.5	1
U-238	5.0E-3	1.2E-3	4.2		1	10
Np-237	3.0E-3	2.2E-3	1.4		0.5	1
Th-230	3.0E-3	2.2E-3	1.4		0.5	1
Cs-135	2.5E-2	2.5E-2	1.0		0.01	0.01
Sn-126	3.1E-3	1.2E-3	2.6		1	5
Pd-107	8.8E-3	8.8E-3	1.0		0.1	0.01
Tc-99	1.0E-2	8.8E-3	1.1		0.1	0.5
Zr-79	1.1E-2	8.8E-3	1.3		0.1	1

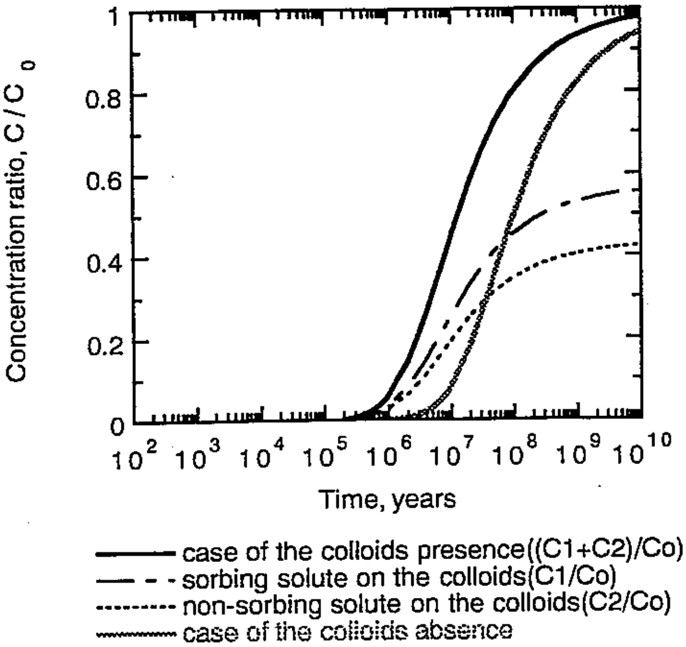


図3.4.3-5　Amの移行(半減期を考慮しない場合)

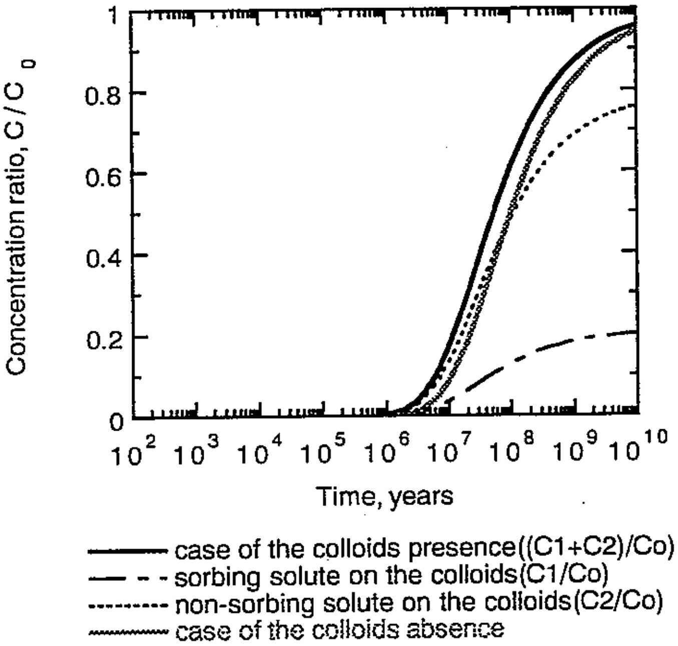


図3.4.3-6　Puの移行(半減期を考慮しない場合)

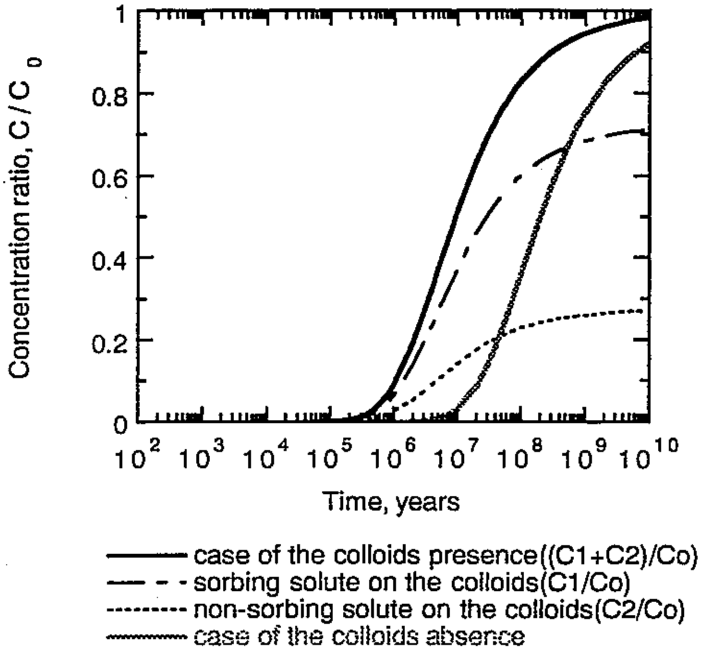


図3.4.3-7　Uの移行(半減期を考慮しない場合)

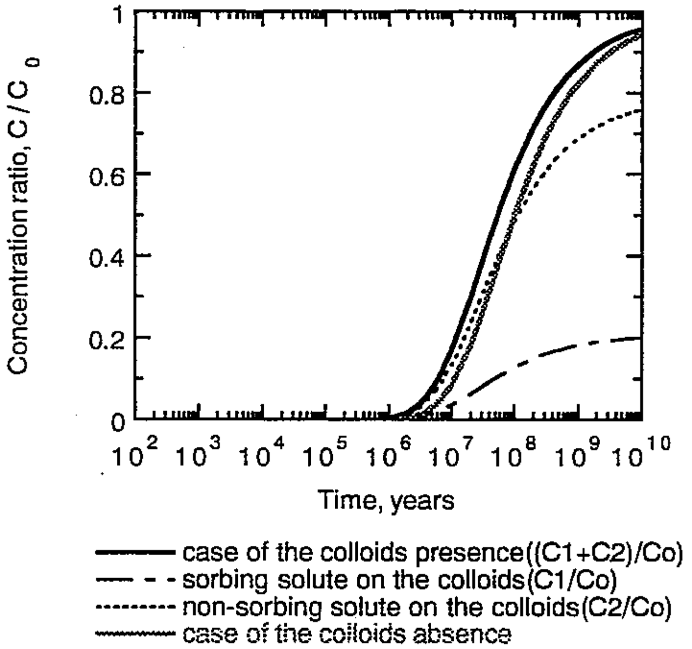


図3.4.3-8　Npの移行(半減期を考慮しない場合)

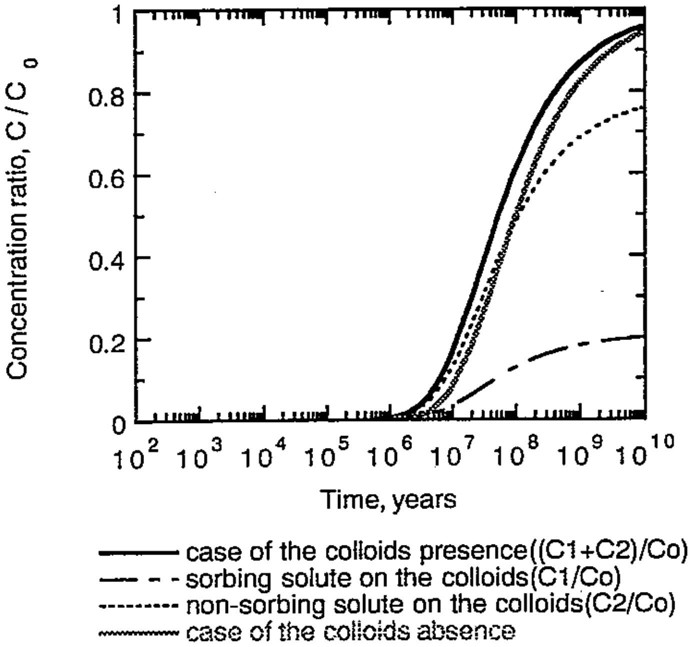


図3.4.3-9 Thの移行(半減期を考慮しない場合)

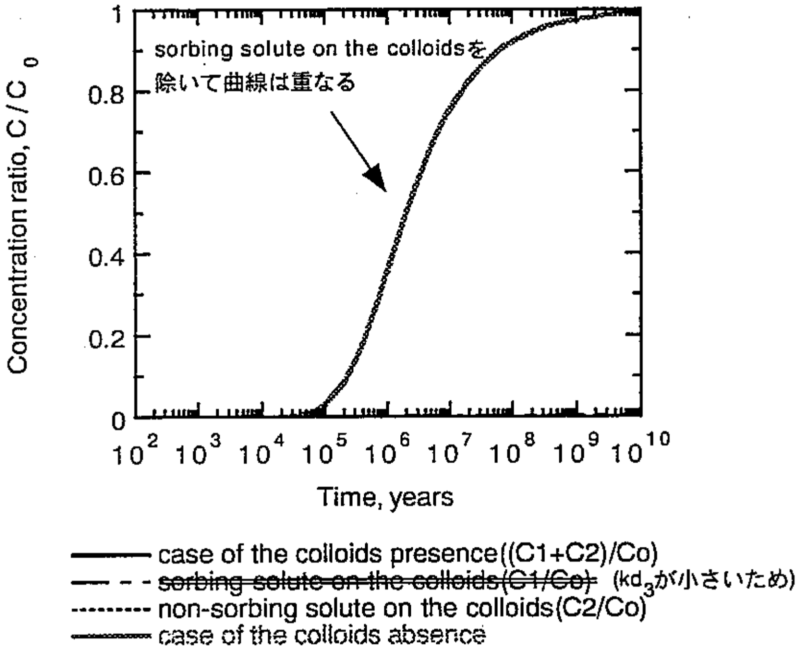


図3.4.3-10 Csの移行(半減期を考慮しない場合)

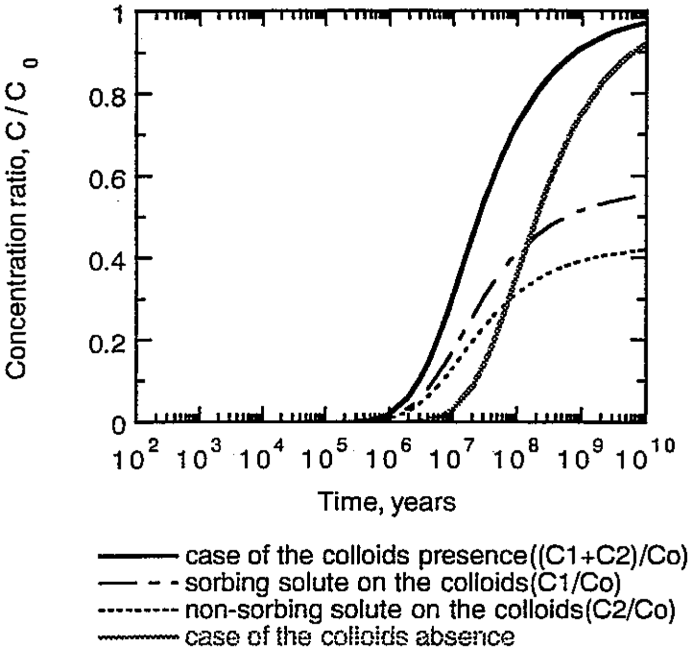


図3.4.3-11　Snの移行(半減期を考慮しない場合)

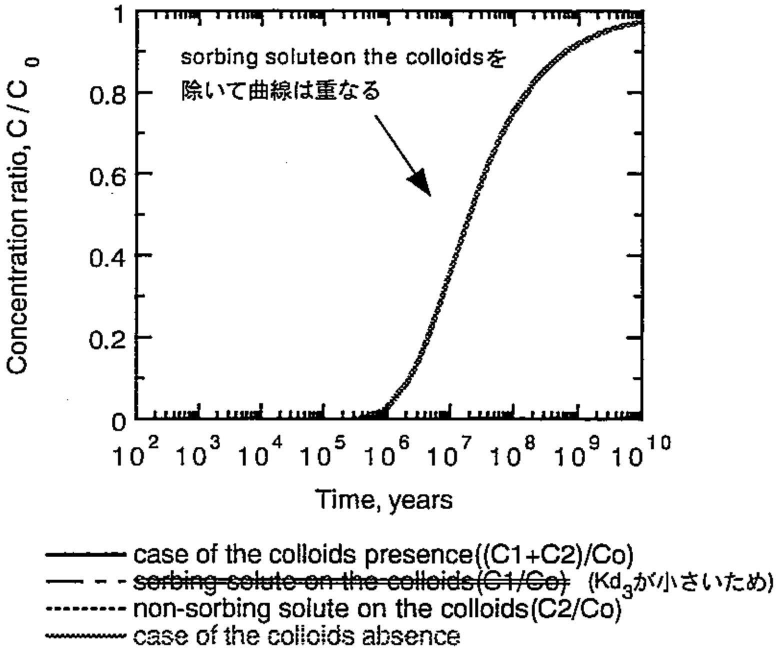


図3.4.3-12　Pdの移行(半減期を考慮しない場合)

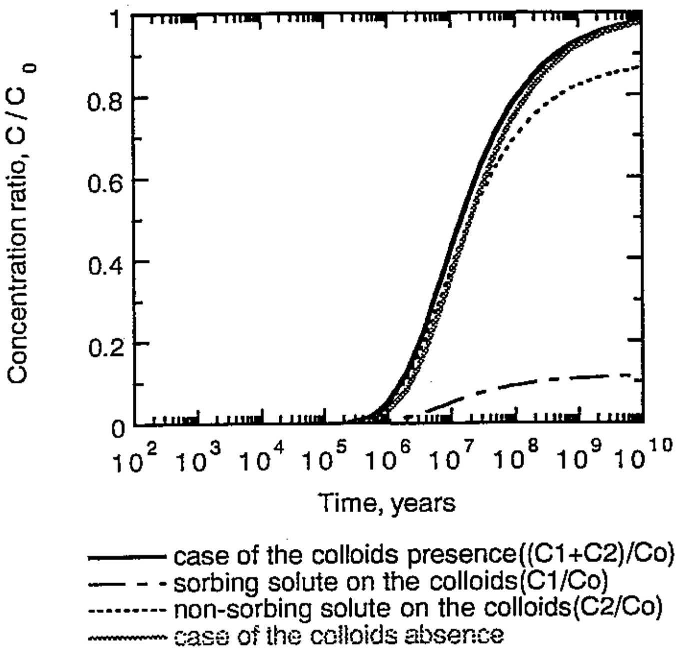


図3.4.3-13　Tcの移行(半減期を考慮しない場合)

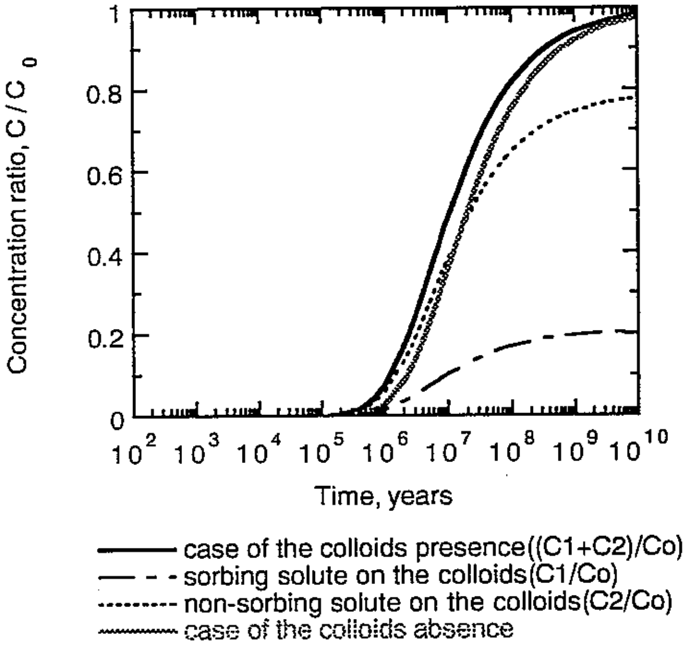


図3.4.3-14　Zrの移行(半減期を考慮しない場合)

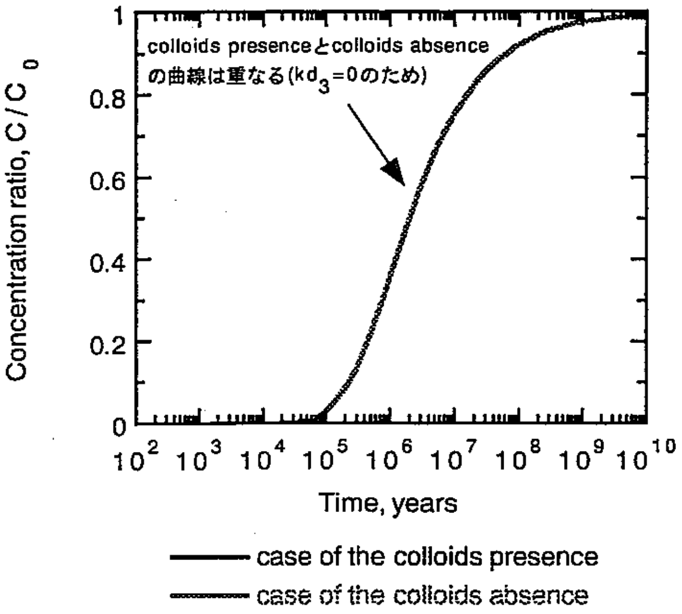


図3.4.3-15　Seの移行(半減期を考慮しない場合)

(ⅱ) 半減期を考慮した場合の解析

ここでは、選定した11核種について、半減期を考慮して核種移行解析を実施した。結果を、図 3.4.3-16～図 3.4.3-26 に示す。図から明らかなように、評価地点(L=100m)での核種移行率は、半減期を考慮することにより移行率は低下している。とくに、選定11核種のうちでは半減期の短いAm-243やPu-239のピーク濃度は、他の核種と比較して著しく低下している。

また、表 3.4.3-8 には、(3.4.3-15 式)のコロイド・核種移行の解析解において、半減期を考慮する項のみを計算した結果を示す。半減期の影響はとくにそれら値を乗じて評価されることから、得られた破過曲線は、それを反映したアウトプットとなっている。

ただし、解析解において半減期の影響を評価する項は、Hwang らの報告する解析解(3.4.3-11 式)と、本研究で導いた解析解(3.4.3-15 式)では一致しておらず、また本研究ではどちらが適切か判断できなかったことから、取り敢えず Hwang らの記述(3.4.3-15 式)に基づいて計算を行った。したがって、計算結果の取り扱いは、あくまでも半減期の影響に関する定性的解釈にとどめるべきであり、その影響を定量的に評価するためにはさらに検討が必要であると考えられる。

表 3.4.3-8　核種の半減期と(3.4.3-15 式)に乗じる値の関係

	半減期(yr) $T_{1/2}$	$\exp\left(-\frac{\sqrt{v^2+4R\lambda D}-v}{2D}x\right)$
Am-243	$7.37\text{x}10^3$	0.22
Pu-239	$2.41\text{x}10^4$	0.40
U-238	$4.47\text{x}10^9$	1.00
Np-237	$2.14\text{x}10^6$	0.99
Th-230	$7.70\text{x}10^4$	0.74
Cs-135	$3.00\text{x}10^6$	1.00
Sn-126	$1.00\text{x}10^5$	0.80
Pd-107	$6.50\text{x}10^6$	1.00
Tc-99	$2.13\text{x}10^5$	0.97
Zr-93	$1.53\text{x}10^6$	1.00
Se-79	$6.50\text{x}10^4$	0.96

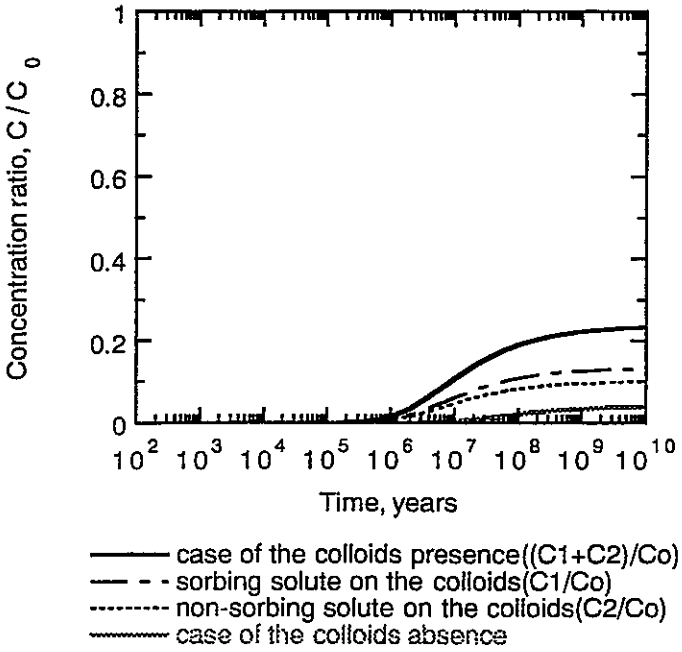


図3.4.3-16　Amの移行(半減期を考慮した場合)

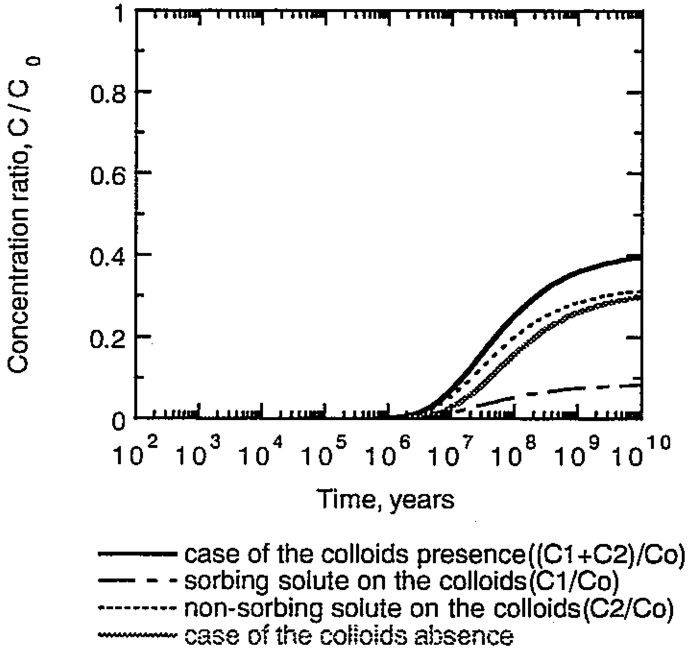


図3.4.3-17　Puの移行(半減期を考慮した場合)

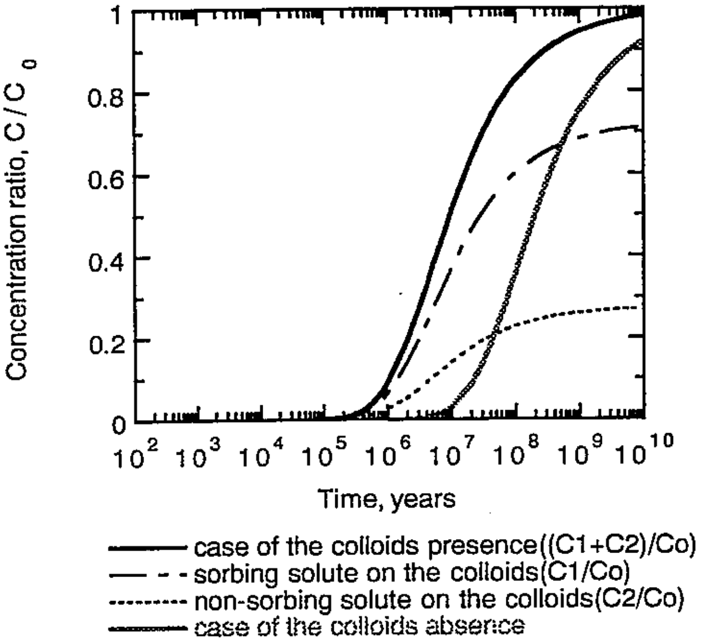


図3.4.3-18　Uの移行(半減期を考慮した場合)

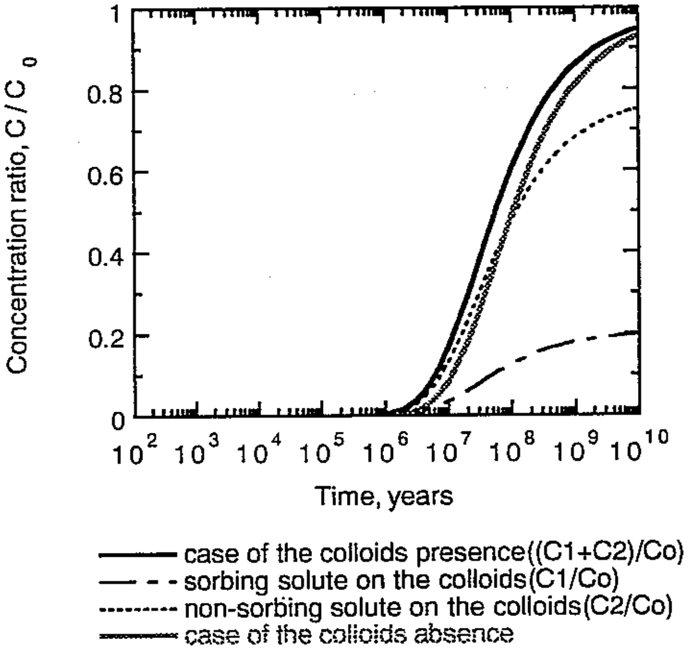


図3.4.3-19　Npの移行(半減期を考慮した場合)

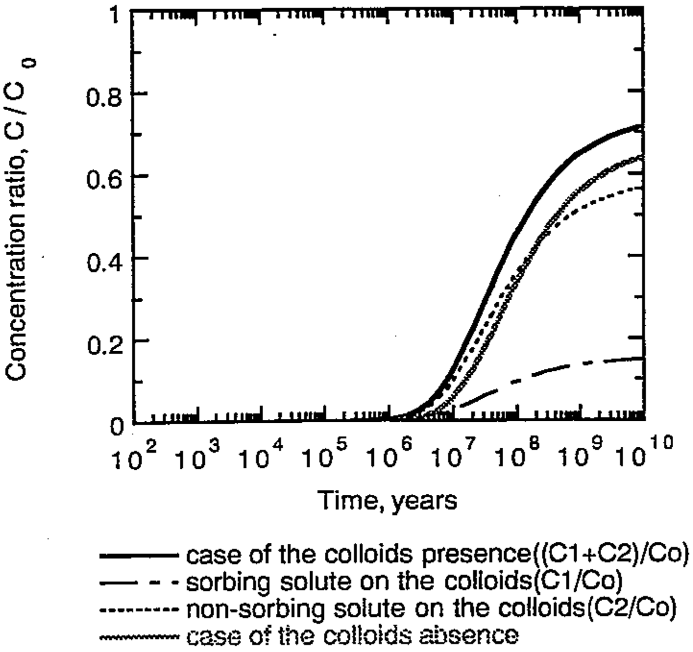


図3.4.3-20　Thの移行(半減期を考慮した場合)

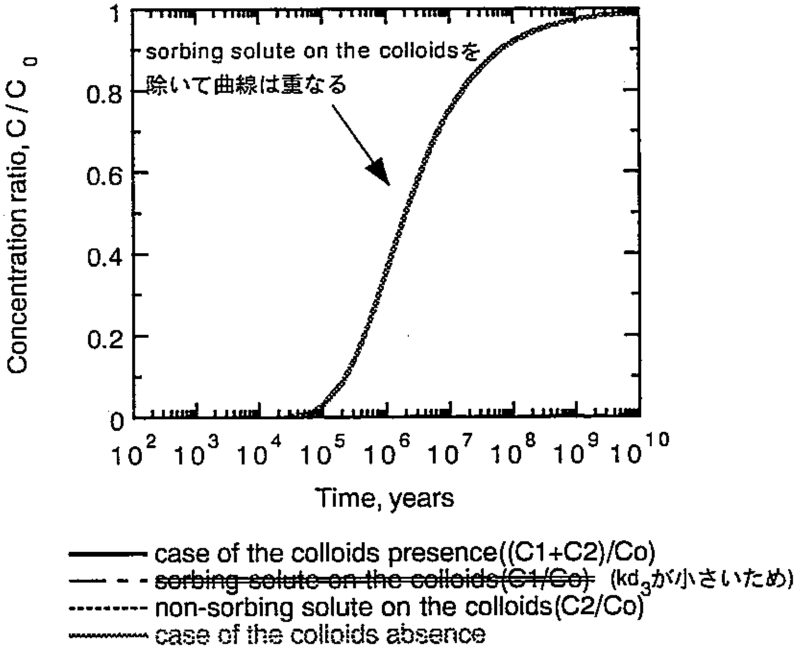


図3.4.3-21　Csの移行(半減期を考慮した場合)

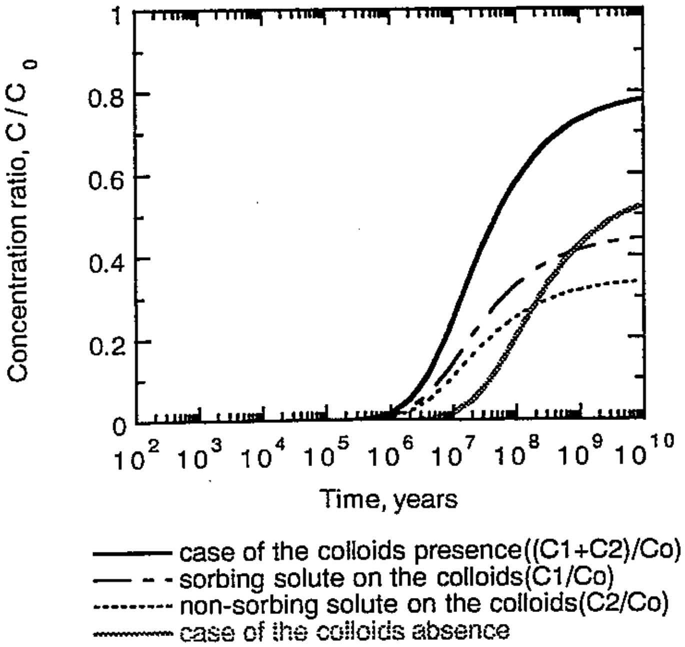
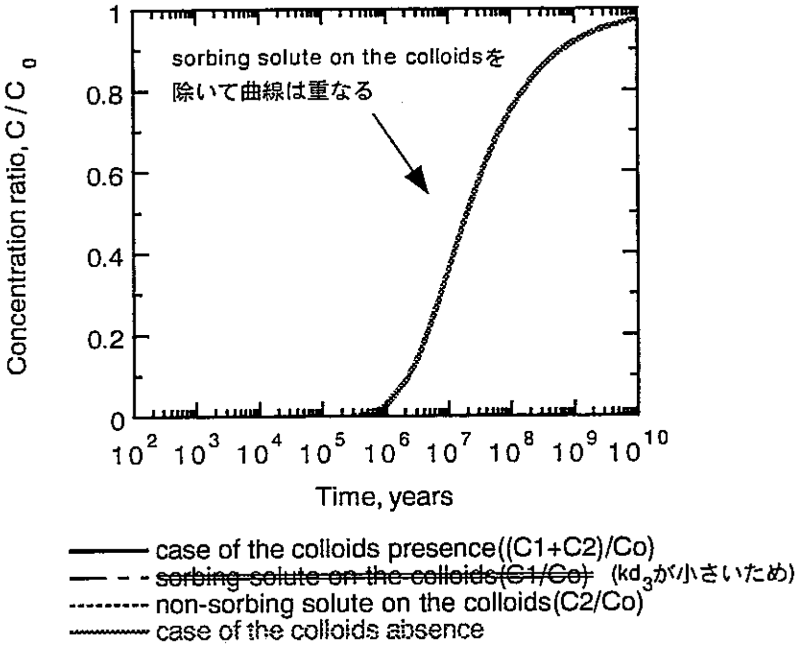


図3.4.3-22　Snの移行(半減期を考慮した場合)



sorbing solute on the colloidsを除いて曲線は重なる

(kd_3が小さいため)

図3.4.3-23　Pdの移行(半減期を考慮した場合)

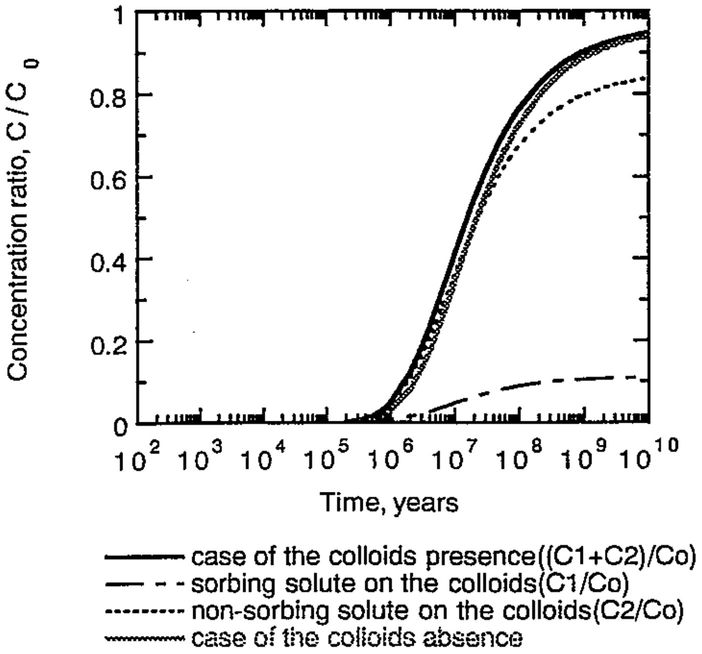


図3.4.3-24　Tcの移行(半減期を考慮した場合)

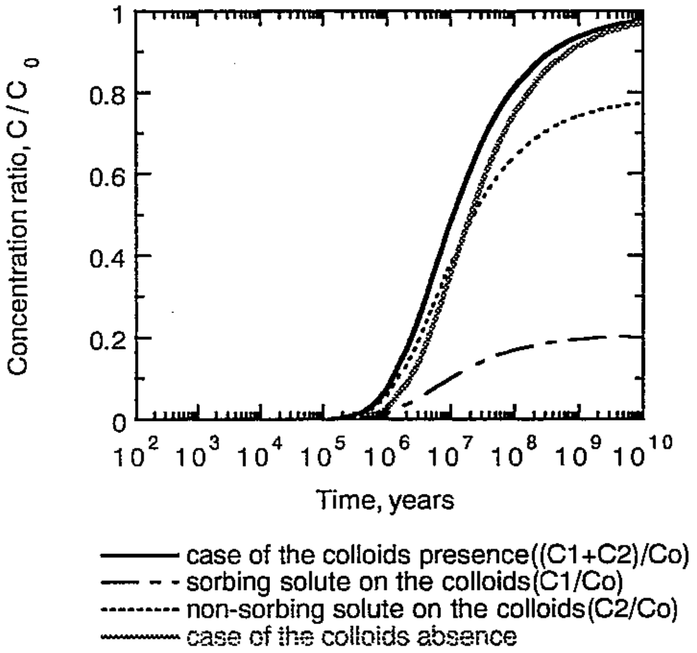


図3.4.3-25　Zrの移行(半減期を考慮した場合)

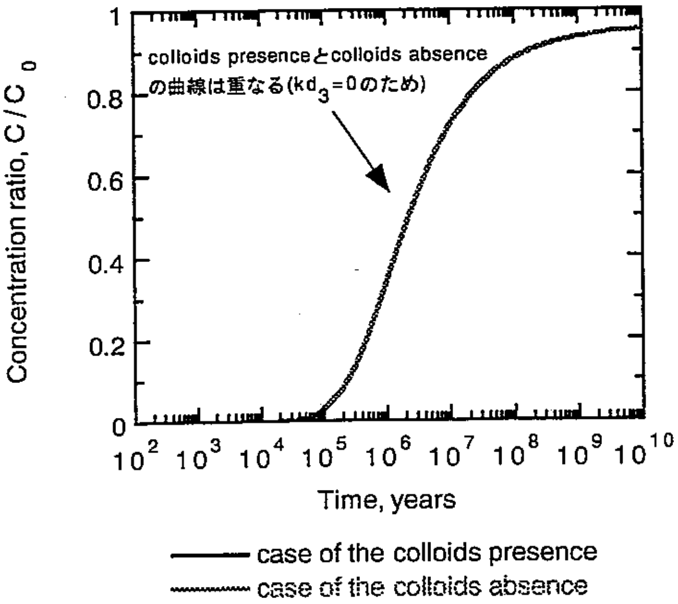


図3.4.3-26　Seの移行(半減期を考慮した場合)

(3) 崩壊連鎖を伴うコロイド共存下での核種移行

Hwang らの文献に記載されているコロイドを含む核種移行の解析解は、崩壊連鎖の上位核種（親核種）に伴う崩壊連鎖の下位核種（娘核種）の挙動は計算できない。また、このような複雑な系については、解析解を解くことは困難である。このため、差分法により数値計算を行うこととした。数値計算では解析解による計算結果と比べ誤差が伴うことから、厳密な解釈を行いたい場合には適さない。また、適用にあたっては計算結果の妥当性を十分吟味することが必要であり、ここでの計算結果の取り扱いについては、あくまでコロイドの移行に関する定性的解釈にとどまる。

(i) モデル

数値解法を行うにあたり、Hwang らのモデルの各パラメータを図 3.4.3-27 のように再定義した。再定義の意図は、実現象との対比に際し扱いに苦慮する事が予想される次の各パラメータの意味を明らかにするためである。

ε_1：亀裂内の空隙率。ここでは核種が移行可能な亀裂内の領域と考えた。これは、空隙内には吸着可能な岩石部分があることを仮定したものであり、換言すると空隙内部は完全な平板状の空間ではなく、一種の多孔質として扱われる。

ξ_1、ξ_2：それぞれ空隙中の移行可能、移行不可能なコロイドの体積分率。このため、亀裂の全体積に対するコロイドの体積分率は、それぞれ $\varepsilon_1\xi_1$、$\varepsilon_1\xi_2$となる。同様に核種の移行可能な領域の体積は $\varepsilon_1(1-\xi_1-\xi_2)$である。

Kd_2、Kd_3：それぞれ核種の岩盤およびコロイドへの分配係数。意味としては Hwang らのモデルと同じ分配係数であるが、単位系を m^3/kg とした。これにより、マスバランスを扱うために岩盤およびコロイドの乾燥密度を式に付加した。なお、コロイド自身の分配係数、すなわち移行可能および不可能なコロイドの比である Kd_1 については元の通り体積比率とした。

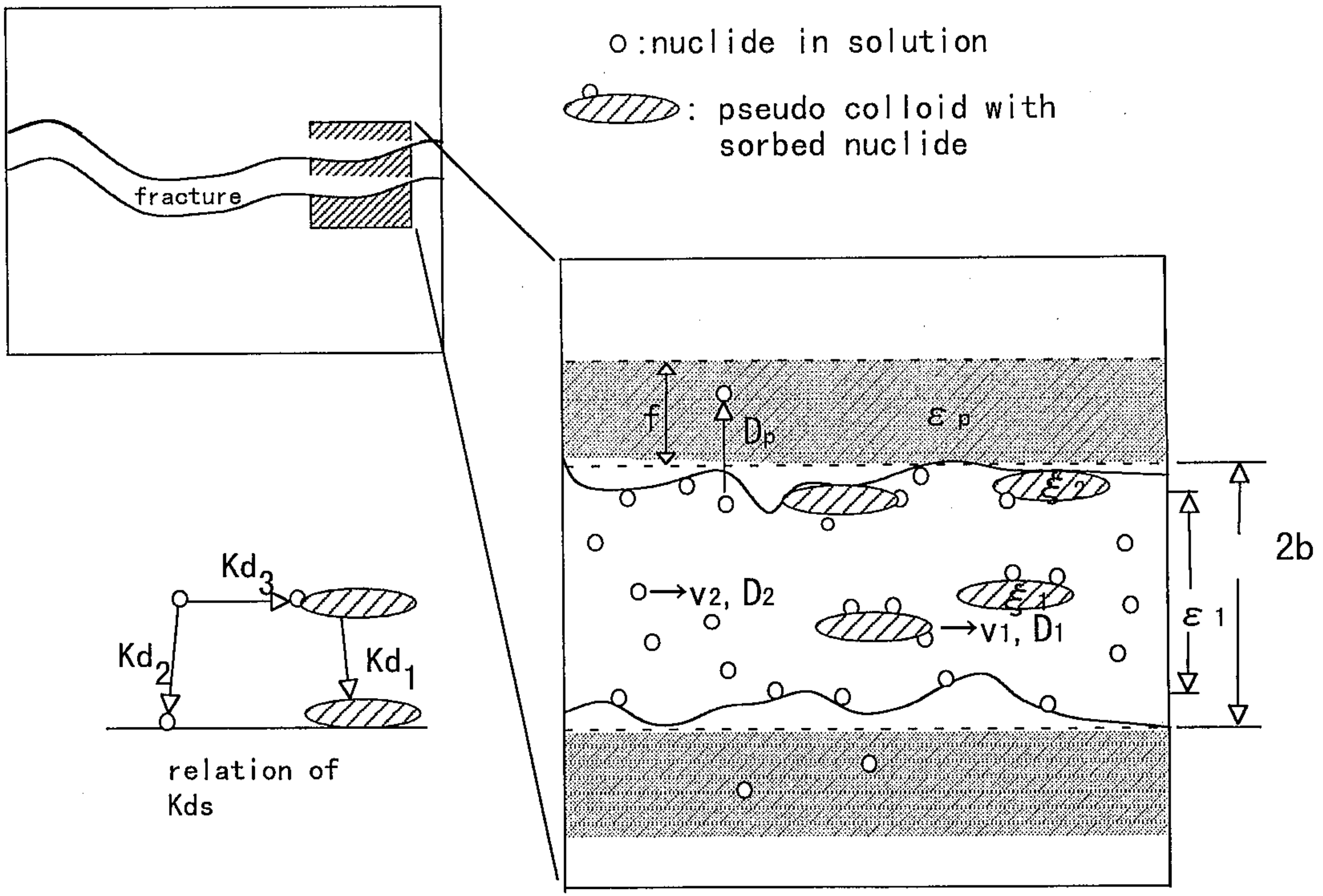


図3.4.3-27　数値計算を行うにあたって定義した各パラメータの概念

(ii) 数値解法

(a) 計算手順

まず Hwang らのモデルを前提とし、(3.4.3-1 式)および(3.4.3-2 式)に示した移流分散方程式(次式)をそれぞれ独自に解く。ここで微分方程式の離散化にあたっては陽解法のうち補正後退差分式を適用した。

・*pseudo－colloid transport*

$$\varepsilon_1\xi_1 \frac{\partial C_1(x,t)}{\partial t} + \varepsilon_1\xi_1 v_1 \frac{\partial C_1(x,t)}{\partial x} + \varepsilon_1 S_1(x,t) + \varepsilon_1 S_2(x,t) - \varepsilon_1\xi_1 D_1 \frac{\partial^2 C_1(x,t)}{\partial x^2} + \varepsilon_1\xi_1\lambda C_1 = 0$$

・*solute transport*

$$\varepsilon_1 \frac{\partial C_2(x,t)}{\partial t} + \varepsilon_1 v_2 \frac{\partial C_2(x,t)}{\partial x} - \varepsilon_1 S_2(x,t) + \varepsilon_1 S_3(x,t) - \varepsilon_1 D_2 \frac{\partial^2 C_2(x,t)}{\partial x^2} + \varepsilon_1\lambda C_2 + \frac{q(x,t)}{b} = 0$$

次いで、コロイド、岩盤、液相の3相間での分配反応計算を行った後、マトリクス拡散およびマトリクス拡散後の岩盤と空隙での核種分配の効果を計算する。ここでマトリクス拡散については次式により近似した。

$$F(t) = -D_p \frac{C_p - C_2}{f/2}\Delta x\Delta t$$

(3.4.3-19 式)

ここで、fは便宜上設定した岩盤内へのマトリクス拡散可能な深さである。また、C_pは岩盤内空隙中の核種濃度平均値である。この近似はマトリクス拡散を性格に扱うものではなく、計算上の便宜的処置である。

この後、マトリクス拡散により液相中核種濃度が変化するため、同じ時間帯において再度分配反応を計算し、離散化された各メッシュにおいて崩壊計算を実施した。

なお、計算にあたっては、メッシュ幅$\Delta\chi$および時間ステップ幅Δtは、次の条件を満足するよう決定した。

$$\frac{v_i\Delta x}{2D_i} + \frac{{v_i}^2\Delta t}{2\varepsilon_p R_i D_i} < 1$$

(3.4.3-20 式)

(b) 境界条件

崩壊系列を考慮した計算時における一番の親核種に関する入り口側境界条件は、次に示すように濃度一定境界とした。

$x=0,\ t \geqq 0$ において $Co=1$　もしくは　$x=0,\ t_1 > t \geqq 0$ において $Co=1$

その他の場合は $Co=0$

(t_1 は任意設定可能)

また、出口側境界条件は次の通りである。

$$C(l=l_{end})=C(l=l_{end}-\Delta x)$$

ここで l_{end} は数値計算時の最終空間メッシュ位置、Δx はメッシュ幅である。上式は出口側境界では濃度勾配がないことを表しているが、数値計算にあたっては補正後退差分法を用いたため、出口側における濃度勾配に $C(l=l_{end}-2\Delta x)$も影響しており、わずかであるが濃度勾配が発生している。

(iii) 計算および計算結果

(a) 移流分散の近似性

数値計算結果と解析解による計算結果を比較することにより、ここで使用した数値計算法が移流分散現象をどの程度近似しているか確認した。計算条件を表3.4.3-9 に示す。計算に際しては、移流分散現象の近似性を容易に確認できるよう、疑似コロイドの効果およびマトリクス拡散の効果は無視した。

計算結果を図 3.4.3-28 に示す。ここで、図中 C は、評価地点における nuclide in solution と pseudocolloid with sorbed nuclide を合わせた濃度である(図 3.4.3-27 参照)。また、Co は亀裂入り口での全核種濃度である。その結果から分かるように、数値計算結果は解析解による結果とほぼ同じであり、移流分散現象については適切に数値計算し得ると判断できる。

表 3.4.3-9　移流分散の近似性確認のための移行評価入力データ

データ項目	親核種	娘核種
v_1:コロイドの亀裂中移行速度(m/y)	考慮せず	考慮せず
v_2:溶質の亀裂中移行速度(m/y)	1.0	
D_1:コロイドの亀裂中分散係数(m^2/y)	考慮せず	
D_2:溶質の亀裂中分散係数(m^2/y)	0.10	
D_p:マトリクス拡散係数（実効拡散）(m^2/y)	考慮せず	
ξ_1:亀裂中の移行可能なコロイド体積分率(－)	考慮せず	
ξ_2:亀裂中の移行不能なコロイド体積分率(－)	考慮せず	
ε_1:亀裂の空隙率(－)	0.9	
ε_p:岩盤の空隙率(－)	考慮せず	
$\rho_{colloid}$:コロイドの真密度(kg/m^3)	考慮せず	
ρ_{rock}:亀裂中岩石部分および岩盤の真密度($kg/\ m^3$)	2.7e3	
2b:亀裂幅(m)	考慮せず	
f:マトリクス拡散深さ(計算上の架空ﾊﾟﾗﾒｰﾀ)(m)	考慮せず	
Kd_1:コロイドの岩盤への吸着率(-)	考慮せず	
Kd_2:溶質の亀裂内岩石への分配係数(m^3/kg)	0.1	
Kd_3:溶質のコロイドへの分配係数(m^3/kg)	考慮せず	
L:核種移行距離(m)	10	
$T_{1/2}$:放射性半減期(y)	考慮せず	
距離0における親核種濃度1の期間	常時	

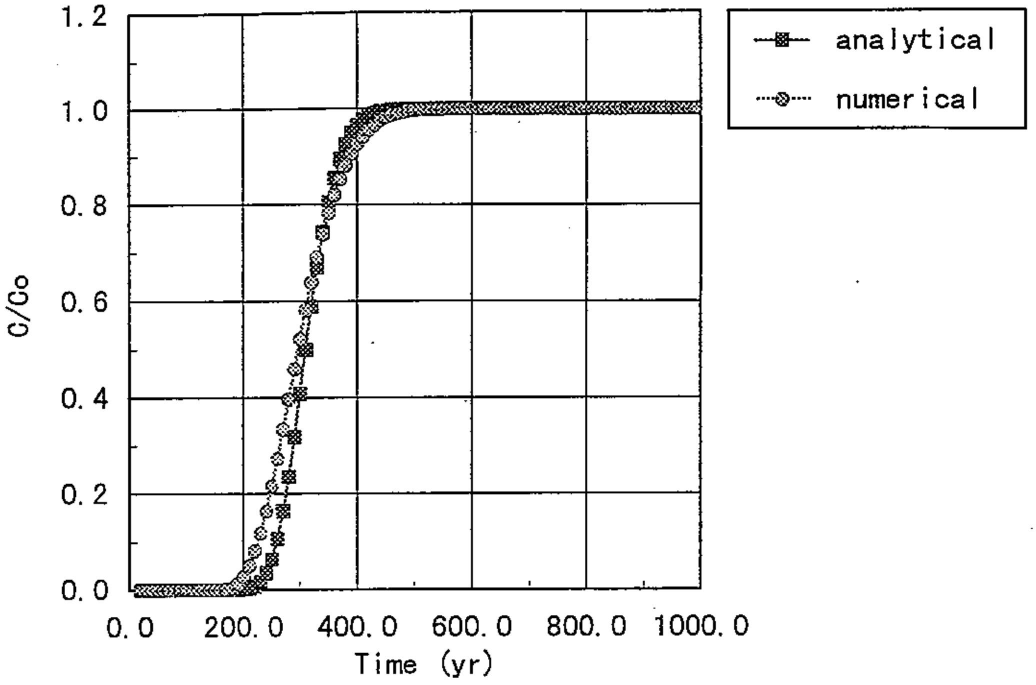


図3.4.3-28　数値計算と解析解の計算結果との比較(L=10m, Vw=1m/yr, Dw=0.1m2/yr, Rf=31)

(b) マトリクス拡散の近似性

ここでは、数値計算結果と解析解による計算結果を比較することにより、使用した数値計算法がマトリクス拡散現象をどの程度近似しているか確認した。計算条件を表 3.4.3-10 に示す。また、計算に際しては、マトリクス拡散の近似性を容易に確認できるよう、疑似コロイドの効果および核種の岩盤への吸着の効果は無視した。

同じ計算条件で、移行距離を 1m にした場合、および 10m にした場合の計算結果をそれぞれ図 3.4.3-29 および図 3.4.3-30 に示す。結果は全て溶液中の核種濃度で表した。疑似コロイド中の核種濃度はこの値に Kd_3 を乗じることによって容易に得られる(3.4.3-7 式参照)。数値解ではマトリクス拡散可能深さfが計算結果に影響する。移行距離 1m の場合には、解析解は f=1m の場合と f=10m の場合の中間に位置している。同じ結果は移行距離 10m の場合にも見られるが、解析解と数値解の差はより大きくなっている。しかしながら、マトリクス拡散の効果により C/Co が一旦立ち上がったのち、1に徐々に近づく傾向は反映されている。このため、本研究ではマトリクス拡散の効果は主な対象ではなくコロイドの効果が検討対象であることから、本計算方法は十分適用可能と判断できる。なお、マトリクス拡散の効果に着目した検討を行うためには、マトリクス拡散の近似方法についてさらに検討する必要がある。

表 3.4.3-10　マトリクス拡散の近似性確認のための移行評価入力データ

データ項目	親核種	娘核種
v_1:コロイドの亀裂中移行速度(m/y)	考慮せず	考慮せず
v_2:溶質の亀裂中移行速度(m/y)	1.0	
D_1:コロイドの亀裂中分散係数(m^2/y)	考慮せず	
D_2:溶質の亀裂中分散係数(m^2/y)	0.10	
D_p:マトリクス拡散係数（実効拡散）(m^2/y)	1e-3	
ξ_1:亀裂中の移行可能なコロイド体積分率(－)	考慮せず	
ξ_2:亀裂中の移行不能なコロイド体積分率(－)	考慮せず	
ε_1:亀裂の空隙率(－)	0.9	
ε_p:岩盤の空隙率(－)	0.02	
$\rho_{colloid}$:コロイドの真密度(kg/m^3)	考慮せず	
ρ_{rock}:亀裂中岩石部分および岩盤の真密度(kg/m^3)	2.7e3	
2b:亀裂幅(m)	0.01	
f:マトリクス拡散深さ(計算上の架空ﾊﾟﾗﾒｰﾀ)(m)	0.1, 1.0, 10	
Kd_1:コロイドの岩盤への吸着率(-)	考慮せず	
Kd_2:溶質の亀裂内岩石への分配係数(m^3/kg)	0	
Kd_3:溶質のコロイドへの分配係数(m^3/kg)	考慮せず	
L:核種移行距離(m)	1, 10	
$T_{1/2}$:放射性半減期(y)	考慮せず	
距離0における親核種濃度1の期間	常時	

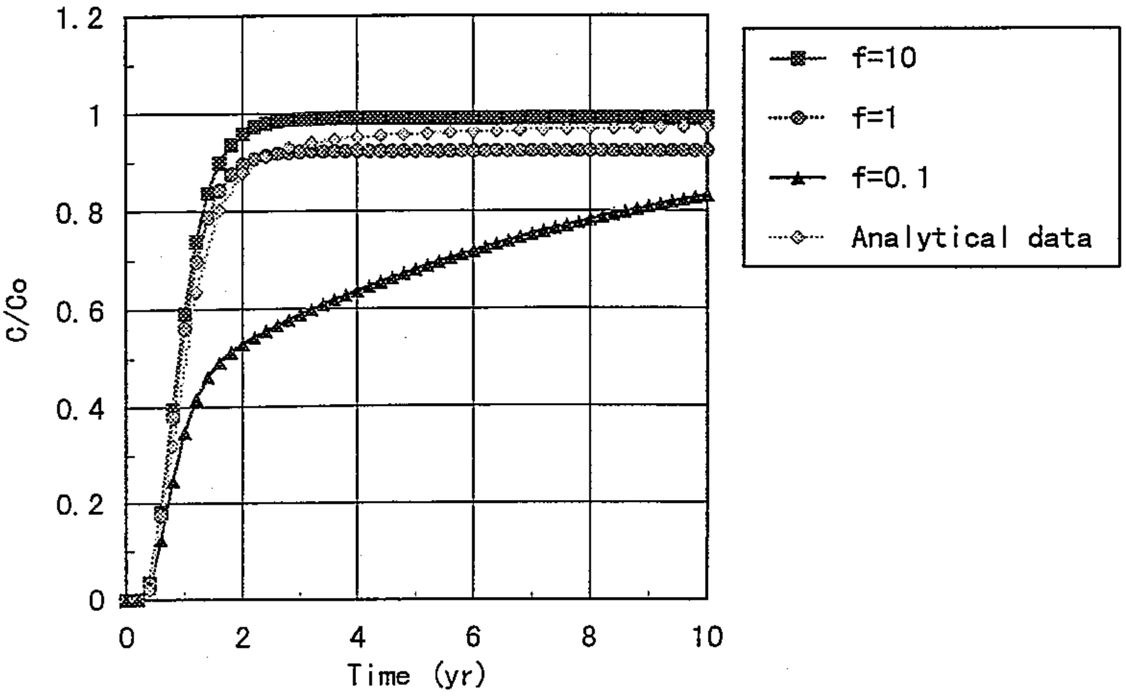


図3.4.3-29　数値計算において核種移行に与えるマトリクス拡散の効果（移行距離1mの場合）
ここで、f: diffusion depth

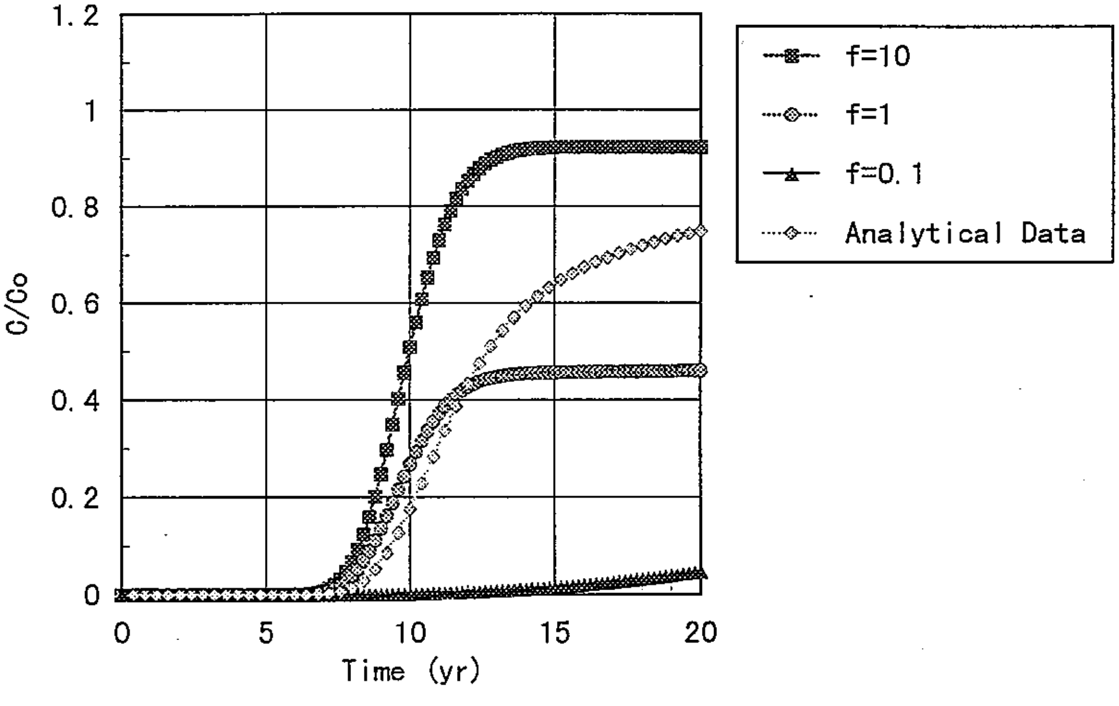


図3.4.3-30　数値計算において核種移行に与えるマトリクス拡散の効果（移行距離10mの場合）
ここで、f: diffusion depth

(c) コロイドおよびマトリクス拡散の効果

コロイドの有無およびマトリクス拡散の有無が核種移行に与える影響について計算した。計算条件を表 3.4.3-11 に示す。計算結果は全て入力パラメータの設定値に依存する。表 3.4.3-11 の計算条件はコロイドの有無やマトリクス拡散の有無が顕著に表れる仮想的設定になっている。なお、前項で記したようにマトリクス拡散の効果は近似的な計算結果である。

図 3.4.3-31 および図 3.4.3-32 に、同じ計算条件における移行距離 1m および 10m の計算結果をそれぞれ示す。図 3.4.3-31 の結果は、比較が容易なアウトプットになっている。マトリクス拡散を無視した条件におけるコロイドの有無の影響は図から明らかなように、疑似コロイドの存在により核種移行は促進される。これに対してマトリクス拡散は、核種移行の遅延と言うよりは C/Co が1になるのを遅らせる効果を示す。この効果は図 3.4.3-32 から明らかなように、移行距離が大きくなるほど顕著になる。これらを次の各項目に整理した。

①マトリクス拡散を無視した場合、コロイド共存により核種移行速度は増加する。

②マトリクス拡散がある場合、コロイド共存により核種移行速度は増加する。

③マトリクス拡散の有無により、平衡時濃度は低下する。(原理的には疑似平衡であり、マトリクス拡散が進展し岩盤に向かう濃度勾配が低下するのに伴い、徐々に濃度増加が生じると考えられる。)

表 3.4.3-11 コロイドおよびマトリクス拡散の影響の比較検討に用いた評価入力データ

データ項目	ｺﾛｲﾄﾞ有 MD^{*1}有	ｺﾛｲﾄﾞ無 MD 有	ｺﾛｲﾄﾞ有 MD 無	ｺﾛｲﾄﾞ無 MD 無
v_1:コロイドの亀裂中移行速度(m/y)	1.5	←^{*2}	←	←
v_2:溶質の亀裂中移行速度(m/y)	1.0	←	←	←
D_1:コロイドの亀裂中分散係数(m^2/y)	0.15	←	←	←
D_2:溶質の亀裂中分散係数(m^2/y)	0.10	←	←	←
D_p:マトリクス拡散係数(実効拡散)(m^2/y)	0.01	0.01	0	0
ξ_1:亀裂中の移行可能なコロイド体積分率(－)	0.001	←	←	←
ξ_2:亀裂中の移行不能なコロイド体積分率(－)	0.00001	←	←	←
ε_1:亀裂の空隙率(－)	0.90	←	←	←
ε_p:岩盤の空隙率(－)	0.02	←	←	←
$\rho_{colloid}$:コロイドの真密度(kg/m^3)	2700	←	←	←
ρ_{rock}:亀裂中岩石部分および岩盤の真密度(kg/ m^3)	2700	←	←	←
2b:亀裂幅(m)	0.01	←	←	←
f: マトリクス拡散深さ(計算上の架空ﾊﾟﾗﾒｰﾀ)(m)	1.0	←	←	←
Kd_1:コロイドの岩盤への吸着率(-)	0.01	←	←	←
Kd_2:溶質の亀裂内岩石への分配係数(m^3/kg)	0.10	←	←	←
Kd_3:溶質のコロイドへの分配係数(m^3/kg)	0.20	0	0.20	0
L:核種移行距離(m)	1, 10	←	←	←
$T_{1/2}$:放射性半減期(y)	無視	←	←	←
距離0における親核種濃度1の期間	常時	←	←	←

＊1)MD:Matrix diffusion

＊2)←の欄は左欄と同じ値を使用する。

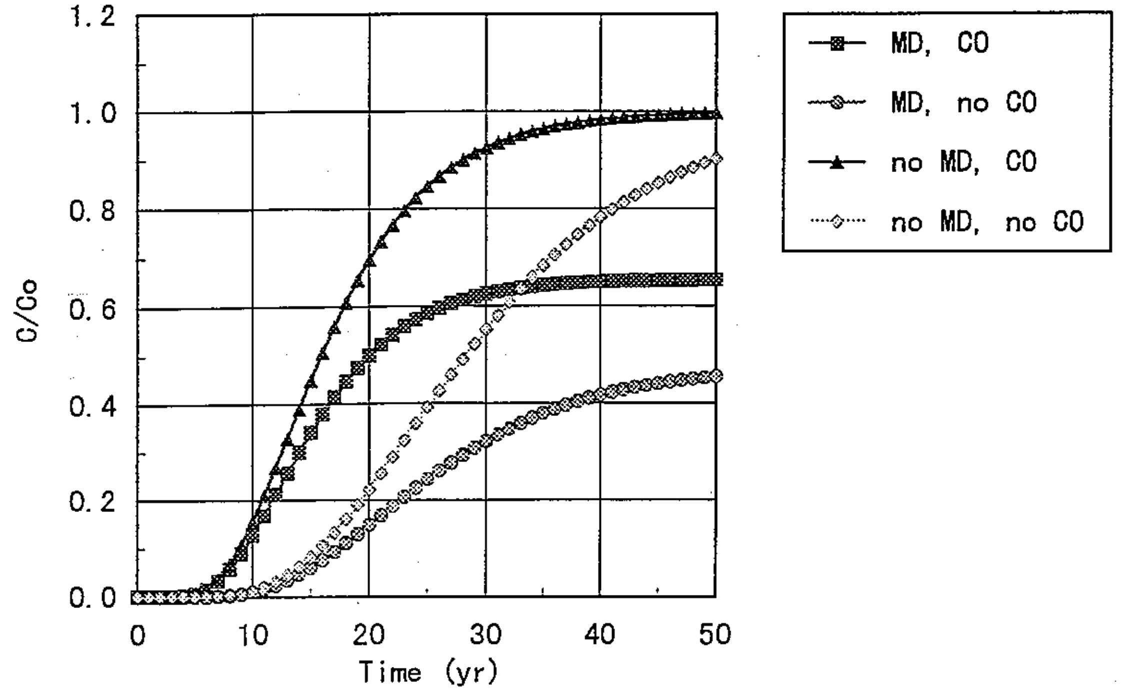


図3.4.3-31 核種移行に与えるコロイドおよびマトリクス拡散の効果(移行距離1mの場合)
ここで、MD: matrix diffusion, CO:colloid

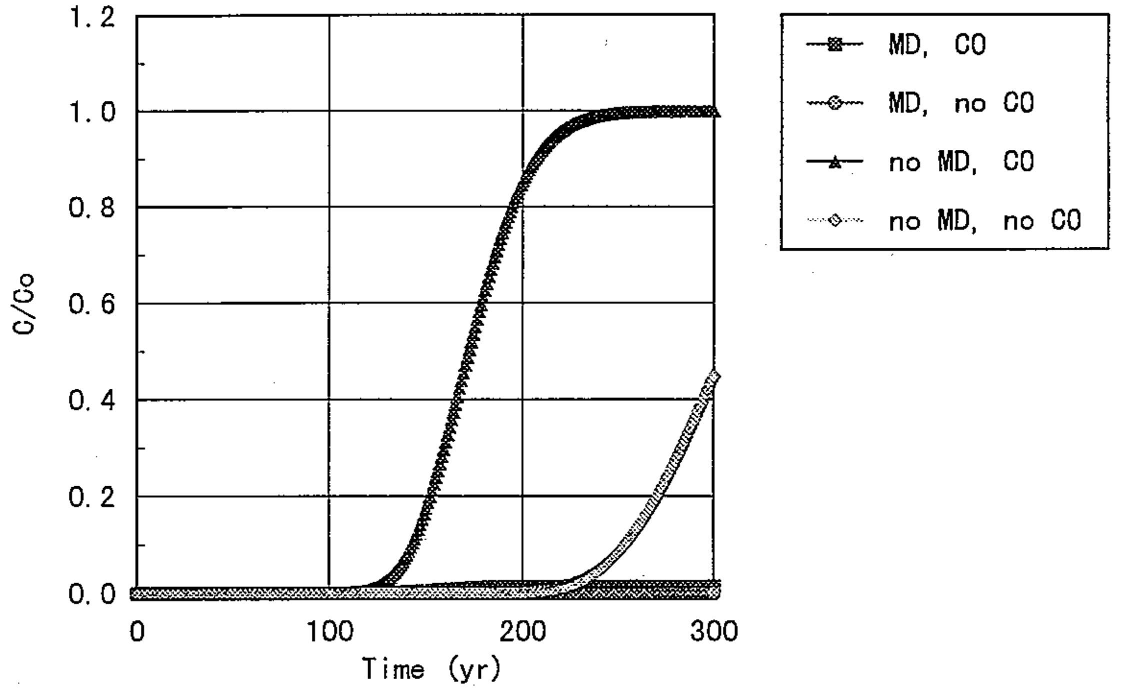


図3.4.3-32 核種移行に与えるコロイドおよびマトリクス拡散の効果(移行距離10mの場合)
ここで、MD: matrix diffusion, CO:colloid

(d) 崩壊連鎖を伴う疑似コロイドの移行

計算は、次の2種類の崩壊系列について実施した。

①Am-243, Pu-239, U-235

②Th-230, Ra-226, Pb -210

これらの崩壊系列は他の核種も多く含んでいる。しかしながら、他の核種も対象にして計算を行う場合、かなりの計算時間を要することが予測されることから、系列上重要性が高いと考えられる3核種のみを計算対象とした。崩壊連鎖の計算では、系列下位核種に進むほど誤差が伝搬し結果の信頼性が低くなることが予想される。

上述2種類の崩壊系列に対し、核種のコロイドへの吸着がある場合およびコロイドへの吸着がない場合をそれぞれ計算した。表 3.4.3-12 および表 3.4.3-13 に計算条件を示す。特筆すべき条件設定は、入り口における濃度設定である。計算開始時(t=0)以降、1000 年間だけ C/Co=1 とし、それ以降の時間では Co=0 とした。これは常時 C/Co=1 とすると娘のビルドアップが激しく計算結果が発散する可能性があったためである。

図 3.4.3-33 および図 3.4.3-34 は、Am-243 系列核種の移行に関する、それぞれコロイドへの核種の吸着がある場合および無い場合の計算結果を横軸に時間、縦軸に所定の移行距離における溶液中の核種濃度でプロットして示したものである。コロイドの影響がない場合の放出核種濃度のピークは約 20 万年において見られるのに対し、コロイドの影響がある場合には数千年であり、コロイドの共存による核種移行の促進効果が見て取れる。また、各ケースとも娘核種の挙動は親核種の挙動に追随する形を取っている。亀裂中の水の移動速度は 3.20e-2m/y であるため、100m の移行時間は 3125 年である。コロイドの影響がない場合、設定値から算出される Am-243 の遅延係数は 151 であり、Am-243 の 100m 地点到達時間として約 50 万年が予想される。図 3.4.3-33 では約 20 万年の時点に Am-243 のピークが見られたのは、Am-243 の半減期が 7370 年であり評価期間に比べて小さいこと、および分散によるピーク濃度低下が起こることが影響している。

コロイドの影響を考慮した図 3.4.3-34 の計算結果は、図 3.4.3-33 と比べ大きく異なっている。Am-243 のピーク到達時期はほとんど水の移行時間と変わらない。ここで計算条件から空隙中の移動可能な核種、すなわちコロイド上に吸着している核種と液相に存在している核種の合計に対するコロイド上に吸着している核種量を算

出する。Kd_3 が $5m^3/kg$ という高い数値であるため、コロイド存在分率は 0.05 であるにも関わらず、99.86%の核種がコロイド上に存在する。この結果、Am-243 はほとんど空隙水と同様の移行挙動を示したものと考えられる。

図 3.4.3-35 および図 3.4.3-36、Th-230 系列核種の移行に関する、それぞれコロイドへの核種の吸着がある場合および無い場合の計算結果である。コロイドの影響が無い場合、親核種である Th-230 よりも娘核種である Ra-226 や Pb-210 の移行が速やかであるが、これは各分配係数の設定値に依存しており、特に Ra-226 の分配係数設定値がきわめて小さいことが影響している。これに対しコロイドの影響がある場合には親核種と娘核種の移行状況の相違は小さくなっている。これは Ra-226 のコロイドへの分配係数を小さく設定したため Ra-226 は岩盤との相互作用によって移行遅延し、コロイドに伴って速やかに移行する Th-230 との移行速度の相違が小さくなったためである。ここで、コロイドの存在により娘核種である Ra-226 や Pb-210 の濃度ピーク値は増加するもの、移行速度は変化していない。これは前述のように Ra-226 のコロイドへの分配係数がきわめて小さく、コロイドの影響がほとんどないためである。このように、崩壊連鎖を考慮した疑似コロイドの核種移行では、親だけでなく娘核種の個々のパラメータ設定がそれぞれ影響してくるため、単純な感度解析的計算により系統的に疑似コロイドの影響の傾向を把握するのは困難である。

表 3.4.3-12 Am-243 系列核種の移行評価入力データ

データ項目	Am-243	Pu-239	U-235
v_1:コロイドの亀裂中移行速度(m/y)	4.48e-2	←*	←
v_2:溶質の亀裂中移行速度(m/y)	3.20e-2	←	←
D_1:コロイドの亀裂中分散係数(m^2/y)	4.48e-2	←	←
D_2:溶質の亀裂中分散係数(m^2/y)	3.20e-2	←	←
D_p:マトリクス拡散係数(実効拡散)(m^2/y)	1.58e-4	←	←
ξ_1:亀裂中の移行可能なコロイド体積分率(－)	5.0e-2	←	←
ξ_2:亀裂中の移行不能なコロイド体積分率(－)	5.0e-5	←	←
ε_1:亀裂の空隙率(－)	0.9	←	←
ε_p:岩盤の空隙率(－)	0.02	←	←
$\rho_{colloid}$:コロイドの真密度(kg/m^3)	2.7e3	←	←
ρ_{rock}:亀裂中岩石部分および岩盤の真密度(kg/ m^3)	2.7e3	←	←
2b:亀裂幅(m)	7.88e-2	←	←
f:マトリクス拡散深さ(計算上の架空ﾊﾟﾗﾒｰﾀ)(m)	1.0	←	←
Kd_1:コロイドの岩盤への吸着率(-)	1.0e-3	←	←
Kd_2:溶質の亀裂内岩石への分配係数(m^3/kg)	0.5	0.5	1.0
Kd_3:溶質のコロイドへの分配係数(m^3/kg)	5.0	0.1	0.5
L:核種移行距離(m)	100	←	←
$T_{1/2}$:放射性半減期(y)	7.37e3	2.41e4	7.04e8
距離0における親核種濃度1の期間	1000 年間	考慮せず	考慮せず

注)コロイドの影響を無視する場合は Kd3=0 とし、その他のパラメータは同じとする。

＊)←の欄は左欄と同じ値を使用する。

表 3.4.3-13 Th-230 系列核種の移行評価入力データ

データ項目	Th-230	Ra-226	Pb-210
v_1:コロイドの亀裂中移行速度(m/y)	4.48e-2	←*	←
v_2:溶質の亀裂中移行速度(m/y)	3.20e-2	←	←
D_1:コロイドの亀裂中分散係数(m^2/y)	4.48e-2	←	←
D_2:溶質の亀裂中分散係数(m^2/y)	3.20e-2	←	←
D_p:マトリクス拡散係数(実効拡散)(m^2/y)	1.58e-4	←	←
ξ_1:亀裂中の移行可能なコロイド体積分率(-)	5.0e-2	←	←
ξ_2:亀裂中の移行不能なコロイド体積分率(-)	5.0e-5	←	←
ε_1:亀裂の空隙率(-)	0.9	←	←
ε_p:岩盤の空隙率(-)	0.02	←	←
$\rho_{colloid}$:コロイドの真密度(kg/m^3)	2.7e3	←	←
ρ_{rock}:亀裂中岩石部分および岩盤の真密度(kg/m^3)	2.7e3	←	←
2b:亀裂幅(m)	7.88e-2	←	←
f:マトリクス拡散深さ(計算上の架空パラメータ)(m)	1.0	←	←
Kd_1:コロイドの岩盤への吸着率(-)	1.0e-3	←	←
Kd_2:溶質の亀裂内岩石への分配係数(m^3/kg)	1.0	0.01	0.01
Kd_3:溶質のコロイドへの分配係数(m^3/kg)	0.1	0.00001	0.01
L:核種移行距離(m)	100	←	←
$T_{1/2}$:放射性半減期(y)	7.54e4	1.60e3	22.3
距離0における親核種濃度1の期間	1000年間	考慮せず	考慮せず

注)コロイドの影響を無視する場合はKd3=0とし、その他のパラメータは同じとする。

＊)←の欄は左欄と同じ値を使用する。

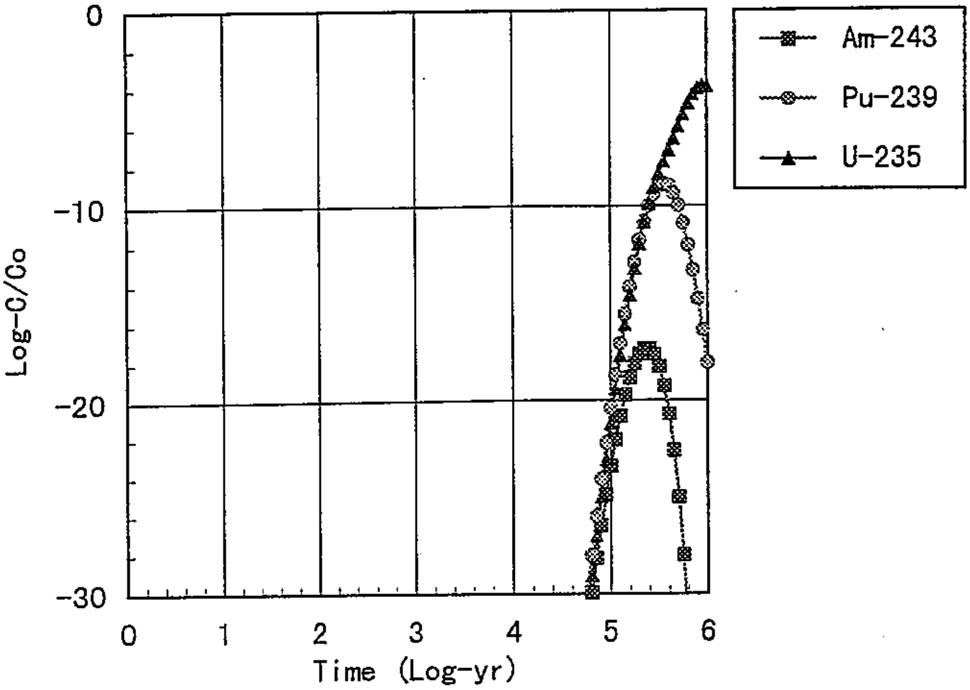


図3.4.3-33　Am-243の崩壊系列に対する移行(コロイドへの吸着がない場合)

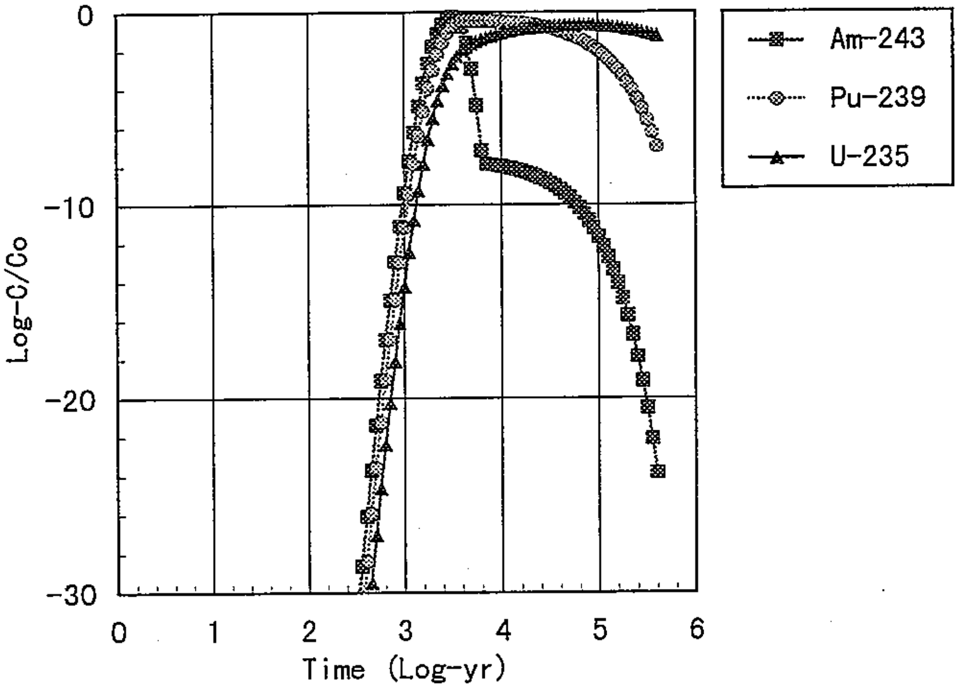


図3.4.3-34　Am-243の崩壊系列に対する移行(コロイドへの吸着がある場合)

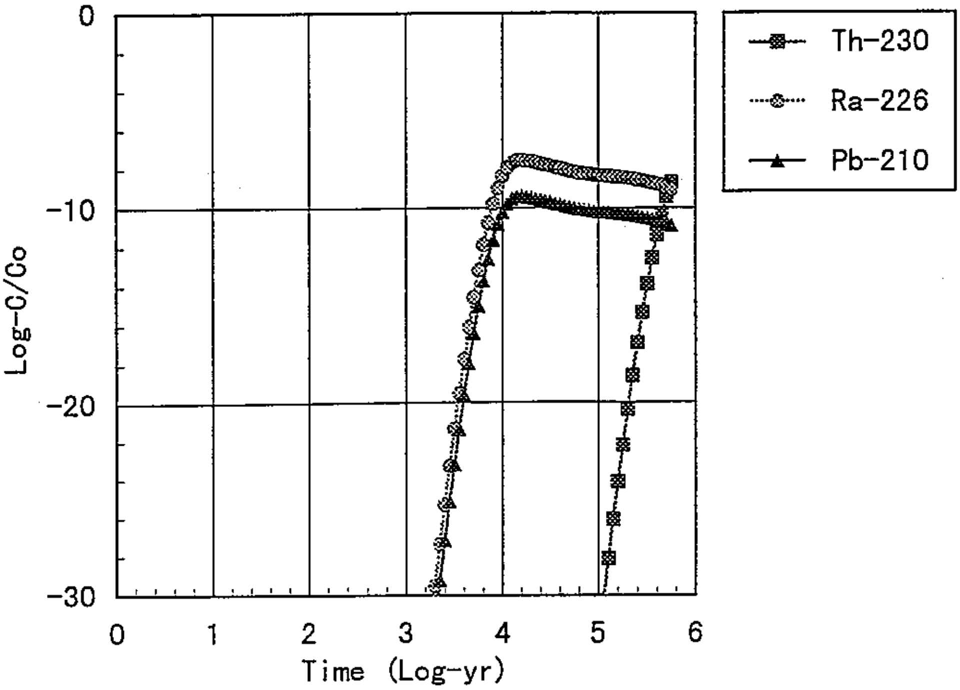


図3.4.3-35　Th-230の崩壊系列に対する移行(コロイドへの吸着がない場合)

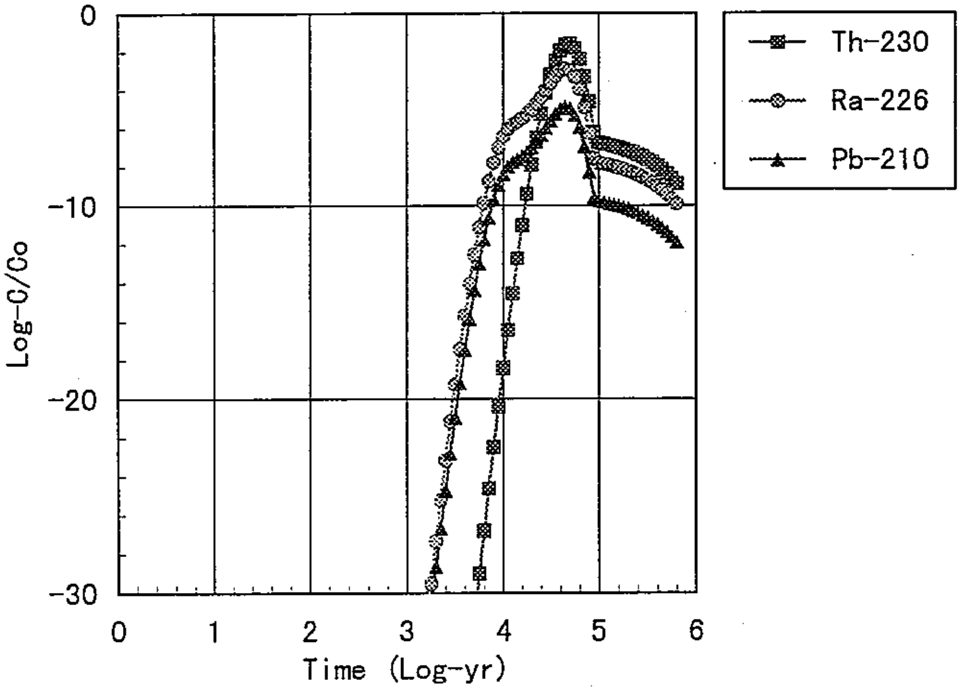


図3.4.3-36　Th-230の崩壊系列に対する移行(コロイドへの吸着がある場合)

(iv) 疑似コロイドの移行の移流分散式に関する考察

崩壊連鎖の娘核種を考慮しない場合、図 3.4.3-27 に示したパラメータの再定義を利用して Hwang らの式は次のように修正される。

$$\frac{\partial (R_{all} C_1)}{\partial t} = \varepsilon_1 \xi_1 \left(-v_1 \frac{\partial C_1}{\partial x} + D_1 \frac{\partial^2 C_1}{\partial x^2} \right) + \varepsilon_1 \left(1 - \xi_1 - \xi_2\right) \left(-v_2 \frac{\partial C_2}{\partial x} + D_2 \frac{\partial^2 C_2}{\partial x^2} \right)$$

$$- \lambda (R_{all} C_1) - \left(1 - \xi_1 - \xi_2\right) D_p \frac{N(x,y,t)}{\partial y} \Big|_{y=b}$$

(3.4.3-21 式)

上式において吸着による質量バランスを表すために用いた定数 R_{all} は次式で表される。

$$R_{all} = \varepsilon_1 \left[1 - \left(1 + Kd_1\right)\xi_1 + \frac{1 - \varepsilon_1}{\varepsilon_1} \rho_{rock} Kd_2 \right] \frac{1}{Kd_3} + \varepsilon_1 \xi_1 \rho_{colloid} \left(1 + Kd_1\right)$$

(3.4.3-22 式)

ここで、次に示す溶液中核種および疑似コロイド核種の濃度を総合し、疑似コロイド上核種濃度の関数として表すことによって得られる加重平均的な移流速度および分散係数を用いる。

$$\bar{v} = v_1 \left[\xi_1 \rho_{colloid} + \frac{v_2}{v_1} \left\{ \frac{1 - \left(1 + Kd_1\right)\xi_1}{Kd_3} \right\} \right]$$

$$\bar{D} = D_1 \left[\xi_1 \rho_{colloid} + \frac{D_2}{D_1} \left\{ \frac{1 - \left(1 + Kd_1\right)\xi_1}{Kd_3} \right\} \right]$$

(3.4.3-23 式)

以上の結果、疑似コロイドを伴う核種移行の移流分散方程式は、次式によって表される。

$$\frac{\partial C_1}{\partial t} = -\frac{\bar{v}}{R_{all}}\frac{\partial C_1}{\partial x} + \frac{\overline{D}}{R_{all}}\frac{\partial^2 C_1}{\partial x^2} - \lambda C_1 - \{1 - (1 + Kd_1)\xi_1\}\frac{D_p}{R_{all}}\frac{N(x,y,t)}{\partial y}\bigg|_{y=b}$$

(3.4.3-24 式)

ここで変換された式は、コロイドを含まない場合の移流分散方程式と全く同じ形式で表されている。これは、疑似コロイドの存在による移行は、単純に核種流速をどのように取り扱うか、またその結果移行速度が速くなるか遅くなるか、といった議論に帰着することを示している。ただし、前述したように崩壊連鎖を含む場合には、関連するパラメータ数が対象核種数に比例して多くなるため、それらの影響を系統的に把握することはきわめて困難である。

以上まとめると、崩壊連鎖を考慮して核種およびコロイドの移行を解く場合、ある程度絞り込まれたパラメータ設定に対して絞り込んだ条件で計算を行い、影響を把握していくことが効率的である。また、崩壊連鎖を考慮した核種およびコロイドの移行に関して解析解を得ることは困難と予想されることから、計算にあたっては今回の検討と同様に数値解法を利用することが適切と考えられる。

3.4.4 参考文献

1) Hwang Y., et al.; Mat. Res. Soc. Symp. Proc., vol.176, p.599(1990).

2) Tang D., et al.; Water Resources Research, vol.17, p.555(1981).

3) 日本粘土学会編; 粘土ハンドブック 第二版, p.132(1987), 技報堂出版.

4．まとめ

本年度の成果を以下にまとめた。

1. 重要元素の核種移行データベースの整備

21 元素に対し、OH^-、CO_3^{2-}、Cl^-、F^-、SO_4^{2-}、PO_4^{3-}を対象とした溶液中の化学種及び固相のデータ整備及びその国際的専門家のレビューを行った。また、岩石などへの17元素の収着データ及び7元素の拡散データ整備を行った。ベントナイトに関しては Pu の収着及び拡散データベースの整備を行った。

2. データベース整備に係わるデータ取得

ベントナイト、花崗閃緑岩、凝灰岩を対象に Th の収着試験を実施した。またベントナイトを対象に Ra、Np、Tc、U、ケイ砂混合ベントナイトを対象に Cs,Se,Ni の拡散試験を実施し、見かけの拡散係数を取得した。

3. ベントナイトの間隙水水質推定モデルの検討

イオン交換モデルにおける吸着化学種の活量補正について評価を行った。また空隙水組成に及ぼす不純物の影響に検討し、空隙水 pH に対して方解石、石膏、硫化鉄の存在が影響することを明らかにした。

4. コロイドの核種移行に与える影響の評価

Hwang らのモデルを確証するためのデータ取得試験を実施するとともに、コロイドの存在が核種移行に与える影響の評価を行った。

添付資料 I

各元素の放射化学純度

核種	半減期 / 年	核種濃度および量			比放射能 (Ci/g)	元素濃度および量		検定日	メーカーおよびコード
		塗布液核種濃度 (Bq/ml)	塗布量1) (ml)	塗布核種量2) (Bq)		塗布液元素濃度 (mol/l)	塗布元素量 (mol)		
Tc-99	2.13E+05	2.5E+04	0.025	6.3E+02	0.017	4.0E-04	1.00E-08	94.6.17	Dupont,NEZ085
Np-237	2.14E+06	1.0E+04	0.025	2.5E+02	キャリアフリー	1.6E-03	4.04E-08	97.10.17	AEA,AE9156
U	4.47E+09	(U-238)	0.025	---	---	1.0E-02	2.50E-07	---	劣化
Ra-226	1600	5.0E+03	0.025	125	キャリアフリー	6.0E-07	1.50E-11	95.4.12	Amersham,RAY.44
Cs-137	30.17	5.0E+04	0.025	1250	1.00E+00	9.9E-06	9.50E-12	96.5.1	Amersham,CDS2
Ni-63	100.1	5.0E+04	0.025	1250	1.00E+01	2.1E-06	2.90E-12	94.4.1	Amersham,NBS1

1)カラム1つあたりの塗布量
2)Tc,Np,Uはストック液中沈殿混みで塗布

添付資料Ⅱ

電気泳動試験結果データ

試験装置	泳動装置	ｱﾄﾞﾊﾞﾝﾃｯｸ東洋社製 PE-2型
	直流電源	GOOD WILL INSTRUMENT社製 GPR-3030
	濾紙	ｱﾄﾞﾊﾞﾝﾃｯｸ東洋社製 No.51A
泳動時間	7時間30分	
印可電圧	25 V	

陽極側

	測定結果 / cpm				
滴下位置からの距離 / cm	Reference		Tc-99		
	Cl-36	Cs-137	1.4g/cm^3	1.8g/cm^3	1.8g/cm^3 （海水系）
9 ～ 10	0.0	0.0	0.0	0.0	1.5
8 ～ 9	0.0	2.6	0.0	5.5	0.0
7 ～ 8	0.0	0.0	0.0	8.7	5.3
6 ～ 7	0.4	0.0	1.3	0.0	1.7
5 ～ 6	758.6	0.0	0.0	7.9	0.0
4 ～ 5	14176.4	0.0	2.5	215.7	2.9
3 ～ 4	19091.0	1.8	267.1	3287.9	0.0
2 ～ 3	1020.6	0.0	3274.9	6262.9	7.5
1 ～ 2	1.2	0.0	5746.9	6750.9	181.3
0 ～ 1	0.0	4.2	11393.3	10707.1	6620.3
0 ～ -1	0.0	0.0	14310.7	7513.9	13234.5
-1 ～ -2	0.0	3.2	518.7	41.3	5535.1
-2 ～ -3	0.0	0.0	3.5	3.7	21.7
-3 ～ -4	0.0	10.4	0.5	0.0	0.0
-4 ～ -5	0.2	3164.4	0.0	2.7	0.0
-5 ～ -6	0.0	21990.5	0.0	4.5	1.5
-6 ～ -7	0.0	10104.0	0.0	1.7	0.0
-7 ～ -8	0.0	862.2	0.9	3.9	0.0
-8 ～ -9	2.2	15.2	1.9	2.1	0.0
-9 ～ -10	0.0	0.0	1.1	1.1	0.0

陰極側

添付資料Ⅲ

拡散試験結果データ

試験条件	
試料	ｸﾆｹﾞﾙV1
核種	Ra-226
検定日	1995/4/12
充填密度	1.4 g/cm3
拡散期間	7.0 日
雰囲気	大気雰囲気
試験液性	蒸留水
試料形状	20 × 20 mm
スライス幅	1mm
トレーサ濃度	5 kBq/ml
トレーサ量	25 μl
分析	液体ｼﾝﾁﾚｰｼｮﾝｶｳﾝﾀｰ

回帰分析の結果	
標本数	14
Y = a·X + b	a = -46070.029 b = 9.350
R2乗	0.994
Da =	9.0E-12 m2/s

表　Ra-226の非定常拡散試験結果①

	試験データ				カラム内濃度分布データ	
スライス片	スライス片中の乾燥重量・含水量測定			スライス片中の トレーサ量	拡散源からの距離	トレーサ濃度
No.	風袋 / g	乾燥前 / g	乾燥後 / g	/ cpm	/ mm	/ cpm·g-1
1	1.066	1.567	1.376	4.3	19.6	8.6
2	1.062	1.593	1.426	3.1	18.6	5.8
3	1.070	1.645	1.475	6.9	17.7	12.0
4	1.079	1.677	1.505	5.5	16.6	9.2
5	1.073	1.646	1.488	7.5	15.6	13.1
6	1.079	1.663	1.500	4.1	14.6	7.0
7	1.067	1.697	1.528	2.3	***13.5***	***3.7***
8	1.071	1.697	1.531	7.5	***12.4***	***12.0***
9	1.059	1.639	1.487	14.9	***11.3***	***25.7***
10	1.082	1.679	1.521	33.1	***10.3***	***55.4***
11	1.076	1.653	1.501	102.1	***9.3***	***176.9***
12	1.076	1.669	1.517	287.7	***8.2***	***485.1***
13	1.072	1.656	1.504	538.1	***7.2***	***921.4***
14	1.072	1.669	1.515	1125.1	***6.2***	***1884.6***
15	1.072	1.660	1.505	1957.1	***5.1***	***3328.4***
16	1.073	1.666	1.513	3201.1	***4.1***	***5398.1***
17	1.069	1.681	1.522	4809.7	***3.0***	***7859.0***
18	1.071	1.647	1.499	6167.3	***2.0***	***10707.1***
19	1.077	1.496	1.381	6425.5	***1.1***	***15335.3***
20	1.068	1.472	1.360	4773.7	***0.4***	***11816.1***

＊太字 *イタリック*のデータを見かけの拡散係数の解析に用いた

試験条件	
試料	ｸﾆｹﾞﾙV1
核種	Ra-226
検定日	1995/4/12
充填密度	1.4 g/cm3
拡散期間	7.0 日
雰囲気	大気雰囲気
試験液性	蒸留水
試料形状	20×20 mm
スライス幅	1mm
トレーサ濃度	5 kBq/ml
トレーサ量	25μl
分析	液体ｼﾝﾁﾚｰｼｮﾝｶｳﾝﾀｰ

回帰分析の結果	
標本数	12
Y = a・X + b	a = −48796.908 b = 9.225
R2乗	0.994
Da =	8.5E−12 m2/s

表　Ra-226の非定常拡散試験結果②

スライス片	試験データ				カラム内濃度分布データ	
	スライス片中の乾燥重量・含水量測定			スライス片中のトレーサ量	拡散源からの距離	トレーサ濃度
No.	風袋 / g	乾燥前 / g	乾燥後 / g	/ cpm	/ mm	/ cpm・g-1
1	1.071	1.571	1.375	4.9	19.6	9.8
2	1.059	1.571	1.407	1.7	18.7	3.3
3	1.061	1.592	1.434	3.7	17.8	7.0
4	1.072	1.623	1.465	1.3	16.9	2.4
5	1.076	1.648	1.492	3.3	15.9	5.8
6	1.071	1.641	1.485	6.9	14.9	12.1
7	1.078	1.827	1.626	2.3	13.8	3.0
8	1.073	1.609	1.467	9.1	12.7	17.0
9	1.081	1.705	1.539	11.7	*11.7*	*18.8*
10	1.074	1.687	1.523	24.7	*10.6*	*40.3*
11	1.068	1.660	1.506	50.9	*9.6*	*86.0*
12	1.068	1.646	1.496	132.3	*8.6*	*228.9*
13	1.075	1.723	1.557	360.9	*7.5*	*556.9*
14	1.080	1.706	1.543	796.9	*6.4*	*1273.0*
15	1.083	1.703	1.540	1387.6	*5.4*	*2238.1*
16	1.071	1.672	1.520	2411.7	*4.3*	*4012.8*
17	1.071	1.660	1.506	3659.1	*3.3*	*6212.4*
18	1.063	1.595	1.444	4733.1	*2.3*	*8896.8*
19	1.068	1.599	1.451	5327.1	*1.4*	*10032.2*
20	1.073	1.637	1.482	6435.4	*0.5*	*11410.3*

＊太字 *イタリック*のデータを見かけの拡散係数の解析に用いた

試験条件

試料	ｸﾆｹﾞﾙV1
核種	Ra-226
検定日	1995/4/12
充填密度	1.8 g/cm3
拡散期間	15.0 日
雰囲気	大気雰囲気
試験液性	蒸留水
試料形状	20×20 mm
スライス幅	1mm
トレーサ濃度	5 kBq/ml
トレーサ量	25μl
分析	液体ｼﾝﾁﾚｰｼｮﾝｶｳﾝﾀｰ

回帰分析の結果

標本数	14
Y = a・X + b	a = −36143.077
	b = 9.111
R2乗	0.989
Da =	5.3E−12 m2/s

表　Ra-226の非定常拡散試験結果①

スライス片	試験データ				カラム内濃度分布データ	
	スライス片中の乾燥重量・含水量測定			スライス片中のトレーサ量	拡散源からの距離	トレーサ濃度
No.	風袋 / g	乾燥前 / g	乾燥後 / g	/ cpm	/ mm	/ cpm・g-1
1	1.040	1.851	1.668	8.3	19.4	10.2
2	1.057	1.690	1.570	4.9	18.3	7.7
3	1.055	1.714	1.588	0.0	17.3	0.0
4	1.065	1.701	1.579	10.1	16.3	15.9
5	1.040	1.693	1.572	5.9	15.4	9.0
6	1.045	1.784	1.652	9.1	14.3	12.3
7	1.045	1.600	1.510	11.3	***13.3***	***20.4***
8	1.058	1.695	1.585	28.1	***12.4***	***44.1***
9	1.049	1.796	1.672	59.1	***11.4***	***79.1***
10	1.064	1.717	1.609	103.7	***10.3***	***158.8***
11	1.059	1.717	1.607	201.5	***9.3***	***306.2***
12	1.049	1.723	1.612	352.9	***8.3***	***523.6***
13	1.046	1.652	1.560	643.7	***7.3***	***1062.2***
14	1.051	1.655	1.561	1071.5	***6.4***	***1774.0***
15	1.051	1.770	1.664	1962.9	***5.4***	***2730.0***
16	1.045	1.697	1.600	2854.1	***4.4***	***4377.5***
17	1.059	1.672	1.584	3870.3	***3.4***	***6313.7***
18	1.060	1.741	1.638	6022.3	***2.4***	***8843.3***
19	1.069	1.744	1.634	8058.7	***1.4***	***11938.8***
20	1.050	1.647	1.545	6618.5	***0.5***	***11086.3***

＊太字*イタリック*のデータを見かけの拡散係数の解析に用いた

試験条件	
試料	ｸﾆｹﾞﾙV1
核種	Ra-226
検定日	1995/4/12
充填密度	1.8 g/cm3
拡散期間	15.0 日
雰囲気	大気雰囲気
試験液性	蒸留水
試料形状	20×20 mm
スライス幅	1mm
トレーサ濃	5 kBq/ml
トレーサ量	25 μl
分析	液体ｼﾝﾁﾚｰｼｮﾝｶｳﾝﾀｰ

回帰分析の結果	
標本数	12
Y = a・X + b	a = -36748.270 b = 9.260
R2乗	0.989
Da =	5.2E-12 m2/s

表　　Ra-226の非定常拡散試験結果②

ライス	試験データ				カラム内濃度分布データ	
	スライス片中の乾燥重量・含水量測定			スライス片中のトレーサ量	拡散源からの距離	トレーサ濃度
No.	風袋 / g	乾燥前 / g	乾燥後 / g	/ cpm	/ mm	/ cpm・g-1
1	1.051	1.787	1.624	4.3	19.4	5.8
2	1.040	1.658	1.538	34.1	18.4	55.2
3	1.056	1.688	1.570	10.3	17.4	16.3
4	1.040	1.674	1.553	3.9	16.4	6.2
5	1.059	1.704	1.587	2.5	15.4	3.9
6	1.077	1.726	1.610	12.9	14.4	19.9
7	1.073	1.840	1.701	29.7	13.3	38.7
8	1.056	1.713	1.606	251.1	12.2	382.2
9	1.062	1.737	1.626	84.7	*11.2*	*125.5*
10	1.058	1.717	1.603	160.7	*10.2*	*243.9*
11	1.048	1.666	1.567	301.9	*9.2*	*488.5*
12	1.051	1.714	1.604	543.8	*8.2*	*820.2*
13	1.055	1.658	1.556	852.9	*7.2*	*1414.4*
14	1.049	1.690	1.586	1434.9	*6.2*	*2238.5*
15	1.057	1.729	1.619	2183.3	*5.2*	*3249.0*
16	1.045	1.626	1.535	2822.5	*4.2*	*4858.0*
17	1.057	1.705	1.601	4198.3	*3.3*	*6478.9*
18	1.061	1.674	1.572	5704.1	*2.3*	*9305.2*
19	1.057	1.794	1.666	7598.9	*1.2*	*10310.6*
20	1.050	1.481	1.401	6819.8	*0.3*	*15823.2*

＊太字*イタリック*のデータを見かけの拡散係数の解析に用いた

試験条件	
試料	ｸﾆｹﾞﾙV1
核種	Ra-226
検定日	1995/4/12
充填密度	1.8 g/cm3
拡散期間	20.0 日
雰囲気	大気雰囲気
試験液性	模擬海水 (3%-NaCl)
試料形状	20 × 20 mm
スライス幅	1mm
トレーサ濃度	5 kBq/ml
トレーサ量	25 μ l
分析	液体ｼﾝﾁﾚｰｼｮﾝｶｳﾝﾀｰ

回帰分析の結果	
標本数	8
Y = a･X + b	a = -83258.027
	b = 9.271
R2乗	0.958
Da =	1.7E-12 m2/s

表　Ra-226の非定常拡散試験結果①（海水系）

スライス片	試験データ				カラム内濃度分布データ	
	スライス片中の乾燥重量・含水量測定			スライス片中のトレーサ量	拡散源からの距離	トレーサ濃度
No.	風袋 / g	乾燥前 / g	乾燥後 / g	/ cpm	/ mm	/ cpm･g-1
1	1.066	1.698	1.579	0.0	19.5	0.0
2	1.058	1.691	1.575	0.0	18.5	0.0
3	1.071	1.743	1.628	0.5	17.6	0.7
4	1.068	1.751	1.634	1.5	16.5	2.2
5	1.076	1.763	1.650	0.0	15.5	0.0
6	1.068	1.664	1.564	0.3	14.5	0.5
7	1.082	1.759	1.644	0.0	13.5	0.0
8	1.075	1.724	1.617	0.0	12.5	0.0
9	1.073	1.825	1.705	0.0	11.4	0.0
10	1.070	1.731	1.622	10.9	10.3	16.5
11	1.075	1.753	1.648	22.1	9.3	32.6
12	1.078	1.737	1.635	59.3	8.3	90.0
13	1.075	1.718	1.620	117.7	***7.3***	***183.0***
14	1.087	1.714	1.621	225.7	***6.3***	***360.0***
15	1.078	1.724	1.633	489.9	***5.4***	***758.4***
16	1.085	1.738	1.645	954.1	***4.4***	***1461.1***
17	1.063	1.717	1.624	1960.3	***3.4***	***2997.4***
18	1.070	1.683	1.606	3572.5	***2.4***	***5827.9***
19	1.066	1.713	1.625	7698.9	***1.4***	***11899.4***
20	1.082	1.695	1.601	10266.5	***0.5***	***16748.0***

＊太字 *イタリック*のデータを見かけの拡散係数の解析に用いた

試験条件	
試料	ｸﾆｹﾞﾙV1
核種	Ra-226
検定日	1995/4/12
充填密度	1.8 g/cm3
拡散期間	20.0 日
雰囲気	大気雰囲気
試験液性	模擬海水 (3%-NaCl)
試料形状	20 × 20 mm
スライス幅	1mm
トレーサ濃度	5 kBq/ml
トレーサ量	25 μl
分析	液体ｼﾝﾁﾚｰｼｮﾝｶｳﾝﾀｰ

回帰分析の結果	
標本数	8
Y = a・X + b	a = -73610.169
	b = 9.255
R2乗	0.943
Da =	2.0E-12 m2/s

表　Ra-226の非定常拡散試験結果②（海水系）

スライス片	試験データ				カラム内濃度分布データ	
	スライス片中の乾燥重量・含水量測定			スライス片中のトレーサ量	拡散源からの距離	トレーサ濃度
No.	風袋 / g	乾燥前 / g	乾燥後 / g	/ cpm	/ mm	/ cpm・g-1
1	1.086	1.729	1.607	20.5	19.5	31.9
2	1.077	1.712	1.606	3.7	18.5	5.8
3	1.083	1.719	1.617	3.5	17.5	5.5
4	1.077	1.718	1.613	0.0	16.6	0.0
5	1.078	1.726	1.626	4.5	15.6	6.9
6	1.078	1.724	1.622	1.7	14.6	2.6
7	1.071	1.714	1.608	0.0	13.6	0.0
8	1.085	1.758	1.653	4.9	12.6	7.3
9	1.073	1.720	1.616	10.9	11.6	16.8
10	1.074	1.729	1.630	16.3	10.6	24.9
11	1.087	1.737	1.633	38.7	9.6	59.5
12	1.070	1.743	1.635	69.7	8.5	103.6
13	1.074	1.734	1.633	163.5	***7.5***	***247.7***
14	1.073	1.808	1.697	335.9	***6.4***	***457.0***
15	1.079	1.701	1.609	580.3	***5.4***	***933.0***
16	1.077	1.745	1.642	1168.9	***4.4***	***1749.9***
17	1.079	1.731	1.632	2019.1	***3.4***	***3096.8***
18	1.076	1.724	1.632	3736.3	***2.4***	***5765.9***
19	1.078	1.723	1.627	8172.3	***1.4***	***12670.2***
20	1.077	1.658	1.562	10167.3	***0.4***	***17499.7***

＊太字 *イタリック*のデータを見かけの拡散係数の解析に用いた

試験条件	
試料	ｸﾆｹﾞﾙV1
核種	Tc-99
検定日	1994/6/17
充填密度	1.4 g/cm3
拡散期間	82.8 日
雰囲気	還元雰囲気 (Ar)
試験液性	蒸留水
試料形状	20×20 mm
スライス幅	0.5 mm
トレーサ濃度	25 kBq/ml
トレーサ量	25μl
分析	液体ｼﾝﾁﾚｰｼｮﾝｶｳﾝﾀｰ

回帰分析の結果	
標本数	3
Co	4201
Da =	6.8E-14 m2/s

表　Tc-99の非定常拡散試験結果①

スライス片	試験データ				カラム内濃度分布データ	
	スライス片中の乾燥重量・含水量測定			スライス片中のトレーサ量	拡散源からの距離	トレーサ濃度
No.	風袋 / g	乾燥前 / g	乾燥後 / g	/ cpm	/ mm	/ cpm・g-1
1	1.070	1.239	1.186	7028.8	0.149	41590.5
2	1.073	1.290	1.226	664.0	***0.490***	***3059.9***
3	1.073	1.320	1.249	281.0	***0.900***	***1137.7***
4	1.076	1.319	1.249	202.8	***1.332***	***834.6***
5	1.075	1.335	1.267	195.2	1.777	750.8
6	1.083	1.335	1.268	160.0	2.229	634.9
7	1.065	1.330	1.260	135.0	2.685	509.4
8	1.067	1.329	1.260	110.0	3.151	419.8
9	1.068	1.334	1.263	84.6	3.617	318.0
10	1.068	1.330	1.263	73.6	4.083	280.9
11	1.067	1.342	1.272	55.8	4.557	202.9
12	1.078	1.333	1.268	49.8	5.025	195.3
13	1.073	1.347	1.275	49.2	5.492	179.6
14	1.075	1.344	1.273	29.6	5.972	110.0
15	1.071	1.356	1.284	25.4	6.461	89.1
16	1.075	1.358	1.286	26.8	6.962	94.7
17	1.080	1.378	1.302	21.6	7.475	72.5
18	1.084	1.373	1.297	21.2	7.994	73.4
19	1.096	1.400	1.324	13.0	8.517	42.8
20	1.084	1.367	1.292	12.4	9.036	43.8
21	1.075	7.142	5.447	-	-	-

＊太字 *イタリック*のデータを見かけの拡散係数の解析に用いた

試験条件	
試料	ｸﾆｹﾞﾙV1
核種	Tc-99
検定日	1997/10/17
充填密度	1.4 g/cm3
拡散期間	108.8 日
雰囲気	還元雰囲気 (Ar)
試験液性	蒸留水
試料形状	20×20 mm
スライス幅	0.2 mm
トレーサ濃度	25 kBq/ml
トレーサ量	25 μl
分析	液体ｼﾝﾁﾚｰｼｮﾝｶｳﾝﾀｰ

回帰分析の結果	
標本数	4
Co	11873
Da =	8.1E-15 m2/s

表　Tc-99の非定常拡散試験結果②

スライス片	試験データ				カラム内濃度分布データ	
	スライス片中の乾燥重量・含水量測定			スライス片中のトレーサ量	拡散源からの距離	トレーサ濃度
No.	風袋 / g	乾燥前 / g	乾燥後 / g	/ cpm	/ mm	/ cpm・g-1
1	1.070	1.129	1.104	6833.0	0.051	115813.6
2	1.074	1.149	1.128	607.4	***0.166***	***8098.7***
3	1.074	1.169	1.144	467.4	***0.312***	***4920.0***
4	1.077	1.175	1.148	206.6	***0.478***	***2108.2***
5	1.088	1.198	1.170	100.6	***0.657***	***914.5***
6	1.083	1.171	1.150	49.0	0.827	556.8
7	1.091	1.213	1.182	91.8	1.008	752.5
8	1.076	1.190	1.166	76.2	1.211	668.4
9	1.083	1.183	1.160	61.8	1.395	618.0
10	1.080	1.188	1.163	103.0	1.574	953.7
11	1.082	11.740	8.838	−	−	−

＊太字 *イタリック*のデータを見かけの拡散係数の解析に用いた

試験条件	
試料	ｸﾆｹﾞﾙV1
核種	Tc-99
検定日	1994/6/17
充填密度	1.8 g/cm3
拡散期間	83.0 日
雰囲気	還元雰囲気 (Ar)
試験液性	蒸留水
試料形状	20 × 20 mm
スライス幅	0.5 mm
トレーサ濃度	25 kBq/ml
トレーサ量	25 μl
分析	液体ｼﾝﾁﾚｰｼｮﾝｶｳﾝﾀｰ

回帰分析の結果	
標本数	3
Co	6153
Da =	1.0E-13 m2/s

表　Tc-99の非定常拡散試験結果①

スライス片	試験データ				カラム内濃度分布データ	
	スライス片中の乾燥重量・含水量測定			スライス片中のトレーサ量	拡散源からの距離	トレーサ濃度
No.	風袋 / g	乾燥前 / g	乾燥後 / g	/ cpm	/ mm	/ cpm・g-1
1	1.086	1.233	1.204	4919.2	0.120	33463.9
2	1.097	1.226	1.201	625.6	***0.345***	***4849.6***
3	1.091	1.380	1.330	974.6	***0.687***	***3372.3***
4	1.085	1.372	1.322	598.2	***1.157***	***2084.3***
5	1.100	1.362	1.319	502.2	1.606	1916.8
6	1.097	1.393	1.347	433.2	2.061	1463.5
7	1.088	1.378	1.330	286.0	2.540	986.2
8	1.085	1.353	1.310	241.6	2.996	901.5
9	1.083	1.365	1.318	189.6	3.445	672.3
10	1.088	1.390	1.341	154.8	3.922	512.6
11	1.099	1.411	1.362	103.6	4.423	332.1
12	1.091	1.360	1.315	68.2	4.898	253.5
13	1.098	1.412	1.361	77.6	5.374	247.1
14	1.090	1.381	1.335	56.2	5.868	193.1
15	1.093	1.388	1.336	41.8	6.346	141.7
16	1.074	1.377	1.327	44.4	6.835	146.5
17	1.078	1.383	1.331	41.0	7.331	134.4
18	1.071	1.391	1.341	37.6	7.842	117.5
19	1.075	1.376	1.327	33.6	8.349	111.6
20	1.076	1.396	1.344	33.2	8.856	103.8
21	1.071	7.734	6.530	－	－	－

＊太字 *イタリック*のデータを見かけの拡散係数の解析に用いた

試験条件	
試料	ｸﾆｹﾞﾙV1
核種	Tc-99
検定日	1997/10/17
充填密度	1.8 g/cm3
拡散期間	108.9 日
雰囲気	還元雰囲気 (Ar)
試験液性	蒸留水
試料形状	20 × 20 mm
スライス幅	0.2 mm
トレーサ濃度	25 kBq/ml
トレーサ量	25 μl
分析	液体ｼﾝﾁﾚｰｼｮﾝｶｳﾝﾀｰ

回帰分析の結果	
標本数	9
Co	5417
Da =	7.5E-14 m2/s

表　Tc-99の非定常拡散試験結果②

スライス片	試験データ				カラム内濃度分布データ	
	スライス片中の乾燥重量・含水量測定			スライス片中のトレーサ量	拡散源からの距離	トレーサ濃度
No.	風袋 / g	乾燥前 / g	乾燥後 / g	/ cpm	/ mm	/ cpm・g-1
1	1.072	1.168	1.150	6785.2	0.077	70679.2
2	1.073	1.093	1.090	86.8	***0.169***	***4340.0***
3	1.080	1.112	1.107	115.4	***0.210***	***3606.3***
4	1.078	1.111	1.108	121.4	***0.262***	***3678.8***
5	1.070	1.116	1.112	288.8	***0.325***	***6278.3***
6	1.076	1.131	1.126	263.0	***0.406***	***4781.8***
7	1.081	1.175	1.167	339.6	***0.525***	***3612.8***
8	1.082	1.249	1.231	487.2	***0.733***	***2917.4***
9	1.077	1.202	1.187	320.2	***0.965***	***2561.6***
10	1.076	1.140	1.133	102.4	***1.116***	***1600.0***
11	1.074	12.886	10.858	-	-	-

＊太字 *イタリック*のデータを見かけの拡散係数の解析に用いた

試験条件

試料	ｸﾆｹﾞﾙV1
核種	Tc−99
検定日	1994/6/17
充填密度	1.8 g/cm3
拡散期間	83.0 日
雰囲気	還元雰囲気 (Ar)
試験液性	模擬海水 (3%−NaCl)
試料形状	20 × 20 mm
スライス幅	0.5 mm
トレーサ濃度	25 kBq/ml
トレーサ量	25 μl
分析	液体ｼﾝﾁﾚｰｼｮﾝｶｳﾝﾀｰ

回帰分析の結果

標本数	4
Co	1371
Da =	3.5E−13 m2/s

表　Tc−99の非定常拡散試験結果①（海水系）

スライス片	試験データ				カラム内濃度分布データ	
	スライス片中の乾燥重量・含水量測定			スライス片中のトレーサ量	拡散源からの距離	トレーサ濃度
No.	風袋 / g	乾燥前 / g	乾燥後 / g	/ cpm	/ mm	/ cpm・g−1
1	1.069	1.290	1.245	9587.4	0.168	43381.9
2	1.067	1.350	1.300	309.0	***0.550***	***1091.9***
3	1.067	1.363	1.307	256.2	***0.989***	***865.5***
4	1.070	1.371	1.314	235.2	***1.442***	***781.4***
5	1.065	1.370	1.315	156.6	***1.902***	***513.4***
6	1.057	1.374	1.320	98.8	2.374	311.7
7	1.059	1.408	1.352	76.6	2.879	219.5
8	1.067	1.407	1.348	46.4	3.401	136.5
9	1.073	1.397	1.339	48.0	3.905	148.1
10	1.068	1.393	1.336	27.6	4.397	84.9
11	1.066	1.390	1.335	30.2	4.890	93.2
12	1.064	1.398	1.340	32.8	5.389	98.2
13	1.063	1.380	1.324	42.8	5.883	135.0
14	1.068	1.398	1.341	45.0	6.373	136.4
15	1.069	1.396	1.339	28.2	6.872	86.2
16	1.068	1.409	1.349	32.0	7.378	93.8
17	1.067	1.464	1.397	28.2	7.938	71.0
18	1.070	1.461	1.396	15.0	8.536	38.4
19	1.068	1.405	1.348	4.2	9.088	12.5
20	1.061	1.385	1.327	5.4	9.590	16.7
21	1.067	7.767	6.519	−	−	−

＊太字 *イタリック*のデータを見かけの拡散係数の解析に用いた

試験条件

試料	ｸﾆｹﾞﾙV1
核種	Tc-99
検定日	1997/10/17
充填密度	1.8 g/cm3
拡散期間	108.9 日
雰囲気	還元雰囲気 (Ar)
試験液性	模擬海水 (3%-NaCl)
試料形状	20 × 20 mm
スライス幅	0.2 mm
トレーサ濃度	25 kBq/ml
トレーサ量	25 μl
分析	液体ｼﾝﾁﾚｰｼｮﾝｶｳﾝﾀｰ

回帰分析の結果

標本数	5
Co	6399
Da =	1.1E-14 m2/s

表　Tc-99の非定常拡散試験結果②（海水系）

スライス片	試験データ				カラム内濃度分布データ	
	スライス片中の乾燥重量・含水量測定			スライス片中のトレーサ量	拡散源からの距離	トレーサ濃度
No.	風袋 / g	乾燥前 / g	乾燥後 / g	/ cpm	/ mm	/ cpm・g-1
1	1.065	1.182	1.160	8377.8	0.089	71605.1
2	1.075	1.110	1.104	143.8	***0.204***	***4108.6***
3	1.078	1.108	1.104	118.4	***0.254***	***3946.7***
4	1.082	1.167	1.155	259.8	***0.341***	***3056.5***
5	1.080	1.188	1.170	171.8	***0.487***	***1590.7***
6	1.078	1.207	1.184	127.6	***0.667***	***989.1***
7	1.088	1.173	1.160	108.2	0.830	1272.9
8	1.080	1.219	1.198	97.6	1.000	702.2
9	1.087	1.209	1.188	77.6	1.198	636.1
10	1.077	1.179	1.164	57.8	1.368	566.7
11	1.075	13.297	11.135	-	-	-

＊太字 *イタリック*のデータを見かけの拡散係数の解析に用いた

試験条件	
試料	ｸﾆｹﾞﾙV1
核種	Np-237
検定日	1997/10/17
充填密度	1.4 g/cm3
拡散期間	50.2 日
雰囲気	還元雰囲気 (Ar)
試験液性	蒸留水
試料形状	20 × 20 mm
スライス幅	0.5 mm
トレーサ濃度	10 kBq/ml
トレーサ量	25 μ l
分析	液体ｼﾝﾁﾚｰｼｮﾝｶｳﾝﾀｰ

回帰分析の結果	
標本数	2
Co	8937
Da =	1.6E-14 m2/s

表　Np-237の非定常拡散試験結果①

スライス片	試験データ				カラム内濃度分布データ	
	スライス片中の乾燥重量・含水量測定			スライス片中のトレーサ量	拡散源からの距離	トレーサ濃度
No.	風袋 / g	乾燥前 / g	乾燥後 / g	/ cpm	/ mm	/ cpm・g-1
1	1.091	1.183	1.152	4067.2	0.083	44208.7
2	1.092	1.287	1.233	634.6	***0.341***	***3254.4***
3	1.097	1.331	1.270	107.4	***0.727***	***459.0***
4	1.092	1.338	1.273	74.6	1.159	303.3
5	1.097	1.339	1.276	63.2	1.598	261.2
6	1.062	1.327	1.258	68.8	2.055	259.6
7	1.059	1.312	1.247	50.0	2.521	197.6
8	1.059	1.320	1.250	47.4	2.983	181.6
9	1.053	1.322	1.252	36.6	3.460	136.1
10	1.052	1.300	1.238	21.0	3.925	84.7
11	1.047	1.316	1.250	15.8	4.391	58.7
12	1.063	1.319	1.255	6.0	4.863	23.4
13	1.109	1.379	1.308	2.2	5.337	8.1
14	1.069	1.329	1.263	0.0	5.814	0.0
15	1.060	1.322	1.255	0.0	6.283	0.0
16	1.063	1.343	1.270	0.0	6.771	0.0
17	1.067	1.354	1.279	1.8	7.281	6.3
18	1.071	1.342	1.272	0.0	7.783	0.0
19	1.068	1.356	1.276	0.0	8.287	0.0
20	1.073	1.348	1.272	0.0	8.793	0.0
21	1.084	7.173	5.472	-	-	-

＊太字 *イタリック*のデータを見かけの拡散係数の解析に用いた

試験条件	
試料	ｸﾆｹﾞﾙV1
核種	Np-237
検定日	1997/10/17
充填密度	1.4 g/cm3
拡散期間	76.2 日
雰囲気	還元雰囲気（Ar）
試験液性	蒸留水
試料形状	20×20 mm
スライス幅	0.2 mm
トレーサ濃度	10 kBq/ml
トレーサ量	25μl
分析	液体ｼﾝﾁﾚｰｼｮﾝｶｳﾝﾀｰ

回帰分析の結果	
標本数	3
Co	3467
Da =	1.6E-14 m2/s

表　Np-237の非定常拡散試験結果②

スライス片	試験データ				カラム内濃度分布データ	
	スライス片中の乾燥重量・含水量測定			スライス片中のトレーサ量	拡散源からの距離	トレーサ濃度
No.	風袋 / g	乾燥前 / g	乾燥後 / g	/ cpm	/ mm	/ cpm・g-1
1	1.071	1.152	1.121	2949.0	0.074	36407.4
2	1.078	1.131	1.112	130.0	***0.196***	***2452.8***
3	1.067	1.132	1.109	105.0	***0.304***	***1615.4***
4	1.068	1.134	1.114	86.3	***0.423***	***1308.0***
5	1.075	1.146	1.124	80.3	0.548	1131.0
6	1.072	1.163	1.135	75.0	0.695	824.5
7	1.073	1.168	1.141	75.3	0.865	792.1
8	1.080	1.161	1.136	61.5	1.025	758.6
9	1.084	1.168	1.140	69.8	1.176	831.4
10	1.081	1.165	1.141	59.9	1.329	712.5
11	1.076	11.276	8.581	–	–	–

＊太字 *イタリック*のデータを見かけの拡散係数の解析に用いた

試験条件	
試料	ｸﾆｹﾞﾙV1
核種	Np-237
検定日	1997/10/17
充填密度	1.8 g/cm3
拡散期間	50.2 日
雰囲気	還元雰囲気 (Ar)
試験液性	蒸留水
試料形状	20 × 20 mm
スライス幅	0.5 mm
トレーサ濃度	10 kBq/ml
トレーサ量	25 μ l
分析	液体ｼﾝﾁﾚｰｼｮﾝｶｳﾝﾀｰ

回帰分析の結果	
標本数	2
Co	2189
Da =	4.9E-14 m2/s

表　Np-237の非定常拡散試験結果①

スライス片	試験データ				カラム内濃度分布データ	
	スライス片中の乾燥重量・含水量測定			スライス片中のトレーサ量	拡散源からの距離	トレーサ濃度
No.	風袋 / g	乾燥前 / g	乾燥後 / g	/ cpm	/ mm	/ cpm・g-1
1	1.063	1.257	1.222	5612.6	0.148	28930.9
2	1.059	1.303	1.260	247.0	*0.481*	*1012.3*
3	1.080	1.382	1.329	111.2	*0.897*	*368.2*
4	1.086	1.395	1.346	111.4	1.362	360.5
5	1.085	1.401	1.349	40.8	1.838	129.1
6	1.088	1.423	1.370	13.2	2.334	39.4
7	1.081	1.410	1.356	2.4	2.840	7.3
8	1.083	1.427	1.371	3.2	3.352	9.3
9	1.084	1.396	1.347	3.0	3.852	9.6
10	1.087	1.416	1.363	0.0	4.340	0.0
11	1.081	1.416	1.364	0.0	4.846	0.0
12	1.077	1.394	1.344	2.4	5.342	7.6
13	1.084	1.414	1.360	2.4	5.835	7.3
14	1.087	1.412	1.360	4.4	6.334	13.5
15	1.081	1.389	1.340	0.0	6.816	0.0
16	1.083	1.424	1.367	1.8	7.310	5.3
17	1.076	1.399	1.348	0.0	7.816	0.0
18	1.086	1.440	1.377	4.6	8.331	13.0
19	1.090	1.393	1.340	0.0	8.832	0.0
20	1.080	1.405	1.353	0.0	9.310	0.0
21	1.119	7.975	6.701	−	−	−

＊太字*イタリック*のデータを見かけの拡散係数の解析に用いた

試験条件	
試料	ｸﾆｹﾞﾙV1
核種	Np-237
検定日	1997/10/17
充填密度	1.8 g/cm3
拡散期間	76.2 日
雰囲気	還元雰囲気 (Ar)
試験液性	蒸留水
試料形状	20 × 20 mm
スライス幅	0.2 mm
トレーサ濃度	10 kBq/ml
トレーサ量	25 μl
分析	液体ｼﾝﾁﾚｰｼｮﾝｶｳﾝﾀｰ

回帰分析の結果	
標本数	6
Co	2432
Da =	3.2E-14 m2/s

表　Np-237の非定常拡散試験結果②

スライス片	試験データ				カラム内濃度分布データ	
	スライス片中の乾燥重量・含水量測定			スライス片中のトレーサ量	拡散源からの距離	トレーサ濃度
No.	風袋 / g	乾燥前 / g	乾燥後 / g	/ cpm	/ mm	/ cpm・g-1
1	1.073	1.181	1.155	3188.0	0.085	29518.5
2	1.074	1.118	1.111	85.6	***0.204***	***1945.5***
3	1.076	1.114	1.109	68.6	***0.269***	***1805.3***
4	1.076	1.134	1.128	98.4	***0.344***	***1696.6***
5	1.073	1.153	1.142	61.6	***0.453***	***770.0***
6	1.072	1.191	1.174	108.4	***0.609***	***910.9***
7	1.076	1.195	1.178	66.8	***0.796***	***561.3***
8	1.082	1.211	1.194	72.4	0.991	561.2
9	1.075	1.185	1.167	61.6	1.179	560.0
10	1.074	1.177	1.161	44.6	1.346	433.0
11	1.077	12.893	10.822	-	-	-

＊太字*イタリック*のデータを見かけの拡散係数の解析に用いた

試験条件	
試料	ｸﾆｹﾞﾙV1
核種	Np-237
検定日	1997/10/17
充填密度	1.8 g/cm3
拡散期間	50.2 日
雰囲気	還元雰囲気 (Ar)
試験液性	模擬海水 (3%-NaCl)
試料形状	20 × 20 mm
スライス幅	0.5 mm
トレーサ濃度	10 kBq/ml
トレーサ量	25 μl
分析	液体ｼﾝﾁﾚｰｼｮﾝｶｳﾝﾀｰ

回帰分析の結果	
標本数	2
Co	362
Da =	2.6E-14 m2/s

表　Np-237の非定常拡散試験結果①（海水系）

スライス片	試験データ				カラム内濃度分布データ	
	スライス片中の乾燥重量・含水量測定			スライス片中のトレーサ量	拡散源からの距離	トレーサ濃度
No.	風袋 / g	乾燥前 / g	乾燥後 / g	/ cpm	/ mm	/ cpm・g-1
1	1.048	1.212	1.184	5253.6	0.133	32034.1
2	1.051	1.296	1.256	29.6	***0.463***	***120.8***
3	1.067	1.360	1.311	6.2	***0.899***	***21.2***
4	1.069	1.369	1.322	0.0	1.378	0.0
5	1.060	1.364	1.316	1.8	1.867	5.9
6	1.059	1.371	1.321	0.8	2.365	2.6
7	1.060	1.400	1.346	0.0	2.892	0.0
8	1.060	1.379	1.328	0.0	3.425	0.0
9	1.056	1.394	1.339	0.0	3.957	0.0
10	1.056	1.381	1.329	0.8	4.493	2.5
11	1.060	1.384	1.333	2.4	5.018	7.4
12	1.054	1.389	1.335	0.0	5.551	0.0
13	1.060	1.376	1.326	0.0	6.077	0.0
14	1.061	1.384	1.331	0.0	6.594	0.0
15	1.060	1.395	1.339	11.4	7.126	34.0
16	1.062	1.383	1.332	0.0	7.657	0.0
17	1.054	1.385	1.329	0.8	8.184	2.4
18	1.051	1.380	1.326	0.0	8.718	0.0
19	1.051	1.386	1.328	0.0	9.255	0.0
20	1.053	1.346	1.296	1.8	9.763	6.1
21	1.092	7.956	6.667	-	-	-

＊太字 *イタリック*のデータを見かけの拡散係数の解析に用いた

試験条件	
試料	ｸﾆｹﾞﾙV1
核種	Np-237
検定日	1997/10/17
充填密度	1.8 g/cm3
拡散期間	76.2 日
雰囲気	還元雰囲気 (Ar)
試験液性	模擬海水 (3%-NaCl)
試料形状	20 × 20 mm
スライス幅	0.2 mm
トレーサ濃度	10 kBq/ml
トレーサ量	25 μ l
分析	液体ｼﾝﾁﾚｰｼｮﾝｶｳﾝﾀｰ

回帰分析の結果	
標本数	3
Co	16906
Da =	1.3E-15 m2/s

表　Np-237の非定常拡散試験結果②（海水系）

スライス片	試験データ				カラム内濃度分布データ	
	スライス片中の乾燥重量・含水量測定			スライス片中のトレーサ量	拡散源からの距離	トレーサ濃度
No.	風袋 / g	乾燥前 / g	乾燥後 / g	/ cpm	/ mm	/ cpm・g-1
1	1.081	1.169	1.150	6460.8	0.067	73418.2
2	1.070	1.089	1.084	102.2	***0.149***	***5378.9***
3	1.066	1.118	1.108	75.0	***0.204***	***1442.3***
4	1.073	1.126	1.117	31.0	***0.284***	***584.9***
5	1.071	1.184	1.163	7.8	0.411	69.0
6	1.071	1.180	1.160	4.0	0.582	36.7
7	1.076	1.228	1.205	4.2	0.782	27.6
8	1.076	1.164	1.152	6.2	0.966	70.5
9	1.080	1.193	1.177	0.0	1.120	0.0
10	1.083	1.203	1.187	0.0	1.298	0.0
11	1.083	13.226	11.140	-	-	-

＊太字*イタリック*のデータを見かけの拡散係数の解析に用いた

試験条件	
試料	ｸﾆｹﾞﾙV1
化学種	U ($UO_2(NO_3)_2 \cdot 6H_2O$)
検定日	−
充填密度	1.4 g/cm3
拡散期間	55.1 日
雰囲気	還元雰囲気 (Ar)
試験液性	蒸留水
試料形状	20 × 20 mm
スライス幅	0.5 mm
トレーサ濃度	約 0.01 mol/l
トレーサ量	25 μl
分析	ICP-MS

回帰分析の結果	
標本数	3
Co	1.24
Da =	1.2E-13 m2/s

表　Uの非定常拡散試験結果①

スライス片	試験データ					カラム内濃度分布データ	
	スライス片中の乾燥重量・含水量測定			スライス片中のトレーサ濃度	B.G	拡散源からの距離	トレーサ濃度
No.	風袋 / g	乾燥前 / g	乾燥後 / g	/ ppb	/ ppb	/ mm	/ mg
1	1.044	1.177	1.121	685.0	16.8	0.12	20.10
2	1.045	1.224	1.150	62.8	20.4	***0.39***	***0.95***
3	1.043	1.257	1.176	52.9	23.1	***0.74***	***0.56***
4	1.051	1.267	1.191	44.6	23.3	***1.11***	***0.39***
5	1.041	1.282	1.199	43.5	25.2	1.51	0.30
6	1.045	1.297	1.213	45.1	26.1	1.95	0.30
7	1.047	1.300	1.223	41.9	26.2	2.39	0.25
8	1.044	1.294	1.215	43.1	26.0	2.83	0.27
9	1.040	1.295	1.218	40.4	26.3	3.27	0.22
10	1.051	1.328	1.250	34.9	28.1	3.74	0.10
11	1.048	1.323	1.246	−	−	−	−
12	1.054	1.331	1.252	−	−	−	−
13	1.049	1.343	1.259	−	−	−	−
14	1.047	1.317	1.241	−	−	−	−
15	1.046	1.349	1.266	−	−	−	−
16	1.043	1.328	1.249	−	−	−	−
17	1.045	1.347	1.266	−	−	−	−
18	1.042	1.346	1.266	−	−	−	−
19	1.047	1.359	1.275	−	−	−	−
20	1.051	1.418	1.323	−	−	−	−
21	1.049	7.183	5.599	−	−	−	−

＊太字*イタリック*のデータを見かけの拡散係数の解析に用いた

試験条件	
試料	ｸﾆｹﾞﾙV1
化学種	U ($UO_2(NO_3)_2 \cdot 6H_2O$)
検定日	-
充填密度	1.4 g/cm3
拡散期間	123.1 日
雰囲気	還元雰囲気 (Ar)
試験液性	蒸留水
試料形状	20 × 20 mm
スライス幅	0.2 mm
トレーサ濃度	約 0.01 mol/l
トレーサ量	25 μl
分析	ICP-MS

回帰分析の結果	
標本数 1	9
Co	1.80
Da =	6.8E-14 m2/s

表　Uの非定常拡散試験結果②

スライス片	試験データ					カラム内濃度分布データ	
	スライス片中の乾燥重量・含水量測定			スライス片中のトレーサ濃度	B.G	拡散源からの距離	トレーサ濃度
No.	風袋 / g	乾燥前 / g	乾燥後 / g	/ ppb	/ ppb	/ mm	/ mg
1	1.073	1.108	1.091	396.0	9.1	0.03	44.22
2	1.074	1.118	1.097	30.2	9.8	***0.10***	***1.86***
3	1.073	1.125	1.105	18.6	10.4	***0.19***	***1.75***
4	1.072	1.134	1.108	24.1	11.2	***0.29***	***1.48***
5	1.073	1.161	1.128	35.0	13.2	***0.43***	***0.99***
6	1.070	1.162	1.132	38.7	13.5	***0.59***	***1.09***
7	1.070	1.162	1.134	37.2	13.5	***0.76***	***1.03***
8	1.072	1.167	1.131	31.8	13.8	***0.92***	***0.76***
9	1.077	1.168	1.137	28.6	13.5	***1.09***	***0.67***
10	1.080	1.180	1.149	27.8	14.2	***1.26***	***0.55***
11	1.072	11.409	8.563	-	-	-	-

＊太字 *イタリック*のデータを見かけの拡散係数の解析に用いた

試験条件	
試料	ｸﾆｹﾞﾙV1
化学種	U ($UO_2(NO_3)_2\cdot 6H_2O$)
検定日	－
充填密度	1.8 g/cm3
拡散期間	96.0 日
雰囲気	還元雰囲気 (Ar)
試験液性	蒸留水
試料形状	20×20 mm
スライス幅	0.5 mm
トレーサ濃度	約 0.01 mol/l
トレーサ量	25 μl
分析	ICP-MS

回帰分析の結果	
標本数	3
Co	0.84
Da =	1.2E-13 m2/s

表　Uの非定常拡散試験結果①

スライス片	試験データ					カラム内濃度分布データ	
	スライス片中の乾燥重量・含水量測定			スライス片中のトレーサ濃度	B.G	拡散源からの距離	トレーサ濃度
No.	風袋 / g	乾燥前 / g	乾燥後 / g	/ ppb	/ ppb	/ mm	/ mg
1	1.053	1.230	1.196	926.0	20.2	0.01	20.47
2	1.055	1.281	1.240	61.5	24.1	***0.04***	***0.66***
3	1.056	1.351	1.297	61.3	29.5	***0.08***	***0.43***
4	1.052	1.373	1.314	55.6	31.5	***0.13***	***0.30***
5	1.051	1.357	1.302	49.4	30.4	0.18	0.25
6	1.051	1.374	1.318	49.0	31.7	0.23	0.21
7	1.051	1.390	1.331	45.7	32.9	0.28	0.15
8	1.050	1.375	1.317	43.2	31.8	0.33	0.14
9	1.050	1.368	1.315	40.1	31.3	0.38	0.11
10	1.049	1.378	1.323	38.7	32.2	0.43	0.08
11	1.053	1.381	1.323	－	－	－	－
12	1.051	1.383	1.326	－	－	－	－
13	1.047	1.362	1.306	－	－	－	－
14	1.043	1.366	1.311	－	－	－	－
15	1.045	1.369	1.313	－	－	－	－
16	1.041	1.379	1.322	－	－	－	－
17	1.043	1.357	1.305	－	－	－	－
18	1.042	1.403	1.337	－	－	－	－
19	1.044	1.360	1.305	－	－	－	－
20	1.043	1.374	1.313	－	－	－	－
21	1.06	7.863	6.615	－	－	－	－

＊太字 *イタリック*のデータを見かけの拡散係数の解析に用いた

試験条件	
試料	ｸﾆｹﾞﾙV1
化学種	U ($UO_2(NO_3)_2 \cdot 6H_2O$)
検定日	-
充填密度	1.8 g/cm3
拡散期間	123.1 日
雰囲気	還元雰囲気 (Ar)
試験液性	蒸留水
試料形状	20×20 mm
スライス幅	0.2 mm
トレーサ濃度	約 0.01 mol/l
トレーサ量	25 μl
分析	ICP-MS

回帰分析の結果	
標本数	4
Co	2.08
Da =	1.1E-14 m2/s

表　Uの非定常拡散試験結果②

	試験データ					カラム内濃度分布データ	
スライス片	スライス片中の乾燥重量・含水量測定			スライス片中のトレーサ濃度	B.G	拡散源からの距離	トレーサ濃度
No.	風袋 / g	乾燥前 / g	乾燥後 / g	/ ppb	/ ppb	/ mm	/ mg
1	1.079	1.168	1.153	407.0	13.3	0.07	17.69
2	1.068	1.123	1.108	26.1	10.6	***0.18***	***1.59***
3	1.066	1.124	1.115	32.1	10.9	***0.26***	***1.31***
4	1.072	1.166	1.148	30.2	13.7	***0.38***	***0.70***
5	1.069	1.127	1.115	21.6	10.9	***0.49***	***0.74***
6	1.070	1.245	1.217	50.4	20.1	0.67	0.69
7	1.070	1.195	1.174	36.3	16.1	0.90	0.65
8	1.068	1.191	1.168	32.4	16.0	1.08	0.53
9	1.070	1.228	1.198	37.8	18.7	1.30	0.48
10	1.074	1.199	1.176	30.8	16.1	1.51	0.47
11	1.059	13.202	11.054	-	-	-	-

＊太字 *イタリック*のデータを見かけの拡散係数の解析に用いた

試験条件	
試料	ｸﾆｹﾞﾙV1
化学種	U ($UO_2(NO_3)_2 \cdot 6H_2O$)
検定日	−
充填密度	1.8 g/cm3
拡散期間	96.0 日
雰囲気	還元雰囲気 (Ar)
試験液性	模擬海水 (3%-NaCl)
試料形状	20 × 20 mm
スライス幅	0.5 mm
トレーサ濃度	約 0.01 mol/l
トレーサ量	25 μ l
分析	ICP-MS

回帰分析の結果	
標本数	2
Co	0.53
Da =	1.8E-14 m2/s

表　Uの非定常拡散試験結果①（海水系）

スライス片	試験データ					カラム内濃度分布データ	
	スライス片中の乾燥重量・含水量測定			スライス片中のトレーサ濃度	B.G	拡散源からの距離	トレーサ濃度
No.	風袋 / g	乾燥前 / g	乾燥後 / g	/ ppb	/ ppb	/ mm	/ mg
1	1.062	1.240	1.197	1246.0	20.3	0.13	27.54
2	1.064	1.314	1.263	39.3	26.0	***0.46***	***0.21***
3	1.070	1.383	1.322	35.4	30.9	***0.88***	***0.06***
4	1.060	1.350	1.296	32.4	29.1	1.34	0.05
5	1.070	1.388	1.329	32.8	31.3	1.80	0.02
6	1.071	1.409	1.348	32.1	32.9	2.29	−
7	1.068	1.398	1.338	32.3	32.2	2.80	0.00
8	1.057	1.380	1.324	33.0	31.7	3.29	0.02
9	1.063	1.384	1.327	31.0	31.5	3.78	−
10	1.074	1.389	1.333	30.8	31.1	4.26	−
11	1.066	1.391	1.335	−	−	−	−
12	1.076	1.402	1.350	−	−	−	−
13	1.059	1.388	1.332	−	−	−	−
14	1.081	1.410	1.353	−	−	−	−
15	1.071	1.408	1.351	−	−	−	−
16	1.062	1.380	1.324	−	−	−	−
17	1.066	1.393	1.332	−	−	−	−
18	1.061	1.387	1.329	−	−	−	−
19	1.060	1.407	1.347	−	−	−	−
20	1.067	1.395	1.334	−	−	−	−
21	1.066	8.03	6.769	−	−	−	−

＊太字 *イタリック*のデータを見かけの拡散係数の解析に用いた

試験条件	
試料	ｸﾆｹﾞﾙV1
化学種	U ($UO_2(NO_3)_2 \cdot 6H_2O$)
検定日	-
充填密度	1.8 g/cm3
拡散期間	123.1 日
雰囲気	還元雰囲気 (Ar)
試験液性	模擬海水 (3%-NaCl)
試料形状	20×20 mm
スライス幅	0.2 mm
トレーサ濃度	約 0.01 mol/l
トレーサ量	25 μl
分析	ICP-MS

回帰分析の結果	
標本数	5
Co	1.76
Da =	2.1E-14 m2/s

表　Uの非定常拡散試験結果②（海水系）

スライス片	試験データ					カラム内濃度分布データ	
	スライス片中の乾燥重量・含水量測定			スライス片中のトレーサ濃度	B.G	拡散源からの距離	トレーサ濃度
No.	風袋 / g	乾燥前 / g	乾燥後 / g	/ ppb	/ ppb	/ mm	/ mg
1	1.062	1.240	1.197	1246.0	20.3	0.08	21.03
2	1.064	1.314	1.263	39.3	26.0	***0.20***	***1.31***
3	1.070	1.383	1.322	35.4	30.9	***0.32***	***0.98***
4	1.060	1.350	1.296	32.4	29.1	***0.47***	***1.14***
5	1.070	1.388	1.329	32.8	31.3	***0.63***	***0.53***
6	1.071	1.409	1.348	32.1	32.9	***0.80***	***0.42***
7	1.068	1.398	1.338	32.3	32.2	0.98	0.43
8	1.057	1.380	1.324	33.0	31.7	1.17	0.41
9	1.063	1.384	1.327	31.0	31.5	1.34	0.44
10	1.074	1.389	1.333	30.8	31.1	1.52	0.36
11	1.048	13.237	11.106	-	-	-	-

＊太字 *イタリック*のデータを見かけの拡散係数の解析に用いた

試験条件	
試料	ｸﾆｹﾞﾙV1＋ｹｲ砂(30%)
核種	Cs-137
検定日	1996/5/1
充填密度	1.8 g/cm3
拡散期間	24.9 日
雰囲気	大気雰囲気
試験液性	蒸留水
試料形状	20×20 mm
スライス幅	1mm
トレーサ濃度	50 kBq/ml
トレーサ量	25μl
分析	液体ｼﾝﾁﾚｰｼｮﾝｶｳﾝﾀｰ

回帰分析の結果	
標本数	20
Y = a·X + b	a = −16674.276
	b = 8.091
R2乗	0.986
Da =	7.0E−12 m2/s

表　Cs-137の非定常拡散試験結果①

スライス片	試験データ				カラム内濃度分布データ	
	スライス片中の乾燥重量・含水量測定			スライス片中のトレーサ量	拡散源からの距離	トレーサ濃度
No.	風袋 / g	乾燥前 / g	乾燥後 / g	/ cpm	/ mm	/ cpm·g-1
1	1.074	1.774	1.632	6.0	***19.5***	***8.6***
2	1.074	1.777	1.649	10.0	***18.4***	***14.2***
3	1.078	1.713	1.608	15.4	***17.4***	***24.3***
4	1.075	1.739	1.630	23.4	***16.4***	***35.2***
5	1.085	1.731	1.626	26.2	***15.3***	***40.6***
6	1.081	1.748	1.636	72.2	***14.3***	***108.2***
7	1.082	1.737	1.630	89.4	***13.3***	***136.5***
8	1.085	1.748	1.642	150.4	***12.3***	***226.8***
9	1.080	1.730	1.631	225.4	***11.3***	***346.8***
10	1.075	1.737	1.631	336.8	***10.3***	***508.8***
11	1.083	1.747	1.640	468.8	***9.3***	***706.0***
12	1.086	1.756	1.653	635.0	***8.2***	***947.8***
13	1.081	1.714	1.615	546.0	***7.2***	***862.6***
14	1.062	1.784	1.666	1185.8	***6.2***	***1642.4***
15	1.064	1.741	1.637	1377.0	***5.1***	***2034.0***
16	1.067	1.706	1.603	1694.0	***4.1***	***2651.0***
17	1.066	1.675	1.568	2026.4	***3.2***	***3327.4***
18	1.068	1.704	1.598	2241.4	***2.2***	***3524.2***
19	1.068	1.725	1.610	2536.4	***1.2***	***3860.6***
20	1.063	1.514	1.420	2455.8	***0.3***	***5445.2***

＊太字 *イタリック*のデータを見かけの拡散係数の解析に用いた

試験条件	
試料	ｸﾆｹﾞﾙV1＋ｹｲ砂(30%)
核種	Cs−137
検定日	1996/5/1
充填密度	1.8 g/cm3
拡散期間	25.0 日
雰囲気	大気雰囲気
試験液性	蒸留水
試料形状	20 × 20 mm
スライス幅	1mm
トレーサ濃度	50 kBq/ml
トレーサ量	25 μl
分析	液体ｼﾝﾁﾚｰｼｮﾝｶｳﾝﾀｰ

回帰分析の結果	
標本数	17
Y = a･X + b	a = −17590.739
	b = 8.119
R2乗	0.994
Da =	6.6E−12 m2/s

表　Cs−137の非定常拡散試験結果②

スライス片	試験データ				カラム内濃度分布データ	
	スライス片中の乾燥重量・含水量測定			スライス片中のトレーサ量	拡散源からの距離	トレーサ濃度
No.	風袋 / g	乾燥前 / g	乾燥後 / g	/ cpm	/ mm	/ cpm･g−1
1	1.069	1.757	1.610	13.6	19.5	19.8
2	1.065	1.750	1.624	7.4	18.4	10.8
3	1.069	1.713	1.599	未測定	17.4	−
4	1.080	1.708	1.600	22.4	***16.4***	***35.7***
5	1.077	1.719	1.612	33.4	***15.4***	***52.0***
6	1.078	1.711	1.602	60.8	***14.4***	***96.1***
7	1.087	1.750	1.637	80.8	***13.4***	***121.9***
8	1.083	1.736	1.628	138.8	***12.4***	***212.6***
9	1.086	1.725	1.626	210.6	***11.4***	***329.6***
10	1.061	1.716	1.613	301.4	***10.4***	***460.2***
11	1.068	1.714	1.614	408.2	***9.4***	***631.9***
12	1.061	1.717	1.610	606.8	***8.4***	***925.0***
13	1.065	1.786	1.676	788.8	***7.3***	***1094.0***
14	1.076	1.766	1.658	1039.4	***6.2***	***1506.4***
15	1.083	1.705	1.612	1253.4	***5.2***	***2015.1***
16	1.077	1.741	1.640	1634.0	***4.2***	***2460.8***
17	1.084	1.704	1.608	1836.0	***3.2***	***2961.3***
18	1.077	1.714	1.613	2070.2	***2.3***	***3249.9***
19	1.082	1.731	1.617	2280.6	***1.3***	***3514.0***
20	1.086	1.584	1.485	2253.4	***0.4***	***4524.9***

＊太字*イタリック*のデータを見かけの拡散係数の解析に用いた

試験条件	
試料	ｸﾆｹﾞﾙV1＋ｹｲ砂(30%)
核種	Ni-63
検定日	1994/7/1
充填密度	1.8 g/cm3
拡散期間	48.0 日
雰囲気	大気雰囲気
試験液性	蒸留水
試料形状	20×20 mm
スライス幅	1mm
トレーサ濃度	50 kBq/ml
トレーサ量	25μl
分析	液体ｼﾝﾁﾚｰｼｮﾝｶｳﾝﾀｰ

回帰分析の結果	
標本数	2
Co	1498
R2乗	-
Da =	1.9E-13 m2/s

表　Ni-63の非定常拡散試験結果①

スライス片 No.	試験データ				カラム内濃度分布データ	
	スライス片中の乾燥重量・含水量測定			スライス片中のトレーサ量	拡散源からの距離	トレーサ濃度
	風袋 / g	乾燥前 / g	乾燥後 / g	/ cpm	/ mm	/ cpm・g-1
1	1.082	1.719	1.568	6.0	19.5	9.4
2	1.080	1.717	1.593	6.6	18.5	10.4
3	1.076	1.705	1.591	0.0	17.6	0.0
4	1.076	1.749	1.622	0.0	16.6	0.0
5	1.085	1.686	1.575	5.4	15.6	9.0
6	1.083	1.779	1.663	7.4	14.6	10.6
7	1.055	1.700	1.592	3.4	13.5	5.3
8	1.081	1.715	1.604	0.0	12.6	0.0
9	1.081	1.710	1.594	7.8	11.6	12.4
10	1.066	1.737	1.618	7.2	10.6	10.7
11	1.049	1.717	1.603	4.2	9.6	6.3
12	1.087	1.751	1.649	3.6	8.5	5.4
13	1.083	1.806	1.684	6.6	7.5	9.1
14	1.082	1.732	1.631	5.8	6.4	8.9
15	1.075	1.736	1.623	10.6	5.4	16.0
16	1.083	1.736	1.625	14.4	4.4	22.1
17	1.087	1.764	1.656	15.4	3.4	22.7
18	1.086	1.714	1.604	55.6	***2.4***	***88.5***
19	1.082	1.708	1.610	249.0	***1.4***	***397.8***
20	1.083	1.672	1.575	813.6	0.5	1381.3

＊太字 *イタリック*のデータを見かけの拡散係数の解析に用いた

試験条件	
試料	ｸﾆｹﾞﾙV1＋ｹｲ砂（30%）
核種	Ni-63
検定日	1994/7/1
充填密度	1.8 g/cm3
拡散期間	56.0 日
雰囲気	大気雰囲気
試験液性	蒸留水
試料形状	20 × 20 mm
スライス幅	1mm
トレーサ濃度	50 kBq/ml
トレーサ量	25 μl
分析	液体ｼﾝﾁﾚｰｼｮﾝｶｳﾝﾀｰ

回帰分析の結果	
標本数	2
Co	4847
R2乗	−
Da =	1.3E-13 m2/s

表　Ni-63の非定常拡散試験結果②

スライス片	試験データ				カラム内濃度分布データ	
	スライス片中の乾燥重量・含水量測定			スライス片中のトレーサ量	拡散源からの距離	トレーサ濃度
No.	風袋 / g	乾燥前 / g	乾燥後 / g	/ cpm	/ mm	/ cpm・g-1
1	0.859	1.575	1.429	4.2	19.5	5.9
2	0.863	1.481	1.367	13.4	18.4	21.7
3	0.867	1.528	1.415	4.2	17.4	6.4
4	0.869	1.481	1.378	10.8	16.5	17.6
5	0.870	1.522	1.406	4.6	15.5	7.1
6	0.870	1.528	1.413	11.4	14.5	17.3
7	0.859	1.490	1.383	12.2	13.5	19.3
8	0.868	1.494	1.384	20.4	12.5	32.6
9	0.864	1.506	1.392	20.8	11.6	32.4
10	0.860	1.529	1.417	12.6	10.6	18.8
11	0.858	1.518	1.407	7.0	9.5	10.6
12	0.857	1.565	1.450	15.4	8.5	21.8
13	0.858	1.488	1.384	4.2	7.5	6.7
14	0.856	1.530	1.420	4.8	6.5	7.1
15	0.855	1.511	1.404	6.2	5.4	9.5
16	0.857	1.499	1.392	4.2	4.4	6.5
17	0.862	1.496	1.391	22.6	3.5	35.6
18	0.860	1.561	1.445	92.6	***2.4***	***132.1***
19	0.850	1.528	1.409	696.4	***1.4***	***1027.1***
20	0.863	1.421	1.328	2032.4	0.4	3642.3

＊太字 *イタリック*のデータを見かけの拡散係数の解析に用いた

試験条件	
試料	ｸﾆｹﾞﾙV1＋ｹｲ砂 (30%)
元素(化学種)	Se (Na_2SeO_3)
検定日	–
充填密度	1.8 g/cm3
拡散期間	13.1 日
雰囲気	低酸素雰囲気
試験液性	蒸留水
試料形状	20×20 mm
スライス幅	1mm
トレーサ濃度	1mol/l
トレーサ量	25μl
分析	ﾌﾚｰﾑﾚｽ原子吸光分析

回帰分析の結果	
標本数	9
Y = a･X + b	a = −20055.693 b = 4.523
R2乗	0.991
Da =	1.1E−11 m2/s

表　Seの非定常拡散試験結果①

スライス片	試験データ				カラム内濃度分布データ	
	スライス片中の乾燥重量・含水量測定			スライス片中のトレーサ濃度	拡散源からの距離	トレーサ濃度
No.	風袋 / g	乾燥前 / g	乾燥後 / g	/ ppb	/ mm	/ mg
1	1.111	2.028	1.747	<1	19.3	–
2	1.090	1.696	1.571	<1	18.1	–
3	1.099	1.681	1.567	<1	17.2	–
4	1.097	1.727	1.612	<1	16.3	–
5	1.098	1.713	1.605	<1	15.4	–
6	1.093	1.720	1.623	1.0	14.4	0.1
7	1.111	1.791	1.689	3.6	13.4	0.4
8	1.110	1.770	1.673	13.7	12.4	1.7
9	1.108	1.677	1.584	26.2	11.5	3.7
10	1.099	1.828	1.708	73.4	10.5	8.1
11	1.113	1.798	1.694	124	***9.4***	***14.5***
12	1.111	1.753	1.658	182	***8.4***	***22.7***
13	1.095	1.681	1.587	238	***7.4***	***32.5***
14	1.090	1.782	1.672	382	***6.5***	***44.2***
15	1.129	1.931	1.804	523	***5.3***	***52.2***
16	1.092	1.759	1.649	514	***4.2***	***61.6***
17	1.109	1.770	1.661	591	***3.2***	***71.5***
18	1.106	1.734	1.627	648	***2.2***	***82.5***
19	1.116	1.674	1.572	627	***1.3***	***89.9***
20	1.122	1.702	1.575	1048	0.4	144.6

＊太字 *イタリック*のデータを見かけの拡散係数の解析に用いた

試験条件	
試料	ｸﾆｹﾞﾙV1＋ｹｲ砂(30%)
元素(化学種)	Se (Na_2SeO_3)
検定日	-
充填密度	1.8 g/cm3
拡散期間	13.1 日
雰囲気	低酸素雰囲気
試験液性	蒸留水
試料形状	20 × 20 mm
スライス幅	1mm
トレーサ濃度	1mol/l
トレーサ量	25 μl
分析	ﾌﾚｰﾑﾚｽ原子吸光分析

回帰分析の結果	
標本数	9
Y = a･X + b	a = −18168.631 b = 4.663
R2乗	0.990
Da =	1.2E−11 m2/s

表　Seの非定常拡散試験結果②

スライス片	試験データ				カラム内濃度分布データ	
	スライス片中の乾燥重量・含水量測定			スライス片中のトレーサ濃度	拡散源からの距離	トレーサ濃度
No.	風袋 / g	乾燥前 / g	乾燥後 / g	/ ppb	/ mm	/ mg
1	1.104	1.803	1.602	<1	19.5	-
2	1.108	1.689	1.582	<1	18.5	-
3	1.115	1.680	1.581	<1	17.6	-
4	1.103	1.719	1.619	1.2	16.7	-
5	1.096	1.768	1.664	<1	15.7	-
6	1.124	1.782	1.686	1.8	14.6	0.2
7	1.125	1.787	1.686	6.4	13.6	0.8
8	1.126	1.742	1.651	10.8	12.6	1.4
9	1.098	1.734	1.635	27.6	11.7	3.5
10	1.093	1.775	1.668	69.8	10.6	8.2
11	1.092	1.777	1.675	153	***9.6***	***17.9***
12	1.113	1.745	1.644	234	***8.6***	***29.6***
13	1.125	1.828	1.721	346	***7.5***	***39.4***
14	1.128	1.860	1.747	484	***6.4***	***52.9***
15	1.125	1.774	1.662	522	***5.4***	***64.3***
16	1.115	1.755	1.647	612	***4.4***	***76.5***
17	1.087	1.740	1.630	703	***3.4***	***86.1***
18	1.110	1.722	1.617	707	***2.4***	***92.4***
19	1.112	1.753	1.643	770	***1.4***	***96.1***
20	1.109	1.706	1.584	1006	0.5	134.8

＊太字*イタリック*のデータを見かけの拡散係数の解析に用いた

PNC ZJ1211 98-001(2/2)

分置01

限定資料

核種移行データベースの開発研究(Ⅱ)

(動力炉・核燃料開発事業団　委託研究報告書：別冊資料)

1998年2月

三菱マテリアル株式会社

本資料についての問合せは下記に願います。

〒107　東京都港区赤坂１－９－13
動力炉・核燃料開発事業団
技術管理部　技術情報室

PNC ZJ1211 98-001(2/2)

限定資料

核種移行データベースの開発研究(Ⅱ)

(動力炉・核燃料開発事業団　委託研究報告書：別冊資料)

1998年2月

三菱マテリアル株式会社

核種移行データベース開発研究（Ⅱ）

別冊資料内容

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1.　熱力学データベースの整備

- Thermodynamic Data for the Speciation and Solubility of Sn, Sb, Pb, Bi, Nb and Pd in Aqueous Solution.
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PNC-TDB
General Information

Thermodynamic Data for the Speciation and Solubility of Sn, Sb, Pb, Bi, Nb, and Pd in Aqueous Solution; Part A - G

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Executive Summary

PNC is planning to submit a new Performance Assessment Report by March 2000. Besides informations on geology, repository design etc., basic data on radionuclide behavior are required for the safety analysis. These basic data include chemical thermodynamic data in aqueous media, requiring the establishment of a chemical thermodynamic database, PNC-TDB, for the interaction of key radionuclides with significant ligands under relevant conditions.

The key elements Sn, Sb, Pb, Bi, Nb, Pd are the subject of the present report. For these elements, element-specific datasets have been developed based exclusively on experimental studies published in the literature, rather than relying on existing compilations. Besides treating hydrolysis in detail, this report focuses on the formation of complexes or compounds with chloride, fluoride, carbonate, nitrate, sulfate and phosphate. Other important inorganic ligands (sulfide for lead and antimony, ammonia in the case of palladium) are also included. For some elements a large number of studies are available, while for others only very few studies have been conducted. Formation constants of aqueous species and solids are proposed in this report for the following ligands:

- Sn: H_2O, Cl^-, F^-, NO_3^-, SO_4^{2-} for Sn(II)
  H_2O for Sn(IV)
  Sn(IV)/Sn(II)/Sn(cr) redox equilibria

- Sb: H_2O, S^{2-} for Sb(III)
  H_2O for Sb(V)
  Sb(V)/Sb(III)/Sb(cr) redox equilibria

- Pb: H_2O, Cl^-, F^-, CO_3^{2-}, SO_4^{2-}, S^{2-}, NO_3^-, PO_4^{3-}
  Pb(II)/Pb(cr) redox equilibrium

- Bi: H_2O, Cl^-, CO_3^{2-}, NO_3^-
  Bi(III)/Bi(cr) redox equilibrium

- Nb: H_2O

- Pd: Cl^-, NH_3

Where data for different ionic strengths are available, the specific ion interaction theory (SIT) approach is used to extrapolate formation constants to zero ionic strength.

Part A of this report contains

- the data selection criteria
- an outline of the extrapolation procedure to I= 0 with the specific ion interaction theory (SIT)
- the selected data for the key elements Sn, Sb, Pb, Bi, Nb, Pd
- the references

In the following parts B - G, the data selection for the individual key elements is discussed in detail:

- Part B: Tin
- Part C: Antimony
- Part D: Lead
- Part E: Bismuth
- Part F: Niobium
- Part G: Palladium

For each element, tables containing the complete data compilation as well as all calculations used in the data evaluation for the individual elements, are made available to PNC.

Seperate reports on actinide elements and Ac are being prepared by Dr. D. Rai and co-workers:

- Thermodynamic data for predicting concentrations of Pu(III), Am(III), and Cm(III) in geological environments
- Thermodynamic data for predicting concentrations of Th(IV), U(IV), Np(IV), and Pu(IV) in geological environments
- Thermodynamic data for predicting concentrations of AnO_2^+ and AnO_2^{2+} species in geological environments

The elements Sm, Ni, Se, Ra, Zr, Tc, and Po are treated by PNC.

The PNC-TDB will be finalized according to the schedule given in the 'Minutes of the PNC-BMG meeting at BMG, Switzerland, March 9-12, 1998' dated March 23, 1998.

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Part A: General information

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1 Introduction

1.1 Background

PNC is planning to submit a new Performance Assessment Report by March 2000. Besides informations on geology, repository design etc., basic data on radionuclide behavior are required for the safety analysis. These basic data include chemical thermodynamic data in aqueous media, requiring the establishment of a chemical thermodynamic database, PNC-TDB, for the interaction of key radionuclides with significant ligands under relevant conditions.

PNC has defined two groups of key elements for the next Performance Assessment Report. They are termed '1st priority elements' and '2nd priority elements', respectively, and are comprised of the following elements:

- 1st priority elements: Pu, U, Np, Th, Am, Ra, Sn, Zr, Ni, Pd, Tc, Se, Pa, Cm and Cs.
- 2nd priority elements: Sm, Ac, Po, Pb, Nb, Bi and Sb.

Ligands considered by PNC include hydroxide, carbonate, chloride, fluoride, sulfate and phosphate. In addition, solid-solution modeling may be considered for Ra, and possibly other elements. Since the aqueous chemistry of Cs is very simple, this element is not treated within the PNC-TDB development.

1.2 Organization of the PNC-TDB project

The PNC-TDB development project involves PNC staff members, an external expert group, and a Japanese expert advisory group. The expert group consists of Dr. H. Wanner, HSK; Dr. D. Rai, Batelle PNNL; Prof. G. Choppin, Florida State University; and Dr. M. Ochs, BMG. The roles and responsibilities of each member of the expert group are defined in Table 1.1. The Japanese expert advisory group comprises Prof. Tochiyama, Tohoku University, Prof. Moriyama, Kyoto University, and Dr. Nakayama, JAERI. The treatment of elements by the different groups is detailed in Table 1.1.

Table 1.1: Assigned responsibilities for the PNC-TDB project for the complete 2-year period of FY96-97:

Elements	Responsibility	Timeframe
Pu, Ac, Th, U, Np, Pa, Am, Cm	PNNL [1]	FY96-97
Pd, Pb, Sb, Bi, Nb, Sn	BMG [2]	FY97
Sm, Ni, Se	PNC (review by PNNL [1])	FY96-97
Ra, Zr, Tc, Po	PNC (review by BMG [2])	FY96-97

[1] This includes Dr. D. Rai and his co-workers at Batelle PNNL, as well as Dr. G. Choppin and his co-workers at Florida State University

[2] This includes Dr. M. Ochs, Dr. B. Lothenbach, and other personnel at BMG Engineering Ltd, with Dr. H. Wanner functioning as external advisor.

The PNC-TDB will be finalized according to the schedule given in the 'Minutes of the PNC-BMG meeting at BMG, Switzerland, March 9-12, 1998' dated March 23, 1998.

1.3 Database development and reporting on key elements

1.3.1 Sn, Sb, Pb, Bi, Nb, Pd

These elements are the subject of the present report. For these elements, element-specific datasets are being developed based exclusively on experimental studies published in the literature, rather than relying on existing compilations. Besides treating hydrolysis in detail, this review focuses on the formation of complexes or compounds with chloride, fluoride, carbonate, nitrate, sulfate and phosphate. Other important inorganic ligands (sulfide for lead and antimony, ammonia in the case of palladium) are also included. For some elements a large number of experimental studies are available, while for others, only very few experimental studies have been conducted in the past. For each element, formation constants of aqueous species and solids are proposed for the following ligands:

- Sn: H_2O, Cl^-, F^-, NO_3^-, SO_4^{2-} for Sn(II)
  H_2O for Sn(IV)
  Sn(IV)/Sn(II)/Sn(cr) redox equilibria
- Sb: H_2O, S^{2-} for Sb(III)
  H_2O for Sb(V)
  Sb(V)/Sb(III)/Sb(cr) redox equilibria
- Pb: H_2O, Cl^-, F^-, CO_3^{2-}, SO_4^{2-}, S^{2-}, NO_3^-, PO_4^{3-}
  Pb(II)/Pb(cr) redox equilibrium
- Bi: H_2O, Cl^-, CO_3^{2-}, NO_3^-
  Bi(III)/Bi(cr) redox equilibrium
- Nb: H_2O
- Pd: Cl^-, NH_3

Where data for different ionic strengths are available, the SIT approach is used to extrapolate formation constants to zero ionic strength.

For each element, tables containing the complete data compilation as well as all calculations used in the data evaluation for the individual elements, are made available to PNC.

1.3.2 Pu, Ac, Th, U, Np, Pa, Am, Cm

1.3.2.1 Trivalent oxidation states

The aqueous chemistry of trivalent actinides and lanthanides is sufficiently similar to allow an analogous treatment. Therefore, all trivalent oxidation states of the above elements are treated through the +III model developed by PNNL. This model uses the Pitzer approach and is based on a large amount of data for Am and Nd, and some data for Pu(III), obtained under a very wide range of conditions.

1.3.2.2 Tetravalent oxidation states

Uniform treatment of the tetravalent actinides is less consistent than for the trivalent actinides. For the present project, the workable approach described below is taken by PNNL, based on the fact that the solubility of An(IV)-oxides decreases from Th to Pu:

- For Th, a complete, Pitzer-based model is developed that addresses the formation of dissolved species with OH^-, Cl^-, CO_3^{2-}, SO_4^{2-}, F^-, and the formation of solid $ThO_2(s)$.
- This model is used for all other tetravalent actinides, with the following exceptions:
  1. The NEA data are used for the hydrolysis of U(IV).
  2. The interaction of U(IV) and Np(IV) with SO_4^{2-} is described using element-specific data.
  3. The solubility products of the solid oxides is element-specific for all tetravalent actinides.

1.3.2.3 Pentavalent and hexavalent oxidation states, redox potentials

These data are treated by Dr. Choppin.

1.3.3 Other elements

The TDB development for Sm, Ni, Se, Ra, Zr, Tc, and Po is being carried out by PNC directly (Table 1.1).

1.4 Symbols, units, notations and conversion factors

1.4.1 Symbols and notation

The symbols for physical and chemical quantities used in this report follow the recommendations of the International Union of Pure and Applied Chemistry, IUPAC [1979WHI]. They are summarized in Table 1.2.

Table 1.2: Symbols and notation

$\Delta_f G°$	the standard molar Gibbs energy of formation [kJ mol^{-1}]
$\Delta_r G°$	the molar Gibbs energy of a reaction [kJ mol^{-1}]
$\Delta_f H°$	the standard molar enthalpy of formation [kJ mol^{-1}]
$S°$	the standard molar entropy [J K^{-1} mol^{-1}]
T	absolute temperature [K]
R	molar gas constant (8.3145 J K^{-1} mol^{-1}]
n	number of electrons involved in a redox reaction
c_B	concentration of a solute B in [mol/L]
m_B	concentration of a solute B in [mol/kg solvent]
γ_B	activity coefficient of a substance B
I	ionic strength [mol/L]
I_m	ionic strength [mol/kg solvent]
ρ	Factor for the conversion of molarity, c_B, to molality, m_B, of substance B [dm^3 solution per kg H_2O]
ν_B	stoichiometric coefficient of a substance B (negative for reactants, positive for products)

1.4.2 Compilation of thermodynamic data

In Part B - G of this report, thermodynamic data are compiled in tables. The following convention have been used throughout:

'Reference': The references are ordered chronologically and alphabetically by the first two authors within each year. A more detailed description is given in Chapter II.1.8 in [1992GRE/FUG]. The references are given in Section 3 of this report.

'Comments': T indicates the temperature to which the given constant refers. Many comments were imported directly from the NEA database.
I indicates the conditions under which the constant was determined, e.g., I = 0.1-1.

'I': I indicates the ionic strength to which the given constant refers. This value is often, but not always identical with the ionic strength given under 'Comments'.

'Medium': indicates, where available, the electrolyte in which the given constant is measured or refers to.

'Method': Abbreviations for the method of measurement are listed in Table 1.3.

Table 1.3: Abbreviations for experimental methods

cat = cation exchange
col = colorimetric analysis
con = conductivity measurements
el = electrophoresis
emf = electromotive force measurements at high temperatures
extr = extraction
fe = fluoride selective electrode
n/a = method not known to the reviewers
NMR = ^{19}F NMR
pol = polarography
pSO_2 = pSO_2 measurements at high temperatures
pot = potentiometry
se = sulfide electrode
sol = solubility measurements
sp = spectrophotometry, NMR
tit = titration (evaluation of equilibrium through pH only)

1.4.3 Phase designators

Chemical formulae may refer to different chemical species and are often required to be specified more clearly in order to avoid ambiguities. For example, $PbCO_3$ occurs as a solid and as aqueous complex. The distinction between the different phases is made by phase designators that immediately follow the chemical formula and appear in parentheses. The only formulae that is not provided with a phase designator in this report are aqueous ions. The use of the phase designators is described below:

- The designator (l) is used for pure liquid substances, e.g., $H_2O(l)$
- The designators ('name'), (cr), (precip) and (s) is used for solid substances. When the solid has a common name, ('name') is used, e.g. $PbCO_3$(cerrusite). (cr) is used when it is known that the solid is crystalline, e.g. PbOHCl(cr). (precip) is used when it is known that the solid was precipitated from solutions. Otherwise, where no such information is available, (s) is used.
- For aqueous species no designators are used, e.g. $PbOH^+$ or $PbCO_3^0$.

1.4.4 Physical constants

The fundamental physical constants are taken from [1992GRE/FUG] and are listed in Table 1.4.

Table 1.4: Fundamental physical constants. These values were taken from [1992GRE/FUG].

R	molar gas constant	8.3145	$J\ K^{-1}\ mol^{-1}$
F	Faraday constant	96 485	$C\ mol^{-1}$

1.4.5 Equilibrium constants

The IUPAC has not explicitly defined the symbols and terminology for equilibrium constants of reactions in aqueous solutions. In this report the conventions (based on the work of Baes and Mesmer, [1976BAE/MES]) given below have been used throughout.

- Formation of an aqueous complex:

$$mM + nL \Leftrightarrow M_mL_n \quad \beta_{m,n} = \frac{[M_mL_n]}{[M]^m[L]^n}$$

- Formation of a solid:

  Conventionally, equilibrium constants involving a solid are denoted as 'solubility constants' rather than as formation constants of the solid. An index 's' to the equilibrium constant indicates that the constant refers to a solubility process, as shown below:

$$M_mL_n(s) \Leftrightarrow mM + nL \quad K_{So} = [M]^m[L]^n$$

  K_{SO} is the conventional solubility product and the subscript '0' indicates that the equilibrium reaction involves only uncomplexed aqueous species.

  In this report, the formation of solid is treated analogously to the formation of aqueous species. I.e., the inverse solubility product is used, denoted with an asterisk:

$$mM + nL \Leftrightarrow M_mL_n(s) \quad K^*{}_{So} = \frac{1}{[M]^m[L]^n}$$

- Further notations used in this report are compiled in Table 1.5.

Table 1.5: Reactions

β	measured cumulative formation constant for a reaction[1] (in molarity units)
β_m	measured cumulative formation constant for a reaction corrected from molarity to molality units
β°	cumulative equilibrium constant valid at $I = 0$
β^b	measured cumulative equilibrium constant for a reaction involving OH^- instead of H^+ [1].
K	consecutive (stepwise) equilibrium constant for a reaction
K_{s0}	Solubility product of a solid [2]. Example: $PbO(cr) + 2H^+ \Leftrightarrow Pb^{2+} + H_2O$; $K_{s0} = \frac{[Pb^{2+}]}{[H^+]^2}$
K^*_{s0}	Formation constant of a solid [2]. Example: $Pb^{2+} + H_2O \Leftrightarrow PbO(cr) + 2H^+$; $K^*_{s0} = \frac{[H^+]^2}{[Pb^{2+}]}$
K^b_{s0}	Solubility product of a solid involving OH^- instead of H^+ [1].
K^{*b}_{s0}	Formation constant of a solid involving OH^- instead of H^+ [1].

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[1] Hydrolysis reactions are formulated in this report using H^+ as component and not OH^-.

[2] In this report, reactions involving a solid are normally formulated as formation reactions.

1.4.6 Redox reactions

Redox reactions are usually quantified in terms of their electrode (half cell) potential E. E is identical to the electromotive force (emf) of a redox reaction that involves the standard hydrogen electrode as an electron donor or acceptor. In this review, electrode potentials are given as reduction potentials relative to the standard hydrogen electrode which acts as an electron donor. The standard redox potential, E°, is related to the Gibbs energy change $\Delta_r G^\circ$ and the equilibrium constant K as outlined below:

$$E^\circ = -\frac{1}{nF}\Delta_r G^\circ = \frac{RT}{nF}\ln K$$

1.5 Data selection criteria

To assure a traceable data selection a list of selection criteria is given below. All studies selected in this review should fulfill the following criteria.

- Experimental study
- I = constant
- No complex formation with electrolyte
- All relevant species included (e.g. polymers)
- Experimental details reported
- $T \approx 298$ K

A more detailed information of the individual papers and additional criteria see discussion of the individual species in Section B - G of this report.

1.6 Ionic strength corrections

Thermodynamic data always refer to a selected standard state. The standard state for a solute B in a solution is a hypothetical solution at the standard state pressure (0.1 MPa) and the standard temperature (298.15 K) in which $m_B = m_0 = 1$ mol/kg, and in which the activity coefficient γ_B is unity. However, for many reactions, measurements cannot be made accurately (or at all) in dilute solutions from which the extrapolation to the standard state would be simple. In this report, thermodynamic data were extrapolated to the standard state (I=0) using the specific ion interaction theory (SIT) as described in [1992GRE/FUG]. An extensive description of this theory and its use can be found in Appendix B of [1992GRE/FUG] and [1995SIL/BID]. Shortly, the correction consists of an extended Debye-Hückel expression, in which the activity coefficients of the reactants and products depend only on the ionic charge of the reactants and the ionic strength of the solution, but it accounts for the medium specific properties by introducing ion pairing between the medium ions and the species involved in the equilibrium reactions. The correction of the measured data to I=0 is made with the following equation:

$$\log\beta^0 = \log\beta_m - \Delta z^2 \times D + \Delta\varepsilon \times I_m$$

$$\textit{Debye} - \textit{Hueckel term}$$

$$D = \frac{0.509 \times \sqrt{I_m}}{1 + 1.5 \times \sqrt{I_m}}$$

$$\log\beta_m = \log\beta + \sum v \times \log\rho$$

$$I_m = I \times \rho$$

where	I	ionic strength [mol/L]
	I_m	ionic strength [mol/kg solvent]
	ρ	Factor for the conversion of molarity, c_B, to molality, m_B, of substance B [dm^3 solution per kg H_2O]
	β	measured cumulative formation constant for a reaction expressed in molarity units
	β_m	measured cumulative formation constant for a reaction corrected from molarity to molality units
	Σv	sum of the stoichiometric coefficients of the reaction.

The factors for the conversion of molarity, c_B, to molality, m_B, of a substance B for the different electrolytes at 298.15 K were taken from Table II.5 in [1995SIL/BID] and from Table II-1 in [1976BAE/MES].

1.7 *Auxiliary Data*

In this section the thermodynamic data for auxiliary compounds and complexes are compiled. Many of the these auxiliary species are used in the evaluation of the recommended data given in Section 2. It is therefore essential to always use these auxiliary data in conjunction with the selected data. The use of other auxiliary data can lead to inconsistencies and erroneous results. Table 1.6 contains the selected thermodynamic data of the auxiliary species considered in this review (all taken from the recent NEA publication of [1995SIL/BID]).

1.7.1 *Selected thermodynamic data for auxiliary complexes*

Table 1.6: Selected thermodynamic data for auxiliary complexes taken from [1995SIL/BID]

complex	$\Delta_fG°$ [kJ/mol]	Reference
Cl^-	-131.217	[1995SIL/BID]
F^-	-281.523	[1995SIL/BID]
SO_4^{2-}	-744.013	[1995SIL/BID]
H_2S^0	-27.648	[1995SIL/BID]
HS^-	12.243	[1995SIL/BID]
NO_3^-	-110.794	[1995SIL/BID]
CO_3^{2-}	-527.899	[1995SIL/BID]
HCO_3^-	-586.845	[1995SIL/BID]
PO_4^{3-}	-1025.491	[1995SIL/BID]
HPO_4^{2-}	-1095.985	[1995SIL/BID]
$H_2PO_4^-$	-1137.152	[1995SIL/BID]
H_2O	-237.140	[1995SIL/BID]
Ca^{2+}	-552.806	[1995SIL/BID]
Na^+	-261.953	[1995SIL/BID]
K^+	-282.510	[1995SIL/BID]

1.7.2 *Conversion of $\Delta_fG°$ values to equilibrium constants*

Experimental papers measure and indicate in most cases log β values. In the few cases the results of experimental studies are given as $\Delta_fG°$ values. To be able to compare these values with the log β or log K values selected in this report, these $\Delta_fG°$ values were converted to β or K values according to

$$K° = e^{-\frac{\Delta_r G°}{RT}}$$

using the $\Delta_fG°$ values of the auxiliary species (Table 1.6) and the $\Delta_fG°$ values of the master species Sn^{2+}, $Sn(OH)_4^0$, $Sb(OH)_3^0$, $Sb(OH)_5^0$, Pb^{2+}, Bi^{3+} selected in this report (Table 1.7).

In many compilations, which were only used for comparison in this report, $\Delta_fG°$ values are compiled instead of log β or log K values (e.g. in [1982WAG/EVA]). In general, these $\Delta_fG°$ values were converted to log β or log K values using the $\Delta_fG°$ values of the auxiliary species (Tables 1.6) and the $\Delta_fG°$ values of the master species Sn^{2+}, $Sn(OH)_4^0$, $Sb(OH)_3^0$, $Sb(OH)_5^0$, Pb^{2+}, Bi^{3+} (Table 1.7) selected in this report. However, some compilations also report $\Delta_fG°$ values for the master species (Table 1.8). In that case the $\Delta_fG°$ values given in the respective compilation is used to minimize inconsistencies.

Table 1.7: Thermodynamic data for the master species Sn^{2+}, $Sn(OH)_4^0$, $Sb(OH)_3^0$, $Sb(OH)_5^0$, Pb^{2+}, Bi^{3+} selected in this report. For $Nb(OH)_5^0$ and Pd^{2+} no thermodynamic data were selected.

complex	$\Delta_fG°$ [kJ/mol]	Reference
Sn^{2+}	-26.3	this report
$Sn(OH)_4^0$	-937	this report
$Sb(OH)_3^0$	-643.9	[1994AKI/ZOT]
$Sb(OH)_5^0$	-993.66	this report
Pb^{2+}	-24.24	[1989COX/WAG]
Bi^{3+}	92.20	this report

Table 1.8: Thermodynamic data for the master species Sn^{2+}, $Sn(OH)_4^0$, $Sb(OH)_3^0$, $Sb(OH)_5^0$, Pb^{2+}, Bi^{3+} given in previous compilations

complex	$\Delta_fG°$ [kJ/mol]	Reference
Sn^{2+}	-26.29	[1952LAT]
	-27.89	[1978COD]
	-29.89	[1980BEN/TEA]
	-27.2	[1982WAG/EVA]
	-27.14	[1985BAB/MAT]
	-27.2	[1985GAL]
	-27.23	[1988PHI/HAL]
	-27.62	[1989COX/WAG]
$Sn(OH)_4^0$	-934.8	[1984KEL/HOU]
	-950.6	[1988PHI/HAL]
$Sb(OH)_3^0$	-647.16	[1985BAB/MAT]
	-644.8	[1985PAS]
	-644.66	[1986ITA/NIS]
	-643.63	[1990SHI/ZOT]

Table 1.8: continued

Pb^{2+}	-24.24	[1989COX/WAG]
	-24.34	[1952LAT]
	-24.44	[1969HEL]
	-24.34	[1977PAU]
	-24.00	[1978COD]
	-24.4	[1978ROB/HEM2]
	-24.43	[1980BEN/TEA]
	-24.06	[1981HEL/KIR]
	-24.39	[1981STU/MOR]
	-24.34	[1982PAU]
	-24.43	[1982WAG/EVA]
	-24.42	[1983LAN]
	-24.42	[1983SAN/BAR]
	-24.4	[1984VIE/TAR]
	-24.42	[1985BAB/MAT]
	-24.34	[1985GAL]
	-24.23	[1985RAI/RYA]
	-24.00	[1988PHI/HAL]
Pb^{4+}	302.43	[1952LAT]
	-302.57	[1983LAN]
	302.44	[1985GAL]
Bi^{3+}	82.79	[1968 ROB/WAL]
	82.80	[1982WAG/EVA]
	91.79	[1985BAB/MAT]
	91.82	[1985LOV/MEK]
$Nb(OH)_5{}^0$	-1448	[1985UDU/VEN]
	-1448	[1982WAG/EVA]
$HNbO_3{}^0$	-985.3	[1985BAB/MAT]
Pd^{2+}	176.5	[1985COL]
	190.34	[1952LAT]
	176.56	[1967IZA/EAT]
	177.37	[1968GOL/HEP]
	176.53	[1980BEN/TEA]
	176.5	[1982WAG/EVA]
	176.53	[1985BAB/MAT]
	176.47	[1988PHI/HAL]

2 Selected data

This chapter presents the thermodynamic data set for bismuth, niobium, lead, palladium, antimony, and tin species selected in this review. The Tables 2.1 to 2.6 contain the recommended thermodynamic constants of chemical equilibrium reactions by which bismuth, niobium, lead, palladium, antimony, and tin compounds and complexes are formed. Besides treating hydrolysis in detail, this review focuses on the formation of complexes or compounds with chloride, fluoride, carbonate, nitrate, sulfate and phosphate. Other important inorganic ligands (sulfide for lead and antimony, ammonia in the case of palladium) are also included. The present report does not include any compounds or complexes containing organic ligands.

It should also be noted that the data set presented in this section may not be 'complete' for all conceivable systems and conditions. Gaps and uncertainties are pointed out in Section 2.2 and in various paragraphs in the Sections B - G.

2.1 Selected data for Sn, Sb, Pb, Bi, Nb and Pd

The Tables 2.1 to 2.6 contain the recommended thermodynamic data and should be read as follows:

Each element has at least one master species whose identity is given in the heading of each table. Redox sensitive elements may have more than one master species, allowing to separate the modeling of the different oxidation states, e. g. in case of kinetic inhibition. Each table contains the formation constants of all the complexes and solids proposed in this report.

Example for reading the contents of the database:

- Species $SnOH^+$ (see Table 2.1) is composed of the following components: 1 × component Sn^{2+}, 1 × H_2O[1], –1 × component H^+. The correct formation reaction for $SnOH^+$ is

  $$Sn^{2+} + H_2O(l) \quad = \quad SnOH^+ + H^+$$

  with a formation constant log β of –3.75

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[1] H_2O has an activity of 1 and is not included in the tables.

Table 2.1: Selected thermodynamic data for reactions involving tin compounds and reactions as selected in Section 4 of this report. All ionic species listed in this table are aqueous species. The data refer to the reference temperature of 298 K and to the standard state, i.e., a pressure of 0.1 MPa and, for aqueous species, infinite dilution (I=0).

components ⇒ **species** ⇓	log β	Sn^{2+}	H^+	Cl^-	F^-	NO_3^-	SO_4^{2-}	e^-
$SnOH^+$	-3.75	1	-1					
$Sn(OH)_2^0$	-7.71	1	-2					
$Sn(OH)_3^-$	-17.54	1	-3					
$Sn_3(OH)_4^{2+}$	-5.20	3	-4					
$SnCl^+$	1.65	1		1				
$SnCl_2^0$	2.31	1		2				
$SnCl_3^-$	2.09	1		3				
$SnOHCl^0$	-2.27	1	-1	1				
SnF^+	3.99	1			1			
SnF_2^0	7.74	1			2			
SnF_3^-	9.61	1			3			
$SnNO_3^+$	1.25	1				1		
$Sn(NO_3)_2^0$	1.74	1				2		
$Sn(NO_3)_3^-$	1.37	1				3		
$SnSO_4^0$	2.91	1					1	
$Sn(SO_4)_2^{2-}$	2.83	1					2	
$Sn(OH)_2$(precip)	-2.84	1	-2					
SnO(cr)	-2.41	1	-2					
SnOHCl(s)	2.41	1	-1	1				
Sn(cr)	-4.61	1						2
Sn^{4+}	-5.04	1						-2
$Sn(OH)_4^0$	-6.64 [1]	1	-4					-2

[1] tentative value (see Section 4.4.3)

Table 2.1: continued

components ⇒ **species** ⇓	log β	**$Sn(OH)_4^0$**	**H^+**
Sn^{4+}	-1.60 [1]	1	4
$SnOH^{3+}$	0.21 [1]	1	3
$Sn(OH)_2^{2+}$	1.14 [1]	1	2
$Sn(OH)_3^+$	1.22 [1]	1	1
$Sn(OH)_5^-$	-8.08	1	-1
$Sn(OH)_6^{2-}$	-18.61	1	-2
SnO_2(precip)	7.59	1	0
SnO_2(cassiterite)	8.06	1	0

[1] tentative values (see Section 4.1.1)

Table 2.2: Selected thermodynamic data for reactions involving antimony compounds and reactions as selected in Section 5 of this report. All ionic species listed in this table are aqueous species. The data refer to the reference temperature of 298 K and to the standard state, i.e., a pressure of 0.1 MPa and, for aqueous species, infinite dilution (I=0).

components ⇒ **species** ⇓	log β	**$Sb(OH)_3^0$**	**H^+**	**HS^-**	**e^-**
$SbOH^{2+}$	0.83	1	2		
$Sb(OH)_2^+$	1.18	1	1		
$Sb(OH)_4^-$	-11.93	1	-1		
$Sb_2(OH)_6^0$	0.08	2	0		
$Sb_2S_4^{2-}$	42.53	2	2	4	
$HSb_2S_4^-$	52.18	2	3	4	
$H_2Sb_2S_4^0$	57.00	2	4	4	
Sb_2O_3(valentinite)	8.51	2	0		
Sb_2S_3(stibnite)	55.41	2	3	3	
Sb(0)	11.83	1	3		3
$HSb(OH)_6$	-21.81	1	-2		-2

components ⇒ **species** ⇓	log β	**$HSb(OH)_6^0$**	**H^+**
$Sb(OH)_2^{3+}$	-6.65	1	3
$Sb(OH)_6^-$	-2.72	1	-1
$Sb_{12}(OH)_{64}^{4-}$	20.34	12	-4
$Sb_{12}(OH)_{65}^{5-}$	16.72	12	-5
$Sb_{12}(OH)_{66}^{6-}$	11.89	12	-6
$Sb_{12}(OH)_{67}^{7-}$	6.07	12	-7
Sb_2O_5(precip)	7.40	2	0

Table 2.3: Selected thermodynamic data for reactions involving lead compounds and reactions as selected in Section 6 of this report. All ionic species listed in this table are aqueous species. The data refer to the reference temperature of 298 K and to the standard state, i.e., a pressure of 0.1 MPa and, for aqueous species, infinite dilution (I=0).

components ⇒ **species** ⇓	log β	Pb^{2+}	H^+	Cl^-	F^-	CO_3^{2-}	NO_3^-	PO_4^{3-}	SO_4^{2-}	HS^-	e^-
$PbOH^+$	-7.50	1	-1								
$Pb(OH)_2^0$	-16.98	1	-2								
$Pb(OH)_3^-$	-27.97	1	-3								
Pb_2OH^{3+}	-7.20	2	-1								
$Pb_4(OH)_4^{4+}$	-20.55	4	-4								
$Pb_3(OH)_4^{2+}$	-22.82	3	-4								
$Pb_3(OH)_5^+$	-31.47	3	-5								
$Pb_6(OH)_8^{4+}$	-42.72	6	-8								
$PbCl^+$	1.54	1		1							
$PbCl_2^0$	2.01	1		2							
$PbCl_3^-$	1.98	1		3							
PbF^+	2.27	1			1						
PbF_2^0	3.01	1			2						
$PbFCl^0$	3.55	1		1	1						
$PbCO_3^0$	7.15	1				1					
$Pb(CO_3)_2^{2-}$	10.10	1				2					
$PbHCO_3^+$	12.96	1	1			1					
$PbNO_3^+$	1.04	1					1				
$Pb(NO_3)_2^0$	1.48	1					2				
$PbHPO_4^0$	15.45	1	1					1			
$PbH_2PO_4^+$	21.05	1	2					1			
$PbSO_4^0$	2.82	1							1		
$Pb(HS)_2^0$	12.34	1								2	
$Pb(HS)_3^-$	13.59	1								3	

Table 2.3: continued

components ⇒ **species** ⇓	log β	Pb^{2+}	H^+	Cl^-	F^-	CO_3^{2-}	NO_3^-	PO_4^{3-}	SO_4^{2-}	HS^-	e^-
PbO(red, litharge)	-12.68	1	-2								
PbO(yellow, massicot)	-12.96	1	-2								
$Pb(OH)_2$(precip)	-13.05	1	-2								
$PbCl_2$(s)	4.81	1		2							
PbOHCl(cr)	-0.62	1	-1	1							
PbF_2(s)	7.52	1			2						
PbFCl(matlockite)	8.82	1		1	1						
$PbCO_3$ (cerrusite)	13.20	1				1					
$Pb_3(CO_3)_2(OH)_2$ (hydrocerrusite)	17.64	3	-2			2					
$Pb_{10}(CO_3)_6(OH)_6O$ (plumbonacrite)	41.21	10	-8			6					
$PbOHNO_3$(cr)	-2.94	1	-1				1				
$PbHPO_4$(s)	23.78	1	1					1			
$Pb_3(PO_4)_2$(s)	44.40	3						2			
$Pb_4(PO_4)_2O$(s)	37.09	4	-2					2			
$Pb(H_2PO_4)_2$(s)	48.94	1	4					2			
$Pb_5(PO_4)_3OH$ (hydroxy pyromorphite)	62.80	5	-1					3			
$Pb_5(PO_4)_3Cl$ (chloro pyromorphite)	84.40	5		1				3			
$Pb_5(PO_4)_3F$ (fluoro pyromorphite)	71.60	5			1			3			
$PbSO_4$(anglesite)	7.81	1							1		
PbS(galena)	12.17	1	-1							1	
Pb(cr)	-4.25	1									2
PbO_2(s)	-48.98 [1]	1	-4								-2
Pb_3O_4(s)	-70.98 [1]	3	-8								-2

[1] tentative values (see Section 6.11.3)

Table 2.4: Selected thermodynamic data for reactions involving bismuth compounds and reactions as selected in Section 7 of this report. All ionic species listed in this table are aqueous species. The data refer to the reference temperature of 298 K and to the standard state, i.e., a pressure of 0.1 MPa and, for aqueous species, infinite dilution (I=0).

components ⇒ **species** ⇓	log β	Bi^{3+}	H^+	Cl^-	CO_3^{2-}	NO_3^-	e^-
$BiOH^{2+}$	-0.92	1	-1				
$Bi(OH)_2^+$	-2.56	1	-2				
$Bi(OH)_3$	-5.31	1	-3				
$Bi(OH)_4^-$	-18.71	1	-4				
$Bi_6(OH)_{12}^{6+}$	1.34	6	-12				
$Bi_9(OH)_{20}^{7+}$	-1.36	9	-20				
$Bi_9(OH)_{21}^{6+}$	-3.25	9	-21				
$Bi_9(OH)_{22}^{5+}$	-4.86	9	-22				
$BiCl^{2+}$	3.65	1		1			
$BiCl_2^+$	5.85	1		2			
$BiCl_3$	7.62	1		3			
$BiCl_4^-$	9.06	1		4			
$BiNO_3^{2+}$	1.78	1				1	
$Bi(NO_3)_2^+$	2.61	1				2	
$Bi(NO_3)_3$	3.18	1				3	
$Bi(NO_3)_4^-$	3.96	1				4	
$BiClNO_3^+$	5.16	1		1		1	
$BiCl(NO_3)_2^0$	5.28	1		1		2	
$BiCl_2NO_3^0$	6.86	1		2		1	
$BiCl_2(NO_3)_2^-$	5.75	1		2		2	
$BiCl_3NO_3^-$	8.09	1		3		1	
α–Bi_2O_3(cr)	-0.76	2	-6				
BiOCl(s)	8.04	1	-2	1			
$(BiO)_2CO_3$(cr)	11.96	2	-4		1		
$(BiO)_4(OH)_2CO_3$(cr)	6.45	4	-10		1		
$BiONO_3$(s)	2.64	1	-2			1	
Bi(cr)	16.15	1					3

Table 2.5: Selected thermodynamic data for reactions involving niobium compounds and reactions as selected in Section 8 of this report. All ionic species listed in this table are aqueous species. The data refer to the reference temperature of 298 K and to the standard state, i.e., a pressure of 0.1 MPa and, for aqueous species, infinite dilution (I=0).

components ⇒ **species** ⇓	log β	***Nb(OH)$_5$^{0}***	**H$^+$**
$Nb_6O_{19}H_3^{5-}$	30.43	6	5
$Nb_6O_{19}H_2^{6-}$	18.80	6	6
$Nb_6O_{19}H^{7-}$	5.57	6	7
$Nb_6O_{19}^{8-}$	-8.72	6	8
$Nb_2O_5(s)$	16.0 [1]	2	

[1] tentative value (see Section 8.2.1)

Nb(OH)$_5$^{0} is a hypothetical species (see Section 8.2.3).

Table 2.6: Selected thermodynamic data for reactions involving palladium compounds and reactions as selected in Section 9 of this report. All ionic species listed in this table are aqueous species. The data refer to the reference temperature of 298 K and to the standard state, i.e., a pressure of 0.1 MPa and, for aqueous species, infinite dilution (I=0).

components ⇒ **species** ⇓	log β	**Pd^{2+}**	**H^+**	**Cl^-**	**NH_3**
$PdCl^+$	5.1	1		1	
$PdCl_2^0$	8.3	1		2	
$PdCl_3^-$	10.9	1		3	
$PdCl_4^{2-}$	11.7	1		4	
$Pd(NH_3)^{2+}$	9.6	1			1
$Pd(NH_3)_2^{2+}$	18.5	1			2
$Pd(NH_3)_3^{2+}$	26.0	1			3
$Pd(NH_3)_4^{2+}$	32.8	1			4

2.2 Gaps and uncertainties

2.2.1 Uncertainties

Some authors report the standard deviations of their experimentally determined formation constants, but these do not represent the quality of the reported values in absolute terms. It is important not to confuse the statistical standard deviation with the accuracy. The standard deviation is calculated from the dispersion of equally weighted points, while the accuracy reflects the reliability and reproducibility of an experimental value and also includes all kinds of systematic errors. The estimation of systematic errors of a method is difficult and can only be made by a person who is familiar with the experimental method. In many cases the determination of the standard deviations is not possible because either only one or two data points are available, or the authors did not report the individual values. In this report no attempt was made to calculate systematically the uncertainties connected to experimentally determined formation constants. For further indication of the reliability of different methods see discussions for the individual species in Sections B - G.

2.2.2 Gaps

For the user it is important to consider that the selected data set presented in Section 2.1 may not be 'complete' with respect to all conceivable systems and conditions; there are gaps in the information, particularly concerning complex formation of tin(IV), antimony and niobium with inorganic ligands as well as the hydrolysis and the solubility of the oxides of niobium and palladium. For each individual key element discussed in this report, gaps are listed below. While some missing data may not be important from a practical point of view (e.g. the exact solubility of a very soluble solid, e.g. $SnCl_2(s)$; or the formation constants for complexes that will only be important in very concentrated solutions, e.g. the formation of tin(IV) nitrates), other missing data (e.g. the formation of solids with sulfide) may be more important. Gaps considered important by the authors of this review are printed in bold.

The gaps also are shortly discussed in the respective sections of the key elements in this report. This information may be used as a basis for the assignment of research priorities.

Tin(II): Gaps in the tin(II) thermodynamic database. Gaps considered important by the authors of this review are printed in bold.

complex or solid	Comments
– $SnCl_2(s)$	very soluble
– $SnF_2(s)$	soluble
– $Sn(NO_3)_2(s)$	very soluble
– $SnSO_4(s)$	moderately soluble
– $SnCO_3(s)$, $SnCO_3^0$ and $Sn(CO_3)_2^{2-}$	
– $Sn_3(PO_4)_2(s)$	
– $SnSO_4(s)$	
– $SnS(s)$	

Tin(IV): Gaps in the tin(IV) thermodynamic database. Gaps considered important by the authors of this review are printed in bold.

complex or solid	Comments
– chloride complexes and solids	weak complexes
– fluoride complexes and solids	weak complexes
– nitrate complexes and solids	weak complexes
– sulfate complexes and solids	weak complexes
– Sn^{4+}, $SnOH^{3+}$, $Sn(OH)_2^{2+}$, $Sn(OH)_3^+$	
– carbonate complexes and solids	
– phosphate complexes and solids	
– sulfide complexes and solids	

Antimony(III): Gaps in the antimony(III) thermodynamic database. Gaps considered important by the authors of this review are printed in bold.

complex or solid	Comments
– Sb^{3+}	stable at pH < 0
– chloride complexes and solids	weak complexes
– fluoride complexes and solids	weak complexes
– nitrate complexes and solids	weak complexes
– sulfate complexes and solids	weak complexes
– carbonate complexes and solids	?
– phosphate complexes and solids	?

Antimony(V): Gaps in the antimony(V) thermodynamic database. Gaps considered important by the authors of this review are printed in bold.

complex or solid	Comments
– Sb^{5+}, $SbOH^{4+}$, $Sb(OH)_2^{3+}$, $Sb(OH)_3^{2+}$, or $Sb(OH)_4^+$	stable at pH < 1
– chloride complexes and solids	weak complexes
– fluoride complexes and solids	weak complexes
– nitrate complexes and solids	weak complexes
– sulfate complexes and solids	weak complexes
– carbonate complexes and solids	?
– phosphate complexes and solids	?
– sulfide complexes and solids	?

Lead: Gaps in the lead thermodynamic database. Gaps considered important by the authors of this review are printed in bold.

complex or solid	Comments
– PbO_2 (s), Pb_3O_4(s)	very oxidizing conditions necessary
– Pb(IV) hydrolysis	very oxidizing conditions necessary

more information needed:
- hydrocerrusite
- phosphate complexes and solids

Bismuth: Gaps in the bismuth thermodynamic database. Gaps considered important by the authors of this review are printed in bold.

complex or solid	Comments
– $BiCl_3$ (s)	very soluble
– fluoride and sulfate complexes	weak complexes
– BiF_3 (s)	?
– **$BiPO_4$(s)**	
– **$Bi_2(SO_4)_3$(s)**	
– **Bi_2S_3(s)**	

Niobium: Gaps in the niobium thermodynamic database. Gaps considered important by the authors of this review are printed in bold.

complex or solid	Comments
– chloride complexes and solids	?
– fluoride complexes and solids	?
– nitrate complexes and solids	?
– sulfate complexes and solids	?
– carbonate complexes and solids	?
– phosphate complexes and solids	?
– sulfide complexes and solids	?
– niobium hydrolysis	in the neutral and acidic pH range

Palladium: Gaps in the palladium thermodynamic database. Gaps considered important by the authors of this review are printed in bold.

complex or solid	Comments
– fluoride complexes and solids	weak complexes
– nitrate complexes and solids	weak complexes
– sulfate complexes and solids	?
– carbonate complexes and solids	probably not important in aqueous solutions
– phosphate complexes and solids	?
– sulfide complexes and solids	?
– hydrolysis	polymerization
– $Pd(OH)_2$ (s)	solubility

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Thermodynamic Data for Predicting Concentrations of Pu(III), Am(III), and Cm(III) in Geologic Environments

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Contents

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Thermodynamic Data for Predicting Concentrations of Pu(III), Am(III), and Cm(III) in Geologic Environments

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INTRODUCTION

The objective of this study is to provide Power Reactor and Nuclear Fuel Development Corporation (PNC) of Japan with reliable values of thermodynamic constants for environmentally important reactions. These values will be used to predict upper concentration limits of trivalent actinides and selected rare earths that can leach out of high-level waste repositories. The Pitzer ion-interaction model is selected for these applications because 1) it is applicable to low as well as high ionic strengths, 2) specific media effects can be reliably ascertained, 3) it provides a mechanism for cross comparison and reinterpretation of thermodynamic data developed under a wide range of ionic strengths and a variety of aqueous media, and 4) over the last few years we have developed a considerable amount of thermodynamic data for trivalent rare earths (primarily Nd, an analog of trivalent actinides) and Am(III) using this approach and have been instrumental in putting together the trivalent actinide model for applications to the low-level waste repository (Waste Isolation Pilot Project, New Mexico); thus, we can take advantage of this expertise and studies conducted under this project.

COMPILATION OF TRIVALENT ACTINIDE THERMODYNAMIC DATA

To develop a comprehensive data base for selecting constants, available pertinent literature was collected. The literature references pertaining to trivalent actinides were collected from several sources including: journal articles and books (e.g., Smith and Martell, 1976; Fuger et al., 1992, Silva et al., 1995), subject indices of several pertinent recent journals, listings of articles on Pu compiled by the Nuclear Energy Agency and provided to us by courtesy of Dr. Hans Wanner, and a computer search of different data bases. Thermodynamic constants reported in these publications were summarized in different tables for each element and ligand (Table A1-A6, Appendix). In addition, these tables provide important information regarding experimental techniques and ligand concentration ranges reported in the publications.

The thermodynamic equilibrium constants of OH^-, Cl^-, F^-, NO_3^-, CO_3^{2-}, SO_4^{2-}, and PO_4^{3-} complexes with Sm(III) and trivalent actinides (Ac(III), Np(III), Pu(III), Am(III), and Cm(III)) are reported and compiled in Appendix (Tables A1-A6). Several general conclusions can be made from these data: 1) The least amount of experimental data exists for Ac (III). 2) Complexes with Cl^- and NO_3^- are very weak. 3) Most studies are conducted at relatively high but constant ionic strength and invariably in different ionic media (for an example of Am sulfate complexes, see Rai et al. 1995), thus making it difficult to extrapolate the results to zero ionic strength because of the lack of information on the specific ionic media dependence of the apparent equilibrium constants. 4) Experimental data for many species, expected to be important for trivalent actinides, are not available. For example, no experimental data are available for $Pu(OH)_2^+$, $Pu(OH)_3^0$, or carbonato complexes of Pu(III). 5) Other than our work for carbonate (Felmy et al.1990 , Rao et al. 1996a) and sulfate systems (Rai et al. 1995), very few attempts have been made to reinterpret the literature data for cross comparisons of values obtained using different experimental techniques, at different ionic strengths, and in different ionic media.

As shown in the compilation of literature data (Tables A1-A6, Appendix), a number of authors have used various approaches (e.g. extrapolation, S.I.T. or Pitzer's approach) to estimate values for stability constants at standard state conditions (I = 0, T = 298.15 K). However, the values for an individual system may vary significantly. To provide a basis for choosing among these values, a screening approach has been used which is based on the strongly ionic nature of the actinide-ligand bonding. A detailed description of this approach is provided in Section A7 of the Appendix. Based on this approach, stability constants of the first complexes of several individual trivalent elements (Sm^{3+}, Am^{3+}, and Pu^{3+}) with relevant ligands were selected and listed in Table A7. This list, including only the constants of the first aqueous complex, is not meant to be used as a complete set of parameters for prediction of the concentrations of Sm(III), Am(III), and Pu(III). Instead, these values can be used for cross-comparison of the stability constants of individual trivalent elements. The values for complexes of Am^{3+} with strongly complexing ligands are essentially the same as those recommended for the Am model described in subsequent sections. Complexation constants of Sm(III) and Am(III) with weakly complexing ligands (Cl^- and NO_3^-) are reported in the literature (Tables A1.2-A1.3, A5.2-A5.3, Appendix) and values selected by the screening approach are compared in Table A7 (Appendix). Although no specific ion-interaction parameters for trivalent actinides with Cl^- and NO_3^- are available, values of these parameters for rare earths are available and they are applicable to very dilute to concentrated electrolyte solutions. We have shown that parameters for Nd^{3+}-Cl^- are directly applicable to Pu^{3+}-Cl^- (Felmy et al. 1989) and Am^{3+}-Cl^- (Rai et al. 1992a). For these reasons, and because of the similarity among the values of different complexes of Am(III), Pu(III) and Sm(III) (Table A7, Appendix), an Am(III) model developed and described in this document is applicable to other trivalent actinides and Sm(III).

Based on the reported data for solid phases of trivalent actinides or on the available data for solid phases of rare earths (which show similar ionic radii and form isostructural compounds with actinides and that are excellent analogs for trivalent actinides), solid compounds of trivalent actinides which may be of significant importance to waste repository include $M(OH)_3$(am), MPO_4(c), MF_3(c), $M(OH)CO_3$(c), $NaM(CO_3)_2.6H_2O$(c), and $M_2(CO_3)_3$(c). These compounds are expected to form readily in geologic environments and they may, under different conditions, help set upper limits on the aqueous concentrations of actinides. Unfortunately, experimental thermodynamic data are not available for all of these solids for all elements. As shown in Table 1, data are available for all Am(III) compounds, but only limited data are available for Pu(III) compounds ($Pu(OH)_3(s)$ and $PuPO_4(s)$) and the only data available for Cm(III) compounds is for $CmF_3(s)$.

Because of the lack of experimental data for several important aqueous complexes and solid phases of all trivalent actinides, completely independent thermodynamic models for specific elements can not be developed. Because trivalent rare earths are excellent analogs for trivalent actinides, as we will show in the next section, and because Pitzer ion-interaction parameters are available for common systems (e.g. Cl^-, ClO_4^-, and NO_3^-) involving trivalent rare earths and for all environmentally important major electrolyte ions, it is currently possible to develop only a generic trivalent model that can be used to estimate upper concentration limits of all trivalent actinides and important rare earths. In the next section, we discuss such a trivalent model based on the Pitzer approach, and we will provide supporting data on the reliability of this model.

Table 1. Availability of Experimental Data for Solubility of Different Trivalent Actinide Compounds[(a)]

Compound	Pu(III)	Am(III)	Cm(III)
$M(OH)_3(s)$	√	√	
$MPO_4(c)$	√	√	
$MF_3(c)$		√	√
$M(OH)CO_3(c)$		√	
$NaM(CO_3)_2{\cdot}H_2O$		√	
$M_2(CO_3)_3(c)$		√	

(a) check mark indicates some data are available

SELECTED THERMODYNAMIC DATA FOR A TRIVALENT ACTINIDE MODEL

Based on extensive experimental studies on Am(III) and Nd(III) and limited studies on Pu(III), a Pitzer model was developed to predict aqueous concentrations in a wide variety of groundwater compositions. While the data specifically pertinent to each actinide element are insufficient for us to develop element-specific models, we do have sufficient data to develop a model for Am. Therefore, modeling parameters specifically for Am(III) are reported in this report. We believe, however, that until more data for other trivalent actinide elements become available, this model can be used to provide reasonable estimates of concentrations for Pu(III), Cm(III), and Sm(III).

The required thermodynamic data for the Am model are reported in Tables 2-8. Tables 2 and 3 provide Pitzer ion-interaction parameters for binary and ternary interactions for the major electrolyte ions (i.e,. Na, K, Ca, Mg, F, Cl, ClO_4, NO_3, CO_3, SO_4, PO_4, MoO_4). Table 4 provides the binary and ternary parameters for Am species. Table 5 provides $\Delta_f G^0/RT$ values for major electrolyte ions and Table 6 for Am species. Thermodynamic equilibrium constants for complexation and solid phase dissolution reactions consistent with the reported $\Delta_f G^0/RT$ values appear in Tables 7 and 8.

This model has been tested for a large number of systems involving ion-interactions/ion-pairs of OH, Cl, F, CO_3, SO_4, and PO_4 with Nd(III), Gd(III), Am(III), and Pu(III) and has been shown to reliably predict the concentrations in dilute to concentrated solutions and in simple as well as mixed electrolyte systems. The basis for selection of the model parameters for Am interactions with different ligands is discussed in detail in the following text.

Table 2. Binary Ion-Interaction Parameters for Major Electrolyte Ions

Species	$\beta^{(0)}$	$\beta^{(1)}$	$\beta^{(2)}$	C^{ϕ}	References
Na^+-Cl^-	0.0765	0.2644	0.00	0.00127	Harvie et al (1984)
Na^+-SO_4^{2-}	0.01958	1.113	0.00	0.00497	Harvie et al (1984)
Na^+-HSO_4^-	0.0454	0.398	0.00	0.00	Harvie et al (1984)
Na^+-OH^-	0.0864	0.253	0.00	0.0044	Harvie et al (1984)
Na^+-HCO_3^-	0.0277	0.0411	0.00	0.00	Harvie et al (1984)
Na^+-CO_3^{2-}	0.0399	1.389	0.00	0.0044	Harvie et al (1984)
K^+-Cl^-	0.04835	0.2122	0.00	-0.00084	Harvie et al (1984)
K^+-SO_4^{2-}	0.04995	0.7793	0.00	0.00	Harvie et al (1984)
K^+-HSO_4^-	-0.0003	0.1735	0.00	0.00	Harvie et al (1984)
K^+-OH^-	0.1298	0.320	0.00	0.0041	Harvie et al (1984)
K^+-HCO_3^-	0.0296	-0.013	0.00	-0.008	Harvie et al (1984)
K^+-CO_3^{2-}	0.1488	1.43	0.00	-0.0015	Harvie et al (1984)
Ca^{2+}-Cl^-	0.3159	1.614	0.00	-0.00034	Harvie et al (1984)
Ca^{2+}-SO_4^{2-}	0.20	3.1973	-54.24	0.00	Harvie et al (1984)
Ca^{2+}-HSO_4^-	0.2145	2.53	0.00	0.00	Harvie et al (1984)
Ca^{2+}-OH^-	-0.1747	-0.2303	-5.72	0.00	Harvie et al (1984)
Ca^{2+}-HCO_3^-	0.4	2.977	0.00	0.00	Harvie et al (1984)
Mg^{2+}-Cl^-	0.35235	1.6815	0.00	0.00519	Harvie et al (1984)
Mg^{2+}-SO_4^{2-}	0.2210	3.343	-37.23	0.025	Harvie et al (1984)
Mg^{2+}-HSO_4^-	0.4746	1.729	0.00	0.00	Harvie et al (1984)
Mg^{2+}-HCO_3^-	0.329	0.6072	0.00	0.00	Harvie et al (1984)
$MgOH^-$-Cl^-	-0.10	1.658	0.00	0.00	Harvie et al (1984)
H^+-Cl^-	0.1775	0.2945	0.00	0.0008	Harvie et al (1984)
H^+-SO_4^{2-}	0.0298	0.00	0.00	0.0438	Harvie et al (1984)
H^+-HSO_4^-	0.2065	0.5556	0.00	0.00	Harvie et al (1984)
Na^+-$H_2PO_4^-$	-0.0533	0.0396	0.00	0.00795	Pitzer & Mayorga (1973)
Na^+-HPO_4^{2-}	-0.0583	1.4655	0.00	0.02938	Pitzer & Mayorga (1973)

Table 2. Binary Ion-Interaction Parameters for Major Electrolyte Ions (cont'd)

Species	$\beta^{(0)}$	$\beta^{(1)}$	$\beta^{(2)}$	C^{ϕ}	References
Na^+-PO_4^{3-}	0.17813	3.8513	0.00	-0.05154	Pitzer & Mayorga (1973)
Na^+-ClO_4^-	0.0554	0.2755	0.00	-0.00118	Pitzer (1991)
H^+-ClO_4^-	0.1747	0.2931	0.00	0.00819	Pitzer (1991)
H^+-NO_3^-	0.1168	0.3546	0.00	-0.00539	Pitzer (1991)
Na^+-NO_3^-	0.0068	0.1783	0.00	-0.00072	Ptizer (1991)
K^+-NO_3^-	-0.0816	0.0494	0.00	0.0066	Pitzer (1991)
Ca^{2+}-NO_3^-	0.211	1.409	0.00	-0.0202	Pitzer (1991)
Mg^{2+}-NO_3^-	0.3671	1.585	0.00	-0.0207	Pitzer (1991)

Table 3. Ternary Ion-Interaction Parameters for Major Electrolyte Ions

Species	Ternary Parameter	References
Na^+-K^+	-0.012	Harvie et al. (1984)
Na^+-K^+-Cl^-	-0.0018	Harvie et al. (1984)
Na^+-K^+-SO_4^{2-}	-0.010	Harvie et al. (1984)
Na^+-K^+-HCO_3^-	-0.003	Harvie et al. (1984)
Na^+-K^+-CO_3^{2-}	0.003	Harvie et al. (1984)
Na^+-K^+-NO_3^-	-0.001	Pitzer (1991)
Na^+-Ca^{2+}	0.07	Harvie et al. (1984)
Na^+-Ca^{2+}-Cl^-	-0.007	Harvie et al. (1984)
Na^+-Ca^{2+}-SO_4^{2-}	-0.055	Harvie et al. (1984)
Na^+-Mg^{2+}	0.07	Harvie et al. (1984)
Na^+-Mg^{2+}-Cl^-	-0.012	Harvie et al. (1984)
Na^+-Mg^{2+}-SO_4^{2-}	-0.015	Harvie et al. (1984)
Na^+-H^+	0.036	Harvie et al. (1984)
Na^+-H^+-Cl^-	-0.004	Harvie et al. (1984)
Na^+-H^+-HSO_4^-	-0.0129	Harvie et al. (1984)
K^+-Ca^{2+}	0.032	Harvie et al. (1984)
K^+-Ca^{2+}-Cl^-	-0.025	Harvie et al. (1984)
K^+-Mg^{2+}-Cl^-	-0.022	Harvie et al. (1984)
K^+-Mg^{2+}-SO_4^{2-}	-0.048	Harvie et al. (1984)
K^+-H^+	0.005	Harvie et al. (1984)
K^+-H^+-Cl^-	-0.011	Harvie et al. (1984)
K^+-H^+-SO_4^{2-}	0.197	Harvie et al. (1984)
K^+-H^+-HSO_4^-	-0.0265	Harvie et al. (1984)
Ca^{2+}-Mg^{2+}	0.007	Harvie et al. (1984)
Ca^{2+}-Mg^{2+}-Cl^-	-0.012	Harvie et al. (1984)
Ca^{2+}-Mg^{2+}-SO_4^{2-}	0.024	Harvie et al. (1984)
Ca^{2+}-H^+	0.092	Harvie et al. (1984)
Ca^{2+}-H^+-Cl^-	-0.015	Harvie et al. (1984)
Mg^{2+}-$MgOH^-$-Cl^-	0.028	Harvie et al. (1984)

Table 3. Ternary Ion-Interaction Parameters for Major Electrolyte Ions (con'td)

Species	Ternary Parameter	References
Mg^{2+}-H^+	0.10	Harvie et al. (1984)
Mg^{2+}-H^+-Cl^-	-0.011	Harvie et al. (1984)
Mg^{2+}-H^+-HSO_4^-	-0.0178	Harvie et al. (1984)
Cl^--SO_4^{2-}	0.02	Harvie et al. (1984)
Cl^--SO_4^{2-}-Na^+	0.0014	Harvie et al. (1984)
Cl^--SO_4^{2-}-Ca^{2+}	-0.018	Harvie et al. (1984)
Cl^--SO_4^{2-}-Mg^{2+}	-0.004	Harvie et al. (1984)
Cl^--HSO_4^-	-0.006	Harvie et al. (1984)
Cl^--HSO_4^--Na^+	-0.006	Harvie et al. (1984)
Cl^--HSO_4^--H^+	0.013	Harvie et al. (1984)
Cl^--OH^-	-0.050	Harvie et al. (1984)
Cl^--OH^--Na^+	-0.006	Harvie et al. (1984)
Cl^--OH^--K^+	-0.006	Harvie et al. (1984)
Cl^--OH^--Ca^{2+}	-0.025	Harvie et al. (1984)
Cl^--HCO_3^-	0.03	Harvie et al. (1984)
Cl^--HCO_3^--Na^+	-0.015	Harvie et al. (1984)
Cl^--HCO_3^--Mg^{2+}	-0.096	Harvie et al. (1984)
Cl^--CO_3^{2-}	-0.02	Harvie et al. (1984)
Cl^--CO_3^{2-}-Na^+	0.0085	Harvie et al. (1984)
Cl^--CO_3^{2-}-K^+	0.004	Harvie et al. (1984)
Cl^--NO_3^-	0.016	Pitzer (1991)
Cl^--NO_3^--Na^+	-0.006	Pitzer (1991)
Cl^--NO_3^--K^+	-0.006	Pitzer (1991)
Cl^--NO_3^--Mg^{2+}	0.00	Pitzer (1991)
Cl^--NO_3^--Ca^{2+}	-0.017	Pitzer (1991)
SO_4^{2-}-HSO_4^--Na^+	-0.0094	Harvie et al. (1984)

Table 3. Ternary Ion-Interaction Parameters for Major Electrolyte Ions (con'td)

Species	Ternary Parameter	References
SO_4^{2-}-HSO_4^--K^+	-0.0677	Harvie et al. (1984)
SO_4^{2-}-HSO_4^--Mg^{2+}	-0.0425	Harvie et al. (1984)
SO_4^{2-}-OH^-	-0.013	Harvie et al. (1984)
SO_4^{2-}-OH^--Na^+	-0.009	Harvie et al. (1984)
SO_4^{2-}-OH^--K^+	-0.050	Harvie et al. (1984)
SO_4^{2-}-HCO_3^-	0.01	Harvie et al. (1984)
SO_4^{2-}-HCO_3^--Na^+	-0.005	Harvie et al. (1984)
SO_4^{2-}-HCO_3^--Mg^{2+}	-0.161	Harvie et al. (1984)
SO_4^{2-}-CO_3^{2-}	0.02	Harvie et al. (1984)
SO_4^{2-}-CO_3^{2-}-Na^+	-0.005	Harvie et al. (1984)
SO_4^{2-}-CO_3^{2-}-K^+	-0.009	Harvie et al. (1984)
OH^--CO_3^{2-}	0.10	Harvie et al. (1984)
OH^--CO_3^{2-}-Na^+	-0.017	Harvie et al. (1984)
OH^--CO_3^{2-}-K^+	-0.01	Harvie et al. (1984)
HCO_3^--CO_3^{2-}	-0.04	Harvie et al. (1984)
HCO_3^--CO_3^{2-}-Na^+	0.002	Harvie et al. (1984)
HCO_3^--CO_3^{2-}-K^+	0.012	Harvie et al. (1984)
CO_2^0-Na^+	0.100	Harvie et al. (1984)
CO_2^0-K^+	0.051	Harvie et al. (1984)
CO_2^0-Ca^{2+}	0.181	Harvie et al. (1984)
CO_2^0-Mg^{2+}	0.183	Harvie et al. (1984)
CO_2^0-Cl^-	-0.005	Harvie et al. (1984)
CO_2^0-SO_4^{2-}	0.097	Harvie et al. (1984)
CO_2^0-HSO_4^-	-0.003	Harvie et al. (1984)
$H_3PO_4^0$-$H_3PO_4^0$	0.0503	Pitzer and Silvester (1976)

Table 3. Ternary Ion-Interaction Parameters for Major Electrolyte Ions (con'td)

Species	Ternary Parameter	References
$H_3PO_4^0$-$H_3PO_4^0$-$H_3PO_4^0$	0.0109	Pitzer and Silvester (1976)
$H_3PO_4^0$-$H_2PO_4^-$	-0.04	Pitzer and Silvester (1976)
$H_3PO_4^0$-H^+	0.29	Pitzer and Silvester (1976)
SO_4^{2-}-ClO_4^-	0.020	Rai et al. (1995)(a)
SO_4^{2-}-ClO_4^--Na^+	0.0014	Rai et al. (1995)(a)

(a) assuming Cl^- parameters reported by Harvie et al. (1984) apply to the ClO_4^- system; Rai et al. (1995) showed these values are reasonable

Table 4. Binary and Ternary Ion-Interaction Parameters for Am Species

Binary Interaction Parameters

Species	$\beta^{(0)}$	$\beta^{(1)}$	$\beta^{(2)}$	C^{ϕ}	References
Am^{3+}-ClO_4^-	0.754	6.53	0	0.0075	Rai et al. (1995)(a)
Am^{3+}-Cl^-	0.6117	5.403	0	-0.019	Rai et al. (1992a)(a)
Am^{3+}-NO_3^-	0.468	5.13	0	-0.0823	This compilation(b)
Am^{3+}-SO_4^{2-}	3.0398	0	-2500	0	Rai et al. (1995)
Am^{3+}-$H_2PO_4^-$	0	0	-92.9	0	This compilation(c)
Na^+-$Am(CO_3)_3^{3-}$	-0.256	5.0	0	0.0443	This compilation(d)

Ternary Interaction Parameters

Cl^--$Am(CO_3)_3^{3-}$	0.168	This compilation(e)
Na^+-Cl^--$Am(CO_3)_3^{3-}$	0.0273	This compilation(e)

(a)Assumed to be analogous to corresponding Nd(III) parameters.

(b)Assumed to be analogous to the parameter for Nd^{3+}-NO_3^- (Pitzer 1991).

(c)Assumed to be analogous to the parameter for Nd^{3+}-$H_2PO_4^-$ (Rai et al. 1991).

(d)Assumed to be analogous to the parameter for Na^+-$Nd(CO_3)_3^{3-}$ (Rao et al. 1996a).

(e)Assumed to be analogous to the parameter for Na^+-Cl^--$Nd(CO_3)_3^{3-}$ (Rao et al. 1996c).

Tables 5. Dimensionless Standard Molar Gibbs Energies of Formation of Major Electrolyte Species

Species	$\Delta_f G^\circ/RT$	References
$H_2O(l)$	-95.6635	Harvie et al. (1984)
Na^+	-105.651	Harvie et al. (1984)
K^+	-113.957	Harvie et al. (1984)
Ca^{2+}	-223.30	Harvie et al. (1984)
Mg^{2+}	-183.468	Harvie et al. (1984)
$MgOH^+$	-251.94	Harvie et al. (1984)
H^+	0.00	Harvie et al. (1984)
Cl^-	-52.955	Harvie et al. (1984)
SO_4^{2-}	-300.386	Harvie et al. (1984)
HSO_4^-	-304.942	Harvie et al. (1984)
OH^-	-63.435	Harvie et al. (1984)
HCO_3^-	-236.751	Harvie et al. (1984)
$CO_3{}^{2-}$	-212.944	Harvie et al. (1984)
$CaCO_3^0$	-443.5	Harvie et al. (1984)
$MgCO_3^0$	-403.155	Harvie et al. (1984)
$CO_2(aq)^0$	-155.68	Harvie et al. (1984)
$CO_2(g)$	-159.092	Harvie et al. (1984)
$Mg(OH)_2(c)$ Brucite	-335.40	Harvie et al. (1984)
$CaCO_3(c)$ Calcite	-455.6	Harvie et al. (1984)
$MgCO_3(c)$ Magnesite	-414.45	Harvie et al. (1984)
$Ca(OH)_2(c)$ Portlandite	-362.12	Harvie et al. (1984)
$H_3PO_4^0$	-460.90	Pitzer and Silvester (1976)
$H_2PO_4^-$	-455.96	Pitzer and Silvester (1976)
HPO_4^{2-}	-439.367	Wagman et al. (1982)
PO_4^{3-}	-410.947	Wagman et al. (1982)
MoO_4^{2-}	-337.366	Wagman et al. (1982)
$HMoO_4^-$	-348.62	Felmy et al. (1995)
$H_2MoO_4^0$	-358.86	Felmy et al. (1995)

Tables 5. Dimensionless Standard Molar Gibbs Energies of Formation of Major Electrolyte Species (cont'd)

Species	$\Delta_f G^\circ/RT$	References
$Mo_7O_{20}(OH)_4^{2-}$	-2152.05	Felmy et al. (1995)
F^-	-112.465	Wagman et al. (1982)
HF(aq)	-119.738	Wagman et al. (1982)
NO_3^-	-43.868	Wagman et al. (1982)

Table 6. Dimensionless Standard Molar Gibbs Energies of Formation of Am Species

Species	$\Delta_f G^\circ/RT$	References
Am^{3+}	-241.694	Fuger and Oetting (1976)
$AmOHCO_3(c)$	-566.888	Silva et al. (1995)
$AmCO_3^+$	-472.598	Silva et al. (1995)
$Am(CO_3)_2^-$	-695.904	Silva et al. (1995)
$Am(CO_3)_3^{3-}$	-915.526	Silva et al. (1995)
$AmPO_4{\cdot}xH_2O(am)$	-709.75	Rai et al. (1992a)
$Am(MoO_4)_2^-$	-942.22	Felmy et al. (1995)
$Am_2Mo_7O_{24}(aq)$	-2644.30	Felmy et al. (1995)
$NaAm(MoO_4)_2(c)$	-1069.29	Felmy et al. (1995)
$Am_2(MoO_4)_3{\cdot}xH_2O$	-1555.59	Felmy et al. (1995)
AmF^{2+}	-361.988	Silva et al. (1995)
AmF_2^+	-479.979	Silva et al. (1995)
AmF_3^0	>-604.878	This compilation(b)
$AmF_3(c)$	-624.00	This compilation(b)
$AmOH^{2+}$	-322.621	Silva et al. (1995)
$Am(OH)_2^+$	-400.554	Silva et al. (1995)
$Am(OH)_3^0$	-469.508	Silva et al. (1995)
$Am(OH)_3(am)$	-489.564	Silva et al. (1995)
$Am(OH)_3(c)$	-493.709	Silva et al. (1995)
$NaAm(CO_3)_2{\cdot}6H_2O(c)$	-1396.48	This compilation(c)

(a) Assumed to be analogous to the values for corresponding Nd(III) species (Felmy et al. 1995).

(b)Assumed to be analogous to the parameters for $NdF_3(c)$ (Rai et al. 1992b).

(c)Assumed to be analogous to the parameters for $NaNd(CO_3)_2{\cdot}6H_2O(c)$ (Rao et al. 1996a).

Table 7 log K^{o}_{sp} Values (25°C) of Am(III) Solid Compounds

Reaction	log K^{o}_{sp}	Reference
$Am(OH)_3(s) \rightleftharpoons Am^{3+} + 3OH^-$	-25.0	Silva et al. 1995
$Am(OH)_3(c) \rightleftharpoons Am^{3+} + 3OH^-$	-26.8	Silva et al. 1995
$AmOHCO_3(c) \rightleftharpoons Am^{3+} + OH^- + CO_3^{2-}$	-21.2	Silva et al. 1995
$NaAm(CO_3)_2.6H_2O(c) \rightleftharpoons$		
$Na^+ + Am^{3+} + 2CO_3^{2-} + 6H_2O$	-21.40	This compilation(a)
$AmPO_4.xH_2O(am) \rightleftharpoons Am^{3+} + PO_4^{3-} + xH_2O$	-24.79	Silva et al. 1995
$AmF_3(c) \rightleftharpoons Am^{3+} + 3F^-$	-19.5	This compilation(b)
$NaAm(MoO_4)_2(c) \rightleftharpoons Na^+ + Am^{3+} + 2MoO_4^{2-}$	-20.5	This compilation(c)
$Am_2(MoO_4)_3.xH_2O \rightleftharpoons 2Am^{3+} + 3MoO_4^{2-} + xH_2O$	-26.1	This compilation(c)

(a) Assumed to be analogous to the value for $NaNd(CO_3)_2.6H_2O(c)$ (Rao et al. 1996a).

(b) Assumed to be analogous to the value for $NdF_3(c)$ (Rai et al. 1992b).

(c) Assumed to be analogous to the values for $NaNd(MoO_4)_2(c)$ and $Nd_2(MoO_4)_3.xH_2O$ (Felmy et al. 1995).

Table 8 log K° Values (25°C) for the Formation of Aqueous Species

Reaction	log K°	Reference
$Mg^{2+} + H_2O \rightleftharpoons MgOH^+ + H^+$	-11.81	Harvie et al. 1984
$Am^{3+} + H_2O \rightleftharpoons Am(OH)^{2+} + H^+$	-6.4	Silva et al. 1995
$Am^{3+} + 2H_2O \rightleftharpoons Am(OH)_2^+ + 2H^+$	-14.1	Silva et al. 1995
$Am^{3+} + 3H_2O \rightleftharpoons Am(OH)_3^0 + 3H^+$	-25.7	Silva et al. 1995
$Mg^{2+} + CO_3^{2-} \rightleftharpoons MgCO_3^0$	2.93	Harvie et al. 1984
$Ca^{2+} + CO_3^{2-} \rightleftharpoons CaCO_3^0$	3.15	Harvie et al. 1984
$Am^{3+} + CO_3^{2-} \rightleftharpoons AmCO_3^+$	7.8	Silva et al. 1995
$Am^{3+} + 2CO_3^{2-} \rightleftharpoons Am(CO_3)_2^-$	12.3	Silva et al. 1995
$Am^{3+} + 3CO_3^{2-} \rightleftharpoons Am(CO_3)_3^{3-}$	15.2	Silva et al. 1995
$Am^{3+} + 2MoO_4^{2-} \rightleftharpoons Am(MoO_4)_2^-$	11.2	This compilation[(a)]
$Am^{3+} + Mo_7O_{20}(OH)_4^{2-} \rightleftharpoons Am_2Mo_7O_{24}(aq) + 4H^+$	3.85	This compilation[(a)]
$Am^{3+} + F^- \rightleftharpoons AmF^{2+}$	3.4	Silva et al. 1995
$Am^{3+} + 2F^- \rightleftharpoons AmF_2^+$	5.8	Silva et al. 1995
$Am^{3+} + 3F^- \rightleftharpoons AmF_3(aq)$	<11.2	This compilation[(b)]

(a) Assumed to be analogous to the values for corresponding Nd(III)/molybdate species (Felmy et al. 1995).

(b) Estimated from the results for solutility of $NdF_3(c)$ (Rai et al. 1992b).

Chloride and Nitrate

Felmy et al.(1989) studied the solubility of $Pu(OH)_3$(am) in dilute solutions and in chloride and sulfate brines (Fig.1). The observed solubility of $Pu(OH)_3$(am) in brine at a given pC_{H^+} was about 3.5 orders of magnitude higher than in dilute solutions. Using the solubility product, calculated from the results of dilute solutions, and assuming that the binary ion-interaction parameters for Nd^{3+}-Cl^- (Pitzer and Mayorga 1973) apply to Pu^{3+}-Cl^-, they were able to very closely predict the solubility of $Pu(OH)_3$(am) in brines in the entire range of measured pC_{H^+} values. These data, as expected, indicated that parameters for Nd^{3+}-Cl^- equally apply to the corresponding Pu(III) system. Since Pu(III) and Am(III) show similar behavior in solubility, ion-interaction parameters for Nd^{3+}-Cl^- are assumed to be applicable to the Am^{3+}-Cl^- system. In fact, these parameters were also found to provide consistent predictions for the solubility of $AmPO_4$(am) in chloride media (Rai et al. 1992a).

Because of the analogous behavior of trivalent rare earths and actinides, binary parameters for Nd^{3+}-NO_3^- reported by Pitzer (1991) are assumed to apply to the corresponding Am system.

Hydroxide

The solubility of Nd, Pu, and Am hydroxides are reported in Fig.2. In general, solubilities of amorphous hydroxides are slightly higher than crystalline hydroxides. There is remarkable similarity in the pH dependence of the solubility behavior. However, different combinations of hydrolysis constants and solubility products may equally explain the observed behavior. For example, the solubility of $Nd(OH)_3$(c) can be reasonably explained by using the values of hydrolysis constants reported by Silva et al. (1995) or by Rai et al. (1983) for Am in combination with the solubility product reported by Rao et al. (1996b) (Fig.3). These values of constants and solubility product also provide reasonable predictions for the solubility of $Pu(OH)_3$(am) (Felmy et al. 1989) and $Am(OH)_3$(am) (Rai et al. 1983). We do notice that the solubilities of $Nd(OH)_3$(c) predicted by Rai et al.(1983) are different from those by Silva et al.(1995) in the pH range above 7 (Fig.3). However, the experimental data in this pH range are quite scattered (close to the detection limit), making it difficult to exclusively justify the constants either by Rai et al.

(1983) or by Silva et al. (1995). Furthermore, data in this pH range are not critical in evaluating the solubility product of $Nd(OH)_3(c)$. To be consistent with the published database (Silva et al. 1995) in the literature, values from Silva et al. (1995) are selected for this compilation.

Fluoride

Fluoride forms strong aqueous complexes and fairly insoluble fluorides with trivalent actinides and rare earths. The values of formation constants of AmF^{2+} and AmF_2^+ from Silva et al. (1995) are selected and, in general, appear to be in close agreement with the values reported for other trivalent actinides (Tables A4.1, A5.1, and A6.1 in Appendix). The solubilities for $AmF_3(c)$ (Phillips 1988) and $PuF_3(c)$ (Wanner 1986) predicted from estimated thermodynamic data are over 4 to 9 orders of magnitude higher than those experimentally determined for $NdF_3(c)$ by Rai et al. (1992b) (Fig.4). These predicted solubilities can not possibly be correct, because they are all expected to be similar. The solubility product selected for the compilation is based on the solubility data reported by Rai et al. (1992b) for $NdF_3(c)$ in NaF solutions ranging in concentrations from 10^{-5} to 1M. Based on the same set of solubility data of $NdF_3(c)$, an upper limit for the formation constant of NdF_3^0 is estimated (11.2) and assumed applicable to AmF_3^0.

Phosphate

Aqueous complexes of phosphate are not very strong, but phosphate forms very insoluble solids. Nd and Am phosphates show similar solubility and pH dependence (Fig.5). Based on the solubility of $NdPO_4(c)$ as a function of $[NaH_2PO_4]$ ranging from 10^{-4} to 1.0 M (Fig.6) and as a function of pH in $10^{-3.5}$ M total phosphate, Rai et al. (1991) developed reliable values of the solubility product of $NdPO_4(c)$ and the ion-interaction parameter $\beta^{(2)}$ for Nd^{3+}-$H_2PO_4^-$. The solubility product of $NdPO_4(c)$ was later found, as expected, to be similar to the solubility product of $AmPO_4.xH_2O$ (Rai et al. 1992a). This value is quoted by Silva et al. (1995) and selected for this review along with the $\beta^{(2)}$ value for Am^{3+}-$H_2PO_4^-$ (identical to the experimentally determined $\beta^{(2)}$ for Nd^{3+}-$H_2PO_4^-$). These values will provide reliable predictions of the solubility of Am phosphate in a large range of pH and phosphate concentrations.

Alternatively, the solubility of Am phosphate as a function of phosphate concentrations can be interpreted by assuming the formation of Am phosphate complexes (e.g., $AmH_2PO_4^{2+}$), instead of using the ion-interaction parameters $\beta^{(2)}$ for Am^{3+}-$H_2PO_4^-$. Rai et al. (1991) calculated the value of $\Delta_fG°/RT$ for $NdH_2PO_4^{2+}$ from the best fit of their solubility data, which corresponds to log β = 2.74 for $Nd^{3+} + H_2PO_4^- \rightleftharpoons NdH_2PO_4^{2+}$. Using either this value to account for the formation of $NdH_2PO_4^{2+}$ or the $\beta^{(2)}$ to account for the ion-interaction of Nd^{3+}-$H_2PO_4^-$, but not the both, provides satisfactory predictions of the solubility of $NdPO_4(c)$ in the presence of phosphate.

Sulfate

A large quantity of data are available on the complexation constants of sulfate with Pu(III), Am(III), and Cm(III) (Tables A4.13, A4.14, A5.11, A5.12, and A6.9 in Appendix). Most of these data were collected at high but constant ionic strengths to avoid variations in activity coefficients. Reliable extrapolations of these data to low or zero ionic strengths is difficult. However, the values obtained by different authors under a constant set of conditions for different trivalent actinides agree closely. For example, values of log β for the formation of MSO_4^+ at I = 2 M reported by Rao et al. (1978) for Pu, Am, and Cm are 1.89, 1.71, and 1.59, respectively, and those reported by Carvalho and Choppin (1967) for Am and Cm are 1.65 and 1.61, respectively. However, there are several difficulties in unambiguously interpreting these data. The major difficulty results from the lack of ion-interaction parameters for bulk electrolyte ions to extrapolate these values to zero ionic strength or to have a capability to predict equilibrium constants at different ionic strengths. To overcome this difficulty, we chose data obtained by McDowell and Coleman (1972) in the absence of bulk electrolyte to determine binary ion-interaction parameters for Am^{3+}-SO_4^{2-} (Rai et al. 1995). Values of $\beta^{(0)} = 3.0398$ and $\beta^{(2)} = -2500$ for Am^{3+}-SO_4^{2-} provided the best representation of McDowell and Coleman's data (Fig.6). To check whether these parameters obtained from a simple system are applicable to mixed systems such as ClO_4^--SO_4^{2-} and $H_2PO_4^-$-SO_4^{2-}, we examined other solvent extraction and ion exchange Am data obtained in 1 M $NaClO_4$ solutions (Sekine 1965; Nair 1968) and data on the solubility of $NdPO_4(c)$ in sulfate solutions (Rai et al. 1995). For these calculations we used $\beta^{(0)} = 3.0398$ and $\beta^{(2)} = -2500$ for Am^{3+}-SO_4^{2-}. We also used ion-interaction parameters for Nd^{3+}-ClO_4^-

reported by Pitzer (1991) to represent Am^{3+}-ClO_4^- interactions for perchlorate systems or Nd^{3+}-$H_2PO_4^-$ parameters discussed above for the $NdPO_4$(c) solubility in sulfate solutions. The calculated concentrations in all cases are in excellent agreement with the solvent extraction and ion exchange data for Am perchlorate systems and with the solubility data of $NdPO_4$(c) in sulfate solutions (Fig.8-10). Several important conclusions can be drawn from these studies: 1) the values of Am^{3+}-SO_4^{2-} interaction parameters are consistent with literature data and are applicable to sulfate concentrations as high as 0.5 M, 2) the values of Am^{3+}-ClO_4^- interactions estimated in this study are reasonable, 3) the interaction parameters obtained for Am^{3+}-SO_4^{2-} apply equally well to Nd^{3+}-SO_4^{2-}, and 4) the Pitzer parameters obtained in this study from simple systems can be used for predictions in concentrated mixed systems containing ClO_4^--SO_4^{2-} or $H_2PO_4^-$-SO_4^{2-}.

Carbonate

Carbonate forms strong complexes with trivalent rare earths and actinides. A large quantity of experimental data are available on carbonato complexes of Am (Tables A5.6-A5.7 in Appendix). Very limited experimental data are available for Cm(III) or Pu(III) (Tables A4.7 and A6.6 in Appendix). Felmy et al. (1990) determined the solubility of $Am(OH)CO_3$(c) in a wide pH range, fixed CO_2(g) atmosphere, and CO_3^{2-} concentrations extending to 0.1 M. Based on these results, Pitzer modeling parameters were developed, including the solubility product of $Am(OH)CO_3$(c) and values of formation constants of mono-, di-, and tricarbonato complexes of Am^{3+}, that closely depicted the solubility of $Am(OH)CO_3$(c) (Figure 11). Felmy et al. (1990) also showed that their model was consistent with the solvent extraction data of Bidoglio (1982) (Figure 12) and the $Am(OH)CO_3$(c) solubility data of Silva and Nitsche (1984) (Figure 11). A recent review of Am thermodynamic data (Silva et al. 1995) based their values on Felmy et al. (1990).

To extend this model to high carbonate concentrations, determine the solubility controlling carbonate solid in the high carbonate region, and obtain reliable values of binary and ternary parameters applicable to concentrated mixed systems (Na_2CO_3/NaCl), Rao et al. (1996a, 1996c) conducted solubility studies in solutions of high [Na_2CO_3] and [NaCl] using $Nd_2(CO_3)_3$(c) and $NaNd(CO_3).6H_2O$(c) as the initial solids (Fig.13 and 14). Several conclusions were drawn from these data: 1) important carbonato complexes and their complexation constants with Nd^{3+} were identical to those for the analogous Am^{3+} system, 2) the solubility controlling solid in solutions of high carbonate concentrations was $NaNd(CO_3).6H_2O(c)$, whereas $Nd_2(CO_3)_3(c)$ is not stable under these conditions, 3) solubility of $NaNd(CO_3).6H_2O(c)$ increased with the increase in [NaCl] up to 4 M, and 4) revised values for the binary and ternary parameters of Nd^{3+} complexes were required to interpret these data. The final model selected in this report is based on these studies and is consistent with all of the previous data for Nd(III)/Am(III)-carbonate systems (Fig.13 and 14).

This model has recently been shown to be applicable to another trivalent rare earth system. The predictions by this model were completely consistent with the measured solubility of Gd(III) compounds in solutions of sodium carbonate and and potassium carbonate (Weger et al. 1998).

As a final test of the robustness of the carbonate model and its ability to reliably predict solubility behavior in mixed and concentrated solutions, the model-predicted concentrations are compared with the experimental data of Runde and Kim (1995) for the solubility of $NaAm(CO_3)_2.6H_2O(c)$ in 5 M NaCl (Fig.15). Close agreement between the predicted and the experimental data showed that the model is applicable to the Am system and that the recommended value of the parameters are reliable.

Molybdate

Based on thermodynamic analysis of solubility measurements of $NdPO_4(c)$ as a function of pH and molybdate, and of $NaNd(MoO_4)_2(c)$ and $Nd_2(MoO_4)_3.xH_2O$ as a function of $NdCl_3$, Felmy et al. (1995) determined the solubility products of $NaNd(MoO_4)_2(c)$ and $Nd_2(MoO_4)_3.xH_2O$ and the equilibrium constants of Nd-molybdate complexes. The predictions based on these constants agreed closely with the extensive experimental data not only for the solubility of molybdate solids but also with the solubility of $NdPO_4(c)$ in molybdate solutions (Figure 16). No other reliable data for these reactions are available. The thermodynamic data selected for the trivalent model are based on this study.

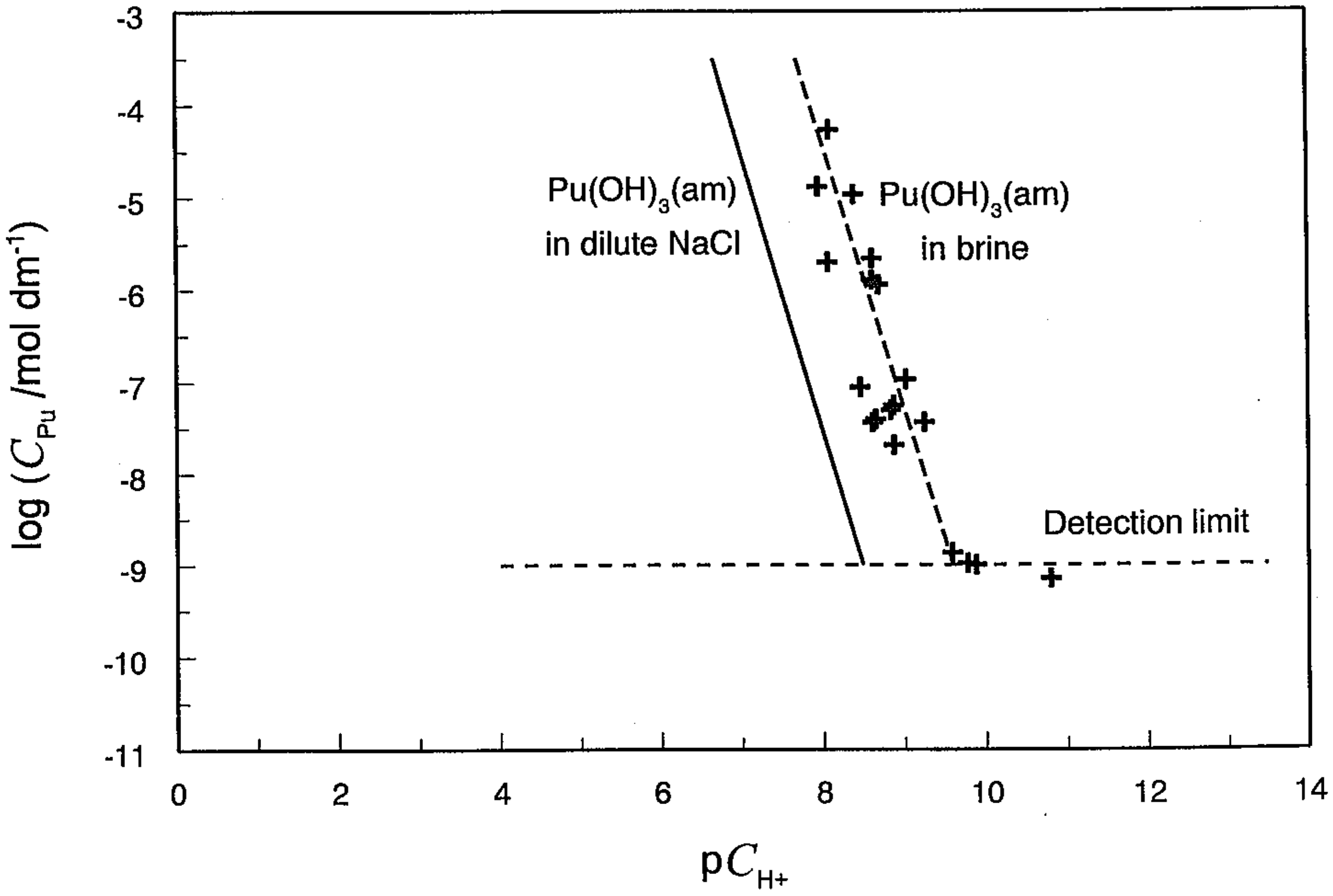

Figure 1 The Effect of PBB1 brine ([Na^+] = 5.2 M, [Ca^{2+}] = 0.034 M, [Cl^-] = 4.6 m, [SO_4^{2-}] = 0.044 M, ionic strength ~ 5.5 M) on the solubility of $Pu(OH)_3$(am) (Felmy et al. 1989).

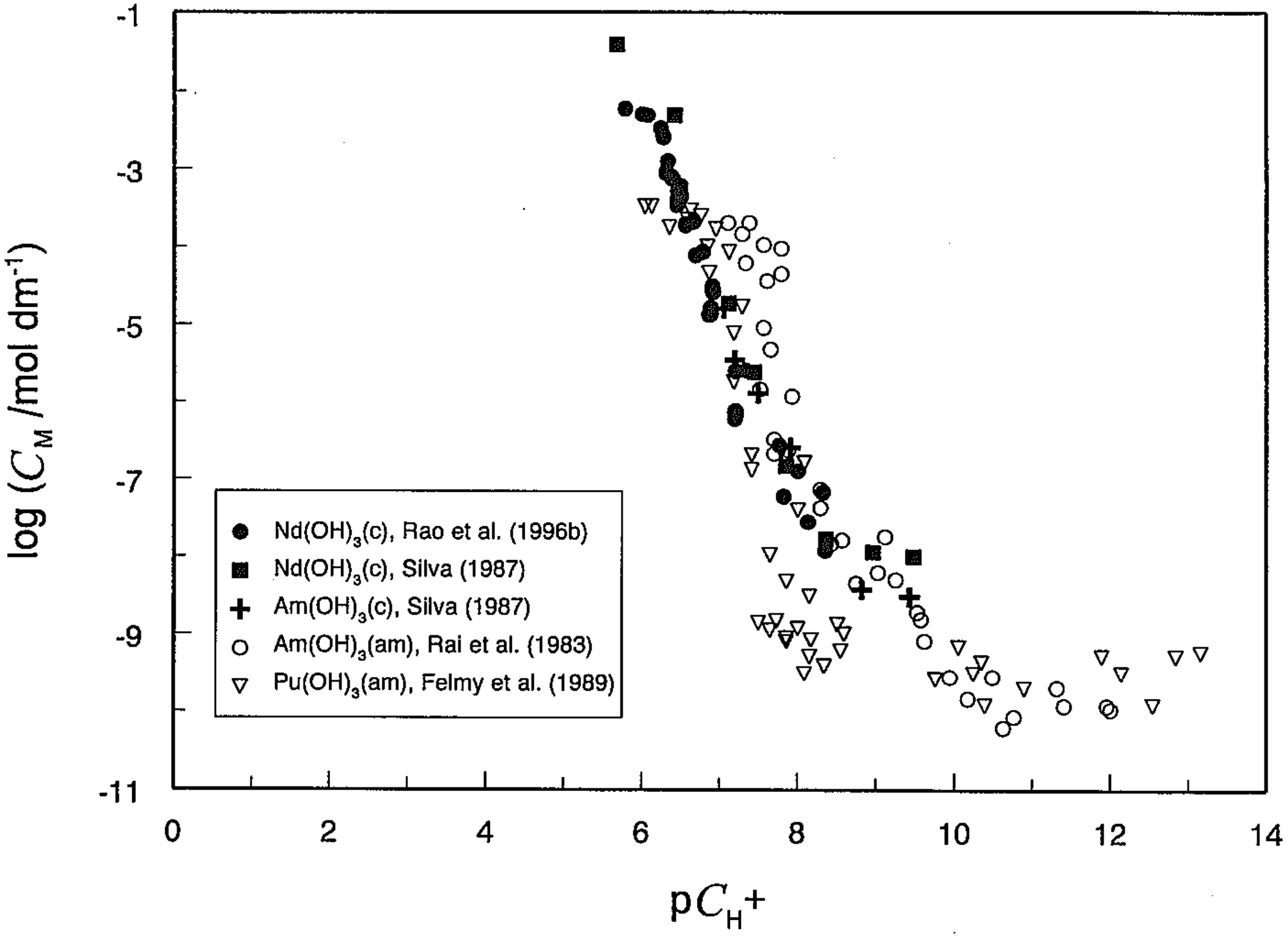

Figure 2 Solubility of trivalent actinide and lanthanide hydroxides.

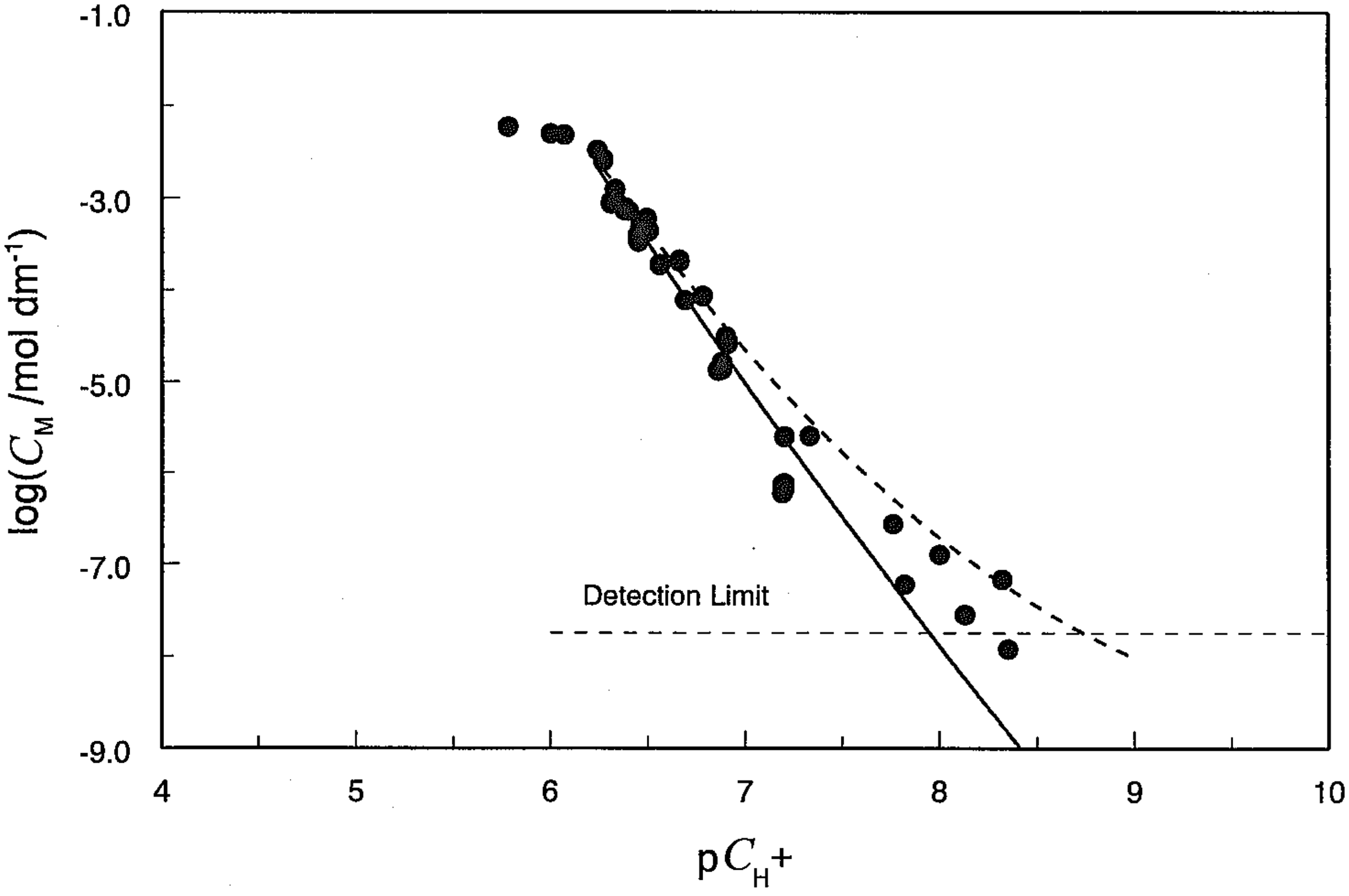

Figure 3 Comparison of measured (points, Rao et al. 1996b) and predicted solubility of Nd(OH)$_3$(c). Predictions are made with the hydrolysis constants from Rai et al. 1983 (solid line) and from Silva et al. 1995 (dashed line).

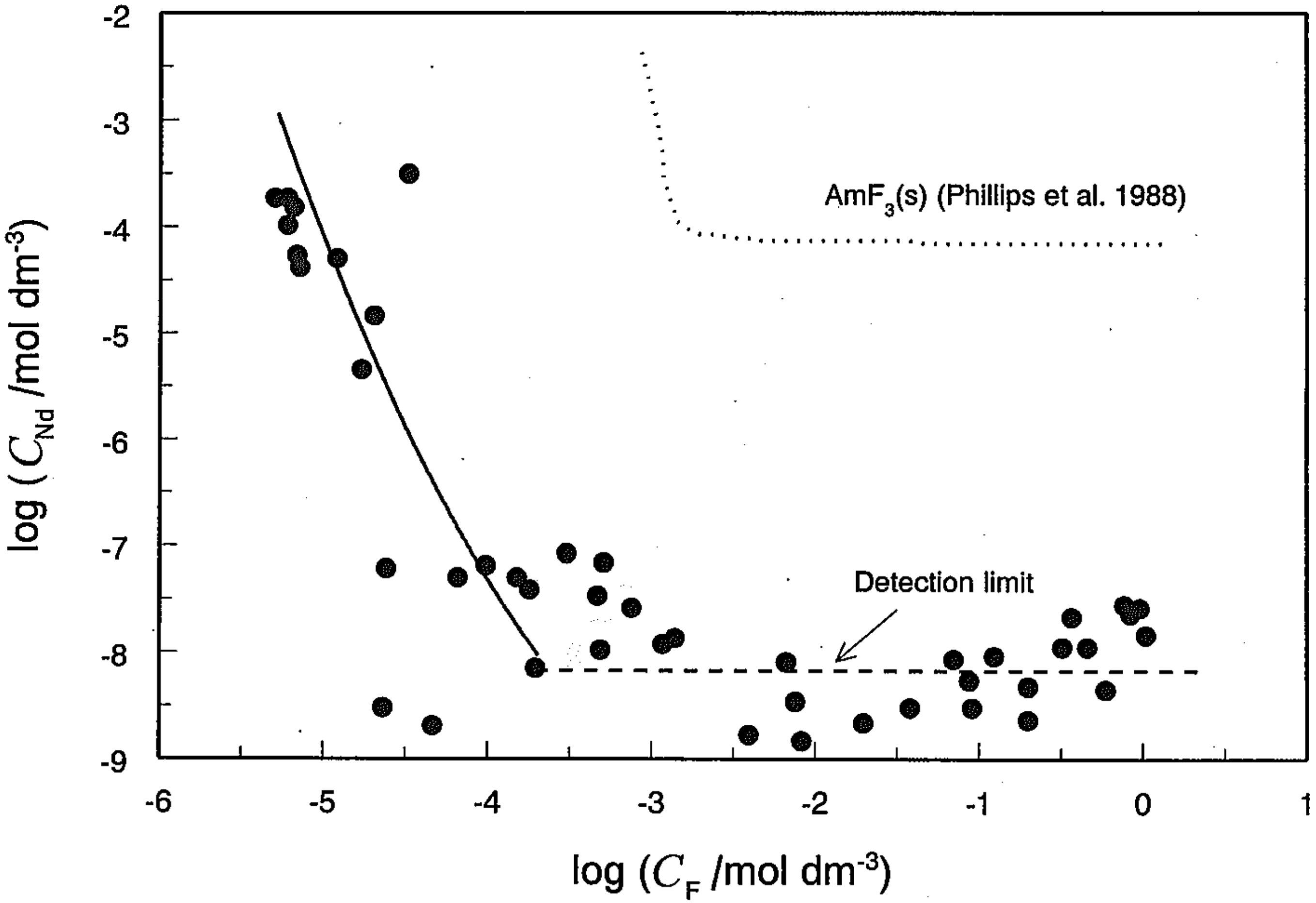

Figure 4 Comparison of experimental solubility of NdF$_3$(c) (Rai et al.1992b) with the predicted solubilities of AmF$_3$(s) (Phillips et al. 1988).

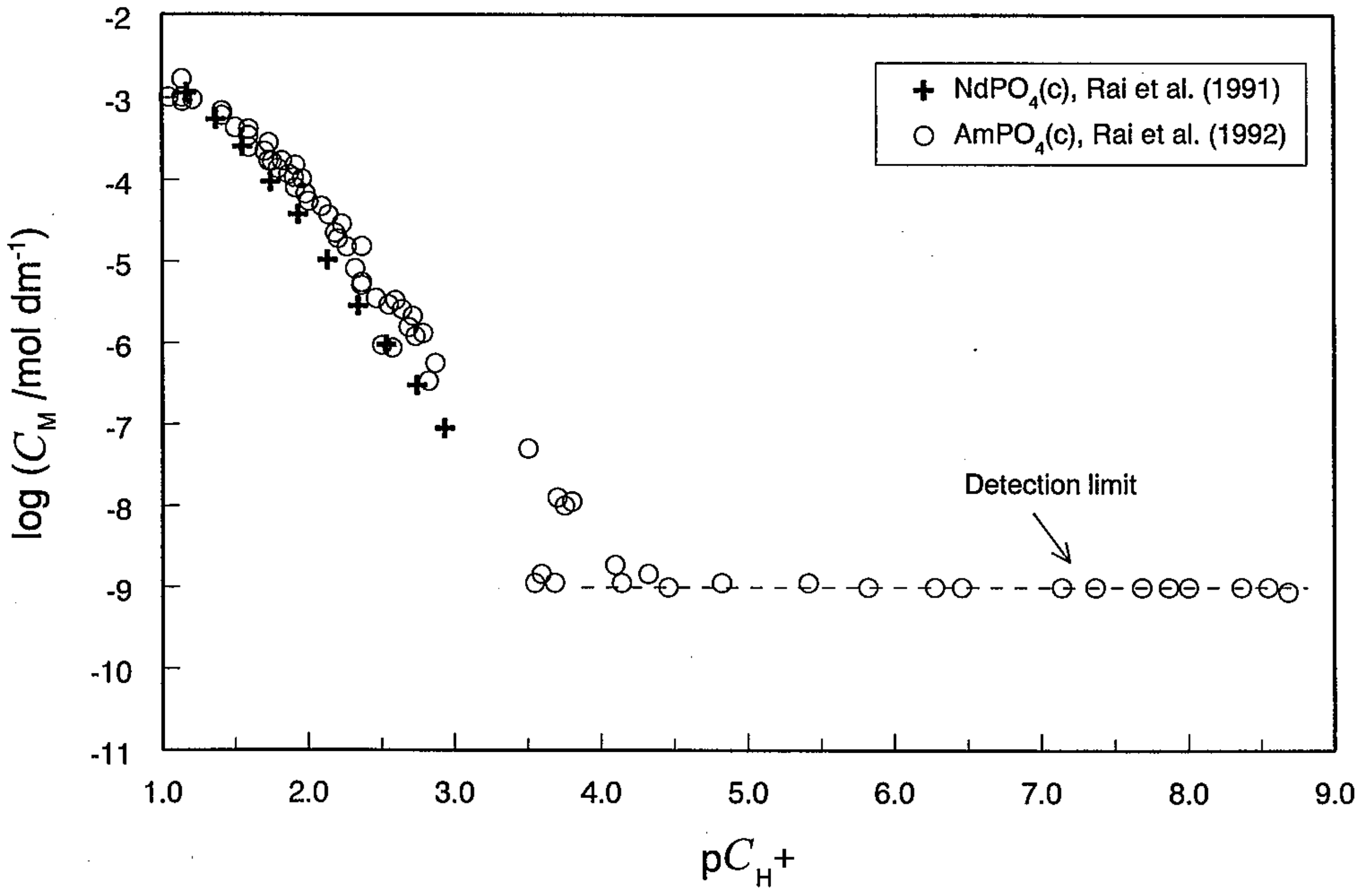

Figure 5 Solubility of Nd(III) and Am(III) phosphates at fixed $[\text{phosphate}]_{\text{total}} \approx 10^{-3.5}$ M.

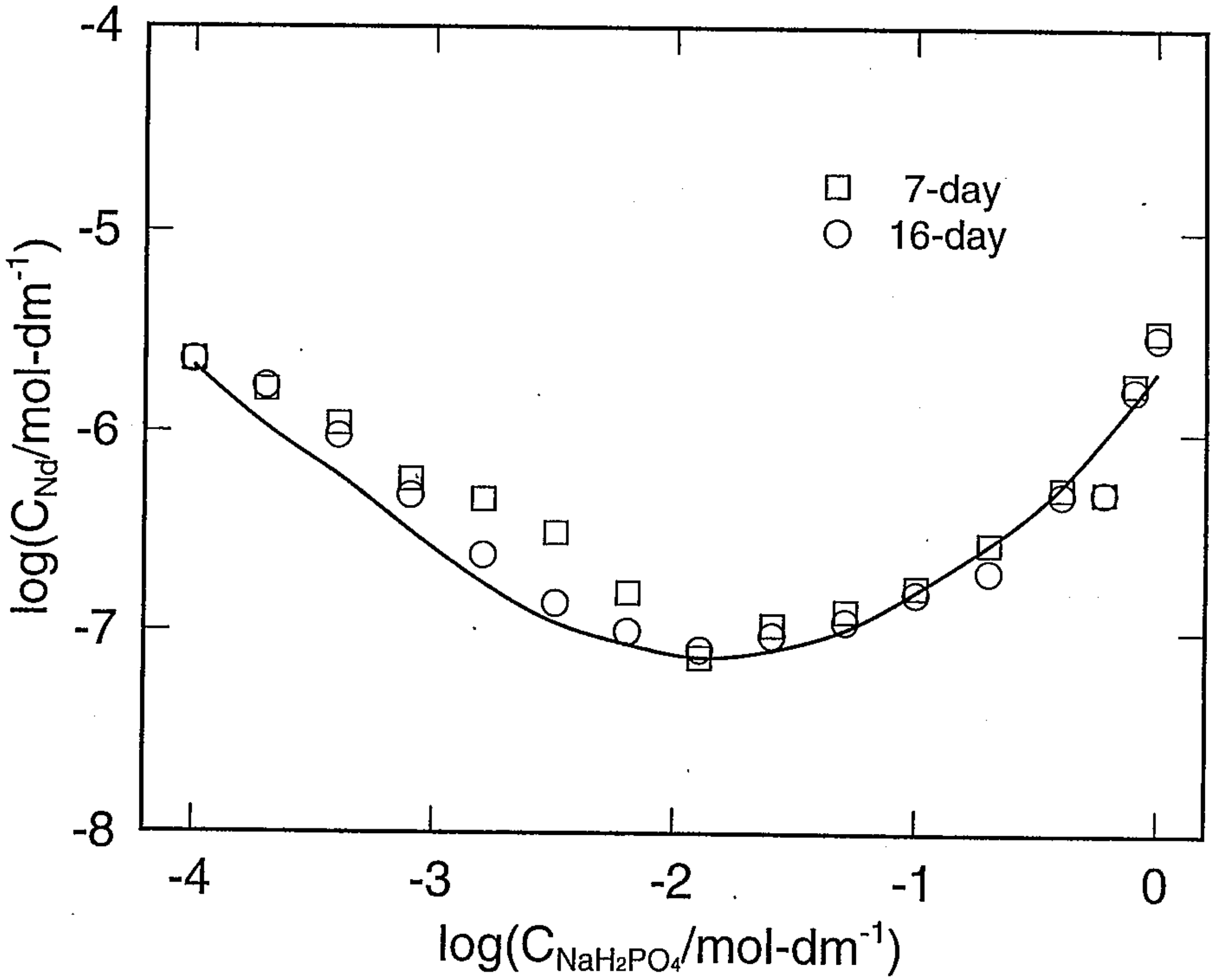

Figure 6 Solubility of $NdPO_4(c)$ as a function of the concentration of NaH_2PO_4 at a constant pH of 2.5 (Rai et al. 1991).

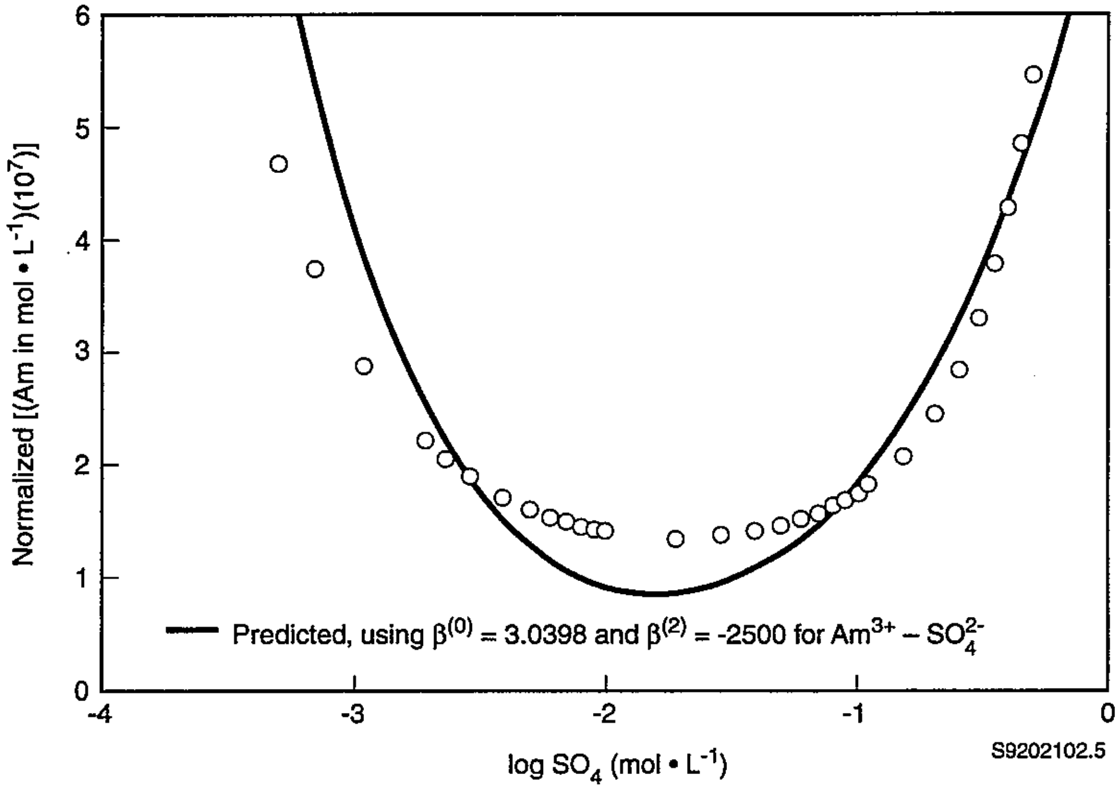

Figure 7 Normalized equilibrium aqueous Am concentrations from solvent extraction data of McDowell and Coleman (1972) obtained at constant acid activity and extractant-phase composition. The solid line represents the predicted concentrations (see text for details). (Rai et al. 1995).

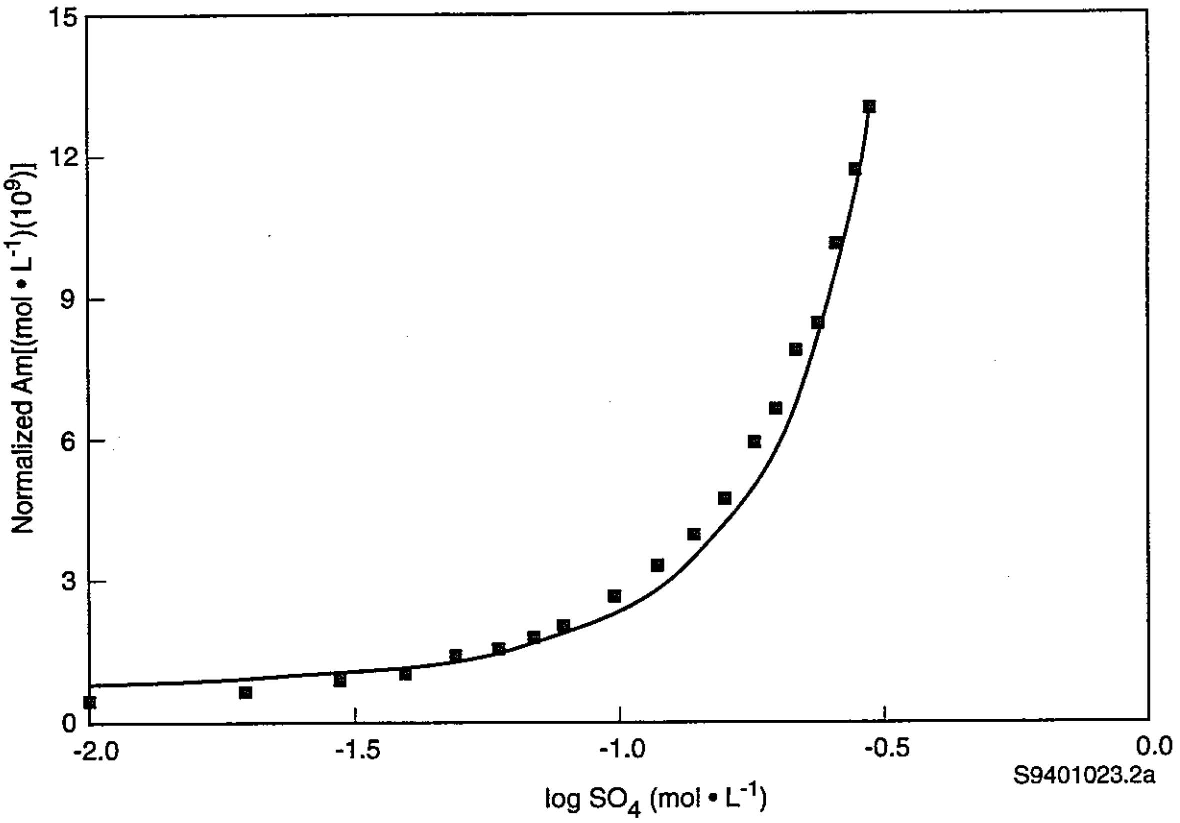

Figure 8 Normalized equilibrium aqueous Am concentrations from ion exchange experimental data of Nair (1968) obtained at constant pH and 1 M $NaClO_4$. The solid line represents the predicted concentrations (see text for details). (Rai et al. 1995).

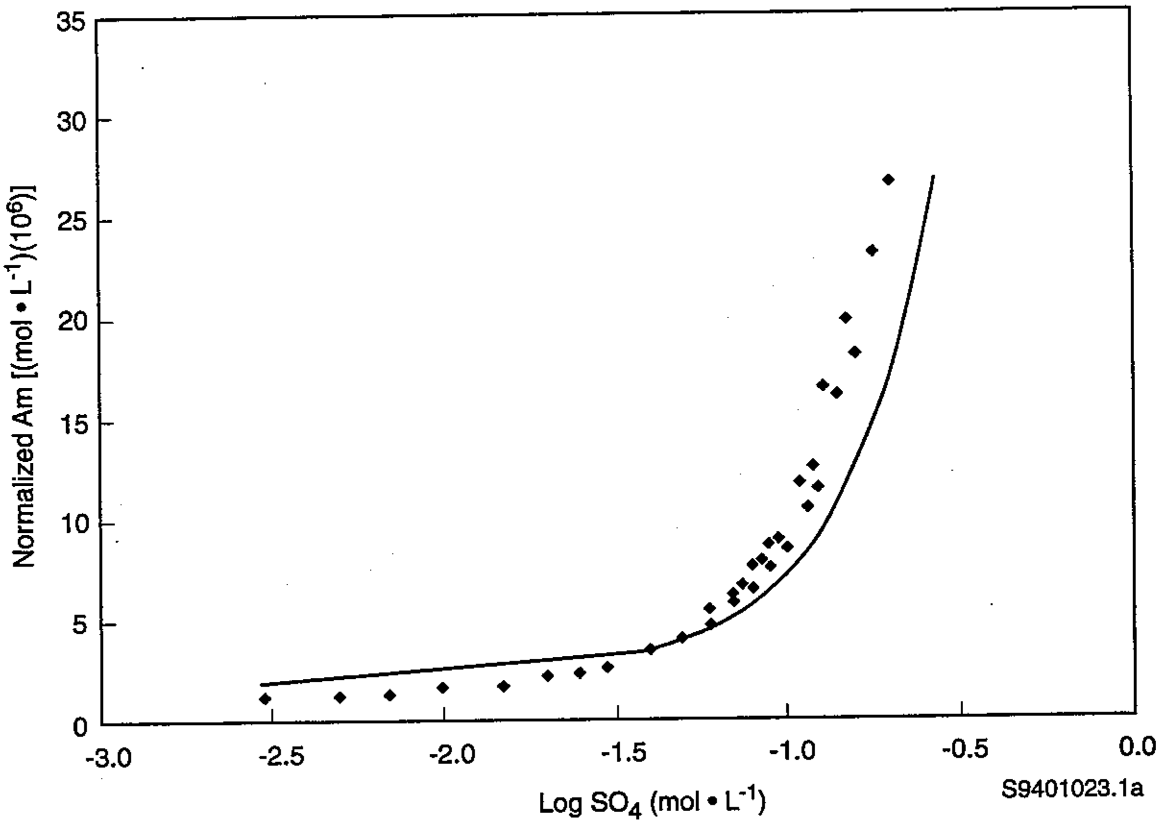

Figure 9 Normalized equilibrium aqueous Am concentrations from solvent extraction data of Sekine (1965) obtained at constant acid activity and extractant-phase composition. The solid line represents the predicted concentrations (see text for details). (Rai et al. 1995).

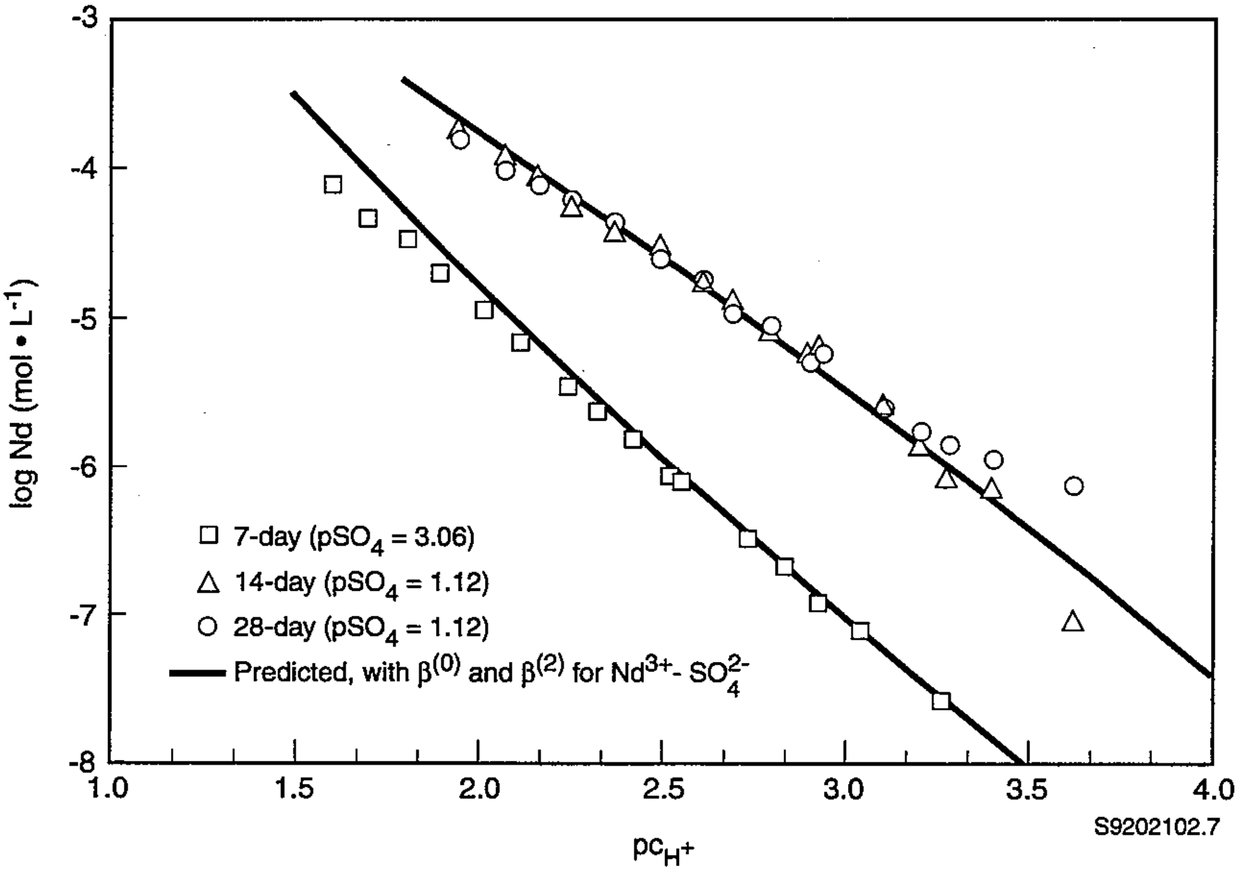

Figure 10 Solubility of $NdPO_4$(c) at [NaH_2PO_4] = $10^{-3.5}$ M and as a function of sulfate concentration. Predicted concentrations based on Pitzer parameters obtained for $Am\text{-}SO_4$ data (see text for details). (Rai et al. 1995).

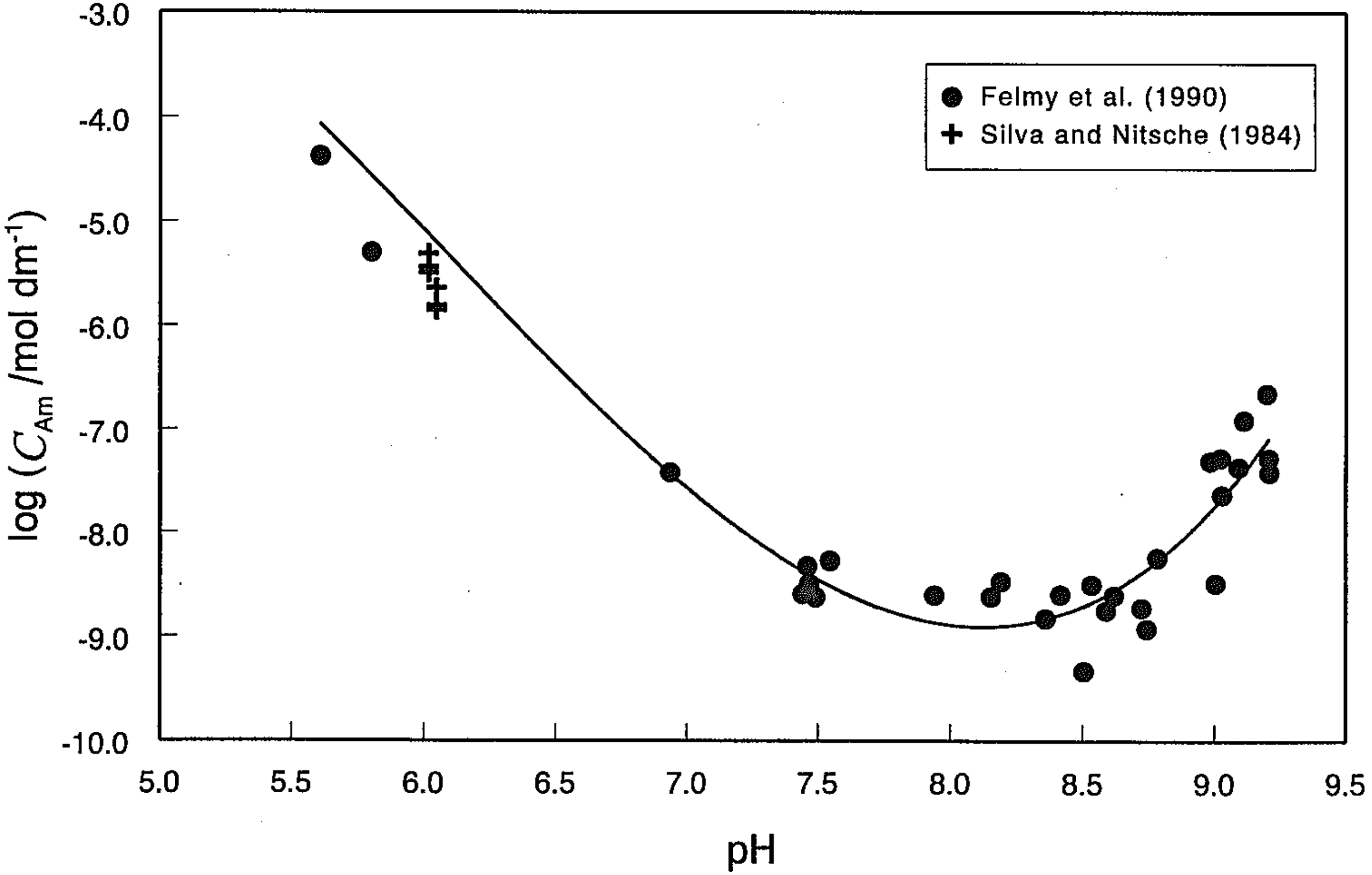

Figure 11 Solubility of $AmOHCO_3(c)$ at a fixed P_{CO2} of 0.001 atm.

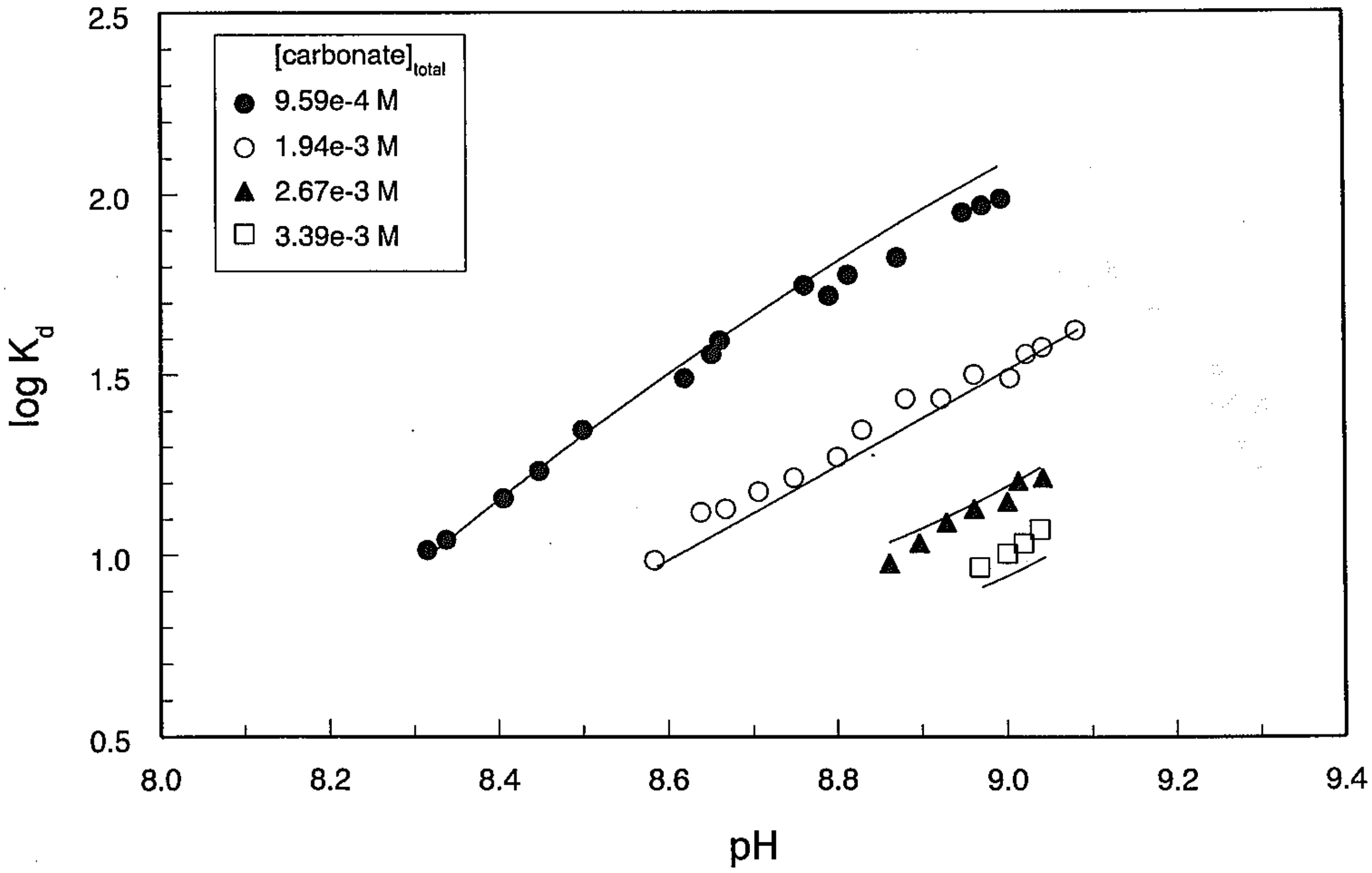

Figure 12 Comparison between the measured K_d by solvent extraction (points, Bidoglio 1982) and the calculated K_d (solid lines, Felmy et al. 1990) at different total carbonate concentrations.

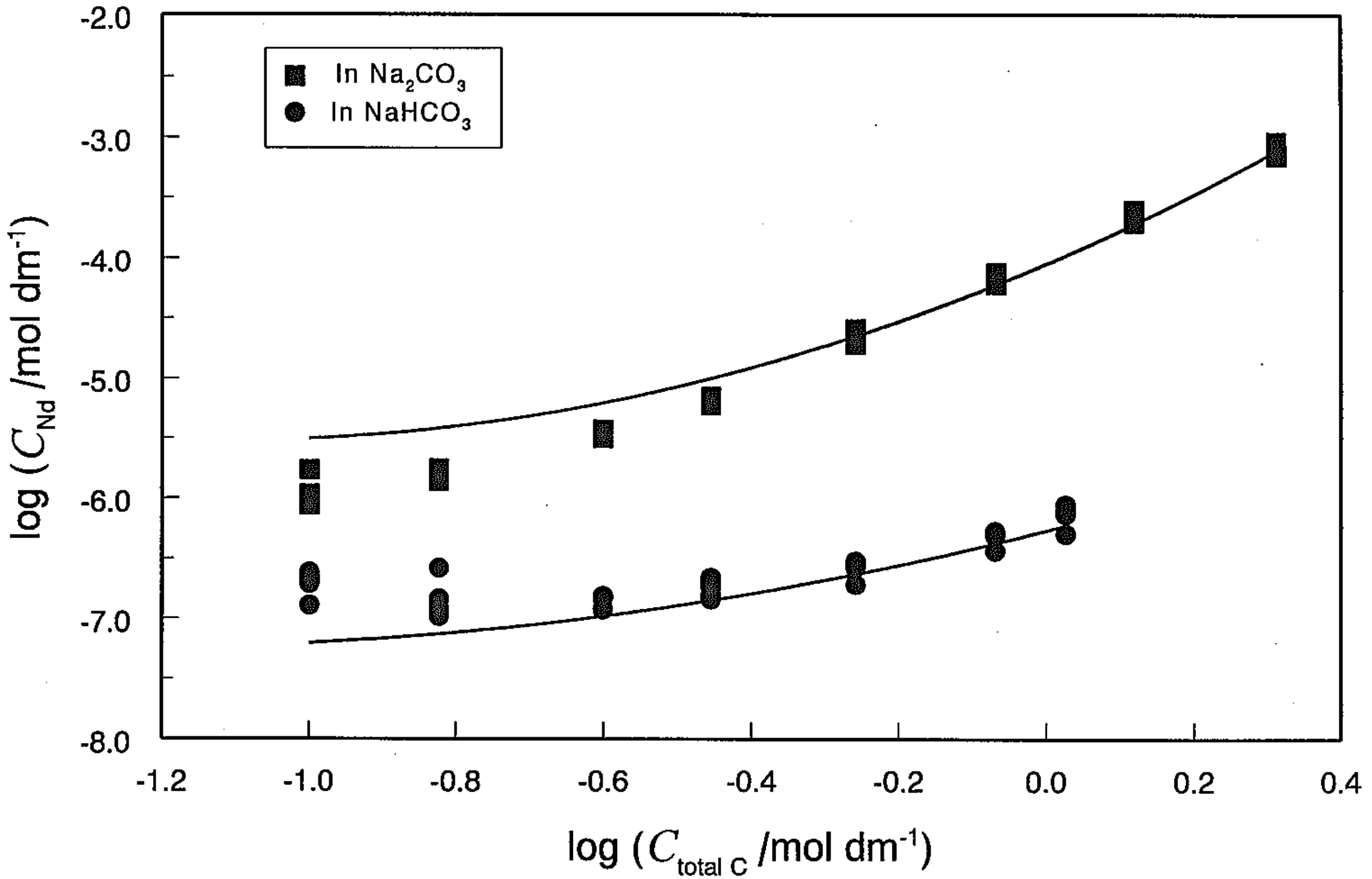

Figure 13 Observed (data points) and model predicted (solid lines, see text for model parameters) solubility of $NaNd(CO_3)_2(s)$ (Rao et al. 1996a).

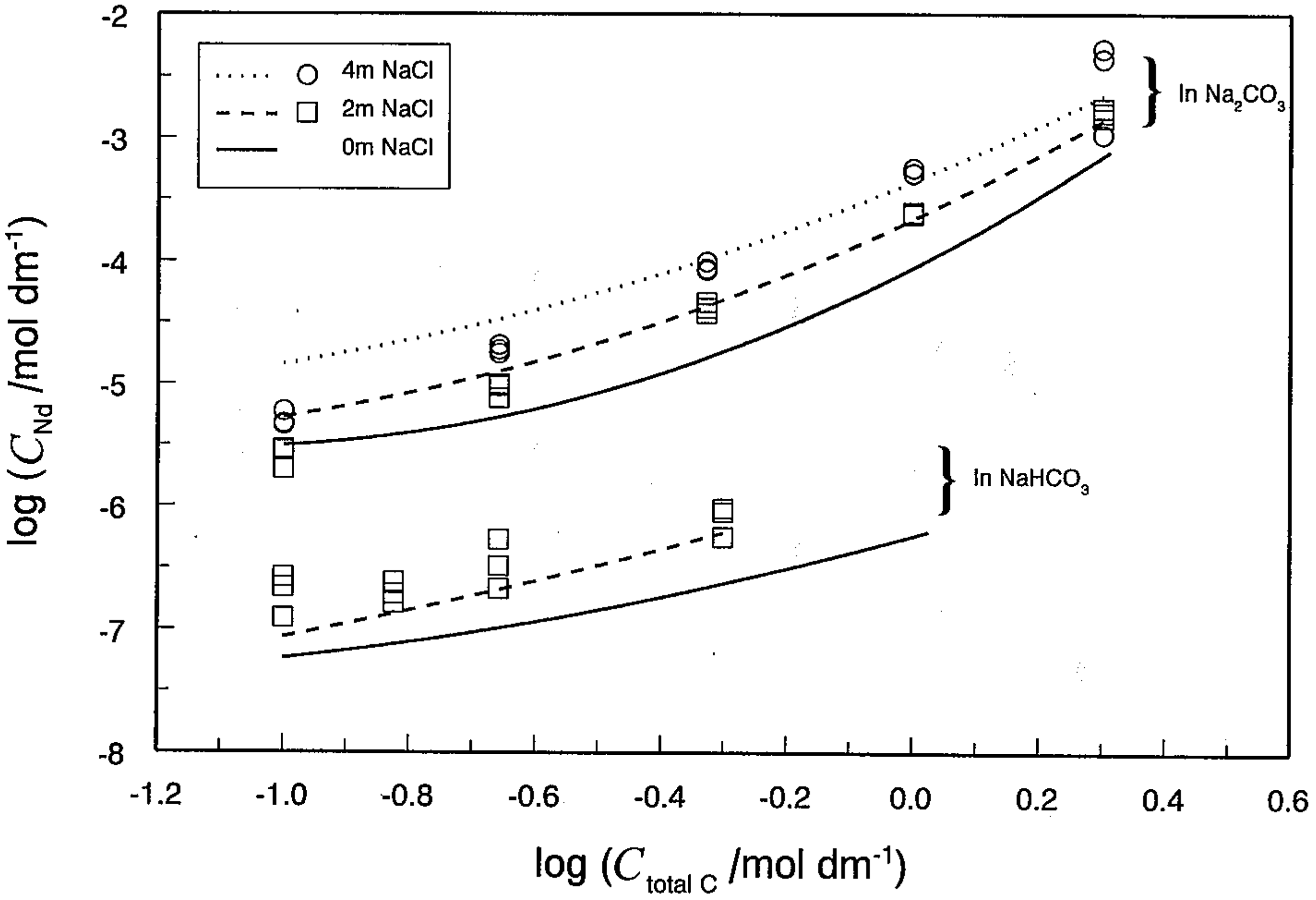

Figure 14 Solubility of $NaNd(CO_3)_2.6H_2O(c)$ in $NaHCO_3$ and Na_2CO_3 solutions, in the absence (solid lines) and presence of NaCl (Rao et al. 1996c).

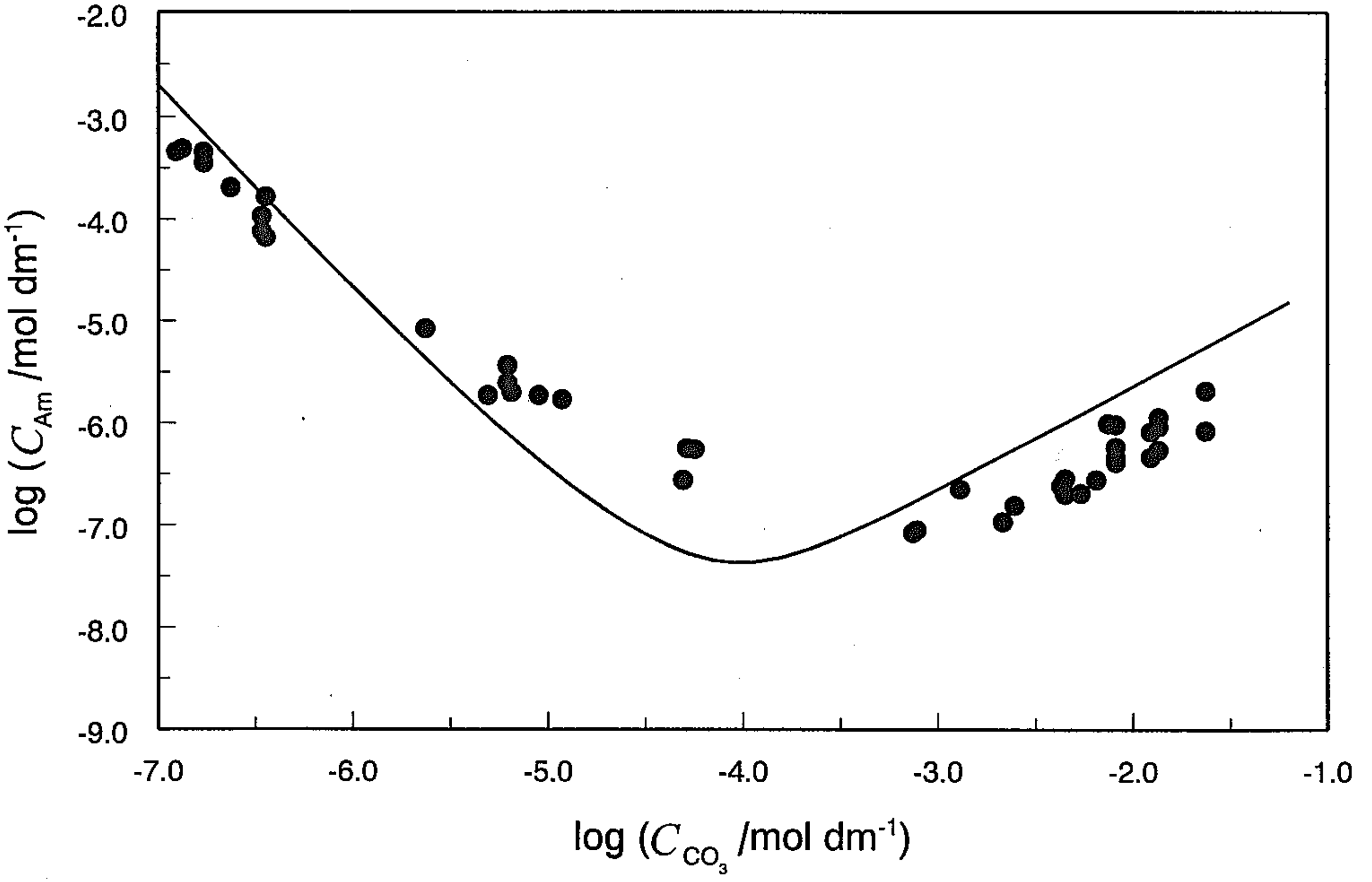

Figure 15 Solubility of $NaAm(CO_3)_2.6H_2O(s)$ as a function of the concentration of carbonate (data points from Runde & Kim 1995, the solid line based on predictions with modeling parameters discussed in the text).

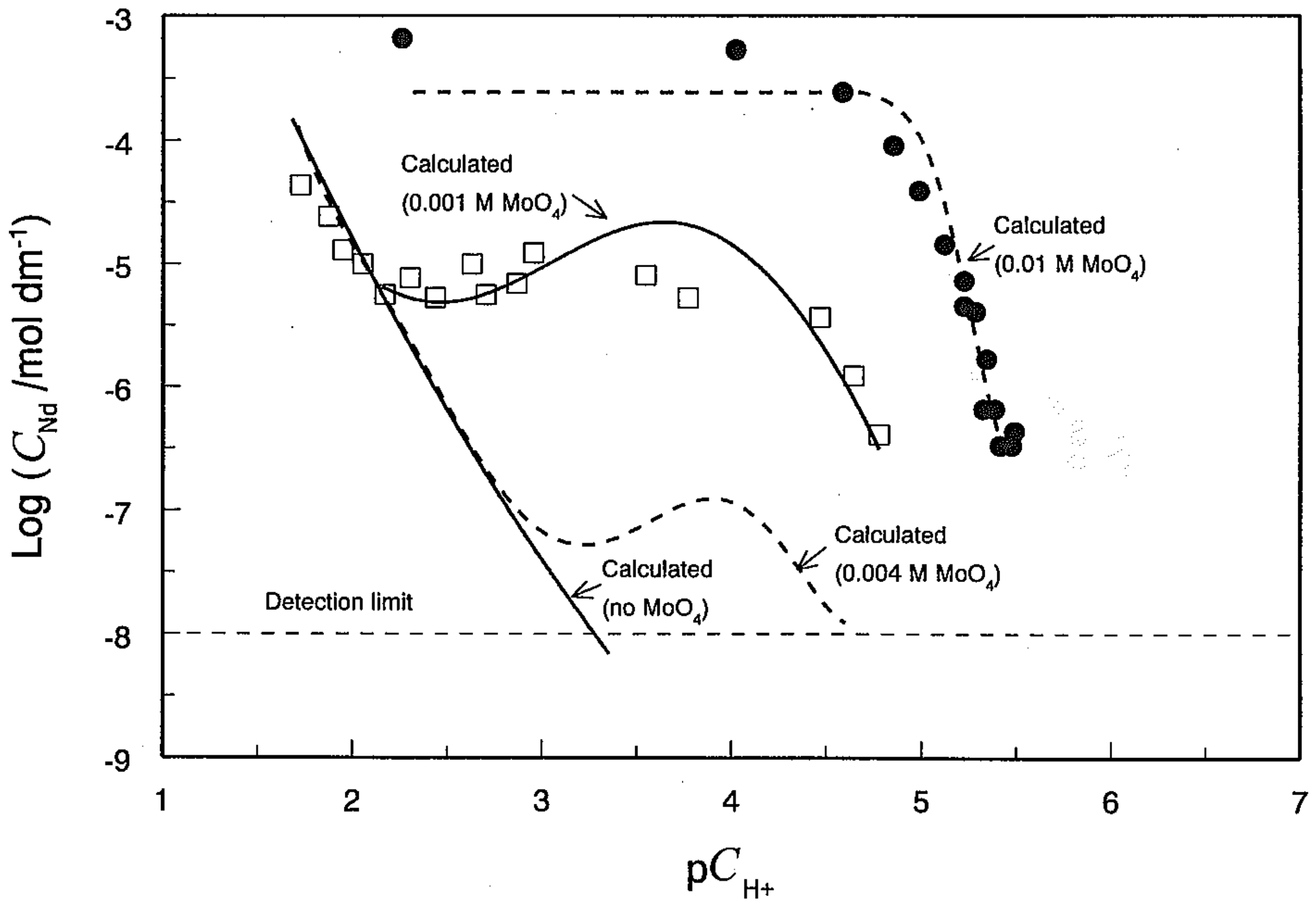

Figure 16 Solubility of $NdPO_4$(c) as functions of pC_{H^+} and molybdate concentrations at fixed [phosphate]$_{total}$ of $10^{-3.5}$ M (Felmy et al. 1995).

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Appendix: Compilation of Thermodynamic Data for Trivalent Actinides

List of Abbreviations Used for Methods

Abbreviation	Method
cal	calorimetry
calc	calculated
chr	chromatography
cix	cation exchange
col	colorimetry
dis	distribution between two phases
emf	electromotive force, not specified
est	estimated
gl	glass electrode
ise-X	ion selective electrode with ion X stated
ix	ion exchange
nmr	nuclear magnetic resonance
pot	potentiometry
recal	recalculation using data from another paper
sol	solubility
sp	spectroscopy
tp	electrical migration or transference number

A1: SAMARIUM

Table A1.1: Equilibrium Constants (β_n) for Formation of Aqueous Sm^{3+} complexes with F^- ($Sm^{3+} + nF^- \rightleftharpoons SmF_n^{(3-n)+}$)

log β_1	log β_2	log β_3	Medium	Maximum Metal/H^+/Ligand Concentration	Method	Reference
4.2			H_2O	n.a.	est	[78ALL/BEA]
4.17			H_2O	n.a.	est	[90WOO]
3.58			H_2O	n.a.	est	[92MIL]
3.15	6.95		0.5M NH_4NO_3	M:1.5mM, H:[1], L:1mM	pot,ise- F^-	[89MEN/JAM]
3.12			1M $NaClO_4$	M:0.01M, H:0.1M, L:2mM	pot	[67WAL/CHO]
3.12			I = 1 M	n.a.	est	[80BON/HEF]
3.09	4.56		1M NaCl	M:0.4mM, H:0.25mM, L:1mM	pot,ise- F^-	[85BEC/BIL]
3.23	5.81	10.54	1M (H,Na)ClO_4	M:1mM, H:1mM, L:0.4mM	pot,ise- F^-	[93SAW/MAH]

1) pH not given in the paper

Table A1.2: Equilibrium Constants (β_n) for Formation of Aqueous Sm^{3+} complexes with Cl^- ($Sm^{3+} + nCl^- \rightleftharpoons SmCl_n^{(3-n)+}$)

log β_1	log β_2	Medium	Maximum Metal/H^+/Ligand Concentration	Method	Reference
0.36		H_2O	n.a.	est	[90WOO]
0.30		H_2O	n.a.	est	[92MIL]
0.09[1]		1M LiCl	M:tr, pH=1.5, L:1M	dis	[75MOU/HUS]
0.13		1M LiCl	M:tr, pH=1.5, L:1M	dis	[75MOU/HUS]
0.29[2]		1M LiCl	M:tr, pH=1.5, L:1M	dis	[75MOU/HUS]
-0.02		3M $Li(Cl,ClO_4)$	M:0.4M, H:[3], L:2.5M	sp	[71KOZ/BAT]
-0.39	-0.60	3M $Li(Cl,ClO_4)$	M:tr, H:0.15M, L:3M	dis	[82FUK/KAW]

1)T=323 K
2) T=273 K
3) Limited experimental details given

Table A1.3: Equilibrium Constants (β_n) for Formation of Aqueous Sm^{3+} complexes with NO_3^- ($Sm^{3+} + nNO_3^- \rightleftharpoons SmNO_3^{(3-n)+}$)

log β_1	Medium	Maximum Metal/H^+/Ligand Concentration	Method	Reference
1.2	H_2O	n.a.	est	[78ALL/BEA]
0.78	H_2O	n.a.	est	[92MIL]
1.06[1]	1M $LiNO_3$	M:tr, pH=1.5, L:1M	dis	[75MOU/HUS]
1.25	1M $LiNO_3$	M:tr, pH=1.5, L:1M	dis	[75MOU/HUS]
1.50[2]	1M $LiNO_3$	M:tr, pH=1.5, L:1M	dis	[75MOU/HUS]

1) T=323 K
2) T=273 K

Table A1.4: Equilibrium Constants (β_{mn})[1] for Formation of Aqueous Sm^{3+} complexes with OH^- ($mSm^{3+} + nH_2O \rightleftharpoons Sm_mOH_n^{(3m-n)+} + nH^+$)

log β_1	log β_2	log β_3	log β_4	Other log β_{mn}	Medium	Maximum Metal/H^+/Ligand Concentration	Method	Reference
-7.9					H_2O	n.a.	est	[81BAE/MES]
-7.9					H_2O	n.a.	est	[90WOO]
-8.19					H_2O	n.a.	est	[92MIL]
-4.4					0.1M (H,Li)ClO_4	M:tr, pH=3	dis	[71GUI/DES]
-7.2	-21.7	-24.9			0.1M $NaClO_4$	M:1mM, pH=5	sol	[95SHI/SHI]
-8.84	-15.73				1M $NaClO_4$	n.a.[2]	gl	[82NAI/CHA]
-7.5	-15.0	-22.7		log $\beta_{(4,3)}$=-19.5	1M $NaClO_4$	M:0.1M, pH=7	sol	[79KRA/CHA]
			-36.7		1M $NaClO_4$	M:0.1M, pH=7	sol	[83KRA/CHA]

1) If m = 1, β_{mn} is written β_n
2) Limited experimental details given

Table A1.5: Equilibrium Constants (β_n) for Formation of Aqueous Sm^{3+} complexes with CO_3^{2-} (Sm^{3+} + nCO3^{2-} $\rightleftharpoons$ $Sm(CO_3)_n^{(3-2n)+}$)

log β_1	log β_2	Medium	Maximum Metal/H$^+$/Ligand Concentration	Method	Reference
7.3	12.11	H_2O	n.a.	est	[92MIL]
8.6	13.4	0.1M $NaClO_4$	M:tr, pH=5, L:1mM	sol	[95SHI/MAK]

Table A1.6: Equilibrium Constants (β_n) for Formation of Aqueous Sm^{3+} complexes with HCO_3^- (mSm^{3+} + nHCO_3^- $\rightleftharpoons$ $Sm_m(HCO_3)_n^{(3m-n)+}$)

log β_1	Medium	Maximum Metal/H$^+$/Ligand Concentration	Method	Reference
1.75	H_2O	n.a.	est	[92MIL]

Table A1.7: Equilibrium Constants (β_n) for Formation of Aqueous Sm^{3+} complexes with HPO_4^{2-} ($mSm^{3+} + nHPO_4^{2-} \rightleftharpoons Sm_m(HPO_4)_n^{(3m-2n)+}$)

log β_1	log β_2	Medium	Maximum Metal/H^+/Ligand Concentration	Method	Reference
5.35	8.96	H_2O	n.a.	est	[92MIL]

Table A1.8: Equilibrium Constants (β_n) for Formation of Aqueous Sm^{3+} complexes with $H_2PO_4^-$ ($mSm^{3+} + nH_2PO_4^- \rightleftharpoons Sm_m(H_2PO_4)_n^{(3m-n)+}$)

log β_1	Medium	Maximum Metal/H^+/Ligand Concentration	Method	Reference
2.23	H_2O	n.a.	est	[92MIL]

Table A1.9: Equilibrium Constants (β_n) for Formation of Aqueous Sm^{3+} complexes with SO_4^{2-} ($Sm^{3+} + nSO4^{2-} \rightleftharpoons Sm(SO_4)_n^{(3-2n)+}$)

log β_1	log β_2	Medium	Maximum Metal/H^+/Ligand Concentration	Method	Reference
3.52	5.19	H_2O	n.a.[1]	cal	[69IZA/EAT]
3.67	5.20	H_2O	n.a.	est	[78ALL/BEA]
3.28		H_2O	n.a.	est	[92MIL]
1.30	1.91	2M $NaClO_4$	M:0.1M, pH=3, L:0.7M	pot	[67CAR/CHO]
4.34		var	n.a.[1]	sol	[54SPE/JAF]

1) Limited experimental details given

Table A1.10: Solubility products (K_{sp}) of the different Sm^{3+} solid phases

Reaction	Log K_{sp}	Medium	Concentration (Molarity) of metal, ligand, H	Method	References
$Sm(OH)_3(s) \rightleftharpoons Sm^{3+} + 3OH^-$	-25.2	0	m:4.3e-5, pH:7.1	col	[62KOV/BAG]
	-25.9	0 (0.02-4 M NaCl)[5]	M:0.3, pH:7.8	sol, gl	[60AKS/SPI]
	-25.20	0 (0.1 M LiCl)[5]	M:6E-4, pH:7	pol, gl	[66KOV/AZH]
	-23.7	$SmCl_3$ in H_2O	M:0.01,pH:6.9	pH	[55KOR]
	-22.08	0.1 M $HClO_4$	M:n.a., pH:7.2	gl	[51MOE/FOG]
	-21.2	0.1 M $Sm(NO_3)_3$, $SmCl_3$ or $Sm(C_2H_3O_2)_3$	M:0.1, OH:0.3	gl	[44MOE/KRE]
$Sm(OH)_3(s) + 3H^+ \rightleftharpoons Sm^{3+} + 3H_2O$	16.5	0	n.a.	est	[76BAE/MES]
	22.12	$HClO_4$ + NaOH[1]	M:0.09, pH:n.a.	gl	[59MEL/VRÁ]
	21.3	$HClO_4$ + NaOH[2]	M:0.09, pH:n.a.	gl	[59MEL/VRÁ]
	20.6	$HClO_4$ + NaOH[3]	M:0.09, pH:n.a.	gl	[59MEL/VRÁ]
	19.9	$HClO_4$ + NaOH[4]	M:0.09, pH:n.a.	gl	[59MEL/VRÁ]
$Sm(OH)_2Cl(s) \rightleftharpoons Sm^{3+} + 2OH^- + Cl^-$	-17.3	0 (0.02-4 M NaCl)[5]	M:0.3, pH:7.8	sol, gl	[60AKS/SPI]
$SmOHCO_3 \cdot 0.5H_2O \rightleftharpoons Sm^{3+} + OH^- + CO_3^{2-} + 0.5H_2O$	-21.0	0 (1 M HCl)[5]	M:0.012,L:0.012,H:1	cal	[96MER/FUG]
$Sm_2(CO_3)_3(s) \rightleftharpoons 2Sm^{3+} + 3CO_3^{2-}$	-32.5	0 (0.1 M $NaClO_4$)[5]	M:0.001, pH:8	sol, gl	[66JOR/HAV]
	-34.41	0.01 M $HClO_4$	M:n.a.,L:n.a.,pH:5.7	pot, sp	[86FIR/MOH]

1: T = 283 K
2: T = 293 K
3: T = 303 K
4: T = 313 K
5: Thermodynamic value calculated using data from medium listed in parenthesis

Table A1.11: Binary Interaction Parameters

Cation	Anion	β^0	β^1	β^2	C^ϕ	Reference
Sm^{3+}	Cl^-	0.6	5.6		-0.0204	[91PIT]
Sm^{3+}	ClO_4^-	0.76	6.53		0.0058	[91PIT]
Sm^{3+}	NO_3^-	0.467	5.13		-0.0504	[91PIT]

A2: ACTINIUM(III)

Table A2.1: Equilibrium constants (β_n) for formation of aqueous Ac^{3+} complexes with F^- ($Ac^{3+} + n F^- \rightleftharpoons AcF_n^{(3-n)+}$)

log β_1	log β_2	log β_3	Medium	Maximum Metal/H^+/Ligand Concentration	Method	Reference
3.6	6.6	9.8	0	n.a.	est	[78ALL/BEA]
2.95			0.1M $NaClO_4$	M:tr, H:0.016M, L:0.01M	tp	[73MAK/STE]
2.72	5.22	7.90	0.5M $NaClO_4$	M:tr, pH=3.6, L:4e-3M	dis	[70AZI/LYL]
2.69	5.18	7.78	0.5	n.a.	est	[80BON/HEF]
2.7	5.2	7.9	0.5	n.a.	est	[92FUG/KHO]

Table A2.2: Equilibrium constants (β_n) for formation of aqueous Ac^{3+} complexes with Cl^- ($Ac^{3+} + nCl^- \rightleftharpoons AcCl_n^{(3-n)+}$)

log β_1	log β_2	Medium	Maximum Metal/H^+/Ligand Concentration	Method	Reference
1.1		0	n.a.	est	[78ALL/BEA]
1.3		0	n.a.	est	[92FUG/KHO]
-0.10	-0.82	1M $H(ClO_4,Cl)$	M:tr, H:1M, L:1M	dis	[68SHA/MAT]
-0.1	-0.8	1	n.a.	est	[92FUG/KOH]
0.27		1M $H(ClO_4,Cl)$	M:tr, H:1M, L:0.5M	dis	[91SZE/KUB]
-0.36	-0.51	3M $Li(Cl,ClO_4)$	M:tr, H:0.15M, L:3M	dis	[82FUK/KAW]
-0.05	-1.0	4M $NaClO_4$	M:tr, H:0.01M, L:[1]	dis	[69SEK/SAK]
-0.05	-1	4	n.a.	est	[92FUG/KHO]

1) No or limited experimental details

Table A2.3: Equilibrium constants (β_n) for formation of aqueous Ac^{3+} complexes with NO_3^- ($Ac^{3+} + nNO_3^- \rightleftharpoons AcNO_3^{(3-n)+}$)

log β_1	log β_2	Medium	Maximum Metal/H^+/Ligand Concentration	Method	Reference
0.12	0.01	1M $H(ClO_4,NO_3)$	M:tr, H:1M, L:1M	dis	[68SHA/MAT]
0.57		1M $H(ClO_4,NO_3)$	M:tr, H:1M, L:0.5M	dis	[91SZE/KUB]
0.1		1	n.a.	est	[92FUG/KHO]

Table A2.4: Equilibrium constants (β_n) for formation of aqueous Ac^{3+} complexes with OH^- ($mAc^{3+} + nH_2O \rightleftharpoons Ac_mOH_n^{(3m-n)+} + nH^+$)

log β_1	Medium	Maximum Metal/H^+/Ligand Concentration	Method	Reference
<-10.4	H_2O	n/a	est	[76BAE/MES]

Table A2.5: Equilibrium constants (β_n) for formation of aqueous Ac^{3+} complexes with $H_2PO_4^-$ ($Ac^{3+} + nH_2PO4^- \rightleftharpoons Ac(H_2PO_4)_n^{(3-n)+}$)

log β_1	Medium	Maximum Metal/H^+/Ligand Concentration	Method	Reference
2.5	0	n.a.	est	[92FUG/KHO]
1.59	0.5M NH_4ClO_4	M:tr, pH=2, L:0.14M	dis	[70RAO/SHA]

Table A2.6: Equilibrium constants (β_n) for formation of aqueous Ac^{3+} complexes with SO_4^{2-} ($Ac^{3+} + nSO4^{2-} \rightleftharpoons Ac(SO_4)_n^{(3-2n)+}$)

$\log\beta_1$	$\log \beta_2$	Medium	Maximum Metal/H^+/Ligand Concentration	Method	Reference
3.6	5.5	0	n.a.	est	[78ALL/BEA]
2.47		0.1M NH_4Cl	M:tr, H:[2], L:9e-4	tp	[73STE]
1.75	2.64	0.5M $NaClO_4$	M:tr, pH=3.6, H:0.12M	dis	[70AZI/LYL]
1.36	2.68	1M $NaClO_4$	M:tr, H:1e-3M, L:[1]	dis	[69SEK/SAK]
1.20	1.85	1M $H(ClO_4,HSO_4)$	M:tr, H:1M, L:0.16M	dis	[68SHA/MAT]

1) Limited experimental details given

Table A2.7: Solubility products (K_{sp}) of the different Ac^{3+} solid phases

Reaction	Log K_{sp}	Medium	Maximum Metal/ Ligand/ H Concentration	Method	References
$Ac(OH)_3$(s,freash) ⇌ Ac^{3+} + $3OH^-$	-18.68	0 (0-0.01 M NH_4NO_3)[1]	M:0.32, pH:10.4	sol	[65ZIV/SHE]
$Ac(OH)_3$ (s,aged) ⇌ Ac^{3+} + $3OH^-$	-20.89	0 (0-0.01 M NH_4NO_3)[1]	M:0.32, pH:10.4	sol	[65ZIV/SHE]

1: Thermodynamic value calculated using data from medium listed in parenthesis

A3: NEPTUNIUM(III)

Table A3.1: Equilibrium constants (β_n) for formation of aqueous Np^{3+} complexes with Cl^- ($Np^{3+} + nCl^- \rightleftharpoons NpCl_n^{(3-n)+}$)

log β_1	log β_2	Medium	Maximum Metal/H^+/Ligand Concentration	Method	Reference
-2.39	-2.89	>7M LiCl	M:[1], H:<7M, L<7M	sp	[64SHI/MAR]

1)Limited experimental details given

Table A3.2: Equilibrium Constants (β_{mn})^1 for Formation of Aqueous Np^{3+} complexes with OH^- ($mNp^{3+} + nOH^- \rightleftharpoons Np_mOH_n^{(3m-n)+}$)

log β_1	log β_2	log β_3	log β_4	Other log β_{mn}	Medium	Maximum Metal/H^+/Ligand Concentration	Method	Reference
7	13	19	23	2,2=15	H_2O	n/a	est	[78ALL/BEA]
6.6	11	15	18	2,2=15	H_2O	n/a	est	[80ALL/KIP]

1) If m = 1, $\beta_{1,x}$ is written β_x

Table A3.3: Equilibrium Constants (β_{mn})^1 for Formation of Aqueous Np^{3+} complexes with OH^- ($mNp^{3+} + nH_2O \rightleftharpoons Np_mOH_n^{(3m-n)+} + nH^+$)

log β_1	log β_2	log β_3	log β_4	Other log β_{mn}	Medium	Maximum Metal/H^+/Ligand Concentration	Method	Reference
-7	-15	-25	-35	2,2=-14	H_2O	n/a	est	[86WAN]
-7.43					I=0.3	n/a	est	[80FUG/KHO]
-7.43					n/a	n/a	est	[74MED/KRO]

1) If m = 1, $\beta_{1,x}$ is written β_x

Table A3.4: Equilibrium constants (β_n) for formation of aqueous Np^{3+} complexes with CO_3^{2-} ($mNp^{3+} + nCO3^{2-} \rightleftharpoons Np(CO_3)_n^{(3-2n)+}$)

log β_1	log β_2	log β_3	Medium	Maximum Metal/H^+/Ligand Concentration	Method	Reference
9.6	12.9	16.2	H_2O	n.a.	est	[86WAN]
7.4	12.3		H_2O	n.a.	calc	[88CAN]

Table A3.5: Equilibrium constants (β_n) for formation of aqueous Np^{3+} complexes with $H_2PO_4^-$ ($Np^{3+} + nH_2PO4^- \rightleftharpoons Np(H_2PO_4)_n^{(3-n)+}$)

log β_1	log β_2	log β_3	Medium	Maximum Metal/H^+/Ligand Concentration	Method	Reference
2.40	3.73	5.64	H_2O	n.a.[1]	ix	[69MOS]
2.5			H_2O	n.a.	est	[92FUG/KHO]

1) Limited experimental details given

A4: PLUTONIUM

Table A4.1: Equilibrium constants (β_n) for formation of aqueous Pu^{3+} complexes with F^- ($Pu^{3+} + nF^- \rightleftharpoons PuF_n^{(3-n)+}$)

log β_1	log β_2	log β_3	Medium	Maximum Metal/H^+/Ligand Concentration	Method	Reference
3.3			H_2O	n.a.	est	[83FUG2]
4.3	7.6	10.8	H_2O	n.a.	est	[86WAN]
3.58	6.40	12.61	1M (H,Na)ClO_4	M:4e-3M:, H:6e-2M, L:5e-3M	pot, ise-F^-	[93SAW/MAH]

Table A4.2: Equilibrium constants (β_n) for formation of aqueous Pu^{3+} complexes with Cl^- ($Pu^{3+} + nCl^- \rightleftharpoons PuCl_n^{(3-n)+}$)

log β_1	log β_2	Medium	Maximum Metal/H^+/Ligand Concentration	Method	Reference
1.1		H_2O	n.a.	est	[78ALL/BEA]
-0.1		H_2O	n.a.	est	[82JEN]
1.2		H_2O	n.a.	est	[83FUG2]
-1.9		H_2O	n.a.	est	[85COW/JEN]
0.35		0.2M HCl	M:tr, H:0.2M, L:0.2M	cix	[56WAR/WEL]
0.24		0.5M HCl	M:tr, H:0.5M, L:0.5M	cix	[56WAR/WEL]
0.25		0.5M HCl/$HClO_4$	M:tr, H:0.5M, L:0.5M	cix	[56WAR/WEL]
0.1		I = 0.5 M	n.a.	est	[92FUG/KHO]
-0.15		1 M $HClO_4$	n.a.	est	[53CON/MCV]
-0.04		1M HCl	M:tr, H:1M, L:1M	cix	[56WAR/WEL]
-0.1		I = 1 M	n.a.	est	[76SMI/MAR]
0.5		I = 1 M	n.a.	est	[92FUG/KHO]
-2.4	-5	3-13M LiCl	M:tr, H:0.5M, L:13M	sp	[66SHI/MAR]

Table A4.3: Equilibrium Constants (β_n) for Formation of Aqueous Pu^{3+} complexes with Cl^- ($mPu^{3+} + nHCl \rightleftharpoons Pu_mCl^{(3m-n)+} + nH^+$)

log β_1	Medium	Maximum Metal/H^+/Ligand Concentration	Method	Reference
-2.40	H_2O	n.a.	est	[77RAI/SER]

Table A4.4: Equilibrium constants (β_n) for formation of aqueous Pu^{3+} complexes with NO_3^- ($Pu^{3+} + nNO_3^- \leftrightarrow PuNO_3^{(3-n)+}$)

log β_1	log β_2	log β_3	Medium	Maximum Metal/H^+/Ligand Concentration	Method	Reference
1.41	2.22	2.52	H_2O	n.a.	est	[85COW/JEN]
0.77			1M $HClO_4$	n.a.[1]	dis	[59SHE/TIM]
1.18	0.07	-0.72	8M $HClO_4$	M:tr, H:8M, L:3M	dis	[70LAH/KNO]

1) Limited experimental details given

Table A4.5: Equilibrium Constants (β_{mn})[1] for Formation of Aqueous Pu^{3+} complexes with OH^- ($mPu^{3+} + nOH^- \rightleftharpoons Pu_mOH_n^{(3m-n)+}$)

log β_1	log β_2	log β_3	log β_4	Other log β_{mn}	Medium	Maximum Metal/H^+/Ligand Concentration	Method	Reference
7					H_2O	n/a	est	[76SMI/MAR]
7.2	14	19	24	2,2=16	H_2O	n/a	est	[78ALL/BEA]
7.2	12.1	16.7	20.2	2,2=16	H_2O	n/a	est	[80ALL/KIP]
6.7					H_2O	n/a	est	[82JEN]
6.5	11.5	15.5	19	2,2=14	H_2O	n/a	est	[83ALL]

1) If m = 1, $\beta_{1,x}$ is written β_x

Table A4.6: Equilibrium constants (β_{mn})[1] for formation of aqueous Pu^{3+} complexes with OH^- ($Pu^{3+} + nH_2O \rightleftharpoons PuOH_n^{(3-n)+} + nH^+$)

log β_1	log β_2	log β_3	log β_4	Other log β_{mn}	Medium	Maximum Metal/H^+/Ligand Concentration	Method	Reference
-5.54					H_2O	n.a.[2]	gl	[49KRA/DAM]
-8					H_2O	n.a.	est	[80LEM/TRE]
-7.5	-16.5	-26.5	-37	2,2=-14	H_2O	n.a.	est	[86WAN]
-7.37					I = 0.024 M	n.a.	est	[80FUG/KHO]
-7.22					I = 0.069	n.a.	est	[80FUG/KHO]
-3.8					0.1M (H,Li)ClO_4	M:tr, pH=2.5	dis	[76HUB/HUS]
-3.8					0.2M $LiClO_4$	M:1e-3M, pH=2.5	dis	[75HUB/HUS]
-3.8					I = 0.2 M	n.a.	est	[80FUG/KHO]

1) If m = 1, $\beta_{1,x}$ is written β_x
2) Limited experimental details given

Table A4.7: Equilibrium constants (β_n) for formation of aqueous Pu^{3+} complexes with CO_3^{2-} ($Pu^{3+} + nCO3^{2-} \rightleftharpoons Pu(CO_3)_n^{(3-2n)+}$)

log β_1	log β_2	log β_3	Medium	Maximum Metal/H^+/Ligand Concentration	Method	Reference
9.6	12.9	16.2	H_2O	n.a.	est	[82JEN]
6	10	13	H_2O	n.a.	est	[83ALL]
6	10	13	H_2O	n.a.	est	[86WAN]
7.5	12.4		H_2O	n.a.	calc	[88CAN]

Table A4.8: Equilibrium constants (β_n) for formation of aqueous Pu^{3+} complexes with PO_4^{3-} (Pu^{3+} + nPO4^{3-} $\rightleftharpoons$ $Pu(PO_4)_n^{(3-3n)+}$)

log β_1	Medium	Maximum Metal/H$^+$/Ligand Concentration	Method	Reference
22	H_2O	n.a.[1]	ix	[69MOS]
19.3	1M NH_4Cl	M:0.015M, H:>0.5M, L:0.25M	sol	[71MOS2]

1) Limited experimental details given

Table A4.9: Equilibrium Constants (β_n) for Formation of Aqueous Pu^{3+} complexes with HPO_4^{2-} (mPu^{3+} + nHPO_4^{2-} $\rightleftharpoons$ $Pu_m(HPO_4)_n^{(3m-2n)+}$)

log β_1	Medium	Maximum Metal/H$^+$/Ligand Concentration	Method	Reference
9.7	H_2O	n/a	est	[80LEM/TRE]

Table A4.10: Equilibrium constants (β_n) for formation of aqueous Pu^{3+} complexes with $H_2PO_4^-$ (Pu^{3+} + nH_2PO4$^-$ $\rightleftharpoons$ $Pu(H_2PO_4)_n^{(3-n)+}$)

log β_1	log β_2	log β_3	log β_4	Medium	Maximum Metal/H$^+$/Ligand Concentration	Method	Reference
2.39	3.7	5.63	6.2	H_2O	n.a.[1]	ix	[69MOS]
1.48	2.2	2.9	3.5	1M NH_4Cl	M:0.015M, H:>0.5M, L:0.25M	sol	[71MOS2]

1) Limited experimental details given

Table A4.11: Equilibrium Constants (β_n) for Formation of Aqueous Pu^{3+} complexes with PO_4^{3-} (Pu^{3+} +nPO_4^{3-} +2nH^+ $\rightleftharpoons$ $Pu(H_2PO_4)_n^{(3-n)+}$)

log β_1	log β_2	Medium	Maximum Metal/H$^+$/Ligand Concentration	Method	Reference
21.64	42.31	H_2O	n/a	est	[85COW/JEN]
22		H_2O	n/a	est	[86WAN]

Table A4.12: Equilibrium Constants (β_n) for Formation of Aqueous Pu^{3+} complexes with PO_4^{3-} (Pu^{3+} +nPO_4^{3-} +nH^+ $\rightleftharpoons$ $Pu(HPO_4)_n^{(3-2n)+}$)

log β_1	Medium	Maximum Metal/H$^+$/Ligand Concentration	Method	Reference
18.3	H_2O	n/a	est	[86WAN]

Table A4.13: Equilibrium Constants (β_n) for Formation of Aqueous Pu^{3+} complexes with SO_4^{2-} (Pu^{3+} + $nSO4^{2-}$ ⇌ $Pu(SO_4)_n^{(3-2n)+}$)

log β_1	log β_2	Medium	Maximum Metal/H^+/Ligand Concentration	Method	Reference
3.7		H_2O	n.a.	est	[78ALL/BEA]
3.5		H_2O	n.a.	est	[80LEM/TRE]0
1.26			n.a.	est	[76SMI/MAR]
1.26			n.a.	est	[82JEN]
3.61	5.47	H_2O	n.a.	est	[82COW/JEN]
3.5	5.2	H_2O	n.a.	est	[86WAN]
4.5	6.7	H_2O	n.a.	est	[92FUG/KHO]
1.26		1M $HClO_4$	M:tr, H:1M, L:0.17M	cix	[67NAI/RAO]
1.99	3.04	1M $HClO_4$	M:tr, H:1M, L:0.7M	dis	[78RAO/BAG1]
1.90	3.18	1M $HClO_4$	M:tr, H:1M, L:0.17M	cix	[67NAI/RAO]
1.73	3.39	1M $HClO_4$	M:tr, H:1M, L:0.9M	cix	[76FAR/BUC]
1.73	3.39	I = 1 M	n.a.	est	[76SMI/MAR]
1.26		I = 1 M	n.a.	est	[79CLE]
1.65	3.29	2M $HClO_4$	M:tr,H:2M, L:0.9M	cix	[76FAR/BUC]
1.89	2.90	2M $HClO_4$	M:tr, H:2M, L:0.7M	dis	[78RAO/BAG1]
1	1.18	2M (Na,H)Cl	M:5e-3M, H:0.3M, L:0.4M	est	[56NEW/BAK]

Table A4.14: Equilibrium Constants (β_n) for Formation of Aqueous Pu^{3+} complexes with SO_4^{2-} ($Pu^{3+} + nHSO4^- \rightleftharpoons Pu(SO_4)_n^{(3-2n)+} + nH^+$)

log β_1	log β_2	Medium	Maximum Metal/H^+/Ligand Concentration	Method	Reference
0.34		I = 2 M	n.a.	est	[83NAS/CLE]

Table A4.15: Solubility products (K_{sp}) of the different Pu^{3+} solid phases

Reaction	Log K_{sp}	Medium	Maximum Metal/ H^+/ Ligand Concentration	Method	References
$PuF3 \rightleftharpoons Pu + 3F$	-15.6	0.06-2.4 M HNO_3	M:0.02, L:7.94, H:2.4	sol	[61MAN/FRA]
$Pu(OH)_3(c) \rightleftharpoons Pu^{3+} + 3OH^-$	-26.2	H_2O	M:0.001, pH:13	sol	[89FEL/RAI]
	-19.7	H_2O	n.a.	est	[76BAE/MES]
$Pu(OH)_{2.5}Cl_{0.5}(s) \rightleftharpoons Pu^{3+} + 2.5OH^- + 0.5Cl^-$	-20.0	0.0073 M $PuCl_3$ + NaOH	M:7E-3, L:0.02, OH:0.025	pot, gl	[50BUS/COW]
$PuPO_4 \cdot xH_2O \rightleftharpoons Pu^{3+} + PO_4^{3-} + xH_2O$	-24.4	0.5 M NH_4ClO_4	M:0.015,L:n.a.,pH:8.9	sol	[71MOS2]

A5: AMERICIUM (For the Americium data, tracer amounts (<1mM) of the metal concentration are assumed unless other notification)

Table A5.1: Equilibrium constants (β_n) for formation of aqueous Am^{3+} complexes with F^- ($Am^{3+} + nF^- \rightleftharpoons AmF_n^{(3-n)+}$)

log β_1	log β_2	log β_3	log β_4	Medium	Maximum Metal/H^+/Ligand Concentration	Method	Reference
3.39	6.11	9		H_2O	n.a.	est	[76SMI/MAR]
4.3	7.5	10.8	14	H_2O	n.a.	est	[78ALL/BEA]
3.39	6.11	9		H_2O	n.a.	est	[82JEN]
4.3	7.4	10.6		H_2O	n.a.	est	[82PHI]
3.4	5.8			H_2O	n.a.	est	[85SIL/BID]
4.3	7.6	10.8		H_2O	n.a.	est	[86WAN]
3.24				H_2O	n.a.	est	[88PHI/HAL]
3.4	5.8			H_2O	n.a.	est	[82JEN]
3.32				0.1M $NaClO_4$	L:0.65mM	emf	[73MAK/STE]
2.59	4.76			0.1M $NaClO_4$	L:0.01M	cix	[84NAS/CLE2]
3.39	6.11			0.5M $NaClO_4$	L:4mM	dis	[69AZI/LYL]
2.39				1M $NaClO_4$		dis	[69JON/CHO]
2.93				1M $NaClO_4$		dis	[75DEG/CHO]
2.39[1]				1M $NaClO_4$		dis	[76CHO/UNR]
2.49				1M $NaClO_4$		dis	[76CHO/UNR]
2.57[2]				1M $NaClO_4$		dis	[76CHO/UNR]
2.71[3]				1M $NaClO_4$		dis	[76CHO/UNR]

1) T=283 K
2) T=313 K
3) T=328 K

Table A5.2: Equilibrium constants (β_n) for formation of aqueous Am^{3+} complexes with Cl^- ($Am^{3+} + nCl^- \rightleftharpoons AmCl_n^{(3-n)+}$)

log β_1	log β_2	Medium	Maximum Metal/H^+/Ligand Concentration	Method	Reference
0.013		H_2O	M:1.4E-3,H:12.6,L:10.75	sp	[69BAR/MIK]
1	0.5	H_2O	n.a.	est	[78ALL/BEA]
-0.1		H_2O	n.a.	est	[82JEN]
1.3	1.4	H_2O	n.a.	est	[92FUG/KHO]
1.05		H_2O	n.a.	est	[95SIL/BID]
0.5		I = 0.1	n.a.	est	[92FUG/KHO]
0.35		0.21M HCl	H:0.21M, L:0.21M	cix	[56WAR/WEL]
0.24		0.5M HCl	H:0.5M, L:0.5M	cix	[56WAR/WEL]
0.1		I = 0.5	n.a.	est	[92FUG/KHO]
-0.05		1M $H(ClO_4,Cl)$	H:1M,L:1M	dis	[62PEP/MAS]
-0.05		1M $H(ClO_4,Cl)$	H:1M,L:1M	cix	[64BAN/PAT]
0.15		1M $Na(ClO_4,Cl)$	L:1M	cix	[64BAN/PAT]
-0.6		1M $Na(ClO_4/Cl)$		dis	[64KHO/SHA]
-0.14	-0.52	1M $H(ClO_4,Cl)$	H:1M,L:1M	dis	[71KHO/NAR]
-0.25		1M $Li(ClO_4,Cl)$	L:1M	dis	[71KHO/NAR]
0.02	-0.37	1M $Na(ClO_4,Cl)$	L:1M	dis	[71KHO/NAR]
0.12	0.03	1M $NH_4(ClO_4,Cl)$	L:1M	dis	[71KHO/NAR]
	-0.09	1M $NH_4(ClO_4,Cl)$	L:1M	dis	[80KHO/MAT]
-0.1	-0.5	I = 1 M	n.a.	est	[92FUG/KHO]
	-0.66	3M (Li,H) (ClO_4,Cl)		dis	[82FUK/KAW]

Table A5.2: Equilibrium constants (β_n) for formation of aqueous Am^{3+} complexes with Cl^- continued

log β_1	log β_2	Medium	Maximum Metal/H^+/Ligand Concentration	Method	Reference
-0.16	-0.74	4M $H(ClO_4,Cl)$	H:4M,L:3.5M	cix	[62GRE]
-0.15	-0.69	4M $Na(ClO_4,Cl)$	L:3.3M	dis	[64SEK]
-0.15	-0.7	I = 4 M	n.a.	est	[92FUG/KHO]
0.03	-0.97	var. LiCl	L:4M	nmr	[66VDO/KOL]
1	0.34	var LiCl		tp	[69MAR2]
-2.21	-4.7	var LiCl	L:13.7M	sp	[69MAR/SHI]
-0.26	-0.05	var LiCl	L:4M	cppt	[69VDO/STE]

Table A5.3: Equilibrium constants (β_n) for formation of aqueous Am^{3+} complexes with NO_3^- ($Am^{3+} + nNO_3^- \rightleftharpoons AmNO_3^{(3-n)+}$)

log β_1	log β_2	log β_3	Medium	Maximum Metal/H^+/Ligand Concentration	Method	Reference
-1	0.5		H_2O	n.a.	est	[78ALL/BEA]
1.5			H_2O	n.a.	est	[92FUG/KHO]
1.33			H_2O	n.a.	est	[95SIL/BID]
0.15	-0.4		1M $H(ClO_4,NO_3)$	H:1M,L:1M	cix	[64BAN/PAT]
0.2			1M $H(ClO_4,NO_3)$	H:1M,L:1M	cix	[64BAN/PAT]
0.6			1M NH_4X	L:1M	cix	[60LEB/PIR]
0.26			1M $H(ClO_4, NO_3)$	H:1M,L:1M	dis	[62PEP/MAS]
0.25			1M $H(ClO_4,NO_3)$	H:1M,L:1M	dis	[65CHO/STR]
0.29			1M $H(ClO_4,NO_3)$	H:1M,L:1M	dis	[71KHO/NAR]
0.30			1M $Li(ClO_4,NO_3)$	L:1M	dis	[71KHO/NAR]
0.26			1M $Na(ClO_4,NO_3)$	L:1M	dis	[71KHO/NAR]
0.23	1.34		1MNH_4 (ClO_4,NO_3)	L:1M	dis	[71KHO/NAR]
0.25			I = 1 M	n.a.	est	[92FUG/KHO]
0.2			2M$NH_4(SCN,NO_3)$	L:2M	dis	[73CHI/DAN]
-0.33	-0.77	-1.4	8M $H(ClO_4,NO_3)$	H:8M,L:8M	dis	[70LAH/KNO]
-1.3			1-15M $H(ClO_4,NO_3)$	H:15M,L:15M	sp	[69SHI/GIV]
-1.3			var $(H,Li)NO_3$		sp	[66GIV]

Table A5.4: Equilibrium constants (β_n) for formation of aqueous Am^{3+} complexes with OH^- ($Am^{3+} + nOH^- \rightleftharpoons AmOH_n^{(3-n)+}$)

log β_1	log β_2	log β_3	Medium	Maximum Metal/H^+/Ligand Concentration	Method	Reference
8.2	15	21	H_2O	n.a.	est	[78ALL/BEA]
7.9			H_2O	n.a.	est	[82JEN]
6.5			H_2O	n.a.	est	[83ALL]
11.3			0.005M $(H,K)ClO_4$		tp	[69MAR/KIK]
10.7	20.09		0.005M NH_4ClO_4	M:0.01M,pH5	tp	[72SHA/STE]
5.85	12.79	16.63	0.1M $NaClO_4$	M:1E-5,pH:10	sol	[84BER/KIM]
6.44	13.8	17.86	0.1M $NaClO_4$	M:1E-5,pH:10	sp	[84BER/KIM]
6.3	12.2	14.4	0.1M $NaClO_4$	M:5Ci/L,pH13	sol	[88STA/KIM]
5.6	11.6	14.1	0.1M $NaClO_4$	M:5Ci/L,pH13	sol	[88STA/KIM]
7.6	14.6	21.7	3M $NaClO_4$	M:0.15M,pH10	sol	[89PAZ]

Table A5.5: Equilibrium constants (β_n) for formation of aqueous Am^{3+} complexes with OH^- ($Am^{3+} + nH_2O \rightleftharpoons AmOH_n^{(3-n)+} + nH^+$)

log β_1	log β_2	log β_3	Medium	Maximum Metal/H^+/Ligand Concentration	Method	Reference
-8.2	-17.1	-27	H_2O	M:1mM,pH11	sol	[83RAI/STR]
-7.5	-16.5	-26.5	H_2O	n.a.	est	[86WAN]
-8	-16.9	-29	H_2O	n.a.	est	[92EWA/SMI]
-6.4	-14.1	-25.7	H_2O	n.a.	est	[95SIL/BID]
-3.3			H_2O	n.a.	est	[80FUG/KHO]
-5.3			0.1M (H;Li)ClO_4	pH:6	dis	[73HUS/HUB]
-2.5	-6.6		0.1M $LiNO_3$		chr, tp	[73KOR2]
-5.3			0.1M (H;Li)ClO_4	pH:6	dis	[76HUB/HUS]
-5.3			I = 0.1 M	n.a.	est	[80FUG/KHO]
-7.7			0.1M $NaClO_4$		sol	[87SIL]
	-16.7		0.1M $NaClO_4$		sol	[84SIL]
-6.9		-23.8	0.1M $XClO_4$		tp	[89ROS/REI]
	-14.76		0.2M $NaClO_4$		dis	[82BID]
-7.5			1M $NaClO_4$	pH:9	dis	[82LUN]
-7.03			1M $NaClO_4$		pot	[82NAI/CHA]
-7.78			1M $NaClO_4$	pcH:7.8	dis	[96CHO/CHE]
-7.83			3M $NaClO_4$	pcH:7.8	dis	[96CHO/CHE]
-8			5M $NaClO_4$	pcH:8.3	dis	[96CHO/CHE]

Table A5.6: Equilibrium constants (β_n) for formation of aqueous Am^{3+} complexes with CO_3^{2-} ($Am^{3+} + nCO3^{2-} \rightleftharpoons Am(CO_3)_n^{(3-2n)+}$)

log β_1	log β_2	log β_3	log β_4	Medium	Maximum Metal/H^+/Ligand Concentration	Method	Reference
			11	H_2O	n.a.	est	[78ALL/BEA]
6	10	13		H_2O	n.a.	est	[83ALL]
7.7	12.8			H_2O	n.a.	calc	[88CAN]
8.3				H_2O	n.a.	est	[92FUG/KHO]
6.4	14	13.38		H_2O	n.a.	est	[92EWA/SMI]
7.8	12.3	15.2		H_2O	n.a.	est	[95SIL/BID]
8.16				H_2O	M:0.14mM,L:1.4x10^{-6}M, pH4.4-6.4	sp	[89NIT/STA]
7.6	15.2	15.2		H_2O	L:0.1M	sol	[90FEL/RAI]
6.69				0.1M $NaClO_4$	M:0.14mM,L:1.4x10^{-6}M, pH4.4-6.4	sp	[89NIT/STA]
6.9				I = 0.1 M	n.a.	est	[92FUG/KHO]
7.7	12.8	12.8		0.1M NaCl		sol	[93GIF/VIT]
5.08	9.27	12.12		0.1-0.3M $NaClO_4$	M:0.01mM,L:0.06M,pH6-10	sol	[84BER/KIM]
5.97	9.58			0.1-0.3M $NaClO_4$	M:0.1mM,L:0.05M,pH6-9	sol	[91MEI/KIM]
6.48	9.94			0.1-0.3M $NaClO_4$	M0.06mM,0.03atm CO_2 at pH9.7	sp	[91MEI/KIM]
	11.45			0.2M $NaClO_4$		dis	[82BID]
5.7	9.4			I = 1 M	n.a.	est	[82ALL]
5.81	9.72			1M $NaClO_4$	1atm CO_2 at pH5-7	dis	[82LUN]
5.3	8.5			1M $NaClO_4$	L:1M,pH7.8	tp	[82LUN]
5.7				I = 1 M	n.a.	est	[92FUG/KHO]

Table A5.6: Equilibrium constants (β_n) for formation of aqueous Am^{3+} complexes with CO_3^{2-} continued

log β_1	log β_2	log β_3	log β_4	Medium	Maximum Metal/H^+/Ligand Concentration	Method	Reference
5.45	8.92	11.44		3M NaCl		sol	[89ROB]
5.3	11.4	11.4		4M NaCl		sol	[93GIF/VIT]

Table A5.7: Equilibrium constants (β_n) for formation of aqueous Am^{3+} complexes with HCO_3^- ($Am^{3+} + nHCO3^- \rightleftharpoons Am(HCO_3)_n^{(3-n)+}$)

log β_1	log β_2	Medium	Maximum Metal/H$^+$/Ligand Concentration	Method	Reference
4.79	8.15	0.2M $NaClO_4$		dis	[82BID]
1.91		0.5M $NaClO_4$	L:0.025M,pH7	dis	[88RAO/MAD]
2		0.5M $NaClO_4$	L:0.30M,pH7	dis	[88RAO/MAD]
2.13	3.83^1	0.5M $NaClO_4$	L:0.05M,pH7	dis	[88RAO/MAD]

1) T=308 K

Table A5.8: Equilibrium constants (β_n) for formation of aqueous Am^{3+} complexes with HPO_4^{2-} ($Am^{3+} + nHPO4^{2-} \rightleftharpoons Am(HPO_4)_n^{(3-2n)+}$)

log β_1	Medium	Maximum Metal/H^+/Ligand Concentration	Method	Reference
4.14	H_2O		dis	[86RAO/MAH]
3.63	0.5M $NaClO_4$	L:0.025M,pH7	dis	[88RAO/MAH]
3.76	0.5M $NaClO_4$	L:0.025M,pH7	dis	[88RAO/MAH]
3.92	0.5M $NaClO_4$	L:0.025M,pH7	dis	[86RAO/MAH]

Table A5.9: Equilibrium constants (β_n) for formation of aqueous Am^{3+} complexes with $H_2PO_4^-$ ($Am^{3+} + nH_2PO4^- \rightleftharpoons Am(H_2PO_4)_n^{(3-n)+}$)

log β_1	log β_2	log β_3	log β_4	Medium	Maximum Metal/H^+/Ligand Concentration	Method	Reference
2.5				H_2O	n.a.	est	[78ALL/BEA]
2.39	3.63	5.62	6.3	H_2O		cix	[69MOS]
2.5				H_2O	n.a.	est	[92FUG/KHO]
3				H_2O	n.a.	est	[95SIL/BID]
2.13				H_2O	n/a	dis	[86RAO/MAH]
1.97				0.5M $(Na,NH_4)ClO_4$	L:0.15M,pH2	dis	[86RAO/MAH]
1.64				0.5M $(Na,NH_4)ClO_4$	L:0.15M,pH2	dis	[88RAO/MAH]
1.69				0.5M $(Na,NH_4)ClO_4$	L:0.15M,pH2	dis	[88RAO/MAH]
2.36[1]				0.5M $(Na,NH_4)ClO_4$	L:0.15M,pH2	dis	[88RAO/MAH]
1.69				0.5M NH_4ClO_4	L:0.1M,pH2	cix	[66BOR/ELE]
1.48	2.1	2.85	3.4	1M NH_4Cl	L:0.72M,pH1.8	cix	[71MOS2]
2.73	3.72			1-13M H_3PO_4	M:8mM,H:1M,L:13M	sp	[79LEB/FRE2]

1) T=314

Table A5.10: Equilibrium Constants (β_n) for Formation of Aqueous Am^{3+} complexes with PO_4^{3-} ($Am^{3+} + nPO4^- + nH^+ \rightleftharpoons Am(HPO_4)_n^{(3-2n)+}$)

log β_1	Medium	Maximum Metal/H^+/Ligand Concentration	Method	Reference
18.4	H_2O	n/a	est	[86WAN]

Table A5.11: Equilibrium constants (β_n) for formation of aqueous Am^{3+} complexes with SO_4^{2-} ($Am^{3+} + nSO4^{2-} \rightleftharpoons Am(SO_4)_n^{(3-2n)+}$)

log β_1	log β_2	log β_3	Medium	Maximum Metal/H^+/Ligand Concentration	Method	Reference
3.76	5.64	5.29	H_2O	H:0.5mM,L:0.5M	sol	[72MCD/COL]
3.6	5.6		H_2O	n.a.	est	[78ALL/BEA]
1.57	2.66		H_2O	n.a.	est	[82JEN]
3.5	5.2		H_2O	n.a.	est	[86WAN]
4.2	6.1		H_2O	n.a.	est	[92FUG/KHO]
3.85	5.4		H_2O	n.a.	est	[95SIL/BID]
2.5	3.1		0.1M Na (ClO_4,HSO_4)	n.a.	tp	[90ROS/REI]
2.45[2]			0.1M NH_4Cl	H:n.a.,L:0.04M	tp	[73STE]
2.41			0.1M NH_4Cl	H:n.a.,L:0.02M	tp	[73STE]
2.48[3]			0.1M NH_4Cl	H:n.a.,L:0.024M	tp	[73STE]
1.86	2.79		0.5M Na(ClO_4,SO_4)	L:0.1M,pH3.6	cix	[68AZI/LYL]
1.85	2.83		0.5M Na(ClO_4,SO_4)	L:0.1M,pH3.6	dis	[68AZI/LYL]
1.86	2.82		I = 0.5 M	n.a.	est	[76SMI/MAR]
1.78			0.75M NH_4 (Cl,SO_4)	L:0.25M,pH3.5-4	cix	[60LEB/PIR]
1.2	1.4		1M H(ClO_4,HSO_4)	H:1M,L:0.14M	cix	[64BAN/PAT]
1.49	2.5		1M Na (ClO_4,SO_4)	L:0.23M,pH3	cix	[64BAN/PAT]
1.57	2.66		1M Na (ClO_4,SO_4)	L:0.50M,pH3-4	dis	[64SEK], [65SEK2]
1.22			1M H(ClO_4,HSO_4)	H:1M,L:1M	cix	[67NAI], [68NAI]
1.49	2.36		1M Na (ClO_4,SO_4)	n.a.	cix	[67NAI], [68NAI]

Table A5.11: Equilibrium constants (β_n) for formation of aqueous Am^{3+} complexes with SO_4^{2-} continued

log β_1	log β_2	log β_3	Medium	Maximum Metal/H^+/Ligand Concentration	Method	Reference
1.82	3.12		1M $H(ClO_4,HSO_4)$	H:1M,L:0.7M	dis	[78RAO/BAG]
1.72			1M NH_4 (ClO_4,SO_4)	L:0.05M,pH3	dis	[80KHO/MAT]
1.76	2.11		1.5M NH_4 (Cl,SO_4)	L:0.51M,pH3.5-4	cix	[60LEB/PIR]
1.43	1.85		2M Na (ClO_4,SO_4)	L:0.1M,pH3	dis	[67CAR/CHO]
1.11[1]	1.73[1]		2M Na (ClO_4,SO_4)	L:0.1M,pH3	dis	[67CAR/CHO2]
1.58[4]	2.03[4]		2M Na (ClO_4,SO_4)	L:0.1M,pH3	dis	[67CAR/CHO2]
2.033	1.56	2.5	2M Na (ClO_4,SO_4)	L:0.44M,pH3.1	pot	[67CAR/CHO2]
1.65[5]	2.38[5]		2M Na (ClO_4,SO_4)	L:0.1M,pH3	dis	[67CAR/CHO2]
1.71			2M $H(ClO_4,HSO_4)$	H:2M,L:0.7M	dis	[78RAO/BAG]

1) T=273 K
2) T=288 K
3) T=308 K
4) T=313 K
5) T=328 K

Table A5.12: Equilibrium constants (β_n) for formation of aqueous Am^{3+} complexes with HSO_4^- ($Am^{3+} + nHSO4^- \rightleftharpoons Am(HSO_4)_n^{(3-n)+}$)

log β_1	Medium	Maximum Metal/H^+/Ligand Concentration	Method	Reference
0.54	1M $H(ClO_4,HSO_4)$	n.a.	cix	[67NAI,68NAI]

Table A5.13: Solubility products (K_{sp}) of the different Am^{3+} solid phases

Reaction	Log K_{sp}	Medium	Maximum Metal/H^+/Ligand Concentration (M)	Method	References
$AmF_3(s) \rightleftharpoons AmF_3(aq)$	-5.09	0.1 M $HClO_4$[1]	n.a.[3]	sol	[54FEA]
	-4.87	0.1 M $HClO_4$	n.a.[3]	sol	[54FEA]
	-4.68	0.1 M $HClO_4$[2]	n.a.[3]	sol	[54FEA]
$AmF_3(s) \rightleftharpoons Am^{3+} + 3F^-$	-13.9	0	n.a.	est	[88PHI/HAL]
$Am(OH)_3(am) + 3H^+ \rightleftharpoons Am^{3+} + 3H_2O$	17.00	0	n.a.	est	[95SIL/BID]
	17.5	0.1 M $NaClO_4$	M:1E-6, pH:10	sol	[83EDE/BUC]
$Am(OH)_3(c) + 3H^+ \rightleftharpoons Am^{3+} + 3H_2O$	15.2	0	n.a.	est	[95SIL/BID]
$Am(OH)_3(s) + 3H^+ \rightleftharpoons Am^{3+} + 3H_2O$	15.9	0 (0.1 M $NaClO_4$)[4]	M:1.6e-5, pH:9.4	sol	[87SIL]
	16.6[5]	0 (0.1 M $NaClO_4$)[4]	M:1.6e-5, pH:9.4	recal	[95SIL/BID][5]
	16.5	0.1 M $NaClO_4$	M:n.a.,pH:9.5	sol	[84SIL]
	17.5	0 (0.0015 $CaCl_2$)[4]	M:1E-3, pH:10	sol	[83RAI/STR]
$Am(OH)_3(s) \rightleftharpoons Am^{3+} + 3OH^-$	-18.7	0	n.a.	est	[76BAE/MES]
	-28.56	0 (0.1 M $NaClO_4$)[3]	M:0.002, pH:13.5	sol	[84KIM/BER]
	-25.7	0.1 M $NaClO_4$	M:0.004, pH:13	sol	[88STA/KIM]
	-27.35	0.002 M $AmCl_3$	M:0.002, pH:7	sol, est	[90PER/SAP]
	-28.89	0.1 M $NaClO_4$	M:2E-5, pH:13	sol	[84BER/KIM]
	-27.16	0.1 M $NaClO_4$	M:0.002, pH:13.5	sol	[84KIM/BER]
	-27.4	3 NH_4ClO_4	M:0.02, pH:9.8	sol	[89PAZ/KOC]
$AmOHCO_3(s) + 2H^+ \rightleftharpoons Am^{3+} + HCO_3^- + H_2O$	2.53	0 (0.1 M $NaClO_4$)[3]	M:3E-6.,L:8E-3 atm,pH:6.1	sol	[85SIL]
	2.77	0.1 M $NaClO_4$	M:3E-6.,L:8E-3 atm,pH:6.1	sol	[85SIL]

Table A5.13: Solubility products (K_{sp}) of the different Am^{3+} solid phases continued

Reaction	Log K_{sp}	Medium	Maximum Metal/ H^+/ Ligand Concentration (M)	Method	References
$AmOHCO_3(s) + 2H^+ \rightleftharpoons Am^{3+} + HCO_3^- + H_2O$	2.74	0.1 M $NaClO_4$	M:n.a.,L:2E-4,pH:6.1	sol	[84SIL] [84SIL/NIT]
$AmOHCO_3(s) \rightleftharpoons Am^{3+} + OH^- + CO_3^{2-}$	-21.20	0	n.a.	est	[95SIL/BID]
	-23.1	0 (1 M HCl)[3]	M:2.4E-3,L:2.4E-3,H:1	cal	[96MER/FUG]
	-22.5	0 (0-0.1 M $NaCO_3$)[3]	M:1E-4,L:0.1,pH:13.0	sol	[90FEL/RAI]
	-18.70	0.1 M $NaClO_4$	M:n.a.,L:1E-7,pH:7	sol	[92RUN/MEI]
	-21.03	0.1 - 0.3 M $NaClO_4$	M:2E-5,L:0.1,pH:13	sol	[84BER/KIM]
$Am_2(CO_3)_3(s) \rightleftharpoons 2Am^{3+} + 3CO_3^-$	-33.40	0	n.a.	est	[95SIL/BID]
	-35.06	0	n.a.	est	[93GIF/VIT]
	-29.89	0.1 M $NaClO_4$	M:1E-4,L:0.05,pH:9.7	sol	[91MEI/KIM]
	-29.45	0.1 M $NaClO_4$	M:n.a.,L:1E-7,pH:7	sol	[92RUN/MEI]
	-34.2	0.1 M NaCl	M:1E-4,L:0.1,pC_H:9.5	sol	[93GIF/VIT]
	-30.16	3.0 M $NaClO_4$	M:1E-4,L:1.0,pH:10.5	sol	[89ROB][6]
	-30.4	4 M NaCl	M:1E-4,L:0.1,pC_H:9.5	sol	[93GIF/VIT]
$NaAm(CO_3)_2(s) \rightleftharpoons Na^+ + Am^{3+} + 2CO_3^{2-}$	-17.38	0	n.a.	sol	[86AVO/BIL][6]
	-18.32	0.1 M	n.a.	sol	[85KIM][6]
	-17.4	5 M NaCl	M:5E-3,L:0.02,pH:8.3	sol	[95RUN/KIM]
$AmPO_4(am) \rightleftharpoons Am^{3+} + PO_4^{3-}$	-24.79	0	n.a.	est	[95SIL/BID]
	-24.79	0	M:1E-3, L:1E-3, pC_H:10	sol	[92RAI/FEL]

1: T = 283 K
2: T = 320 K

3: Information obtained from [64SIL/MAR] or [71SIL/MAR]
4: Thermodynamic value calculated using data from medium listed in parenthesis
5: Recalculation of data from [87SIL]
6: Information obtained from [95SIL/BID]

Table A5.14: Binary Interaction Parameters

Cation	Anion	β^0	β^1	β^2	C^ϕ	Reference
Am^{3+}	SO_4^{2-}	3.0398	0	-2500	0	[95RAI/FEL]
Am^{3+}	ClO_4^-	0.80	5.35	0	-0.0048	[90FEL/RAI]
		0.754	6.53	0	0.0075	[95RAI/FEL]
Na^+	$Am(CO_3)_3^{3-}$	0.24	8.1	0	0	[90FEL/RAI]

Table A6.1: Equilibrium Constants (β_n) for Formation of Aqueous Cm^{3+} complexes with F^- ($mCm^{3+} + nF^- \rightleftharpoons Cm_mF_n^{(3m-n)+}$)

log β_1	log β_2	log β_3	Medium	Maximum Metal/H^+/Ligand Concentration	Method	Reference
4.3	7.6	10.9	H_2O	n.a.	est	[78ALL/BEA]
3.34	6.18	9.1	H_2O	n.a.	est	[82JEN]
3.34	6.17	9.07	0.5M $NaClO_4$	n.a.	est	[80BON/HEF]
	6.2	9.1	I=0.5	n.a.	est	[92FUG/KHO]

Table A6.2: Equilibrium constants (β_n) for formation of aqueous Cm^{3+} complexes with Cl^- ($Cm^{3+} + nCl^- \rightleftharpoons CmCl_n^{(3-n)+}$)

log β_1	log β_2	Medium	Maximum Metal/H$^+$/Ligand Concentration	Method	Reference
1.3		H_2O	n.a.	est	[92FUG/KHO]
0.18		0.195M HCl	H:0.195M, L:0.195M	cix	[56WAR/WEL]
0.37		0.5M HCl	H:0.5M, L:0.5M	cix	[82JEN]
0.215	-0.027	1M NH_4ClO_4	L:n.a.	dis	[80KHO/MAT]

Table A6.3: Equilibrium constants (β_n) for formation of aqueous Cm^{3+} complexes with NO_3^- ($Cm^{3+} + nNO_3^- \rightleftharpoons CmNO_3^{(3-n)+}$)

log β_1	log β_2	Medium	Maximum Metal/H^+/Ligand Concentration	Method	Reference
0.57		1.0M NH_4Cl	L:1.0M	dis	[60LEB/PIR]
0.34	0.097	1M NH_4ClO_4	L:1.0M	dis	[80KHO/MAT]
-0.125		2.01M NH_4SCN	L:2.01M	dis	[73CHI/DAN]

Table A6.4: Equilibrium constants (β_n) for formation of aqueous Cm^{3+} complexes with OH^- ($Cm^{3+} + nOH^- \rightleftharpoons CmOH_n^{(3-n)+}$)

log β_1	log β_2	Medium	Maximum Metal/H^+/Ligand Concentration	Method	Reference
8.4		H_2O	n.a.	est	[78ALL/BEA]
7.9		H_2O	n.a.	est	[82JEN]
10.6	18.9	0.005M NH_4ClO_4	M:10^{-5}M,pH5	tp	[72SHA/STE]
6.67	12.06	0.1M $NaClO_4$	pH7	sp	[92WIM/KEL]
6.09	11.32	0.011m NaCl	pH:8.6	sp	[94FAN/KIM]
5.76	11.1	0.099m NaCl	pH:8.6	sp	[94FAN/KIM]
5.58	10.98	0.576m NaCl	pH:8.6	sp	[94FAN/KIM]
5.47	11.01	0.985m NaCl	pH:8.6	sp	[94FAN/KIM]
5.48	10.9	0.99m NaCl	pH:8.6	sp	[94FAN/KIM]
5.6	11.15	1.00m NaCl	pH:8.6	sp	[94FAN/KIM]
5.72	11.39	1.022m NaCl	pH:8.6	sp	[94FAN/KIM]
6.06	12.19	2.00m NaCl	pH:8.6	sp	[94FAN/KIM]
6.16	12.24	2.648m NaCl	pH:8.6	sp	[94FAN/KIM]
6.26	12.39	3.476m NaCl	pH:8.6	sp	[94FAN/KIM]
6.39	13	3.743m NaCl	pH:8.6	sp	[94FAN/KIM]
6.43	12.7	3.828m NaCl	pH:8.6	sp	[94FAN/KIM]
6.21	13.25	4.00m NaCl	pH:8.6	sp	[94FAN/KIM]
6.6	13.23	4.244m NaCl	pH:8.6	sp	[94FAN/KIM]
6.6	13.22	4.981m NaCl	pH:8.6	sp	[94FAN/KIM]

Table A6.4: Equilibrium constants (β_n) for formation of aqueous Cm^{3+} complexes with OH^- continued

log β_1	log β_2	Medium	Maximum Metal/H^+/Ligand Concentration	Method	Reference
6.48	13.96	5.357m NaCl	pH:8.6	sp	[94FAN/KIM]
6.62	13.24	5.693m NaCl	pH:8.6	sp	[94FAN/KIM]
6.8	14.1	6.15m NaCl	pH:8.6	sp	[94FAN/KIM]

Table A6.5: Equilibrium constants (β_n) for formation of aqueous Cm^{3+} complexes with OH^- ($Cm^{3+} + nH_2O \rightleftharpoons CmOH_n^{(3-n)+} + nH^+$)

log β_1	Medium	Maximum Metal/H^+/Ligand Concentration	Method	Reference
-2.7	0.005M KCl	n.a.	tp	[68MAR/KIK]
-3.30[1]	0.01 NaAc	pH:4.5	dis	[89MOH]
-5.92	0.1M $LiClO_4$	pH:6	dis	[69DES/HUS]
-6.05	0.1M $LiClO_4$	n.a.	dis	[69GUI/FER]
-5.4	0.1M $LiClO_4$	pH:6	dis	[73HUB/HUS]
-7.7	I=0.1	n.a.	gl	[83EDE/BUC]

1) T=303 K

Table A6.6: Equilibrium constants (β_n) for formation of aqueous Cm^{3+} complexes with CO_3^{2-} ($Cm^{3+} + nCO3^{2-} \rightleftharpoons Cm(CO_3)_n^{(3-2n)+}$)

log β_1	log β_2	log β_3	Medium	Maximum Metal/H^+/Ligand Concentration	Method	Reference
7.7	12.8		H_2O	n.a.	calc	[88CAN]
6.65[a]	9.6[b]	10.7[c]	O.1M $NaClO_4$	L:100%CO_2 at pH6 (a), 9.4(b) and 1M $NaCO_3$(c)	sp	[92WIM/KIM]
6.32			n.a.	n.a.	sol	[91MEI]

Table A6.7: Equilibrium constants (β_n) for formation of aqueous Cm^{3+} complexes with PO_4^{3-} ($Cm^{3+} + nPO4^{3-} \rightleftharpoons Cm(PO_4)_n^{(3-3n)+}$)

log β_1	log β_2	Medium	Maximum Metal/H$^+$/Ligand Concentration	Method	Reference
20.2	36.8	H_2O	n.a.	sol, ix	[69MOS]
17.5	34.1	1M NH_4Cl	M:0.015M, pH:1.8, L:0.57M	sol, ix	[71MOS2]

Table A6.8: Equilibrium constants (β_n) for formation of aqueous Cm^{3+} complexes with $H_2PO_4^-$ ($Cm^{3+} + nH_2PO4^- \rightleftharpoons Cm(H_2PO_4)_n^{(3-n)+}$)

log β_1	log β_2	log β_3	log β_4	Medium	Maximum Metal/H$^+$/Ligand Concentration	Method	Reference
2.4	3.6	5.61	6.2	H_2O	n.a.	sol, ix	[69MOS]
1.48	2.08	2.84	3.1	1M NH_4Cl	M:0.015M, pH:1.8, L:0.57M	sol, ix	[71MOS2]

Table A6.9: Equilibrium constants (β_n) for formation of aqueous Cm^{3+} complexes with SO_4^{2-} ($Cm^{3+} + nSO4^{2-} \rightleftharpoons Cm(SO_4)_n^{(3-2n)+}$)

log β_1	log β_2	log β_3	Medium	Maximum Metal/H^+/Ligand Concentration	Method	Reference
3.88	5.7	5.15	H_2O	L:0.5M,H5x10^{-4}M	sol	[72MCD/COL]
3.6	5.6		H_2O	n.a.	est	[78ALL/BEA]
1.86	2.7		H_2O	n.a.	est	[82JEN]
4.2	6.1		H_2O	n.a.	est	[92FUG/KHO]
2.41[4]			0.1M NH_4Cl	L:5mM,pH1.8	tp	[73STE]
2.45			0.1M NH_4Cl	L:9mM,pH1.8	tp	[73STE]
2.48[5]			0.1M NH_4Cl	L:5mM,pH1.8	tp	[73STE]
1.85	2.7		0.5M $NaClO_4$	L:0.1M,pH3.6	dis	[68AZI/LYL]
1.86	2.37		0.5M $NaClO_4$	L:0.1M,pH3.6	ix	[68AZI/LYL]
1.75			0.75M NH_4Cl	L:0.25M,pH4	dis	[60LEB/PIR]
1.7	3.19		1M $HClO_4$	H:1M,L:0.7M	dis	[78RAO/BAG]
1.509	2.382		1M NH_4ClO_4	L:0.05M,pH3	dis	[80KHO/MAT]
1.34	1.86		2M $NaClO_4$	L:0.1M,pH3	dis	[67CAR/CHO]
1.08[1]	1.66[1]		2M $NaClO_4$	L:0.1M,pH3	dis	[67CAR/CHO2]
1.49[2]	2.05[2]		2M $NaClO_4$	L:0.1M,pH3	dis	[67CAR/CHO2]
1.61[3]	2.30[3]		2M $NaClO_4$	L:0.1M,pH3	dis	[67CAR/CHO2]
1.59	3.11		2M $HClO_4$	H:1M,L:0.7M	dis	[78RAO/BAG]
0.93	0.61		3m $Na(Cl,SO_4)$	L:0.367m,pH2	sp	[96PAV/FAN]

1)T=273K
2) T=313K
3) T=328K
4) T=288K
5) T=308K

Table A6.10: Solubility products (K_{sp}) of the different Cm^{3+} solid phases

Reaction	Log K_{sp}	Medium	Maximum Metal/ H^+/ Ligand Concentration	Method	References
CmF_3 (s) = CmF_3(aq)	-5.22	0.1 M $HClO_4$[2]	n.a.	sol	[54FEA][1]
	-4.91	0.1 M $HClO_4$	n.a.	sol	[54FEA][1]
	-4.75	0.1 $HClO_4$[3]	n.a.	sol	[54FEA][1]

1: Information obtained from [64SIL/MAR] or [71SIL/MAR]
2: T = 283 K
3: T = 320 K

Table A6.11: Binary Interaction Parameters

Cation	Anion	β^0	β^1	β^2	C^ϕ	Reference
Cm^{3+}	OH^-	-0.6	3.0		0.2	[94FAN/KIM]
$Cm(OH)_2^+$	Cl^-	-0.58	-0.9		0	[94FAN/KIM]
Cm^{3+}	Cl^-	0.5856	5.6		-0.019	[94FAN/KIM2]

A7: Selection of log β_1° Values with the Screening Approach

A number of authors have used various approaches (e.g., extrapolation, S.I.T. or Pitzer modeling, etc.) to estimate values at classical standard state (I = 0, T = 298K) conditions for stability constants. These have been cited in Tables A1 - A6. However, the values for an individual system may vary significantly. To provide a basis for choosing among these values, a screening approach has been used which is based on the strongly ionic nature of the actinide-ligand bonding. An extended Born equation is used for estimation of log $\beta°_{101}$ for AnX complexation of various actinide cations with the same ligand X where An includes both simple and dioxo cations [94CHO/RIZ]. The equation takes into account the different "effective" ionic charges of the actinide cations, the different effective dielectric constants for these and the differences in

An - X bond distances:

$$\Delta G_{101} = \frac{Ne^2 Z_1 Z_2}{418.7\ D_e d_{12}} - \nu RT\ln\ 55.51$$

z_1 = +3 D_e = 57 d_{12} = based on Shannon radii [76SHA]

= +4 = 40

= +2.2 (NpO_2^+) = 70

= +3.3 (UO_2^{2+}) = 50

The screening method calculated the unknown log β°(An^{11}) values from known values of another actinide, log β (An^1), by the formula:

$$\log\ \beta°(An^{11}) = \log\ \beta(An^{1}) \cdot \frac{Z_1(An^{11})}{Z_1(An^{1})} \cdot \frac{D_e(An^{1})}{D_e(An^{11})} \cdot \frac{d_{12}(An^{1})}{d_{12}(An^{11})}$$

Sm(III) values of log β° were obtained from measurements by a variety of techniques at concentrations above tracer scale. For this reason, they were chosen as a reliable set of more reliable known values and unknown values of log β° were calculated for the An^{3+}, An^{4+}, AnO_2^+ and AnO_2^{2+} complexation. UO_2^{2+} values of log β° from the careful evaluation of the NEA seem reliable and were used in a second series of calculations of unknown values for the III - VI series of actinide cations. Only values for the 1:1 complexation were calculated as the use of the Born equation for 1:2, etc., requires more "extension" and results in less reliable estimates. However, it is reasonable to assume that values for 1:2, 1:3, etc. from the authors responsible for the most reliable 1:1 values would be the values to use.

The values from the Sm^{3+} and UO_2^{2+} based estimates were compared and found to be in acceptable agreement. In turn, they were used to select, by the degree of agreement, a set of values from those at I = 0 in the data tables. These selected values which best agreed with these estimates are listed below as our recommended values for I = 0.

Table A7: Values of log β_1^0 selected with the screening approach

Trivalent Ions	Cl^-	F^-	NO_3^-	OH^-	CO_3^{2-}	HPO_4^-	$H_2PO_4^-$	SO_4^{2-}
Sm^{3+}		3.58^{1}	1.2^{3}	6.8^{1}		$5.35^{(1)}$	$2.23^{(1)}$	3.67^{5}
Am^{3+}	1.05^{1}	3.4^{2}	1.33^{2}	7.6^{2}	7.8^{2}	5.35^{1}	3^{2}	3.85^{2}
Pu^{3+}	(1.03)	3.3^{3}	1.41^{4}	7.6	(7.7)	(5.31)	2.95	(3.80)

( ) = estimate

1 [92MIL]

2 [95SIL/BID]

3 [86WAN]

4 [83FUG2]

5 [78ALL/BEA]

A8: REFERENCES

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Thermodynamic Data for Predicting Concentrations of Th(IV), U(IV), Np(IV), and Pu(IV) in Geologic Environments

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Thermodynamic Data for Predicting Concentrations of Th(IV), U(IV), Np(IV), and Pu(IV) in Geologic Environments

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Introduction

The objective of this study is to provide Power Reactor and Nuclear Fuel Development Corporation (PNC) of Japan with reliable values of thermodynamic constants for environmentally important reactions. These values will be used to predict upper concentration limits of tetravalent actinides that can leach out of high-level waste repositories. The Pitzer ion-interaction model is selected for these applications because 1) it is applicable to low as well as high ionic strengths, 2) specific media effects can be reliably ascertained, and 3) it provides a mechanism for cross comparison and reinterpretation of thermodynamic data developed under a wide range of ionic strengths and a variety of aqueous media. Over the last few years, a considerable amount of thermodynamic data for Th(IV), as well as a limited amount of data for U(IV), Np(IV), and Pu(IV), have been developed in our laboratory under several research projects using the Pitzer approach; we can take advantage of the expertise and experience in the thermodynamic data analysis.

Due to programmatic constraints in terms of funding and time frame on this project, this report is not intended to be a comprehensive and critical review of all thermodynamic data for tetravalent actinides. Instead, based on a thorough compilation of the available data, expert review has been performed to analyze the data using the Pitzer's ion-interaction approach and select thermodynamic data sets which, we believe, can provide reasonable estimates of the solubilities of tetravalent actinides under conditions relevant to the geologic environments.

Compilation of Tetravalent Actinide Thermodynamic Data

To develop a comprehensive database for selecting constants, available pertinent literature was collected. The references pertaining to tetravalent actinides were collected from the literature and databases available to us. The thermodynamic equilibrium constants of F^-, Cl^-, NO_3^- OH^-, CO_3^{2-}, PO_4^{3-} and SO_4^{2-} complexes with Th(IV), U(IV), Np(IV), and Pu(IV) were compiled in different tables for each element and ligand (Appendix, Tables A1-A4). No attempt was made to prioritize any data in the compilation. In addition to the values of constants, these tables also include the experimental techniques used to obtain the results and the experimental conditions such as ionic media and ligand concentration ranges.

Some of the general conclusions that can be made from these data are that: 1) the solubilities of the hydrous oxides of tetravalent actinides are extremely low and decrease drastically in the order of $ThO_2(am) >> UO_2(am) > NpO_2(am) > PuO_2(am)$; 2) in contrast to the drastic difference in the solubilities of hydrous oxides, stability constants of the aqueous complexes of Th(IV), U(IV), Np(IV), and Pu(IV) reported in the compilation (Appendix, Tables A1-A4) vary less than 2-3 orders of magnitude for most of the ligands.

As a result, unlike the systems for trivalent actinide elements where we reported a general trivalent model based on the similarities in the solubility and complexation among trivalent actinides and lanthanides, it is not feasible to develop a general model for tetravalent actinides. As for element-specific models, currently available data allow us to develop such a model only for Th(IV), for which extensive studies have been reported and reliable data covering wide ranges of ionic media exist. The Th(IV) model is discussed in the following sections. Potential use of the Th(IV) model for estimating the upper limit of aqueous concentrations of other tetravalent actinides under repository conditions is also discussed. In addition, brief comments are made on the available thermodynamic data for U(IV), Np(IV), and Pu(IV). These data, though not sufficient to develop reliable models, are nevertheless helpful in dealing with the specific element in a particular medium.

Selected Thermodynamic Data for Thorium

The compilation of literature data on tetravalent actinides (Appendix,Tables A1-A4) clearly indicates that extensive experimental studies covering wide ranges of pH and ionic media have been conducted on thorium hydrous oxide solubilities and on the complexation of Th(IV) with ligands including hydroxide, chloride, sulfate, fluoride, and carbonate while only limited data are available for other tetravalent actinides including U(IV), Np(IV), and Pu(IV).

Based on the literature compilation, thermodynamic parameters in the Th(IV) model that best represent a large amount of experimental data on the solubility of Th(IV) hydrous oxide in the presence of a variety of ligands, and on the complexation of Th(IV) with environmentally important ligands are selected in this report in Tables 1-7. Sufficient data do exist for Th(IV), which allows us to develop a Th(IV)-specific model for predicting aqueous concentrations of Th(IV) in a wide variety of groundwater compositions. Tables 1 and 2 provide thermodynamic equilibrium constants for solid phase dissolution and complexation reactions involving species of Th(IV). Table 3 summarizes the Pitzer ion-interaction parameters for Th(IV) species. Table 4 provides $\Delta_f G^0/RT$ values for Th(IV) species. Tables 5-7 summarize $\Delta_f G^0/RT$ values and Pitzer ion-interaction parameters for the major electrolyte ions (i.e., Na, K, Ca, Mg, F, Cl, ClO_4, NO_3, CO_3, SO_4, PO_4), which are identical to those reported in a previous report (Tables 2, 3, and 5 in Rai et al. 1998a, PNC report).

In tests of several systems containing ligands relevant to nuclear waste disposal (OH, Cl, F, CO_3, and SO_4), the Th(IV) model has been shown to reliably predict the concentrations of Th(IV) in dilute to concentrated solutions and in simple as well as mixed systems. The basis for selection of the model parameters for Th(IV) interactions with each ligand is discussed individually in the subsequent sections.

Though the Th(IV) model cannot be used as a general model for all tetravalent actinides because of the drastically different solubilities of their hydrous oxides, we suggest using the

Th(IV) model to estimate the upper limit of the aqueous concentrations of U(IV), Np(IV), and Pu(IV) under conditions relevant to nuclear waste repositories based on the following considerations:

1) The hydrous oxides of tetravalent actinides are likely to be the solubility-controlling solid phase because of their extremely low solubility.

2) The solubilities of hydrous oxides of tetravalent actinides decrease in the order of ThO_2(am) >> UO_2(am) > NpO_2(am) > PuO_2(am), with the K_{sp} value for ThO_2(am) 8 orders of magnitude higher than that for UO_2(am); and the K_{sp} values for UO_2(am) (-53.45), NpO_2(am) (-54.5) and PuO_2(am) (-56.85) decrease by only 3 orders of magnitude.

3) The stability constants of the aqueous complexes of Th(IV), U(IV), Np(IV), and Pu(IV) are quite similar (within 2-3 orders of magnitude) for most of the ligands reported in the compilation (see previous section). Such a smaller difference in aqueous complexation is not expected to compensate for the large difference in the solubility of hydrous oxides among tetravalent actinides.

4) Because of the extremely low solubilities of the hydroxides and the strong tendency of the tetravalent actinides toward hydrolysis, the concentration of Th(IV) reaches the detection limit at pH above 5 and the concentrations of U(IV), Np(IV) and Pu(IV) reach the detection limits at even lower pH (e.g., pH about 3.3-3.5 for U(IV)). The pH of most groundwaters is expected to be higher than this. Only the ligands (e.g., sulfate, carbonate) that form very strong complexes with tetravalent actinides can significantly increase their concentrations in groundwaters. However, even for these ligands, very high ligand concentrations (e.g., from 0.1 M up to 5 M for carbonate) would be required to have a significant impact on tetravalent actinide concentrations in acidic solutions. Such high concentrations of ligands are unlikely to be encountered in most groundwaters.

As a result, we believe, in the absence of sufficient data specific to individual tetravalent actinides, the Th(IV) model can be reliably used to estimate the upper limit for the aqueous concentrations of U(IV), Np(IV), and Pu(IV) in nuclear waste repositories.

In addition to detailed discussions on the thermodynamic data for the Th(IV) model, brief comments on thermodynamic data for U(IV), Np(IV), and Pu(IV) are also provided in the following sections along with the selected recommended values of thermodynamic parameters for important systems. These data, though insufficient to generate element-specific models, can be helpful when estimation of the aqueous concentration of the specific actinide in a particular groundwater system is needed.

Table 1. log K^o_{sp} Values (25°C) of Reactions Involving Solid Compounds of Th(IV)

Reaction	log K^o_{sp}	Reference
$ThO_2(am) + 2H_2O \rightleftharpoons Th^{4+} + 4OH^-$	-45.5	Felmy et al. 1991
$Th(OH)_4(c) \rightleftharpoons Th^{4+} + 4OH^-$	-54.14	Ryan & Rai 1987
$ThO_2(am) + H^+ + H_2O + CO_3^{2-} \rightleftharpoons Th(OH)_3CO_3^-$	6.78	Osthols et al. 1994[a]
$ThO_2(am) + 4H^+ + 5CO_3^{2-} \rightleftharpoons Th(CO_3)_5^{6-} + 2H_2O$	37.6	Felmy et al. 1997
$ThF_4 \cdot nH_2O(s) + 4H^+ \rightleftharpoons Th^{4+} + 4HF + nH_2O$	-16.29	Felmy et al. 1993
$ThF_4 \cdot NaF \cdot H_2O(c) + 5H^+ \rightleftharpoons Th^{4+} + Na^+ + 5HF + H_2O$	-18.23	Felmy et al. 1993
$ThF_4 \cdot NH_4F(s) + 5H^+ \rightleftharpoons Th^{4+} + NH_4^+ + 5HF$	-18.09	Felmy et al. 1993

(a)The same value Felmy et al. (1997) adopted in their final model.

Table 2. log K° Values (25°C) of Reactions Involving Solution Species of Th(IV)

Reaction	log K°	Reference
$Th^{4+} + 2SO_4^{2-} \rightleftharpoons Th(SO_4)_2(aq)$	11.59	Felmy & Rai 1992
$Th^{4+} + 3SO_4^{2-} \rightleftharpoons Th(SO_4)_3^{2-}$	12.42	Felmy & Rai 1992
$Th^{4+} + 3F^- \rightleftharpoons ThF_3^+$	18.89	Felmy et al 1993
$Th^{4+} + 4F^- \rightleftharpoons ThF_4(aq)$	22.33	Felmy et al 1993
$Th^{4+} + 5F^- \rightleftharpoons ThF_5^-$	24.76	Felmy et al 1993
$Th^{4+} + 6F^- \rightleftharpoons ThF_6^{2-}$	25.56	Felmy et al 1993
$Th^{4+} + NO_3^- \rightleftharpoons ThNO_3^{3+}$	(2.5)	This compilation(a)

(a) Based on the screening approach described in Section A5, Appendix.

Table 3. Relevant Pitzer Ion-Interaction Parameters for Th(IV) Species

Species	$\beta^{(0)}$	$\beta^{(1)}$	$\beta^{(2)}$	C^{ϕ}	Reference
H^+-$Th(SO_4)_3^{2-}$	0.84				Felmy & Rai 1992
Na^+-$Th(SO_4)_3^{2-}$	0.12				Felmy & Rai 1992
K^+-$Th(SO_4)_3^{2-}$	0.90				Felmy & Rai 1992
Li^+-$Th(SO_4)_3^{2-}$	0.52				Felmy & Rai 1992
NH_4^+-$Th(SO_4)_3^{2-}$	0.26				Felmy & Rai 1992
NH_4^+-ThF_6^{2-}	-1.3				Felmy & Rai 1993
Th^{4+}-Cl^-	1.092	13.7	-160	-0.112	Roy et al. 1992
Th^{4+}-HSO_4^-	1.44				Felmy & Rai 1992
Th^{4+}-SO_4^{2-}	1.56				Felmy & Rai 1992
Na^+-$Th(CO_3)_5^{6-}$	1.31	30.0			Felmy et al. 1997

Species	θ	ψ	Reference
H^+-Th^{4+}	0.60		Felmy & Rai 1992
H^+-Th^{4+}-Cl^-		0.08	Felmy & Rai 1992
Na^+-Th^{4+}	0.42		Rai et al. 1997a
Na^+-Th^{4+}-Cl^-		0.21	Rai et al. 1997a
NH_4^+-Th^{4+}	-0.44		Felmy & Rai 1992
NH_4^+-Th^{4+}-SO_4^{2-}		0.06	Felmy & Rai 1992
Mg^{2+}-Th^{4+}	0.60		Rai et al. 1997a
Mg^{2+}-Th^{4+}-Cl^-		0.21	Rai et al. 1997a
ClO_4^--$Th(CO_3)_5^{6-}$	5.5 (proposed)		Felmy et al. 1997

Species	λ	Reference
$Th(SO_4)_2$-Cl^-	0.29	Felmy & Rai 1992
$Th(SO_4)_2$-HSO_4^-	0.68	Felmy & Rai 1992

Table 4. Dimensionless Standard Molar Gibbs Energies of Formation of Th(IV) Species

Species	$\Delta_f G^\circ/RT$	References
Th^{4+}	-284.227	Fuger and Oetting (1976)
$Th(OH)_3CO_3^-$	-775.63	Felmy et al. (1997)
$Th(CO_3)_5^{6-}$	-1411.39	Felmy et al. (1997)
$Th(SO_4)_2(aq)$	-911.69	Felmy & Rai (1992)
$Th(SO_4)_3^{2-}$	-1214.0	Felmy et al. (1992)
ThF_3^+	-665.12	Felmy et al.(1993)
$ThF_4(aq)$	-785.507	Felmy et al.(1993)
ThF_5^-	-903.571	Felmy et al.(1993)
ThF_6^{2-}	-1017.875	Felmy et al.(1993)
$ThO_2(am)$	-451.408	Felmt et al.(1991)
$Th(OH)_4(c)$	-662.63	Ryan & Rai (1987)
$ThF_4{\cdot}nH_2O(s)$	-800.694	Felmy et al.(1993)
$ThF_4{\cdot}NaF{\cdot}H_2O(c)$	-1126.22	Felmy et al.(1993)
$ThF_4{\cdot}NH_4F(s)$	-956.60	Felmy et al.(1993)

Table 5. Dimensionless Standard Molar Gibbs Energies of Formation of Major Electrolyte Species

Species	$\Delta_f G^\circ/RT$	References
$H_2O(l)$	-95.6635	Harvie et al. (1984)
Na^+	-105.651	Harvie et al. (1984)
K^+	-113.957	Harvie et al. (1984)
Ca^{2+}	-223.30	Harvie et al. (1984)
Mg^{2+}	-183.468	Harvie et al. (1984)
$MgOH^+$	-251.94	Harvie et al. (1984)
H^+	0.00	Harvie et al. (1984)
Cl^-	-52.955	Harvie et al. (1984)
SO_4^{2-}	-300.386	Harvie et al. (1984)
HSO_4^-	-304.942	Harvie et al. (1984)
OH^-	-63.435	Harvie et al. (1984)
HCO_3^-	-236.751	Harvie et al. (1984)
CO_3^{2-}	-212.944	Harvie et al. (1984)
$CaCO_3^0$	-443.5	Harvie et al. (1984)
$MgCO_3^0$	-403.155	Harvie et al. (1984)
$CO_2(aq)^0$	-155.68	Harvie et al. (1984)
$CO_2(g)$	-159.092	Harvie et al. (1984)
$Mg(OH)_2(c)$ Brucite	-335.40	Harvie et al. (1984)
$CaCO_3(c)$ Calcite	-455.6	Harvie et al. (1984)
$MgCO_3(c)$ Magnesite	-414.45	Harvie et al. (1984)
$Ca(OH)_2(c)$ Portlandite	-362.12	Harvie et al. (1984)
$H_3PO_4^0$	-460.90	Pitzer and Silvester (1976)
$H_2PO_4^{-1}$	-455.96	Pitzer and Silvester (1976)
HPO_4^{2-}	-439.367	Wagman et al. (1982)
PO_4^{3-}	-410.947	Wagman et al. (1982)
MoO_4^{2-}	-337.366	Wagman et al. (1982)
$HMoO_4^-$	-348.62	Felmy et al. (1995)

$H_2MoO_4^0$	-358.86	Felmy et al. (1995)
$Mo_7O_{20}(OH)_4^{2-}$	-2152.05	Felmy et al. (1995)
F^-	-112.465	Wagman et al. (1982)
HF(aq)	-119.738	Wagman et al. (1982)
NO_3^-	-43.868	Wagman et al. (1982)

Table 6. Binary Ion-Interaction Parameters for Major Electrolyte Ions

Species	$\beta^{(0)}$	$\beta^{(1)}$	$\beta^{(2)}$	C^{ϕ}	References
Na^{+}-Cl^{-}	0.0765	0.2644	0.00	0.00127	Harvie et al (1984)
Na^{+}-SO_4^{2-}	0.01958	1.113	0.00	0.00497	Harvie et al (1984)
Na^{+}-HSO_4^{-}	0.0454	0.398	0.00	0.00	Harvie et al (1984)
Na^{+}-OH^{-}	0.0864	0.253	0.00	0.0044	Harvie et al (1984)
Na^{+}-HCO_3^{-}	0.0277	0.0411	0.00	0.00	Harvie et al (1984)
Na^{+}-CO_3^{2-}	0.0399	1.389	0.00	0.0044	Harvie et al (1984)
K^{+}-Cl^{-}	0.04835	0.2122	0.00	-0.00084	Harvie et al (1984)
K^{+}-SO_4^{2-}	0.04995	0.7793	0.00	0.00	Harvie et al (1984)
K^{+}-HSO_4^{-}	-0.0003	0.1735	0.00	0.00	Harvie et al (1984)
K^{+}-OH^{-}	0.1298	0.320	0.00	0.0041	Harvie et al (1984)
K^{+}-HCO_3^{-}	0.0296	-0.013	0.00	-0.008	Harvie et al (1984)
K^{+}-CO_3^{2-}	0.1488	1.43	0.00	-0.0015	Harvie et al (1984)
Ca^{2+}-Cl^{-}	0.3159	1.614	0.00	-0.00034	Harvie et al (1984)
Ca^{2+}-SO_4^{2-}	0.20	3.1973	-54.24	0.00	Harvie et al (1984)
Ca^{2+}-HSO_4^{-}	0.2145	2.53	0.00	0.00	Harvie et al (1984)
Ca^{2+}-OH^{-}	-0.1747	-0.2303	-5.72	0.00	Harvie et al (1984)
Ca^{2+}-HCO_3^{-}	0.4	2.977	0.00	0.00	Harvie et al (1984)
Mg^{2+}-Cl^{-}	0.35235	1.6815	0.00	0.00519	Harvie et al (1984)
Mg^{2+}-SO_4^{2-}	0.2210	3.343	-37.23	0.025	Harvie et al (1984)
Mg^{2+}-HSO_4^{-}	0.4746	1.729	0.00	0.00	Harvie et al (1984)
Mg^{2+}-HCO_3^{-}	0.329	0.6072	0.00	0.00	Harvie et al (1984)
$MgOH^{-}$-Cl^{-}	-0.10	1.658	0.00	0.00	Harvie et al (1984)
H^{+}-Cl^{-}	0.1775	0.2945	0.00	0.0008	Harvie et al (1984)
H^{+}-SO_4^{2-}	0.0298	0.00	0.00	0.0438	Harvie et al (1984)
H^{+}-HSO_4^{-}	0.2065	0.5556	0.00	0.00	Harvie et al (1984)
Na^{+}-$H_2PO_4^{-}$	-0.0533	0.0396	0.00	0.00795	Pitzer & Mayorga (1973)
Na^{+}-HPO_4^{2-}	-0.0583	1.4655	0.00	0.02938	Pitzer & Mayorga (1973)

Na^+-PO_4^{3-}	0.17813	3.8513	0.00	-0.05154	Pitzer & Mayorga (1973)
Na^+-ClO_4^-	0.0554	0.2755	0.00	-0.00118	Pitzer (1991)
H^+-ClO_4^-	0.1747	0.2931	0.00	0.00819	Pitzer (1991)
H^+-NO_3^-	0.1168	0.3546	0.00	-0.00539	Pitzer (1991)
Na^+-NO_3^-	0.0068	0.1783	0.00	-0.00072	Ptizer (1991)
K^+-NO_3^-	-0.0816	0.0494	0.00	0.0066	Pitzer (1991)
Ca^{2+}-NO_3^-	0.211	1.409	0.00	-0.0202	Pitzer (1991)
Mg^{2+}-NO_3^-	0.3671	1.585	0.00	-0.0207	Pitzer (1991)

Table 7. Ternary Ion-Interaction Parameters for Major Electrolyte Ions

Species	Ternary parameters	References
Na^+-K^+	-0.012	Harvie et al. (1984)
Na^+-K^+-Cl^-	-0.0018	Harvie et al. (1984)
Na^+-K^+-SO_4^{2-}	-0.010	Harvie et al. (1984)
Na^+-K^+-HCO_3^-	-0.003	Harvie et al. (1984)
Na^+-K^+-CO_3^{2-}	0.003	Harvie et al. (1984)
Na^+-K^+-NO_3^-	-0.001	Pitzer (1991)
Na^+-Ca^{2+}	0.07	Harvie et al. (1984)
Na^+-Ca^{2+}-Cl^-	-0.007	Harvie et al. (1984)
Na^+-Ca^{2+}-SO_4^{2-}	-0.055	Harvie et al. (1984)
Na^+-Mg^{2+}	0.07	Harvie et al. (1984)
Na^+-Mg^{2+}-Cl^-	-0.012	Harvie et al. (1984)
Na^+-Mg^{2+}-SO_4^{2-}	-0.015	Harvie et al. (1984)
Na^+-H^+	0.036	Harvie et al. (1984)
Na^+-H^+-Cl^-	-0.004	Harvie et al. (1984)
Na^+-H^+-HSO_4^-	-0.0129	Harvie et al. (1984)
K^+-Ca^{2+}	0.032	Harvie et al. (1984)
K^+-Ca^{2+}-Cl^-	-0.025	Harvie et al. (1984)
K^+-Mg^{2+}-Cl^-	-0.022	Harvie et al. (1984)
K^+-Mg^{2+}-SO_4^{2-}	-0.048	Harvie et al. (1984)
K^+-H^+	0.005	Harvie et al. (1984)
K^+-H^+-Cl^-	-0.011	Harvie et al. (1984)
K^+-H^+-SO_4^{2-}	0.197	Harvie et al. (1984)
K^+-H^+-HSO_4^-	-0.0265	Harvie et al. (1984)
Ca^{2+}-Mg^{2+}	0.007	Harvie et al. (1984)
Ca^{2+}-Mg^{2+}-Cl^-	-0.012	Harvie et al. (1984)
Ca^{2+}-Mg^{2+}-SO_4^{2-}	0.024	Harvie et al. (1984)
Ca^{2+}-H^+	0.092	Harvie et al. (1984)

Ca^{2+}-H^{+}-Cl^{-}	-0.015	Harvie et al. (1984)
Mg^{2+}-$MgOH^{-}$-Cl^{-}	0.028	Harvie et al. (1984)
Mg^{2+}-H^{+}	0.10	Harvie et al. (1984)
Mg^{2+}-H^{+}-Cl^{-}	-0.011	Harvie et al. (1984)
Mg^{2+}-H^{+}-HSO_4^{-}	-0.0178	Harvie et al. (1984)
Cl^{-}-SO_4^{2-}	0.02	Harvie et al. (1984)
Cl^{-}-SO_4^{2-}-Na^{+}	0.0014	Harvie et al. (1984)
Cl^{-}-SO_4^{2-}-Ca^{2+}	-0.018	Harvie et al. (1984)
Cl^{-}-SO_4^{2-}-Mg^{2+}	-0.004	Harvie et al. (1984)
Cl^{-}-HSO_4^{-}	-0.006	Harvie et al. (1984)
Cl^{-}-HSO_4^{-}-Na^{+}	-0.006	Harvie et al. (1984)
Cl^{-}-HSO_4^{-}-H^{+}	0.013	Harvie et al. (1984)
Cl^{-}-OH^{-}	-0.050	Harvie et al. (1984)
Cl^{-}-OH^{-}-Na^{+}	-0.006	Harvie et al. (1984)
Cl^{-}-OH^{-}-K^{+}	-0.006	Harvie et al. (1984)
Cl^{-}-OH^{-}-Ca^{2+}	-0.025	Harvie et al. (1984)
Cl^{-}-HCO_3^{-}	0.03	Harvie et al. (1984)
Cl^{-}-HCO_3^{-}-Na^{+}	-0.015	Harvie et al. (1984)
Cl^{-}-HCO_3^{-}-Mg^{2+}	-0.096	Harvie et al. (1984)
Cl^{-}-CO_3^{2-}	-0.02	Harvie et al. (1984)
Cl^{-}-CO_3^{2-}-Na^{+}	0.0085	Harvie et al. (1984)
Cl^{-}-CO_3^{2-}-K^{+}	0.004	Harvie et al. (1984)
Cl^{-}-NO_3^{-}	0.016	Pitzer (1991)
Cl^{-}-NO_3^{-}-Na^{+}	-0.006	Pitzer (1991)
Cl^{-}-NO_3^{-}-K^{+}	-0.006	Pitzer (1991)
Cl^{-}-NO_3^{-}-Mg^{2+}	0.00	Pitzer (1991)
Cl^{-}-NO_3^{-}-Ca^{2+}	-0.017	Pitzer (1991)
SO_4^{2-}-HSO_4^{-}-Na^{+}	-0.0094	Harvie et al. (1984)
SO_4^{2-}-HSO_4^{-}-K^{+}	-0.0677	Harvie et al. (1984)
SO_4^{2-}-HSO_4^{-}-Mg^{2+}	-0.0425	Harvie et al. (1984)
SO_4^{2-}-OH^{-}	-0.013	Harvie et al. (1984)

SO_4^{2-}-OH^--Na^+	-0.009	Harvie et al. (1984)
SO_4^{2-}-OH^--K^+	-0.050	Harvie et al. (1984)
SO_4^{2-}-HCO_3^-	0.01	Harvie et al. (1984)
SO_4^{2-}-HCO_3^--Na^+	-0.005	Harvie et al. (1984)
SO_4^{2-}-HCO_3^--Mg^{2+}	-0.161	Harvie et al. (1984)
SO_4^{2-}-CO_3^{2-}	0.02	Harvie et al. (1984)
SO_4^{2-}-CO_3^{2-}-Na^+	-0.005	Harvie et al. (1984)
SO_4^{2-}-CO_3^{2-}-K^+	-0.009	Harvie et al. (1984)
OH^--CO_3^{2-}	0.10	Harvie et al. (1984)
OH^--CO_3^{2-}-Na^+	-0.017	Harvie et al. (1984)
OH^--CO_3^{2-}-K^+	-0.01	Harvie et al. (1984)
HCO_3^--CO_3^{2-}	-0.04	Harvie et al. (1984)
HCO_3^--CO_3^{2-}-Na^+	0.002	Harvie et al. (1984)
HCO_3^--CO_3^{2-}-K^+	0.012	Harvie et al. (1984)
CO_2^0-Na^+	0.100	Harvie et al. (1984)
CO_2^0-K^+	0.051	Harvie et al. (1984)
CO_2^0-Ca^{2+}	0.181	Harvie et al. (1984)
CO_2^0-Mg^{2+}	0.183	Harvie et al. (1984)
CO_2^0-Cl^-	-0.005	Harvie et al. (1984)
CO_2^0-SO_4^{2-}	0.097	Harvie et al. (1984)
CO_2^0-HSO_4^-	-0.003	Harvie et al. (1984)
$H_3PO_4^0$-$H_3PO_4^0$	0.0503	Pitzer and Silvester (1976)
$H_3PO_4^0$-$H_3PO_4^0$-$H_3PO_4^0$	0.0109	Pitzer and Silvester (1976)
$H_3PO_4^0$-$H_2PO_4^-$	-0.04	Pitzer and Silvester (1976)
$H_3PO_4^0$-H^+	0.29	Pitzer and Silvester (1976)
SO_4^{2-}-ClO_4^-	0.020	Rai et al. (1995a)(a)
SO_4^{2-}-ClO_4^--Na^+	0.0014	Rai et al. (1995a)(a)

(a) Assuming Cl^- parameters reported by Harvie et al. (1984) apply to the ClO_4^- system; Rai et al. (1995a) showed these values are reasonable.

Hydroxide

There have been a number of studies to determine the solubility product of ThO_2(am) and the hydrolysis constants of Th(IV). Numerous mononuclear and polynuclear hydrolysis species have been proposed to fit the experimental data, including $ThOH^{3+}$, $Th(OH)_2^{2+}$, $Th(OH)_4^0$, $Th_2(OH)_2^{6+}$, $Th_4(OH)_8^{8+}$, $Th_4(OH)_{12}^{4+}$, and $Th_6(OH)_{15}^{9+}$. The relative importance of these species may be highly dependent on the concentration ranges of Th(IV), pH, and ionic strength. For example, the hydrolysis constants have impact on the concentration of Th(IV) only in solutions of low pH (around 3.5), but not in near neutral or basic solutions as encountered in groundwaters. Since different combinations of hydrolysis constants and solubility products may equally explain the observed experimental data, the potential importance of hydrolysis species is usually difficult to be uniquely defined from these experimental data. Consequently, a simple model which can interpret all the reliable data but invoke the fewest number of necessary species is preferred.

The solubility product of Th(IV) hydrous oxide was calculated by Felmy et al. (1991) from the data of Ryan and Rai (1987) for systems of low total Th(IV) concentration (~ 1×10^{-5} M) and low ionic strength (~ 0.005 M). In this calculation, polynuclear Th(IV) species should not be important, and formation of mononuclear hydrolysis species was neglected. The calculation yields log K = -45.5 for the reaction: $ThO_2(am) + 2H_2O \rightleftharpoons Th^{4+} + 4OH^-$, which is in excellent agreement with that of Ryan and Rai (1987), if their correction for hydrolysis species is ignored. With this constant, Rai et al. (1997a) could interpret their solubility results of Th(IV) hydrous oxides in concentrated NaCl and $MgCl_2$ solutions by including several ion-interaction parameters: $\beta^{(o)}$, $\beta^{(1)}$, $\beta^{(2)}$, and C^ϕ for Th^{4+}-Cl^- from Roy et al. (1992); θ for H^+-Th^{4+} and ψ for H^+-Th^{4+}-Cl^- from Roy et al. (1992); and θ for Na^+-Th^{4+} and Mg^{2+}-Th^{4+}, ψ for Na^+-Th^{4+}-Cl^- and Mg^{2+}-Th^{4+}-Cl^- from their own results. It appears that, although the importance of hydrolysis species in these solutions cannot be entirely discounted, the changes in solubilities of ThO_2(am) can be modeled without invoking numerous hydrolysis species. Therefore, Th(IV) hydrolysis species are not included in our final model for Th(IV). This model provides equally satisfactory predictions of ThO_2(am) solubility as other models which include hydrolysis constants. Test calculations in the presence of strongly complexing ligands concentrated electrolytes indicate that the concentrations of $ThOH^{3+}$ never contribute significantly to the total calculated Th concentration (Rai et al. 1997a).

Chloride

Roy et al.(1992) developed a set of ion-interaction parameters (for Th^{4+}-Cl^-: $\beta^{(o)} = 1.092$, $\beta^{(1)} = 13.7$, $\beta^{(2)} = -160$, and $C^{\phi} = -0.112$) for the HCl-$ThCl_4$-H_2O system from EMF measurements of solutions of a wide range of ionic strengths (0.006 to 3.0 $mol{\cdot}kg^{-1}$). These binary interaction parameters, together with the ternary interaction parameters (θ for H^+-$Th^{4+} = 0.60$, θ for Na^+-$Th^{4+} = 0.42$, θ for Mg^{2+}-$Th^{4+} = 0.60$; ψ for H^+-Th^{4+}-$Cl^- = 0.08$, ψ for Na^+-Th^{4+}-$Cl^- = 0.21$, ψ for Mg^{2+}-Th^{4+}-$Cl^- = 0.21$) developed from the solubility studies of ThO_2(am) in the presence of sulfate (Felmy et al. 1992) and in the presence of NaCl and $MgCl_2$ (Rai et al. 1997a), could well interpret all the data on ThO_2(am) solubility in NaCl and $MgCl_2$ solutions up to high chloride concentrations, as well as the existing osmotic data on $ThCl_4$ solutions (Robinson 1955) and the EMF data in the HCl-$ThCl_4$-H_2O system (Roy et al. 1992).

Instead of developing ion-interaction parameters for Th^{4+}-Cl^- based on experimental data, a number of authors elected to assume the formation of Th(IV) chloride complexes and calculated the formation constants as cited in the Appendix. It is not surprising that these complexes are very weak (log β_1 about 1). At present, using either the ion-interaction parameters described in the previous section or the formation constants is a matter of personal preference. However, to be consistent with the Pitzer's approach used for other systems and because extensive and reliable experimental data are available for this approach, we recommend that the ion interaction parameters be used.

Nitrate

There are no values of ion-interaction parameters for Th^{4+}-NO_3^- available in the literature, but there are a few values of the stability constants for Th(IV)-nitrate complexes reported (Table A1.14, Appendix). These constants were obtained at a limited number of relatively high ionic strengths (0.5 M, 2 M, 4 M and 5.97 M). Consequently, it is difficult to analyze or extrapolate these values to obtain the constant at zero ionic strength.

Because the ion-interaction parameters for Th^{4+}-NO_3^- are not available and the data of the formation constants for Th(IV)-nitrate complexes are scarce, a screening approach described in Section A5 of the Appendix is taken to estimate the formation constant of the first complex ($ThNO_3^{3+}$). This approach is based on the strongly ionic nature of the actinide-ligand bonding. The value of log β_1 for $ThNO_3^{3+}$ is estimated to be 2.5 and included in Table 2.

Sulfate

A limited amount of data is available on the complexation constants of sulfate with Th(IV), U(IV), Np(IV), and Pu(IV) (Tables A1.6-1.7, A2.6-2.7, A3.5-3.6, A4.4-4.5, Appendix). All of these data, except the Th(IV) data by Allen and McDowell (1963) and the Np(IV) data by Xia et al. (1997), were collected at high and constant ionic strengths to avoid variations in aqueous phase ionic activity coefficients, and in strongly acidic solutions to eliminate complications of hydrolysis and oxidation of U(IV), Np(IV), and Pu(IV). Reliable extrapolations of these data to low or zero ionic strengths is difficult. To overcome this difficulty, Felmy and Rai (1992) chose the solubility data of $Th(SO_4)_2 \cdot 9H_2O$ in various ionic media including Na_2SO_4, K_2SO_4, $(NH_4)_2SO_4$, Li_2SO_4, HCl, and H_2SO_4 (Linke 1965) and the solvent extraction data by Allen and McDowell (1963) to determine necessary ion-interaction parameters for Th(IV)/sulfate systems and to calculate the thermodynamic equilibrium constants for the formation of $Th(SO_4)_2(aq)$ and $Th(SO_4)_3^{2-}$, because these data cover a wide range of electrolyte concentrations from zero to about 2 M. The constants and parameters that were developed are listed in Tables 2-4. As shown by Felmy and Rai (1992), the extraction of Th(IV) from Na_2SO_4 solutions is well interpreted by the model including the formation constants of Th(IV)/sulfate species and necessary ion-interaction parameters.

In a recent study of the solubility of $NpO_2(am)$ in the presence of 0.01m and 0.0025 m Na_2SO_4, use of the complexation constants of Th(IV)/sulfate (Felmy and Rai 1992) as analogous values for Np(IV)/sulfate was tested (Rai et al. 1997b). Results indicate that the constants and parameters for Th(IV)/sulfate provide equally good interpretation of the effect of sulfate on the solubility of NpO_2(am) as a set of constants and parameters specifically developed for Np(IV)/sulfate from solvent extraction experiments (Xia et al. 1997).

Carbonate

Osthols et al. (1994) reviewed the past results of the studies on Th(IV)-carbonate systems and reported values of the solubility of ThO_2(act) in 0.5 M $NaClO_4$ as a function of pH and partial pressure of CO_2(g). Based on the experimental results, presence of two aqueous Th(IV)-carbonate complexes, $Th(OH)_3(CO_3)^-$ and $Th(CO_3)_5^{6-}$, were suggested and the equilibrium formation constants of these complexes were calculated using the S.I.T. activity coefficient model. The formation constant for $Th(OH)_3(CO_3)^-$ was later found to be in good agreement with the value obtained by Felmy et al. (1997) using Pitzer's ion-interaction approach, based on solubility data for ThO_2(am) in concentrated $NaHCO_3$ and Na_2CO_3 solutions (Rai et al. 1995b). As a result, the value obtained by Osthols et al. (1994) and verified by Felmy et al. (1997) for the formation of $Th(OH)_3(CO_3)^-$ is selected in the present Th(IV) model.

Osthols's experiment was conducted in solutions of relatively low carbonate concentrations (about 0.1 M). As a result, there might be higher uncertainty in their formation constant for $Th(CO_3)_5^{6-}$, because this complex is expected to be dominant only in solutions of high concentrations of carbonate. To extend the study of the Th(IV)/carbonate system to higher carbonate concentrations, Rai et al. (1995b) determined the solubility of ThO_2(am) in concentrated $NaHCO_3$ and Na_2CO_3 solutions (up to 2 M) and confirmed the presence of $Th(CO_3)_5^{6-}$ using the EXAFS technique. Based on the experimental results of Osthols et al. (1994) and Rai et al. (1995b), Felmy et al. (1997) established a simple model which was able to interpret all the solubility data of ThO_2(am) in the presence of carbonate from dilute to nearly saturated solutions. The Th(IV) model includes the two aqueous Th(IV) complexes that Osthols et al. suggested as well as two ion-interaction parameters, $\beta^{(0)}$ and $\beta^{(1)}$, for Na^+-$Th(CO_3)_5^{6-}$ (Felmy et al. 1997). The parameters of the Th(IV)-carbonate model are summarized in Tables 1-4.

Fluoride

Fluoride ions can interact strongly with aqueous Th(IV) to form a series of aqueous complexes including ThF^{3+}, ThF_2^{2+}, ThF_3^+, and $ThF_4(aq)$ as literature data indicate (Tables A1.11, A1.12, Appendix). The stability constants from different studies have been reviewed (Wagman et al. 1982) and shown to be in reasonable agreement, given the difference in experimental methods and ionic media. However, these studies were generally conducted in acidic solutions of high ionic strengths, in which the dominant aqueous fluoride species was HF(aq) and the free fluoride concentration was quite low (~ 0.001 M), with no evidence of anionic thorium fluoride complexes observed.

Felmy et al. (1993) conducted a study of thorium fluorides in solutions of NaF and NH_4F over a wide range of aqueous fluoride concentrations (0.0001 M to 1.0 M). It was found that ThF_3^+ and $ThF_4(aq)$ are the dominant aqueous Th(IV) species in solutions of 0.0001 M to 0.003 M in fluoride. However, at higher fluoride concentrations, the solubility data support the existence of anionic Th(IV)/F complexes including ThF_5^- and ThF_6^{2-}. Inclusion of these anionic species into the thermodynamic model was found necessary to interpret the solubility data in the whole range of fluoride concentrations. The stability constants and ion-interaction parameters developed based on this study are listed in Table 1-4. This model has been shown to provide good prediction of the concentration of Th(IV) over a wide range of fluoride concentrations.

Selected Thermodynamic Data for U(IV), Np(IV) and Pu(IV)

The compilation of the data in the literature on tetravalent actinides (see Appendix) indicates that thermodynamic data for U(IV), Np(IV), and Pu(IV) are not as extensive as the data for Th(IV), and currently available data do not allow us to develop thermodynamic models specifically for U(IV), Np(IV), and Pu(IV). Lack of thermodynamic models makes it difficult to predict the aqueous concentrations of these elements under a variety of conditions in nuclear waste repositories. However, we do believe 1) the Th(IV) model can be used to estimate the upper limit of the aqueous concentrations of these elements; and 2) a limited amount of reliable data on U(IV), Np(IV), and Pu(IV) does exist and can help to make more accurate estimations for the specific element in a particular medium. Individual data for U(IV), Np(IV), and Pu(IV) are briefly discussed in the following sections.

U(IV)

For the hydrolysis of U^{4+} and the solubility of UO_2(am), reliable data are obtained from a combination of several studies covering wide ranges of ionic media including dilute solutions (Rai et al.1990), concentrated NaCl/$MgCl_2$ solutions (Rai et al. 1997a), and Na_2SO_4 solutions (Rai et al. 1998b). The value of log K°_{sp} has been proven consistent with the observed solubilities of UO_2(am) in all the above-mentioned systems.

For the U(IV)/sulfate system, we recommend the use of all the constants and parameters from corresponding Np(IV)/sulfate systems.

A recent study by Rai et al. (1998c) on U(IV)/carbonate system provides the formation constants for $U(CO_3)_5^{6-}$ and $U(OH)_2(CO_3)_2^{2-}$ and interaction parameters of Na^+-$U(CO_3)_5^{6-}$. The existence of $U(CO_3)_5^{6-}$ was consistent with the observation for the Th(IV)/carbonate system and supported by EXAFS measurements.

The recommended values of the constants and parameters for the hydroxide, chloride, nitrate, fluoride, sulfate, and carbonate systems are included in Table 8.

Table 8. Recommended Thermodynamic Data for U(IV)

Reaction	log K^{o}_{sp}	Reference
$UO_2(am) + 2H_2O \rightleftharpoons U^{4+} + 4OH^-$	-53.45	Rai et al. 1997a
$UO_2(am) + 2HCO_3^- \rightleftharpoons U(OH)_2(CO_3)_2^{2-}$	-4.8	Rai et al. 1998c
$UO_2(am) + 4H^+ + 5CO_3^{2-} \rightleftharpoons U(CO_3)_5^{6-} + 2H_2O$	33.8	Rai et al. 1998c

Reaction	log K^{o}	Reference
$U^{4+} + H_2O \rightleftharpoons UOH^{3+} + H^+$	-0.50	Rai et al. 1990
$U^{4+} + SO_4^{2-} \rightleftharpoons USO_4^{2+}$	9.0	This compilation(a)
$U^{4+} + 2SO_4^{2-} \rightleftharpoons U(SO_4)_2(aq)$	11.7	This compilation(a)
$U^{4+} + 5CO_3^{2-} \rightleftharpoons U(CO_3)_5^{6-}$	31.29	Rai et al. 1998c
$U^{4+} + 2CO_3^{2-} + 2OH^- \rightleftharpoons U(OH)_2(CO_3)_2^{2-}$	41.33	Rai et al. 1998c
$U^{4+} + NO_3^- \rightleftharpoons UNO_3^{3+}$	(2.1)	This compilation(b)
$U^{4+} + F^- \rightleftharpoons UF^{3+}$	(6.0)	This compilation(b)

Pitzer Ion-Interaction Parameters

Species	$\beta^{(0)}$	$\beta^{(1)}$	$\beta^{(2)}$	C^{ϕ}	Reference
U^{4+}-Cl^-	1.644	15.5		0.0995	Rai et al. 1997a
U^{4+}-ClO_4^-	1.644	15.5		0.0995	Rai et al. 1997a
UOH^{3+}-Cl^-	1.0	7.856			Rai et al. 1997a
UOH^{3+}-ClO_4^-	1.0	7.856			Rai et al. 1997a
USO_4^{2+}-Cl^-	1.64			-0.2635	This compilation(a)
USO_4^{2+}-ClO_4^-	1.735			-0.2635	This compilation(a)
Na^+-$U(CO_3)_5^{6-}$	1.5	31.3			Rai et al. 1998c
K^+-$U(CO_3)_5^{6-}$	1.5	31.3			Rai et al. 1998c

Species	λ	Reference
$U(SO_4)_2$-Cl^-	0.29	This compilation(a)
$U(SO_4)_2$-ClO_4^-	0.81	This compilation(a)

(a) Assumed to be identical with values for corresponding Np(IV) species.

(b) Based on the screening approach described in Section A5, Appendix.

Np(IV)

In Table 9, the data for hydroxide, chloride, nitrate, fluoride, sulfate and carbonate systems are listed. The data for Np(IV) sulfate systems are based on recent results obtained by solvent extraction (Xia et al.1997) and solubility measurements (Rai et al 1997b). The formation constants for $NpSO_4^{2+}$ and $Np(SO_4)_2$ and the ion-interaction parameters included in Table 9 provide good interpretation of the results of solvent extraction as well as solubility. The value of log K^{o}_{sp} for NpO_2(am) has been found reliable in predicting the concentrations of Np(IV) in solutions of 0, 0.02 M, and 0.1 M Na_2SO_4. The values for the formation of carbonato complexes are estimated from solubility studies of NpO_2(am) in carbonate solutions, conducted for PNC (Rai et al., unpublished data).

Table 9. Recommended Thermodynamic Data for Np(IV)

Reaction	log K^o_{sp}	Reference
$Np^{4+} + H_2O \rightleftharpoons NpOH^{3+} + H^+$	-0.50	This compilation[(a)]
$NpO_2(am) + 2H_2O \rightleftharpoons Np^{4+} + 4OH^-$	-54.5	Rai et al. 1987

Reaction	log K^o	Reference
$Np^{4+} + SO_4^{2-} \rightleftharpoons NpSO_4^{2+}$	9.0	Xia et al. 1997
$Np^{4+} + 2SO_4^{2-} \rightleftharpoons Np(SO_4)_2(aq)$	11.7	Xia et al. 1997
$Np^{4+} + 5CO_3^{2-} \rightleftharpoons Np(CO_3)_5^{6-}$	(32.3)	This compilation[(b)]
$Np^{4+} + 2CO_3^{2-} + 2OH^- \rightleftharpoons Np(OH)_2(CO_3)_2^{2-}$	(42.3)	This compilation[(b)]
$Np^{4+} + NO_3^- \rightleftharpoons NpNO_3^{3+}$	(2.2)	This compilation[(c)]
$Np^{4+} + F^- \rightleftharpoons NpF^{3+}$	(5.8)	This compilation[(c)]

	Pitzer Ion-Interaction Parameters				
Species	$\beta^{(0)}$	$\beta^{(1)}$	$\beta^{(2)}$	C^{ϕ}	Reference
Np^{4+}-Cl^-	1.644	15.5		0.0995	Xia et al. 1997[(a)]
Np^{4+}-ClO_4^-	1.644	15.5		0.0995	Xia et al. 1997[(a)]
$NpOH^{3+}$-Cl^-	1.0	7.856			Xia et al. 1997[(a)]
$NpOH^{3+}$-ClO_4^-	1.0	7.856			Xia et al. 1997[(a)]
$NpSO_4^{2+}$-Cl^-	1.64			-0.2635	Xia et al. 1997
$NpSO_4^{2+}$-ClO_4^-	1.735			-0.2635	Xia et al. 1997

Species	λ	Reference
$Np(SO_4)_2$-Cl^-	0.29	Xia et al. 1997[(d)]
$Np(SO_4)_2$-ClO_4^-	0.81	Xia et al. 1997

[(a)] Assumed to be identical with values for corresponding U(IV) species.

[(b)] Value was estimated based on unpublished data from Rai et al.

[(c)] Based on the screening approach described in Section A5, Appendix.

[(d)] Assumed to be identical with values for corresponding Th(IV) species.

Pu(IV)

Solubility studies of PuO_2(am) are usually difficult because of the complications with various oxidation states. Data obtained by Rai et al. (1984) were currently recommended because the redox potential was carefully measured and the oxidation states were analyzed by solvent extraction and spectrophotometry. The tendency of the decrease in log K^{o}_{sp} for ThO_2(am), UO_2(am), NpO_2(am), and PuO_2(am) show a good correlation with the change in the atomic radii of these elements (Rai et al. 1987). For the Pu(IV)/sulfate system, the constants and parameters from corresponding Np(IV)/sulfate systems are recommended in Table 10. The values for the formation of carbonato complexes are estimated from solubility studies of PuO_2(am) in carbonate solutions, conducted for PNC (Rai et al., unpublished data).

Table 10. Recommended Thermodynamic Data for Pu(IV)

Reaction	log K°_{sp}	Reference
$Pu^{4+} + H_2O \rightleftharpoons PuOH^{3+} + H^+$	-0.50	This compilation[a]
$PuO_2(am) + 2H_2O \rightleftharpoons Pu^{4+} + 4OH^-$	-56.85	Rai 1984

Reaction	log K°	Reference
$Pu^{4+} + SO_4^{2-} \rightleftharpoons PuSO_4^{2+}$	9.0	This compilation[b]
$Pu^{4+} + 2SO_4^{2-} \rightleftharpoons Pu(SO_4)_2(aq)$	11.7	This compilation[b]
$Pu^{4+} + 5CO_3^{2-} \rightleftharpoons Pu(CO_3)_5^{6-}$	(34.7)	This compilation[c]
$Pu^{4+} + 2CO_3^{2-} + 2OH^- \rightleftharpoons Pu(OH)_2(CO_3)_2^{2-}$	(44.7)	This compilation[c]
$Pu^{4+} + NO_3^- \rightleftharpoons PuNO_3^{3+}$	(2.6)	This compilation[d]
$Pu^{4+} + F^- \rightleftharpoons PuF^{3+}$	(5.8)	This compilation[d]

	Pitzer Ion-Interaction Parameters				
Species	$\beta^{(0)}$	$\beta^{(1)}$	$\beta^{(2)}$	C^Φ	Reference
Pu^{4+}-Cl^-	1.644	15.5		-0.0995	This compilation[a]
Pu^{4+}-ClO_4^-	1.644	15.5		-0.0995	This compilation[a]
$PuOH^{3+}$-Cl^-		7.856			This compilation[a]
$PuOH^{3+}$-ClO_4^-		7.856			This compilation[a]
$PuSO_4^{2+}$-Cl^-	1.64			-0.2635	This compilation[b]
$PuSO_4^{2+}$-ClO_4^-	1.735			-0.2635	This compilation[b]

Species	λ	Reference
$Pu(SO_4)_2$-Cl^-	0.29	This compilation[b]
$Pu(SO_4)_2$-ClO_4^-	0.81	This compilation[b]

[a] Assumed to be identical with values for corresponding U(IV) species.
[b] Assumed to be identical with values for corresponding Np(IV) species.
[C] Value was estimated based on unpublished data from Rai et al.
[d] Based on the screening approach described in Section A5, Appendix.

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Appendix

Compilation of Thermodynamic Data for Tetravalent Actinides

Table of Contents

List of Abbreviations Used for Methods

Abbreviation	Method
ads	adsorption
Ag, Cd, ect...	e.m.f. with electrode of metal stated
cal	calorimetry
cix	cation exchange
cop	coprecipitation
cou	coulometry
dis	distribution between two phases
E	electromotive force, not specified
est	estimated
gl	glass electrode
ise-X	ion selective electrode with ion X stated
ix	ion exchange
lat	labeled atom
nmr	nuclear magnetic resonance
pH	pH method, not specified
pol	polarography
prx	proton relaxation
qh	quinhydrone electrode
recl	recalculation using data from another paper
red	e.m.f. with redox electrode
rev	review
SIT	Thermodynamic value calculated using the specific ion interaction theory
sol	solubility
sp	spectroscopy
tls	thermal lensing spectroscopy
xas	X-ray absorption spectroscopy
ΔG	combination of thermodynamic data

Thorium(IV)

Table A1.1: Equilibrium constants $(\beta_{mn})^1$ for formation of aqueous Th^{4+} complexes with OH^- ($mTh^{4+} + nH_2O \rightleftharpoons Th_m(OH)_n^{4m-n} + nH^+$)
(Stability values for polynuclear species are rounded to the first decimal place)

log β_1	log β_2	log β_3	log β_4	Other Species log $\beta_{m,n}$	Medium	Concentration (Molarity) of metal, H	Method	References
-3.8	-8.1			none	H_2O	M≤0.01 pH = 3.8-4.2	gl	[55PAN/HSE]
-3.27			-14.3	none	I = 0	n.a.	est	[91GRE/LAG2]
	-6.99			none	KOH<0.2 m $Th(NO_3)_4$ ≤0.1	M<0.1, p[OH] = 1.7-3.7	sol	[63BIL/FGR]
-3.61	-7.62	-11.17	-14.43	none	0.01-0.04 M HNO_3/HCl/$HClO_4$	M≤1E-2, pH=3-4.5	gl,sp	[71KIC/STE]
-3.9	-8.1			none	0.05 M $NaClO_4$	M≤0.01 pH = 3.8-4.2	gl	[55PAN/HSE]
-4.36				none	0.1 M $NaClO_4$	M≤1E-4 pH < 4	ix,sp	[86DAV/TOR]
-4.0	-8.1			none	0.1 $NaClO_4$	M≤0.01 pH = 3.8-4.2	gl	[55PAN/HSE]
-2.98				4,12 = -30.6; 6,15 = -34.4	0.1 M KNO_3	M≤2E-3 pH=3.1-4.0	pH	[83BRO/ELL]
-4.1	-8.2			none	0.3 $NaClO_4$	M≤0.01 pH = 3.8-4.2	gl	[55PAN/HSE]
-4.3	-8.3			none	0.5 M NaClO	M≤0.01 pH = 3.8-4.2	gl	[55PAN/HSE]
-4.12				none	0.5 M KNO_3	M=0.01 M pH=1.5-3.7	dis	[84NAK/ZIM]
				2,2 = -4.9; 3,2 = -7.7	0.5 NaCl	M≤0.01 M pH=2.2-3	pol,cal	[81MIL]
				2,2 = -5.1; 6,15 = -38.06	0.5 M $NaNO_3$	M≤0.01 M pH = 2-3.5	gl,Ag	[82MIL/ŠUR]
				2,2=-5.8;3,2=-7.6	0.5 M KCl	M=n.a.,pH=2-3.5	E	[81ŠUR/MIL]
-4.3	-7.8			2,2=-4.8,2,3 =-8	1 M (Na,H)ClO_4	M≤0.015M pC_H=1-4.5	gl	[54KRA/HOL]
-4.32[2]	-8.48[2]			2,2 = -5.6; 4,8 = -22.8; 6,15 = -43.8	1 m (Na,H)ClO_4	M≤0.029 pC_H=1-4.5	gl,sol	[65BAE/MEY]

Table A1.1 continued.

$\log \beta_1$	$\log \beta_2$	$\log \beta_3$	$\log \beta_4$	Other Species $\log \beta_{m,n}$	Medium	Concentration (Molarity) of metal, H	Method	References
-4.12	-7.81			2,2 = -4.6; 4,8 = -19.0;, 6,15 = -36.8	1 m (Na,H)ClO_4,	M≤0.029 pC_H=1 - 4.5	gl,sol	[65BAE/MEY]
-2.29[3]	-4.50[3]			2,2 = -2.6; 4,8 = -10.5; 6,15 = -20.6	1 m (Na,H)ClO_4	M≤0.029 pC_H=1 - 4.5	gl, sol	[65BAE/MEY]
				2,2 = -4.9; 3,2 = -7.9	1.0 NaCl	M≤0.01M pH=2.2-3	pol,cal	[81MIL]
				2,2 = -5.1; 6,15 = -39.56	1.0 M $NaNO_3$	M≤0.01 M pH = 2-3.5	gl,Ag	[82MIL/ŠUR]
			<-19.7	1,5 < -33.1	0.28-1.3 M LiOH, 0.1 M $NaClO_4$	M<0.02, OH = 0.28-1.38	sol, ΔG	[87RYA/RAI]
				2,2 = -5.0; 3,2 = -8.0	1.5 NaCl	M≤0.01M pH=2.2-3	pol,cal	[81MIL]
				2,2 = -5.1; 6,15 = -39.56	1.0 M $NaNO_3$	M≤0.01 M pH = 2-3.5	gl,Ag	[82MIL/ŠUR]
				2,2 = -5.0; 3,2 = -8.0	1.5 NaCl	M≤0.01 M pH=2.2-3	pol,cal	[81MIL]
				2,2 = -5.1; 6,15 = -40.47	1.5 M $NaNO_3$	M≤0.01 M pH = 2-3.5	gl,Ag	[82MIL/ŠUR]
				2,2 = -4.9; 3,2 = -8.0	1.5 M KCl	M=n.a.,pH=2-3.5	E	[81ŠUR/MIL]
				2,2 = -5.2; 6,15 = -41.10	2.0 M $NaNO_3$	M≤0.01 M pH = 2-3.5	gl,Ag	[82MIL/ŠUR]
				2,2 = -5.0; 3,2 = -8.1	2.0 M KCl	M=n.a.,pH=2-3.5	E	[81ŠUR/MIL]
				2,1= -2.8; 2,2 = -5.0	2.2 M (Na,Th)Cl	M=0.5 pC_H =0.7-13.6	H,Ag	[59HIE/SIL]
				2,2 = -5.1; 3,2 = -8.1	2.5 NaCl	M≤0.01 M pH=2.2-3	pol,cal	[81MIL]
				2,2 = -5.2; 6,15 = -41.77	2.5 M $NaNO_3$	M≤0.01 M pH = 2-3.5	gl,Ag	[82MIL/ŠUR]
				2,2 = -4.9; 3,2 = -8.3	2.5 M KCl	M=n.a.,pH=2-3.5	E	[81ŠUR/MIL]
-4.35			-16.65	2,2 = -5.1; 2,3 = -7.9; 4,8= -19.6; 4,12 = -34.9; 6,14 = -33.7; 6:16 = -42.9	3 M $NaClO_4$	M≤6E-3, pH=2.2-4.5	pol	[91GRE/LAG2]

Table A1.1 continued.

log β_1	log β_2	log β_3	log β_4	Other Species log $\beta_{m,n}$	Medium	Concentration (Molarity)of metal, H	Method	References
-4.13			-15.7	2,2 = -4.7; 4,8 = -19.2; 6,14 = -33.8	3 M (Na)ClO_4	M≤0.02, pH=2.5-4.5	pol	[87BRU/CAS]
				2,2 = -5.1; 2,3 = -8.2	3.0 M NaCl	M≤0.01 M pH=2.2-3	pol,cal	[81MIL]
-4.9				2,1=-2.8; 2,2 = -4.8; 2,3= -8.8; 2,5= -17.2; 3,1= -1.5; 3,2 = -4.1; 3,3= -6.8; 4,8 = -21.1; 4,9 = -24.3; 5,11= -29.1; 5,12= -32.2; 6,14= -36.4; 10,25= -65.4	3 M NaCl	M≤0.1, pH=2-4	H,gl	[68HIE/SIL][5]
				2,1= -2.9; 2,2 = -5.1	3 M (Na,Th)Cl	M=0.7, pC_H =0.7-13.6	H,Ag	[59HIE/SIL]
	-9.0			2,1=-2.6; 2,2 = -4.7; 2,3 = -8.8; 6,14 = -36.5; 6, 15 = -40.4	3.0 M NaCl	M≤0.1 ,pH=n.a.	pol,pH	[64HIE/SIL]
				2,2 = -5.2; 6,15 = -42.32	3.0 M$NaNO_3$	M≤0.01 M pH = 2-3.5	gl,Ag	[82MIL/ŠUR]
				2,2 = -4.9; 3,2 = -8.4	3.0 M KCl	M=n.a.,pH=2-3.5	E	[81ŠUR/MIL]
				2,2 = -5.0; 2,3 = -8.2	3.0 M KCl	M≤0.01 M pH=2.2-3	pol,cal	[81MIL]
				2,2 = -5.2; 2,3 = -8.3	3.0 M LiCl	M≤0.01 M pH=2.2-3	pol,cal	[81MIL]
				2,2 = -5.14, 3,5 = -14.23	3.0 M $LiNO_3$	M= 5E-3, pH=2-3.5	E	[71MIL]
				2,2 = -5.10; 2,3 = -8.98	3.0 M KNO_3	M=5E-3, pH=2-3.5	E	[71MIL]
				2,2 = -5.17 5,3 = -14.29	3.0 M $MgNO_3$	M=5E-3, pH=2-3.5	E	[71MIL]
				2,1 = -2.7; 2,4 = -10.5; 3,6 = -17.9; 4,12 = -19.2; 6,14 = -36.2	4 M $NaClO_4$	M≤0.5, pH=2-3.5	qh	[68DAN/MAG]
				2,2 = -5.5; 4,12 = -37.2	4 M $NaNO_3$	M≤0.5, pH=2-3.5	qh	[68DAN/MAG]

Table A1.1 continued.

log β_1	log β_2	log β_3	log β_4	Other Species log $\beta_{m,n}$	Medium	Concentration (Molarity) of metal, H	Method	References
				2,2=--4.9 to -5.2; 2,3 = -7.5 to -8.5	0.5 -3.0 M LiCl	M=n.a.,pH=2-3.5	E	[81ŠUR/MIL]
				2,2 = -4.9 to -5.1; 2,3 = -7.6 to -8.6	0.5 - 3.0 M MgCl	M≤0.01, pH=2-3.5	pol	[82ŠUR/MIL]
				2,2=-4.9 to -5.0; 2,3 = -7.6 to -8.4	0.5- 2.5 M CaCl	M≤0.01,pH=2-3.1	pol	[82ŠUR/MIL]
				2,2 = -5.5 to -4.9; 2,3 = -7.7 to -8.5	0.5 - 3.0 M SrCl	M≤0.01, pH=2-3.1	pol	[82ŠUR/MIL]
				2,2 = -5.6 to -4.9; 3,2 = -7.6 to -8.5	0.5 - 3.0 M BaCl	M≤0.01, pH = 2 - 3.1	pol	[82ŠUR/MIL]
				other[4]	0.6-3 M NaCl, 0.6 M KCl	M≤0.007 pC_H =3-11	sol	[91FEL/RAI]
				other[4]	0-6 m NaCl, 0-3 m $MgCl_2$	M<0.02,pC_H=2-5.5	sol	[97 RAI/FEL]

1: If m = 1, β_{mn} is written as β_n
2: T = 273.1 K
3: T = 368.1 K
4: No stability constants are given, but parameters for the Pitzer Equations are determined.
5: Several speciation models were used to calculate stability constants. The value listed is the summary and average of all the different models. Not all species listed were included in all of the models.

TableA1.2: Equilibrium constants (β_{mn})[1] for formation of aqueous Th^{4+} complexes with OH^- ($mTh^{4+} + nOH^- \rightleftharpoons Th_m(OH)_n^{4m-n}$): Mononuclear Species. (Stability Values for polynuclear species are rounded to the first decimal place)

log β_1	log β_2	log β_3	log β_4	Other Species log $\beta_{m,n}$	Medium	Concentration (Molarity) of metal, H	Method	References
12.42	22.46	34.36	42.58		0.1 M $NaClO_4$	$M \leq 0.03$, pH = 1.5 - 13	sol	[89MOO]
9.43	18.2	26.7	34.8		0.1 M $NaClO_4$	$M \leq 2.5E\text{-}3$, pH =3.4-7.0	sol	[64NAB/KUD]
11.64	22.44	33.06	43.51		0.5M $NaClO_4$	$M \leq 5E\text{-}7$, pH = 1-4	cix	[67BER]
12.58	22.33	34.42	42.76	2,2 = 30.0; 2,3 = 32.2; 2,4 = 59.1	0.5 M $NaClO_4$	$M \leq 0.03$, pH= 1.5 - 13	sol	[89MOO]
9.1	19.0	26.2	33.1		1.0 M $NaClO_4$	$M \leq 1E\text{-}4$, pH = 2 - 12	dis	[92ENG/ALB]

[1] If m = 1, β_{mn} is written as β_n

Table A1.3: Other equilibrium constants (β) for the following hydrolysis reactions of Th^{4+}

Reaction	Log β	Medium	Concentration (Molarity) of metal, H	Method	References
$Th((OH)_3Th)_n^{4+n} + Th^{4+} + 3H_2O \rightleftharpoons Th(OH)_3Th)_{n+1}^{5+n} + 3H^+$	-7.5	1 M $NaClO_4$	$M \leq 0.1$, pH=2-4.1	qh	[54HIE]

Table A1.4: Equilibrium constants (β_n) for formation of aqueous Th^{4+} complexes with Cl^- ($Th^{4+} + nCl^- = Th(Cl)_n^{4-n}$)

log β_1	log β_2	log β_3	log β_4	log β_5	Medium	Concentration (Molarity) of metal, ligand, H	Method	References
0.45					0	n.a.	ads	[76SOU/SHA][1]
0.35					0.5 M (H,Na)(ClO_4,Cl)	M≤0.1, L≤0.5, H=0.2	dis	[52WAG/STO]
0.25					0.5 M H(ClO_4, Cl)	M≤1E-6,L≤0.5,H=0.5	dis	[50DAY/STO]
0.25					0.7 M (H,Na)(ClO_4,Cl)	M≤0.1,L≤=4, H≤0.2	dis	[52WAG/STO]
0.18					1.0 M (H,Na)(ClO_4,Cl)	M≤0.1, L≤1, H=0.2	dis	[52WAG/STO]
0.11	-0.3				2.0M H(ClO_4, Cl)	M=trace,L=1, H=2	dis	[75PAT/RAM]
0.08	-1.0	-0.70			2.0 M (H,Na)(ClO_4,Cl)	M≤0.1, L≤2, H=0.2	dis	[52WAG/STO]
0.23	-0.85	-1.0	-1.74		4.0 M (H,Na)(ClO_4,Cl)	M≤0.1, L≤4, H=0.32	dis	[52WAG/STO]
0.11	-0.90	-1.43	-1.85		4.0 M (H,Na)(ClO_4,Cl)	M≤5E-4,L≤4, H=0.1	dis	[51ZEB/ALT]
0.20	-0.80	-0.85	-1.46	-2.46	4.0M H(NO_3, Cl)	M=1E-3, L≤4, H≤4	dis	[64NAB/KUD2]
0.32	-0.26	-0.46			6.0 M (Na)ClO_4	M≤0.1, L≤2, H=0.32	dis	[52WAG/STO]

[1] Used data from [76SOU/ABD]

Table A1.5: Pitzer ion-interaction parameters for Th(IV) and Chloride

Binary Interaction Parameters

Cation	Anion	β^0	β^1	β^2	C^{Φ}	Reference
Th^{4+}	Cl^-	1.014	13.3	-200	-0.103	[91FEL/RAI]
		1.092	13.7	-160	-0.112	[92ROY/VOG]

Ternary Interaction Parameters

Cation	Cation	θ	ψ with Cl^-	Reference
H^+	Th^{4+}	0.60	0.08	[92FEL/RAI]
		0.60	0.37	[92ROY/VOG]
Na^+	Th^{4+}	0.42	0.21	[97RAI/FEL]
NH_4^+	Th^{4+}	-0.44		[92FEL/RAI]
Mg^{2+}	Th^{4+}	0.60	0.21	[97RAI/FEL]

Table A1.6: Equilibrium constants (β_n) for formation of aqueous Th^{4+} complexes with HSO_4^- ($Th^{4+} + nHSO_4^- \rightleftharpoons Th(SO_4)_n^{4-2n} + nH^+$)

log β_1	log β_2	Medium	Concentration (Molarity) of metal, ligand, H	Method	References
2.3	3.4	1.7 M $HClO_4$	M=n.a., L=0.05, H=1.7	dis	[58MAI/FOM]
2.20	3.45	2.0 M $NaClO_4$	M=5E-4, L=0.04, H=2	dis	[51ZEB/ALT]
2.34[1]	3.59[1]	2.0 M $H(ClO_4, HSO_4)$	M=n.a., L$\leq$ 0.096, H = 2	dis	[72PAT/RAM]
2.26	3.56	2.0 M $H(ClO_4, HSO_4)$	M=n.a., L$\leq$ 0.096, H = 2	dis	[72PAT/RAM]
2.24[2]	3.5[2]	2.0 M H (ClO_4, HSO_4)	M=n.a., L$\leq$ 0.096, H = 2	dis	[72PAT/RAM]
2.22	3.56	2.00 M $(H, Na)ClO_4$	M=1E-5, L$\leq$ 0.2, H = 1 or 2	cix	[59ZIE]

1 T=283 K

2 T=313 K

Table A1.7: Equilibrium Constants (β) for the Formation of the Following Complexation Reactions of Aqueous Th^{4+} with HSO_4^{-1} and SO_4^{-2}

Reaction	log β	Medium	Concentration (Molarity) of metal, ligand, H	Method	Reference
$Th^{4+} + 2SO_4^{2-} \rightleftharpoons Th(SO_4)_2^0$	11.59	0	n.a.	recl	[92FEL/RAI]
$Th^{4+} + 3SO_4^{2-} \rightleftharpoons Th(SO_4)_3^{2-}$	12.42	0	n.a.	recl	[92FEL/RAI]
$Th^{4+} + 2HSO_4^- \rightleftharpoons Th(HSO_4SO_4)^+ + H^+$	- 2.9	2.0 M $NaClO_4$	M=5E-4, L$\leq$ 0.04, H = 0.09	dis	[51ZEB/ALT]
$Th(SO_4)_2^0 + SO_4^{2-} \rightleftharpoons Th(SO_4)_3^{2-}$	0.8	0-1.2 M $(Na_2, H_2)SO_4$	M=5E-3, L$\leq$ 1.2, H=0.19	dis	[63ALL/MCD]
$Th(SO_4)_3^{2-} + SO_4^{2-} \rightleftharpoons Th(SO_4)_4^{4-}$	-2.0	0-1.2 M $(Na_2, H_2)SO_4$	M=5E-3, L$\leq$ 1.2, H=0.19	dis	[63ALL/MCD]
$Th^{4+} + HSO_4^- + HNO_3^0 \rightleftharpoons Th(NO_3)(SO_4)^+ + 2H^+$	3.3	1.7 M $HClO_4$	M=n.a., L$\leq$ 0.05, H=1.7	dis	[58MAI/FOM]
$Th^{4+} + HSO_4^- + 2HNO_3^0 \rightleftharpoons Th(NO_3)_2(SO_4)^0 + 3H^+$	3.0	1.7 M $H(ClO_4, NO_3)$	M=n.a., $SO_4 \leq 0.05$, $NO_3 \leq 1.7$, H=1.7	dis	[58MAI/FOM]

Table A1.8: Pitzer ion-interaction parameters for Th and sulfate

Binary Interaction Parameters

Cation	Anion	β^0	β^1	β^2	C^Φ	Reference
H^+	$Th(SO_4)_3^{2-}$	0.84				[92FEL/RAI]
Na^+	$Th(SO_4)_3^{2-}$	0.12				[92FEL/RAI]
K^+	$Th(SO_4)_3^{2-}$	0.90				[92FEL/RAI]
Li^+	$Th(SO_4)_3^{2-}$	0.52				[92FEL/RAI]
NH_4^+	$Th(SO_4)_3^{2-}$	0.26				[92FEL/RAI]
Th^{4+}	HSO_4^-	1.44				[92FEL/RAI]
Th^{4+}	SO_4^{2-}	1.56				[92FEL/RAI]

Ternary Interaction Parameters

Cation	Cation	θ	ψ with SO_4^{2-}	Reference
H^+	Th^{4+}	0.60		[92FEL/RAI]
		0.60		[92ROY/VOG]
Na^+	Th^{4+}	0.42		[97RAI/FEL]
NH_4^+	Th^{4+}	-0.44	0.06	[92FEL/RAI]
Mg^{2+}	Th^{4+}	0.60		[97RAI/FEL]

Interaction Parameters for Neutral Aqueous Th^{4+} complexes

Neutral Ion	Charged Ion	λ	Reference
$Th(SO_4)_2$	Cl^-	0.29	[92FEL/RAI]
$Th(SO_4)_2$	HSO_4^-	0.68	[92FEL/RAI]

Table A1.9: Equilibrium constants (β) for the following complexation reactions of Th^{4+} with carbonate ($Th^{4+} + 5CO_3^{2-} \rightleftharpoons Th(CO_3)_5^{-6}$)

Reaction	log β	Medium	Concentration (Molarity) of metal, H, ligand	Method	Reference
$Th^{4+} + 5CO_3^{2-} \rightleftharpoons Th(CO_3)_5^{-6}$	32.33	0	n.a.	SIT	[94ÖST/BRU]
	32.75	0.5 M $NaClO_4$	$M \leq 1E\text{-}3$, pH =3-8, P_{CO2} = 10%, 100%	sol	[94ÖST/BRU]
	26.2	1 M $NH_4(NO_3, CO_3)$	$M \leq 1.1E\text{-}3$, L= 0.26 M, pH=10.2	dis	[87JOÅ/BIG]
	26.3	2.5 M $NH_4(NO_3, CO_3)$	$M \leq 1.1E\text{-}3$, L=0.5 M, pH=10.2	dis	[87JOÅ/BIG]

Table A1.10: Pitzer ion-interaction parameters for Th with carbonate

Binary Interaction Parameters

Cation	Anion	β^0	β^1	β^2	C^Φ	Reference
Na^+	$Th(CO_3)_5^{6-}$	1.31	30.0			[97FEL/RAI]

Ternary Interaction Parameters

Cation	Cation	θ	Reference
ClO_4^-	$Th(CO_3)_5^{6-}$	5.5 (proposed)	[97FEL/RAI]

Table A1.11: Equilibrium constants (β_n) for formation of aqueous Th^{4+} complexes with F^- ($Th^{4+} + nHF \rightleftharpoons ThF_n^{4-n} + nH^+$)

log β_1	log β_2	log β_3	log β_4	Medium	Concentration (Molarity) of metal, ligand, H	Method	References
4.7	7.5			0.5 M $NaClO_4$	n.a.	dis	[51ZEB/ALT]
4.6	7.5			0.5 M $HClO_4$	M=1E-6, L≤0.002, H=0.5	dis	[50DAY/STO]
4.65	7.46	8.96		0.5 M Na,$HClO_4$	M≤0.005,L≤0.018, H=0.3	red	[49DOD/ROL]
4.43				2.0 M H(ClO_4, Cl)	M=trace,L≤0.01, H=2	dis	[75PAT/RAM]
4.52	7.26	8.9		3 M (H, Na)(ClO_4, F)	M≤0.06,L<3, H≤1	ise-F	[71KLO/MUK]
4.68	7.65			4 M $HClO_4$	M=0.18M,L≤4.5E-3,H=4M	ise-F	[69NOR]
3.8	6.8	9.0	10.4	4 M HNO_3	M≤0.66M,L≤0.38M,H=4M	sol	[81SMI/MES]
3.7[1]	6.6[1]	8.6[1]	9.8[1]	4 M HNO_3	M≤ 0.52M,L≤0.30M,H=4M	sol	[81SMI/MES]
3.3[2]	6.0[2]	8.2[2]	9.8[2]	4 M HNO_3	M≤0.58M,L≤0.24M,H=4M	sol	[81SMI/MES]
3.2	5.9	8.2	10.1	8 M HNO_3	M≤0.47M,L≤0.10M,H=8M	sol	[81SMI/MES]
2.9[1]	5.4[1]	7.5[1]	9.2[1]	8 M HNO_3	M≤0.34M,L≤0.099M,H=8M	sol	[81SMI/MES]
2.9[2]	5.5[2]	7.9[2]	10.1[2]	8 M HNO_3	M≤0.50M,L≤0.18M,H=8M	sol	[81SMI/MES]
2.7	5.4	8.2	11.0	13 M HNO_3	M≤0.43M,L≤0.53M,H=13M	sol	[81SMI/MES]
2.8[1]	5.8[1]	9.1[1]	12.6[1]	13 M HNO_3	M≤0.42M,L≤0.04M,H=13M	sol	[81SMI/MES]
2.7[2]	5.5[2]	8.5[2]	11.6[2]	13 M HNO_3	M≤0.51M,L≤0.05M,H=13M	sol	[81SMI/MES]
			other[3]	1 M (Na, NH_4)F	M≤1E-5,L≤ 1,pH=4.2-6.5	sol	[93FEL/RAI]

[1] T = 323 K

[2] T = 373 K

[3] No stability constants are given, but parameters for the Pitzer Equations are determined.

Table A1.12: Equilibrium constants (β_n) for formation of aqueous Th^{4+} complexes with F^- ($Th^{4+} + nF^- \rightleftharpoons ThF_n^{4-n}$)

log β_1	log β_2	log β_3	log β_4	log β_5	log β_6	Medium	Concentration (Molarity) of metal, ligand, H	Method	References
		18.89	22.33	24.76	25.56	0^3 (1 M NaF, NH_4F)	M≤1E-5, L≤1, pH=4.2-6.5	sol	[93FEL/RAI]
8.46^1	15.01^1	19.82^1	23.23^1			0	n.a.	est	[70BAU]
8.44	15.06	19.81	23.17			0	n.a.	est	[70BAU]
8.32^2	14.80^2	19.53^2				0	n.a.	est	[70BAU]
8.11^1	14.40^1	19.04^1	22.37^1			0.01 M NH_4NO_3	M≤3.8E-4, L≤2.7E-4, H=1.2E-3	ise-F	[70BAU]
8.08	14.44	19.01	22.29			0.01 M NH_4NO_3	M≤3.8E-4, L≤2.7E-4, H=9.4E-4	ise-F	[70BAU]
7.95^2	14.15^2	18.70^2				0.01 M NH_4NO_3	M≤3.8E-4, L≤2.7E-4, H=1.5E-3	ise-F	[70BAU]
5.9	8.75					varied (H,Na,Ca)F, $Th(NO_3)_4$	M≤0.5, L≤0.45, H=0.45	sol	[59TAN/LU]
7.61	13.42	17.65	23.67			1 M NaF, $HClO_4$	M≤0.02, L≤0.048, H=0.48	ise-F	[90SAW/CHA]

1 T = 278 K

2 T = 373 K

3: Thermodynamic value calculated using data from medium listed in parenthesis.

Table A1.13: Pitzer ion-interaction parameters for Th with fluoride

Binary Interaction Parameters

Cation	Anion	β^0	β^1	β^2	C^ϕ	Reference
NH_4^+	ThF_6^{2-}	-1.3				[93FEL/RAI]

Table A1.14: Equilibrium constants (β_{mn})[1] for formation of aqueous Th^{4+} complexes with NO$_3^-$ (Th^{4+} + nNO$_3^-$ = Th(NO3)$_n^{4-n}$)

log β_1	log β_2	log β_3	log β_4	log β_5	log β_6	Medium	Concentration (Molarity) of metal, ligand, H	Method	References
0.40						0	M=n.a., L=1, H=1	ix	[76SOU/SHA]
0.67						0.5 M H(ClO$_4$, NO$_3$)	M=1E-6, L≤0.5, H=0.5	dis	[50DAY/STO]
1.22	1.5	1.1				2 M H(ClO$_4$, NO$_3$)	M=6.6E-5, L≤ 1, H=2	cix	[68TED/DER]
0.78	1.1	1.0	0.74			2 M H(ClO$_4$, NO$_3$)	M=trace, L≤ 2, H=2	dis	[56FOM/MAI]
0.55	0.32	-0.30	-0.72	-1.5	-2.4	4 M H(ClO$_4$, NO$_3$)	M=1E-3, L≤4, H=4	dis	[64NAB/KUD2]
0.45	0.15					5.97 M (H, Na)(ClO$_4$, NO$_3$)	M=5E-4, L≤ 4.9, H=2	dis	[51ZEB/ALT]

Table A1.15: Equilibrium constants (β) for formation of the following complexation reactions of aqueous Th^{4+} complexes with Phosphate

Reaction	Log β	Medium	Concentration (Molarity) of metal, ligand, H	Method	Reference
$Th^{4+} + H_3PO_4 \rightleftharpoons Th(H_3PO_4)^{4+}$	1.89	2.0 M (H, Na)ClO_4	M=5E-4, L≤ 0.01, H≤ 2	dis	[51ZEB/ALT]
$Th^{4+} + H_3PO_4 \rightleftharpoons Th(H_2PO_4)^{3+} + H^+$	2.18	2.0 M (H, Na)ClO_4	M=5E-4, L ≤ 0.01, H≤ 2	dis	[51ZEB/ALT]
$Th^{4+} + 2H_3PO_4 \rightleftharpoons Th(H_2PO_4H_3PO_4)^{3+} + H^+$	4.15	2.0 M (H, Na)ClO_4	M=5E-4, L ≤ 0..01, H≤ 2	dis	[51ZEB/ALT]
$Th^{4+} + 2H_3PO_4 \rightleftharpoons Th(H_2PO_4)_2^{2+} + 2H^+$	3.90	2.0 M (H, Na)ClO_4	M=5E-4, L ≤ 0.01, H≤ 2	dis	[51ZEB/ALT]
$Th(HPO_4)^{2+}$ [1]	10.8	0.35 M $HClO_4$, var. H_3PO_4	M<4E-4, L≤ 1.5, H≥0.35	sol	[67MOS/ESS]
$Th(HPO_4)_2$ [1]	22.8	0.35 M $HClO_4$, var. H_3PO_4	M<4E-4, L≤ 1.5, H≥0.35	sol	[67MOS/ESS]
$Th(HPO_4)_3^{2-}$ [1]	31.3	0.35 M $HClO_4$, var. H_3PO_4	M<4E-4, L≤ 1.5, H≥0.35	sol	[67MOS/ESS]
$Th^{4+} + 4H_2O + PO_4^{3-} \rightleftharpoons Th(OH)_4PO_4^{3-} + 4H^+$	-14.9	1.0 M $NaClO_4$	M≤ 3E-6, L≤ 0.1, pH=5-13	sol	[95ÖST]
$ThO(HPO_4)_3(H_2PO_4)^{5-}$	exists	KH_2PO_4, NaOH	M≤ 1.5E-6, L≤ 0.8, pH=5.9-8	sol	[94FOU/BAG]
$ThO(HPO_4)_3(H_2PO_4)_2^{6-}$	exists	KH_2PO_4, NaOH	M≤ 1.5E-6, L≤ 0.8, pH=5.9-8	sol	[94FOU/BAG]

[1] Reaction not given

Table A1.16: Equilibrium solubility product (K_{sp}) for the following Th^{4+} solid phases[1]

Reaction	Log K_{sp}	Medium	Concentration (Molarity) of metal, ligand, H	Method	References
$ThO_2(c)+2H_2O \rightleftharpoons Th^{4+} + 4OH^-$	-54.14	n.a.	n.a.	ΔG	[87RYA/RAI]
$ThO_2(lc)^2 + 4H^+ \rightleftharpoons Th^{4+} + 2H_2O$	7.31	0^3 (0.5 M $NaClO_4$)	M ≤ 1E-3,pH =3-8, P_{CO2} = 10%, 100%	SIT	[94ÖST/BRU]
	9.37	0.5 M $NaClO_4$	M ≤ 1E-3,pH =3-8, P_{CO2} = 10%, 100%	sol	[94ÖST/BRU]
$ThO_2(am)+2H_2O \rightleftharpoons Th^{4+} + 4OH^-$	-45.5	0^3 (0.6-3 M NaCl,0.6 M KCl)	M ≤ 0.007 pC_H=3-11	sol	[91FEL/RAI]
	-44.8	0.28-1.3 M LiOH, 0.1 M $NaClO_4$	M<0.02, OH = 0.28-1.38	sol	[87RYA/RAI]
$Th(OH)_4(s) \rightleftharpoons Th^{4+} + 4OH^-$	-44.7	0^3 (0-4 M KNO_3)	M=3.5E-3, pH=2.5-5	col	[61KOV/BAG]
	-45.7	KOH<0.2 M $Th(NO_3)_4$ ≤ 0.1 M	M<0.1, p[OH] = 1.7-3.7	sol	[63BIL/FGR]
	-41.1	0.1 M $NaClO_4$	M ≤ 2.5E-3, pH =3.4-7.0	sol	[64NAB/KUD]
	-50.76	0.1 M (H, Na)ClO_4	M ≤ 0.03,pH=1.5-13	sol	[89MOO]
$Th(OH)_4(s) \rightleftharpoons Th(OH)_2^{2+} + 2OH^-$	-24.3	KOH<0.2 M $Th(NO_3)_4$ ≤ 0.1 M	M<0.1,p[OH]=1.7-3.7	sol	[63BIL/FGR]
$Th(OH)_4(s) + H^+ + H_2O \rightleftharpoons Th(OH)_3^+$	3.3	0.1 M (H, Na)ClO_4	M ≤ 0.1,pH=1.1-7.4	pH	[80ZHI/KOL]
$ThO_2(s) + H^+ + H_2O \rightleftharpoons Th(OH)_3^+$	3.30	0.1 M $NaClO_4$	M ≤ 0.1,pH=1.1-7.4	pH	[80ZHI/KOL]
$ThO_2(s) + 2H_2O \rightleftharpoons Th(OH)_4^0$	6.66	0.1 M (H, Na)ClO_4	M ≤ 0.1,pH=1.1-7.4	pH	[80ZHI/KOL]
$ThO(OH)_2(s) + 2H^+ \rightleftharpoons ThO^{2+} + 2H_2O$	4.74	0.02-0.81 M $HClO_4$	M<0.36, H=0.02-0.81	sol	[54GAY/LEI]
$ThO(OH)_2(s) \rightleftharpoons ThO^{2+} + 2OH^-$	-23.3	0.01-0.865 M NaOH	M<2E-5, OH=0.01-0.865	sol	[54GAY/LEI]
$ThO_2(c) + H^+ + H_2O + CO_3^{2-} \rightleftharpoons Th(OH)_3CO_3^-$	6.78	0^3 (0.5 M $NaClO_4$)	M ≤ 1E-3,pH =3-8, P_{CO2} = 10%, 100%	SIT	[94ÖST/BRU]
	6.11	0.5 M $NaClO_4$	M ≤ 1E-3,pH =3-8, P_{CO2} = 10%, 100%	sol	[94ÖST/BRU]

Table A1.16 continued

Reaction	Log K_{sp}	Medium	Concentration (Molarity) of metal, ligand, H	Method	References
$ThO_2(c) + 4H^+ + 5CO_3^{2-} \rightleftharpoons Th(CO_3)_5^{6-} + 2H_2O$	39.64	0^3 (0.5 M $NaClO_4$)	M ≤ 1E-3, pH = 3-8, P_{CO2} = 10%, 100%	SIT	[94ÖST/BRU]
	42.12	0.5 M $NaClO_4$	M ≤ 1E-3, pH = 3-8, P_{CO2} = 10%, 100%	sol	[94ÖST/BRU]
$ThO_2(am) + 4H^+ + 5CO_3^{2-} \rightleftharpoons Th(CO_3)_5^{6-} + 2H_2O$	37.6	0	n.a.	recl	[97FEL/RAI]
$Th(SO_4)_2 \bullet 9H_2O \rightleftharpoons Th^{4+} + 2SO_4^{2-} + 9H_2O$	-13.00	0	n.a.	recl	[92FEL/RAI]
$Th(SO_4)_2 \bullet 8H_2O \rightleftharpoons Th^{4+} + 2SO_4^{2-} + 8H_2O$	-12.90	0	n.a.	recl	[92FEL/RAI]
$ThF_4 \bullet nH_2O + 4H^+ \rightleftharpoons Th^{4+} + 4HF(aq) + nH_2O$	-16.30	0^3 (1 M (Na, NH_4)F)	M ≤ 1E-5, L ≤ 0.001-1, pH=4.2-6.5	sol	[93FEL/RAI]
$ThF_4^0 + 4H^+ \rightleftharpoons Th^{4+} + 4HF$	-15.17	3 M (H, Na)ClO_4	M ≤ 0.06, L ≤ 0.5, H=1	ise-F	[71KLO/MUK]
$ThF_4(s) + 4H^+ \rightleftharpoons Th^{4+} + 4HF$	-16.2	4 M HNO_3	M≤0.66M, L≤0.38M, H=4M	sol	[81SMI/MES]
	-15.4^1	4 M HNO_3	M≤ 0.52M, L≤0.30M, H=4M	sol	[81SMI/MES]
	-14.6^2	4 M HNO_3	M≤0.58M, L≤0.24M, H=4M	sol	[81SMI/MES]
	-15.3	8 M HNO_3	M≤0.47M, L≤0.10M, H=8M	sol	[81SMI/MES]
	-14.3^1	8 M HNO_3	M≤0.34M, L≤0.099M, H=8M	sol	[81SMI/MES]
	-14.5^2	8 M HNO_3	M≤0.50M, L≤0.18M, H=8M	sol	[81SMI/MES]
	-15.4	13 M HNO_3	M≤0.43M, L≤0.53M, H=13M	sol	[81SMI/MES]
	-16.4^1	13 M HNO_3	M≤0.42M, L≤0.04M, H=13M	sol	[81SMI/MES]
	-15.6^2	13 M HNO_3	M≤0.51M, L≤0.05M, H=13M	sol	[81SMI/MES]

Table A1.16 continued

Reaction	Log K_{sp}	Medium	Concentration (Molarity) of metal, ligand, H	Method	References
$ThF_4 \cdot NaF \cdot H_2O(c) + 5H^+ \rightleftharpoons Th^{4+} + Na^+ + 5HF + H_2O$	-18.23	0^3 (1 M NaF)	M≤ 1E-5, L≤ 1, pH=4.2-6.5	sol	[93FEL/RAI]
$ThF_4 \cdot NH_4F(s) + 5H^+ \rightleftharpoons Th^{4+} + NH_4^+ + 5HF$	-18.09	0^3 (1 M NH_4F)	M≤ 1E-5, L≤ 1, pH=4.2-6.5	sol	[93FEL/RAI]
$Th_3(PO_4)_4(s) \rightleftharpoons 3Th^{4+} + 4PO_4^{3-}$	-78.6 -57.6	0.01 HNO_3	M < 4.5E-3, L≤ 4.5E-3,pH=1.6-2.05	sol lat	[56CHU/STE]
$Th(HPO_4)_2(s) \rightleftharpoons Th^{4+} + 2HPO_4^{2-}$	-21.0 -19.9	0.01 HNO_3	M < 4.5E-3, L ≤ 4.5E-3, pH=1.6-2.05	sol lat	[56CHU/STE]
$Th(HPO_4)_2 \cdot 4H_2O(s) \rightleftharpoons Th^{4+} + 2HPO_4^{2-} + 4H_2O$	-26.9	0.35 M $HClO_4$	M=1.4E-4, L≤ 0.03, H=0.35	sol	[67MOS/ESS]

1: T = 323 K

2: T = 373 K

3: Thermodynamic value calculated using data from medium listed in parenthesis.

URANIUM(IV)

Table A2.1: Equilibrium constants (β_{mn})^1 for formation of aqueous U^{4+} complexes with OH^- ($mU^{4+} + nH_2O \rightleftharpoons U_m(OH)_n^{4m-n} + nH^+$)^1

log β_1	log β_2	log β_3	log β_4	Other Species log $\beta_{m,n}$	Medium	Concentration (Molarity) of metal, H	Method	References
-1.11^2					0	n.a.	recl	[67SOL/TSV]
			-9.0		0(dilute NaCl)	M≤3E-4, pH=2-12	sol	[95YAJ/KAW]
-0.68					0^3 (0.017-2.0 M $NaClO_4$)	M≤0.012, H≤0.3	sp	[50KRA/NEL]
-0.50					var. NaOH	M≤0.01, pH=2-12	sol	[90RAI/FEL]
-2.5	-6.2	-10.4	-16.4		self (≤5.6e-4 M UF_4)	M≤1.4E-4, pH=3.5-4.6	pot, sol	[61NIK/LUK]
-1.4^4					0.19 M (Na, H)ClO_4	M=8.5e-3, H=0.104	sp	[55BET]
-1.1					0.19 M (Na, H)ClO_4	M=8.5e-3, H=0.104	sp	[55BET]
-1.44 to -1.72					0.25 m $HClO_4$ to 1.09 m $HClO_4$	n.a.	sp	[78NIK]^5
-1.90^6					0.50 M (Na, H)ClO_4	M=7.3e-4, H=0.002-0.512	sp	[55KRA/NEL]
-1.00^7					0.50 M (Na, H)ClO_4	M=7.3e-4, H=0.04-0.512	sp	[55KRA/NEL]
		-1.1	-5.4		0.5 M $NaClO_4$	M<0.001, pH=2-10.5	sol	[87BRU/CAS]
-0.56 to -1.00^8					0.51 m $HClO_4$ to 1.09 m $HClO_4$	n.a.	sp	[78NIK]^5
-0.25 to -0.55^9					0.51 m $HClO_4$ to 1.2 m $HClO_4$	n.a.	sp	[78NIK]^5
-0.21 to -0.56^{10}					0.65 m $HClO_4$ to 1.68 m $HClO_4$	n.a.	sp	[78NIK]^5
-1.57					0.93 M (Li, H)ClO_4 0.07 M HNO_3	M=0.04, H≤0.05	sp	[64MCK/WOO]

Table A2.1 continued[1]

$\log \beta_1$	$\log \beta_2$	$\log \beta_3$	$\log \beta_4$	Other Species $\log \beta_{m,n}$	Medium	Concentration (Molarity) of metal, H	Method	References
-0.09 to -0.43[11]					1.09 m $HClO_4$ to 1.68 m $HClO_4$	n.a.	sp	[78NIK][5]
-1.68					2.00 M (Na, H) ClO_4	M=n.a., H=0.05	sp	[59SUL/HIN]
-1.65	<-4.5				3.00 M $NaClO_4$	M=1e-5, H=0.0015-1	tls	[89GRE/BID]
-2.1[12]				6:15 = -16.9[12]	3.00 M $NaClO_4$	n.a.	recl	[76BAE/MES]
-1.95				(1+n):3n =-1.22 - 3.4n	3.00 M $NaClO_4$	M≤0.035, H=0.005-0.18	pot	[56HIE] [56HIE2]
				1:5 ≤ -22.7	0.045-10.5 M NaOH	M≤1.5E-4, OH≤10.5	sol	[83RYA/RAI]

1 Information obtained with the aid of the compilation in [92WAN/FOR]
2 recalculated using data from [50KRA/NEL]
3 Thermodynamic value calculated using data from medium listed in parenthesis.
4 T = 288 K
5 Values are from summary in [92WAN/FOR]
6 T = 316
7 T = 316 K
8 T = 348 K
9 T = 373 K
10 T = 398 K
11 T = 423 K
12 recalculated using data from [56HIE/SIL]

Table A2.2: Equilibrium constants (β_{mn})[1] for formation of aqueous U^{4+} complexes with OH^- ($mU^{4+} + nOH^- \rightleftharpoons U_m(OH)_n^{4m-n}$)[1]

log β_1	log β_2	log β_3	log β_4	Other Species log $\beta_{m,n}$	Medium	Concentration (Molarity) of metal, H	Method	References
12.5	23.9				0.001-0.5 M HCl	M≤0.05,H=0.001-0.5	sp	[75DAV/EFR]
	-26.2[2]				n.a.	n.a.	recl	[69VDO/STE]
12.5					n.a.	M=0.03,pH=0.4-2.0	prx	[63VDO/ROM]
12.5	23.9				0.5 M (NH_4, H)Cl 0.5 M (Na, H)ClO_4	M≤1E-5, H=0.001-0.5	sp	[75DAV/EFR]

[1] Information obtained with the aid of the compilation in [92WAN/FOR]

[2] recalculated using data from [63VDO/ROM]

Table A2.3: Pitzer ion-interaction parameters for U(IV) with hydroxide

Binary Interaction Parameters

Cation	Anion	β^0	β^1	β^2	C^Φ	Reference
UOH^{3+}	Cl^-	1.00	7.856	0	0.0	[97RAI/FEL]

Table A2.4: Equilibrium constants (β_n) for formation of aqueous U^{4+} complexes with Cl^- ($U^{4+} + nCl^- \rightleftharpoons U(Cl)_n^{4-n}$)[1]

log β_1	log β_2	Medium	Concentration (Molarity) of metal, ligand, H	Method	References
1.3		0	n.a.	rev	[78LAN]
3.0		0	n.a.	rev	[80LEM/TRE]
2.6		0[2]	n.a.	E	[77NIK]
0.85		0[3] (0.024 to 2 M HCl)	M≤0.012, L≤2,H≤0.3	E	[50KRA/NEL]
0.60		0.25 M $H(Cl,ClO_4)$	M = 0.13, L ≤ 0.18, H=0.25	E	[61SOB]
0.47		0.64 $H(Cl,ClO_4)$	M = 0.13, L ≤ 0.48, H=0.64	E	[61SOB]
0.40		1 M $H(Cl,ClO_4)$	M = 0.13, L ≤ 0.71, H=1	E	[61SOB]
0.30		1 M (H,Na)(Cl, ClO_4)	M≤0.06, L≤0.5, H=0.6	E	[54AHR/LAR2]
0.33		1.44 M $H(Cl,ClO_4)$	M≤0.06, L≤0.98, H=1.4	E	[61SOB]
0.52[4]		2 M (H,Na)(Cl, ClO_4)	M≤0.0037, L≤2, H=1	dis	[55DAY/WIL]
0.08	0.06	2 M (H,Na)(Cl, ClO_4)	M≤0.0037, L≤2, H=1	dis	[55DAY/WIL]
-0.04[5]	-0.10[5]	2 M (H,Na)(Cl, ClO_4)	M≤0.0037, L≤2, H=1	dis	[55DAY/WIL]
-0.51		2.06 M H(ClO_4, Cl.)	M≤3E-4, L≤2, H=2.06	cix	[74BUN]
0.78		~ 2.5 M (H, Na)(Cl,ClO_4)	M=0.077, L≤0.5, H=2	nmr	[63VDO/ROM3]
0.26		2.25 M $H(Cl,ClO_4)$	M=0.077, L≤1.43, H=2.25	E	[61SOB]
-0.12		3.0 M H(ClO_4, Cl)	M≤3e-4, L≤2, H=3	cix	[74BUN]
0.01		3.93 M H(ClO_4, Cl)	M≤3e-4, L≤2, H=3.93	cix	[74BUN]
[6]		0.01-6 m NaCl, 1-3 m $MgCl_2$	M≤0.01, L≤6 H≤0.01	sol	[97RAI/FEL]

[1] Information obtained with the aid of the compilation in [92WAN/FOR]

2 Thermodynamic value at 298 K has been calculated by the formula given by the author which models temperature effect from 298 to 423 K. Values taken from [92WAN/FOR]

3 Thermodynamic value calculated using data from medium listed in parenthesis.

4 T = 283 K

5 T = 313 K

6 Authors calculated Pitzer parameters from the data

Table A2.5: Pitzer ion-interaction parameters for U(IV) with chloride

Binary Interaction Parameters

Cation	Anion	β^0	β^1	β^2	C^Φ	Reference
U^{4+}	Cl^-	1.644	15.5	0	0.1	[97RAI/FEL]
UOH^{3+}	Cl^-	1.00	7.856	0	0.0	[97RAI/FEL]

Table A2.6: Equilibrium constants (β_n) for formation of aqueous U^{4+} complexes with HSO_4^- ($U^{4+} + nHSO_4^- \rightleftharpoons U(SO_4)_n^{4-2n} + nH^+$)[1]

log β_1	log β_2	Medium	Concentration (Molarity) of metal, ligand, H	Method	References
2.53	2.40	2 M (H, Na)ClO_4	M=0.0035, L≤0.092, H≤1.99	dis	[50BET/LEI]
2.41[2]	3.72[2]	2 M $HClO_4$	n.a.	recl	[52SUL/HIN]
2.63[3]	3.97[3]	2 M (H, Na)ClO_4	M≤0.0037, L≤0.1, H=1	dis	[55DAY/WIL]
2.52	3.87	2 M (H, Na)ClO_4	M≤0.0037, L≤0.1, H=1	dis	[55DAY/WIL]
2.38[4]	3.76[4]	2 M (H, Na)ClO_4	M≤0.0037, L≤0.1, H=1	dis	[55DAY/WIL]
2.36	3.73	3.8 M (Na,H)(ClO_4, NO_3) NO_3 = 1 M	M=0.01, L≤0.1, H=1	dis	[69RAO/PAI]

1 Information obtained with the aid of the compilation in [92WAN/FOR]
2 Recalculation of data from [50BET/LEI]
3 T=283 K
4 T=313 K

Table A2.7: Equilibrium constants (β_n) for Formation of aqueous U^{4+} complexes with SO_4^{2-} ($U^{4+} + nSO_4^{-} = U(SO_4)_n^{4-2n}$)[1]

log β_1	log β_2	Medium	Concentration (Molarity) of metal, ligand, H	Method	References
5.46	9.75	0	n.a.	rev	[78LAN]
5	10	0	n.a.	rev	[80LEM/TRE]
8.0	10.9	0[2] (0.4-2 M $NaClO_4$)	n.a.	pot	[77NIK/TSV][3]
5.1	6.8	0.4 M $NaClO_4$	n.a.	pot	[77NIK/TSV][3]
4.5	5.7	1.1 M $NaClO_4$	n.a.	pot	[77NIK/TSV][3]
4.3	5.4	1.4 M $NaClO_4$	n.a.	pot	[77NIK/TSV][3]
4.1	5.3	1.6 M $NaClO_4$	n.a.	pot	[77NIK/TSV][3]
4.0	5.2	1.8 M $NaClO_4$	n.a.	pot	[77NIK/TSV][3]
1.70		2 M $HClO_4$	$M=0.127, L \leq 0.33, H=2$	nmr	[63VDO/ROM3]
3.8	4.9	2 M $NaClO_4$	n.a.	pot	[77NIK/TSV][3]

1 Information obtained with the aid of the compilation in [92WAN/FOR]

2 Thermodynamic value calculated using data from medium listed in parenthesis.

3 Value at 298 K has been calculated by the formula given by the author which models temperature effect from 298 to 423 K. Values taken from [92WAN/FOR]

Table A2.8: Equilibrium constants (β) for the following complexation reactions of U^{4+} with carbonate ($U^{4+} + 5CO_3^{2-} \rightleftharpoons U(CO_3)_5^{-6}$)[1]

Reaction	log β	Medium	Concentration (Molarity) of metal, ligand, H	Method	Reference
$U^{4+} + 5CO_3^{2-} \rightleftharpoons U(CO_3)_5^{6-}$	34.0[2]	0	n.a.	recl	[92WAN/FOR]
	31.29	0[3](3E-4-5M $(Na/K)_2CO_3$, 0.01-1.0 M (Na/K)OH	M<0.01,L≤5,OH≤1	sp,dis,xas	[98RAI/FEL]
	40.0	3 M $NaClO_4$	M≤0.01, pH=8-9, CO_2=0.02-0.1 atm	sp, E	[83CIA/FER]
	36.86[2]	3 M $NaClO_4$	n.a.	recl	[92WAN/FOR]
$U^{4+} + 2CO_3^{2-} + 2OH^- \rightleftharpoons U(OH)_2(CO_3)_2^{2-}$	41.33	0[3](3E-4-5M $(Na/K)_2CO_3$, 0.01-1.0 M (Na/K)OH	M<0.01,L≤5,OH≤1	sp,dis,xas	[98RAI/FEL]
$U(CO_3)_4^{4-} + CO_3^{2-} \rightleftharpoons U(CO_3)_5^{6-}$	-1.12	0[3] (0.51-3.5 M $NaClO_4$)	n.a.	SIT	[89BRU/GRE]
	-0.86	0.51 M $NaClO_4$	M≤2.2e-3, L ≤0.24, pH=7.3-8.9	sp	[89BRU/GRE]
	-1.16	1.05 M $NaClO_4$	M≤4.4e-3, L ≤0.19, pH=7.3-9.3	sp	[89BRU/GRE]
	-0.96	2.21 M $NaClO_4$	M≤4.4e-3, L ≤0.08, pH=6.9-9.1	sp	[89BRU/GRE]
	-0.59	3.50 M $NaClO_4$	M≤4.3e-3, L ≤0.09, pH=7.0-9.3	sp	[89BRU/GRE]

1 Information obtained with the aid of the compilation in [92WAN/FOR]
2 Value recalculated using data from [83CIA/FER]
3 Thermodynamic value calculated using data from medium listed in parenthesis.

Table A2.9: Pitzer ion-interaction parameters for U and carbonate
Binary Interaction Parameters

Cation	Anion	β^0	β^1	β^2	C^Φ	Reference
Na^+	$U(SO_4)_5^{6-}$	1.5	31.3			[98RAI/FEL]
K^+	$U(SO_4)_5^{6-}$	1.5	31.3			[98RAI/FEL]

Table A2.10: Equilibrium constants (β_n) for formation of aqueous U^{4+} complexes with F^- $mU^{4+} + nHF \rightleftharpoons UF_n^{4-n} + nH^+$)[1]

log β_1	log β_2	log β_3	log β_4	Medium	Concentration (Molarity) of metal, ligand, H	Method	References
5.02[2]	7.98[2]	9.48[2]	10.64[2]	1 M (Na, H)Cl	n.a.	recl	[92WAN/FOR]
4.82				1 M $HClO_4$	n.a.	ise-F	[76CHO/UNR]
~6	~ 8			2 M (H, Na)(ClO_4, F)	n.a.	dis	[55DAY/WIL]
5.37	8.29	9.45		4.0 M (H, Na)ClO_4	M≤0.12, L≤0.045, H=0.6	red	[69GRE/VAR]
5.54	8.72	10.68		4 M $HClO_4$	M≤0.011, L≤0.03, H=4	ise-F	[69NOR]

1 Information obtained with the aid of the compilation in [92WAN/FOR]
2 Corrected for Cl^- complexation by [92WAN/FOR]

Table A2.11: Equilibrium constants (β_n) for formation of aqueous Th^{4+} complexes with F^- ($U^{4+} + nF^- \rightleftharpoons UF_n^{4-n}$)[1]

log β_1	log β_2	log β_3	log β_4	Medium	Concentration (Molarity) of metal, ligand, H	Method	References
7.3	13.1	17.5	21.8	1 M (Na,H)Cl	M≤0.01, L≤1e-4, H>0.1	ise-F^-	[74KAK/ISH]
8.48	14.66	19.51	23.92	1 M NaF, $HClO_4$	M≤0.02, L≤0.048, H=0.48	ise-F	[90SAW/CHA]
7.15	12.4	17.7	23.1	2 M $HClO_4$	M=0.025, L≤ 0.075, H=1	nmr	[63VDO/ROM2]

1 Information obtained with the aid of the compilation in [92WAN/FOR]

Table A2.12: Equilibrium constants (β_n) for formation of aqueous U^{4+} complexes with NO_3^- ($U^{4+} + nNO_3^- \rightleftharpoons U(NO3)_n^{4-n}$)[1]

log β_1	log β_2	log β_3	log β_4	Medium	Concentration (Molarity) of metal, ligand, H	Method	References
0.04	-0.30			1.0 M $H(ClO_4,NO_3)$	M=0.014, L≤1.07, H=1	sp	[64MCK/WOO]
0.06	0.00			1.0 M $H(ClO_4,NO_3)$, 1.0 M $Li(ClO_4,NO_3)$	M=0.014, L≤2.07, H=1	sp	[64MCK/WOO]
0.20	0.17	-0.018	-0.46	2.0 M $H(ClO_4,NO_3)$	M=0.019, L≤2, H=2	sp	[62ERM/KRO]
0.21	0.19	0.025	-0.31	2.5 M $H(ClO_4,NO_3)$	M=0.019, L≤2.5, H=2.5	sp	[62ERM/KRO]
0.28	0.31	0.17	-0.15	3.0 M $H(ClO_4,NO_3)$	M=0.019, L≤3, H=3	sp	[62ERM/KRO]
0.22	0.18	-0.17	-0.40	3 M $H(ClO_4,NO_3)$	M=0.013, L≤1.8, H=3	pot	[85GUO/LIU]
0.20	0.30			1.0 M $H(ClO_4,NO_3)$, 2.0 M $Li(ClO_4,NO_3)$	M=0.014, L≤3.07, H=1	sp	[64MCK/WOO]
0.36	0.47	0.42	0.18	3.5 M $H(ClO_4,NO_3)$	M=0.019, L≤3, H=3.5	sp	[62ERM/KRO]
0.30	0.42	0.38	0.18	3.5 M $H(ClO_4,NO_3)$	M=0.019, L≤3, H=1	cix	[62ERM/KRO]
0.08				3.8 M $(H,Na)(ClO_4,NO_3)$	M=0.01, L≤3.8, H=1	dis	[69RAO/PAI]
0.18	0.78			1.0 M $H(ClO_4,NO_3)$, 3.0 M $Li(ClO_4,NO_3)$	M=0.014, L≤4.07, H=1	sp	[64MCK/WOO]
-0.08	0.58	-0.43	-0.30	8 M $H(ClO_4,NO_3)$	M=trace, L≤1.0, H=8	dis	[70LAH/KNO]

[1] Information obtained with the aid of the compilation in [92WAN/FOR]

Table A2.13: Equilibrium solubility product (K_{sp}) for the following U^{4+} solid phases[1]

Reaction	Log K_{sp}	Medium	Concentration (Molarity) of metal, ligand, H	Method	References
$UO_2 \bullet xH_2O(am) \rightleftharpoons U^{4+} + 4OH^- + (x-2)H_2O$	-52.0	dilute NaOH	M≤0.01, pH=2-12	sol	[90RAI/FEL]
	-53.45[2]	0 (0.01-6 m NaCl, 1-3 m $MgCl_2$)	M≤0.01, H≤0.01	sol	[97RAI/FEL]
$UO_2(c) + 4H^+ \rightleftharpoons U^{4+} + 2H_2O$	0.34	dilute NaCl	M≤3E-4, pH=2-12	sol	[95YAJ/KAW]
	-1.6	0 (3 M $NaClO_4$)	M≤0.004, H≤0.05	SIT	[86BRU/FER]
	-1.2	3 M $NaClO_4$	M≤0.004, H≤0.05	pot	[86BRU/FER]
$UO_2(c) + 2H_2O \rightleftharpoons U(OH)_4^0$	-8.7	0(dilute NaCl)	M≤3E-4, pH=2-12	sol	[95YAJ/KAW]
	-9.47[3]	0.02 LiCl	M≤2e-7, pH=1-10	sol	[88PAR/POH]
$UO_2(c) + 2H_2O + OH^- \rightleftharpoons U(OH)_5^-$	-5.8[4]	0.003 and 0.03 LiOH	M<1e-7, pOH = 1.5, 2.5	sol	[81TRE/CHE]
$UO_2 \bullet xH_2O(s) + 3H^+ \rightleftharpoons UOH^{3+} + (x+1)H_2O$	3.5	dilute NaOH	M≤0.01, pH=2-12	sol	[90RAI/FEL]
	0.72	0.5 M $NaClO_4$	M≤0.03,pH=2-5	cop	[85BRU/GRE]
$U(OH)_4(s) + OH^- \rightleftharpoons H_3UO_4^- + H_2O$	-3.77	0.04-0.39 m $HClO_4$	M=0.21, H=0.04-0.39	sol	[57GAY/LEI]
$UO_2(am) + 4H^+ + 5CO_3^{2-} \rightleftharpoons U(CO_3)_5^{6-} + 2H_2O$	33.8	0[3](3E-4-5M (Na/K)$_2$CO$_3$, 0.01-1.0 M (Na/K)OH	M<0.01,L≤5,OH≤1	sp,dis,xas	[98RAI/FEL]
$UO_2(am) + 2HCO_3^- \rightleftharpoons U(OH)_2(CO_3)_2^{2-}$	-4.8	0[3](3E-4-5M (Na/K)$_2$CO$_3$, 0.01-1.0 M (Na/K)OH	M<0.01,L≤5,OH≤1	sp,dis,xas	[98RAI/FEL]
	[5]	0-7.4 NaOH	M≤8.4e-5, OH≤7.4	sol	[60GAL/STE]
$NaH_3UO_4 + H_2O \rightleftharpoons U(OH)_4^0 + NaOH$	exists	0-7.4 NaOH	M≤8.4e-5, OH≤7.4	sol	[60GAL/STE]
$UF_4 \bullet 2.5H_2O(cr) \rightleftharpoons UF_2^{2+} + 2F^- + 2.5H_2O$	-12.45	0.12 m $HClO_4$	M≤0.0014, L≤0.015, H=0.12	sol	[60SAV/BRO]
$UF_4 \bullet 2.5H_2O(cr) \rightleftharpoons UF_3^+ + F^- + 2.5H_2O$	-8.24	0.12 m $HClO_4$	M≤0.0014, L≤0.015, H=0.12	sol	[60SAV/BRO]
$UF_4 \bullet 2.5H_2O(cr) \rightleftharpoons UF_4^0(aq) + 2.5H_2O$	-3.96	0.12 m $HClO_4$	M≤0.0014, L≤0.015, H=0.12	sol	[60SAV/BRO]

Table A2.13 Continued[1]

Reaction	Log K_{sp}	Medium	Concentration (Molarity) of metal, ligand, H	Method	References
$UF_4 \bullet 2.5H_2O(cr) + F^- \rightleftharpoons UF_5^- + 2F^- + 2.5H_2O$	-2.39	0.12 m $HClO_4$	M≤0.0014, L≤0.015, H=0.12	sol	[60SAV/BRO]
$UF_4 \bullet 2.5H_2O(cr) + 2F^- \rightleftharpoons UF_6^{2-} + 2F^- + 2.5H_2O$	-0.08	0.12 m $HClO_4$	M≤0.0014, L≤0.015, H=0.12	sol	[60SAV/BRO]
$U(OH)_2SO_4 \rightleftharpoons U^{4+} + 2OH^- + SO_4^{2-}$	-31.2	0.01 M $(NH_4,H,U)SO_4$	M=0.002,L=0.008,H=0.0013	pot	[62STE/GAL]
$U(HPO_4)_2 \bullet 4H_2O(c) + 4H^+ \rightleftharpoons U^{4+} + 2H_3PO_4 + 4H_2O$	-9.96	0.35 $MHClO_4$, H_3PO_4	M≤1e-4,L≤1, H=0.35	sol	[92WAN/FOR][6]
	-11.79	0	n.a.	SIT	[92WAN/FOR][6]

1 Information obtained with the aid of the compilation in [92WAN/FOR]
2 Thermodynamic value calculated using data in the medium listed in parenthesis
3 T = 373 to 573 K, P = 50 Mpa.
4 T = 298-373 C,
5 confirmed value of [57GAY/LEI] up to 0.5 N NaOH
6 Value recalculated from data presented in [67MOS/ESS][64MAR/VER].

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Table A3.1: Equilibrium constants (β_n) for formation of aqueous Np^{4+} complexes with OH^- ($Np^{4+} + nH_2O \rightleftharpoons Np(OH)_n^{4-n} + nH^+$)

log β_1	log β_2	log β_4	log β_5	Medium	Concentration (Molarity) of metal, H	Method	References
-0.50				0[1] (0.1-5.0 M NaCl, $NaClO_4$)	M=120 cpm,H≤0.01	dis	[97XIA/RAO]
0.37	-0.91			0	n.a.	est	[77DUP/GUI]
			<-24.7	0.05 M $Na_2S_2O_4$	M=1E-3, pH=6-14.2	sol	[85RAI/RYA]
-0.52	-1.5			1 M (Li, H)ClO_4	M=n.a.,pH=0-3	dis	[77DUP/GUI]
-2.25				1 M $HClO_4$	M≤1E-3, H = 1 M	sp	[78FED/PER]
		-9±1		1 M $HClO_4$	M ≤3E-7, pH=10-13	sol	[85EWA/GOR]
-2.30				2 M (Na, H)ClO_4	M≤2.7E-3, pH >1.0	sp	[59SUL/HIN]

1 Thermodynamic value calculated using data from medium listed in parenthesis.

Table A3.2: Pitzer ion-interaction parameters for Np(IV) and hydroxide

Binary Interaction Parameters

Cation	Anion	β^0	β^1	β^2	C^ϕ	Reference
$NpOH^{3+}$	Cl^-	1.0	7.856	0	0	[97XIA/RAO]
$NpOH^{3+}$	ClO_4^-	1.0	7.856	0	0	[97XIA/RAO]

Table A3.3: Equilibrium constants (β_n) for formation of aqueous Np^{4+} complexes with Cl^- ($Np^{4+} + nCl^- \rightleftharpoons Np(Cl)_n^{4-n}$)

log β_1	log β_2	log β_3	Medium	Concentration (Molarity) of metal, ligand, H	Method	References
0.34			0	n.a.	ads	[76SOU/SHA][1]
0.15			0.5 M H(Cl, ClO_4)	M=1E-5, L≤0.5, H=0.5	dis	[66SHI/NAZ]
-0.04	-0.24	-0.48	1.0 M H(Cl, ClO_4)	M=1E-5, L≤1.0 H=1.0	dis	[66SHI/NAZ]
0.01	-0.15		2.0 M H(Cl, ClO_4)	M=1E-5, L≤2.0, H=2.0	dis	[66SHI/NAZ]
-0.28			0 - 3.7 M Cl	M=n.a.,L=0-3.7M,H=n.a.	sp	[62SYK/TAY]
-0.05	-0.15		2 M H(ClO_4, Cl)	M=trace, L≤1.0,H=2	dis	[75PAT/PAM]
-0.11	-0.10		4 M (Na, H)(ClO_4, Cl)	M≤0.045,L≤4 M, H= 1M	dis	[71DAN/CHI]
2.12	3.0		9 M H(ClO_4, Cl)	M=2E-3, L≤1.0, H=9M	sp	[73BAR/MUR]

[1] Used data from [76SOU/ABD]

Table A3.4: Pitzer ion-interaction parameters for Np(IV) and chloride and perchlorate

Binary Interaction Parameters

Cation	Anion	β^0	β^1	β^2	C^Φ	Reference
Np^{4+}	Cl^-	1.644	15.5	0	0.0995	[97XIA/RAO]
Np^{4+}	ClO_4^-	1.644	15.5	0	0.0995	[97XIA/RAO]
$NpOH^{3+}$	Cl^-	1.0	7.856	0	0	[97XIA/RAO]

Table A3.5: Equilibrium constants (β_n) for formation of aqueous Np^{4+} complexes with HSO_4^- ($Np^{4+} + nHSO_4^- \rightleftharpoons Np(SO_4)_n^{4-2n} + nH^+$)

$\log \beta_1$	$\log \beta_2$	Medium	Concentration (Molarity) of metal, ligand, H	Method	References
2.43	3.47	2.0 M $H(ClO_4, HSO_4)$	$M \leq 3E\text{-}4$, $L \leq 0.13$, H=2	dis	[54SUL/HIN]
2.49	3.51	2.0 M $H(ClO_4, HSO_4)$	M=n.a., $L \leq 0.096$, H=2	dis	[73PAT/RAM]
2.53	4.04	2.0 M $H(ClO_4, HSO_4)$	M=n.a.,$L \leq 0.096$, H=2	dis	[76BAG/RAM]
2.49	3.58	3.0 M $(H, Na)(ClO_4, HSO_4)$	M=1E-4,$L \leq 0.25$, H<0.25	pol	[63MUS]
2.70	4.26	4.0 M $HClO_4$	$M \leq 0.02$, $L \leq 0.5$, H=4	cix	[66AHR/BRA]

1 Thermodynamic value calculated using data from medium listed in parenthesis.

Table A3.6: Equilibrium constants (β_n) for formation of aqueous Np^{4+} complexes with SO_4^{2-} ($Np^{4+} + nSO_4^{2-} \rightleftharpoons Np(SO_4)_n^{4-2n}$)

$\log \beta_1$	$\log \beta_2$	Medium	Concentration (Molarity) of metal, ligand, H	Method	References
9.0	11.7	0[1] (0.1-5 M NaCl, $NaClO_4$)	M=120 cpm,$L \leq 0.008$,$H \leq 0.01$	dis	[97XIA/RAO]
3.51		2.0 M $NaClO_4$	n.a.	sp	[62SYK/TAY]

Table A3.7: Pitzer ion-interaction parameters for NP(IV) and sulfate

Binary Interaction Parameters

Cation	Anion	β^0	β^1	β^2	C^Φ	Reference
Cl^-	$NpSO_4^{2+}$	1.64	0	0	-0.2635	[97XIA/RAO]
ClO_4^-	$NpSO_4^{2+}$	1.735	0	0	-0.2635	[97XIA/RAO]

Interaction Parameters for Neutral Aqueous Th^{4+} complexes

Neutral Ion	Charged Ion	λ	Reference
$Np(SO_4)_2^0$	Cl^-	0.29	[97XIA/RAO]
$Np(SO_4)_2^0$	ClO_4^-	0.81	[97XIA/RAO]

Table A3.8: Equilibrium constants (β) for the following complexation reactions of Np^{4+} with carbonate

Reaction	log β	Medium	Concentration (Molarity) of metal, H	Method	Reference
$Np(OH)_4 + CO_3^{2-} \rightleftharpoons Np(OH)_4CO_3^{2-}$	53.08	0-2.2 M $(NH_4)_2CO_3$	M≤0.022, L≤ 2.2 M,pH=8.7	sol	[71MOS4]
$Np^{4+} + nCO_3^{2-} \rightleftharpoons Np(CO_3)_n^{4-2n}$	n=1: < 22.5 n=2: < 27.9 n=3: < 33.2 n=4: < 38.5 n=5: < 41.6	0.05 M $Na_2S_2O_4$	M=0.001, L=0.01, pH =6-14.2	sol	[85RAI/RYA]

Table A3.9: Equilibrium constants (β_n) for formation of aqueous Np^{4+} complexes with F^- ($Np^{4+} + nHF \rightleftharpoons NpF_n^{4-n} + nH^+$)

log β_1	log β_2	log β_3	log β_4	Medium	Concentration (Molarity) of metal, ligand, H	Method	References
8.17	14.52	20.05	25.95	1.0 M (H, Na)ClO_4	M≤6E-3,L≤8.2E-3,H≤0.93	ise-F	[90SAW/CHA]
4.56				1.0 M $HClO_4$	M=6.4E-8,L≤3.2E-2,H=1.0	ix	[69KRY/KOM3]
4.23				1.0 M HNO_3	M=6.4E-8,L≤3.2E-2,H=1.0	ix	[69KRY/KOM4]
4.70				2.0 M $HClO_4$	M=6.4E-8, L≤3.2E-2, H=2.0	ix	[69KRY/KOM3]
4.60	7.49			2.0 M $HClO_4$	M=trace, L≤0.01, H=2	dis	[75PAT/RAM]
4.70	7.38			2.0 M $HClO_4$	M=n.a, L≤8E-4, H=2	dis	[76BAG/RAM]
4.11				2.0 M HNO_3	M=6.4E-8,L≤3.2E-2,H=2.0	ix	[69KRY/KOM4]
4.82	7.57			4.0 M $HClO_4$	M≤0.02, L≤0.015, H=4	cix	[66AHR/BRA]
	7.51	9.85	~11.15	4.0 M $HClO_4$	M≤0.02, L≤0.04, H=4	red	[66AHR/BRA]

Table A3.10: Equilibrium Constants (β_n) for Formation of Aqueous Np^{4+} complexes with NO_3^- ($Np^{4+} + nNO_3^- \rightleftharpoons Np(NO_3)_n^{4-n}$)

log β_1	log β_2	log β_3	log β_4	Medium	Concentration (Molarity) of metal, ligand, H	Method	References
0.45				0-0.89 M HNO_3	M=n.a.,$L \leq 0.89$, $H \leq 0.89$	ads	[76SOU/SHA]
0.45				0.5 M $H(ClO_4, NO_3)$	M=1E-5, $L \leq 0.5$, $H \leq 0.5$	dis	[66SHI/NAZ]
0.34	0.08	-0.26		1.0 M $H(ClO_4, NO_3)$	M=1E-5, $L \leq 1.0$, $H \leq 1.0$	dis	[66SHI/NAZ]
0.36				1.5 M $H(ClO_4, NO_3)$	M=1E-5, $L \leq 1.5$, $H \leq 1.5$	dis	[66SHI/NAZ]
0.30	0.34			2.0 M $H(ClO_4, NO_3)$	M=1E-5, $L \leq 2.0$, $H \leq 2.0$	dis	[66SHI/NAZ]
0.11				2.0 M $NaClO_4$	n.a.	sp	[62SYK/TAY]
0.83	1.30	1.55	1.55	2.0 M (Li, H)(ClO_4, NO_3)	M=trace, $L \leq 2.0$, $H \leq 2$	dis	[71MOS1]
0.72	1.08	1.23	1.16	4.0 M (Li, H)(ClO_4, NO_3)	M=trace, $L \leq 4.0$, $H \leq 2$	dis	[71MOS1]
-0.15	-0.74			4.0 M (Na, H)(ClO_4, NO_3)	$M \leq 0.045$, $L \leq 4.0$, H=1	dis	[71DAN/CHI]
-1.52[1]	-0.17[1]	-0.82[1]	-0.89[1]	8 M $H(ClO_4, NO_3)$	M=trace,$L \leq 1.0$, H=8	dis	[70LAH/KNO]

Table A3.11: Solubility products (K_{sp}) of the different Np^{4+} solid phases

Reaction	Log K_{sp}	Medium	Concentration (Molarity) of metal, ligand, H	Method	References
$NpO_2 \cdot xH_2O(am) \rightleftharpoons Np^{4+} + 4OH^- + (x-2)H_2O$	-54.5	0.01 M NaCl; 0.001 M $CuCl_2$	M<2E-4, pH=1.5-2.5	sol	[87RAI/SWA]
$Np(OH)_4(am) + 2HCO_3^- \rightleftharpoons Np(OH)_2(CO_3)_2^{2-} + 2H_2O$	-0.35	0.1 M $Na_2S_2O_4$	M≤6E-5 L≤5E-3, pH=8-12.5	sol	[90PRA/MOR]
$Np(OH)_4(am) + 2HCO_3^- \rightleftharpoons Np(OH)_4(HCO_3)_2^{2-}$	-0.35	0.1 M $Na_2S_2O_4$	M≤6E-5 L≤5E-3, pH=8-12.5	sol	[90PRA/MOR]
$Np(OH)_4(am) + 2CO_3^{2-} \rightleftharpoons Np(OH)_4(CO_3)_2^{4-}$	-1.43	0.1 M $Na_2S_2O_4$	M≤6E-5 L≤5E-3, pH=8-12.5	sol	[90PRA/MOR]

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Table A4.1: Equilibrium constants (β_n) for formation of aqueous Pu^{4+} complexes with OH^- ($[Pu^{4+}] + n[H_2O] \rightleftharpoons [PuOH_n^{(4-n)+}] + n[H^+]$)

log β_1	log β_2	log β_3	log β_4	Medium	Concentration (Molarity) of metal, H	Method	Reference
-1.48				0.06M $HClO_4$	M=1.6E-2, H=0.06	sp	[68CLE]
-1.96				0.19M $HClO_4$	M=1.6E-2, H=0.19	sp	[68CLE]
-1.60				0.5M $(Na,K,H)ClO_4$	M=7E-4, H≤0.5	sp	[50KRA/NEL]
-1.65				0.5M (Na,K,H)Cl	M=7E-4, H≤0.5	sp	[50KRA/NEL]
-1.57				0.5M $(H, Na)ClO_4$	M=1.3E-4, pH=0.42-1.83	sp	[96NIT/SIL]
-1.51				1M $(Na,H)ClO_4$	M=4E-4, H≤1	red	[51RAB/LEM]
-0.45	-0.75	-3.30	-6.3	1M $(Li,H)ClO_4$	M=trace, H≤1	dis	[72MET/GUI]
-1.55				1.11M $(H, Na)ClO_4$	M=1.4E-2, H≤1.1E-3	sp	[49HIN]
-1.41[1]				2M $(Li,H)ClO_4$	M=8E-3, H≤2	red	[57RAB]
-1.26				2M $(Li,H)ClO_4$	M=8E-3, H≤2	red	[57RAB]
-1.06[2]				2M (Li,H) $HClO_4$	M=8E-3, H≤2	red	[57RAB]
-1.7				2M $(Na, H)ClO_4$	M=n.a., H≤0.1	sp	[60RAB/KLI]

1) T = 288 K
2) T = 307.5 K

Table A4.2: Equilibrium constants (β_n) for formation of aqueous Pu^{4+} complexes with OH^- ($[Pu^{4+}] + n[OH^-] \rightleftharpoons [PuOH_n^{(m-n)+}]$)

log β_1	log β_2	log β_3	log β_4	Medium	Concentration (Molarity) of metal, H	Method	Reference
12.48	24.28	35.53	46.43	3M (H, Na) ClO_4	M≤0.1M, pH=1.5-10.3	sol	[90PAZ/KUD]

Table A4.3: Equilibrium Constants (β_n) for Formation of Aqueous Pu^{4+} complexes with Cl^-, ($[Pu^{4+}] + n[Cl^-] \rightleftharpoons [PuCl_n^{(4-n)+}]$)

log β_1	log β_2	log β_3	Medium	Concentration (Molarity) of metal, ligand, H	Method	Reference
0.36			0	n.a.	ads	[76SOU/SHA][1]
-0.24			1M $H(Cl,ClO_4)$	M=1E-3, H=1, L≤1	red	[51RAB/LEM]
-0.25			1M $H(Cl,ClO_4)$	M=1E-3, H=1, L≤1	red	[55RAB/COW]
0.14	-0.17		1M $HClO_4$	n.a.	red	[58RAB/ASP]
-0.42			2M $H(Cl,ClO_4)$	M=4E-3, H=2, L≤2	sp	[49HIN3]
-0.23			2M $H(Cl, ClO_4)$	M=1E-3, H=2, L≤1	red	[55RAB/COW]
0.15	-0.64		2M $H(Cl,ClO_4)$	M=trace, H=2, L≤1	dis	[76BAG/RAM]
0.15	0.08		4M $H(Cl,ClO_4)$	M=trace, H=4, L≤3.5	cix	[60GRE/NOR]
0.30	-0.80	-1	4M(Cl,ClO_4)	M=trace, H=4, L≤4	dis	[66DAN/ORL]
-0.1	-0.3	0.3	1-5M ($HClO_4$, KCl)	M=2.5E-3, H=5, L≤5	red	[60KAB/PAL]

[1] Used data from [76SOU/ABD]

Table A4.4: Equilibrium Constants (β_n) for Formation of Aqueous Pu^{3+} complexes with SO_4^{2-} ($[Pu^{3+}] + n[HSO4^-] \rightleftharpoons [Pu(SO_4)_n^{(3-2n)+}] + n[H^+]$)

log β_1	log β_2	log β_3	Medium	Concentration (Molarity) of metal, ligand, H	Method	Reference
2.30	5.0		0.3M HNO_3, 0-0.1 H_2SO_4	M=n.a. , H≥0.3, L≤ 0.1	sp	[70MOS]
0.98	1.30	2.10	0.5M H(ClO_4, HSO_4)	M=7E-6, H=0.5, L≤0.2	cix	[61MAR/CHM]
3.24	4.71		2M (H,Na) (NO_3,ClO_4)	M=1E-6, H≤ 1.2, L≤0.09	dis	[64LAX/PAT]
2.72	4.46		2M H(ClO_4, HSO_4)	M=trace, H=2, L≤0.1	dis	[73PAT/RAM2]
2.75	4.36		2M H(ClO_4, HSO_4)	M≤5E-5, H=2, L≤.1	dis	[73PAT/RAM]
2.81[1]	4.36[1]		2M H(ClO_4, HSO_4)	M=trace, H=2, L≤0.1	dis	[73PAT/RAM]
2.68[2]	4.40[2]		2M H(ClO_4, HSO_4)	M=trace, H=2, L≤0.1	dis	[73PAT/RAM]
2.75	4.43		2M (H,Na)(ClO_4, HSO_4)	M=trace, H=2, L≤0.2	cix	[74FAR/PEA]
2.83	4.63		2M H(ClO_4, HSO_4)	M=trace, H=2, L≤0.1	dis	[76BAG/RAM2]
2.78[1]	4.52[1]		2M H(ClO_4, HSO_4)	M=trace, H=2, L≤0.1	dis	[77BAG/RAM]
2.46[3]			2M (H,Na)(ClO_4, HSO_4)	M=2e-7, H=1, L≤0.1	dis	[83NAS/CLE2]
2.59[1]			2M (H,Na)(ClO_4, HSO_4)	M=2e-7, H=1, L≤0.1	dis	[83NAS/CLE2]
2.77			2M (H,Na)(ClO_4, HSO_4)	M=2e-7, H=1, L≤0.1	dis	[83NAS/CLE2]
2.85[4]			2M (H,Na)(ClO_4, HSO_4)	M=2e-7, H=1, L≤0.1	dis	[83NAS/CLE2]
2.48			2.33M H(ClO_4, HSO_4)	M=7E-6, H=2.33, L≤0.41	cix	[61MAR/CHM]

1: T=283 K
2: T=313 K
3: T=273 K
4: T=308 K

Table A4.5: Equilibrium constants (β_n) for formation of aqueous Pu^{4+} complexes with SO_4^{2-} and HSO_4^-

Reaction	log β	Medium	Concentration (Molarity) of metal, ligand, H	Method	Reference
$Pu^{4+} + SO_4^{2-} = PuSO_4^{2+}$	3.66	1M $HClO_4$	M=1E-3, H=1, L≤7E-3	red	[51RAB/LEM]
$PuSO4^{2+} + HSO_4^- = Pu(SO_4)^0 + H^+$	0.58	1M $(Na,H)NO_3$	M=1E-6, H=0.5M, L≤0.2M	dis	[64LUC]

Table A4.6: Equilibrium constants (β_n) for Formation of aqueous Pu^{4+} complexes with CO_3^{2-} ($[Pu^{4+}] + n[CO3^{2-}] \rightleftharpoons [Pu(CO_3)_n^{(4-2n)+}]$)

log β_1	log β_2	log β_3	log β_4	log β_5	Medium	Concentration (Molarity) of metal, ligand, H	Method	Reference
<12.9					0.5M $NaClO_4$	M=1.3E-4, H=n.a.,L≤1	sp	[96NIT/SIL]
~17.0[1]	~29.9[1]	39.1	42.9	44.5	1M $NaClO_4$	M≤:1E-4, pH=10, L≤:1E-3	sol, sp	[86LIE/KIM]
47.0					10 M K(Cl, ClO_4)	M≤:1.7E-3, H=n.a., L≤3.6	sol	[58MOS/GEL]

[1] Estimates

Table A4.7: Step-wise equilibrium constants for the formation of aqueous Pu^{4+} complexes with CO_3^{2-}

Reaction	log K	Medium	Concentration (Molarity) of metal, ligand, H	Method	Reference
$Pu(CO_3)_4^{4-} + CO_3^{2-} \rightleftharpoons Pu(CO_3)_5^{6-}$	-1.36	0[1] (0.1-1.5 M Na_2CO_3, $NaHCO_3$)	M=1E-3, H=n.a., L≤1.5	sp	[96CAP/VIT]

[1]: Thermodynamic value calculated using data from medium listed in parenthesis.

Table A4.8: Equilibrium constants (β_n) for formation of aqueous Pu^{4+} complexes with F^- ($[Pu^{4+}] + n[HF] \rightleftharpoons [PuF_n^{(4-n)+}] + n[H^+]$)

log β_1	log β_2	Medium	Concentration (Molarity) of metal, ligand, H	Method	Reference
4.23		1M HNO_3	M=7E-3, H=1, L≤0.088	sp	[49MCL]
4.20		1M $HClO_4$	M=trace, H=1, L≤0.13	cix	[69KRY/KOM]
4.04		1M HNO_3	M=trace, H=1, L≤1E-4	cix	[69KRY/KOM2]
4.66	7.32	1M $HClO_4$	M:2E-3, H=1, L≤1E-3	cou	[79CHI/TAL]
4.04		2M HCl	M:6E-3, H=2, L≤4E-3	red	[49MCL]
4.45		2M $HClO_4$	M=trace, H=2, L≤1E-4	cix	[69KRY/KOM]
3.78		2M HNO_3	M=trace, H=2, L≤1E-4	cix	[69KRY/KOM2]
4.60	7.60	2M $HClO_4$	M=trace, H=2, L≤1E-3	dis	[76BAG/RAM1]
4.70[1]	7.65[1]	2M $HClO_4$	M=trace, H=2, L≤1E-3	dis	[77BAG/RAM]
4.52[2]	7.69[2]	2M $HClO_4$	M=trace, H=2, L≤5E-3	dis	[84NAS/CLE]
4.50[3]	7.54[3]	2M $HClO_4$	M=trace, H=2, L≤5E-3	dis	[84NAS/CLE]
4.50[4]	7.54[4]	2M $HClO_4$	M=trace, H=2, L≤5E-3	dis	[84NAS/CLE]
4.47	7.46	2M $HClO_4$	M=trace, H=2, L≤5E-3	dis	[84NAS/CLE]
4.37	7.35	2M $(Na,H)ClO_4$	M=trace, H=1, L≤5E-3	dis	[84NAS/CLE]

1) T=283 K
2) T=274 K
3) T=280.5 K
4) T=288 K

Table A4.9: Equilibrium constants (β_n) for formation of aqueous Pu^{4+} complexes with F^- ($[Pu^{4+}] + n[F^-] \rightleftharpoons [PuF_n^{(4-n)+}]$

log β_1	log β_2	log β_3	log β_4	Medium	Concentration (Molarity) of metal, ligand, H	Method	Reference
7.61	14.77	20.11	26.07	1M (H,Na)ClO_4	M≤4E-3, H ≤0.5, L ≤0.018	ise-F	[90SAW/CHA]

Table A4.10: Equilibrium constants (β_n) for formation of aqueous Pu^{4+} complexes with NO_3^-, ($[Pu^{4+}] + n[NO_3^-] \rightleftharpoons [PuNO_3^{(4-n)+}]$)

log β_1	log β_2	log β_3	log β_4	Medium	Concentration (Molarity) of metal, ligand, H	Method	Reference
0.57				0-0.89 M HNO_3	M=trace, H≤0.89, L≤0.89	ads	[76SOU/SHA]
0.54				1M $HClO_4$	M=1E-3, H=1M, L≤:0.06	red	[51RAB/LEM]
0.72	0.97	0.63		1M $H(NO_3,ClO_4)$	M=trace, H=1M, L≤1	dis	[64LAX/PAT]
0.38	0.43			1M (H,Li) (NO_3,ClO_4)	M=trace, H≤1, L≤1	dis	[71MOS]
0.61	0.85	0.64	0.11	1.9M (H,Na) (NO_3,ClO_4)	M=trace, H=0.6M, L≤1.9	dis	[64LAX/PAT]
0.46				2M $H(ClO_4,NO_3)$	M=5E-3, H=2M, L≤2	sp	[49HIN2]
0.84	1.32	1.56		I=2	n.a.	n.a.	[73MOS3]
0.65	1.12			2M $H(NO_3,ClO_4)$	M=trace, H=2M, L≤1	dis	[76BAG/RAM]
0.57	1.15			2M $H(ClO_4, NO_3)$	M=trace, H=2M, L≤1	dis	[77BAG/RAM]
0.74	1.37	1.18		4M $H(NO_3,ClO_4)$	M=trace, H=4M, L≤2.5	cix	[60GRE/NOR]
0.97	1.43	-0.39		4M $H(NO_3,ClO_4)$	M=trace, H=4M, L≤4	dis	[66DAN/ORL]
0.69	1.12	1.08	0.66	4.7M (H,Na) (NO_3,ClO_4)	M=trace, H=0.7M, L≤1.5	dis	[64LAX/PAT]
0.67	0.65	0.17		I=6	n.a.	dis	[49ZEB/NEU]
0.92[1]				I=6	n.a.	dis	[49ZEB/NEU]
1.00	1.36	-0.01		6M $H(NO_3,ClO_4)$	M=trace, H=6M, L≤4	dis	[66DAN/ORL]
0.68	0.42		-0.72	8M $H(ClO_4,NO_3)$	M=trace, H=8M, L≤8	dis	[70LAH/KNO]

Table A4.11: Equilibrium constants (β_n) for formation of aqueous Pu^{4+} complexes with HPO_4^{2-} ($[Pu^{4+}] + n[HPO_4^{2-}] \rightleftharpoons [Pu(HPO_4)_n^{(4-2n)+}]$)

log β_1	log β_2	log β_3	log β_4	log β_5	Medium	Concentration (Molarity) of metal, ligand, H	Method	Reference
12.9	23.7	33.4	43.2	52.0	2M HNO_3, 0.012-2 M H_3PO_4	M≤3E-3, H≤2, L≤2	sol	[60DEN/MOS]

Table A4.12: Solubility products (K_{sp}) of the different Pu^{4+} solid phases

Reaction	Log K_{sp}	Medium	Concentration (Molarity) of metal, ligand, H	Method	References
$PuO_2 \bullet xH_2O(am) \rightleftharpoons Pu^{4+} + 4OH^- + (x-2)H_2O$	-56.85	0[1] (1e-5-0.5 M HNO_3)	M=4.7e-3, H≤0.5	sol	[84RAI]
	~ -50.2	0.0015 M $CaCl_2$	M=4e-5, pH=3.8-7.3	sol	[80RAI/SER]
	-57.85	0[1] (1 M $HClO_4$)	M=0.03, H=1	sol	[89KIM/KAN]
	-53.7	1 M $NaClO_4$	M=3.7e-4, pH=1.4	sp	[86LIE/KIM]
	-56.3	0[1] (3E-4-0.29 M $HClO_4$)	M=1.2e-4, pH=0.54-3.5	sol	[65PER]
	-49.3	0[1] (3E-4-0.29 M $HClO_4$)	M=1.2e-4, pH=0.54-3.5	sol	[65PER]
	-51.4	3 M (H, Na)ClO_4	M≤0.1,pH=1.5-10.3	sol	[90PAZ/KUD]
$PuO_2(c) + 2H_2O \rightleftharpoons Pu^{4+} + 4OH^-$	-64.0	0	n.a.	ΔG	[86LIE/KIM]
	-60.20	0[1] (1 M $HClO_4$)	M=2.3e-4, H=1	sol	[89KIM/KAN]
	-63.8	0	n.a.	ΔG	[89KIM/KAN]
	-62.5	0	n.a.	ΔG	[76BAE/MES]
	-63.3	0	n.a.	ΔG	[86KAT/SEA]
	-64.1	0	n.a.	ΔG	[87RAI/SWA]
$PuO_2 \bullet xH_2O + 2HCO_3^- \rightleftharpoons Pu(OH)_2(CO_3)_2^{2-} + xH_2O$	-2.7	0.1 M K(Cl,CO_3,OH)	M≤1.3e-6, pH=9.4-13	sol	[94YAM/SAK]
$PuO_2 \bullet xH_2O + 2CO_3^{2-} \rightleftharpoons Pu(OH)_4(CO_3)_2^{4-} + (x-2)H_2O$	-4.98	0.1 M K(Cl,CO_3,OH)	M≤1.3e-6, pH=9.4-13	sol	[94YAM/SAK]
$PuF_4(s) \rightleftharpoons Pu_4^+ + 4F^-$	-15.6	2.5e-4 M PuF_4	M=2.5e-4, H=n.a.,I=self[5]	sol	[61MAN/FRA]
	-20.1 to -18.6	0.015 to 3.19 M HNO_3	M≤4.4E-2, H≤3.2, I=self[5]	sol	[61MAN/FRA]

Table A4.12 continued

Reaction	Log K_{sp}	Medium	Concentration (Molarity) of metal, ligand, H	Method	References
$Pu(HPO_4)_2{\bullet}xH_2O \rightleftharpoons Pu^{4+} + 2HPO_4^{2-} + xH_2O$	-27.7^2	2 M (H/Na)ClO_4 2 M $LiNO_3$ 2 M (Li/H)NO_3	M≤2.8e-3,H≤2,L=self^5	sol	[60DEN/MOS2]
$Pu(HPO_4)_2{\bullet}xH_2O + (n+4)H^+ \rightleftharpoons PuH_n^{n+4} + 2H_3PO_4 + xH_2O$	$-9.15^{3,4}$	0.83 M HNO_3	M:2.7e-4, H>0.8, L:1.2	sol	[49KIN]
	$-7.45^{3,4}$	2.08 M HNO_3	M:2.7e-4, H>0.8, L:1.2	sol	[49KIN]
$Pu(HPO_4)_2{\bullet}xH_2O + (n+1)H^+ \rightleftharpoons Pu(PO_4)H_n^{n+1} + H_3PO_4 + xH_2O$	-6.85^4	0.83 M HNO_3	M:2.7e-4, H>0.8, L:1.2	sol	[49KIN]
	-5.25^4	2.08 M HNO_3	M:2.7e-4, H>0.8, L:1.2	sol	[49KIN]
$Pu(HPO_4)_2{\bullet}xH_2O + (n-2)H^+ \rightleftharpoons Pu(PO_4)_2H_n^{n-2} + xH_2O$	-5.3^4	0.83 M HNO_3	M:2.7e-4, H>0.8, L:1.2	sol	[49KIN]
	-4.5^4	2.08 M HNO_3	M:2.7e-4, H>0.8, L:1.2	sol	[49KIN]
$Pu(HPO_4)_2{\bullet}xH_2O + (n-5)H^+ + H_3PO_4 \rightleftharpoons Pu(PO_4)_3H_n^{n-5} + xH_2O$	-4.2^3	0.83 M HNO_3	M:2.7e-4, H>0.8, L:1.2	sol	[49KIN]
	-3.6^3	2.08 M HNO_3	M:2.7e-4, H>0.8, L:1.2	sol	[49KIN]
$Pu(HPO_4)_2{\bullet}xH_2O + (n-8)H^+ + 2\,H_3PO_4 \rightleftharpoons Pu(PO_4)_4H_n^{n-8} + xH_2O$	-3.8^4	0.83 M HNO_3	M:2.7e-4, H>0.8, L:1.2	sol	[49KIN]
	-3.3^4	2.08 M HNO_3	M:2.7e-4, H>0.8, L:1.2	sol	[49KIN]
$Pu(HPO_4)_2{\bullet}xH_2O + (n-11)H^+ + 3H_3PO_4 \rightleftharpoons Pu(PO_4)_5H_n^{n-11} + xH_2O$	-4.0^3	0.83 M HNO_3	M:2.7e-4, H>0.8, L:1.2	sol	[49KIN]
	-3.5^3	2.08 M HNO_3	M:2.7e-4, H>0.8, L:1.2	sol	[49KIN]

1: Thermodynamic value calculated using data from medium listed in parenthesis.

2: Value is the average of the three ionic media

3: Assuming that the following species are formed: $Pu(PO_4)_mH_n^{4+n-3m}$: n=0,1,3,5. The K value reported is independent of the (n-x)H^+ on the left hand side of the reaction.

4: Assuming that the following species are formed: $Pu(PO_4)_mH_n^{4+n-3m}$: n=0,1,2,4. The K value is independent of the (n-x)H^+ on the left hand side of the reaction.

5: Any ligand in solution is from dissolution of the solid

A5: Selection of log $\beta_1°$ Values with the Screening Approach

A number of authors have used various approaches (e.g., extrapolation, S.I.T. or Pitzer modeling, etc.) to estimate values at classical standard state (I = 0, T = 298K) conditions for stability constants. These have been cited in Tables A1 - A4. However, the values for an individual system may vary significantly. To provide a basis for choosing among these values, a screening approach has been used which is based on the strongly ionic nature of the actinide-ligand bonding. An extended Born equation is used for estimation of log $\beta°_{101}$ for AnX complexation of various actinide cations with the same ligand X where An includes both simple and dioxo cations [94CHO/RIZ]. The equation takes into account the different "effective" ionic charges of the actinide cations, the different effective dielectric constants for these and the differences in An - X bond distances:

$$\Delta G_{101} = \frac{Ne^2 Z_1 Z_2}{418.7\ D_e d_{12}} - \nu RT \ln 55.51$$

z_1 = +3 D_e = 57 d_{12} = based on Shannon radii [76SHA]
= +4 = 40
= +2.2 (NpO_2^+) = 70
= +3.3 (UO_2^{2+}) = 50

The screening method calculated the unknown log $\beta°(An^{11})$ values from known values of another actinide, log β (An^1), by the formula:

$$\log\ \beta°(An^{11}) = \log\ \beta(An^{1}) \cdot \frac{Z_1(An^{11})}{Z_1(An^{1})} \cdot \frac{D_e(An^{1})}{D_e(An^{11})} \cdot \frac{d_{12}(An^{1})}{d_{12}(An^{11})}$$

Sm(III) values of log $\beta°$ were obtained from measurements by a variety of techniques at concentrations above tracer scale. For this reason, they were chosen as a reliable set of more reliable known values and unknown values of log $\beta°$ were calculated for the An^{3+}, An^{4+}, AnO_2^+ and AnO_2^{2+} complexation. UO_2^{2+} values of log $\beta°$ from the careful evaluation of the NEA seem reliable and were used in a second series of calculations of unknown values for the III - VI series of actinide cations. Only values for the 1:1 complexation were calculated as the use of the Born equation for 1:2, etc., requires more "extension" and results in less reliable estimates. However, it is reasonable to assume that values for 1:2, 1:3, etc. from the authors responsible for the most reliable 1:1 values would be the values to use.

The values from the Sm^{3+} and UO_2^{2+} based estimates were compared and found to be in acceptable agreement. In turn, they were used to select, by the degree of agreement, a set of values from those at I = 0 in the data tables. These selected values which best agreed with these estimates are listed below as our recommended values for I = 0.

The screening approach was taken to estimate the stability constants of the complexes of tetravalent actinides with NO_3^- and F^-. The estimated log β value for $ThNO_3^{3+}$ is provided in the section of "Selected Thermodynamic Data for Thorium: Nitrate" of this report. The estimated values for the complexes of U(IV), Np(IV) and Pu(IV) with these ligands are included in Table 8 (for U(IV)), Table 9 (for Np(IV)) and Table 10 (for Pu(IV)) of this report.

3.　収着現象のモデル化とモデルの適応性の検討

Development and Application of a Simple Sorption Model for Nickel on Bentonite.

Database Development Project: Sorption Modeling

Development and Application of a Simple Sorption Model for Nickel on Bentonite

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Executive Summary

Thermodynamic ('mechanistic') sorption models are effective tools for supporting and facilitating the selection of K_d values. The sorption behavior of Ni in bentonite-groundwater systems is described by simultaneously addressing ion exchange and surface complexation reactions, as well as the solution speciation of Ni. Where necessary, the formation of solid Ni-phases is also considered. At the same time, the model is used to calculate the solution composition and bentonite surface speciation as a function of the solid/water ratio, based on the bentonite model described in the FY97 companion report on the reference case analysis. An ion exchange constant for Ni on montmorillonite was selected from the literature and incorporated in the bentonite model. Edge site (surface complexation) constants for Ni were re-evaluated to be consistent with the respective bentonite model, using raw experimental data of Lothenbach et al. (1997). A comparison of model results and independent experimental sorption studies shows that the model used is able to predict K_d values for Ni that are in very good agreement with experimentally derived values over a very wide range of conditions.

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Appendix:

1 Introduction

K_d values for Ac, Am, Bi, Cm, Nb, Np, Pa, Pb, Pd, Po, Pu, Ra, Sb, Sm, Th, U, and Zr on rock materials reported in the literature are collected in an accompanying report (Ochs and Lothenbach, 1998a). No attempt was made so far to model these systems, due to a lack of fundamental solution and surface chemical data. In previous reports, models were developed to compute the sorption of Ra/Sr (Ochs and Wanner, 1996) and Pb (Ochs and Lothenbach, 1997) on montmorillonite. These models have recently been published (Ochs et al., 1998). A model for Cs sorption on montmorillonite has been developed earlier by Wanner et al. (1996).

The present effort is directed at interpreting published experimental distribution coefficients by modeling the solution and surface speciation using Ni as a key element. For Ni, similar to Pb (Ochs and Lothenbach, 1997), both ion exchange and surface complexation are expected as adsorption mechanisms, depending on pH (Lothenbach et al., 1997, Bradbury and Baeyens, 1997). Sorption studies carried out with the well-known bentonites SWy-1 and Kunigel-V1 over a range of experimental conditions are available (Lothenbach et al., 1997, Bradbury and Baeyens, 1997, Shibutani, 1997). This allows to test a defined ion exchange and surface complexation model under different conditions and to evaluate the influence of experimental parameters on K_d.

In the following chapter, a Ni model consistent with the bentonite model used for the porewater calculations described in the companion report by Ochs and Lothenbach (1998b) is developed. This model development has been carried out based on the following steps:

- review of available sorption models for nickel in the literature,
- selection of a cation exchange constant from the literature,
- selection of published experimental data to re-evaluate surface complexation constants,
- re-evaluation of surface complexation constants that are consistent with relevant bentonite models,
- testing of the model against independent experimental data taken from the studies of Bradbury and Baeyens (1997) and Shibutani et al. (1996).

2 Review of previous studies

2.1 Selection of a cation exchange constant

Several Ni sorption studies on montmorillonite can be found in the literature. Ion exchange constants reported in the literature are given in Table 2.1. For ease of comparison, the ion exchange constants in Table 2.1 are given according to the mole fraction formalism (K_V) and according to the equivalent fraction formalism (K_{GT}). A detailed description of the different ion exchange models and of the relation between the different constants can be found in section 1 of the companion report 'Reference Case Analysis' by Ochs and Lothenbach (1998b).

The ion exchange constants for Ni on montmorillonite listed in Table 2.1 are all very similar to each other. These values are also only slightly higher than the cation exchange constants observed for the Ca^{2+} and Mg^{2+} exchange on montmorillonite (Fletcher and Sposito, 1989). These data suggest that montmorillonite has no strong preference for Ni^{2+} compared to Ca^{2+} and Mg^{2+}. In the bentonite model that was used as a basis for the optimization procedure with GRFIT, the ion exchange constants of Fletcher and Sposito (1989) are used for Ca^{2+} and Mg^{2+}; thus, the ion exchange constant for Ni^{2+} is also taken from Fletcher and Sposito (1989).

Table 2.1: Comparison of ion exchange constants ($\log_{10} K^\circ$) for Ni^{2+} on montmorillonite for the reaction $Ni^{2+} + 2Z^- = Z_2Ni$. The values are based on an ion exchange constant of 10^{20} for the formation reaction $Na^+ + Z^- = ZNa$.

Surface species	equivalent fraction model log K_{GT}	mole fraction model log K_V	Reference
Z_2Ni	40.55 [1]	40.25	Fletcher and Sposito (1989)
	40.49	40.19 [2]	Bradbury and Baeyens (1997)
	40.47 [3]	40.17 [3]	Lothenbach et al. (1997)

[1] After conversion to the equivalent fraction model

[2] After conversion to the mole fraction model

[3] After correction for ionic strength using the Davies equation and conversion to the equivalent or mole fraction model

2.2 *Review of surface complexation constants*

The selection of surface complexation constants proved to be more difficult. The few constants reported for nickel sorption on montmorillonite in the literature (Lothenbach et al., 1997, Bradbury and Baeyens, 1997), are based on a surface complexation model without electrostatic terms and with protonation/deprotonation constants different from those used in bentonite models based on the extended Wanner model (cf. Table 2.2). Bradbury and Baeyens (1997) used weak and strong sorbing edge sites (wSOH and sSOH) to model their Ni adsorption data. In their model, 5% of the total edge sites correspond to the strong sorbing sSOH sites, the rest (95%) corresponds to the weak sorbing wSOH sites. Lothenbach et al. (1997) also used the bentonite model of Bradbury and Baeyens (1997) to derive their constants for nickel sorption on the bentonite edge sites.

Table 2.2: Surface complexation constants reported for nickel on montmorillonite, river sediment and hydrous ferric oxide (HFO). The corresponding SOH hydrolysis constants are also given (w = weak sites, s = strong sites).

	montmorillonite [1]	montmorillonite [2]	HFO [3]	HFO [4]	River sediment [5]
Surface site master species: SOH			(surface complexation), $\log_{10} K^\circ$		
$wSONi^+$	-3.1	-3.6	-3.25	– 2.5	-3.8
$wSOH_2^+$	4.5	4.5	5.1	7.3	nr
wSO^-	– 7.9	– 7.9	– 8.1	– 8.9	nr
$sSONi^+$	-0.1	-0.1			
$sSOH_2^+$	4.5	4.6			
sSO^-	-7.9	-7.9			
electrostatic model	none	none	constant capacitance	diffuse layer	nr

[1] Bradbury and Baeyens (1997); [2] Lothenbach et al. (1997); corrected for ionic strength; [3] Nowack (1996); [4] Dzombak and Morel (1992); HFO: hydrous ferric oxide; [5] Mouvet and Bourg (1983); nr: not reported

It is, therefore, not possible to use the surface complexation constants of Bradbury and Baeyens (1997) or Lothenbach et al. (1997) directly with the present bentonite model. On one hand, the model of Bradbury and Baeyens (1997) and Lothenbach et al. (1997) assumes the presence of two surface sites (weak and strong sorbing) and, on the other hand, they use no electrostatic model for the edge sites. However, the derivation of surface complexation constants for metal ions is strongly influenced by the choice of the respective electrostatic model and bentonite edge surface protonation constants. Therefore, a surface complexation constant K_{SONi} for Ni on bentonite has to be re-fitted to be consistent with the surface model employed for other purposes, e.g. porewater calculations.

3 Deriving a surface complexation constant for Ni on bentonite

Based on the Extended Wanner Model/Version 2 and the cation exchange constant of Fletcher and Sposito (1989) for Ni^{2+}, the experimental data reported by Lothenbach et al. (1997) were used to re-fit a surface complexation constant K_{SONi} for Ni on the edge sites of the montmorillonite. For fitting the program GRFIT (Ludwig, 1992) was used, which is based on the well known code FITEQL (Westall, 1982). GRFIT uses a non-linear, least-squares optimization technique to calculate equilibrium constants from chemical data.

3.1 *Thermodynamic database for Ni*

Any surface chemical model is implicitly based on the thermodynamic data used to describe the formation of dissolved species of the respective element; for model application, the formation of solid species may also be important. The thermodynamic data used to calculate the aqueous speciation of nickel and all other elements considered in the present model are given in Appendix A of this report. The nickel data in the thermodynamic database given in Appendix A are based on the NAGRA TDB (Pearson and Berner, 1991; Pearson et al., 1992). The formation constants for nickel carbonate and bicarbonate species and for the formation of $NiCO_3(s)$ given in that database seem to be incorrect, however.

Several authors (e.g. Mouvet and Bourg, 1983; Larsen and Postma, 1997; PSI, 1996) remarked that the often used log K value of ≈ 6 for the reaction $Ni^{2+} + CO_3^{2-} \Leftrightarrow NiCO_3^0$ is much too high, leading to a strong overestimation of dissolved nickel concentrations at higher pH values in the presence of carbonate. In a internal report, Bradbury and Baeyens (1996) showed that only the 1:1 nickel carbonate complex is important and that no nickel bicarbonate complex is formed up to a bicarbonate concentration of 10^{-2} M. They determined a log K value of 4.3 for the reaction $Ni^{2+} + CO_3^{2-} \Leftrightarrow NiCO_3^0$.

The value given for the formation of $NiCO_3(s)$ given in Appendix A ($\log K^*_{S0} = 6.97$) is too low, in comparison with the formation constants of carbonate compounds of other transition metals. According to a study focusing on the quality of solubility data for some transition metal carbonates, a log $K_{S0}{}^*$ of 11.2 for the reaction $Ni^{2+} + CO_3^{2-} \Leftrightarrow NiCO_3(s)$ is proposed by Grauer (1994). Recently, Carlson and Aalto (1998) confirmed this value as an upper limit for the solubility product of $NiCO_3(s)$. In the absence of better data, a log $K_{S0}{}^*$ of 11.2 is used in the present calculations.

3.2 *Fitting the surface complexation constant K_{SONi} for Ni*

The experimental details and the constants used for fitting the surface complexation constant K_{SONi} for Ni on the edge sites of montmorillonite are given in Table 3.3 and Table 3.4. Using the experimental data of Lothenbach et al. (1997) for nickel sorption on montmorillonite in 0.1 M $NaClO_4$, a log K_{SONi} of –4.35 was obtained for the reaction $Ni^{2+} + SOH \Leftrightarrow SONi^+ + H^+$. Correction of this constant with the Davies-equation gives a log K_{SONi} of –4.04 at I = 0.

Table 3.3: Montmorillonite characteristics and experimental details of the experiments of Lothenbach et al. (1997). These data were used to obtain a surface complexation constant K_{SONi} for Ni on the edge sites of the SWy-1 montmorillonite.

Concentration of montmorillonite:	2 g/L	Lothenbach et al. (1997)
Ionic strength:	0.1 M $NaClO_4$	Lothenbach et al. (1997)
Nickel concentration:	0.0001 M	Lothenbach et al. (1997)
Surface site density (SOH):	2.84×10^{-5} mol/g	Wieland et al. (1994)
CEC (Z):	86 meq/100 g	Lothenbach et al. (1997)
exchangeable Na^+:	100 %	Lothenbach et al. (1997)
exchangeable K^+:	0 %	Lothenbach et al. (1997)
exchangeable Ca^+:	0 %	Lothenbach et al. (1997)
exchangeable Mg^+:	0 %	Lothenbach et al. (1997)

Table 3.4: Ion exchange and surface complexation parameters for nickel on montmorillonite. The corresponding SOH hydrolysis constants are also given.

Species	log K^o	Reference
Surface site master species:		Z (ion exchange), log K^o
ZNa	20.00 (by definition)	Wanner (1986)
ZH	20.10	Fletcher and Sposito (1989)
ZK	20.26	Fletcher and Sposito (1989)
Z_2Mg	40.47 [1]	Fletcher and Sposito (1989)
Z_2Ca	40.47 [1]	Fletcher and Sposito (1989)
Z_2Ni	40.55 [1]	Fletcher and Sposito (1989)
Surface site master species:		SOH (surface complexation), log K^o
$SONi^+$	-4.04 [2]	this study
SOH_2^+	5.4 [2]	Wanner et al. (1994)
SO^-	-6.7 [2]	Wanner et al. (1994)

[1] Corresponding to the equivalent fraction model

[2] Corresponding to the diffuse double layer model

4 Model testing and interpretation of Ni sorption in batch experiments

A comparison of all model results and experimental K_d values is provided in Figure 4.1 and Table 4.5. All model results are calculated using the constants given in Table 3.4, i. e., in no case were the constants modified in order to obtain a better fit. Figure 4.1 shows that the model used is able to predict K_d values for Ni well over a very wide range of conditions, including 0.001 - 0.1 M NaCl and a pH range of 4.5 to 10.8. It becomes apparent that a major factor governing the distribution of Ni is pH. At pH values below 7, ion exchange dominates adsorption, whereas at higher pH values, surface complexation limits the dissolved Ni concentrations. In supersaturated systems (i.e., at high initial Ni concentrations), the precipitation of $NiCO_3$, NiO or $Ni(OH)_2$ has to be taken into account (Lothenbach et al., 1997). The influence of the precipitation of solid phases on experimentally measured, apparent, K_d values is discussed in more detail in the following sections. At low pH values, the composition of the electrolyte, i.e., the solution concentration of cations able to compete for the available ion exchange sites, influences the distribution of Ni (Table 4.5). This stresses the importance of the composition of the input solution and the amount of soluble impurities contained in the different bentonites for Ni sorption. The modeling approaches used and the corresponding results are discussed in detail for each system in the following sections.

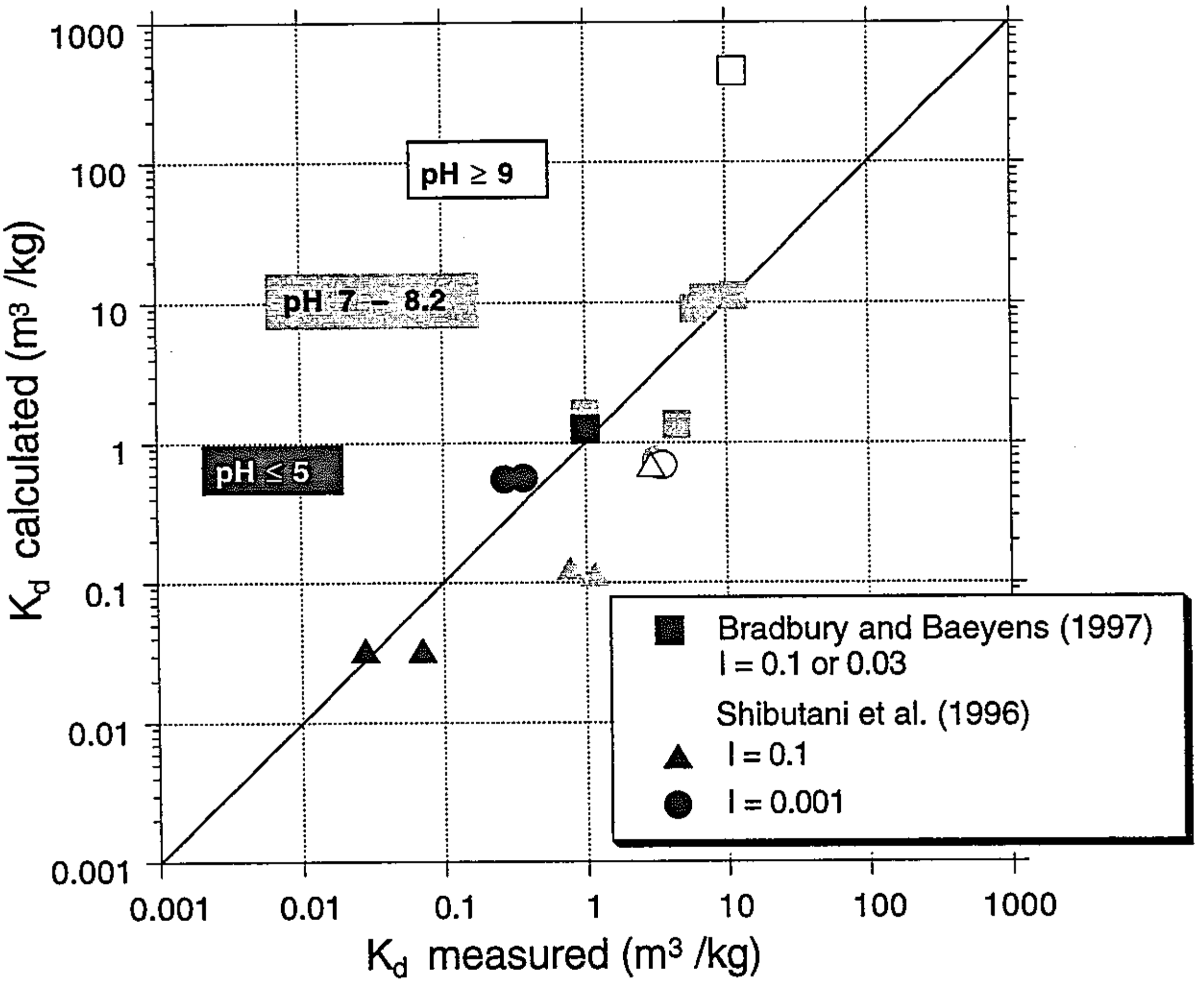

Figure 4.1: A comparison of calculated and measured K_d values. The model parameters are given in Table 3.4, the measured K_d values are given, together with relevant experimental conditions, in Table 4.5.

Table 4.5: Experimental conditions and measured K_d values for the references used in Figure 4.1. For details on bentonite characteristics used, see explanations in the text.

reference	solid phase	water type	[Ni] initial (M)	water/solid ratio (mL/g)	pH measured	K_d (m^3/kg) measured
Shibutani (1997)	Kunigel–V1	0.001 NaCl	1.0 E-4	100	4.66	0.27
	Kunigel–V1	0.001 NaCl	1.0 E-4	100	5.05	0.37
	Kunigel–V1	0.001 NaCl	1.0 E-4	100	7.34	3.17
	Kunigel–V1	0.001 NaCl	1.0 E-4	100	7.47	3.17
	Kunigel–V1	0.001 NaCl	1.0 E-6	100	10.96	3.57
	Kunigel–V1	0.1 NaCl	1.0 E-4	100	5.1	0.070
	Kunigel–V1	0.1 NaCl	1.0 E-4	100	4.91	0.028
	Kunigel–V1	0.1 NaCl	1.0 E-4	100	7.63	1.15
	Kunigel–V1	0.1 NaCl	1.0 E-4	100	7.64	0.77
	Kunigel–V1	0.1 NaCl	1.0 E-6	100	10.83	2.91
	Kunigel V1	0.1 NaCl	1.0 E-6	100	10.78	2.91
Baeyens and Bradbury (1997)	SWy-1	0.03 $NaClO_4$	3.0 E-7	909	4.7	1
	SWy-1	0.03 $NaClO_4$	3.0 E-7	909	7	4.5
	SWy-1	0.03 $NaClO_4$	3.0 E-7	909	8	6.0
	SWy-1	0.03 $NaClO_4$	3.0 E-7	909	9	11.2
	SWy-1	0.1 $NaClO_4$	1.0 E-8	4167	8.2	11.4
	SWy-1	0.1 $NaClO_4$	1.0 E-7	4167	8.2	7.1
	SWy-1	0.1 $NaClO_4$	1.0 E-5	4167	8.2	1

4.1 Experiments by Shibutani et al. (1996)

In his experiments, Shibutani et al. (1996) used Kunigel-V1 (Kunimine Industries Co.), a crude bentonite, whose composition is given below. As electrolyte solution, Shibutani et al. (1996) used 0.1 and 0.001 M. The pH was adjusted with acid and base without reporting the total amount of acid or base added. For all modeling purposes, the appropriate amount of acid and base were added to reach the experimental pH values reported.

The mineralogical analysis and CEC of Kunigel-V1 is given by Sasaki et al. (1995), the amount of soluble impurities is taken from Wanner and Wieland (1993), and the proportion of exchangeable cations is used as given by PNC (1992) (Table 4.6). Kunigel-V1 contains a number of minerals other than clays in various proportions, which are of importance in determining the composition of the surrounding solution.

Table 4.6: Composition and other specific parameters of Kunigel-V1.

Parameters	Kunigel-V1	Reference
Minerals:		
smectite	46-49 %	Sasaki et al. (1995)
quartz	29-38 %	Sasaki et al. (1995)
feldspar	2.7-5.5 %	Sasaki et al. (1995)
calcite	2.1-2.6 %	Sasaki et al. (1995)
dolomite	2.0-3.8 %	Sasaki et al. (1995)
zeolite	3.0-3.5 %	Sasaki et al. (1995)
pyrite	0.5-0.7 %	Sasaki et al. (1995)
Soluble impurities:		
NaCl	0.001 %	Wanner and Wieland (1993)
KCl	0.004 %	Wanner and Wieland (1993)
$CaSO_4$	0.38 %	Wanner and Wieland (1993)
Surface sites and cation exchange parameters:		
SOH sites	1.36E-5 mol/g	Wieland et al. (1994) *
CEC	60.1 meq/100g	Sasaki et al. (1995)
exchangeable Na^+	82.7 %	PNC (1992)
exchangeable K^+	0.9 %	PNC (1992)
exchangeable Mg^{2+}	2.4 %	PNC (1992)
exchangeable Ca^{2+}	14.0 %	PNC (1992)
Structural parameters:		
specific density	2700 kg/m^3	Sato et al. (1993)
surface area of layer sites	810 m^2/g	Sato et al. (1995)
surface area of edge sites	3 m^2/g	Wieland et al. (1994) **

* Corrected for the smectite content of Kunigel-V1

** Obtained for pretreated MX-80 which had a CEC of 108 meq/100g

The solution and surface speciation of Ni is modeled for the bentonite/water ratio corresponding to the experiments (10 g/L; see Table 4.5) using the parameters given in Table 3.4 and Table 4.6. According to the composition of Kunigel-V1, equilibrium with quartz, calcite and all soluble impurities was assumed (Table 4.6). Dissolution of the other minerals present was not considered. With respect to CO_2, an open system in equilibrium with the atmosphere is assumed.

The results of all model calculations referring to the experimental data of Shibutani et al. (1996) are plotted separately in Figure 4.2. There is a very good agreement between calculated K_d values and the K_d values measured by Shibutani et al. (1997).

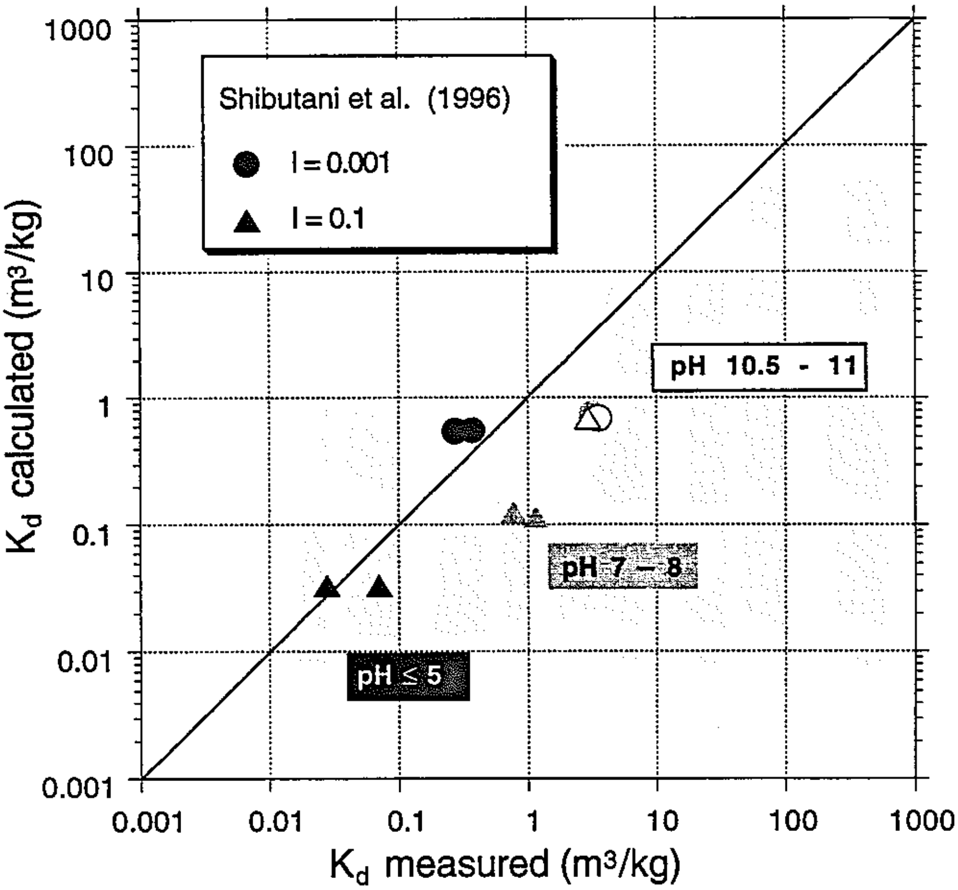

Figure 4.2: A comparison of calculated K_d values and K_d values measured by Shibutani et al. (1997). The K_d values were calculated either in presence of 0.1 M NaCl (triangles) or 0.001 M NaCl (circles), using the model parameters given in Table 3.4 and Table 4.6.

Figure 4.2 shows the critical role that the concentration of the electrolyte plays at low pH values where Ni sorbs mainly through an ion exchange mechanism. The same observation has also been made for Pb (Ochs et al., 1998). In presence of 0.1 M $NaClO_4$, less Ni adsorbs on the ion exchange sites due to competition by Na (Figure 4.2), resulting in smaller K_d values than in presence of a less concentrated electrolyte. In presence of 0.001 M NaCl, more than 80% of Ni is adsorbed on the ion exchange sites. At pH values above 10, ionic strength is strongly influenced by the presence of carbonate – in equilibrium with atmospheric CO_2 – and the influence of the original electrolyte solution is quite small as shown by both the calculated and measured values (Figure 4.2 and Table 4.5).

A major factor influencing the distribution coefficient of Ni is the pH value, as was already observed earlier for Pb (Ochs et al., 1998). In Figure 4.3 the speciation of Ni in the experiments by Shibutani et al. (1996) is shown as a function of pH. In the pH range of 4 to 6, ion exchange reactions are most important process with regard to the distribution of Ni. In presence of 0.001 M NaCl, more than 80% of Ni is adsorbed on the ion exchange sites. Ni adsorption on surface complexation sites increases at pH values > 7 (Figure 4.3).

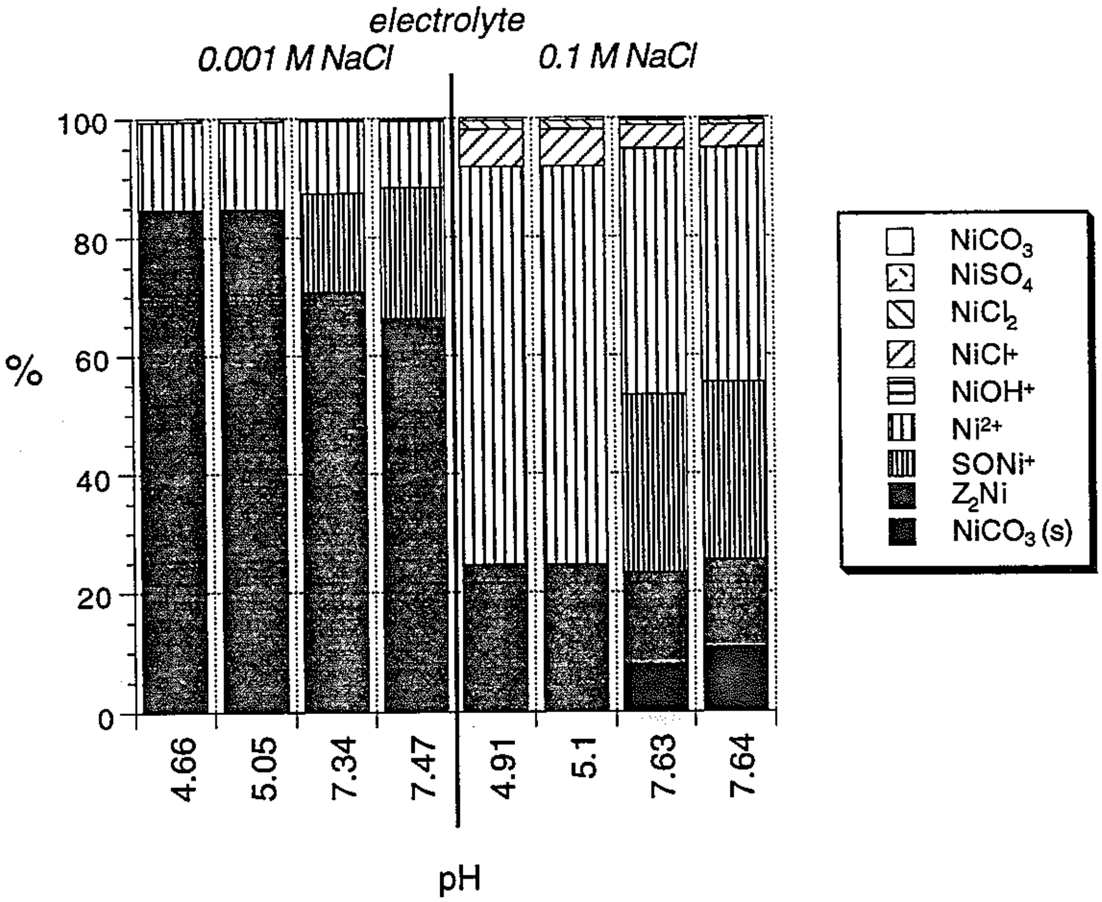

Figure 4.3: Influence of the electrolyte concentration and pH on calculated Ni speciation at a Ni concentration of 10^{-4} M in the experiments by Shibutani et al. (1996).

4.2 Experiments by Baeyens and Bradbury, 1997

Some experimental K_d values published by Baeyens and Bradbury (1997) were recalculated with the model presented in Table 3.4. In their experiments, Baeyens and Bradbury (1997) washed the SWy-1 montmorillonite three times with 1 M NaCl and removed the > 0.5 μm fraction by centrifugation. The washing and centrifugation procedures removed most of the impurities originally present in the SWy-1 montmorillonite (Baeyens and Bradbury, 1997). As input solution, Baeyens and Bradbury (1997) employed 0.1 or 0.03 M $NaClO_4$ solutions containing 10^{-8} – 10^{-5} M Ni (see Table 4.5) and adjusted the pH with buffer solutions. They demonstrated clearly that these buffer solutions did not influence the sorption behavior of nickel to any significant extent. The distribution of Ni between solution and solid phase is calculated for a bentonite/water ratio of 1.1 and 0.24 g/L (Baeyens and Bradbury, 1997). For the calculations, the parameters given in Table 3.4 and a CEC of 87 meq/100 g (Baeyens and Bradbury, 1997) are used. All model calculations are carried out with Na^+ as the only exchangeable cation present, in the absence of any impurities. With respect to CO_2, an open system with a $pCO_2 < 10^{-5.5}$ (N_2 atmosphere glove box) is reported by Baeyens and Bradbury (1997). For the present calculation a pCO_2 of $10^{-5.5}$ was used.

The K_d values calculated by the model used are shown in Figure 4.1. Again, the influence of pH can be seen. At low pH both calculated and measured K_d values are small, while they increase with increasing pH values. The agreement between experimental and calculated data is good in most cases. However, at pH 9, the model somewhat overestimates K_d values in comparison with the measurements by Baeyens and Bradbury (1997).

Figure 4.4 shows the influence of nickel concentration on the distribution of Ni at a pH value of 8.2. Due to the relatively high pH, Ni sorbs predominantly at the edge sites of the montmorillonite. While at the lower two Ni concentrations, only a small percentage of total available edge sites are occupied by Ni^{2+} cations, at a Ni concentration of 10^{-5} M already 25% of the total edge sites are occupied by Ni^{2+} (Table 4.7). Table 4.7 shows that the speciation of the surface complexation sites is drastically changed in the presence of 10^{-5} M Ni in comparison with lower Ni concentrations. At a solution concentration of 10^{-5} M, Ni starts to displace protons from the surface complexation sites, and this competition leads to a lower K_d value.

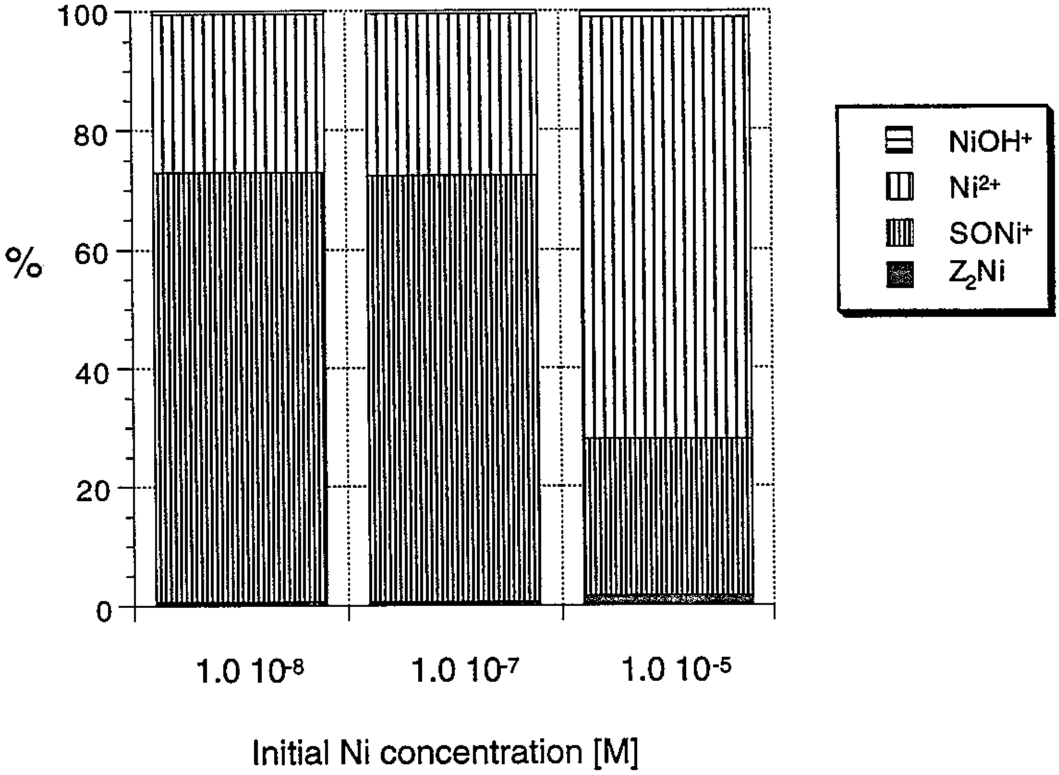

Figure 4.4: Influence of initial Ni concentration on calculated Ni speciation in the experiments by Baeyens and Bradbury (1997). Ni speciation was calculated in absence of soluble impurities at a pH of 8.2 and a bentonite concentration of 0.24 g L^{-1}.

Table 4.7: Calculated speciation of Ni, ion exchange, and surface complexation sites of bentonite at pH 8.2, calculated at a water/solid ratio of 4167 mL/g (0.24 g L^{-1}) and nickel concentrations of 10^{-8}, 10^{-7}, and 10^{-5} M with the help of the present model for the experiments by Baeyens and Bradbury (1997).

species Ni	concentration (% of total)	species Z^-	concentration (% of total)	species SOH	concentration (% of total)
Ni concentration = 10^{-8} M,			*K_d = 11.2 m^3/kg, I=0.1 M*		
Ni^{2+}	26.6	Z_2Ni	100	SOH	63.8
$NiOH^+$	0.4	ZNa	0	SOH_2^+	8.2
Z_2Ni	0.6			SO^-	24.7
$SONi^+$	72.4			$SONi^+$	< 0.1
Ni concentration = 10^{-7} M,			*K_d = 10.9 m^3/kg, I=0.1 M*		
Ni^{2+}	27.3	Z_2Ni	100	SOH	62.8
$NiOH^+$	0.4	ZNa	0	SOH_2^+	7.9
Z_2Ni	0.6			SO^-	25.0
$SONi^+$	71.7			$SONi^+$	0.8
Ni concentration = 10^{-5} M,			*K_d = 1.62 m^3/kg, I=0.1 M*		
Ni^{2+}	70.9	Z_2Ni	99.8	SOH	29.4
$NiOH^+$	1.1	ZNa	0.2	SOH_2^+	1.1
Z_2Ni	1.6			SO^-	38.7
$SONi^+$	26.4			$SONi^+$	27.5

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Appendix A

Calculational Tools

A Calculational tools

A.1 The speciation code MIN_SURF

MIN_SURF (Berner, 1993) is a surface and solution chemical speciation code based on MINEQL/PSI and DSURF (cf. Dzombak and Morel, 1990). MIN_SURF uses the diffuse double layer model to calculate surface complexation reactions in the solid surface/water interface, cf. Dzombak and Morel (1990) and Stumm and Morgan (1996). The formalisms used to calculate double layer characteristics are based on Hunter (1981) and de Levie (1990).

The BMG-version of MIN_SURF includes the possibility to model ion exchange reactions, using either the mole fraction or equivalent fraction approach (cf. Sposito, 1981) to calculate the activity of the exchanger species.

The code MINEQL/PSI corresponds to the code MINEQL/EIR (EIR was the former Swiss Federal Institute for Reactor Research, now named Paul Scherrer Institute, PSI). Under the latter name, it was made available for the NEA data bank in 1986 (OECD/NEA, 1986, 1994). This code is an extension of the well-known speciation code MINEQL (Westall, Zachary and Morel, 1976) and was developed at EIR as documented in two technical notes (Schweingruber, 1982, 1984) which are reproduced in the NEA user's guide (OECD/NEA, 1986). The extension essentially consists in the inclusion of activity coefficients and temperature dependence routines. Ionic strength corrections are done by using the Davies-equation.

A.2 Thermodynamic database (TDB)

The TDB version of May 1992 of the MIN_SURF code includes the contents of the Nagra TDB (Pearson and Berner, 1991; Pearson, Berner and Hummel, 1992) but contains also additional species which were part of earlier versions of MINEQL. These additional species have been partly revised and listed by Pearson, Berner and Hummel (1992). In the BMG-version, the recent uranium and americium data of Grenthe et al. (1992) and Silva et al. (1995) have also been included.

Note that thermodynamic databases are in a permanent process of improvement, extension and revision. The quality of the data is not uniform. Some data are updated and of high quality, such as the core data (Pearson and Berner, 1991) and the uranium and americium data from the NEA-TDB (Grenthe et al., 1992; Silva et al., 1995), while other data may not correspond to the state of the art.

In Appendix A.3, data of the MIN_SURF TDB relevant for the present project are reproduced for convenience and traceability. The TDB consists of a table identifying the master species used as components in the speciation calculations, a log K° table in which the ID's and the compositions of the complexes are defined, and a reference list containing literature citations.

A.3 TDB used with MIN_SURF

A.3.1 Table of Master Species

Each element has at least one master species whose ID and chemical characteristics are shown in this table. Redox sensitive elements may have more than one master species, allowing to separate the modeling of the different oxidation states, e. g. in case of kinetic inhibition.

1	CA+2	2	MG+2	3	SR+2	4	K+	IDKO 10
5	NA+	6	FE+3	7	FE+2	8	MN+2	IDKO 20
9	CU+2	10	BA+2	11	CD+2	12	ZN+2	IDKO 30
13	NI+2	14	HG+2	15	PB+2	16	CO+2	IDKO 40
17	CO+3	18	AG+	19	CR+3	20	AL+3	IDKO 50
21	CS+	22	LI+	23	BE+2	24	SC+3	IDKO 60
25	TIO+2	26	SN+2	27	SN+4	28	LA+3	IDKO 70
29	CE+3	30	AU+	31	TH+4	32	UO2+2	IDKO 80
33	CU+	34	ND+3	35	PUO2+2	36	PUO2+	IDKO 90
37	PU+4	38	PU+3	39	U+3	40	U+4	IDKO 100
41	UO2+	42	NP+3	43	NP+4	44	NPO2+	IDKO 110
45	NPO2+2	46	TC+2	47	TCO+2	48	EU+3	IDKO 120
49	SM+3	50	H+	51	ZR+4	52	PD+2	IDKO 130
53	PA+4	54	PAO2+	55	AM+3	56	TCO+	IDKO 140
57	SB(OH)3	58	SB(OH)5	59	BI(OH)3	60		IDKO 150
61		62		63		64		IDKO 160
65		66		67		68	RB+	IDKO 170
69	RA+2	70		71		72		IDKO 180
73		74		75		76		IDKO 190
77		78		79		80	PSI-X	IDKO 200
81	=XSOH	82	=XWOH	83		84		IDKO 210
85	PSI-Y	86	=YSOH	87	=YWOH	88		IDKO 220
89		90	PSI-Z	91	=ZSOH	92	=ZWOH	IDKO 230
93		94		95		96		IDKO 240
97		98		99	E-	100		IDKO 250
101	CO3-2	102	SO4-2	103	CL-	104	F-	IDKO 260
105	BR-	106	I-	107	NH3	108	HS-	IDKO 270
109	PO4-3	110	P2O7-4	111	P3O10-5	112	H2SIO4-2	IDKO 280
113	S2O3-2	114	CN-	115	AC-	116	ACAC-	IDKO 290
117	CIT-3	118	OX-2	119	SAL-2	120	TART-2	IDKO 300
121	EN	122	DIP	123	SUSAL-3	124	GLY-	IDKO 310
125	GLU-2	126	PIC-	127	NTA-3	128	EDTA-4	IDKO 320
129	DCTA-4	130	CYST-2	131	NOC-3	132	PHTH-2	IDKO 330
133	ARG-	134	ORN-	135	LYS-	136	HIS-	IDKO 340
137	ASP-	138	SER-	139	ALA-	140	TYR-2	IDKO 350
141	MET-	142	VAL-	143	THR-	144	PHE-	IDKO 360
145	ISO-	146	LEU-	147	PRO-	148	B(OH)4-	IDKO 370
149	SO3-2	150	SCN-	151	NH2OH	152	MOO4-2	IDKO 380
153	WO4-2	154	ASO4-3	155	HVO4-2	156	SEO3-2	IDKO 390
157	NO3-	158	TRIS	159	TCO4-	160	ASO2-	IDKO 400
161	NBO3-	162		163	TCO4-2	164		IDKO 410
165	ZET-	166	EDG-	167	TCO4-3	168		IDKO 420
169		170	CLO-	171	CLO2-	172	CLO4-	IDKO 430
173	BRO-	174		175	IO3-	176		IDKO 440
177	HSE-	178	SEO4-2	179		180	N3-	IDKO 450
181	NO2-	182		183		184		IDKO 460
185		186		187		188		IDKO 470
189		190		191		192		IDKO 480
193		194		195		196		IDKO 490
197	CH4(AQ)	198	N2(AQ)	199	H2(AQ)	200	O2(AQ)	

A.3.2 Table of Formation Constants

This Table contains the formation constants of all the complexes and solids of the May 1992 version of the MIN_SURF database. A large part of it was published by Pearson and Berner (1991) and Pearson, Berner and Hummel (1992). The ID number is followed by the $\log_{10} K^\circ$ value and by the ID's and stoichiometric coefficients of the master species of which the corresponding complexes are composed of. The species type number is a MINEQL-specific code number: 1: master species; 2: aqueous complexes; 3: boundary conditions; 4: precipitated solids (calculation-specific); 5: potential solids; 6: species excluded from the mass balance. The information and references are given in Appendix A.3.3

Example for reading the contents of the database:

ID	log K°	stoichiometric coefficients	type, info
1000	3.224	1 1 101 1	2 CORE (7602) 1.6.90
32037	-0.88	32 2 101 1 50 -3	3.0 2 NEA (NEW) 20.7.90

- Species 1000 is composed of the components 1 and 101 (one of each). Component 1 is Ca^{2+}, and component 101 is CO_3^{2-}. Species 1000 thus represents $CaCO_3$ with a formation constant of $\log K^\circ = 3.224$. The species type is 2, meaning that $CaCO_3$ is an aqueous species (and not solid $CaCO_3$). The "info" column indicates that this species is part of the Nagra core database (cf. Pearson and Berner, 1991), and its origin is from Ref. 7602, i.e. Smith and Martell (1976), cf. Appendix A.3.3. The last update was made on 1 June 1990.
- Species 32037 is composed of the following components: 2 × component 32, 1 × component 101 and –3 × component 50. Component 32 is UO_2^{2+}, 101 is CO_3^{2-}, and 50 is H^+. Negative coefficients with H^+ stand for "$H_2O - H^+$" (H_2O is not explicitly considered by MINEQL) and indicate OH^-. Species 32037 thus represents $(UO_2)_2CO_3(OH)_3^-$. The correct formation reaction is

  $$2\ UO_2^{2+} + CO_3^{2-} + 3\ H_2O(l) \quad = \quad (UO_2)_2CO_3(OH)_3^- + 3\ H^+$$

  with a formation constant of $\log K^\circ = -0.88$.

The number 3.0 just before the species type code (2 = aqueous complex) is currently not used by the MINEQL code. It represents the number of H_2O molecules involved in the formation reaction. "NEA" means that the value is from the NEA-TDB (Grenthe et al., 1992), and "new" indicates that this species was not included in earlier versions of the MINEQL database at PSI. The last update was on 20 July 1990.

The complete database contains more than 1800 aqueous complexes (species type 2), 28 fixed boundary conditions (species type 3, e.g., redox reactions), 415 potential solids (species type 5) and 30 species which by default are excluded from the mass balance (species type 6, e.g., gaseous species and test species or uncertain species). Below, only the species relevant for the present study are listed.

A) Bentonite porewater

ID	log K	ID1	c1	ID2	c2	ID3	c3	(etc.)	type	Info + Ref.	last update
1000	3.224	1	1	101	1				2	CORE (7602)	1.6.90
1010	11.435	1	1	101	1	50	1		2	CORE	1.6.90
1020	2.30	1	1	102	1				2	CORE (7602)	1.6.90
1350	-12.78	1	1	50	-1			1.0	2	CORE	1.6.90
1360	2.98	2	1	101	1				2	CORE (7602)	1.6.90
1370	11.397	2	1	101	1	50	1		2	CORE	1.6.90
1380	2.37	2	1	102	1				2	CORE (7602)	1.6.90
1740	-11.44	2	1	50	-1			1.0	2	CORE (7602)	1.6.90
1749	11.514	3	1	101	1	50	1		2	CORE (8401)	21.3.91
1950	-13.29	3	1	50	-1			1.0	2	CORE (7602)	1.6.90
1951	2.805	3	1	101	1				2	CORE (8300*)	1.6.90
1952	2.29	3	1	102	1				2	CORE (7602)	1.6.90
1953	0.00	3	1	103	2				2	8201	17/2/83
1959	-14.46	4	1	50	-1			1.0	2	CORE	1.6.90
1960	0.85	4	1	102	1				2	CORE (7602)	1.6.90
1999	-14.18	5	1	50	-1			1.0	2	CORE	1.6.90
2000	1.27	5	1	101	1				2	CORE	1.6.90
2001	10.079	5	1	101	1	50	1		2	CORE	1.6.90
2010	0.70	5	1	102	1				2	CORE (7602)	1.6.90
12530	10.329	50	1	101	1				2	CORE	1.6.90
12540	16.681	50	2	101	1				2	CORE	1.6.90
12550	1.988	50	1	102	1				2	CORE	1.6.90
12710	13.33	50	1	112	1				2	CORE (NEA) (7602)	1.6.90
12712	27.28	50	2	112	2				2	STAND (NEA)	2.9.90
12713	38.18	50	3	112	2				2	STAND (NEA)	2.9.90
12715	40.82	50	3	112	3				2	STAND (NEA) CYCL.	2.9.90
12716	39.42	50	3	112	3				2	STAND (9005) LIN.	2.9.90
12718	54.56	50	4	112	4				2	STAND (9005)	2.9.90
12719	67.06	50	5	112	4				2	STAND (NEA)	2.9.90
12720	23.14	50	2	112	1				2	CORE (NEA) (7602)	1.6.90
12726	14.93	50	1	112	1	5	1		2	STAND (9005)	2.9.90
13595	-14.00	50	-1					1.0	2	CORE	1.6.90
20000	8.48	1	1	101	1				5	CORE CALCITE	1.6.90
20001	8.336	1	1	101	1				5	CORE ARAGONITE	1.6.90
20010	4.581	1	1	102	1			2.0	5	CORE GYPSUM	1.6.90
20011	4.357	1	1	102	1				5	CORE ANHYDRITE	1.6.90
20130	-22.81	1	1	50	-2			2.0	5	CORE (7601) PORTLAN.	1.6.90
20140	8.04	2	1	101	1				5	8301 MAGNESITE	14.2.84
20145	17.09	1	1	2	1	101	2		5	CORE DOLOMITE ord.	21.3.91
20149	16.54	1	1	2	1	101	2		5	CORE DOLOMITE disord	21.3.91
20200	-16.84	2	1	50	-2			2.0	5	CORE BRUCITE	1.6.90
20210	9.271	3	1	101	1				5	CORE STRONTIANITE	1.6.90
20220	6.632	3	1	102	1				5	CORE CELESTITE	1.6.90
21440	27.12	50	2	112	1			-2.0	5	CORE QUARTZ (3.98)	1.6.90
21441	25.85	50	2	112	1			-2.0	5	CORE SiO2 am. (2.71)	1.6.90
21442	26.691	50	2	112	1			-2.0	5	CORE CHALCED. (3.55)	1.6.90
25000	18.149	50	2	101	1			-1.0	6	CORE CO2-gas	1.6.90

B) Nickel

ID	log K	ID1	c1	ID2	c2	ID3	c3	(etc.)	type	Info + Ref.	last update
6765	5.78*	13	1	101	1				2	7902	21.3.91
6766	10.11*	13	1	101	2				2	8105	21.3.91
6767	13.41*	13	1	101	1	50	1		2	7902	21.3.91
6770	2.31	13	1	102	1				2	8208	21.3.91
6771	3.2	13	1	102	2				2	8102	21.3.91
6780	0.4	13	1	103	1				2	8105	21.3.91
6781	0.96	13	1	103	2				2	SUPPL 8105	NiCl2
7590	-9.71	13	1	50	-1			1.0	2	8208	21.3.91
7591	-20.0	13	1	50	-2			2.0	2	7602	21.3.91
7592	-30.0	13	1	50	-3			3.0	2	7601	21.3.91
7593	-44.00	13	1	50	-4			4.0	2	7601	21.3.91
7594	-10.70	13	2	50	-1			1.0	2	7601	21.3.91
7595	-27.74	13	4	50	-4			4.0	2	7601	21.3.91
20710	6.97*	13	1	101	1				5	7102 NiCO3	21.3.91
20711	-5.33	13	1	102	1				5	8208 NiSO4	21.3.91
20712	2.01	13	1	102	1			6.0	5	7805 NiSO4.6H2O	21.3.91
20713	2.02	13	1	102	1			7.0	5	7805 NiSO4.7H2O	21.3.91
20715	-8.36	13	1	103	2				5	7903 NiCl2	21.3.91
20716	-3.89	13	1	103	2			2.0	5	8208 NiCl2.2H2O	21.3.91
20717	-3.8	13	1	103	2			4.0	5	8208 NiCl2.4H2O	21.3.91
20718	-3.09	13	1	103	2			6.0	5	8208 NiCl2.6H2O	21.3.91
20737	25.2	13	1	112	1			-1.0	5	7704 NiSiO3	21.3.91
20738	3.83	13	2	112	1	50	-2		5	8403 NiSiO4 olivine	21.3.91
20739	2.43	13	2	112	1	50	-2		5	8403 NiSiO4 spinel	21.3.91
20750	-12.73	13	1	50	-2			2.0	5	8208 Ni(OH)2	21.3.91
20751	-12.45	13	1	50	-2			1.0	5	8208 NiO bunsenite	21.3.91
20752	-19.2	13	2	103	1	50	-3	3.0	5	8204 Ni(OH)1.5Cl0.5	21.3.91
20753	-44.	13	4	103	1	50	-7	7.0	5	8204 Ni(OH)1.75Cl0.25	21.3.91

* instead of these values, the following, corrected values are used:

ID	log K	ID1	c1	ID2	c2	ID3	c3	(etc.)	type	Info + Ref.	last update
6765	4.30	13	1	101	1				2	PSI 1997	4.2.98
6766	not included any more								2	PSI 1997	4.2.98
6767	not included any more								2	PSI 1997	4.2.98
20710	11.20	13	1	101	1				5	Grauer 1994	4.2.98

A.3.3 List of References Cited in the Data Files of Appendix A.3.2

This Appendix presents the reference list supplied with the database of the code MIN_SURF (Berner, 1993). The data files in Appendix A.3.2 ($\log_{10} K^{\circ}$) contain a column with a reference code consisting of 4 digits plus a 1-digit qualifier. The first 2 digits of the reference code refer to the year of publication. The qualifier contains information on deviations from standard and/or reference conditions (A-I), on the quality of the value (U, X, *) if it has been assessed, or on ionic strength corrections performed on the original data (Z, Y), see the list below. Reference codes consisting of letters, e.g. CORE, SUPPL, STAND, NEA, etc., are explained at the end of this Appendix.

THE FOLLOWING QUALIFIERS 'Q' ARE USED IN THE THERMODYNAMIC DATABASE (X = IONIC STRENGTH, T = TEMPERATURE) IN THE FIFTH POSITION OF THE REFERENCE FIELD:

	X = 0	X ≤ 0.5	X = 1.0	X = 2.0	X = 3.0
T = 25	BLANK	A	B	C	D
T ≠ 25	E	F	G	H	I

AND:
U - UNCERTAIN
X - LACK OF X/T - INDICATION
* - GUESS

NEW:
Z - VALUES ARE CORRECTED TO IONIC STRENGTH I=0 USING THE DAVIES EQUATION.

Y - VALUES ARE CORRECTED TO IONIC STRENGTH I=0 USING THE SPECIFIC ION-INTERACTION THEORY (SIT).
GRENTHE I., WANNER H.,
GUIDELINES FOR THE EXTRAPOLATION TO ZERO IONIC STRENGTH
TDB-2.1, OECD NEA, 1989

7102 NAUMOV G.B.,RYZHENKO B.N., KHODAKOVSKI I.L.,
HANDBOOK OF THERMODYNAMIC DATA,
MOSCOW ATIOMIZSAT. 1971 (TRANSL.FROM RUSSIAN BY G.H. SOLEIMANI,
I.BARNER AND Y.SPELTSZ,EDS.), REPORT WRD-74-01 U.S.GEOL.SURVEY,
MENLO PARK, CA, 328 P., 1974.

7601 BAES C.F., MESMER R.E.
THE HYDROLYSIS OF CATIONS
NEW YORK: JOHN WILEY, PP.158-192, 1976.

7602 SMITH R.M., MARTELL A.E.
CRITICAL STABILITY CONSTANTS
NEW YORK: PLENUM PRESS, 1976.

7602Y VALUES FROM REF. 7602; IONIC STRENGHT CORRECTED FROM I=1 M (NACLO4)
OR I=0.5 TO I=0 WITH S.I.T (SPECIFIC ION INTERACTION THEORY)
USING E (AM+3, CLO4-) = 0.47
E (SO4-2,NA+) =-0.12
E (AMSO4+,CLO4-) = 0.31
E (EU(SO4)2-, NA+) = 0.0
E (F-, NA+) = 0.02
E (AMF+2, CLO4-) = 0.3
E (AMF2+, CLO4-) = 0.3
E: ION INTERACTION COEFFICIENT
SEE PSI-REPORT NO. ?? (TO BE PUBLISHED)

7602Z VALUES FROM REFERENCE 7602; IONIC STRENGHT CORRECTION
TO ZERO IONIC STRENGHT MADE BY APPLYING THE
DAVIES EQUATION USING A LINEAR "I"-CORRECTION OF -0.3
CONCERNS ONLY CITRATE EQUILIBRIA

7704 TARDY Y., GARRELS R.M.,
PREDICTIONS OF GIBBS ENERGY OF FORMATION OF COMPOUNDS FROM THE
ELEMENTS: II. MONOVALENT AND DIVALENT METAL SILICATES,
GEOCHIM.COSMOCHIM.ACTA, **41** (1977) 87-92.

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THERMODYNAMIC PROPERTIES OF MINERALS AND RELATED SUBSTANCES AT 298K
AND 1 BAR PRESSURE AND AT HIGHER TEMPERATURES.
U.S.GEOL.SURVEY BULLETIN NO. 1452, 456 P., 1978 (REV. 1979)

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CHEMICAL MODELLING OF TRACER METAL EQULIBRIA IN CONTAMINATED SOIL
SOLUTIONS USING THE COMPUTER PROGRAM GEOCHEM,
IN: CHEMICAL MODELLING IN AQUEOUS SYSTEMS (E.A. JENNE, ED.) PP.
837-856, ACS SYMP. NO. 93, AMER.CHEM.SOC., WASHINGTON D.C., 1979.

7903 KUBASCHEWSKI O., ALCOCK C.B.,
METALLURGICAL THERMODYNAMICS, 5TH ED.
OXFORD: PERGAMON PRESS, 449 P., 1979.

8102 TURNER D.L. ET AL.
GEOCHIM. COSMOCHIM. ACTA, **45** (1981) 855-881.

8105 BALL J.W., NORDSTROM D.K., JENNE E.A.,
ADDITIONAL AND REVISED THERMOCHEMICAL DATA AND COMPUTER CODE FOR
WATEQ2 - A COMPUTERIZED CHEMICAL MODEL FOR TRACE AND MAJOR ELEMENT
SPECIATION AND MINERAL EQUILIBRIA OF NATURAL WATERS,
U.S.GEOL.SURVEY WATER RECOURCES INVEST.
WRI 78-116, 1980 (2ND PRINTING 1981)

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HYDROLYSIS AND FORMATION CONSTANTS AT 25 C.
LBL-14313 / UC-70, LAWRENCE BERKELEY LABORATORY (1982).
LBL-14313 LAWRENCE LIVERMORE LAB. 65 P., 1985.

8208 WAGMAN D.D., ET AL.
THE NBS TABLES OF CHEMICAL THERMODYNAMIC PROPERTIES: SELECTED
VALUES FOR INORGANIC AND C1 AND C2 ORGANIC SUBSTANCES IN SI-UNITS.
J. PHYS. CHEM. REF. DATA, **11 (SUPPL 2)**, (1982) 1-392.

8300 SCHWEINGRUBER M.
PERSONAL ESTIMATES, 1983.

8401 BUSENBERG E., PLUMMER L.N., PARKER V.B.
GEOCHIM. COSMOCHIM. ACTA, **48** (1984) 2021.

8403 ROBIE R.A., ET AL.,
HEAT CAPACITY AND ENTROPY OF NI2SIO4-OLIVINE FROM 5 TO 1000 K AND
HEAT CAPACITY OF CO2SIO4 FROM 360 TO 1000 K.
AMER.MINERAL., **69** (1984) 1096-1101.

9005 EIKENBERG J.,
ON THE PROBLEM OF SILICA SOLUBILITY AT HIGH PH
PSI REPORT NR. 74, WUERENLINGEN/VILLIGEN, 1990.

THE RECOMMENDED USE OF THE SILICA EQUILIBRIA
IN THE PRESENT DATABASE DEPENDS ON THE CONCENTRATION
LEVEL OF SILICA IN SOLUTION AND ON THE PH-VALUE:

AT PH-LEVELS BELOW 10 IT IS SUFFICIENT TO USE THE EQUILIBRIA
NUMBERED WITH 12710 AND 12720 (H4SIO4, H3SIO4-).

IT IS PROPOSED TO INCLUDE THE EQUILIBRIA NUMBERED WITH
12712, 12713, 12715, 12716, 12718, 12719, SIMULTANEOUSLY IN ORDER
TO DESCRIBE THE SPECIATION OF SILICA UP TO A PH OF 11.2 IF
AMORPHOUS SILICA IS THE SOLUBILITY LIMITING PHASE. (POLYMERIC
SPECIES)

THE (POLYMERIC) EQUILIBRIA MAY BE USED UP TO A PH OF 12.2 IF QUARTZ LIMITS SILICA SOLUBILITY.

AT SILICA LEVELS AROUND 10**-5 TO 10**-6 (FOR EXAMPLE CSH-GEL OF HYDRATED CEMENT) THE POLYMERIC EQUILIBRIA MAY BE USED UP TO A PH OF 13.

UPDATED JUNE 1990 BY U.BERNER
****

DURING THIS UPDATING PROCEDURE A QUALITY ASPECT HAS BEEN INTRODUCED INTO THE PRESENT VERSION OF THE DATABASE. ITS ASSUMED THAT THE DATA DESCRIBING THE BASIC GROUNDWATER CHEMISTRY ARE NOW SUFFICIENTLY WELL KNOWN AND ARE AVAILABLE IN A GOOD QUALITY. THESE DATA ARE REFERENCED WITH "CORE" AND ARE MAINLY TAKEN FROM REFERENCES 9001 (MAIN SOURCE), 9101 AND "NEA".

UPDATED MARCH 1991 BY U.BERNER
****

THIS UPDATE OF THE DATABASE HAS SEVERAL REASONS:

1. THE SULPHIDE SYSTEM IS NOW EXPRESSED WITH HS- AS THE BASIC COMPONENT. THEREFORE, ALL EQUILIBRIA CONTAINING S-2 HAVE LOG K-VALUES DIFFERING FROM FORMER VERSIONS OF THE DATABASE.

2. DATA ON PD, NI AND SE FROM REFERENCE 8902 ARE INCLUDED IN THE DATABASE. REFERENCE 8902 IS NOT CITED IN THE DATABASE, SINCE THE ORIGINAL REFERENCE IS GIVEN FOR PARTICUALR EQUILIBRIA.

3. SOME OF THE "CORE"-EQULIBRIA HAD TO BE CHANGED (DIGIT CORRECTIONS) IN ORDER TO ACHIEVE COMPLETE AGREEMENT WITH THE VALUES GIVEN IN REFERENCE 9101.

4. FINAL CHANGES IN THE QUALITY PARAMETERS "CORE" AND "SUPPL"

5. CLEARING OF TYPOGRAPHICAL ERRORS

CORE	DATA FROM REFERENCE 9001, 9101 OR "NEA" WHICH ARE ASSUMED TO BE OF GOOD QUALITY. THESES DATA WILL NOT BE SUBJECT OF FURTHER UPDATING DURING AN APPROPRIATE PERIOD OF TIME (SAY 5 YEARS).
SUPPL	DATA FROM REFERENCE 9101.
STAND	SAME SOURCES AS "CORE" BUT NOT INCLUDED IN THE BASIC CORE DATA. A MODERATE TO GOOD QUALITY IS ASSIGNED TO THESE DATA. DATA WITH THE REFERENCE "STAND" ARE THE SOURCE FOR THE "SUPPL" DATA. AFTER FINAL REVISION "STAND" WILL BE CHANGED TO "SUPPL"
DEP.	EQUILIBRIA CHANGED DUE TO DEPENDENCY ON CHANGED CORE DATA (CONCERNS MAINLY CHANGES IN PROTONATION CONSTANTS OF ANIONS). THIS CHANGE KEEPS THE DEPENDENT DATA CONSISTENT WITH FORMER VERSIONS OF THE DATABASE SEE ALSO THE FILE "DEPENDENT.EQUILIBRIA".
NEA	GRENTHE I., FUGER J., LEMIRE R.J., MULLER A.B., NGUYEN-TRUNG C., WANNER H. NEA -TDB, CHEMICAL THERMODYNAMICS OF URANIUM NUCLEAR ENERGY AGENCY (OECD), GIF-SUR-YVETTE, FRANCE FINAL DRAFT OF MARCH 1990.

NEA1 GRENTHE I., FUGER J., LEMIRE R.J., MULLER A.B.,
NGUYEN-TRUNG C., WANNER H.
NEA -TDB, CHEMICAL THERMODYNAMICS OF URANIUM
NUCLEAR ENERGY AGENCY (OECD), GIF-SUR-YVETTE, FRANCE
DRAFT VERSION OF JUNE 1991.

NEA2 SILVA, R.J., BIDOGLIO, G., RAND, M.H., ROBOUCH, P.B., WANNER, H.,
PUIGDOMENECH, I.
NEA -TDB, CHEMICAL THERMODYNAMICS OF AMERICIUM
AMSTERDAM, NORTH-HOLLAND, 1995.

SULPH DURING THE UPDATE OF 23.3.91 THE BASIC SPECIES FOR THE SULPHIDE SYSTEM HAS BEEN CHANGED FROM S-2 TO HS- .
IN A FORMER VERSION (OCTOBER 1990) ALL SULPHIDE EQUILIBRIA HAD BEEN CHANGED BY 5.1 LOG K UNITS PER S-2 BASED ON A 5.1 LOG K - CHANGE IN THE EQUILIBRIUM S-2 + H+ = HS- . THIS CHANGE IS BACK-CORRECTED IN THE 1991-VERSION OF THE DATABASE. ALL SUPLPHIDE EQUILIBRIA ARE NOW EXPRESSED USING HS- AS THE BASIC SULPHIDE SPECIES. TO PERFORM THE CORRECTION IT WAS ASSUMED THAT ALL EQUILIBRIA CONTAINING THE SULPHIDE ION S-2 WERE ORIGINALLY BASED ON LOG K = 13.9 FOR THE REACTION S-2 + H+ = HS- AS GIVEN IN REFERENCE 7602.

4.　ベントナイトの間隙水水質モデルの検討

Model Simulations of Porewater Chemistry in Compacted
Bentonite under Near-Field Conditions.

Reference Case Analysis

Model Simulations of Porewater Chemistry in Compacted Bentonite under Near-Field Conditions.

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Executive Summary

The generic nature of PNC's performance assessment activities makes it difficult to rely exclusively on experimental evidence, and therefore, thermodynamic/mechanistic models are used to support parameter setting, porewater definition, and so on. In line with this approach, the different types of reference groundwaters considered in PNC's performance analysis have largely been defined based on geochemical modeling (PNC, 1992). In this report, the results of different activities related to the definition of porewater chemistry through the use of geochemical models are presented.

The porewater composition in compacted bentonite is dependent on the composition of the surrounding groundwater, and on the characteristics of the bentonite itself. Two mechanisms may be distinguished through which bentonite influences the respective porewater composition: surface chemical reactions (ion exchange, surface complexation) and the dissolution of soluble impurities. With respect to the calculation of porewater compositions, (1) the treatment and predicted effects of bentonite surface chemistry as influenced by the choice of models is evaluated, and (2) a sensitivity analysis for the effect of soluble impurities is performed. Finally, (3) the composition of bentonite porewaters is calculated for a large number of conditions.

(1) *Evaluation of model properties and input parameters:* Different approaches commonly used for ion exchange modeling are presented and evaluated. The use of the equivalent fraction model is recommended. The simple complexation model is not well accepted by experts, and the respective constants are conditional in nature and need to be back-calculated for each case based on either K_V or K_{GT}. If neither K_V or K_{GT} are known, K_{no} cannot be extrapolated at all. Both mole fraction and equivalent fraction approaches are thermodynamically valid, accepted, and the constants can be extrapolated to different systems if the experimental conditions are known. The equivalent fraction model is easy to use with any speciation code, whereas the mole fraction model requires additional programming.

(2) *Performance of sensitivity analyses:* In compacted bentonite it is possible that only a part of the soluble impurities is actually available to the porewater, i. e., is able to dissolve. Since this quantity is unknown, but may be very important at the same time, sensitivity analyses were performed to check the influence of differnt assumptions regarding the dissolution of impurities on the respective predicted porewater composition. These model calculations indicate that:

- The presence of calcite, gypsum and pyrite strongly influences the pH in the compacted bentonite. Equilibrium with calcite increases the pH, while dissolution of gypsum, or large amounts of NaCl, lowers the pH. Oxidation of pyrite strongly lowers pH in the compacted Kunigel-V1 bentonite.
- The pH in compacted bentonite is buffered both by the acid/base equilibria at the edge sites of the bentonite and by the carbonate buffer system.
- The assumption of a closed system with respect to CO_2 results in high CO_2 partial pressures due to calcite dissolution.

(3) *Calculations of bentonite porewater compositions:* Based on the findings discussed under (1) and (2) above, a large number of calculations were carried out to support the definition of the porewater in the backfill (compacted bentonite) of nuclear waste repositories. These calculations were performed for five different PNC reference groundwaters that were assumed to be in equilibrium with compacted bentonite. In addition, the presence of corrosion products stemming from the carbon steel overpack of the waste was modeled for each set of conditions. In connection with these calculations, the relevance of different mineral and redox equilibria for the PNC Reference Case Analysis is discussed.

Table of Contents

1 Introduction

For its next comprehensive performance assessment report (H-12 report), PNC is conducting a generic performance analysis. According to the multi-barrier concept that forms the basis for the deep geological disposal of high-level nuclear waste in Japan, PNC requires solubility, sorption, and diffusion data for 22 key elements that are applicable to (i) the bentonite backfill, and (ii) to rock types relevant for the far-field of possible repository sites. Therefore, a wide variety of geological materials has to be considered, and transport parameter setting has to be carried out for a number of different systems, including different types of groundwater.

The generic nature of PNC's performance assessment activities makes it difficult to rely exclusively on experimental evidence, and thermodynamic/mechanistic models have to be used to support parameter setting, porewater definition, and so on. In line with this approach, the different types of reference groundwaters considered in PNC's performance analysis have largely been defined based on geochemical modeling (PNC, 1992).

The Japanese disposal concept for high-level radioactive waste envisages the use of compacted bentonite as a backfill material (PNC, 1992). The backfill is an effective, and possibly the most predictable barrier on the entire migration path. This renders the transport parameter setting for compacted bentonite very important. The generic nature of the reference groundwaters, and the inaccessibility of compacted bentonite to most experimental techniques make it impossible to rely exclusively on experimental evidence, and thermodynamic/mechanistic models or expert judgment have to be used instead. Therefore, PNC attributes great importance to the thorough understanding of the processes affecting porewater chemistry and radionuclide transport in compacted bentonite. In order to provide a framework with respect to documentation and traceabilty for this approach, an Integrated Sorption/Diffusion (ISD) database system was suggested in our previous contract work (Wanner, 1995).

In Figure 1.1, the ISD concept is extended to the present application, providing an overview of the structure of this system. The boxes represent data records and models, respectively. The arrows represent input/output data transfers. Both the data records and the models carry labels in the form of names or version numbers. Hence, the resulting porewater composition, and K_d and D_a values for a specific nuclide can be referred to a well-defined bentonite (e.g., Kunigel-V1), TDB, groundwater type, sorption model, and diffusion model, ensuring full internal consistency.

In this report, the results of different activities related to the definition of porewater chemistry through the use of geochemical models are presented:

- evaluation of model properties and input parameters,
- performance of sensitivity analyses,
- calculations of bentonite porewater compositions.

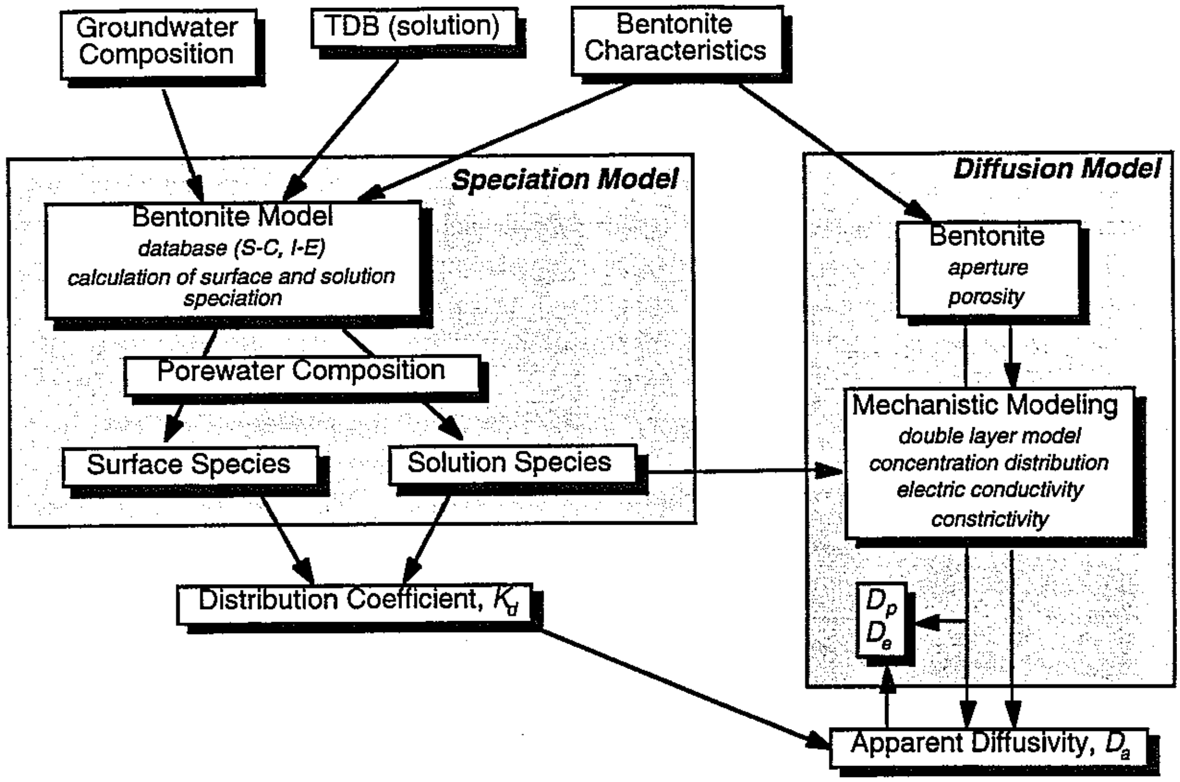

Figure 1.1 Overview of the Integrated Sorption/Diffusion (ISD) database system originally proposed in our FY95 report (Wanner, 1995). For the present application, this system is extended to specifically include the calculation of bentonite porewater characteristics.

2 Model characteristics

As shown in Figure 1.1, the porewater composition in compacted bentonite is dependent on

- the composition of the surrounding groundwater, and on
- the characteristics of the bentonite itself.

In dilute suspensions typical for experimental batch systems, the solution composition is largely dominated by the respective input solution, but with increasing degree of compaction, the influence of the bentonite itself becomes dominant.

Two mechanisms may be distinguished through which bentonite influences the respective porewater composition:

- Surface chemical reactions (ion exchange, surface complexation) affect the concentrations of the major cations in the pore solution. Ion exchange taking place at the layer sites of clay minerals is very important with respect to the distribution of Ca^{2+}, Mg^{2+}, K^+, Na^+, and at $pH < \approx 5\text{-}6$, H^+. Surface complexation taking place at the edge sites of clay

minerals functions like a pH buffer through the uptake or release of H^+ ions at surface-SOH groups.
- Dissolution of soluble impurities influences porewater composition through the respective mineral equilibria. Salts like NaCl may dissolve completely, minerals like calcite or gypsum may dissolve according to their solubility product.

In the following sections, these mechanisms are discussed in view of the model choices that have to be made in order to carry out porewater calculations.

2.1 Approaches to ion exchange modeling

Models used for quantitative descriptions of ion exchange reactions can be divided into two basic categories (see e. g. Babcock, 1963; Sposito, 1981):

- double layer models, and
- models based on mass-action theory.

2.1.1 Double layer models

All double models basically rely on the Gouy equations to describe the distribution of ions at the interface between clay layer surface and solution. In order to do this, the following assumptions are typically made:

1. The exchange sites form a continuum of negative charge on an infinite planar surface; i. e., there are no discrete exchange sites.
2. All exchangeable cations are completely dissociated form the surface and interact electronically with the surface and each other; i. e., no complexes are formed.
3. The mean electric potential at a given distance x from the surface is proportional to the average energy required to bring an ion from infinite distance to distance x.
4. The water in the system has a uniform dielectric constant.

Based on these assumptions, the total charge density of the surface σ can be related to the concentration of counterions at a certain distance from the surface:

$$\sigma = -\int_0^d \rho(x)\,dx \qquad (2.1)$$

where $\rho(x)$ is the net amount of positive ionic charge per volume between x and $x + dx$ near the surface, and d is the distance where charge balance between solution and surface is achieved; x is the distance from the surface, with $x = 0$ directly at the surface. With only one surface present, d is at infinity; with two surfaces present (i. e., in the interlayer of clays), d is located midway between the surfaces. Note that equation (2.1) also forms the basis for the definition of constrictivity in the mechanistic diffusion model of Sato et al. (1995).

An important limitation of double layer models is the inability to explain cation selectivity in many cases. It is a direct consequence of assumption 2. above that cations of the same valency cannot display any selectivity among each other.

2.1.2 *Mass-action or site-binding models*

The basic assumption of this type of model is that a suspension consists of two distinct phases, namely the exchanger phase, including the exchangeable cations, and the solution. This clear separation of ions located at the surface and in solution allows the formulation of mass-action laws and equilibrium constants. Depending on the actual model used, further assumptions are important. Typical assumptions are:

1. The exchange reactions occur on discrete, identical sites, through chemical interactions between exchange site and cations.
2. The exchange process is the replacement of cations according to electroneutrality; i. e., a cation of charge +*u* will occupy *u* sites. The relative affinity of cations for the surface may be described through thermodynamic equilibrium constants.
3. The exchange sites are covered at all times with exchangeable cations, in accordance with assumption 2.
4. The cations on the sites do not interact with one another.

Through these assumptions, cation exchange reactions may be formulated analogous to complex formation in solution by treating exchange sites as hypothetical ligands. In other words, ion exchange sites may be used in exchange reactions in the same way as the free electron in redox reactions.

The above model does not consider any change in the activity of the exchanger phase, but experience suggests that the activity of the exchanger phase does not remain perfectly constant in the course of an exchange experiment. Thus, several models have been developed that allow to correct the activity of the exchanger phase as a function of its composition; i. e., as a function of the composition of the cations bound to the exchange sites. The most common approaches for such activity corrections are the mole-fraction (Vanselow) and equivalent-fraction (Gaines-Thomas) convention.

All bentonite models discussed in this report are based on this mass-action approach. Its implementation in a speciation code such as MIN_SURF allows to formulate ion exchange equilibria using either the mole- or equivalent fraction approach, or to use no activity corrections. This is discussed in detail below.

2.1.3 *Ion exchange equilibria*

Typically, ion exchange reactions are formulated as follows:

$$2\ \mathrm{NaZ} + \mathrm{Ca}^{2+} \rightleftarrows \mathrm{CaZ}_2 + 2\ \mathrm{Na}^{+} \tag{2.2}$$

Mass action models treat the surface species NaZ and CaZ_2 as hypothetical aqueous species with the following equilibrium constant:

$$K = \frac{\{\mathrm{CaZ_2}\}\ \{\mathrm{Na^+}\}^2}{\{\mathrm{NaZ}\}^2\{\mathrm{Ca^{2+}}\}} \tag{2.3}$$

where { } denote activities.

In equation (2.3), the activity of the dissolved species can be calculated in the usual fashion, e. g. by using the Davies equation. The activity of the surface species is not well defined, however. Therefore, researchers adopted a simplified concept (that of an ideal mixture) to calculate the activities. In order to do this, different approaches (mole fraction, equivalent fraction) have been developed to represent the activities of the exchanger species, leading to slightly different, but equally valid and consistent solid-phase activity coefficients. The activity of the sorbed ions is taken to be unity.

2.1.4 *Mole fraction convention*

In the mole fraction or Vanselow model, the equilibrium constant of reaction (2.2) is expressed by the following equation:

$$K_V = \frac{N_{(\mathrm{CaZ_2})}\ \{\mathrm{Na^+}\}^2}{(N_{(\mathrm{NaZ})})^2\{\mathrm{Ca^{2+}}\}} \tag{2.4a}$$

where *N* are the mole fractions defined as follows:

$$N_{(\mathrm{CaZ_2})} = \frac{[\mathrm{CaZ_2}]}{[\mathrm{CaZ_2}] + [\mathrm{NaZ}]} \tag{2.4b}$$

$$N_{(\mathrm{NaZ})} = \frac{[\mathrm{NaZ}]}{[\mathrm{CaZ_2}] + [\mathrm{NaZ}]} \tag{2.4c}$$

The correction term needed for the conversion from concentration units (equation 2.3) to mole fraction units (equation 22.4) can be obtained by dividing K_V by K and has the following form:

$$K_V = K([CaZ_2] + [NaZ]) \tag{2.4d}$$

Note that this correction factor, $[CaZ_2]+[ZNa]$, is not equal to the cation exchange capacity (CEC), since CEC = $2[CaZ_2]+[ZNa]$ in a system containing only Na and Ca as exchangeable ions.

2.1.5 *Equivalent fraction convention*

In the equivalent fraction or Gaines-Thomas model, the equilibrium constant of reaction (2.2) is expressed by the following equation:

$$K_{GT} = \frac{E_{(CaZ_2)} \; \{Na^+\}^2}{(E_{(NaZ)})^2 \{Ca^{2+}\}} \tag{2.5a}$$

where E are the mole fractions defined as follows:

$$E_{(CaZ_2)} = \frac{2[CaZ_2]}{2[CaZ_2] + [NaZ]} \tag{2.5b}$$

$$E_{(NaZ)} = \frac{[NaZ]}{2[CaZ_2] + [NaZ]} \tag{2.5c}$$

Again, the correction term needed for the conversion from concentration units (equation 2.2) to equivalent fraction units (equation 2.5) can be obtained by dividing K_{GT} by K and has the following form:

$$K_{GT} = K\,2(2[CaZ_2] + [NaZ]) \tag{2.5d}$$

Note that this correction factor, $2(2[CaZ_2]+[ZNa])$, is equal to twice the cation exchange capacity (CEC), *expressed in molar units,* since CEC = $2[CaZ_2]+[ZNa]$ in a system containing only Na and Ca as exchangeable ions.

2.1.6 *Implications for MIN_SURF or other equilibrium speciation codes*

As explained in several earlier reports prepared within our PNC contract work, ion exchange reactions are treated by splitting the exchange reaction in equation (2.2) into half-reactions (formation reactions) involving the exchanger site Z^-:

$$NaZ = Na^+ + Z^-, \; \frac{1}{K_{(NaZ)}} \tag{2.6a}$$

$$Ca^{2+} + 2Z^- = CaZ_2,\ K_{(CaZ_2)} \tag{2.6b}$$

Using the half-reactions given in equations (2.6a-b), the equilibrium constants corresponding to equations (2.2), (2.4a), and (2.5a) can be expressed as follows:

$$K = \frac{K_{(CaZ_2)}}{\left(K_{(NaZ)}\right)^2} \tag{2.7a}$$

$$K_V = \frac{K_{(CaZ_2)}\left([CaZ_2] + [NaZ]\right)}{\left(K_{(NaZ)}\right)^2} \tag{2.7b}$$

$$K_{GT} = \frac{K_{(CaZ_2)}\ 2\,CEC}{\left(K_{(NaZ)}\right)^2} \tag{2.7c}$$

Note that these correction terms cancel out for homovalent exchange. Since the constants used in the bentonite models discussed in this report are based on the definition that the formation constant for the species NaZ = 10^{20}, only the constants for divalent ions (Ca^{2+}, Mg^{2+}, Ra^{2+}, Sr^{2+}, Ni^{2+}, Pb^{2+}) are model-dependent; the constants for K^+ and H^+ are identical for each approach discussed here.

A comparison of equations (2.7a-c) shows that the equivalent fraction approach involves only a relatively simple correction (2 CEC, expressed in molar units) that will remain constant during the course of a speciation calculation. The correction factor for the mole fraction approach, however, depends on the actual composition of the exchanger phase and needs to be updated after each iteration step (this necessitates to link this correction with the iteration procedure of a speciation code).

Thus, for the PNC performance assessment, it appears that the equivalent fraction approach is promising (as an alternative to simply using the complexation model without any correction), since this could also be used with PHREEQC or HYDRAQL, by performing the necessary correction by hand for each calculation.

2.2 *Comparison of mole fraction model, equivalent fraction model, and complexation model ('uncorrected model')*

The influence of different ion exchange models on the ion exchange constants and the calculated porewater compositions for Kunigel-V1 is assessed in this section.

2.2.1 *Ion exchange constants*

Henceforth, the following terminology is used:

- mole fraction constants: K_V
- equivalent fraction constants: K_{GT}
- complexation (non-corrected) constants: K_{no}

In Table 2.1, the formation constants for the half-reaction:

$$M^{2+} + 2\,Z^- = MZ_2$$

are given for the experimental system that these constants were derived from (Wanner et al., 1992). Under the experimental conditions used by these authors, the correction factor to convert K_{no} (the non-corrected complexation constant) to K_V (the mole fraction constant) is very close to unity. However, this is only a coincidence: in other situations, these constants will be different (see Table 2.1).

Table 2.1: Formation constants of the surface species Z_2Mg and Z_2Ca. K_{GT} and K_V are generally valid, K_{no} is valid only for the experimental conditions considered in Wanner et al. (1992). Details regarding the conversion are given in the footnotes. Note that each set of constants must only be used together with the respective model.

Surface species	complexation model (no correction) log K_{no}	equivalent fraction model [1] log K_{GT}	mole fraction model [2] log K_V	Reference
Z_2Mg	40.13	40.46 [3]	40.13 [4]	Wanner et al. (1992)
Z_2Ca	40.2	40.53 [3]	40.2 [4]	Wanner et al. (1992)

CEC' is the CEC in moles/L; i. e., accounts for the solid/water ratio.

[1] $\log K_{GT} = \log K_{no} + \log(2 \times CEC')$

[2] $\log K_V = \log K_{no} + \log([MgZ_2] + [CaZ_2] + [NaZ])$

[3] CEC = 76.4 meq/100g; s/w = 1.4 g/mL: CEC' = 1.07 mol/L; $\log(2 \times CEC') = 0.33$

[4] $[MgZ_2] + [CaZ_2] + [NaZ] \approx 0.93 \times CEC' = 0.99$ mol/L; $\log CEC' = -0.003$ (CEC = 76.4 meq/100g; s/w = 1.4 g/mL)

It is very important to realize that only K_V and K_{GT} can be directly applied to other experimental systems; K_{no} (i. e., the constant referring to the simple complexation model) is a conditional constant containing implicitly information on the solid/water ratio used, the CEC of the respective solid etc., and is only valid under the experimental conditions used to derive it. In other words: in order to use constants derived from e. g. MX-80 or taken from the literature to calculate the porewater of Kunigel-V1, these constants must be based on the mole fraction or equivalent fraction format. Calculations can then be carried out directly with these constants by using the mole or equivalent fraction models. In order to use the complexation (non-corrected) model, K_V and K_{GT} need to be back-calculated to K, using the correct conditions (solid/water ratio, CEC).

In Table 2.2, the same dataset given in Table 2.1 is modified for the input of a model calculation with 1800 kg/m^3 Kunigel-V1. Note that the values for K_{GT} and K_V are the same as in Table 2.1, whereas K_{no} had to be recalculated (from either K_{GT} or K_V) for this particular case.

Table 2.2: Formation constants of the surface species Z_2Mg and Z_2Ca for the input of a model calculation with 1800 kg/m^3 Kunigel-V1. Details regarding the conversion are given in the footnotes. Note that each set of constants must only be used together with the respective model.

Surface species	equivalent fraction model [1] log K_{GT}	mole fraction model [1] log K_V	complexation model [2] log K_{no}	Reference
Z_2Mg	40.46	40.13	39.65	Wanner et al. (1992)
Z_2Ca	40.53	40.2	39.72	Wanner et al. (1992)

CEC' is the CEC in moles/L; i. e., accounts for the solid/water ratio.

[1] The constants for the mole fraction and equivalent fraction model can be used without further corrections

[2] $\log K_{no} = \log K_{GT} - \log(2 \times CEC')$; CEC = 60.1 meq/100g; s/w = 5.4 g/mL: CEC' = 3.25 mol/L

2.2.2 *Influence of different ion exchange models on calculated porewater compositions*

The results of the respective model calculations are given in Table 2.3, using the PNC reference groundwater SRHP as input solution. Note that the correct use of either model, together with the appropriate constants, leads to practically identical results. However, failing to recalculate K_{no} from K_{GT} or K_V leads to erroneous results.

Table 2.3: Influence of different ion exchange models on calculated porewater compositions for Kunigel-V1 (dry density = 1800 kg/m^3) in contact with SRHP PNC reference groundwater, as calculated (at 25 °C) with the extended Wanner model. The respective surface speciation is given in Table 2.4.

parameter	equivalent fraction model (K_{GT}, Table 2.2)	mole fraction model (K_V, Table 2.2)	complexation model (K_{no} recalculated from K_{GT}, Table 2.2)	complexation model (K_{no} not recalculated, Table 2.1) [1]
Ca	2.80E-02	2.81E-02	2.79E-02	1.73E-02
Mg	6.35E-03	6.36E-03	6.33E-03	3.57E-03
Na	5.66E-01	5.66E-01	5.67E-01	6.42E-01
K	5.21E-03	5.21E-03	5.21E-03	6.00E-03
Al	2.05E-11	2.05E-11	2.05E-11	2.05E-11
Fe(II)	1.52E-13	1.52E-13	1.52E-13	1.52E-13
Cl	5.58E-1	5.58E-1	5.58E-1	5.58E-1
SO_4	2.93E-2	2.93E-2	2.94E-1	5.17E-2
HS	2.65E-2	2.65E-2	2.65E-2	2.65E-2
CO_3	5.93E-3	5.93E-3	5.95E-3	8.67E-3
SiO_4	1.06E-4	1.06E-4	1.06E-4	1.06E-4
total H^+	1.61E-2	1.61E-2	1.61E-2	1.61E-2
pH	6.59	6.59	6.59	6.68
ionic strength	0.69	0.69	0.69	0.74
precipitated minerals [2]	calcite gypsum	calcite gypsum	calcite gypsum	calcite gypsum

[1] Note that this approach is for illustration only, it is not valid, however!

[2] Calcite and gypsum are originally present as soluble impurities contained in Kunigel-V1. Upon dissolution of the impurities, the surrounding solution becomes supersaturated, and these minerals precipitate as separate solid phases.

Based on these findings, we recommend the use of the equivalent fraction model and constants. The complexation model is not well accepted by experts, and the respective constants are conditional in nature and need to be back-calculated for each case based on either KV or KGT. If neither KV or KGT are known, Kno cannot be extrapolated at all. Both mole fraction and equivalent fraction approaches are thermodynamically valid, accepted, and the constants are generally valid; i. e., can be extrapolated to different systems if the experimental conditions are known. The equivalent fraction model is easy to use with any speciation code, whereas the mole fraction model requires additional programming.

Table 2.4: Influence of different ion exchange models on calculated surface speciation of Kunigel-V1 (dry density = 1800 kg/m^3) in contact with SRHP PNC reference groundwaters, as calculated (at 25 °C) with the extended Wanner model. The respective solution speciation is given in Table 3.

parameter	equivalent fraction model (K_{GT}, Table 2.2)	mole fraction model (K_V, Table 2.2)	complexation model (K_{no} recalculated from K_{GT}, Table 2.2)	complexation model (K_{no} not recalculated, Table 2.1) [1]
Speciation of ion exchange sites (%)				
ZNa	86.34	86.35	86.33	84.00
ZK	1.44	1.44	1.44	1.41
Z_2Mg	1.92	1.92	1.92	2.09
Z_2Ca	10.26	10.25	10.27	12.47
ZH	0.05	0.05	0.05	0.04
Speciation of surface complexation sites (%)				
SO^-	18.5	18.5	18.5	19.0
SOH	68.7	68.7	68.7	68.6
SOH_2^+	12.8	12.8	12.8	12.4

[1] Note that this approach is for illustration only, it is not valid, however!

3 Sensitivity analyses (1): Porewater calculations

3.1 Selection of ion exchange constants

In Wanner et al. (1992), Wieland et al. (1994) and Fletcher and Sposito (1989) different values for the ion exchange of Ca^{2+}, Mg^{2+} and H^+ vs. Na^+ are given (cf. Table 3.1 and Table 3.3). The influence of the different constants from Wanner et al. (1992), Wieland et al. (1994) or Fletcher and Sposito (1989) on the calculated porewater composition of compacted bentonite is examined in this section.

Three different sets of ion exchange constants are compared in this report:

- Extended Wanner Model/Version 1 (Table 3.1 and Table 3.2), which uses ion exchange constants given by Wanner et al. (1992) and Wieland et al. (1994),
- Extended Wanner Model/Version 2 (Table 3.3 and Table 3.4), which uses the ion exchange constants of Ca^{2+}, Mg^{2+} and H^+ as given by Fletcher & Sposito (1989),
- Bentonite Model/RCA.1 (Table 3.5 and Table 3.6), which uses the ion exchange constants for Ca^{2+} and Mg^{2+} given by Wanner et al. (1992) and the H^+ vs. Na^+ constant from Wieland et al. (1994).

The constants used for each model are given according to both the mole fraction equivalent fraction formalism.

Table 3.1: Bentonite model used in Ochs and Wanner (1996) and Ochs and Lothenbach (1997) ('Extended Wanner Model/Version 1'), corresponding to the mole fraction formalism.

Surface species	$\log_{10} K^\circ$	Reference
Surface site master species: Z^-		
Surface site density:		bentonite specific
ZNa	20.0	Wanner (1986)
ZK	20.26	Fletcher and Sposito (1989)
Z_2Mg	40.13	Wanner et al. (1992)
Z_2Ca	40.2	Wanner et al. (1992)
ZH	23.0	Wieland et al. (1994)
Surface site master species: SOH		
Surface site density:		2.84×10^{-5} mol/g [1]
SOH_2^+	5.4	Wanner et al. (1994)
SO^-	–6.7	Wanner et al. (1994)

[1] Obtained for pretreated MX-80 which had a CEC of 108 meq/100 g.

Table 3.2: Bentonite model used in Ochs and Wanner (1996) and Ochs and Lothenbach (1997) ('Extended Wanner Model/Version 1'), corresponding to the equivalent fraction formalism.

Surface species	$\log_{10} K^\circ$	Reference
Surface site master species: Z^-		
Surface site density:		bentonite specific
ZNa	20.0	Wanner (1986)
ZK	20.26	Fletcher and Sposito (1989)
Z_2Mg	40.46	Wanner et al. (1992)
Z_2Ca	40.53	Wanner et al. (1992)
ZH	23.0	Wieland et al. (1994)
Surface site master species: SOH		
Surface site density:		2.84×10^{-5} mol/g [1]
SOH_2^+	5.4	Wanner et al. (1994)
SO^-	–6.7	Wanner et al. (1994)

[1] Obtained for pretreated MX-80 which had a CEC of 108 meq/100 g.

Table 3.3: Extended Wanner Model/Version 2. Bentonite model adapted for Kunigel-V1, which uses the ion exchange constants of Ca^{2+}, Mg^{2+} and H^+ as given by Fletcher and Sposito (1989). Corresponding to the mole fraction formalism.

Surface species	$\log_{10} K^\circ$	Reference
Surface site master species: Z^-		
Surface site density:		bentonite specific
ZNa	20.0	by definition
ZK	20.26	Fletcher and Sposito (1989)
Z_2Mg	40.17	Fletcher and Sposito (1989)
Z_2Ca	40.17	Fletcher and Sposito (1989)
ZH	20.1	Fletcher and Sposito (1989)
Surface site master species: SOH		
Surface site density (bentonite specific):		1.36×10^{-5} mol/g [1]
SOH_2^+	5.4	Wanner et al. (1994)
SO^-	−6.7	Wanner et al. (1994)

[1] Corrected for the smectite content of Kunigel-V1

Table 3.4: Extended Wanner Model/Version 2. Bentonite model adapted for Kunigel-V1, which uses the ion exchange constants of Ca^{2+}, Mg^{2+} and H^+ as given by Fletcher and Sposito (1989). Corresponding to the equivalent fraction formalism.

Surface species	$\log_{10} K^\circ$	Reference
Surface site master species: Z^-		
Surface site density:		bentonite specific
ZNa	20.0	by definition
ZK	20.26	Fletcher and Sposito (1989)
Z_2Mg	40.47	Fletcher and Sposito (1989)
Z_2Ca	40.47	Fletcher and Sposito (1989)
ZH	20.1	Fletcher and Sposito (1989)
Surface site master species: SOH		
Surface site density (bentonite specific):		1.36×10^{-5} mol/g [1]
SOH_2^+	5.4	Wanner et al. (1994)
SO^-	−6.7	Wanner et al. (1994)

[1] Corrected for the smectite content of Kunigel-V1

Table 3.5: Bentonite Model/RCA.1. Bentonite model adapted for Kunigel-V1, which uses the ion exchange constant H^+ as given by Fletcher and Sposito (1989). Corresponding to the mole fraction formalism.

Surface species	$\log_{10} K^\circ$	Reference
Surface site master species: Z^-		
Surface site density:		bentonite specific
ZNa	20.0	by definition
ZK	20.26	Fletcher and Sposito (1989)
Z_2Mg	40.13	Wanner et al. (1992)
Z_2Ca	40.2	Wanner et al. (1992)
ZH	20.1	Fletcher and Sposito (1989)
Surface site master species: SOH		
Surface site density (bentonite specific):		1.36×10^{-5} mol/g [1]
SOH_2^+	5.4	Wanner et al. (1994)
SO^-	−6.7	Wanner et al. (1994)

[1] Corrected for the smectite content of Kunigel-V1

Table 3.6: Bentonite Model/RCA.1. Bentonite model adapted for Kunigel-V1, which uses the ion exchange constant H^+ as given by Fletcher and Sposito (1989). Corresponding to the equivalent fraction formalism.

Surface species	$\log_{10} K^\circ$	Reference
Surface site master species: Z^-		
Surface site density:		bentonite specific
ZNa	20.0	by definition
ZK	20.26	Fletcher and Sposito (1989)
Z_2Mg	40.46	Wanner et al. (1992)
Z_2Ca	40.53	Wanner et al. (1992)
ZH	20.1	Fletcher and Sposito (1989)
Surface site master species: SOH		
Surface site density (bentonite specific):		1.36×10^{-5} mol/g [1]
SOH_2^+	5.4	Wanner et al. (1994)
SO^-	−6.7	Wanner et al. (1994)

[1] Corrected for the smectite content of Kunigel-V1

3.1.1 Influence of ion exchange constants on calculated porewater chemistry

To perform this sensitivity analysis, different sets of constants determined by Wanner et al. (1992), Wieland et al. (1994), and Fletcher and Sposito (1989), for cation exchange of H^+, Ca^{2+} and Mg^{2+} vs. Na^+ on Kunigel-V1 have been selected for porewater calculations. Calculations have been carried out to quantify the influence of the different sets of cation exchange constants (Table 3.1 - Table 3.6) on calculated porewater composition.

3.1.1.1 H^+ vs. Na^+ exchange on the bentonite layer sites: log K_{HX} = 20.1

Calculations were carried out to assess the influence of the use of a log K_{HX} of 20.1 (Fletcher and Sposito, 1989) instead of 23.0 (Extended Wanner Model/Version 1; Table 2.2) for the H^+ vs. Na^+ exchange on the bentonite layer sites on calculated porewater composition.

For this purpose, Figure 2.2 and Figure 2.5 in our FY 96 Technical Report: 'Sensitivity analysis of key parameters in the bentonite model' (Lothenbach and Ochs, 1997) were recalculated using a log K_{HX} of 20.1 instead of 23.0 (without changing the Mg^{2+} and Ca^{2+} ion exchange constants; corresponding to the Bentonite Model/RCA.1 as given in Table 3.5 and Table 3.6.

Recalculation of Figure 2.2 of our FY 96 Technical Report shows that in the presence of $CaCO_3(s)$, the influence of the log K_{HX} value on calculated pH values is negligible (Figure 3.1), as the whole system is dominated by the carbonate buffer system (cf. also Figure 2.6 in our FY 96 Technical Report). On the other hand, if only a small amount of $CaCO_3(s)$ is available for dissolution, no equilibrium with precipitated calcite may be reached. In that case, the change in the log K_{HX} value has a notable influence on the calculated porewater pH (Figure 3.1), as the H^+ concentration in solution is controlled by the edge and layer sites of the bentonite (cf. Figure 2.6 our FY 96 Technical Report).

Recalculation of Figure 2.5 of our FY 96 Technical Report (given in Figure 3.2) shows again that in the presence of $CaCO_3(s)$, the influence of the log K_{HX} value on pH value is negligible as the whole system is dominated by the carbonate buffer system and pyrite dissolution. If depletion of calcite occurs, the porewater pH calculated with a log K_{HX} of 20.1 will be lower than calculated previously K_{HX} = 23.0. However, in the presence of calcite, the usage of log K_{HX} = 20.1 has only a negligible influence on the calculated porewater pH.

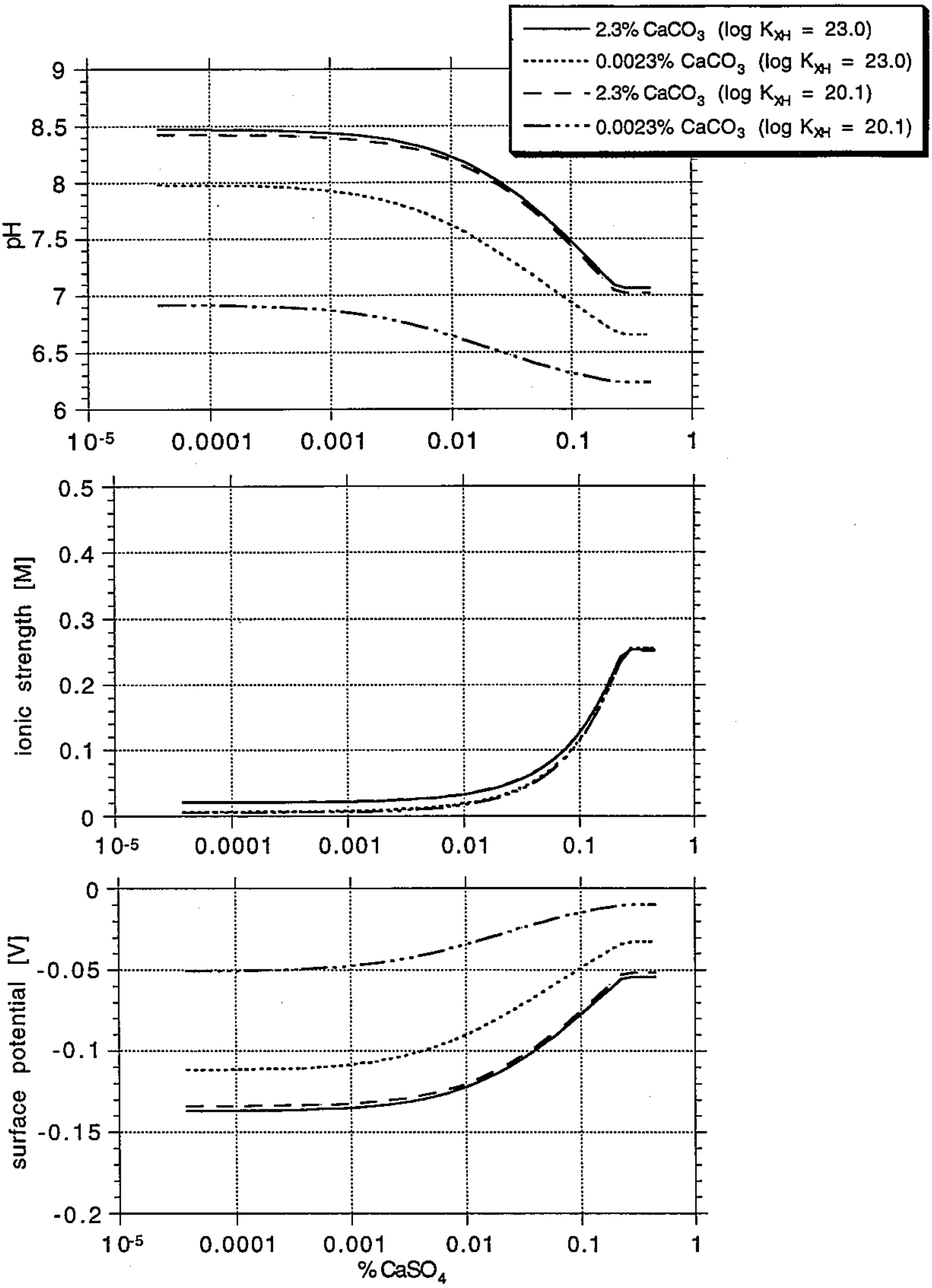

Figure 3.1: Plot of pH, ionic strength and edge surface potential vs. % $CaSO_4$ impurity dissolved in the porewater of compacted Kunigel-V1 (dry density = 1800 kg/m^3). All (corresponding to 2.3 weight % of Kunigel-V1) and 0.1% of the total $CaCO_3$(s) (corresponding to 0.0023 weight % of Kunigel-V1) impurity present dissolved. All NaCl dissolved. Different K_{HX} values are compared.

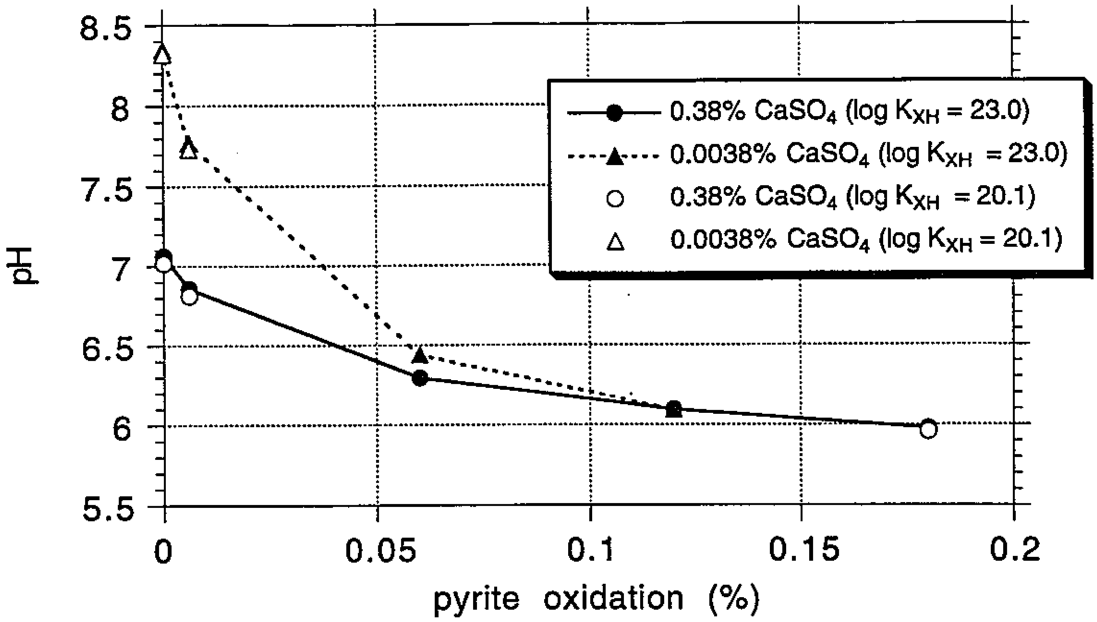

Figure 3.2: Influence of log K_{HX} on calculated pH as a function of pyrite oxidation in the porewater of compacted Kunigel-V1 with 0.0038 and 0.38% $CaSO_4$ dissolved. Calculated in presence of $CaCO_3(s)$ and 0.001% NaCl dissolved. Total pyrite content is 0.6%.

3.1.1.2 Ca^{2+} and Mg^{2+} vs. Na^+ exchange on the bentonite layer sites: log K_{CaX_2} = 40.17 and log K_{MgX_2} = 40.17

The use of the cation exchange constants for Ca^{2+} and Mg^{2+} of Fletcher and Sposito (1989) (Table 3.3) instead of the constants given by Wanner et al. (1992) (Table 3.1) had in all cases discussed in this report a negligible influence on the calculated porewater composition.

3.2 Testing of alternative bentonite models

Recently, Baeyens and Bradbury (Baeyens and Bradbury, 1997; Bradbury and Baeyens, 1997) published a bentonite model based on titration experiments carried out with SWy-1 montmorillonite. In their publication, Bradbury and Baeyens fitted the hydrolysis constants of the bentonite edge sites using the diffuse layer model (Table 3.7). The evaluation of sorption experiments involving Zn caused Bradbury and Baeyens (1997) to reject the diffuse layer model and to fit hydrolysis constants instead without any electrostatic correction term (Table 3.8). In this section, the influence of the different bentonite models (as given in Table 3.2, Table 3.6, Table 3.7 and Table 3.8) on the calculated porewater pH is investigated.

3.2.1 The bentonite models of Bradbury and Baeyens (1997)

The bentonite models given by Bradbury and Baeyens are given in Table 3.7 and Table 3.8. Bradbury and Baeyens (1997) calculated hydrolysis constants of the bentonite edge sites using a diffuse layer model (Table 3.7) and using no electrostatic model (Table 3.8). For the present application, their surface site concentration was adapted to the smectite content of Kunigel-V1 and for Mg, the same ion exchange constant as for Ca was used, following the approach of Fletcher and Sposito.

Table 3.7: Bradbury and Baeyens: diffuse layer model. Bentonite model given by Bradbury and Baeyens (1997), adapted for Kunigel-V1. Ion exchange constants of Ca^{2+}, Mg^{2+} and H^+ as given by Fletcher & Sposito (1989); corresponding to the equivalent fraction formalism. The surface area is 35 m^2/g (Bradbury and Baeyens, 1997).

Surface species	$\log_{10} K^\circ$	Reference
Surface site master species: Z^-		
Surface site density (bentonite specific [1]):		60.1 meq/100 g
ZNa	20.0	by definition
ZK	20.26	Fletcher and Sposito (1989)
Z_2Ca	40.61	Baeyens and Bradbury (1997)
Z_2Mg	40.61	– (analogy with Ca)
ZH	20.0	Baeyens and Bradbury (1997)
Surface site master species: SOH		
Surface site density (bentonite specific [1]):		3.84×10^{-5} mol/g
SOH_2^+	6.2	Bradbury and Baeyens (1997)
SO^-	-8.4	Bradbury and Baeyens (1997)

[1] Corrected for the smectite content of Kunigel-V1 (48%).

Table 3.8: Bradbury and Baeyens: no electrostatic model. Bentonite model given by Bradbury and Baeyens (1997), adapted for Kunigel-V1. Ion exchange constants of Ca^{2+}, Mg^{2+} and H^+ as given by Fletcher & Sposito (1989); corresponding to the equivalent fraction formalism.

Surface species	$\log_{10} K^\circ$	Reference
Surface site master species: Z^-		
Surface site density:		60.1 meq/100 g [1]
ZNa	20.0	by definition
ZK	20.26	Fletcher and Sposito (1989)
Z_2Ca	40.61	Baeyens and Bradbury (1997)
Z_2Mg	40.61	– (analogy with Ca)
ZH	20.0	Baeyens and Bradbury (1997)
Surface site master species: sSOH		9.6×10^{-7} mol/g [1]
Surface site master species: w1SOH		1.92×10^{-5} mol/g [1]
Surface site master species: w2SOH		1.92×10^{-5} mol/g [1]
$sSOH_2^+$	4.5	Bradbury and Baeyens (1997)
sSO^-	-7.9	Bradbury and Baeyens (1997)
$w1SOH_2^+$	4.5	Bradbury and Baeyens (1997)
$w1SO^-$	-7.9	Bradbury and Baeyens (1997)
$w2SOH_2^+$	6.0	Bradbury and Baeyens (1997)
$w2SO^-$	-10.5	Bradbury and Baeyens (1997)

[1] Corrected for the smectite content of Kunigel-V1 (48%).

3.2.2 *Calculated porewater pH values in Kunigel-V1*

Figure 3.3 shows the porewater pH values calculated with different bentonite models in compacted Kunigel-V1 bentonite using FRHP groundwater as input. Figure 3.4 shows the same comparison in compacted Kunigel-V1 bentonite using SRLP groundwater as input. The difference between porewater pH calculated with the extended Wanner Model/Version 1 and Bentonite Model/RCA.1 is small (< 0.05 pH units) for both groundwaters. The pH values calculated with the two bentonite models published by Bradbury and Baeyens (1997) show a larger difference (0.1 to 0.5 pH units) in the case of the FRHP input water. In the saline system (SRHP), these models also behave similar to each other.

The two bentonite models published by Bradbury and Baeyens (1997) have a higher edge site concentration which leads to higher buffer capacity of the edge sites and to calculated pH which are near to the zero point of charge (≈ pH 7.2) of these bentonite models. In comparison, the extended Wanner Model/Version 1 and Bentonite Model/RCA.1 correspond to a smaller edge site concentration and thus also a smaller pH buffer capacity. In summary, it can be said that the models with higher edge site density (by Bradbury and Baeyens, 1997) have a stronger tendency to buffer the pH around the respective pH_{zpc}. In comparison with the model based on Wieland et al. (1994), they tend to predict lower pH values at low ionic strength and higher pH values at high ionic strength

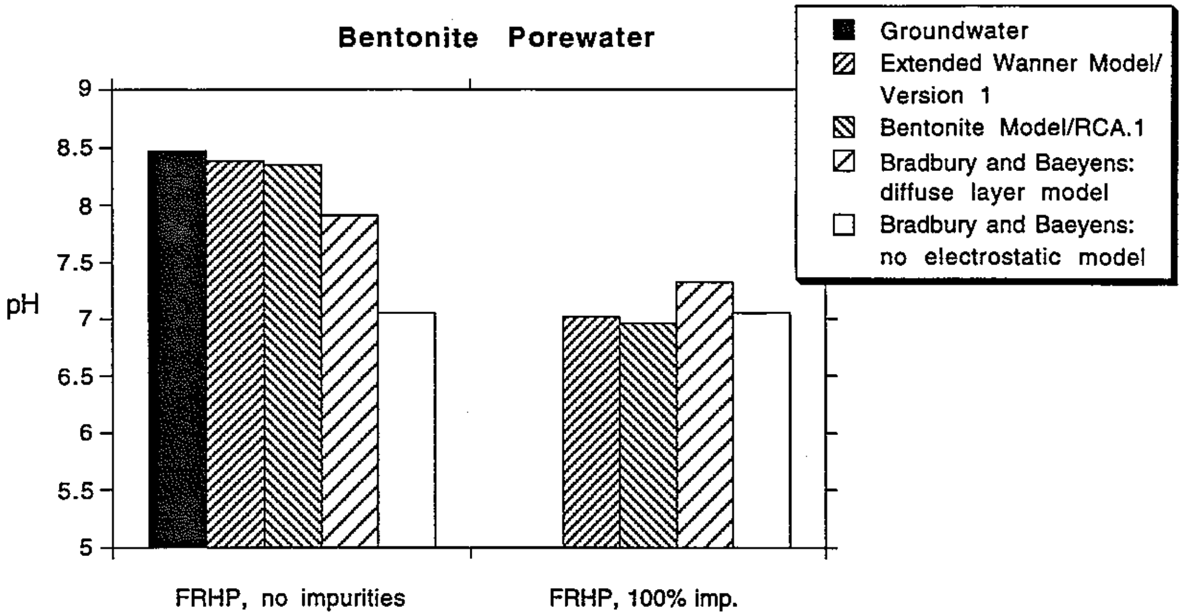

Figure 3.3: Calculated porewater pH in compacted Kunigel-V1 in presence of FRHP groundwater. Calculated with different bentonite models: Extended Wanner Model/Version 1 (Table 2.2); Bentonite Model/RCA.1 (Table 2.6); Bradbury and Baeyens: diffuse layer model (Table 2.7) and Bradbury and Baeyens: no electrostatic model (Table 2.8).

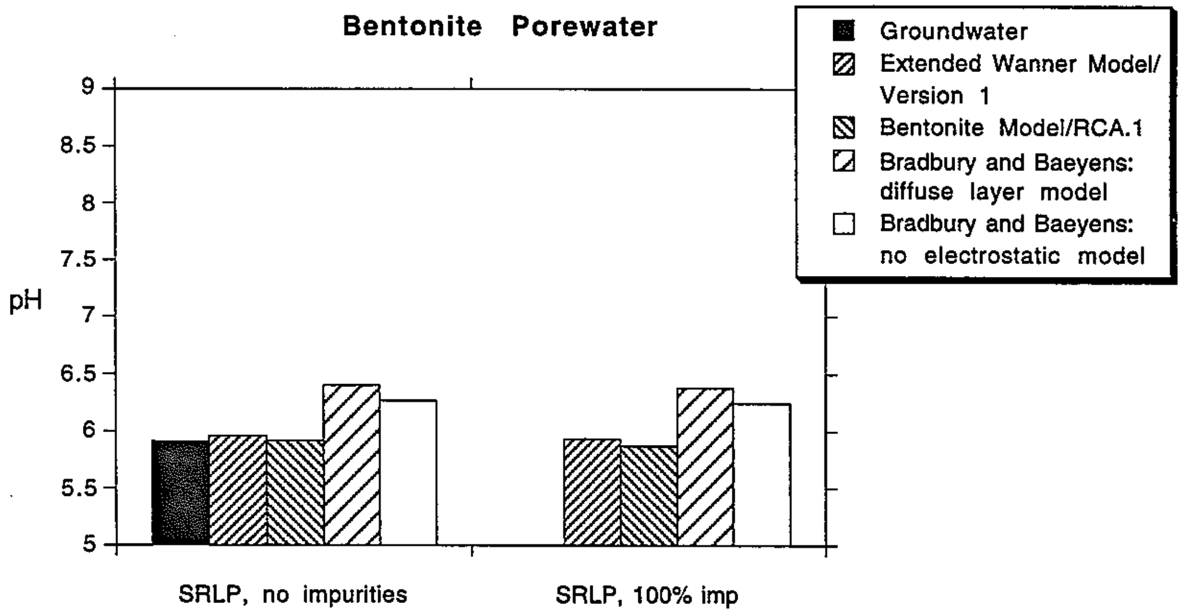

Figure 3.4: Calculated porewater pH in compacted Kunigel-V1 in presence of SRLP groundwater. Calculated with different bentonite models: Extended Wanner Model/Version 1 (Table 2.2); Bentonite Model/RCA.1 (Table 2.6); Bradbury and Baeyens: diffuse layer model (Table 2.7) and Bradbury and Baeyens: no electrostatic model (Table 2.8).

4 Sensitivity analyses (2): Dissolution of soluble impurities:

The discussion in the previous section deals with the influence that the choice of bentonite model and ion exchange constants have on the calculated porewater composition. In this section, the sensitivity of the calculated porewater composition in compacted bentonite with respect to the treatment of soluble impurities by a given bentonite model is examined.

As shown in section 5 and the appendices to this report, soluble impurities may have a significant impact on the porewater chemistry in compacted bentonite, in particular in the case of dilute input solutions such as the PNC FRHP reference groundwater. Traditionally, this effect has not received much attention, mainly because it is almost negligible in batch measurements with low solid/water ratios. Unfortunately, only limited information is therefore available on the amount of soluble impurities that should realistically be expected for bentonites under repository conditions. Furthermore, it is possible that only a fraction of the soluble impurities is actually available to the porewater in compacted bentonite. Since this quantity is unknown, but may be very important at the same time, the sensitivity analyses in the present report are performed by:

- varying the amounts of $CaSO_4$ between $1/10^4$ and 1/1 of the total quantities present,
- varying the amounts of NaCl between $1/10^4$ and $10^3/1$ of the total quantities present.

$CaSO_4$ and NaCl are not considered to be in contact with the porewater as individual solid. Instead, in the model calculations they are strictly treated as part of the bentonite. I.e., the $CaSO_4$ and NaCl in the bentonite are allowed to dissolve, leading to the buildup of Ca^{2+}/SO_4^{2-} and Na^+/Cl^- in the solution. NaCl dissolves completely, while $CaSO_4(s)$ is allowed to precipitate upon supersaturation and is then treated as a separate solid phase in equilibrium with the pore solution.

4.1 Input parameters

The bentonite considered in this sensitivity analysis is Kunigel-V1 (Kunimine Industries Co.), a crude bentonite that contains significant amounts of soluble impurities. In all model calculations presented in this section, distilled water is used as input solution.

The mineralogical analysis and CEC of Kunigel-V1 is given by Sasaki et al. (1995), the amount of soluble impurities is taken from Wanner and Wieland (1993). Kunigel-V1 contains a number of minerals other than clays in various proportions (Table 4.1), which are of importance in determining the porewater composition. The solution and surface speciation for Kunigel-V1 in equilibrium with pure water is modeled by using the following set of assumptions throughout:

1) Feldspar and zeolite are neglected, since these minerals exhibit slow dissolution kinetics, and are present in small quantities compared to quartz and smectite. Dolomite is also not considered. Effects of dolomite dissolution (supply of carbonate and bivalent cations) can be estimated by considering calcite.
2) The solution is under all conditions assumed to be in equilibrium with chalcedony, NaCl and KCl. The amount of dissolved calcite, gypsum, and pyrite is varied.

3) A dry density of ρ_d=1800 kg/m^3, corresponding to a total porosity of ε=33% and, hence, to a solid/water ratio of s/w=5400 kg/m^3, is used in the calculations.

Table 4.1: Composition and other specific parameters of Kunigel-V1.

Parameters	Kunigel-V1	Reference
Minerals:		
smectite	46-49 %	Sasaki et al. (1995)
quartz	29-38 %	Sasaki et al. (1995)
feldspar	2.7-5.5 %	Sasaki et al. (1995)
calcite	2.1-2.6 %	Sasaki et al. (1995)
dolomite	2.0-3.8 %	Sasaki et al. (1995)
zeolite	3.0-3.5 %	Sasaki et al. (1995)
pyrite	0.5-0.7 %	Sasaki et al. (1995)
Soluble impurities:		
NaCl	0.001 %	Wanner and Wieland (1993)
KCl	0.004 %	Wanner and Wieland (1993)
$CaSO_4$	0.38 %	Wanner and Wieland (1993)
Surface sites and cation exchange parameters:		
SOH sites	1.363E-5 mol/g [1]	Wieland et al. (1994)
CEC	60.1 meq/100g	Sasaki et al. (1995)
exchangeable Na^+	82.7 %	PNC (1992)
exchangeable K^+	0.9 %	PNC (1992)
exchangeable Mg^{2+}	2.4 %	PNC (1992)
exchangeable Ca^{2+}	14.0 %	PNC (1992)
Structural parameters:		
specific density	2700 kg/m^3	Sato et al. (1993)
surface area of layer sites	810 m^2/g	Sato et al. (1995)
surface area of edge sites	3 m^2/g	Wieland et al. (1994)

[1] taken from Wieland et al. (1994) (Table 3.2), adjusted to the amount of smectite contained in Kunigel-V1.

4.2 *Variation of $CaSO_4$ and $CaCO_3$ impurities in Kunigel-V1*

Figure 4.1 - Figure 4.4 show the strong dependence of ionic strength, edge surface potential, and pH as a function of the increasing dissolution of $CaSO_4$, which in this respect is the most relevant impurity in Kunigel-V1. The effects of $CaSO_4$ dissolution are shown for systems where:

- $CaCO_3$ precipitates, assuming systems that are closed (Figure 4.1) or open (Figure 4.2) with respect to atmospheric CO_2;
- $CaCO_3$ does not precipitate, assuming systems that are closed (Figure 4.3) or open (Figure 4.4) with respect to atmospheric CO_2.

Since the ionic strength strongly influences the edge surface potential and thus the protonation/deprotonation of the edge sites, both pH and edge surface potential generally show a very similar picture (the more negative the surface potential, the higher the pH).

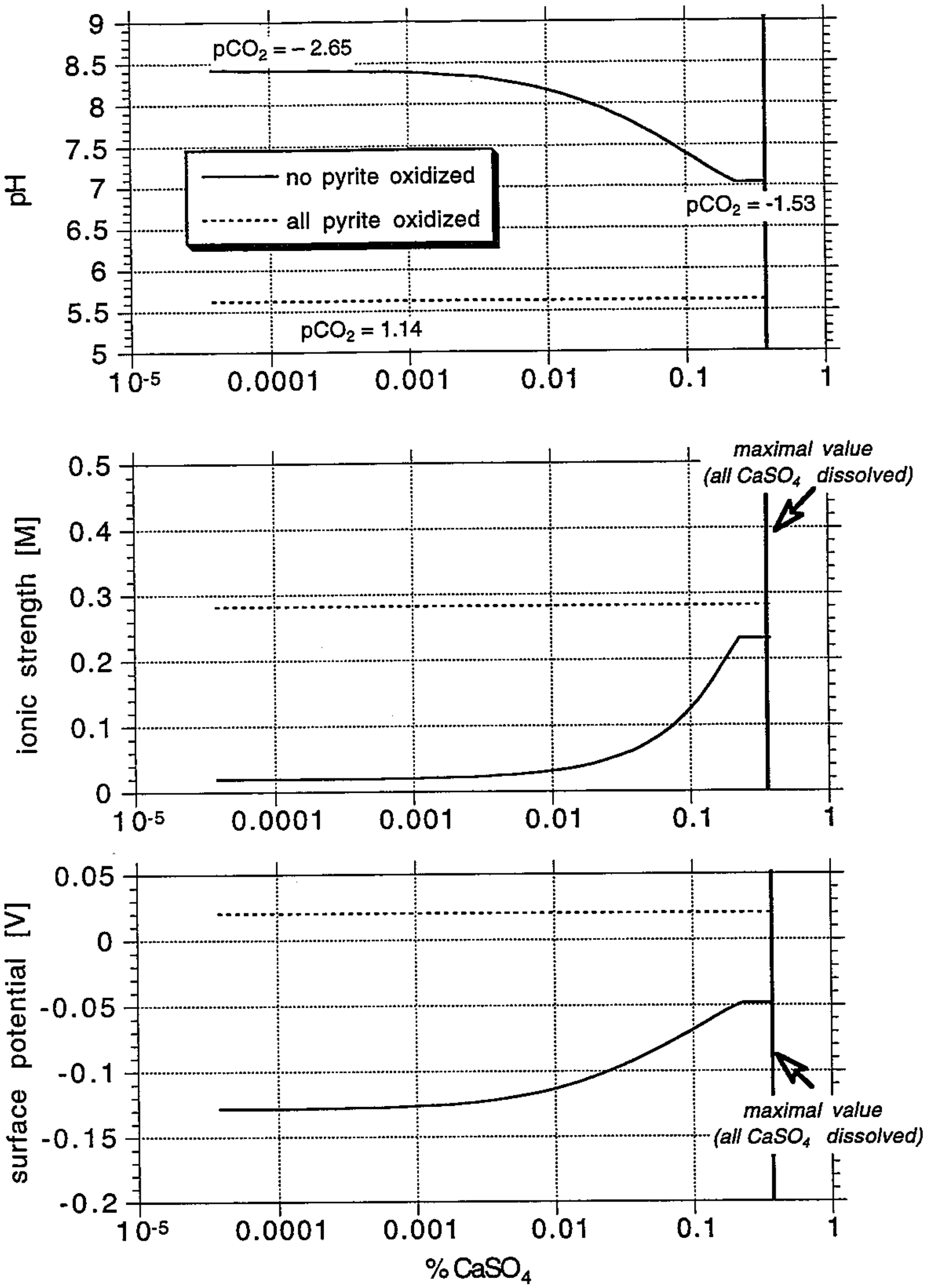

Figure 4.1: Plot of pH, ionic strength and edge surface potential vs. % $CaSO_4$ dissolved in the porewater of compacted Kunigel-V1 (dry density = 1800 kg/m^3) with all and with no pyrite oxidized. System closed with respect to CO_2, $CaCO_3$(s) present, all NaCl dissolved. Model: Bentonite Model/RCA.1.

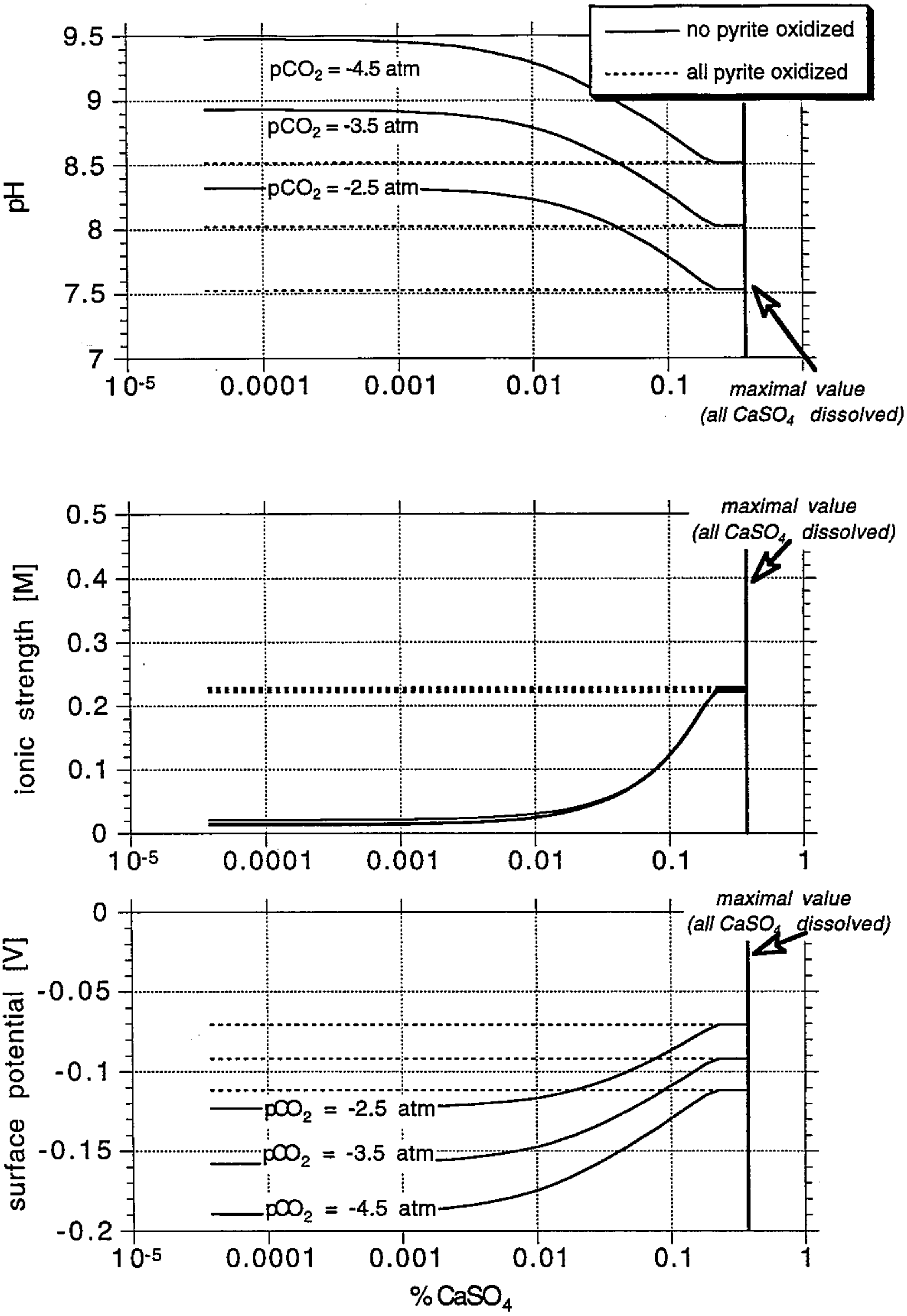

Figure 4.2: Plot of pH, ionic strength and edge surface potential vs. % $CaSO_4$ dissolved in the porewater of compacted Kunigel-V1 (dry density = 1800 kg/m^3) with all and with no pyrite oxidized. System open with respect to CO_2, $CaCO_3$(s) present, all NaCl dissolved.

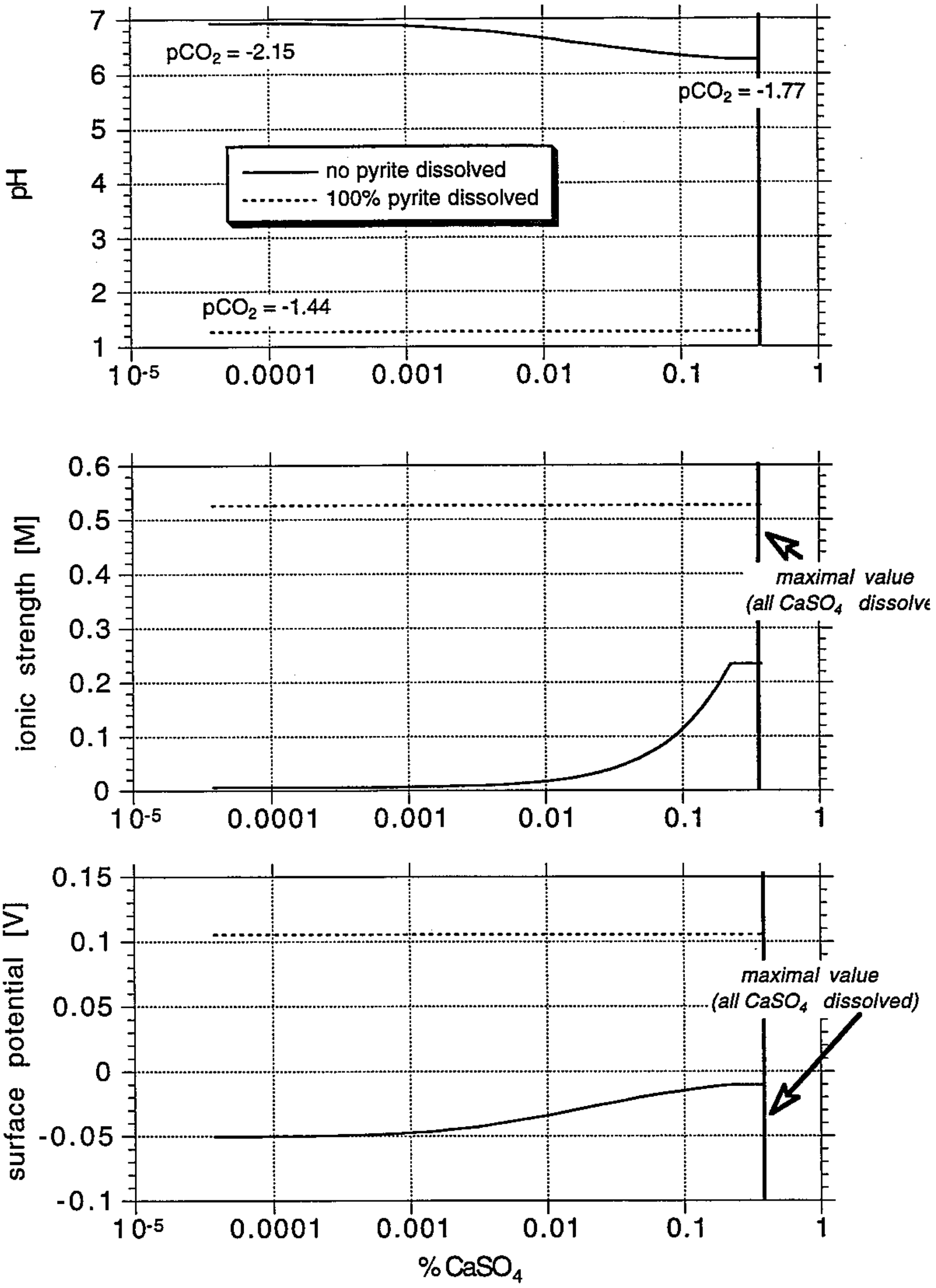

Figure 4.3: Plot of pH, ionic strength and edge surface potential vs. % $CaSO_4$ dissolved in the porewater of compacted Kunigel-V1 (dry density = 1800 kg/m^3) with all and with no pyrite oxidized. System closed with respect to CO_2, 0.1% of the total $CaCO_3$ impurity present dissolved, all NaCl dissolved. Model: Bentonite Model/RCA.1.

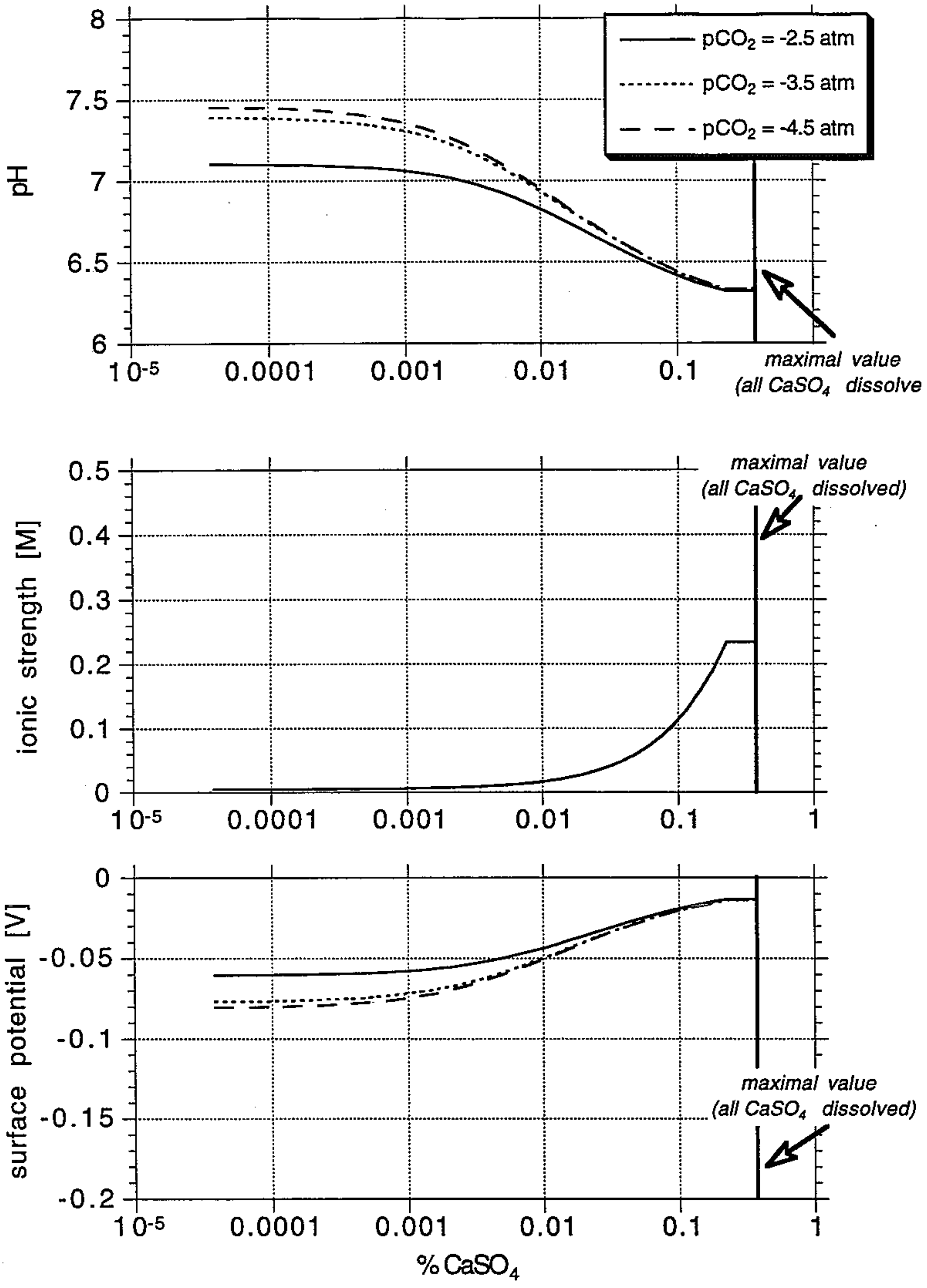

Figure 4.4: Plot of pH, ionic strength and edge surface potential vs. % $CaSO_4$ dissolved in the porewater of compacted Kunigel-V1 (dry density = 1800 kg/m^3). System open with respect to CO_2, 0.1% of the total $CaCO_3$ impurity present dissolved, all NaCl dissolved. Model: Bentonite Model/RCA.1.

The dissolution of $CaSO_4$ in the presence of carbonate (Figure 4.1 and Figure 4.2) according to the overall reaction

$$CaSO_4 = Ca^{2+} + SO_4^{2-} \tag{4.1a}$$

$$Ca^{2+} + HCO_3^- = CaCO_3(s) + H^+ \tag{4.1b}$$

leads to the precipitation of calcite upon supersaturation. This reaction produces H^+ and also reduces the pH value, in addition to the ionic strength effect. The contribution of this reaction can be estimated by comparing the top panels of Figure 4.1 and Figure 4.3.

The lowering of pH due to the dissolution of $CaSO_4$ leads to a higher solubility of $CaCO_3$, and in closed system, to an increase of CO_2 partial pressure. This increase of CO_2 partial pressure leads to an increased importance of the $CaCO_3$-CO_2 buffer system in comparison with the edge site buffer system of the bentonites. Thus, in equilibrium with $CaSO_4$ and $CaCO_3$, the resulting pH value is dominated much more by the carbonate buffer system than by bentonite surface reactions.

Figure 4.1 - Figure 4.4 also show that in equilibrium with either 0.1 and 100% of $CaCO_3$ present, the extent of $CaSO_4$ dissolution reaches a maximum according to the solubility product of $CaSO_4(s)$.

4.3 *Variation of NaCl impurities in Kunigel-V1*

To illustrate the effect of ionic strength alone, i. e., without considering the influence of Ca stemming from $CaSO_4$ dissolution, the amount of NaCl available for dissolution was varied between $1/10^4$ and $10^3/1$ of the total quantity present. I. e., the maximum amount of NaCl that may dissolve has been increased by a factor of 1000 in comparison to the actual amount of NaCl present in Kunigel-V1. The results are summarized in Figure 4.5; they are comparable with the effect of $CaSO_4$ dissolution in the absence of $CaCO_3(s)$ precipitation.

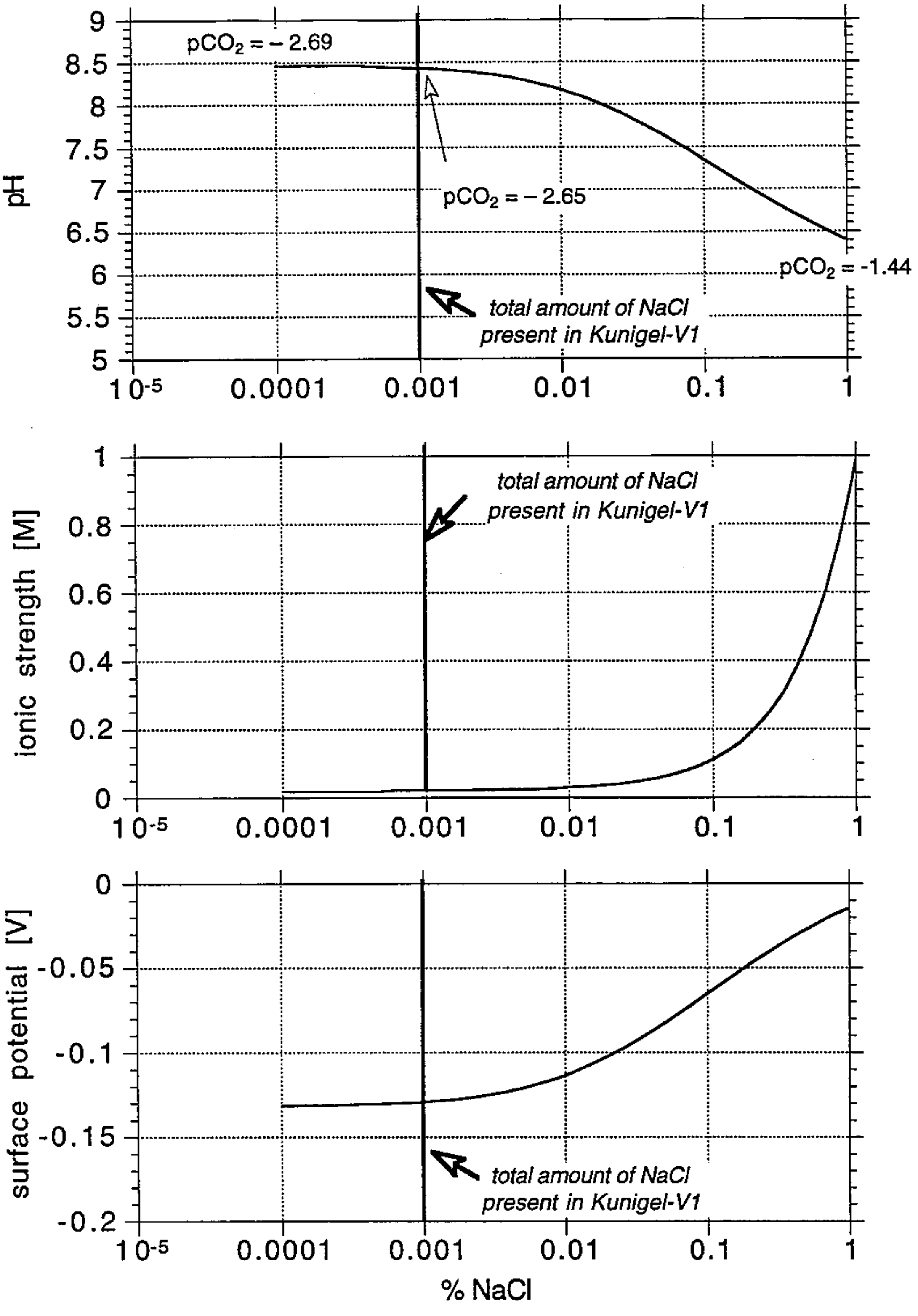

Figure 4.5: Plot of pH, ionic strength and edge surface potential vs. % NaCl dissolved in the porewater of compacted Kunigel-V1 (dry density = 1800 kg/m^3). System closed with respect to CO_2, equilibrium with $CaCO_3$(s), no $CaSO_4$ present. Model: Bentonite Model/RCA.1.

4.4 *Summary*

The sensitivity analyses performed in the present study, as well as our FY96 Technical Report on this topic (Lothenbach and Ochs, 1997) cover large variations in the dissolution of soluble impurities ($CaSO_4$, $CaCO_3$) and less soluble minerals (pyrite), contained in compacted Kunigel-V1 bentonite. The main interest in these sensitivity calculations lies in the range of pH values (as an important representative parameters for the porewater chemistry) to be realistically expected in the near field of a nuclear waste repository. The water used as input for the calculations of the present study is distilled water, and the results will be different if distilled water is replaced, e.g., by the saline-reducing low pH PNC reference water (See Section 5 of this report).

Figure 4.6 gives an overview of the different parameters and the relative influence of the carbonate and edge site buffer systems. Figure 4.7 shows the influence of these parameters on the resulting porewater pH in compacted Kunigel-V1. The following general conclusions can be drawn from the sensitivity analyses carried out for compacted Kunigel-V1:

- The pH of the porewater in compacted bentonite lies in most cases between 5.6 and 9.5. Only the assumption that all pyrite dissolves while at the same time calcite is not in equilibrium with the bentonite porewater leads to theoretical pH of 1.3. This assumption, however, is not realistic. Additionally, at such a pH, the bentonite would start to dissolve, buffering the pH.

- The presence of calcite, gypsum and pyrite strongly influences the pH in the compacted bentonite. Equilibrium with calcite increases pH, while the dissolution of gypsum lowers pH. Oxidation of pyrite strongly lowers pH in compacted Kunigel-V1 (Figure 4.7, left hand side).

- In the absence of calcite (Figures 4.6 and 4.7, right hand side), the pH is significantly affected by the acid/base equilibria at the edge sites of the bentonite in addition to the carbonate buffer system.

- In absence of a solid $CaCO_3(s)$ phase and in presence of $CaSO_4(s)$ in equilibrium with the porewater solution, the calculated porewater pH is relatively low (≈ 6.3) and more or less independent of CO_2 partial pressure.

- Calculations carried out under the assumption of a system closed with respect to atmospheric CO_2 result in relatively low pH values, because the dissolution of $CaCO_3(s)$ produces a CO_2 partial pressures ten to hundred times larger than atmospheric CO_2 partial pressure.

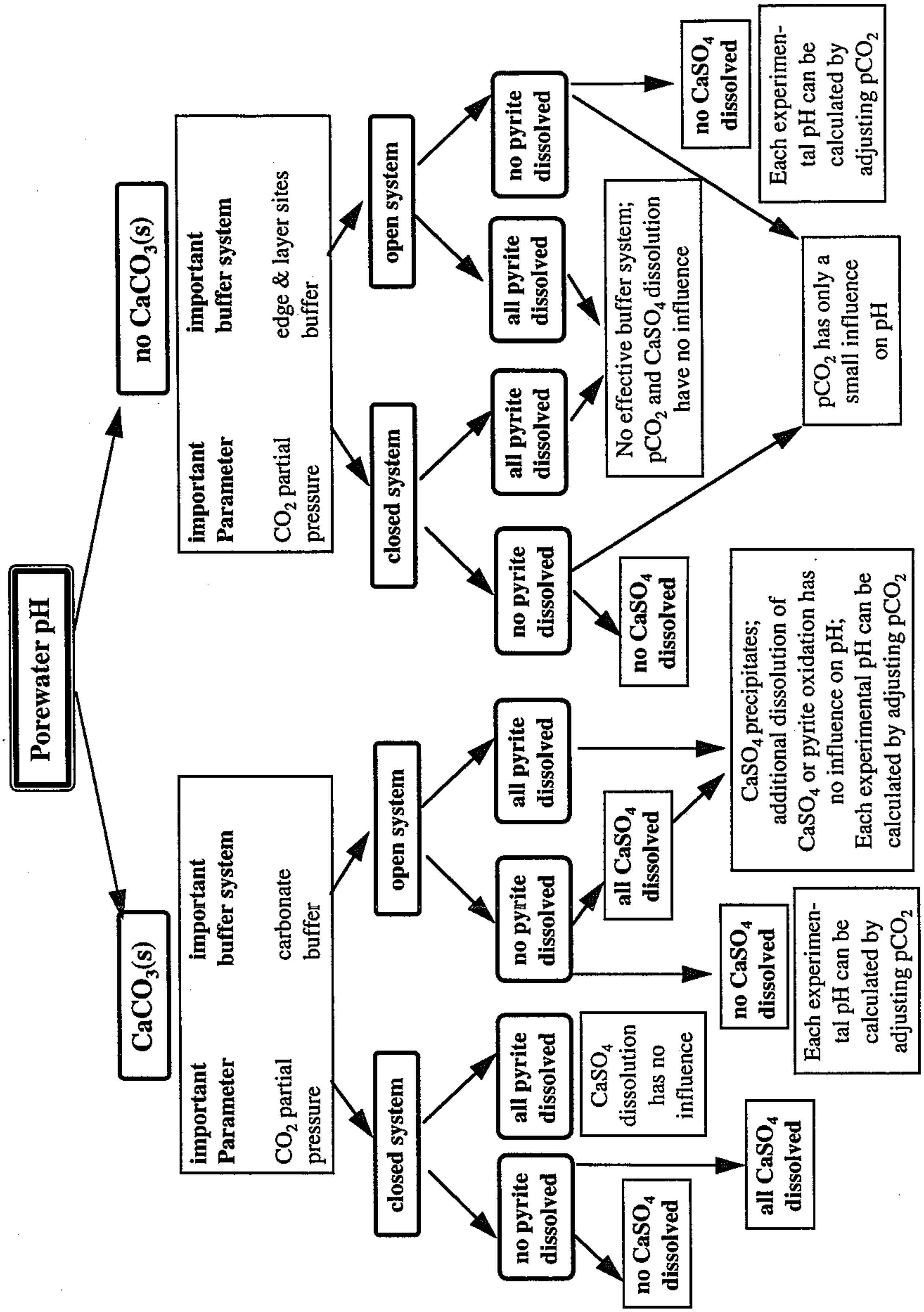

Figure 4.6: Overview of the influence of different parameters (dissolution of $CaCO_3(s)$, $CaSO_4(s)$ and pyrite) on the dominating buffer systems in compacted Kunigel-V1 (dry density = 1800 kg/m3). However, always both buffer system, carbonate and edge site, will influence porewater pH. Approximate pCO_2 and pH are given in Figure 4.7.

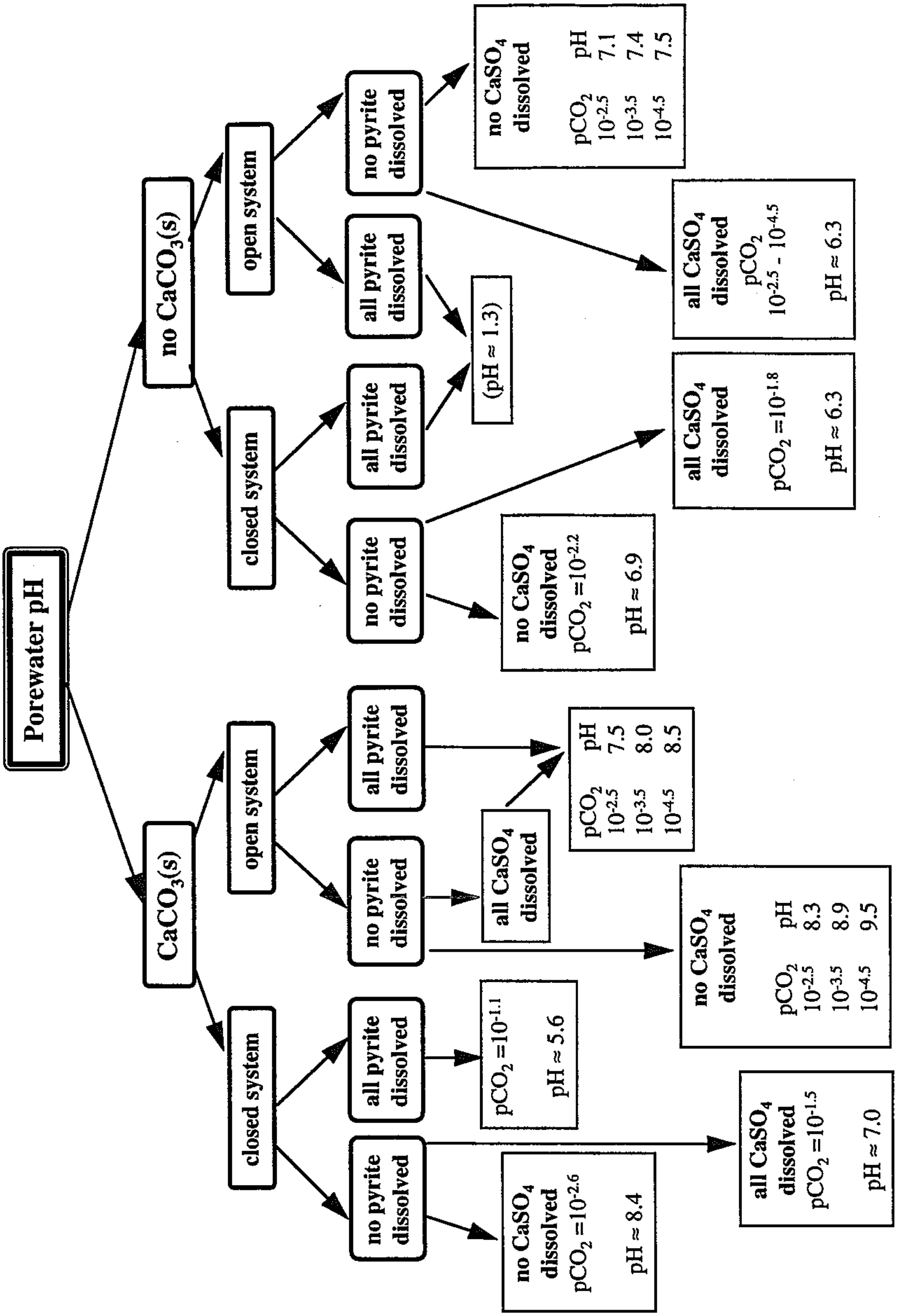

Figure 4.7: Overview of the influence of different parameters (dissolution of $CaCO_3(s)$, $CaSO_4(s)$ and pyrite) on approximate porewater pH and pCO$_2$ in compacted Kunigel-V1 (dry density = 1800 kg/m3). Dominating buffer systems are given in Figure 4.6.

5 Porewater calculations

5.1 *General conditions*

5.1.1 *Input: PNC reference groundwaters FRHP, FRLP, MRNP, SRHP, SRLP*

As input for the porewater calculations, reference groundwater compositions as reported by PNC (Yui and Sasamoto, 1997) were used. The reported groundwater compositions included the dissolved total concentrations of Al, B, Br, Ca, Cl, F, Fe (incl. Fe(II) and Fe(III)), SiO_2, K, Mg, Na, N, PO_4 and S, pH, pCO_2 and p[e] (see below).

For the calculations of the porewater composition, pH, pCO_2 and pe can not be used as fixed input parameters because these parameters actually are the result of the calculations. Thus, the distribution of the redox-sensitive elements according to the indicated redox state and the total amount of bound plus dissolved H^+ for each PNC groundwater are used as input parameters. Based on the information from PNC, the distribution of the redox sensitive species and the total amount of bound and dissolved H^+ was calculated for each groundwater with the help of the code MINEQL under fixed pH, pCO_2 and pe conditions. This detailed distribution of the relevant elements (cf. 'Input groundwater' in the result sheets of the porewater calculations) was then used as input for the porewater calculations.

The term pe is difficult to interpret in the PHREEQE output, as the same hypothetical E^- concentration is reported under the column concentration and in the column activity (i. e., the activity coefficient is taken as unity). Depending on the calculated ionic strength this may translate to a difference of up to 0.15 pe units in comparison to the true (activity-corrected) pe. For the present porewater calculations, the term pe was interpreted as the negative logarithm of the hypothetical E^- concentration ($-\log[E^-]$).

5.1.2 *Calculation of the B1&2 porewaters*

A bentonite model based on the extended Wanner model, a surface chemical speciation model that simultaneously addresses ion exchange and surface complexation equilibria, were used to model bentonite/groundwater interactions. To calculate ion exchange reactions, the equivalent fraction approach was used. A summary of the model parameters is provided in section 3, Table 3.6. Computations are performed with the aid of the computer code MIN_SURF (Berner, 1993) which is an extended version of the computer code MINEQL. A constant temperature of 25 °C or 60 °C and a closed system are assumed. For further details see Figure 5.1.

The PNC groundwaters were equilibrated with Kunigel-V1 (5.4 g/mL) at 25 or at 60 °C. The composition of the exchangeable cations on the surface sites and the soluble impurities are listed in section 4.1, Table 4.1. For the calculations, it was assumed that the system is in equilibrium with chalcedony, calcite and pyrite; and that 0, 50 or 100% of the soluble impurities are accessible to the porewater and are therefore dissolved.

5.1.3 Calculation of the B3 porewaters

For the calculation of the B3 porewaters it is assumed that the system is in equilibrium only with chalcedony and pyrite; and that all soluble impurities are depleted (Figure 5.1). Calcium is assumed to be the only exchangeable cation on the layer sites. As for the B1&2 porewaters, the PNC groundwaters are equilibrated with Kunigel-V1 (5.4 g/mL) at 25 °C or at 60 °C in a system closed with respect to CO_2.

5.1.4 Calculations of the C2 porewaters

For the calculation of the C2 porewaters (Figure 5.1) it is assumed that the system is in equilibrium with chalcedony, calcite and magnetite (as steel corrosion product) and again, that 0, 50 or 100% of the soluble impurities are accessible to the porewater and are therefore dissolved. As input water, the porewater composition calculated for the different B1&2 porewaters was used. Also, the composition of the exchangeable cations on the surface sites corresponding to equilibrium with the different B1&2 porewaters was used. This input was equilibrated with magnetite at 25 °C or at 60 in a system closed with respect to CO_2.

5.1.5 Calculations of C3 porewaters

For the calculation of the C3 porewaters (Figure 5.1) it is assumed that the system is in equilibrium with chalcedony and magnetite (as steel corrosion product), and that all soluble impurities are depleted. As input water, the porewater composition calculated for the different B3 porewaters is used. Also, the composition of the exchangeable cations on the surface sites corresponding to equilibrium with the different B3 porewaters (which is dominated by calcium) is used. This input is equilibrated with magnetite at 25 °C or at 60 in a system closed with respect to CO_2.

So far, C3 porewaters have been modeled assuming that these solutions are not in equilibrium with calcite (Figure 5.1). However, the sensitivity analyses carried out for the present report, as well as for our FY96 Technical Report (Lothenbach and Ochs, 1997), demonstrate that the absence of calcite is unlikely. If more than 0.1 % of the $CaCO_3$ *in Kunigel-V1 (i. e., more than 0.0023 %) dissolve, calcite will precipitate in solution. It is planned, therefore, to include calcite in the C3 box.*

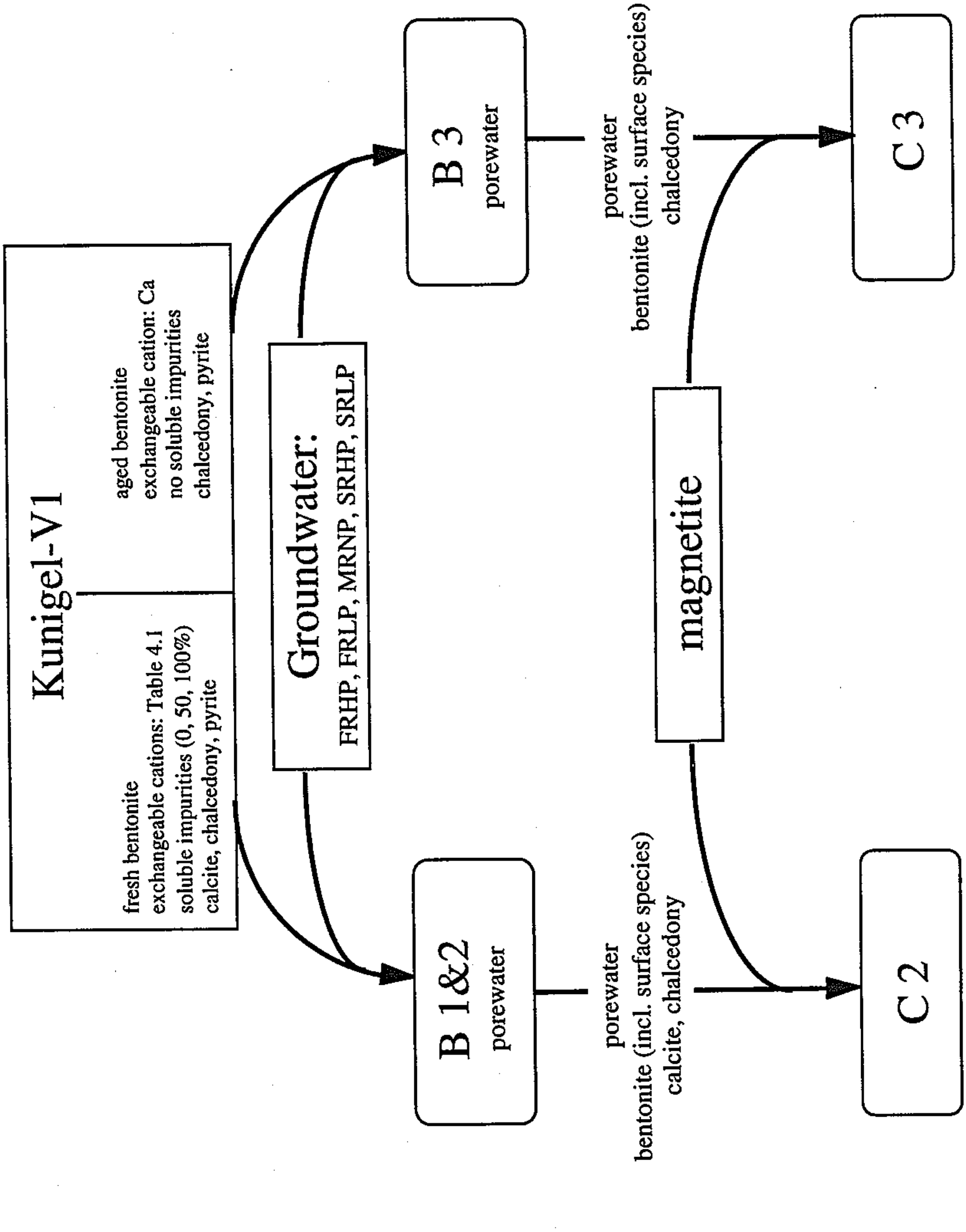

Figure 5.1: Porewater calculations carried out in compacted Kunigel-V1.

5.2 Mineral equilibria

Some input groundwaters are already oversaturated with respect to F-apatite and fluorite. The degree of oversaturation with respect to OH-apatite, F-apatite, fluorite, hematite, kaolinite, quartz, siderite(crystalline) and C(0) is calculated for each bentonite porewater (see the tables of calculated porewater composition in this section and in the appendices to this report). The possible precipitation of F-apatite, fluorite and hematite, and its influence on porewater pe and pH is discussed in the following paragraphs. Details on the treatment of mineral equilibria in the porewater calculations are given in Figure 5.1 with respect to the different solids.

5.2.1 Fluorite and apatite

5.2.1.1 PNC groundwater FRHP, FRLP, MRNP, SRHP, SRLP

As input for the porewater calculations, groundwater compositions as reported by PNC (Yui and Sasamoto, 1997) are used. The dissolved total concentrations of the major element in the PNC reference groundwaters has been derived through geochemical modeling, while the concentrations of B, Br, Cl, F, NH_4, and PO_4 has been calculated from the statistical data analysis of measurements in different types of Japanese groundwaters. This leads to the situation that the input groundwaters (with exception of the FRLP groundwater) are strongly (up to a factor of 10^8) oversaturated with respect to F-apatite. Oversaturation of the input groundwaters with respect to fluorite occurs only in the SRLP groundwater (the solution is oversaturated by a factor of 1.6). While it is known that natural groundwaters are not always in equilibrium with relevant minerals, such a large degree of oversaturation with respect to F-apatite is not considered to be realistic, and is difficult to account for in groundwaters whose composition is largely based on geochemical modeling.

5.2.1.2 Bentonite porewaters

Similarly to the respective input groundwaters, the bentonite porewaters calculated with the help of the computer code MIN_SURF as described in section 5.1 are strongly oversaturated with respect to F-apatite. Some of the calculated bentonite porewaters are also – to a lesser extent, however – oversaturated with respect to OH-apatite and fluorite (see section 0). The presence or absence of apatite and fluorite precipitation has no influence on the resulting porewater pH or pe in the bentonite, but has a large effect on PO_4 and F concentrations.

The concentration of PO_4 and F may strongly influence the solubility of various key radionuclides. As an example may serve the control of Am concentrations through the precipitation of $AmPO_4$; depending on pH and the concentration of other ligands present, the precipitation of $AmPO_4$ may significantly reduce the calculated Am solubility in the near-field of a nuclear waste repository. E.g., in B1&2 bentonite porewater an Am concentration of 1.0×10^{-11} M was calculated in absence of apatite and fluorite precipitation (i. e., in the presence of relatively high PO_4 and F concentrations), while in presence of apatite and fluorite precipitation, a much higher dissolved Am concentration of 2.6×10^{-9} M resulted.

Based on published experimental studies on mineral dissolution and precipitation, it cannot be expected that there are any kinetic restrictions with respect to the precipitation of apatite and fluorite. Apatite is reported (Van Capellen and Berner, 1991; Zhang and Nancollas, 1990) to precipitate from homogenous solutions within a short time (a few hours). Fluorite is a very simple compound and will precipitate in a similar period of time in solutions (Stumm and Morgan, 1996).

5.2.2 *Hematite and goethite*

5.2.2.1 *Influence on porewater pe and pH*

In the absence of iron corrosion products (bentonite porewaters B1&2 and B3; see Figure 5.1), only the FRHP-derived porewaters are calculated to be slightly oversaturated with respect to hematite. Its presence or absence has only a minor influence on calculated porewater pH or pe, however.

In contrast, in the presence of magnetite as corrosion product (bentonite porewaters C2 and C3; see Figure 5.1), the absence of hematite leads to an increase of pe, while its influence on pH is small. Since the dissolution of magnetite produces both Fe(III) and Fe(II), magnetite is as a source of Fe(III) linked to the precipitation of minerals that may serve as a sink of Fe(III). If precipitation of hematite or goethite does not occur, i.e., if a sink for dissolved Fe(III) is missing, a major fraction of dissolved Fe(III) has to remain in solution and is reduced to dissolved Fe(II), decreasing the hypothetical E^- concentration and increasing the pe.

This may be illustrated by pe-pH diagrams that can be found e. g. in Brookins (1988; Fig. 39 and 40). Such diagrams show the stability field of magnetite in presence and absence of goethite precipitation. In presence of goethite the stability field of magnetite is restricted to a relatively narrow range of pe conditions. In presence of hematite, the stability field of magnetite is even smaller. However, in absence of goethite and hematite, magnetite exists over a wide range of pe values, including even oxidizing conditions. In presence of both magnetite and goethite, the calculated theoretical pe has to lie on the line separating the stability fields of magnetite and goethite (similarly in the presence of hematite and magnetite), while the calculated pe may lie somewhere (depending on pH) inside the stability field of magnetite if only magnetite is present.

5.2.2.2 *Solubility control of Fe(III)*

In solutions oversaturated with respect to Fe(III)-(hydr)oxides, amorphous ferrihydrite precipitates which will transform to thermodynamically more stable structures such as goethite or hematite. At room temperature the transformation of ferrihydrite to goethite or hematite takes place within weeks to years (Ford et al., 1997, Baltpurvins et al., 1997), depending on pH and solution composition. At higher temperature the formation of hematite will be promoted. Thus in bentonite porewaters, hematite or goethite will not precipitate directly from solutions, but are likely to be formed after some time. I. e., hematite will probably not control Fe(III) solubility if

Fe(III) is continuously supplied by e.g. container corrosion, but with time it will be present as a solid phase. Such a system is not in thermodynamic equilibrium, since two Fe(III)(hydr)oxides are present.

5.2.3 $Fe(OH)_2(s)$

Magnetite is the stable solid phase in equilibrium with Fe(II) under the pe-pH conditions considered here, but the formation of the metastable solid $Fe(OH)_2(s)$ may be preferred kinetically. Thus, during continuous steel corrosion, $Fe(OH)_2(s)$ might precipitate and control Fe solubility. This system, however, is not in thermodynamic equilibrium. With time $Fe(OH)_2(s)$ will be transformed into the thermodynamically stable Fe_3O_4(magnetite) (Baes and Mesmer, 1986). These observations also correspond to the findings reported in the fax by Mr. M. Shibata (dated 2 May 1997), where in presence of iron powder and distilled water after one week a solid magnetite phase was detected by X-ray analysis, while the solution chemistry seemed to be dominated by the more reactive $Fe(OH)_2(s)$.

Porewater calculations carried out in presence of $Fe(OH)_2(s)$ instead of magnetite (Appendix D2) result in a pH of 12.1 and a pe of -11.3. For porewater calculations, however, where long-term processes have to be considered, equilibrium relations are more important than short-term kinetic considerations. Thermodynamically, Fe_3O_4(magnetite) is the stable iron oxidation product which should be considered for safety analysis. $Fe(OH)_2(s)$ is thermodynamically not stable in the $Fe(cr)/Fe_3O_4$ system, and its use as corrosion product may be difficult to defend.

5.3 Redox conditions

The occurrence of redox reactions in the bentonite is a difficult topic. Redox equilibria like $H_2/H_2O/O_2$ or Fe(II)/Fe(III) are not expected to depend on microbiological activity and are therefore always included in the calculations of the porewater composition.

The NH_3/NH_4^+ oxidation to N_2 (due to the low pe values, oxidation to NO_3 is negligible anyway) is not likely to occur in absence of microorganisms. We do not have any indication that NH_4 oxidizing microorganism exist under repository conditions. The NH_3/NH_4^+ oxidation to N_2 is included in the first two sets of porewater calculations (cf. section 0), while the latter three sets were calculated assuming no equilibrium between these redox couples.

Up to now, the redox pairs S(-II)/S(+VI) was assumed to be in equilibrium, as the presence of sulfate reducing microorganism (e.g. thiobacillus ssp) is probable under repository conditions (West et al., 1985; McNeil and McKay, 1994). The CO_2/CH_4 redox pair is also influenced by the presence of sulfate reducing microorganism. The S(-II)/S(+VI) and CO_2/CH_4 redox pairs are always included in the calculations of the porewater composition included in this report.

For the next set of porewater calculations, these equilibria will not be considered because it is not expected that microorganisms are able to exist in the bentonite backfill itself.

5.4 *Sets of porewater calculations*

The porewater composition in compacted bentonite was calculated assuming different sets of boundary conditions concerning the precipitation of solid phases, redox equilibria, the number of edge sites and the bentonite model used (Figure 5.1). A summary of the calculated porewater composition is given in Table 5.2 to Table 5.6 (calculations D) and in the Appendix (Calculations A, B, C, D1 and D2; cf. Figure 5.1).

The tables give the concentration of each component of the porewater, the calculated pH, pe and pCO_2. The tables have also a list of precipitated and a list of oversaturated solids. Additionally, the amount of dissolved or precipitated pyrite and calcite is given.

A

T = 60 °C
Redox reactions: $H_2/H_2O/O_2$; Fe(II)/Fe(III); HS/SO_4; CH_4/CO_3; NH_3/N_2
no precipitation of quartz, C(0), kaolinite
Bentonite model/RCA.1
Edge site density: 2.84×10^{-5} mol/g

B

T = 25 °C
Redox reactions: $H_2/H_2O/O_2$; Fe(II)/Fe(III); HS/SO_4; CH_4/CO_3; NH_3/N_2
no precipitation of quartz, C(0), kaolinite
Bentonite model/RCA.1
Edge site density: 2.84×10^{-5} mol/g

C

T = 25 °C
Redox reactions: $H_2/H_2O/O_2$; Fe(II)/Fe(III); HS/SO_4; CH_4/CO_3
no precipitation of quartz, C(0), kaolinite,
no precipitation of fluorite, apatite, hematite, goethite
Bentonite model/RCA.1
Edge site density: 2.84×10^{-5} mol/g

D

T = 25 °C
Redox reactions: $H_2/H_2O/O_2$; Fe(II)/Fe(III); HS/SO_4; CH_4/CO_3
no precipitation of quartz, C(0), kaolinite, fluorite,
no precipitation of fluorite, apatite, hematite, goethite
Bentonite model/RCA.1
Edge site density: 1.36×10^{-5} mol/g

D1

as version D
with exception of the
bentonite model:
Extended Wanner model/
Version 2

D2

as version D1
with exception of:
$Fe(OH)_2(s)$ instead of
magnetite present in
C 1&2 porewater

Figure 5.1: Different sets of porewater calculations carried out for compacted Kunigel-V1 and different PNC groundwaters (FRHP, FRLP, MRNP, SRHP, SRLP). The calculated porewater compositions are given in Table 5.2 to Table 5.6 and in the Appendices A, B, C, D1 and D2.

Table 5.2: Porewater calculations set D (cf. Figure 5.1). Kunigel-V1(5.4 g/mL) equilibrated with FRHP groundwater at 25 °C, system closed.

	Input groundwater FRHP	Porewater B1 & B2: no impurities (with pyrite & calcite)	Magnetite precipitates in box B1&2. Therefore box C2 is not calculated
	(M)	(M)	
Al	3.5E-07	3.48E-07	
B(OH)4	6.4E-04	6.42E-04	
Br	1.1E-05	1.13E-05	
Ca	1.1E-04	6.30E-05	
CH4(aq)	1.5E-16	3.69E-12	
Cl	5.8E-04	5.81E-04	
CO3	3.2E-03	1.35E-02	
F	6.4E-04	6.40E-04	
Fe(II)	6.2E-05	5.07E-09	
Fe(III)	8.3E-10	6.02E-15	
H2(aq)	5.4E-12	4.46E-11	
H2SIO4	3.5E-04	3.00E-04	
K	6.1E-05	1.43E-04	
Mg	–	1.10E-05	
Na	3.5E-03	2.40E-02	
NH3	1.1E-03	1.06E-03	
O2(aq)	2.2E-70	3.12E-72	
PO4	1.3E-05	1.31E-05	
S(-II)	3.6E-12	1.74E-08	
SO4	1.3E-04	1.20E-04	
SOH2+		7.08E-03	
SO-		1.72E-02	
NaX		2.66E+00	
HX		2.59E-06	
CaX2		2.38E-01	
MgX2		3.89E-02	
KX		2.91E-02	
calculated pH	8.47	8.35	
calculated pe	-4.39	-4.73	
calculated -log [E$^-$]*	-4.42	-4.79	
calculated log pCO_2	-3.20	-2.48	
calculated I	0.005	0.02	
solids present		calcite chalcedony pyrite	
precipitated solids		magnetite	
oversaturated solids (saturation index)			
fluorite		–	
OH-apatite		13.71	
F-apatite		3.36E+05	
hematite		1.85	
goethite		–	–
kaolinite		11.22	
quartz		2.69	
C(0)		–	
calcite precipitated		-1.03E-02	
pyrite precipitated		2.83E-06	
(negative values indicate dissolution)			
bound and unbound H+		1.54E-02	

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* -log [E$^-$] refers to the hypothetical E$^-$ concentration. The expression 'pe' refers normally to the hypothetical E$^-$ activity.

Table 5.3: Porewater calculations set D (cf. Figure 5.1). Kunigel-V1(5.4 g/mL) equilibrated with FRLP groundwater at 25 °C, system closed.

	Input groundwater FRLP	Porewater B1 & B2: no impurities (with pyrite & calcite)	Porewater C2: no impurities (with magnetite & calcite)
	(M)	(M)	(M)
Al	3.1E-08	3.10E-08	3.10E-08
B(OH)4	6.4E-04	6.42E-04	6.42E-04
Br	1.1E-05	1.13E-05	1.13E-05
Ca	1.1E-04	2.26E-04	2.24E-04
CH4(aq)	1.1E-05	1.08E-05	1.07E-05
Cl	4.2E-04	4.21E-04	4.21E-04
CO3	1.9E-02	3.97E-02	3.97E-02
F	6.4E-04	6.40E-04	6.40E-04
Fe(II)	3.1E-08	2.41E-08	1.07E-06
Fe(III)	2.7E-18	8.95E-17	3.99E-15
H2(aq)	5.4E-10	8.43E-10	8.41E-10
H2SIO4	3.3E-04	2.83E-04	2.83E-04
K	6.1E-05	2.69E-04	2.69E-04
Mg	–	4.40E-05	4.30E-05
Na	3.5E-03	4.37E-02	4.37E-02
NH3	1.0E-03	1.03E-03	1.03E-03
O2(aq)	2.2E-74	8.89E-75	8.92E-75
PO4	1.3E-05	1.31E-05	1.31E-05
S(-II)	6.2E-08	4.79E-08	7.18E-09
SO4	1.9E-12	2.85E-10	4.30E-11
SOH2+		8.16E-03	8.16E-03
SO-		1.54E-02	1.54E-02
NaX		2.64E+00	2.64E+00
HX		3.49E-06	3.48E-06
CaX2		2.47E-01	2.47E-01
MgX2		3.89E-02	3.89E-02
KX		2.90E-02	2.90E-02
calculated pH	5.70	7.42	7.43
calculated pe	-2.62	-4.44	-4.44
calculated -log [E$^-$]*	-2.65	-4.52	-4.52
calculated log pCO_2	-0.34	-1.12	-1.12
calculated I	0.005	0.04	0.04
solids present		calcite chalcedony pyrite	calcite chalcedony magnetite pyrite
precipitated solids			
oversaturated solids (saturation index)			
fluorite		–	–
OH-apatite		–	–
F-apatite		4.38E+04	4.36E+04
hematite		–	–
goethite		-	–
kaolinite		1.43	1
quartz		2.69	3
C(0)		8.75	9
calcite precipitated		-2.04E-02	-7.40E-06
pyrite precipitated		6.94E-09	2.05E-08
(negative values indicate dissolution)			
bound and unbound H+		4.44E-02	4.44E-02

* -log [E$^-$] refers to the hypothetical E$^-$ concentration. The expression 'pe' refers normally to the hypothetical E$^-$ activity.

Table 5.4: Porewater calculations set D (cf. Figure 5.1). Kunigel-V1(5.4 g/mL) equilibrated with MRNP groundwater at 25°C, system closed.

	Input groundwater MRNP	Porewater B1 & B2: no impurities (with pyrite & calcite)	Porewater C2: no impurities (with magnetite & calcite)
	(M)	(M)	(M)
Al	6.1E-10	6.10E-10	6.10E-10
B(OH)4	1.0E-02	1.03E-02	1.03E-02
Br	1.9E-03	1.87E-03	1.87E-03
Ca	5.1E-04	1.07E-02	1.06E-02
CH4(aq)	1.4E-05	1.38E-05	2.00E-10
Cl	3.3E-01	3.33E-01	3.33E-01
CO3	1.1E-01	7.97E-02	7.96E-02
F	1.5E-04	1.47E-04	1.47E-04
Fe(II)	3.2E-05	3.22E-05	1.98E-04
Fe(III)	1.6E-14	2.37E-15	5.88E-14
H2(aq)	5.8E-10	4.38E-10	2.71E-11
H2SIO4	3.0E-04	2.82E-04	2.82E-04
K	1.1E-01	8.33E-03	8.33E-03
Mg	3.5E-04	2.46E-03	2.46E-03
Na	3.2E-01	3.25E-01	3.25E-01
NH3	1.4E-02	1.44E-02	1.44E-02
O2(aq)	1.8E-74	3.28E-74	8.59E-72
PO4	1.3E-05	1.31E-05	1.31E-05
S(-II)	1.0E-10	6.22E-09	6.21E-10
SO4	1.7E-12	8.43E-12	5.81E-08
SOH2+		1.14E-02	1.14E-02
SO-		1.14E-02	1.14E-02
NaX		2.67E+00	2.67E+00
HX		1.26E-05	1.26E-05
CaX2		1.86E-01	1.86E-01
MgX2		3.68E-02	3.68E-02
KX		1.26E-01	1.26E-01
calculated pH	7.01	6.05	6.05
calculated pe	-3.95	-2.93	-2.32
calculated -log $[E^-]$*	-4.08	-3.06	-2.46
calculated log pCO_2	-0.38	0.12	0.12
calculated I	0.43	0.38	0.38
solids present		calcite chalcedony pyrite	calcite chalcedony magnetite pyrite
precipitated solids			
oversaturated solids (saturation index)			
fluorite		–	–
OH-apatite		–	–
F-apatite		2.39E+04	2.26E+04
hematite		–	2
goethite		–	–
kaolinite		-	–
quartz		2.69	3
C(0)		41.30	–
calcite precipitated		1.46E-03	4.41E-04
pyrite precipitated		-3.06E-09	-2.63E-08
(negative values indicate dissolution)			
bound and unbound H+		1.50E-01	1.49E-01

* -log $[E^-]$ refers to the hypothetical E^- concentration. The expression 'pe' refers normally to the hypothetical E^- activity.

Table 5.5: Porewater calculations set D (cf. Figure 5.1). Kunigel-V1(5.4 g/mL) equilibrated with SRHP groundwater at 25 °C, system closed.

	Input groundwater SRHP	Porewater B1 & B2: no impurities (with pyrite & calcite)	Porewater C2: no impurities (with magnetite & calcite)
	(M)	(M)	(M)
Al	3.8E-09	3.83E-09	3.83E-09
B(OH)4	1.0E-02	1.03E-02	1.03E-02
Br	1.9E-03	1.88E-03	1.88E-03
Ca	3.5E-04	2.75E-02	2.75E-02
CH4(aq)	2.4E-06	2.43E-06	1.36E-11
Cl	6.2E-01	6.19E-01	6.19E-01
CO3	1.2E-02	1.05E-02	1.04E-02
F	1.5E-04	1.48E-04	1.48E-04
Fe(II)	5.7E-08	5.57E-08	3.34E-05
Fe(III)	2.4E-15	1.19E-17	3.24E-14
H2(aq)	1.2E-09	5.23E-10	2.54E-11
H2SIO4	2.9E-04	2.83E-04	2.89E-04
K	1.2E-02	4.05E-03	4.05E-03
Mg	2.3E-04	5.51E-03	5.50E-03
Na	6.1E-01	5.48E-01	5.48E-01
NH3	1.4E-02	1.41E-02	1.41E-02
O2(aq)	4.8E-75	2.30E-74	9.72E-72
PO4	1.3E-05	1.32E-05	1.32E-05
S(-II)	7.8E-08	7.60E-08	6.83E-10
SO4	1.4E-09	2.37E-10	3.81E-07
SOH2+		9.49E-03	9.48E-03
SO-		1.35E-02	1.35E-02
NaX		2.74E+00	2.74E+00
HX		3.84E-06	3.83E-06
CaX2		1.99E-01	1.99E-01
MgX2		3.37E-02	3.37E-02
KX		3.70E-02	3.70E-02
calculated pH	7.98	6.34	6.34
calculated pe	-5.06	-3.25	-2.60
calculated -log [E$^-$]*	-5.19	-3.38	-2.72
calculated log pCO_2	-2.31	-0.94	-0.95
calculated I	0.63	0.66	0.66
solids present		calcite chalcedony pyrite	calcite chalcedony magnetite pyrite
precipitated solids			
oversaturated solids (saturation index)			
fluorite		2.24	2
OH-apatite		216.77	217
F-apatite		8.05E+07	8.02E+07
hematite		–	2
goethite		–	–
kaolinite		–	–
quartz		2.69	3
C(0)		5.11	–
calcite precipitated		1.46E-03	3.02E-05
pyrite precipitated		1.57E-09	-1.53E-07
(negative values indicate dissolution)			
bound and unbound H+		3.93E-02	3.93E-02

* -log [E$^-$] refers to the hypothetical E$^-$ concentration. The expression 'pe' refers normally to the hypothetical E$^-$ activity.

Table 5.6: Porewater calculations set D (cf. Figure 5.1). Kunigel-V1(5.4 g/mL) equilibrated with SRLP groundwater at 25 °C, system closed.

	Input groundwater SRLP	Porewater B1 & B2: no impurities (with pyrite & calcite)	Porewater C2: no impurities (with magnetite & calcite)
	(M)	(M)	(M)
Al	3.0E-08	3.00E-08	3.00E-08
B(OH)4	1.0E-02	1.03E-02	1.03E-02
Br	1.9E-03	1.88E-03	1.88E-03
Ca	3.0E-02	3.07E-02	3.07E-02
CH4(aq)	1.4E-07	1.42E-07	2.07E-13
Cl	6.0E-01	5.97E-01	5.97E-01
CO3	4.2E-02	4.05E-02	4.04E-02
F	1.5E-04	1.48E-04	1.48E-04
Fe(II)	5.7E-08	7.50E-09	1.59E-04
Fe(III)	6.5E-18	8.64E-19	9.87E-14
H2(aq)	1.6E-10	1.63E-10	5.65E-12
H2SIO4	2.9E-04	2.82E-04	2.82E-04
K	1.2E-02	3.97E-03	3.96E-03
Mg	2.0E-02	8.09E-03	7.79E-03
Na	4.9E-01	5.20E-01	5.19E-01
NH3	1.5E-02	1.45E-02	1.45E-02
O2(aq)	2.5E-73	2.39E-73	1.97E-70
PO4	1.3E-05	1.32E-05	1.32E-05
S(-II)	3.7E-07	2.78E-07	3.55E-10
SO4	2.4E-08	1.63E-08	1.43E-05
SOH2+		1.23E-02	1.22E-02
SO-		1.05E-02	1.06E-02
NaX		2.66E+00	2.66E+00
HX		1.03E-05	1.02E-05
CaX2		2.25E-01	2.25E-01
MgX2		5.07E-02	5.07E-02
KX		3.70E-02	3.70E-02
calculated pH	5.91	5.92	5.93
calculated pe	-2.57	-2.58	-1.86
calculated -log [E^-]*	-2.69	-2.71	-1.98
calculated log pCO_2	-0.13	-0.14	-0.15
calculated I	0.66	0.65	0.65
solids present		calcite chalcedony pyrite	calcite chalcedony magnetite pyrite
precipitated solids			
oversaturated solids (saturation index)			
fluorite		2	2
OH-apatite		–	–
F-apatite		837529	7.96E+05
hematite		–	4
goethite		–	–
kaolinite		–	–
quartz		2	3
C(0)		3	–
calcite precipitated		1.01E-03	1.33E-04
pyrite precipitated		4.98E-08	-7.00E-06
(negative values indicate dissolution)			
bound and unbound H+		9.03E-02	9.02E-02

* -log [E^-] refers to the hypothetical E^- concentration. The expression 'pe' refers normally to the hypothetical E^- activity.

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Appendix

Results of Porewater Calculations

Appendix

This appendix contains a complete listing of results for all porewater calculations carried out in FY97 (except the data given in section 5). The tables are organized according to the structure given in Figure 5.1.

Table A.1: Porewater calculations set A (cf. Figure 5.1). Kunigel-V1(5.4 g/ml) equilibrated with FRHP groundwater at 60 °C, system closed.

	Input groundwater (M)	Porewater B1 & B2 no impurites (with pyrite & calcite) (M)	Porewater B1 & B2 50% impurites (with pyrite & calcite) (M)	Porewater B1 & B2 100% impurites (with pyrite & calcite) (M)	Porewater B3 no impurites (with pyrite) (M)
Al	3.5E-07	3.5E-07	3.5E-07	3.5E-07	3.5E-07
B(OH)4	6.4E-04	6.4E-04	6.4E-04	6.4E-04	6.4E-04
Br	1.1E-05	1.1E-05	1.1E-05	1.1E-05	1.1E-05
Ca	1.1E-04	4.5E-05	5.8E-03	1.1E-02	1.6E-03
CH4(aq)	1.5E-16	2.8E-13	1.2E-17	5.4E-18	7.8E-16
Cl	5.8E-04	5.8E-04	2.5E-03	4.4E-03	5.8E-04
CO3	3.1E-03	1.3E-02	8.9E-03	7.9E-03	3.1E-03
F	6.4E-04	6.4E-04	4.1E-04	3.2E-04	2.5E-04
Fe(II)	6.2E-05	3.9E-10	4.7E-08	9.4E-08	5.0E-08
Fe(III)	8.3E-10	2.8E-14	2.7E-14	3.0E-14	3.1E-14
H2(aq)	5.4E-12	2.6E-10	1.2E-11	9.5E-12	3.7E-11
H2SIO4	3.5E-04	1.5E-03	7.5E-04	7.3E-04	6.7E-04
K	6.1E-05	2.2E-04	1.6E-03	2.2E-03	6.9E-07
Mg	–	9.7E-06	1.5E-03	2.7E-03	0.0E+00
N2(aq)	5.3E-04	5.3E-04	5.3E-04	5.3E-04	5.3E-04
Na	3.5E-03	2.3E-02	1.5E-01	1.9E-01	7.1E-05
NH3	1.8E-07	1.1E-06	1.7E-07	1.6E-07	1.3E-06
O2(aq)	2.2E-70	1.4E-63	6.7E-61	1.1E-60	7.0E-62
PO4	1.3E-05	4.2E-07	8.2E-08	6.7E-08	7.4E-08
S(-II)	3.8E-12	1.7E-07	6.6E-09	5.0E-09	5.2E-09
SO4	1.3E-04	1.2E-04	7.5E-02	1.0E-01	1.2E-04
calculated pH	8.47	8.10	6.81	6.66	6.54
calculated pe	-4.39	-4.90	-2.94	-2.74	-2.91
calculated -log [E$^-$]*	-4.42	-4.96	-3.07	-2.88	-2.95
calculated pCO$_2$	-3.20	-2.05	-1.07	-1.00	-1.21
calculated I	0.005	0.019	0.200	0.258	0.005
solids present		chalcedony calcite pyrite	chalcedony calcite pyrite	chalcedony calcite pyrite	chalcedony pyrite
precipitated solids		hematite F-apatite	hematite F-apatite fluorite	gypsum hematite F-apatite fluorite	hematite F-apatite fluorite
bound and unbound H+	4.3E-03	1.6E-02	1.2E-02	1.1E-02	6.0E-03

Table A.1: continued

	Porewater C2 no impurites (with magnetite & calcite) (M)	Porewater C2 50% impurites (with magnetite & calcite) (M)	Porewater C2 100% impurites (with magnetite & calcite) (M)	Porewater C3 no impurites (with magnetite) (M)
Al	3.5E-07	3.5E-07	3.5E-07	3.5E-07
B(OH)4	6.4E-04	6.4E-04	6.4E-04	6.4E-04
Br	1.1E-05	1.1E-05	1.1E-05	1.1E-05
Ca	4.1E-05	5.6E-04	1.2E-03	1.6E-03
CH4(aq)	5.2E-10	2.1E-14	8.6E-15	3.1E-09
Cl	5.8E-04	2.5E-03	4.4E-03	5.8E-04
CO3	1.3E-02	1.2E-04	7.8E-05	3.1E-03
F	6.4E-04	4.1E-04	3.2E-04	2.5E-04
Fe(II)	9.4E-10	2.0E-12	1.8E-12	1.9E-07
Fe(III)	2.8E-14	4.6E-13	5.4E-13	2.8E-14
H2(aq)	1.7E-09	1.7E-09	1.7E-09	1.7E-09
H2SIO4	1.5E-03	8.1E-02	1.2E-01	6.7E-04
K	2.2E-04	7.3E-04	1.0E-03	6.7E-07
Mg	8.8E-06	4.2E-05	3.6E-05	0.0E+00
N2(aq)	5.2E-04	5.3E-04	5.3E-04	3.9E-04
Na	2.3E-02	1.0E-01	1.4E-01	7.1E-05
NH3	1.9E-05	7.4E-06	7.4E-06	2.8E-04
O2(aq)	3.2E-65	3.2E-65	3.2E-65	3.2E-65
PO4	4.2E-07	8.4E-10	5.3E-10	4.6E-08
S(-II)	2.8E-07	1.3E-05	1.6E-05	1.6E-08
SO4	1.0E-07	3.2E-04	4.8E-04	1.1E-10
calculated pH	8.12	9.77	9.82	6.67
calculated pe	-5.33	-6.98	-7.03	-3.88
calculated -log $[E^-]$ *	-5.39	-7.08	-7.14	-3.91
calculated pCO_2	-2.07	-6.46	-6.86	-1.31
calculated I	0.019	0.067	0.098	0.005
solids present	chalcedony calcite magnetite	chalcedony calcite magnetite	chalcedony calcite magnetite	chalcedony magnetite
solids precipitated	pyrite hematite F-apatite	pyrite hematite F-apatite brucite	pyrite hematite F-apatite brucite	pyrite hematite F-apatite fluorite
bound and unbound H+	1.6E-02	9.9E-02	1.4E-01	6.1E-03

* -log $[E^-]$ refers to the hypothetical E^- concentration. The expression 'pe' refers normally to the hypothetical E^- activity.

Table A.2: Porewater calculations set A (cf. Figure 5.1). Kunigel-V1(5.4 g/ml) equilibrated with FRLP groundwater at 60 °C, system closed.

	Input groundwater (M)	Porewater B1 & B2 no impurites (with pyrite & calcite) (M)	Porewater B1 & B2 50% impurites (with pyrite & calcite) (M)	Porewater B1 & B2 100% impurites (with pyrite & calcite) (M)	Porewater B3 no impurites (with pyrite) (M)
Al	3.1E-08	3.1E-08	3.1E-08	3.1E-08	3.1E-08
B(OH)4	6.4E-04	6.4E-04	6.4E-04	6.4E-04	6.4E-04
Br	1.1E-05	1.1E-05	1.1E-05	1.1E-05	1.1E-05
Ca	1.1E-04	1.6E-04	6.5E-03	1.2E-02	1.7E-03
CH4(aq)	1.1E-05	5.6E-05	1.2E-12	7.0E-13	1.1E-05
Cl	4.2E-04	4.2E-04	2.3E-03	4.2E-03	4.2E-04
CO3	1.9E-02	3.8E-02	2.9E-02	2.7E-02	1.9E-02
F	6.4E-04	6.4E-04	3.9E-04	3.2E-04	2.5E-04
Fe(II)	3.1E-08	6.2E-08	3.9E-16	5.1E-16	1.1E-07
Fe(III)	2.7E-18	7.1E-15	1.2E-23	1.0E-23	2.6E-16
H2(aq)	5.4E-10	1.4E-08	1.3E-10	1.1E-10	6.4E-09
H2SIO4	3.3E-04	7.8E-04	6.9E-04	6.8E-04	6.5E-04
K	6.1E-05	3.9E-04	1.7E-03	2.2E-03	6.9E-07
Mg	–	3.3E-05	1.6E-03	2.7E-03	0.0E+00
N2(aq)	7.1E-08	6.1E-05	5.1E-04	5.1E-04	9.4E-07
Na	3.5E-03	4.1E-02	1.6E-01	2.0E-01	7.1E-05
NH3	1.0E-03	9.1E-04	1.6E-05	1.7E-05	1.0E-03
O2(aq)	2.2E-74	4.6E-67	5.7E-63	7.9E-63	2.4E-66
PO4	1.3E-05	9.1E-07	3.6E-07	3.0E-07	3.4E-06
S(-II)	6.2E-08	1.2E-07	3.9E-04	3.9E-04	2.3E-07
SO4	1.9E-12	1.2E-12	7.5E-02	1.0E-01	1.6E-13
calculated pH	5.70	7.19	6.36	6.23	5.63
calculated pe	-2.62	-4.86	-3.01	-2.85	-3.12
calculated -log $[E^-]^*$	-2.65	-4.94	-3.14	-2.98	-3.16
calculated pCO_2	-0.34	-0.71	-0.20	-0.16	0.01
calculated I	0.005	0.039	0.207	0.261	0.006
solids present		chalcedony calcite pyrite	chalcedony calcite pyrite	chalcedony calcite pyrite	chalcedony pyrite
solids precipitated		F-apatite	F-apatite fluorite	gypsum F-apatite fluorite	F-apatite fluorite
bound and unbound H+	3.7E-02	4.4E-02	4.0E-02	3.9E-02	3.7E-02

Table A.2: continued

	Porewater C2 no impurites (with magnetite & calcite) (M)	Porewater C2 50% impurites (with magnetite & calcite) (M)	Porewater C2 100% impurites (with magnetite & calcite) (M)	Porewater C3 no impurites (with magnetite) (M)
Al	3.1E-08	3.1E-08	3.1E-08	3.1E-08
B(OH)4	6.4E-04	6.4E-04	6.4E-04	6.4E-04
Br	1.1E-05	1.1E-05	1.1E-05	1.1E-05
Ca	1.7E-04	3.9E-04	7.6E-04	1.7E-03
CH4(aq)	5.7E-05	3.5E-14	1.5E-14	8.4E-06
Cl	4.2E-04	2.3E-03	4.2E-03	4.2E-04
CO3	3.8E-02	1.5E-04	1.0E-04	1.9E-02
F	6.4E-04	3.9E-04	3.2E-04	2.5E-04
Fe(II)	1.4E-07	2.2E-12	1.9E-12	3.8E-05
Fe(III)	1.6E-14	4.2E-13	4.8E-13	9.2E-14
H2(aq)	1.4E-08	1.7E-09	1.7E-09	6.0E-09
H2SIO4	7.8E-04	6.7E-02	9.1E-02	6.5E-04
K	3.9E-04	6.4E-04	8.5E-04	6.9E-07
Mg	3.3E-05	4.8E-05	4.1E-05	0.0E+00
N2(aq)	6.1E-05	5.1E-04	5.1E-04	1.2E-06
Na	4.1E-02	9.0E-02	1.2E-01	7.1E-05
NH3	9.1E-04	7.3E-06	7.3E-06	1.0E-03
O2(aq)	4.6E-67	3.2E-65	3.2E-65	2.7E-66
PO4	9.1E-07	1.2E-09	7.2E-10	3.4E-06
S(-II)	8.2E-08	1.2E-05	1.4E-05	1.2E-08
SO4	7.7E-13	2.5E-04	3.7E-04	1.1E-14
calculated pH	7.19	9.73	9.78	5.64
calculated pe	-4.86	-6.94	-6.99	-3.11
calculated -log $[E^-]$*	-4.94	-7.03	-7.10	-3.15
calculated pCO_2	-0.71	-6.25	-6.61	0.00
calculated I	0.039	0.056	0.077	0.006
solids present	chalcedony calcite magnetite	chalcedony calcite magnetite	chalcedony calcite magnetite	chalcedony magnetite
solids precipitated	pyrite F-apatite	pyrite hematite F-apatite brucite	pyrite hematite F-apatite brucite	pyrite fluorite
bound and unbound H+	4.4E-02	8.3E-02	1.1E-01	3.7E-02

* -log $[E^-]$ refers to the hypothetical E^- concentration. The expression 'pe' refers normally to the hypothetical E^- activity.

Table A.3: Porewater calculations set A (cf. Figure 5.1). Kunigel-V1(5.4 g/ml) equilibrated with MRNP groundwater at 60°C, system closed.

	Input groundwater (M)	Porewater B1 & B2 no impurites (with pyrite & calcite) (M)	Porewater B1 & B2 50% impurites (with pyrite & calcite) (M)	Porewater B1 & B2 100% impurites (with pyrite & calcite) (M)	Porewater B3 no impurites (with pyrite) (M)
Al	6.1E-10	6.1E-10	6.1E-10	6.1E-10	6.1E-10
B(OH)4	1.0E-02	1.0E-02	1.0E-02	1.0E-02	1.0E-02
Br	1.9E-03	1.9E-03	1.9E-03	1.9E-03	1.9E-03
Ca	4.9E-04	7.8E-03	2.1E-02	2.1E-02	1.4E-01
CH4(aq)	1.4E-05	1.7E-06	8.3E-12	8.3E-12	3.2E-08
Cl	3.3E-01	3.3E-01	3.3E-01	3.4E-01	3.3E-01
CO3	1.1E-01	7.7E-02	7.4E-02	7.3E-02	6.2E-02
F	1.5E-04	1.4E-04	1.4E-04	1.4E-04	9.3E-05
Fe(II)	3.2E-05	3.2E-05	4.4E-17	4.4E-17	3.2E-05
Fe(III)	1.6E-14	6.2E-14	2.1E-25	2.1E-25	2.8E-14
H2(aq)	5.8E-10	3.0E-09	1.4E-10	1.4E-10	1.1E-09
H2SIO4	3.0E-04	6.7E-04	6.7E-04	6.7E-04	6.5E-04
K	1.1E-01	9.2E-03	1.2E-02	1.2E-02	8.4E-03
Mg	3.5E-04	2.3E-03	5.8E-03	5.8E-03	3.4E-05
N2(aq)	1.7E-03	1.6E-03	7.0E-03	7.0E-03	1.6E-03
Na	3.2E-01	3.2E-01	4.0E-01	4.0E-01	4.3E-02
NH3	1.1E-02	1.1E-02	3.3E-04	3.3E-04	1.1E-02
O2(aq)	1.8E-74	1.1E-65	5.0E-63	5.0E-63	8.3E-65
PO4	1.3E-05	1.2E-06	9.1E-07	9.1E-07	5.5E-07
S(-II)	1.0E-10	1.2E-08	3.4E-03	3.4E-03	2.4E-08
SO4	1.7E-12	1.5E-12	5.4E-02	5.3E-02	2.0E-11
calculated pH	7.01	5.83	5.67	5.67	5.16
calculated pe	-3.95	-3.16	-2.33	-2.33	-2.27
calculated -log [E⁻]*	-4.08	-3.30	-2.47	-2.47	-2.41
calculated pCO_2	-0.38	0.49	0.53	0.53	0.54
calculated I	0.425	0.370	0.416	0.468	0.467
solids present		chalcedony calcite pyrite	chalcedony calcite pyrite	chalcedony calcite pyrite	chalcedony pyrite
solids precipitated		F-apatite	gypsum S(0) F-apatite	gypsum S(0) F-apatite	calcite F-apatite fluorite
bound and unbound H+	1.5E-01	1.4E-01	1.4E-01	1.4E-01	1.4E-01

Table A.3: continued

	Porewater C2 no impurites (with magnetite & calcite) (M)	Porewater C2 50% impurites (with magnetite & calcite) (M)	Porewater C2 100% impurites (with magnetite & calcite) (M)	Porewater C3 no impurites (with magnetite) (M)
Al	6.1E-10	6.1E-10	6.1E-10	6.1E-10
B(OH)4	1.0E-02	1.0E-02	1.0E-02	1.0E-02
Br	1.9E-03	1.9E-03	1.9E-03	1.9E-03
Ca	7.8E-03	6.9E-03	6.9E-03	1.3E-01
CH4(aq)	1.7E-06	2.0E-08	2.1E-08	2.1E-07
Cl	3.3E-01	3.3E-01	3.4E-01	3.3E-01
CO3	7.7E-02	1.5E-02	1.6E-02	6.0E-02
F	1.4E-04	1.4E-04	1.4E-04	9.3E-05
Fe(II)	4.6E-05	2.9E-06	3.1E-06	5.5E-04
Fe(III)	8.8E-14	4.4E-14	4.5E-14	3.9E-13
H2(aq)	3.0E-09	1.7E-09	1.7E-09	1.7E-09
H2SIO4	6.7E-04	7.1E-04	7.1E-04	6.5E-04
K	9.2E-03	9.3E-03	9.4E-03	8.4E-03
Mg	2.3E-03	2.1E-03	2.1E-03	3.4E-05
N2(aq)	1.6E-03	5.7E-03	5.7E-03	5.8E-04
Na	3.2E-01	3.2E-01	3.2E-01	4.3E-02
NH3	1.1E-02	3.0E-03	3.0E-03	1.3E-02
O2(aq)	1.1E-65	3.2E-65	3.2E-65	3.2E-65
PO4	1.2E-06	1.8E-07	1.9E-07	5.5E-07
S(-II)	1.0E-08	1.2E-08	1.2E-08	7.3E-09
SO4	1.3E-12	9.0E-11	8.6E-11	9.3E-13
calculated pH	5.83	6.32	6.31	5.17
calculated pe	-3.16	-3.53	-3.52	-2.38
calculated -log $[E^-]$*	-3.30	-3.67	-3.66	-2.52
calculated pCO_2	0.49	-0.48	-0.46	0.53
calculated I	0.352	0.357	0.359	0.466
solids present	chalcedony calcite magnetite	chalcedony calcite magnetite	chalcedony calcite magnetite	chalcedony magnetite
solids precipitated	pyrite	pyrite hematite F-apatite	pyrite hematite F-apatite	pyrite hematite calcite
bound and unbound H+	1.4E-01	3.5E-02	3.5E-02	1.3E-01

* -log $[E^-]$ refers to the hypothetical E^- concentration. The expression 'pe' refers normally to the hypothetical E^- activity.

Table A.4: Porewater calculations set A (cf. Figure 5.1). Kunigel-V1(5.4 g/ml) equilibrated with SRHP groundwater at 60 °C, system closed.

	Input groundwater (M)	Porewater B1 & B2 no impurites (with pyrite & calcite) (M)	Porewater B1 & B2 50% impurites (with pyrite & calcite) (M)	Porewater B1 & B2 100% impurites (with pyrite & calcite) (M)	Porewater B3 no impurites (with pyrite) (M)
Al	3.8E-09	3.8E-09	3.8E-09	3.8E-09	3.8E-09
B(OH)4	1.0E-02	1.0E-02	1.0E-02	1.0E-02	1.0E-02
Br	1.9E-03	1.9E-03	1.9E-03	1.9E-03	1.9E-03
Ca	3.5E-04	2.1E-02	3.4E-02	3.4E-02	2.4E-01
CH4(aq)	2.4E-06	3.5E-08	4.0E-12	4.0E-12	1.5E-09
Cl	6.2E-01	6.2E-01	6.2E-01	6.2E-01	6.2E-01
CO3	1.2E-02	8.7E-03	8.9E-03	8.9E-03	3.6E-03
F	1.5E-04	1.4E-04	1.4E-04	1.4E-04	8.8E-05
Fe(II)	5.7E-08	7.2E-08	3.5E-17	3.5E-17	8.6E-08
Fe(III)	2.4E-15	5.7E-16	5.7E-25	5.7E-25	3.4E-16
H2(aq)	1.1E-09	2.2E-09	2.2E-10	2.2E-10	1.2E-09
H2SIO4	2.9E-04	7.1E-04	7.1E-04	7.1E-04	6.6E-04
K	1.2E-02	5.9E-03	6.6E-03	6.7E-03	1.3E-03
Mg	2.3E-04	5.3E-03	8.1E-03	8.1E-03	3.9E-05
N2(aq)	4.3E-03	4.3E-03	6.9E-03	6.9E-03	4.3E-03
Na	6.1E-01	5.6E-01	5.9E-01	6.0E-01	1.1E-01
NH3	5.4E-03	5.4E-03	2.6E-04	2.6E-04	5.4E-03
O2(aq)	4.8E-75	2.0E-65	2.0E-63	2.0E-63	6.7E-65
PO4	1.3E-05	7.0E-08	6.8E-08	6.7E-08	2.7E-08
S(-II)	7.8E-08	1.1E-07	1.9E-03	1.9E-03	1.4E-07
SO4	1.5E-09	2.4E-10	3.2E-02	3.2E-02	1.7E-09
calculated pH	7.98	6.13	6.05	6.05	5.73
calculated pe	-5.06	-3.39	-2.81	-2.81	-2.86
calculated -log $[E^-]^*$	-5.19	-3.52	-2.94	-2.94	-2.98
calculated pCO_2	-2.31	-0.64	-0.59	-0.59	-0.96
calculated I	0.629	0.648	0.677	0.679	0.858
solids present		chalcedony calcite pyrite	chalcedony calcite pyrite	chalcedony calcite pyrite	chalcedony pyrite
solids precipitated		F-apatite	gypsum F-apatite	gypsum F-apatite	calcite F-apatite fluorite
bound and unbound H+	2.7E-02	2.9E-02	2.6E-02	2.6E-02	2.2E-02

Table A.4: continued

	Porewater C2 no impurites (with magnetite & calcite) (M)	Porewater C2 50% impurites (with magnetite & calcite) (M)	Porewater C2 100% impurites (with magnetite & calcite) (M)	Porewater C3 no impurites (with magnetite) (M)
Al	3.8E-09	3.8E-09	3.8E-09	3.8E-09
B(OH)4	1.0E-02	1.0E-02	1.0E-02	1.0E-02
Br	1.9E-03	1.9E-03	1.9E-03	1.9E-03
Ca	2.1E-02	2.7E-02	2.7E-02	2.4E-01
CH4(aq)	3.5E-08	2.1E-12	2.1E-12	5.2E-09
Cl	6.2E-01	6.2E-01	6.2E-01	6.2E-01
CO3	8.7E-03	8.2E-05	8.2E-05	3.0E-03
F	1.4E-04	1.4E-04	1.4E-04	8.8E-05
Fe(II)	6.8E-06	1.2E-09	1.2E-09	2.6E-05
Fe(III)	5.5E-14	2.7E-14	2.7E-14	1.0E-13
H2(aq)	2.2E-09	1.7E-09	1.7E-09	1.7E-09
H2SIO4	7.1E-04	5.4E-03	5.3E-03	6.6E-04
K	5.9E-03	6.5E-03	6.6E-03	1.3E-03
Mg	5.3E-03	5.9E-03	5.9E-03	3.9E-05
N2(aq)	4.3E-03	7.0E-03	7.0E-03	3.4E-03
Na	5.6E-01	5.9E-01	6.0E-01	1.1E-01
NH3	5.4E-03	9.5E-05	9.5E-05	7.3E-03
O2(aq)	2.0E-65	3.2E-65	3.2E-65	3.2E-65
PO4	7.0E-08	4.0E-10	4.0E-10	2.2E-08
S(-II)	1.1E-08	2.5E-07	2.4E-07	8.4E-09
SO4	2.4E-11	3.1E-07	3.0E-07	3.0E-11
calculated pH	6.13	7.99	7.99	5.79
calculated pe	-3.39	-5.20	-5.20	-3.00
calculated -log [E^-] *	-3.52	-5.33	-5.33	-3.11
calculated pCO_2	-0.64	-4.47	-4.47	-1.07
calculated I	0.648	0.676	0.678	0.858
solids present	chalcedony calcite magnetite	chalcedony calcite magnetite	chalcedony calcite magnetite	chalcedony magnetite
solids precipitated	pyrite	pyrite hematite F-apatite	pyrite hematite F-apatite	calcite pyrite hematite F-apatite fluorite
bound and unbound H+	2.9E-02	1.5E-02	1.5E-02	2.3E-02

* -log [E^-] refers to the hypothetical E^- concentration. The expression 'pe' refers normally to the hypothetical E^- activity.

Table A.5: Porewater calculations set A (cf. Figure 5.1). Kunigel-V1(5.4 g/ml) equilibrated with SRLP groundwater at 60 °C, system closed.

	Input groundwater (M)	Porewater B1 & B2 no impurities (with pyrite & calcite) (M)	Porewater B1 & B2 50% impurites (with pyrite & calcite) (M)	Porewater B1 & B2 100% impurites (with pyrite & calcite) (M)	Porewater B3 no impurites (with pyrite) (M)
Al	3.0E-08	3.0E-08	3.0E-08	3.0E-08	3.0E-08
B(OH)4	1.0E-02	1.0E-02	1.0E-02	1.0E-02	1.0E-02
Br	1.9E-03	1.9E-03	1.9E-03	1.9E-03	1.9E-03
Ca	3.0E-02	2.4E-02	3.8E-02	3.8E-02	2.4E-01
CH4(aq)	1.4E-07	1.7E-06	1.0E-11	1.0E-11	7.4E-08
Cl	6.0E-01	6.0E-01	6.0E-01	6.0E-01	6.0E-01
CO3	4.2E-02	3.7E-02	3.8E-02	3.8E-02	3.0E-02
F	1.5E-04	1.4E-04	1.4E-04	1.4E-04	9.3E-05
Fe(II)	5.7E-08	5.1E-08	3.2E-17	3.2E-17	1.0E-07
Fe(III)	6.5E-18	8.1E-17	1.7E-25	1.7E-25	8.1E-17
H2(aq)	1.6E-10	3.6E-09	1.7E-10	1.7E-10	1.6E-09
H2SIO4	2.9E-04	6.7E-04	6.7E-04	6.7E-04	6.5E-04
K	1.2E-02	5.8E-03	6.4E-03	6.6E-03	1.3E-03
Mg	2.0E-02	7.8E-03	1.2E-02	1.2E-02	3.3E-03
N2(aq)	7.4E-04	7.4E-04	7.0E-03	7.0E-03	7.4E-04
Na	4.9E-01	5.2E-01	5.6E-01	5.6E-01	9.1E-02
NH3	1.3E-02	1.3E-02	5.0E-04	5.0E-04	1.3E-02
O2(aq)	2.5E-73	7.6E-66	3.2E-63	3.2E-63	3.6E-65
PO4	1.3E-05	3.7E-07	3.5E-07	3.5E-07	2.8E-07
S(-II)	3.7E-07	3.8E-07	4.1E-03	4.1E-03	4.8E-07
SO4	2.4E-08	2.0E-11	3.0E-02	3.0E-02	1.5E-10
calculated pH	5.91	5.69	5.62	5.62	5.17
calculated pe	-2.57	-3.05	-2.33	-2.33	-2.37
calculated -log $[E^-]^*$	-2.69	-3.19	-2.46	-2.46	-2.49
calculated pCO_2	-0.13	0.21	0.24	0.24	0.18
calculated I	0.66	0.64	0.67	0.67	0.83
solids present		chalcedony calcite pyrite	chalcedony calcite pyrite	chalcedony calcite pyrite	chalcedony pyrite
precipitated solids		F-apatite	gypsum S(0) F-apatite	gypsum S(0) F-apatite	calcite F-apatite fluorite
bound and unbound H+	9.1E-02	8.6E-02	7.9E-02	7.9E-02	7.6E-02

Table A.5: continued

	Porewater C2 no impurites (with magnetite & calcite) (M)	Porewater C2 50% impurites (with magnetite & calcite) (M)	Porewater C2 100% impurites (with magnetite & calcite) (M)	Porewater C3 no impurites (with magnetite) (M)
Al	3.0E-08	3.0E-08	3.0E-08	3.0E-08
B(OH)4	1.0E-02	1.0E-02	1.0E-02	1.0E-02
Br	1.9E-03	1.9E-03	1.9E-03	1.9E-03
Ca	2.4E-02	2.5E-02	2.5E-02	2.4E-01
CH4(aq)	1.7E-06	8.8E-09	8.9E-09	9.1E-08
Cl	6.0E-01	6.0E-01	6.0E-01	6.0E-01
CO3	3.7E-02	6.0E-03	6.1E-03	2.9E-02
F	1.4E-04	1.4E-04	1.4E-04	9.3E-05
Fe(II)	7.1E-05	4.5E-06	4.5E-06	4.6E-04
Fe(III)	1.1E-13	5.1E-14	5.1E-14	3.6E-13
H2(aq)	3.5E-09	1.7E-09	1.7E-09	1.7E-09
H2SIO4	6.7E-04	7.2E-04	7.2E-04	6.5E-04
K	5.7E-03	6.0E-03	6.2E-03	1.3E-03
Mg	7.8E-03	7.9E-03	7.9E-03	3.3E-03
N2(aq)	7.5E-04	5.4E-03	5.4E-03	6.6E-04
Na	5.2E-01	5.3E-01	5.3E-01	9.0E-02
NH3	1.3E-02	3.7E-03	3.7E-03	1.3E-02
O2(aq)	7.7E-66	3.2E-65	3.2E-65	3.2E-65
PO4	3.7E-07	4.7E-08	4.7E-08	2.8E-07
S(-II)	1.0E-08	1.1E-08	1.1E-08	7.3E-09
SO4	5.4E-13	8.0E-11	7.8E-11	1.8E-12
calculated pH	5.69	6.20	6.20	5.18
calculated pe	-3.05	-3.42	-3.41	-2.39
calculated -log $[E^-]$*	-3.19	-3.55	-3.54	-2.51
calculated pCO_2	0.21	-0.85	-0.84	0.17
calculated I	0.637	0.638	0.640	0.833
solids present	chalcedony calcite magnetite	chalcedony calcite magnetite	chalcedony calcite magnetite	chalcedony magnetite
solids precipitated	pyrite	pyrite hematite F-apatite	pyrite hematite F-apatite	calcite pyrite hematite fluorite
bound and unbound H+	8.6E-02	2.3E-02	2.3E-02	7.5E-02

* -log $[E^-]$ refers to the hypothetical E^- concentration. The expression 'pe' refers normally to the hypothetical E^- activity.

Table B.1: Porewater calculations set B (cf. Figure 5.1). Kunigel-V1(5.4 g/ml) equilibrated with FRHP groundwater at 25 °C, system closed.

	Input groundwater (M)	Porewater B1 & B2 no impurites (with pyrite & calcite) (M)	Porewater B1 & B2 50% impurites (with pyrite & calcite) (M)	Porewater B1 & B2 100% impurites (with pyrite & calcite) (M)	Porewater B3 no impurites (with pyrite) (M)
Al	3.5E-07	3.5E-07	9.3E-08	9.9E-08	3.5E-07
B	6.4E-04	6.4E-04	6.4E-04	6.4E-04	6.4E-04
Br	1.1E-05	1.1E-05	1.1E-05	1.1E-05	1.1E-05
Ca	1.1E-04	5.5E-05	5.8E-03	9.4E-03	1.6E-03
CH4(aq)	1.5E-16	4.9E-12	2.3E-16	1.3E-16	6.1E-15
Cl	5.8E-04	5.8E-04	2.5E-03	4.4E-03	5.8E-04
CO3	3.1E-03	1.5E-02	1.2E-02	1.1E-02	3.1E-03
F	6.4E-04	6.4E-04	2.5E-04	2.1E-04	1.6E-04
Fe(II)	6.2E-05	4.1E-09	3.8E-07	6.3E-07	1.1E-06
Fe(III)	8.3E-10	4.4E-15	6.6E-15	7.6E-15	1.1E-14
H2(aq)	5.4E-12	4.6E-11	2.1E-12	1.8E-12	5.1E-12
SiO2	3.5E-04	3.0E-04	2.8E-04	2.8E-04	2.8E-04
K	6.1E-05	2.6E-04	1.7E-03	2.1E-03	6.8E-07
Mg	–	1.3E-05	1.1E-03	1.6E-03	0.0E+00
N2(aq)	5.3E-04	5.3E-04	5.3E-04	5.3E-04	5.2E-04
Na	3.5E-03	2.7E-02	1.6E-01	1.9E-01	7.1E-05
NH3	1.8E-07	6.0E-06	1.2E-06	1.2E-06	1.0E-05
O2(aq)	2.2E-70	2.9E-72	1.4E-69	2.0E-69	2.4E-70
PO4	1.3E-05	2.2E-07	5.7E-08	4.9E-08	1.2E-07
S(-II)	3.8E-12	2.0E-08	8.9E-10	7.3E-10	6.2E-10
SO4	1.3E-04	1.2E-04	7.5E-02	9.5E-02	1.2E-04
calculated pH	8.5	8.3	7.1	6.9	6.6
calculated pe	-4.39	-4.74	-2.78	-2.63	-2.50
calculated -log [E^{-}]*	-4.42	-4.80	-2.91	-2.76	-2.54
calculated pCO_2	-3.2	-2.4	-1.4	-1.3	-1.5
calculated I	0.005	0.02	0.21	0.25	0.005
solids present		chalcedony calcite pyrite	chalcedony calcite pyrite	chalcedony calcite pyrite	chalcedony pyrite
precipitated solids		F-apatite fluorite	hematite gibbsite F-apatite fluorite	gypsum hematite gibbsite F-apatite fluorite	hematite F-apatite fluorite
bound and unbound H+	4.3E-03	1.6E-02	1.4E-02	1.4E-02	5.4E-03

Table B.1: continued

	Porewater C2 no impurites (with magnetite & calcite) (M)	Porewater C2 50% impurites (with magnetite & calcite) (M)	Porewater C2 100% impurites (with magnetite & calcite) (M)	Porewater C3 no impurites (with magnetite) (M)
Al	3.5E-07	9.3E-08	9.9E-08	1.3E-07
B	6.4E-04	6.4E-04	6.4E-04	6.4E-04
Br	1.1E-05	1.1E-05	1.1E-05	1.1E-05
Ca	5.2E-05	1.5E-03	2.3E-03	1.6E-03
CH4(aq)	6.3E-09	1.3E-14	6.3E-15	3.7E-08
Cl	5.8E-04	2.5E-03	4.4E-03	5.8E-04
CO3	1.5E-02	4.2E-05	3.4E-05	3.1E-03
F	6.4E-04	2.5E-04	2.1E-04	1.6E-04
Fe(II)	9.3E-09	1.1E-12	8.5E-13	2.3E-06
Fe(III)	4.5E-15	1.5E-13	1.9E-13	7.4E-15
H2(aq)	2.8E-10	2.8E-10	2.8E-10	2.8E-10
SiO2	3.0E-04	7.9E-03	1.1E-02	2.8E-04
K	2.5E-04	1.1E-03	1.3E-03	6.9E-07
Mg	1.2E-05	1.7E-04	1.2E-04	0.0E+00
N2(aq)	4.9E-04	5.3E-04	5.3E-04	8.0E-05
Na	2.6E-02	1.2E-01	1.3E-01	7.1E-05
NH3	8.3E-05	9.7E-06	9.6E-06	9.0E-04
O2(aq)	7.8E-74	7.8E-74	7.8E-74	7.8E-74
PO4	2.2E-07	2.4E-10	2.1E-10	4.3E-08
S(-II)	3.4E-08	5.6E-06	7.0E-06	2.1E-09
SO4	1.5E-07	6.1E-03	1.0E-02	1.2E-10
calculated pH	8.4	10.6	10.7	6.9
calculated pe	-5.15	-7.34	-7.44	-3.65
calculated -log [E^-]*	-5.21	-7.45	-7.55	-3.68
calculated pCO$_2$	-2.5	-8.2	-8.5	-1.7
calculated I	0.02	0.07	0.09	0.01
solids present	chalcedony calcite magnetite	chalcedony calcite magnetite	chalcedony calcite magnetite	chalcedony magnetite
solids precipitated	pyrite hematite	pyrite hematite F-apatite brucite	pyrite hematite F-apatite brucite	pyrite hematite gibbsite F-apatite
bound and unbound H+	1.6E-02	7.7E-03	1.0E-02	5.9E-03

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* -log [E^-] refers to the hypothetical E^- concentration. The expression 'pe' refers normally to the hypothetical E^- activity.

Table B.2: Porewater calculations set B (cf. Figure 5.1). Kunigel-V1(5.4 g/ml) equilibrated with FRLP groundwater at 25 °C, system closed.

Total dissolved concentrations	Input groundwater (M)	Porewater B1 & B2 no impurites (with pyrite & calcite) (M)	Porewater B1 & B2 50% impurites (with pyrite & calcite) (M)	Porewater B1 & B2 100% impurites (with pyrite & calcite) (M)	Porewater B3 no impurites (with pyrite) (M)
Al	3.1E-08	3.1E-08	3.1E-08	3.1E-08	3.1E-08
B	6.4E-04	6.4E-04	6.4E-04	6.4E-04	6.4E-04
Br	1.1E-05	1.1E-05	1.1E-05	1.1E-05	1.1E-05
Ca	1.1E-04	2.0E-04	6.5E-03	9.8E-03	1.7E-03
CH4(aq)	1.1E-05	2.7E-05	1.3E-10	8.5E-11	1.1E-05
Cl	4.2E-04	4.2E-04	2.3E-03	4.2E-03	4.2E-04
CO3	1.9E-02	4.1E-02	3.3E-02	3.1E-02	1.9E-02
F	6.4E-04	6.4E-04	2.4E-04	2.0E-04	1.6E-04
Fe(II)	3.1E-08	2.6E-08	1.5E-16	1.8E-16	6.8E-08
Fe(III)	2.7E-18	1.0E-16	1.4E-25	1.4E-25	6.3E-18
H2(aq)	5.4E-10	1.1E-09	3.7E-11	3.2E-11	5.4E-10
SiO2	3.3E-04	2.8E-04	2.8E-04	2.8E-04	2.8E-04
K	6.1E-05	4.5E-04	1.7E-03	2.1E-03	6.9E-07
Mg	–	4.3E-05	1.2E-03	1.6E-03	0.0E+00
N2(aq)	7.1E-08	2.2E-05	4.2E-04	4.2E-04	9.4E-08
Na	3.5E-03	4.7E-02	1.7E-01	1.9E-01	7.1E-05
NH3	1.0E-03	9.9E-04	1.9E-04	2.0E-04	1.0E-03
O2(aq)	2.2E-74	5.3E-75	4.7E-72	6.0E-72	2.1E-74
PO4	1.3E-05	4.2E-07	2.0E-07	1.7E-07	4.1E-06
S(-II)	6.2E-08	5.2E-08	3.2E-04	3.2E-04	1.4E-07
SO4	1.9E-12	1.3E-10	7.5E-02	9.2E-02	6.5E-12
calculated pH	5.7	7.5	6.7	6.6	5.8
calculated pe	-2.62	-4.55	-2.99	-2.87	-2.69
calculated -log [E^-] *	-2.65	-4.63	-3.12	-3.00	-2.72
calculated pCO_2	-0.3	-1.2	-0.6	-0.6	-0.4
calculated I	0.005	0.04	0.22	0.25	0.006
solids present		chalcedony calcite pyrite	chalcedony calcite pyrite	chalcedony calcite pyrite	chalcedony pyrite
solids precipitated		F-apatite	F-apatite fluorite	gypsum F-apatite fluorite	F-apatite fluorite
bound and unbound H+	3.7E-02	4.6E-02	4.3E-02	4.2E-02	3.7E-02

Table B.2: continued

	Porewater C2 no impurites (with magnetite & calcite) (M)	Porewater C2 50% impurites (with magnetite & calcite) (M)	Porewater C2 100% impurites (with magnetite & calcite) (M)	Porewater C3 no impurites (with magnetite) (M)
Al	3.1E-08	3.1E-08	3.1E-08	3.1E-08
B	6.4E-04	6.4E-04	6.4E-04	6.4E-04
Br	1.1E-05	1.1E-05	1.1E-05	1.1E-05
Ca	1.9E-04	1.0E-03	1.5E-03	1.6E-03
CH4(aq)	2.7E-05	2.0E-14	1.2E-14	4.2E-07
Cl	4.2E-04	2.3E-03	4.2E-03	4.2E-04
CO3	4.1E-02	5.0E-05	4.2E-05	1.2E-02
F	6.4E-04	2.4E-04	2.0E-04	1.6E-04
Fe(II)	9.6E-07	1.1E-12	9.9E-13	1.3E-04
Fe(III)	3.7E-15	1.4E-13	1.6E-13	3.1E-14
H2(aq)	1.1E-09	2.8E-10	2.8E-10	2.8E-10
SiO2	2.8E-04	6.8E-03	8.3E-03	2.8E-04
K	4.5E-04	9.9E-04	1.1E-03	6.8E-07
Mg	4.2E-05	1.8E-04	1.5E-04	0.0E+00
N2(aq)	2.2E-05	5.1E-04	5.1E-04	2.1E-06
Na	4.7E-02	1.0E-01	1.1E-01	7.1E-05
NH3	9.9E-04	9.6E-06	9.5E-06	1.0E-03
O2(aq)	5.3E-75	7.8E-74	7.8E-74	7.8E-74
PO4	4.2E-07	3.0E-10	2.6E-10	1.4E-06
S(-II)	8.6E-09	5.1E-06	5.9E-06	1.3E-09
SO4	2.2E-11	4.9E-03	6.8E-03	2.6E-12
calculated pH	7.5	10.5	10.6	6.0
calculated pe	-4.55	-7.32	-7.37	-2.81
calculated -log [E$^-$]*	-4.63	-7.41	-7.47	-2.84
calculated pCO_2	-1.2	-8.0	-8.2	-0.6
calculated I	0.04	0.06	0.07	0.01
solids present	chalcedony calcite magnetite	chalcedony calcite magnetite	chalcedony calcite magnetite	chalcedony magnetite
solids precipitated	pyrite	pyrite hematite F-apatite brucite	pyrite hematite F-apatite brucite	pyrite hematite siderite F-apatite
bound and unbound H+	4.6E-02	6.7E-03	8.1E-03	2.2E-02

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* -log [E$^-$] refers to the hypothetical E$^-$ concentration. The expression 'pe' refers normally to the hypothetical E$^-$ activity.

Table B.3: Porewater calculations set B (cf. Figure 5.1). Kunigel-V1(5.4 g/ml) equilibrated with MRNP groundwater at 25 °C, system closed.

	Input groundwater (M)	Porewater B1 & B2 no impurites (with pyrite & calcite) (M)	Porewater B1 & B2 50% impurites (with pyrite & calcite) (M)	Porewater B1 & B2 100% impurites (with pyrite & calcite) (M)	Porewater B3 no impurites (with pyrite) (M)
Al	6.1E-10	6.1E-10	6.1E-10	6.1E-10	6.1E-10
B	1.0E-02	1.0E-02	1.0E-02	1.0E-02	1.0E-02
Br	1.9E-03	1.9E-03	1.9E-03	1.9E-03	1.9E-03
Ca	4.9E-04	8.2E-03	1.9E-02	1.9E-02	1.4E-01
CH4(aq)	1.4E-05	1.8E-07	9.5E-10	9.5E-10	3.5E-09
Cl	3.3E-01	3.3E-01	3.3E-01	3.4E-01	3.3E-01
CO3	1.1E-01	8.2E-02	7.9E-02	7.9E-02	6.5E-02
F	1.5E-04	1.4E-04	1.4E-04	1.4E-04	4.7E-05
Fe(II)	3.2E-05	3.2E-05	2.3E-17	2.3E-17	3.2E-05
Fe(III)	1.6E-14	4.5E-15	4.1E-27	4.1E-27	2.4E-15
H2(aq)	5.8E-10	1.5E-10	4.0E-11	4.0E-11	5.4E-11
SiO2	3.0E-04	2.8E-04	2.8E-04	2.8E-04	2.8E-04
K	1.1E-01	9.5E-03	1.2E-02	1.2E-02	8.6E-03
Mg	3.5E-04	2.4E-03	4.4E-03	4.4E-03	3.5E-05
N2(aq)	1.7E-03	1.6E-03	5.3E-03	5.3E-03	1.6E-03
Na	3.2E-01	3.3E-01	4.0E-01	4.0E-01	4.4E-02
NH3	1.1E-02	1.1E-02	3.7E-03	3.7E-03	1.1E-02
O2(aq)	1.8E-74	2.8E-73	4.0E-72	4.0E-72	2.2E-72
PO4	1.3E-05	5.3E-07	4.1E-07	4.1E-07	2.4E-07
S(-II)	1.0E-10	3.3E-09	2.7E-03	2.7E-03	6.5E-09
SO4	1.7E-12	4.2E-10	4.6E-02	4.5E-02	5.4E-09
calculated pH	7.0	6.1	6.0	6.0	5.4
calculated pe	-3.95	-2.76	-2.34	-2.33	-1.86
calculated -log $[E^-]^*$	-4.08	-2.90	-2.47	-2.47	-2.00
calculated pCO_2	-0.4	0.1	0.1	0.1	0.2
calculated I	0.42	0.38	0.42	0.47	0.47
solids present		chalcedony calcite pyrite	chalcedony calcite pyrite	chalcedony calcite pyrite	chalcedony pyrite
solids precipitated		F-apatite	gypsum F-apatite fluorite	gypsum F-apatite fluorite	calcite F-apatite fluorite
bound and unbound H+	1.5E-01	1.5E-01	1.4E-01	1.4E-01	1.4E-01

Table B.3: continued

	Porewater C2 no impurites (with magnetite & calcite)	Porewater C2 50% impurites (with magnetite & calcite)	Porewater C2 100% impurites (with magnetite & calcite)	Porewater C3 no impurites (with magnetite)
	(M)	(M)	(M)	(M)
Al	6.1E-10	6.1E-10	6.1E-10	6.1E-10
B	1.0E-02	1.0E-02	1.0E-02	1.0E-02
Br	1.9E-03	1.9E-03	1.9E-03	1.9E-03
Ca	6.7E-03	6.8E-03	6.9E-03	1.4E-01
CH4(aq)	4.2E-07	4.2E-07	4.2E-07	4.2E-07
Cl	3.3E-01	3.3E-01	3.4E-01	3.3E-01
CO3	2.5E-02	2.5E-02	2.5E-02	1.3E-02
F	1.4E-04	1.4E-04	1.4E-04	4.7E-05
Fe(II)	4.0E-05	4.0E-05	4.0E-05	6.4E-04
Fe(III)	1.6E-14	1.6E-14	1.6E-14	6.1E-14
H2(aq)	2.8E-10	2.8E-10	2.8E-10	2.8E-10
SiO2	2.8E-04	2.8E-04	2.8E-04	2.8E-04
K	9.2E-03	9.3E-03	9.5E-03	8.6E-03
Mg	2.1E-03	2.1E-03	2.1E-03	3.4E-05
N2(aq)	1.6E-03	1.6E-03	1.6E-03	1.2E-04
Na	3.2E-01	3.2E-01	3.2E-01	4.4E-02
NH3	1.1E-02	1.1E-02	1.1E-02	1.4E-02
O2(aq)	7.8E-74	7.8E-74	7.8E-74	7.8E-74
PO4	1.4E-07	1.4E-07	1.4E-07	4.6E-08
S(-II)	1.7E-09	1.7E-09	1.7E-09	1.3E-09
SO4	8.7E-11	8.6E-11	8.6E-11	8.5E-12
calculated pH	6.5	6.5	6.5	5.9
calculated pe	-3.30	-3.30	-3.30	-2.64
calculated -log $[E^-]$[*]	-3.43	-3.43	-3.43	-2.77
calculated pCO_2	-0.6	-0.6	-0.6	-0.6
calculated I	0.36	0.36	0.37	0.47
solids present	chalcedony calcite magnetite	chalcedony calcite magnetite	chalcedony calcite magnetite	chalcedony magnetite
solids precipitated	pyrite hematite siderite F-apatite	pyrite hematite siderite F-apatite	pyrite hematite siderite F-apatite	calcite pyrite hematite siderite F-apatite
bound and unbound H+	5.5E-02	5.5E-02	5.5E-02	4.6E-02

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[*] -log $[E^-]$ refers to the hypothetical E^- concentration. The expression 'pe' refers normally to the hypothetical E^- activity.

Table B.4: Porewater calculations set B (cf. Figure 5.1). Kunigel-V1(5.4 g/ml) equilibrated with SRHP groundwater at 25 °C, system closed.

	Input groundwater (M)	Porewater B1 & B2 no impurities (with pyrite & calcite) (M)	Porewater B1 & B2 50% impurities (with pyrite & calcite) (M)	Porewater B1 & B2 100% impurities (with pyrite & calcite) (M)	Porewater B3 no impurities (with pyrite) (M)
Al	3.8E-09	3.8E-09	3.8E-09	3.8E-09	3.8E-09
B	1.0E-02	1.0E-02	1.0E-02	1.0E-02	1.0E-02
Br	1.9E-03	1.9E-03	1.9E-03	1.9E-03	1.9E-03
Ca	3.5E-04	2.2E-02	3.1E-02	3.2E-02	2.5E-01
CH4(aq)	2.4E-06	3.7E-09	3.1E-10	3.1E-10	1.5E-10
Cl	6.2E-01	6.2E-01	6.2E-01	6.2E-01	6.2E-01
CO3	1.2E-02	1.2E-02	1.2E-02	1.2E-02	5.5E-03
F	1.5E-04	1.1E-04	1.0E-04	1.0E-04	4.0E-05
Fe(II)	5.7E-08	6.8E-08	4.0E-17	4.0E-17	2.2E-07
Fe(III)	2.4E-15	3.6E-17	2.2E-26	2.2E-26	5.9E-17
H2(aq)	1.1E-09	1.0E-10	5.4E-11	5.4E-11	5.1E-11
SiO2	2.9E-04	2.8E-04	2.8E-04	2.8E-04	2.8E-04
K	1.2E-02	6.0E-03	6.5E-03	6.7E-03	1.4E-03
Mg	2.3E-04	5.3E-03	6.8E-03	6.8E-03	4.0E-05
N2(aq)	4.3E-03	4.3E-03	5.7E-03	5.7E-03	4.3E-03
Na	6.1E-01	5.6E-01	5.9E-01	5.9E-01	1.2E-01
NH3	5.4E-03	5.4E-03	2.7E-03	2.7E-03	5.4E-03
O2(aq)	4.8E-75	6.1E-73	2.2E-72	2.2E-72	2.5E-72
PO4	1.3E-05	4.1E-08	3.9E-08	3.9E-08	1.8E-08
S(-II)	7.8E-08	2.9E-08	1.0E-03	1.0E-03	2.5E-08
SO4	1.5E-09	7.1E-08	2.6E-02	2.6E-02	3.8E-07
calculated pH	8.0	6.4	6.3	6.3	5.9
calculated pe	-5.06	-2.94	-2.74	-2.74	-2.32
calculated -log [E$^-$]*	-5.19	-3.06	-2.87	-2.86	-2.43
calculated pCO_2	-2.3	-0.9	-0.9	-0.9	-1.1
calculated I	0.63	0.65	0.68	0.68	0.86
solids present		chalcedony calcite pyrite	chalcedony calcite pyrite	chalcedony calcite pyrite	chalcedony pyrite
solids precipitated		F-apatite fluorite	gypsum F-apatite fluorite	gypsum F-apatite fluorite	calcite F-apatite fluorite
bound and unbound H+	2.7E-02	3.2E-02	3.0E-02	3.0E-02	2.5E-02

Table B.4: continued

	Porewater C2 no impurites (with magnetite & calcite) (M)	Porewater C2 50% impurites (with magnetite & calcite) (M)	Porewater C2 100% impurites (with magnetite & calcite) (M)	Porewater C3 no impurites (with magnetite) (M)
Al	3.8E-09	3.8E-09	3.8E-09	3.8E-09
B	1.0E-02	1.0E-02	1.0E-02	1.0E-02
Br	1.9E-03	1.9E-03	1.9E-03	1.9E-03
Ca	2.1E-02	2.5E-02	2.5E-02	2.4E-01
CH4(aq)	1.5E-07	2.9E-10	3.0E-10	5.6E-08
Cl	6.2E-01	6.2E-01	6.2E-01	6.2E-01
CO3	9.0E-03	2.7E-04	2.7E-04	2.7E-03
F	1.1E-04	1.0E-04	1.0E-04	4.0E-05
Fe(II)	4.0E-05	8.6E-08	8.8E-08	1.7E-04
Fe(III)	1.7E-14	4.4E-15	4.4E-15	3.3E-14
H2(aq)	2.8E-10	2.8E-10	2.8E-10	2.8E-10
SiO2	2.8E-04	3.3E-04	3.3E-04	2.8E-04
K	5.9E-03	6.4E-03	6.6E-03	1.3E-03
Mg	5.2E-03	5.6E-03	5.7E-03	3.9E-05
N2(aq)	1.4E-03	6.4E-03	6.4E-03	3.9E-04
Na	5.6E-01	5.9E-01	5.9E-01	1.2E-01
NH3	1.1E-02	1.2E-03	1.3E-03	1.3E-02
O2(aq)	7.8E-74	7.8E-74	7.8E-74	7.8E-74
PO4	3.0E-08	6.7E-10	6.8E-10	8.5E-09
S(-II)	1.7E-09	1.1E-08	1.1E-08	1.4E-09
SO4	9.9E-11	4.3E-08	4.2E-08	5.2E-11
calculated pH	6.5	7.8	7.8	6.1
calculated pe	-3.26	-4.57	-4.56	-2.90
calculated -log $[E^-]$ *	-3.39	-4.69	-4.69	-3.02
calculated pCO_2	-1.1	-3.8	-3.8	-1.5
calculated I	0.65	0.67	0.67	0.86
solids present	chalcedony calcite magnetite	chalcedony calcite magnetite	chalcedony calcite magnetite	chalcedony magnetite
solids precipitated	pyrite hematite F-apatite	pyrite hematite F-apatite	pyrite hematite F-apatite	calcite pyrite hematite F-apatite
bound and unbound H+	3.4E-02	1.2E-02	1.2E-02	2.8E-02

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* -log $[E^-]$ refers to the hypothetical E^- concentration. The expression 'pe' refers normally to the hypothetical E^- activity.

Table B.5: Porewater calculations set B (cf. Figure 5.1). Kunigel-V1(5.4 g/ml) equilibrated with SRLP groundwater at 25 °C, system closed.

	Input groundwater	Porewater B1 & B2 no impurities (with pyrite & calcite)	Porewater B1 & B2 50% impurities (with pyrite & calcite)	Porewater B1 & B2 100% impurities (with pyrite & calcite)	Porewater B3 no impurities (with pyrite)
	(M)	(M)	(M)	(M)	(M)
Al	3.0E-08	3.0E-08	3.0E-08	3.0E-08	3.0E-08
B	1.0E-02	1.0E-02	1.0E-02	1.0E-02	1.0E-02
Br	1.9E-03	1.9E-03	1.9E-03	1.9E-03	1.9E-03
Ca	3.0E-02	2.5E-02	3.5E-02	3.5E-02	2.4E-01
CH4(aq)	1.4E-07	2.0E-07	1.1E-09	1.1E-09	8.2E-09
Cl	6.0E-01	6.0E-01	6.0E-01	6.0E-01	6.0E-01
CO3	4.2E-02	4.2E-02	4.2E-02	4.2E-02	3.2E-02
F	1.5E-04	1.1E-04	1.0E-04	1.0E-04	4.1E-05
Fe(II)	5.7E-08	6.7E-09	2.1E-17	2.1E-17	2.6E-08
Fe(III)	6.5E-18	8.2E-19	4.1E-27	4.1E-27	1.8E-18
H2(aq)	1.6E-10	1.8E-10	4.7E-11	4.7E-11	8.0E-11
SiO2	2.9E-04	2.8E-04	2.8E-04	2.8E-04	2.8E-04
K	1.2E-02	5.8E-03	6.4E-03	6.6E-03	1.3E-03
Mg	2.0E-02	7.9E-03	1.0E-02	1.0E-02	3.3E-03
N2(aq)	7.4E-04	7.4E-04	4.7E-03	4.7E-03	7.4E-04
Na	4.9E-01	5.3E-01	5.6E-01	5.6E-01	9.2E-02
NH3	1.3E-02	1.3E-02	5.1E-03	5.1E-03	1.3E-02
O2(aq)	2.5E-73	2.0E-73	2.8E-72	2.8E-72	9.9E-73
PO4	1.3E-05	1.7E-07	1.7E-07	1.7E-07	1.2E-07
S(-II)	3.7E-07	2.8E-07	3.0E-03	3.0E-03	2.6E-07
SO4	2.4E-08	1.4E-08	2.4E-02	2.4E-02	7.6E-08
calculated pH	5.9	6.0	5.9	5.9	5.4
calculated pe	-2.57	-2.65	-2.31	-2.31	-1.95
calculated -log [E⁻]*	-2.69	-2.78	-2.44	-2.44	-2.07
calculated pCO_2	-0.1	-0.2	-0.1	-0.1	-0.1
calculated I	0.66	0.64	0.67	0.67	0.84
solids present		chalcedony calcite pyrite	chalcedony calcite pyrite	chalcedony calcite pyrite	chalcedony pyrite
precipitated solids		F-apatite fluorite	gypsum F-apatite fluorite	gypsum F-apatite fluorite	calcite F-apatite fluorite
bound, unbound H+	9.1E-02	9.0E-02	8.6E-02	8.6E-02	8.0E-02

Table B.5: continued

	Porewater C2 no impurites (with magnetite & calcite) (M)	Porewater C2 50% impurites (with magnetite & calcite) (M)	Porewater C2 100% impurites (with magnetite & calcite) (M)	Porewater C3 no impurites (with magnetite) (M)
Al	3.0E-08	3.0E-08	3.0E-08	3.0E-08
B	1.0E-02	1.0E-02	1.0E-02	1.0E-02
Br	1.9E-03	1.9E-03	1.9E-03	1.9E-03
Ca	2.4E-02	2.4E-02	2.4E-02	2.4E-01
CH4(aq)	4.2E-07	2.5E-07	2.5E-07	4.2E-07
Cl	6.0E-01	6.0E-01	6.0E-01	6.0E-01
CO3	1.8E-02	1.2E-02	1.2E-02	1.3E-02
F	1.1E-04	1.0E-04	1.0E-04	4.1E-05
Fe(II)	1.4E-04	7.9E-05	8.0E-05	1.3E-03
Fe(III)	2.7E-14	2.2E-14	2.2E-14	8.4E-14
H2(aq)	2.8E-10	2.8E-10	2.8E-10	2.8E-10
SiO2	2.8E-04	2.8E-04	2.8E-04	2.8E-04
K	5.8E-03	6.0E-03	6.1E-03	1.3E-03
Mg	7.7E-03	7.7E-03	7.7E-03	3.3E-03
N2(aq)	5.8E-04	8.9E-04	8.8E-04	6.2E-05
Na	5.3E-01	5.3E-01	5.3E-01	9.2E-02
NH3	1.3E-02	1.3E-02	1.3E-02	1.4E-02
O2(aq)	7.8E-74	7.8E-74	7.8E-74	7.8E-74
PO4	6.8E-08	4.6E-08	4.6E-08	4.7E-08
S(-II)	1.4E-09	1.5E-09	1.5E-09	1.3E-09
SO4	3.1E-11	5.2E-11	5.2E-11	7.0E-12
calculated pH	6.2	6.3	6.3	5.7
calculated pe	-3.00	-3.12	-3.11	-2.47
calculated -log $[E^-]$*	-3.13	-3.24	-3.24	-2.59
calculated pCO_2	-0.6	-0.9	-0.9	-0.6
calculated I	0.64	0.64	0.64	0.84
solids present	chalcedony calcite magnetite	chalcedony calcite magnetite	chalcedony calcite magnetite	chalcedony magnetite
solids precipitated	pyrite hematite siderite F-apatite	pyrite hematite F-apatite	pyrite hematite F-apatite	calcite pyrite hematite siderite F-apatite
bound and unbound H+	5.0E-02	4.0E-02	4.1E-02	4.6E-02

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* -log $[E^-]$ refers to the hypothetical E^- concentration. The expression 'pe' refers normally to the hypothetical E^- activity.

Table C.1: Porewater calculations set C (cf. Figure 5.1). Kunigel-V1(5.4 g/ml) equilibrated with FRHP groundwater at 25 °C, system closed.

	Input groundwater (M)	Porewater B1 & B2 no impurites (with pyrite & calcite) (M)	Porewater B1 & B2 50% impurites (with pyrite & calcite) (M)	Porewater B3 no impurites (with pyrite) (M)
Al	3.5E-07	3.5E-07	3.5E-07	3.5E-07
B(OH)4	6.4E-04	6.4E-04	6.4E-04	6.4E-04
Br	1.1E-05	1.1E-05	1.1E-05	1.1E-05
Ca	1.1E-04	6.3E-05	7.1E-03	1.8E-03
CH4(aq)	1.5E-16	3.4E-12	1.2E-16	5.3E-15
Cl	5.8E-04	5.8E-04	2.5E-03	5.8E-04
CO3	3.2E-03	1.4E-02	1.1E-02	3.2E-03
F	6.4E-04	6.4E-04	6.4E-04	6.4E-04
Fe(II)	6.2E-05	6.1E-09	1.0E-06	1.8E-06
Fe(III)	8.3E-10	6.0E-15	1.6E-14	2.0E-14
H2(aq)	5.4E-12	4.2E-11	1.8E-12	5.0E-12
H2SIO4	3.5E-04	3.0E-04	2.8E-04	2.8E-04
K	6.1E-05	1.5E-04	1.0E-03	7.3E-07
Mg	0.0E+00	1.2E-05	1.1E-03	-1.0E-25
Na	3.5E-03	2.5E-02	1.5E-01	7.6E-05
NH3	1.1E-03	1.1E-03	1.1E-03	1.1E-03
O2(aq)	2.2E-70	3.6E-72	2.0E-69	2.5E-70
PO4	1.3E-05	1.3E-05	1.3E-05	1.3E-05
S(-II)	3.6E-12	1.5E-08	5.2E-10	4.5E-10
SO4	1.3E-04	1.2E-04	7.5E-02	1.2E-04
SOH2+		1.9E-02	1.9E-02	2.3E-02
SO-		2.9E-02	2.9E-02	2.4E-02
NaX		2.7E+00	2.5E+00	3.4E-03
HX		7.7E-07	2.9E-06	1.4E-05
CaX2		2.4E-01	3.0E-01	1.6E+00
MgX2		3.9E-02	3.8E-02	1.0E-25
KX		2.9E-02	3.0E-02	6.0E-05
calculated pH	8.47	8.30	7.02	6.64
calculated pe	-4.39	-4.67	-2.69	-2.54
calculated -log $[E^-]^*$	-4.42	-4.73	-2.82	-2.58
calculated pCO_2	-3.20	-2.42	-1.37	-1.53
calculated I	0.005	0.02	0.21	0.006
solids present		calcite chalcedony pyrite	calcite chalcedony pyrite	chalcedony pyrite
precipitated solids		magnetite	magnetite	magnetite
oversaturated solids (saturation index)				
fluorite		–	8	17
OH-apatite		12	114	11
F-apatite		3.4E+05	4.9E+07	1.4E+07
hematite		2	5	4
kaolinite		14	6	–
quartz		3	3	3
C(0)		–	–	–
calcite precipitated (negative values indicate dissolution)		-1.1E-02	6.1E-01	–
bound and unbound H+		1.6E-02	1.5E-02	6.4E-03

Table C.1: continued

	Porewater C2 no impurities (magnetite & calcite) (M)	Porewater C2 50% impurities (magnetite & calcite) (M)	Porewater C3 no impurities (magnetite) (M)
Al	3.5E-07	3.5E-07	3.5E-07
B(OH)4	6.4E-04	6.4E-04	6.4E-04
Br	1.1E-05	1.1E-05	1.1E-05
Ca	5.9E-05	7.1E-03	1.8E-03
CH4(aq)	3.3E-12	1.2E-16	5.3E-15
Cl	5.8E-04	2.5E-03	5.8E-04
CO3	1.4E-02	1.1E-02	3.2E-03
F	6.4E-04	6.4E-04	6.4E-04
Fe(II)	5.7E-09	1.0E-06	1.8E-06
Fe(III)	6.0E-15	1.6E-14	2.0E-14
H2(aq)	4.2E-11	1.8E-12	5.0E-12
H2SIO4	3.0E-04	2.8E-04	2.8E-04
K	1.5E-04	1.0E-03	7.3E-07
Mg	1.1E-05	1.1E-03	-1.0E-25
Na	2.5E-02	1.5E-01	7.6E-05
NH3	1.1E-03	1.1E-03	1.1E-03
O2(aq)	3.5E-72	2.0E-69	2.5E-70
PO4	1.3E-05	1.3E-05	1.3E-05
S(-II)	1.5E-08	5.2E-10	4.5E-10
SO4	1.2E-04	7.5E-02	1.2E-04
SOH2+	1.9E-02	1.9E-02	2.3E-02
SO-	2.9E-02	2.9E-02	2.4E-02
NaX	2.7E+00	2.5E+00	3.4E-03
HX	7.5E-07	2.9E-06	1.4E-05
CaX2	2.4E-01	3.0E-01	1.6E+00
MgX2	3.9E-02	3.8E-02	1.0E-25
KX	2.9E-02	3.0E-02	6.0E-05
calculated pH	8.32	7.02	6.64
calculated pe	-4.68	-2.69	-2.54
calculated -log $[E^-]$*	-4.74	-2.82	-2.58
calculated pCO_2	-2.44	-1.37	-1.53
calculated I	0.02	0.21	0.006
solids present	calcite chalcedony magnetite	calcite chalcedony magnetite	chalcedony magnetite
precipitated solids		pyrite	pyrite
oversaturated solids (saturation index)			
fluorite	–	8	17
OH-apatite	13	114	11
F-apatite	3.4E+05	4.9E+07	1.4E+07
hematite	2	5	4
goethite	–	–	–
kaolinite	13	6	–
quartz	3	3	3
C(0)	–	–	–
calcite precipitated (negative values indicate dissolution)	1.4E-04	1.2E-06	–
bound and unbound H+	1.6E-02	1.5E-02	6.4E-03

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* -log $[E^-]$ refers to the hypothetical E^- concentration. The expression 'pe' refers normally to the hypothetical E^- activity.

Table C.2: Porewater calculations set C (cf. Figure 5.1). Kunigel-V1(5.4 g/ml) equilibrated with FRLP groundwater at 25 °C, system closed.

	Input groundwater	Porewater B1 & B2 no impurites (with pyrite & calcite)	Porewater B1 & B2 50% impurites (with pyrite & calcite)	Porewater B3 no impurites (with pyrite)
	(M)	(M)	(M)	(M)
Al	3.1E-08	3.1E-08	3.1E-08	3.1E-08
B(OH)4	6.4E-04	6.4E-04	6.4E-04	6.4E-04
Br	1.1E-05	1.1E-05	1.1E-05	1.1E-05
Ca	1.1E-04	2.3E-04	7.8E-03	1.9E-03
CH4(aq)	1.1E-05	1.1E-05	3.6E-12	1.1E-05
Cl	4.2E-04	4.2E-04	2.3E-03	4.2E-04
CO3	1.9E-02	4.0E-02	3.1E-02	1.9E-02
F	6.4E-04	6.4E-04	6.4E-04	6.4E-04
Fe(II)	3.1E-08	2.4E-08	6.3E-14	6.8E-08
Fe(III)	2.7E-18	8.5E-17	8.2E-23	6.5E-18
H2(aq)	5.4E-10	8.3E-10	1.5E-11	5.4E-10
H2SIO4	3.3E-04	2.8E-04	2.8E-04	2.8E-04
K	6.1E-05	2.6E-04	1.1E-03	7.3E-07
Mg	0.0E+00	4.3E-05	1.2E-03	0.0E+00
Na	3.5E-03	4.4E-02	1.6E-01	7.6E-05
NH3	1.0E-03	1.0E-03	1.0E-03	1.0E-03
O2(aq)	2.2E-74	9.1E-75	2.8E-71	2.1E-74
PO4	1.3E-05	1.3E-05	1.3E-05	1.3E-05
S(-II)	6.2E-08	4.8E-08	1.1E-05	1.4E-07
SO4	1.9E-12	2.9E-10	7.5E-02	6.8E-12
SOH2+		2.0E-02	2.1E-02	2.4E-02
SO-		2.8E-02	2.6E-02	2.3E-02
NaX		2.6E+00	2.5E+00	3.4E-03
HX		3.6E-06	7.2E-06	1.0E-04
CaX2		2.5E-01	3.1E-01	1.6E+00
MgX2		3.9E-02	3.8E-02	0.0E+00
KX		2.9E-02	3.0E-02	6.0E-05
calculated pH	5.70	7.41	6.61	5.77
calculated pe	-2.62	-4.42	-2.74	-2.69
calculated -log $[E^-]^*$	-2.65	-4.50	-2.87	-2.73
calculated pCO_2	-0.34	-1.10	-0.59	-0.36
calculated I	0.005	0.04	0.22	0.007
solids present		calcite chalcedony pyrite	calcite chalcedony pyrite	chalcedony pyrite
precipitated solids				
oversaturated solids (saturation index)				
fluorite		–	9	17
OH-apatite		–	1	–
F-apatite		4.4E+04	1.2E+06	2.3E+02
hematite		–	–	–
kaolinite		1	–	–
quartz		3	3	3
C(0)		9	–	21
calcite precipitated (negative values indicate dissolution)		-2.1E-02	6.1E-01	–
bound and unbound H+		4.5E-02	4.2E-02	3.7E-02

Table C.2: continued

	Porewater C2 no impurites (with magnetite & calcite) (M)	Porewater C2 50% impurites (with magnetite & calcite) (M)	Porewater C3 no impurites (with magnetite) (M)
Al	3.1E-08	3.1E-08	3.1E-08
B(OH)4	6.4E-04	6.4E-04	6.4E-04
Br	1.1E-05	1.1E-05	1.1E-05
Ca	2.3E-04	7.8E-03	1.9E-03
CH4(aq)	1.1E-05	9.5E-17	1.8E-12
Cl	4.2E-04	2.3E-03	4.2E-04
CO3	4.0E-02	3.1E-02	1.9E-02
F	6.4E-04	6.4E-04	6.4E-04
Fe(II)	1.1E-06	6.5E-06	1.3E-04
Fe(III)	4.0E-15	3.2E-14	9.1E-14
H2(aq)	8.3E-10	1.1E-12	1.1E-11
H2SIO4	2.8E-04	2.8E-04	2.8E-04
K	2.6E-04	1.1E-03	7.3E-07
Mg	4.3E-05	1.2E-03	0.0E+00
Na	4.4E-02	1.6E-01	7.6E-05
NH3	1.0E-03	1.0E-03	1.0E-03
O2(aq)	9.1E-75	5.5E-69	5.2E-71
PO4	1.3E-05	1.3E-05	1.3E-05
S(-II)	7.0E-09	2.8E-10	4.2E-10
SO4	4.2E-11	7.5E-02	1.4E-07
SOH2+	2.0E-02	2.1E-02	2.4E-02
SO-	2.8E-02	2.6E-02	2.3E-02
NaX	2.6E+00	2.5E+00	3.4E-03
HX	3.6E-06	7.2E-06	1.0E-04
CaX2	2.5E-01	3.1E-01	1.6E+00
MgX2	3.9E-02	3.8E-02	0.0E+00
KX	2.9E-02	3.0E-02	6.0E-05
calculated pH	7.41	6.61	5.80
calculated pe	-4.42	-2.17	-1.87
calculated -log [E$^-$] *	-4.50	-2.30	-1.91
calculated pCO_2	-1.10	-0.59	-0.36
calculated I	0.04	0.22	0.007
solids present	calcite chalcedony magnetite	calcite chalcedony magnetite	chalcedony magnetite
precipitated solids	pyrite	pyrite	
oversaturated solids (saturation index)			
fluorite	–	9	17
OH-apatite	–	1	–
F-apatite	4.4E+04	1.2E+06	2.4E+02
hematite	–	6	3
goethite	–	–	–
kaolinite	1	–	–
quartz	3	3	3
C(0)	9	–	–
calcite precipitated (negative values indicate dissolution)	-9.2E-06	8.5E-06	–
bound and unbound H+	4.5E-02	4.2E-02	3.6E-02

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* -log [E$^-$] refers to the hypothetical E$^-$ concentration. The expression 'pe' refers normally to the hypothetical E$^-$ activity.

Table C.3: Porewater calculations set C (cf. Figure 5.1). Kunigel-V1(5.4 g/ml) equilibrated with MRNP groundwater at 25 °C, system closed.

	Input groundwater (M)	Porewater B1 & B2 no impurites (with pyrite & calcite) (M)	Porewater B1 & B2 50% impurites (with pyrite & calcite) (M)	Porewater B3 no impurites (with pyrite) (M)
Al	6.1E-10	6.1E-10	6.1E-10	6.1E-10
B(OH)4	1.0E-02	1.0E-02	1.0E-02	1.0E-02
Br	1.9E-03	1.9E-03	1.9E-03	1.9E-03
Ca	5.1E-04	1.1E-02	2.1E-02	1.4E-01
CH4(aq)	1.4E-05	1.4E-05	1.3E-16	1.4E-05
Cl	3.3E-01	3.3E-01	3.3E-01	3.3E-01
CO3	1.1E-01	8.0E-02	7.7E-02	6.5E-02
F	1.5E-04	1.5E-04	1.5E-04	1.5E-04
Fe(II)	3.2E-05	3.2E-05	2.4E-05	3.2E-05
Fe(III)	1.6E-14	2.4E-15	3.1E-14	8.5E-16
H2(aq)	5.8E-10	4.4E-10	7.6E-13	4.2E-10
H2SIO4	3.0E-04	2.8E-04	2.8E-04	2.8E-04
K	1.1E-01	8.3E-03	9.9E-03	8.6E-03
Mg	3.5E-04	2.5E-03	4.2E-03	3.5E-05
Na	3.2E-01	3.3E-01	3.7E-01	4.4E-02
NH3	1.4E-02	1.4E-02	1.4E-02	1.4E-02
O2(aq)	1.8E-74	3.3E-74	1.1E-68	3.5E-74
PO4	1.3E-05	1.3E-05	1.3E-05	1.3E-05
S(-II)	1.0E-10	6.2E-09	3.8E-10	1.8E-08
SO4	1.7E-12	8.4E-12	4.0E-02	3.9E-12
SOH2+		2.4E-02	2.4E-02	2.8E-02
SO-		2.4E-02	2.3E-02	2.0E-02
NaX		2.7E+00	2.6E+00	2.7E-01
HX		1.3E-05	1.4E-05	3.8E-05
CaX2		1.9E-01	2.1E-01	1.4E+00
MgX2		3.7E-02	3.5E-02	3.1E-04
KX		1.3E-01	1.3E-01	9.6E-02
calculated pH	7.01	6.05	5.96	5.45
calculated pe	-3.95	-2.93	-1.45	-2.31
calculated -log [E$^-$]*	-4.08	-3.06	-1.58	-2.45
calculated pCO$_2$	-0.38	0.12	0.14	0.18
calculated I	0.43	0.38	0.46	0.48
solids present		calcite chalcedony pyrite	calcite chalcedony pyrite	chalcedony pyrite
precipitated solids			gypsum	calcite
oversaturated solids (saturation index)				
fluorite		–	1	10
OH-apatite		–	–	–
F-apatite		2.4E+04	4.5E+04	5.4E+05
hematite		–	–	–
kaolinite		–	–	–
quartz		3	3	3
C(0)		41	–	44
calcite precipitated (negative values indicate dissolution)		3.1E-02	6.5E-01	4.6E-02
bound and unbound H+		1.5E-01	1.5E-01	1.4E-01

Table C.3: continued

	Porewater C2 no impurites (with magnetite & calcite) (M)	Porewater C2 50% impurites (with magnetite & calcite) (M)	Porewater C3 no impurites (with magnetite) (M)
Al	6.1E-10	6.1E-10	6.1E-10
B(OH)4	1.0E-02	1.0E-02	1.0E-02
Br	1.9E-03	1.9E-03	1.9E-03
Ca	1.1E-02	2.1E-02	1.4E-01
CH4(aq)	1.9E-15	4.3E-24	6.7E-23
Cl	3.3E-01	3.3E-01	3.3E-01
CO3	8.0E-02	7.7E-02	6.5E-02
F	1.5E-04	1.5E-04	1.5E-04
Fe(II)	7.6E-05	2.4E-05	2.0E-04
Fe(III)	9.5E-14	2.7E-13	7.6E-13
H2(aq)	1.5E-12	1.0E-14	2.0E-14
H2SIO4	2.8E-04	2.8E-04	2.8E-04
K	8.3E-03	9.9E-03	8.6E-03
Mg	2.5E-03	4.2E-03	3.5E-05
Na	3.2E-01	3.7E-01	4.4E-02
NH3	1.4E-02	1.4E-02	1.4E-02
O2(aq)	2.8E-69	6.0E-65	1.6E-65
PO4	1.3E-05	1.3E-05	1.3E-05
S(-II)	6.3E-16	1.2E-17	4.2E-22
SO4	6.2E-09	4.0E-02	1.8E-08
SOH2+	2.4E-02	2.4E-02	2.8E-02
SO-	2.4E-02	2.3E-02	2.0E-02
NaX	2.7E+00	2.6E+00	2.7E-01
HX	1.3E-05	1.4E-05	3.8E-05
CaX2	1.9E-01	2.1E-01	1.4E+00
MgX2	3.7E-02	3.5E-02	3.1E-04
KX	1.3E-01	1.3E-01	9.6E-02
calculated pH	6.05	5.96	5.45
calculated pe	-1.69	-0.52	-0.15
calculated -log [E$^-$] *	-1.83	-0.65	-0.28
calculated pCO_2	0.12	0.14	0.18
calculated I	0.38	0.46	0.48
solids present	calcite chalcedony magnetite	calcite chalcedony magnetite	chalcedony magnetite
precipitated solids	siderite		calcite
oversaturated solids (saturation index)			
fluorite	–	1	10
OH-apatite	–	–	–
F-apatite	2.4E+04	4.4E+04	5.2E+05
hematite	6	30	24
goethite	–	–	–
kaolinite	–	–	–
quartz	3	3	3
C(0)	–	–	–
calcite precipitated (negative values indicate dissolution)	5.1E-05	-5.9E-05	1.6E-04
bound and unbound H+	1.5E-01	1.5E-01	1.4E-01

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* -log [E$^-$] refers to the hypothetical E$^-$ concentration. The expression 'pe' refers normally to the hypothetical E$^-$ activity.

Table C.4: Porewater calculations set C (cf. Figure 5.1). Kunigel-V1(5.4 g/ml) equilibrated with SRHP groundwater at 25 °C, system closed.

	Input groundwater	Porewater B1 & B2 no impurites (with pyrite & calcite)	Porewater B1 & B2 50% impurites (with pyrite & calcite)	Porewater B3 no impurites (with pyrite)
	(M)	(M)	(M)	(M)
Al	3.8E-09	3.8E-09	3.8E-09	3.8E-09
B(OH)4	1.0E-02	1.0E-02	1.0E-02	1.0E-02
Br	1.9E-03	1.9E-03	1.9E-03	1.9E-03
Ca	3.5E-04	2.8E-02	3.7E-02	2.5E-01
CH4(aq)	2.4E-06	2.4E-06	7.5E-13	2.4E-06
Cl	6.2E-01	6.2E-01	6.2E-01	6.2E-01
CO3	1.2E-02	1.1E-02	1.0E-02	5.4E-03
F	1.5E-04	1.5E-04	1.5E-04	1.5E-04
Fe(II)	5.7E-08	5.6E-08	1.6E-12	8.4E-08
Fe(III)	2.4E-15	1.2E-17	1.9E-21	6.9E-18
H2(aq)	1.2E-09	5.2E-10	1.2E-11	5.8E-10
H2SIO4	2.9E-04	2.8E-04	2.8E-04	2.8E-04
K	1.2E-02	4.1E-03	4.4E-03	1.4E-03
Mg	2.3E-04	5.5E-03	6.8E-03	4.0E-05
Na	6.1E-01	5.5E-01	5.7E-01	1.2E-01
NH3	1.4E-02	1.4E-02	1.4E-02	1.4E-02
O2(aq)	4.8E-75	2.4E-74	4.2E-71	1.9E-74
PO4	1.3E-05	1.3E-05	1.3E-05	1.3E-05
S(-II)	7.8E-08	7.7E-08	2.4E-06	1.3E-07
SO4	1.4E-09	2.4E-10	2.2E-02	1.2E-10
SOH2+		2.2E-02	2.2E-02	2.5E-02
SO-		2.6E-02	2.6E-02	2.3E-02
NaX		2.7E+00	2.7E+00	4.9E-01
HX		3.9E-06	4.0E-06	8.3E-06
CaX2		2.0E-01	2.1E-01	1.4E+00
MgX2		3.4E-02	3.2E-02	1.9E-04
KX		3.7E-02	3.8E-02	1.0E-02
calculated pH	7.98	6.33	6.30	5.92
calculated pe	-5.06	-3.24	-2.40	-2.85
calculated -log $[E^-]^*$	-5.19	-3.37	-2.52	-2.96
calculated pCO_2	-2.31	-0.92	-0.93	-1.11
calculated I	0.63	0.66	0.70	0.87
solids present		calcite chalcedony pyrite	calcite chalcedony pyrite	chalcedony pyrite
precipitated solids			gypsum	calcite
oversaturated solids (saturation index)				
fluorite		2	3	14
OH-apatite		192	232	2109
F-apatite		7.3E+07	9.4E+07	1.6E+09
hematite		–	–	–
kaolinite		–	–	–
quartz		3	3	3
C(0)		5	–	4
calcite precipitated (negative values indicate dissolution)		1.1E-03	6.2E-01	6.6E-03
bound and unbound H+		4.0E-02	3.9E-02	3.3E-02

Table C.4: continued

	Porewater C2 no impurities (with magnetite & calcite) (M)	Porewater C2 50% impurities (with magnetite & calcite) (M)	Porewater C3 no impurities (with magnetite) (M)
Al	3.8E-09	3.8E-09	3.8E-09
B(OH)4	1.0E-02	1.0E-02	1.0E-02
Br	1.9E-03	1.9E-03	1.9E-03
Ca	2.8E-02	3.7E-02	2.5E-01
CH4(aq)	2.2E-12	7.6E-17	2.3E-21
Cl	6.2E-01	6.2E-01	6.2E-01
CO3	1.1E-02	1.0E-02	5.3E-03
F	1.5E-04	1.5E-04	1.5E-04
Fe(II)	3.0E-05	1.6E-05	3.1E-05
Fe(III)	3.6E-14	5.8E-14	1.9E-13
H2(aq)	1.6E-11	1.2E-12	1.0E-13
H2SIO4	2.8E-04	2.8E-04	2.8E-04
K	4.1E-03	4.4E-03	1.4E-03
Mg	5.5E-03	6.8E-03	4.0E-05
Na	5.5E-01	5.7E-01	1.2E-01
NH3	1.4E-02	1.4E-02	1.4E-02
O2(aq)	2.5E-71	4.2E-69	6.2E-67
PO4	1.3E-05	1.3E-05	1.3E-05
S(-II)	2.2E-11	2.4E-10	1.4E-19
SO4	7.7E-08	2.2E-02	1.3E-07
SOH2+	2.2E-02	2.2E-02	2.5E-02
SO-	2.6E-02	2.6E-02	2.3E-02
NaX	2.7E+00	2.7E+00	4.9E-01
HX	3.9E-06	4.0E-06	8.3E-06
CaX2	2.0E-01	2.1E-01	1.4E+00
MgX2	3.4E-02	3.2E-02	1.9E-04
KX	3.7E-02	3.8E-02	1.0E-02
calculated pH	6.33	6.30	5.92
calculated pe	-2.49	-1.90	-0.97
calculated -log $[E^-]$*	-2.61	-2.02	-1.09
calculated pCO_2	-0.93	-0.93	-1.11
calculated I	0.66	0.70	0.87
solids present	calcite chalcedony magnetite	calcite chalcedony magnetite	chalcedony magnetite
precipitated solids		pyrite	calcite
oversaturated solids (saturation index)			
fluorite	2	3	14
OH-apatite	191	231	2133
F-apatite	7.3E+07	9.3E+07	1.6E+09
hematite	3	6	14
goethite	–	–	–
kaolinite	–	–	–
quartz	3	3	3
C(0)	–	–	–
calcite precipitated (negative values indicate dissolution)	2.6E-05	1.3E-05	2.3E-05
bound and unbound H+	4.0E-02	3.9E-02	3.3E-02

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* -log $[E^-]$ refers to the hypothetical E^- concentration. The expression 'pe' refers normally to the hypothetical E^- activity.

Table C.5: Porewater calculations set C (cf. Figure 5.1). Kunigel-V1(5.4 g/ml) equilibrated with SRLP groundwater at 25 °C, system closed.

	Input groundwater (M)	Porewater B1 & B2 no impurites (with pyrite & calcite) (M)	Porewater B1 & B2 50% impurites (with pyrite & calcite) (M)	Porewater B3 no impurites (with pyrite) (M)
Al	3.0E-08	3.0E-08	3.0E-08	3.0E-08
B(OH)4	1.0E-02	1.0E-02	1.0E-02	1.0E-02
Br	1.9E-03	1.9E-03	1.9E-03	1.9E-03
Ca	3.0E-02	3.1E-02	4.0E-02	2.4E-01
CH4(aq)	1.4E-07	1.4E-07	1.5E-13	1.3E-07
Cl	6.0E-01	6.0E-01	6.0E-01	6.0E-01
CO3	4.2E-02	4.0E-02	4.0E-02	3.2E-02
F	1.5E-04	1.5E-04	1.5E-04	1.5E-04
Fe(II)	5.7E-08	7.5E-09	1.3E-10	3.0E-08
Fe(III)	6.5E-18	8.6E-19	7.5E-20	1.5E-18
H2(aq)	1.6E-10	1.6E-10	5.2E-12	1.6E-10
H2SIO4	2.9E-04	2.8E-04	2.8E-04	2.8E-04
K	1.2E-02	4.0E-03	4.3E-03	1.3E-03
Mg	2.0E-02	8.1E-03	9.8E-03	3.3E-03
Na	4.9E-01	5.2E-01	5.4E-01	9.2E-02
NH3	1.5E-02	1.5E-02	1.5E-02	1.5E-02
O2(aq)	2.5E-73	2.4E-73	2.4E-70	2.5E-73
PO4	1.3E-05	1.3E-05	1.3E-05	1.3E-05
S(-II)	3.7E-07	2.8E-07	4.1E-07	3.3E-07
SO4	2.4E-08	1.6E-08	2.1E-02	6.4E-09
SOH2+		2.5E-02	2.5E-02	2.9E-02
SO-		2.3E-02	2.2E-02	1.9E-02
NaX		2.7E+00	2.6E+00	4.0E-01
HX		1.0E-05	1.1E-05	2.5E-05
CaX2		2.3E-01	2.4E-01	1.4E+00
MgX2		5.1E-02	4.9E-02	1.6E-02
KX		3.7E-02	3.8E-02	1.0E-02
calculated pH	5.91	5.93	5.90	5.45
calculated pe	-2.57	-2.58	-1.81	-2.10
calculated -log [E^-]*	-2.69	-2.71	-1.93	-2.21
calculated pCO_2	-0.13	-0.14	-0.14	-0.15
calculated I	0.66	0.65	0.68	0.84
solids present		calcite chalcedony pyrite	calcite chalcedony pyrite	chalcedony pyrite
precipitated solids			gypsum	calcite
oversaturated solids (saturation index)				
fluorite		2	3	13
OH-apatite		–	1	2
F-apatite		8.5E+05	1.0E+06	5.0E+06
hematite		–	–	–
kaolinite		–	–	–
quartz		3	3	3
C(0)		3	–	3
calcite precipitated (negative values indicate dissolution)		1.1E-03	6.2E-01	9.2E-03
bound and unbound H+		9.0E-02	9.0E-02	8.2E-02

Table C.5: continued

Total dissolved concentrations	Porewater C2 no impurities (with magnetite & calcite) (M)	Porewater C2 50% impurities (with magnetite & calcite) (M)	Porewater C3 no impurities (with magnetite) (M)
Al	3.0E-08	3.0E-08	3.0E-08
B(OH)4	1.0E-02	1.0E-02	1.0E-02
Br	1.9E-03	1.9E-03	1.9E-03
Ca	3.1E-02	4.0E-02	2.4E-01
CH4(aq)	2.2E-31	1.4E-32	4.9E-41
Cl	6.0E-01	6.0E-01	6.0E-01
CO3	4.0E-02	4.0E-02	3.2E-02
F	1.5E-04	1.5E-04	1.5E-04
Fe(II)	5.0E-06	4.9E-06	5.6E-06
Fe(III)	5.5E-13	6.6E-13	4.0E-12
H2(aq)	1.8E-16	9.1E-17	7.0E-19
H2SIO4	2.8E-04	2.8E-04	2.8E-04
K	4.0E-03	4.3E-03	1.3E-03
Mg	8.1E-03	9.8E-03	3.3E-03
Na	5.2E-01	5.4E-01	9.2E-02
NH3	1.5E-02	1.5E-02	1.5E-02
O2(aq)	1.9E-61	7.6E-61	1.3E-56
PO4	1.3E-05	1.3E-05	1.3E-05
S(-II)	7.6E-30	3.9E-26	6.9E-39
SO4	2.9E-07	2.1E-02	3.4E-07
SOH2+	2.5E-02	2.5E-02	2.9E-02
SO-	2.3E-02	2.3E-02	1.9E-02
NaX	2.7E+00	2.6E+00	4.0E-01
HX	1.0E-05	1.1E-05	2.5E-05
CaX2	2.3E-01	2.4E-01	1.4E+00
MgX2	5.1E-02	4.9E-02	1.6E-02
KX	3.7E-02	3.8E-02	1.0E-02
calculated pH	5.93	5.90	5.45
calculated pe	0.39	0.57	2.08
calculated -log [E^-]*	0.27	0.45	1.96
calculated pCO_2	-0.15	-0.14	-0.15
calculated I	0.65	0.68	0.84
solids present	calcite chalcedony magnetite	calcite chalcedony magnetite	chalcedony magnetite
precipitated solids			calcite
oversaturated solids (saturation index)			
fluorite	2	2	13
OH-apatite	–	1	2
F-apatite	8.4E+05	1.0E+06	5.0E+06
hematite	116	146	740
goethite	1	2	3
kaolinite	–	–	–
quartz	3	3	3
C(0)	–	–	–
calcite precipitated (negative values indicate dissolution)	3.7E-06	-4.1E-05	4.8E-06
bound and unbound H+	9.0E-02	9.0E-02	8.2E-02

* -log [E^-] refers to the hypothetical E^- concentration. The expression 'pe' refers normally to the hypothetical E^- activity.

Table D1.1: Porewater calculations set D1 (cf. Figure 5.1). Kunigel-V1(5.4 g/ml) equilibrated with FRHP groundwater at 25 °C, system closed.

	Input groundwater (M)	Porewater B1 & B2 no impurites (with pyrite & calcite) (M)
Al	3.5E-07	3.48E-07
B(OH)4	6.4E-04	6.42E-04
Br	1.1E-05	1.13E-05
Ca	1.1E-04	6.43E-05
CH4(aq)	1.5E-16	3.33E-12
Cl	5.8E-04	5.81E-04
CO3	3.2E-03	1.31E-02
F	6.4E-04	6.40E-04
Fe(II)	6.2E-05	5.39E-09
Fe(III)	8.3E-10	6.00E-15
H2(aq)	5.4E-12	4.30E-11
H2SIO4	3.5E-04	3.00E-04
K	6.1E-05	1.39E-04
Mg	–	9.98E-06
Na	3.5E-03	2.34E-02
NH3	1.1E-03	1.06E-03
O2(aq)	2.2E-70	3.41E-72
PO4	1.3E-05	1.31E-05
S(-II)	3.6E-12	1.62E-08
SO4	1.3E-04	1.19E-04
SOH2+		7.18E-03
SO-		1.70E-02
NaX		2.66E+00
HX		7.79E-07
CaX2		2.37E-01
MgX2		3.89E-02
KX		2.91E-02
calculated pH	8.47	8.33
calculated pe	-4.39	-4.70
calculated -log [E$^-$]*	-4.42	-4.76
calculated log pCO$_2$	-3.20	-2.47
calculated I	0.005	0.02
solids present		calcite chalcedony pyrite
precipitated solids		magnetite
oversaturated solids (saturation index)		
fluorite		–
OH-apatite		16
F-apatite		4.28E+05
hematite		1.9
kaolinite		12.7
quartz		2.7
C(0)		–
calcite precipitated		-9.96E-03
pyrite precipitated		2.83E-06
(negative values indicate dissolution)		
bound and unbound H+		1.51E-02

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* -log [E$^-$] refers to the hypothetical E$^-$ concentration. The expression 'pe' refers normally to the hypothetical E$^-$ activity.

Table D1.2: Porewater calculations set D1 (cf. Figure 5.1). Kunigel-V1(5.4 g/ml) equilibrated with FRLP groundwater at 25 °C, system closed.

	Input groundwater (M)	Porewater B1 & B2 no impurites (with pyrite & calcite) (M)
Al	3.1E-08	3.10E-08
B(OH)4	6.4E-04	6.42E-04
Br	1.1E-05	1.13E-05
Ca	1.1E-04	2.47E-04
CH4(aq)	1.1E-05	1.08E-05
Cl	4.2E-04	4.21E-04
CO3	1.9E-02	3.92E-02
F	6.4E-04	6.40E-04
Fe(II)	3.1E-08	2.40E-08
Fe(III)	2.7E-18	8.04E-17
H2(aq)	5.4E-10	8.30E-10
H2SIO4	3.3E-04	2.84E-04
K	6.1E-05	2.54E-04
Mg	–	3.84E-05
Na	3.5E-03	4.27E-02
NH3	1.0E-03	1.03E-03
O2(aq)	2.2E-74	9.17E-75
PO4	1.3E-05	1.31E-05
S(-II)	6.2E-08	4.79E-08
SO4	1.9E-12	2.74E-10
SOH2+		8.28E-03
SO-		1.52E-02
NaX		2.64E+00
HX		3.85E-06
CaX2		2.47E-01
MgX2		3.89E-02
KX		2.90E-02
calculated pH	5.70	7.39
calculated pe	-2.62	-4.40
calculated -log $[E^-]$*	-2.65	-4.48
calculated log pCO_2	-0.34	-1.10
calculated I	0.005	0.04
solids present		calcite chalcedony pyrite
precipitated solids		
oversaturated solids (saturation index)		
fluorite		1.06
OH-apatite		–
F-apatite		5.24E+04
hematite		–
kaolinite		1.18
quartz		2.69
C(0)		9.02
calcite precipitated		-1.99E-02
pyrite precipitated		6.96E-09
(negative values indicate dissolution)		
bound and unbound H+		4.41E-02

* -log $[E^-]$ refers to the hypothetical E^- concentration. The expression 'pe' refers normally to the hypothetical E^- activity.

Table D1.3: Porewater calculations set D1 (cf. Figure 5.1). Kunigel-V1(5.4 g/ml) equilibrated with MRNP groundwater at 25 °C, system closed.

	Input groundwater (M)	Porewater B1 & B2 no impurites (with pyrite & calcite) (M)
Al	6.1E-10	6.10E-10
B(OH)4	1.0E-02	1.03E-02
Br	1.9E-03	1.87E-03
Ca	5.1E-04	1.18E-02
CH4(aq)	1.4E-05	1.38E-05
Cl	3.3E-01	3.33E-01
CO3	1.1E-01	7.88E-02
F	1.5E-04	1.47E-04
Fe(II)	3.2E-05	3.22E-05
Fe(III)	1.6E-14	2.27E-15
H2(aq)	5.8E-10	4.37E-10
H2SIO4	3.0E-04	2.82E-04
K	1.1E-01	8.24E-03
Mg	3.5E-04	2.35E-03
Na	3.2E-01	3.21E-01
NH3	1.4E-02	1.44E-02
O2(aq)	1.8E-74	3.30E-74
PO4	1.3E-05	1.31E-05
S(-II)	1.0E-10	6.46E-09
SO4	1.7E-12	8.02E-12
SOH2+		1.15E-02
SO-		1.13E-02
NaX		2.68E+00
HX		1.35E-05
CaX2		1.84E-01
MgX2		3.69E-02
KX		1.26E-01
calculated pH	7.01	6.03
calculated pe	-3.95	-2.90
calculated -log $[E^-]$ *	-4.08	-3.03
calculated log pCO_2	-0.38	0.13
calculated I	0.43	0.38
solids present		calcite chalcedony pyrite
precipitated solids		
oversaturated solids (saturation index)		
fluorite		1.05
OH-apatite		–
F-apatite		2.84E+04
hematite		–
kaolinite		–
quartz		2.69
C(0)		41.59
calcite precipitated		3.19E-02
pyrite precipitated		-3.18E-09
(negative values indicate dissolution)		
bound and unbound H+		1.49E-01

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* -log $[E^-]$ refers to the hypothetical E^- concentration. The expression 'pe' refers normally to the hypothetical E^- activity.

Table D1.4: Porewater calculations set D1 (cf. Figure 5.1). Kunigel-V1(5.4 g/ml) equilibrated with SRHP groundwater at 25 °C, system closed.

	Input groundwater (M)	Porewater B1 & B2 no impurities (with pyrite & calcite) (M)
Al	3.8E-09	3.83E-09
B(OH)4	1.0E-02	1.03E-02
Br	1.9E-03	1.88E-03
Ca	3.5E-04	3.03E-02
CH4(aq)	2.4E-06	2.43E-06
Cl	6.2E-01	6.19E-01
CO3	1.2E-02	1.02E-02
F	1.5E-04	1.48E-04
Fe(II)	5.7E-08	5.67E-08
Fe(III)	2.4E-15	1.15E-17
H2(aq)	1.2E-09	5.24E-10
H2SIO4	2.9E-04	2.83E-04
K	1.2E-02	4.01E-03
Mg	2.3E-04	5.25E-03
Na	6.1E-01	5.42E-01
NH3	1.4E-02	1.41E-02
O2(aq)	4.8E-75	2.30E-74
PO4	1.3E-05	1.32E-05
S(-II)	7.8E-08	7.80E-08
SO4	1.4E-09	2.26E-10
SOH2+		9.62E-03
SO-		1.34E-02
NaX		2.75E+00
HX		4.08E-06
CaX2		1.96E-01
MgX2		3.39E-02
KX		3.70E-02
calculated pH	7.98	6.32
calculated pe	-5.06	-3.23
calculated -log $[E^-]$*	-5.19	-3.36
calculated log pCO$_2$	-2.31	-0.94
calculated I	0.63	0.66
solids present		calcite chalcedony pyrite
precipitated solids		
oversaturated solids (saturation index)		
fluorite		2.47
OH-apatite		246.04
F-apatite		9.59E+07
hematite		–
kaolinite		–
quartz		2.69
C(0)		5.11
calcite precipitated		1.75E-03
pyrite precipitated (negative values indicate dissolution)		5.91E-10
bound and unbound H+		3.90E-02

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* -log $[E^-]$ refers to the hypothetical E^- concentration. The expression 'pe' refers normally to the hypothetical E^- activity.

Table D1.5: Porewater calculations set D1 (cf. Figure 5.1). Kunigel-V1(5.4 g/ml) equilibrated with SRLP groundwater at 25 °C, system closed.

	Input groundwater (M)	Porewater B1 & B2 no impurites (with pyrite & calcite) (M)
Al	3.0E-08	3.00E-08
B(OH)4	1.0E-02	1.03E-02
Br	1.9E-03	1.88E-03
Ca	3.0E-02	3.37E-02
CH4(aq)	1.4E-07	1.41E-07
Cl	6.0E-01	5.97E-01
CO3	4.2E-02	4.01E-02
F	1.5E-04	1.48E-04
Fe(II)	5.7E-08	7.98E-09
Fe(III)	6.5E-18	8.84E-19
H2(aq)	1.6E-10	1.62E-10
H2SIO4	2.9E-04	2.82E-04
K	1.2E-02	3.92E-03
Mg	2.0E-02	7.73E-03
Na	4.9E-01	5.14E-01
NH3	1.5E-02	1.45E-02
O2(aq)	2.5E-73	2.41E-73
PO4	1.3E-05	1.32E-05
S(-II)	3.7E-07	2.80E-07
SO4	2.4E-08	1.54E-08
SOH2+		1.24E-02
SO-		1.04E-02
NaX		2.66E+00
HX		1.10E-05
CaX2		2.22E-01
MgX2		5.10E-02
KX		3.71E-02
calculated pH	5.91	5.90
calculated pe	-2.57	-2.56
calculated -log [E⁻]*	-2.69	-2.69
calculated log pCO_2	-0.13	-0.14
calculated I	0.66	0.65
solids present		calcite chalcedony pyrite
precipitated solids		
oversaturated solids (saturation index)		
fluorite		2
OH-apatite		–
F-apatite		961612
hematite		–
kaolinite		–
quartz		3
C(0)		3
calcite precipitated		1.46E-03
pyrite precipitated		4.98E-08
(negative values indicate dissolution)		
bound and unbound H+		9.01E-02

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* -log [E⁻] refers to the hypothetical E⁻ concentration. The expression 'pe' refers normally to the hypothetical E⁻ activity.

Table D2.1: Porewater calculations set D2 (cf. Figure 5.1). Kunigel-V1(5.4 g/ml) equilibrated with FRHP groundwater at 25 °C, system closed.

	Input groundwater (M)	Porewater B1 & B2 no impurities (with pyrite & calcite) (M)	Porewater C2 no impurities (with $Fe(OH)_2$(s) & calcite) (M)
Al	3.5E-07	3.48E-07	3.48E-07
B(OH)4	6.4E-04	6.42E-04	6.42E-04
Br	1.1E-05	1.13E-05	1.13E-05
Ca	1.1E-04	6.43E-05	7.40E-02
CH4(aq)	1.5E-16	3.33E-12	5.30E-01
Cl	5.8E-04	5.81E-04	5.81E-04
CO3	3.2E-03	1.31E-02	6.85E-06
F	6.4E-04	6.40E-04	6.40E-04
Fe(II)	6.2E-05	5.39E-09	2.44E-09
Fe(III)	8.3E-10	6.00E-15	2.87E-09
H2(aq)	5.4E-12	4.30E-11	1.13E-05
H2SIO4	3.5E-04	3.00E-04	8.74E-01
K	6.1E-05	1.39E-04	2.38E-03
Mg	–	9.98E-06	3.58E-07
Na	3.5E-03	2.34E-02	8.31E-01
NH3	1.1E-03	1.06E-03	1.06E-03
O2(aq)	2.2E-70	3.41E-72	4.92E-83
PO4	1.3E-05	1.31E-05	1.31E-05
S(-II)	3.6E-12	1.62E-08	1.44E+00
SO4	1.3E-04	1.19E-04	6.21E-19
SOH2+		7.18E-03	2.78E-10
SO-		1.70E-02	7.36E-02
NaX		2.66E+00	1.86E+00
HX		7.79E-07	7.61E-12
CaX2		2.37E-01	6.81E-01
MgX2		3.89E-02	1.15E-06
KX		2.91E-02	2.69E-02
calculated pH	8.47	8.33	12.14
calculated pe	-4.39	-4.70	-11.22
calculated -log $[E^-]$ *	-4.42	-4.76	-11.34
calculated log pCO_2	-3.20	-2.47	-12.94
calculated I	0.005	0.02	0.72
solids present		calcite chalcedony pyrite	calcite chalcedony magnetite pyrite
precipitated solids		magnetite	brucite Fe(OH)3 aged FeS sulph
oversaturated solids (saturation index)			
fluorite		–	123
OH-apatite		16	3E+17
F-apatite		4.28E+05	7E+17
hematite		1.9	3E+05
goethite-A		–	63
goethite-B		–	2
kaolinite		12.7	–
quartz		2.7	3
larnite		–	542
fayalite		–	7E+04
magnetite		–	3E+10
calcite precipitated		-9.96E-03	-5.17E-01
pyrite precipitated		2.83E-06	–
$Fe(OH)_2$(c) precipitated		–	-4.24E+00
(negative values indicate dissolution)			
bound and unbound H+		1.51E-02	8.43E-01

* -log $[E^-]$ refers to the hypothetical E^- concentration. The expression 'pe' refers normally to the hypothetical E^- activity.

Appendix A

Sorption data tables

A.1 User's manual

A.2 Sorption data

A.3 Footnotes

A.4 Auxiliary tables

A Sorption database

A.1 User's manual

1) Kd values are listed in the same order as in the FY97 report in individual spreadsheets
For each element, Kd values are listed according to literature source and solid phase used.

2) Headers of columns that contain footnotes or references to auxiliary tables are tagged
by an asterisk *, and a number (e. g. *3).

3) Footnotes and references to auxiliary tables can be found in the spreadsheet: footnotes
Footnotes can be found according to a code, consisting of the column header tag and the corresponding entry in the column 'code REF'.
These codes have the following format: <column header tag>[<code REF>], e.g. *2 [Pu3]

4) Where no information on a given item could be found in the literature used, it is indicated by n.r. (not reported) in the table.

5) General informations and abbreviations for each column are given below:

column header	tag	information/abbreviations
element	-	-
redox state	*1	(e) = evaluated by BMG (not explicitly reported)
solid phase	*2	where details on the sorbents used are reported, they are given in the spreadsheets 'footnotes' and/or 'auxiliary tables'
specific surf. area	*3	no remark = BET, EGME = ethylene glycol monoethyl ether adsorption, EG = ethylene glycol adsorption
CEC	*4	details in spreadsheet 'footnotes' and/or 'auxiliary tables'
solution vol.	-	-
solid weight	-	-
s/w ratio	*5	details in spreadsheet 'footnotes' and/or 'auxiliary tables'
w/s ratio	*5	details in spreadsheet 'footnotes' and/or 'auxiliary tables'
temp.	-	-
water type	*6	details in spreadsheet 'footnotes' and/or 'auxiliary tables', PW = pure water
pH init	*7	details in spreadsheet 'footnotes' and/or 'auxiliary tables', T = Titration experiment
pH end	*7	details in spreadsheet 'footnotes' and/or 'auxiliary tables', T = Titration experiment
C init.	-	-
reaction time	*8	details in spreadsheet 'footnotes' and/or 'auxiliary tables'
phase sep.	*9	c = centrifugation (rpm, no units=g/time in min), f = filtration (pore size in µm, MWCO = molecular weight cutoff), ISE = ion selective electrode, DPASV = differential pulse anodic stripping voltammetry.
Eh init	-	-
Eh end	-	-
atm./redox condition	-	where no specific information is reported, but enough circumstantial information is given in a paper, conditions are reported as follows: n.r. (conditions)
Kd	-	-
type of info	-	ads. = adsorbed, diss. = dissolved, (p) = plot, no () = table
reference	-	see FY97 report by BMG
replicates, n	-	T = titration (i. e., individual measurements are not repeated, but there is a large number of measurements), bT = titration curve constructed from batch experiments I = isotherms (i. e., individual measurements are not repeated, but there is a large number of measurements), C = column experiments (i. e., individual measurements are not repeated, but there is a large number of measurements) (e) = replicates of the complete experiment (s) = one experiment is sampled repeatedly (a) = only the analytical determination is replicated
additional information, remarks	-	SCM =surface complexation modeling/DDL = diffuse double layer model, CC = constant capacitance model, TL = triple layer model Ex = ion exchange modeling/V = Vanselow approach, GT = Gaines-Thomas approach
code REF	-	-
calculations	-	-
calculations	-	-

6) The contents of the speadsheets in this file may be sorted according to e. g. Kd value, author, or any other entry by using the Excel-functions in the menu <data - sort>.
It is recommended to copy the data into a separate file beforehand, in order to preserve the present file structure.
Note that the entries in the spreadsheets 'footnotes' and 'Auxiliary Tables' are preceded by two columns of code (e. g. column 1 = *6, column 2 = [Pb12]), so that both parts of the code may be used separately for sorting procedures.

Table 1: Compilation of batch distribution coefficients for Th on rocks

solid phase *2	CEC *4 (meq/100g)	w/s ratio (mL/g)	water type *6	pH end *7	C init. (M)	phase sep. *9	Eh end (mV)	atm./redox condition	K_d (Th) (m^3/kg)	reference	additional information, remarks	code REF
a) plutonic rocks												
granite *2	n.r.	11	synthetic groundwater (aq293) *6	~8	~1E-11	c(4000/50)	-150 - -210	reducing (Fe(II))	4.0	Allard et al. (1978)	careful experimental work	Ra1
granite *2	n.r.	11	synthetic groundwater (aq293) *6	~8	~1E-11	c(4000/50)	n.r.	atmospheric conditions	4.0	Allard et al. (1978)	not so clear if the values are measured in reducing or oxidizing environment	Ra1
tonalite*2	n.r.	10	synthetic groundwater *6	8.9	1E-13 - 1E-15	C(8000 rpm, 60 min)	n.r.	oxic	>1	Koskinen et al. (1985)		Th3
tonalite*2	n.r.	10	synthetic groundwater *6	8.9	1E-13 - 1E-15	C(8000 rpm, 60 min); f(0.45 µm)	n.r.	oxic	>1	Koskinen et al. (1985)		Th3
mica gneiss*2	n.r.	10	synthetic groundwater *6	8.7	1E-13 - 1E-15	C(8000 rpm, 60 min)	n.r.	oxic	>1	Koskinen et al. (1985)		Th3
mica gneiss*2	n.r.	10	synthetic groundwater *6	8.7	1E-13 - 1E-15	C(8000 rpm, 60 min); f(0.45 µm)	n.r.	oxic	>1	Koskinen et al. (1985)		Th3
b) volcanic rocks												
tuff *2	n.r.	50	synthetic groundwater *6	7-8	1.00E-11	f (0.45 µm, 30000 MWCO)	n.r.	N_2 atmosphere *10	0.21-0.45	Berry et al. (1995)	Blank experiments to monitor radionuclide behavior, also experiments with fractured infill materials	U3
tuff *2	n.r.	50	high-pH synthetic groundwater *6	12-13	1.00E-11	f (0.45 µm, 30000 MWCO)	n.r.	N_2 atmosphere *10	0.24-5.8	Berry et al. (1995)	The K_d ranges represent several experiments with different tuff samples	U3
grey-green tuff *2	n.r.	50	synthetic groundwater *6	~8	2E-11	f (0.45 µm, 30000 MWCO)	n.r.	N_2 atmosphere *10	0.2	Baston et al. (1994)	Blank experiments to monitor radionuclide behavior.	Th2
red tuff *2	n.r.	50	synthetic groundwater *6	~8	2E-11	f (0.45 µm, 30000 MWCO)	n.r.	N_2 atmosphere *10	0.37	Baston et al. (1994)	Phase separation technique (no f; f(0.45 µm); f (30'000 MWCO)) had no influence on K_d values	Th2
grey-green tuff *2	n.r.	50	synthetic groundwater *6	~12	2E-11	f (0.45 µm, 30000 MWCO)	n.r.	N_2 atmosphere *10	0.54	Baston et al. (1994)	See Table 15, FY95 BMG-report: Ochs and Wanner, 1996	Th2
red tuff *2	n.r.	50	synthetic groundwater *6	~12	2E-11	f (0.45 µm, 30000 MWCO)	n.r.	N_2 atmosphere *10	7.15	Baston et al. (1994)		Th2
c) sedimentary rocks												
mudrock *2	n.r.	50	cement-equilibrated water *6	10.1	2E-11	c (1500 g/15)	n.r.	N_2 atmosphere *10	3.0	Baston et al. (1992b)	See Table 15, FY95 BMG-report: Ochs and Wanner, 1996	Th1
mudrock *2	n.r.	50	cement-equilibrated water *6	9.9	2E-11	c (1500 g/15)	n.r.	N_2 atmosphere *10	1.9	Baston et al. (1992b)		Th1
mudrock *2	n.r.	5	cement-equilibrated water *6	11.5	2E-11	c (1500 g/15)	n.r.	N_2 atmosphere *10	0.64	Baston et al. (1992b)		Th1
mudrock *2	n.r.	5	cement-equilibrated water *6	11.5	2E-11	c (1500 g/15)	n.r.	N_2 atmosphere *10	0.23	Baston et al. (1992b)		Th1
mudrock *2	n.r.	50	cement-equilibrated water *6	10.1	2E-11	c(1500 g/15), f(0.45 µm)	n.r.	N_2 atmosphere *10	2.8	Baston et al. (1992b)		Th1
mudrock *2	n.r.	50	cement-equilibrated water *6	9.9	2E-11	c(1500 g/15), f(0.45 µm)	n.r.	N_2 atmosphere *10	2.0	Baston et al. (1992b)		Th1
mudrock *2	n.r.	5	cement-equilibrated water *6	11.5	2E-11	c(1500 g/15), f(0.45 µm)	n.r.	N_2 atmosphere *10	2.8	Baston et al. (1992b)		Th1
mudrock *2	n.r.	5	cement-equilibrated water *6	11.5	2E-11	c(1500 g/15), f(0.45 µm)	n.r.	N_2 atmosphere *10	3.4	Baston et al. (1992b)		Th1
mudrock *2	n.r.	50	cement-equilibrated water *6	10.1	2E-11	c(1500 g/15), f(30000 MWCO)	n.r.	N_2 atmosphere *10	2.9	Baston et al. (1992b)		Th1
mudrock *2	n.r.	50	cement-equilibrated water *6	9.9	2E-11	c(1500 g/15), f(30000 MWCO)	n.r.	N_2 atmosphere *10	1.9	Baston et al. (1992b)		Th1
mudrock *2	n.r.	5	cement-equilibrated water *6	11.5	2E-11	c(1500 g/15), f(30000 MWCO)	n.r.	N_2 atmosphere *10	9.2	Baston et al. (1992b)		Th1
mudrock *2	n.r.	5	cement-equilibrated water *6	11.5	2E-11	c(1500 g/15), f(30000 MWCO)	n.r.	N_2 atmosphere *10	7.3	Baston et al. (1992b)		Th1
mudrock *2	n.r.	50	cement-equilibrated water *6	8.5	2E-11	c (1500 g/15)	n.r.	N_2 atmosphere *10	1.20	Baston et al. (1992b)		Th1
mudrock *2	n.r.	50	cement-equilibrated water *6	8.5	2E-11	c (1500 g/15)	n.r.	N_2 atmosphere *10	1.20	Baston et al. (1992b)		Th1
mudrock *2	n.r.	5	cement-equilibrated water *6	8.5	2E-11	c (1500 g/15)	n.r.	N_2 atmosphere *10	1.30	Baston et al. (1992b)		Th1
mudrock *2	n.r.	5	cement-equilibrated water *6	8.1	2E-11	c (1500 g/15)	n.r.	N_2 atmosphere *10	0.82	Baston et al. (1992b)		Th1
mudrock *2	n.r.	50	cement-equilibrated water *6	8.5	2E-11	c(1500 g/15), f(0.45 µm)	n.r.	N_2 atmosphere *10	1.10	Baston et al. (1992b)		Th1
mudrock *2	n.r.	50	cement-equilibrated water *6	8.5	2E-11	c(1500 g/15), f(0.45 µm)	n.r.	N_2 atmosphere *10	1.20	Baston et al. (1992b)		Th1
mudrock *2	n.r.	5	cement-equilibrated water *6	8.5	2E-11	c(1500 g/15), f(0.45 µm)	n.r.	N_2 atmosphere *10	3.00	Baston et al. (1992b)		Th1
mudrock *2	n.r.	5	cement-equilibrated water *6	8.1	2E-11	c(1500 g/15), f(0.45 µm)	n.r.	N_2 atmosphere *10	1.10	Baston et al. (1992b)		Th1
mudrock *2	n.r.	50	cement-equilibrated water *6	8.5	2E-11	c(1500 g/15), f(30000 MWCO)	n.r.	N_2 atmosphere *10	1.10	Baston et al. (1992b)		Th1
mudrock *2	n.r.	50	cement-equilibrated water *6	8.5	2E-11	c(1500 g/15), f(30000 MWCO)	n.r.	N_2 atmosphere *10	1.20	Baston et al. (1992b)		Th1
mudrock *2	n.r.	5	cement-equilibrated water *6	8.5	2E-11	c(1500 g/15), f(30000 MWCO)	n.r.	N_2 atmosphere *10	2.40	Baston et al. (1992b)		Th1
mudrock *2	n.r.	5	cement-equilibrated water *6	8.1	2E-11	c(1500 g/15), f(30000 MWCO)	n.r.	N_2 atmosphere *10	1.10	Baston et al. (1992b)		Th1
marl	1 - 80	7.0	groundwater	n.r.	1E-10	n.r.	n.r.	n.r.	0.569	Meier et al. (1994)	Short overview about wide range of experimental work. Lack of experimental details.	Pb3
marl	1 - 80	3.5	groundwater	n.r.	1E-10	n.r.	n.r.	n.r.	0.369	Meier et al. (1994)	Increase of s/w ratio decreases sorption.	Pb3
marl	1 - 80	1.4	groundwater	n.r.	1E-10	n.r.	n.r.	n.r.	0.214	Meier et al. (1994)	desorption coefficients investigated	Pb3
marl	1 - 80	1.0	groundwater	n.r.	1E-10	n.r.	n.r.	n.r.	0.17	Meier et al. (1994)		Pb3

Table 1: continued

solid phase *2	CEC *4 (meq/100g)	w/s ratio (mL/g)	water type *6	pH end *7	C init. (M)	phase sep. *9	Eh end (mV)	atm./redox condition	K_d (Th) (m^3/kg)	reference	additional information, remarks	code REF
St. Bees sandstone *2	n.r.	50	cement-equilibrated water *6	11.8	2E-11	c(1500 g/15), f(30000 MWCO)	n.r.	N_2 atmosphere *10	2.60	Baston et al. (1992b)		Th1
St. Bees sandstone *2	n.r.	50	cement-equilibrated water *6	11.8	2E-11	c(1500 g/15), f(30000 MWCO)	n.r.	N_2 atmosphere *10	2.30	Baston et al. (1992b)		Th1
St. Bees sandstone *2	n.r.	5	cement-equilibrated water *6	11.7	2E-11	c(1500 g/15), f(30000 MWCO)	n.r.	N_2 atmosphere *10	1.40	Baston et al. (1992b)		Th1
St. Bees sandstone *2	n.r.	50	cement-equilibrated water *6	8.1	2E-11	c(1500 g/15), f(30000 MWCO)	n.r.	N_2 atmosphere *10	2.10	Baston et al. (1992b)		Th1
St. Bees sandstone *2	n.r.	50	cement-equilibrated water *6	8.8	2E-11	c(1500 g/15), f(30000 MWCO)	n.r.	N_2 atmosphere *10	1.90	Baston et al. (1992b)		Th1
St. Bees sandstone *2	n.r.	5	cement-equilibrated water *6	7.6	2E-11	c(1500 g/15), f(30000 MWCO)	n.r.	N_2 atmosphere *10	0.92	Baston et al. (1992b)		Th1
St. Bees sandstone *2	n.r.	5	cement-equilibrated water *6	8.6	2E-11	c(1500 g/15), f(30000 MWCO)	n.r.	N_2 atmosphere *10	0.86	Baston et al. (1992b)		Th1
Caithness flagstones *2	n.r.	50	cement-equilibrated water *6	11.8	2E-11	c (1500 g/15)	n.r.	N_2 atmosphere *10	1.2	Baston et al. (1992b)	Phase separation procedure has hardly an influence on Kd values	Th1
Caithness flagstones *2	n.r.	5	cement-equilibrated water *6	11.0	2E-11	c (1500 g/15)	n.r.	N_2 atmosphere *10	0.93	Baston et al. (1992b)	Kd values decrease with increasing s/w ratios.	Th1
Caithness flagstones *2	n.r.	50	cement-equilibrated water *6	11.8	2E-11	c(1500 g/15), f(0.45 µm)	n.r.	N_2 atmosphere *10	1.2	Baston et al. (1992b)	Kd values slightly increase with increasing pH	Th1
Caithness flagstones *2	n.r.	5	cement-equilibrated water *6	11.0	2E-11	c(1500 g/15), f(0.45 µm)	n.r.	N_2 atmosphere *10	1.4	Baston et al. (1992b)		Th1
Caithness flagstones *2	n.r.	50	cement-equilibrated water *6	11.8	2E-11	c(1500 g/15), f(30000 MWCO)	n.r.	N_2 atmosphere *10	1.7	Baston et al. (1992b)		Th1
Caithness flagstones *2	n.r.	5	cement-equilibrated water *6	11.0	2E-11	c(1500 g/15), f(30000 MWCO)	n.r.	N_2 atmosphere *10	1.2	Baston et al. (1992b)		Th1
Caithness flagstones *2	n.r.	50	cement-equilibrated water *6	9.0	2E-11	c (1500 g/15)	n.r.	N_2 atmosphere *10	0.95	Baston et al. (1992b)		Th1
Caithness flagstones *2	n.r.	50	cement-equilibrated water *6	7.9	2E-11	c (1500 g/15)	n.r.	N_2 atmosphere *10	1.10	Baston et al. (1992b)		Th1
Caithness flagstones *2	n.r.	5	cement-equilibrated water *6	8.3	2E-11	c (1500 g/15)	n.r.	N_2 atmosphere *10	0.12	Baston et al. (1992b)		Th1
Caithness flagstones *2	n.r.	50	cement-equilibrated water *6	9.0	2E-11	c(1500 g/15), f(0.45 µm)	n.r.	N_2 atmosphere *10	0.95	Baston et al. (1992b)		Th1
Caithness flagstones *2	n.r.	50	cement-equilibrated water *6	7.9	2E-11	c(1500 g/15), f(0.45 µm)	n.r.	N_2 atmosphere *10	1.10	Baston et al. (1992b)		Th1
Caithness flagstones *2	n.r.	5	cement-equilibrated water *6	8.3	2E-11	c(1500 g/15), f(0.45 µm)	n.r.	N_2 atmosphere *10	0.15	Baston et al. (1992b)		Th1
Caithness flagstones *2	n.r.	50	cement-equilibrated water *6	9.0	2E-11	c(1500 g/15), f(30000 MWCO)	n.r.	N_2 atmosphere *10	0.82	Baston et al. (1992b)		Th1
Caithness flagstones *2	n.r.	50	cement-equilibrated water *6	7.9	2E-11	c(1500 g/15), f(30000 MWCO)	n.r.	N_2 atmosphere *10	1.00	Baston et al. (1992b)		Th1
Caithness flagstones *2	n.r.	5	cement-equilibrated water *6	8.3	2E-11	c(1500 g/15), f(30000 MWCO)	n.r.	N_2 atmosphere *10	0.14	Baston et al. (1992b)		Th1
d) other												
eichsel glacial sediment * 2	n.r.	2.5	Low salinity groundwater G1 *6	6.1	1.00E-08	*9	70	99% Ar. 1% CO_2	0.248	Lieser et al. (1990)	Kd is calculated from the distribution of Pb	Pb1
Elster glacial sediment * 2	n.r.	2.5	Medium salinity groundwater G8 *6	7.5	1.00E-08	*9	-160	99% Ar. 1% CO_2	0.094	Lieser et al. (1990)	between coarse+fine particles and the	Pb1
Elster glacial sediment * 2	n.r.	2.5	Medium salinity groundwater G9 *6	7.7	1.00E-08	*9	-430	99% Ar. 1% CO_2	0.498	Lieser et al. (1990)	molecular fraction	Pb1
sandy sediments *2	1 - 80	1.0	groundwater + EDTA	n.r.	1E-10	n.r.	n.r.	n.r.	0.015	Meier et al. (1994)	EDTA decreases Th sorption.	Pb3

Table 2: Compilation of batch distribution coefficients for Pa on rocks

redox state *1	solid phase *2	CEC *4 (meq/100g)	w/s ratio (mL/g)	temp. (°C)	water type *6	pH end *7	C init. (M)	phase sep. *9	Eh end (mV)	atm./redox condition	K_d (Pa) (m³/kg)	reference	additional information, remarks	code REF
a) plutonic rock														
n.r.	granodiorite	n.r.	5	Room	de-ionised water*6	10.1	3.6E-11	centrifuged	-480	strong reducing conditions	1.7	Baston et al. (1997b)		Ac1
n.r.	granodiorite	n.r.	5	Room	de-ionised water*6	10.1	3.6E-11	f (0.45 µm)	-480	strong reducing conditions	>160	Baston et al. (1997b)		Ac1
n.r.	granodiorite	n.r.	5	Room	de-ionised water*6	10.1	3.6E-11	10000 MWCO	-480	strong reducing conditions	>300	Baston et al. (1997b)		Ac1
n.r.	granodiorite	n.r.	5	Room	de-ionised water*6	10.1	3.8E-11	centrifuged	-480	strong reducing conditions	0.75	Baston et al. (1997b)		Ac1
n.r.	granodiorite	n.r.	5	Room	de-ionised water*6	10.1	3.8E-11	f (0.45 µm)	-480	strong reducing conditions	>140	Baston et al. (1997b)		Ac1
n.r.	granodiorite	n.r.	5	Room	de-ionised water*6	10.1	3.8E-11	10000 MWCO	-480	strong reducing conditions	>210	Baston et al. (1997b)		Ac1
n.r.	granodiorite	n.r.	5	60	de-ionised water*6	9.6	3.8E-11	centrifuged	-340	strong reducing conditions	0.25	Baston et al. (1997b)		Ac1
n.r.	granodiorite	n.r.	5	60	de-ionised water*6	9.6	3.6E-11	f (0.45 µm)	-340	strong reducing conditions	2	Baston et al. (1997b)		Ac1
n.r.	granodiorite	n.r.	5	60	de-ionised water*6	9.6	3.8E-11	10000 MWCO	-340	strong reducing conditions	>210	Baston et al. (1997b)		Ac1
n.r.	granodiorite	n.r.	5	60	de-ionised water*6	9.6	3.6E-11	centrifuged	-340	strong reducing conditions	0.52	Baston et al. (1997b)		Ac1
n.r.	granodiorite	n.r.	5	60	de-ionised water*6	9.6	3.6E-11	f (0.45 µm)	-340	strong reducing conditions	7.8	Baston et al. (1997b)		Ac1
n.r.	granodiorite	n.r.	5	60	de-ionised water*6	9.6	3.8E-11	10000 MWCO	-340	strong reducing conditions	>240	Baston et al. (1997b)		Ac1
+V	Inada granite	n.r.	30.0	room	PW	ca. 7	ca.1E-4 (237Np)	f (0.45 µm)	n.r.	n.r. (ambient conditions)	0.0025	Nakayama et al. (1986)	surface area of solids reported See Appendix A2, Table 4, FY96 BMG-report: Ochs and Lothenbach, 1997	Pa2
+V	Inada granite	n.r.	30.0	room	PW	ca. 7	ca.1E-4 (237Np)	f (0.45, 0.1 µm)	n.r.	n.r. (ambient conditions)	0.0033	Nakayama et al. (1986)		Pa2
+V	Inada granite	n.r.	30.0	room	PW	ca. 7	ca.1E-4 (237Np)	f (0.45, 0.1, 0.025 µm)	n.r.	n.r. (ambient conditions)	0.0062	Nakayama et al. (1986)		Pa2
+V	Inada granite	n.r.	30.0	room	PW	ca. 11	ca.1E-4 (237Np)	f (0.45 µm)	n.r.	n.r. (ambient conditions)	0.0024	Nakayama et al. (1986)		Pa2
+V	Inada granite	n.r.	30.0	room	PW	ca. 11	ca.1E-4 (237Np)	f (0.45, 0.1 µm)	n.r.	n.r. (ambient conditions)	0.0056	Nakayama et al. (1986)		Pa2
+V	Inada granite	n.r.	30	room	PW	ca. 11	ca.1E-4 (237Np)	f (0.45, 0.1, 0.025 µm)	n.r.	n.r. (ambient conditions)	0.0073	Nakayama et al. (1986)		Pa2
b) volcanic rock														
n.r.	tuff	n.r.	5	Room	de-ionised water*6	9.4	3.8E-11	centrifuged	-180	strong reducing conditions	>120	Baston et al. (1997b)		Ac1
n.r.	tuff	n.r.	5	Room	de-ionised water*6	9.4	3.8E-11	f (0.45 µm)	-180	strong reducing conditions	>190	Baston et al. (1997b)		Ac1
n.r.	tuff	n.r.	5	Room	de-ionised water*6	9.4	3.8E-11	10000 MWCO	-180	strong reducing conditions	>210	Baston et al. (1997b)		Ac1
n.r.	tuff	n.r.	5	Room	de-ionised water*6	9.4	3.8E-11	centrifuged	-180	strong reducing conditions	>160	Baston et al. (1997b)		Ac1
n.r.	tuff	n.r.	5	Room	de-ionised water*6	9.4	3.8E-11	f (0.45 µm)	-180	strong reducing conditions	>210	Baston et al. (1997b)		Ac1
n.r.	tuff	n.r.	5	Room	de-ionised water*6	9.4	3.8E-11	10000 MWCO	-180	strong reducing conditions	>120	Baston et al. (1997b)		Ac1
n.r.	tuff	n.r.	5	60	de-ionised water*6	9.2	3.6E-11	centrifuged	-70	strong reducing conditions	2.9	Baston et al. (1997b)		Ac1
n.r.	tuff	n.r.	5	60	de-ionised water*6	9.2	3.8E-11	f (0.45 µm)	-70	strong reducing conditions	9.4	Baston et al. (1997b)		Ac1
n.r.	tuff	n.r.	5	60	de-ionised water*6	9.2	3.8E-11	10000 MWCO	-70	strong reducing conditions	>220	Baston et al. (1997b)		Ac1
n.r.	tuff	n.r.	5	60	de-ionised water*6	9.2	3.6E-11	centrifuged	-70	strong reducing conditions	2.7	Baston et al. (1997b)		Ac1
n.r.	tuff	n.r.	5	60	de-ionised water*6	9.2	3.8E-11	f (0.45 µm)	-70	strong reducing conditions	8.2	Baston et al. (1997b)		Ac1
n.r.	tuff	n.r.	5	60	de-ionised water*6	9.2	3.8E-11	10000 MWCO	-70	strong reducing conditions	12	Baston et al. (1997b)		Ac1
+V	Ohya tuff	n.r.	30.0	room	PW	ca. 7	ca.1E-4 (237Np)	f (0.45 µm)	n.r.	n.r. (ambient conditions)	0.0015	Nakayama et al. (1986)	surface area of solids reported See Appendix A2, Table 4, FY96 BMG-report: Ochs and Lothenbach, 1997	Pa2
+V	Ohya tuff	n.r.	30.0	room	PW	ca. 7	ca.1E-4 (237Np)	f (0.45, 0.1 µm)	n.r.	n.r. (ambient conditions)	0.04	Nakayama et al. (1986)		Pa2
+V	Ohya tuff	n.r.	30.0	room	PW	ca. 7	ca.1E-4 (237Np)	f (0.45, 0.1, 0.025 µm)	n.r.	n.r. (ambient conditions)	0.052	Nakayama et al. (1986)		Pa2
+V	Ohya tuff	n.r.	30.0	room	PW	ca. 11	ca.1E-4 (237Np)	f (0.45 µm)	n.r.	n.r. (ambient conditions)	0.0034	Nakayama et al. (1986)		Pa2
+V	Ohya tuff	n.r.	30.0	room	PW	ca. 11	ca.1E-4 (237Np)	f (0.45, 0.1 µm)	n.r.	n.r. (ambient conditions)	0.042	Nakayama et al. (1986)		Pa2
+V	Ohya tuff	n.r.	30	room	PW	ca. 11	ca.1E-4 (237Np)	f (0.45, 0.1, 0.025 µm)	n.r.	n.r. (ambient conditions)	0.065	Nakayama et al. (1986)		Pa2

Table 2: continued

redox state *1	solid phase *2	CEC *4 (meq/100g)	w/s ratio (mL/g)	temp. (°C)	water type *6	pH end *7	C init. (M)	phase sep. *9	Eh end (mV)	atm./redox condition	K_d (Pa) (m³/kg)	reference	additional information, remarks	code REF
c) sedimentary rock														
+V (e)	dolomitic marl	n.r.	2.5	n.r.	groundwater	n.r.	n.r.	f(0.45 µm)	n.r.	aerobic (const. O2)	24	Bode (1989)	desorption coefficients	Pa3
+V (e)	dolomitic marl	n.r.	2.5	n.r.	groundwater	n.r.	n.r.	f(0.45 µm)	n.r.	aerobic (const. O2)	6.2	Bode (1989)	desorption coefficients	Pa3
+V (e)	marl	n.r.	2.5	n.r.	groundwater	n.r.	n.r.	f(0.45 µm)	n.r.	aerobic (const. O2)	12.7	Bode (1989)	desorption coefficients	Pa3
+V (e)	dolomitic marl	n.r.	2.5	n.r.	groundwater	n.r.	n.r.	f(0.45 µm)	n.r.	aerobic (const. O2)	4.8	Bode (1989)	desorption coefficients	Pa3
+V (e)	marl/limestone	n.r.	2.5	n.r.	groundwater	n.r.	n.r.	f(0.45 µm)	n.r.	aerobic (const. O2)	7.3	Bode (1989)	desorption coefficients	Pa3
+V (e)	marl/dolomite + anhydrite	n.r.	2.5	n.r.	groundwater	n.r.	n.r.	f(0.45 µm)	n.r.	aerobic (const. O2)	5.5	Bode (1989)	desorption coefficients	Pa3
+V (e)	reddish claystone	n.r.	2.5	n.r.	groundwater	n.r.	n.r.	f(0.45 µm)	n.r.	aerobic (const. O2)	6.6	Bode (1989)	desorption coefficients	Pa3
+V (e)	green claystone	n.r.	2.5	n.r.	groundwater	n.r.	n.r.	f(0.45 µm)	n.r.	aerobic (const. O2)	9.4	Bode (1989)	desorption coefficients	Pa3
+V (e)	claystone	n.r.	2.5	n.r.	groundwater	n.r.	n.r.	f(0.45 µm)	n.r.	aerobic (const. O2)	6.85	Bode (1989)	desorption coefficients	Pa3
+V (e)	claystone	n.r.	2.5	n.r.	groundwater	n.r.	n.r.	f(0.45 µm)	n.r.	aerobic (const. O2)	3.5	Bode (1989)	desorption coefficients	Pa3
d) other														
+V/ +IV	marl & sandy sediments *2	n.r.	1.5	n.r.	natural groundwater *6	n.r.	6.9E-12	n.r.	-146	Ar + 1% CO2	0	Kim et al. (1994)	breakthrough curve, sorption low because of high organic content in groundwater (80 mg C/L).	Pa1

Table 3: Compilation of batch distribution coefficients for U on rocks

redox state *1	solid phase *2	CEC *4 (meq/100g)	w/s ratio (mL/g)	water type *6	pH and *7	C init. (M)	phase sep. *9	Eh end (mV)	atm./redox condition	K_d (U) (m^3/kg)	reference	additional information, remarks	code REF
a) plutonic rock													
+IV	granite *2	n.r.	11	synthetic groundwater (aq293) *6	~8	~1E-8	c(4000/50)	-150 - -210	reducing (Fe(II))	2.0	Allard et al. (1976)	careful experimental work	Ra1
+VI	granite *2	n.r.	11	synthetic groundwater (aq293) *6	~8	~1E-8	c(4000/50)	n.r.	atmospheric conditions	0.0063	Allard et al. (1976)		Ra1
+VI	Climax Stock granite CS5 *2	<1 *4	20	pre-equilibrated synthetic groundwater *6	~8	~5E-8	4 times c(16'000 rpm, 1h)	n.r.	atmospheric conditions	0.0044	Erdal et al. (1979)	desorption values are also recorded	U2
+VI	Climax Stock granite CS7 *2	<1-2 *4	20	pre-equilibrated synthetic groundwater *6	~8	~5E-8	4 times c(16'000 rpm, 1h)	n.r.	atmospheric conditions	0.0042	Erdal et al. (1979)		U2
IV	granodiorite *2	n.r.	50	de-ionised water	10.2	1.5E-07	c (1100 g), f (0.45 μm)	-440	reducing (2.5 mM Na-hydrosulphite, N$_2$)	6.9	Baston et al. (1995)	Blank experiments to monitor radionuclide behavior.	U4
IV	granodiorite *2	n.r.	50	de-ionised water	10.2	1.5E-07	c (1100 g), f (0.45 μm, 30000 MWCO)	-440	reducing (2.5 mM Na-hydrosulphite, N$_2$)	12	Baston et al. (1995)	Kd values on tuff lower at a s/w = 5 g/L under strongly reducing conditions.	U4
IV	granodiorite *2	n.r.	50	de-ionised water	10.1	1.5E-07	c (1100 g), f (0.45 μm)	-440	reducing (2.5 mM Na-hydrosulphite, N$_2$)	9.1	Baston et al. (1995)		U4
IV	granodiorite *2	n.r.	50	de-ionised water	10.1	1.5E-07	c (1100 g), f (0.45 μm, 30000 MWCO)	-440	reducing (2.5 mM Na-hydrosulphite, N$_2$)	18	Baston et al. (1995)		U4
IV	granodiorite *2	n.r.	50	seawater	8.5	1.5E-07	c (1100 g), f (0.45 μm)	-420	reducing (2.5 mM Na-hydrosulphite, N$_2$)	41	Baston et al. (1995)		U4
IV	granodiorite *2	n.r.	50	seawater	8.5	1.5E-07	c (1100 g), f (0.45 μm, 30000 MWCO)	-420	reducing (2.5 mM Na-hydrosulphite, N$_2$)	81	Baston et al. (1995)		U4
IV	granodiorite *2	n.r.	50	seawater	8.4	1.5E-07	c (1100 g), f (0.45 μm)	-460	reducing (2.5 mM Na-hydrosulphite, N$_2$)	71	Baston et al. (1995)		U4
IV	granodiorite *2	n.r.	50	seawater	8.4	1.5E-07	c (1100 g), f (0.45 μm, 30000 MWCO)	-460	reducing (2.5 mM Na-hydrosulphite, N$_2$)	280	Baston et al. (1995)		U4
VI	granodiorite *2	n.r.	50	de-ionised water	10	1.5E-07	c (1100 g), f (0.45 μm)	280	N$_2$ atmosphere *10	0.05	Baston et al. (1995)		U4
VI	granodiorite *2	n.r.	50	de-ionised water	10	1.5E-07	c (1100 g), f (0.45 μm, 30000 MWCO)	280	N$_2$ atmosphere *10	0.05	Baston et al. (1995)		U4
VI	granodiorite *2	n.r.	50	seawater	8.4	1.5E-07	c (1100 g), f (0.45 μm)	310	N$_2$ atmosphere *10	<0.02	Baston et al. (1995)		U4
VI	granodiorite *2	n.r.	50	seawater	8.4	1.5E-07	c (1100 g), f (0.45 μm, 30000 MWCO)	310	N$_2$ atmosphere *10	<0.01	Baston et al. (1995)		U4
n.r.	granodiorite	n.r.	5	seawater	8.5	1.4E-07	centrifuged	-420	strongly reducing conditions	1.2	Baston et al. (1997b)	data exist also for non-reducing conditions	Ac1
n.r.	granodiorite	n.r.	5	seawater	8.5	1.4E-07	f (0.45 μm)	-420	strongly reducing conditions	19	Baston et al. (1997b)		Ac1
n.r.	granodiorite	n.r.	5	seawater	8.5	1.4E-07	10000 MWCO	-420	strongly reducing conditions	>10	Baston et al. (1997b)	partly, these are the same data as reported by Baston et al. (1995) [U4], and Baston et al. (1997a) [Np6]	Ac1
n.r.	granodiorite	n.r.	5	seawater	8.4	1.4E-07	centrifuged	-430	strongly reducing conditions	0.84	Baston et al. (1997b)		Ac1
n.r.	granodiorite	n.r.	5	seawater	8.4	1.4E-07	f (0.45 μm)	-430	strongly reducing conditions	>10	Baston et al. (1997b)		Ac1
n.r.	granodiorite	n.r.	5	seawater	8.4	1.4E-07	10000 MWCO	-430	strongly reducing conditions	>10	Baston et al. (1997b)		Ac1
n.r.	granodiorite	n.r.	50	seawater	8.5	1.4E-07	centrifuged	-420	strongly reducing conditions	2.6	Baston et al. (1997b)		Ac1
n.r.	granodiorite	n.r.	50	seawater	8.5	1.4E-07	f (0.45 μm)	-420	strongly reducing conditions	41	Baston et al. (1997b)		Ac1
n.r.	granodiorite	n.r.	50	seawater	8.5	1.4E-07	10000 MWCO	-420	strongly reducing conditions	81	Baston et al. (1997b)		Ac1
n.r.	granodiorite	n.r.	50	seawater	8.4	1.4E-07	centrifuged	-460	strongly reducing conditions	0.48	Baston et al. (1997b)		Ac1
n.r.	granodiorite	n.r.	50	seawater	8.4	1.4E-07	f (0.45 μm)	-460	strongly reducing conditions	71	Baston et al. (1997b)		Ac1
n.r.	granodiorite	n.r.	50	seawater	8.4	1.4E-07	10000 MWCO	-460	strongly reducing conditions	280	Baston et al. (1997b)		Ac1
n.r.	granodiorite	n.r.	5	deionized water*6	10.1	1.4E-07	centrifuged	-450	strongly reducing conditions	0.54	Baston et al. (1997b)		Ac1
n.r.	granodiorite	n.r.	5	deionized water*6	10.1	1.4E-07	f (0.45 μm)	-450	strongly reducing conditions	6.3	Baston et al. (1997b)		Ac1
n.r.	granodiorite	n.r.	5	deionized water*6	10.1	1.4E-07	10000 MWCO	-450	strongly reducing conditions	28	Baston et al. (1997b)		Ac1
n.r.	granodiorite	n.r.	5	deionized water*6	10.1	1.4E-07	centrifuged	-450	strongly reducing conditions	0.36	Baston et al. (1997b)		Ac1
n.r.	granodiorite	n.r.	5	deionized water*6	10.1	1.4E-07	f (0.45 μm)	-450	strongly reducing conditions	4.7	Baston et al. (1997b)		Ac1
n.r.	granodiorite	n.r.	5	deionized water*6	10.1	1.4E-07	10000 MWCO	-450	strongly reducing conditions	6.3	Baston et al. (1997b)		Ac1
n.r.	granodiorite	n.r.	50	deionized water*6	10.1	1.4E-07	centrifuged	-440	strongly reducing conditions	1.1	Baston et al. (1997b)		Ac1
n.r.	granodiorite	n.r.	50	deionized water*6	10.1	1.4E-07	f (0.45 μm)	-440	strongly reducing conditions	6.9	Baston et al. (1997b)		Ac1
n.r.	granodiorite	n.r.	50	deionized water*6	10.1	1.4E-07	10000 MWCO	-440	strongly reducing conditions	12	Baston et al. (1997b)		Ac1
n.r.	granodiorite	n.r.	50	deionized water*6	10.2	1.4E-07	centrifuged	-440	strongly reducing conditions	0.95	Baston et al. (1997b)		Ac1
n.r.	granodiorite	n.r.	50	deionized water*6	10.2	1.4E-07	f (0.45 μm)	-440	strongly reducing conditions	9.1	Baston et al. (1997b)		Ac1
n.r.	granodiorite	n.r.	50	deionized water*6	10.2	1.4E-07	10000 MWCO	-440	strongly reducing conditions	18	Baston et al. (1997b)		Ac1
n.r.	granodiorite	n.r.	5	synthetic deionized water	10.1	1.0E-07	f (0.45 μm)	-450	Reducing - (N2-Atmosphere)	6.3	Baston et al. (1997a)	strongly reducing conditions with sodium	Np6
n.r.	granodiorite	n.r.	5	synthetic deionized water	10.1	1.0E-07	10000 MWCO	-450	Reducing - (N2-Atmosphere)	28	Baston et al. (1997a)	strongly reducing conditions with sodium	Np6
n.r.	granodiorite	n.r.	5	synthetic deionized water	10.1	1.0E-07	f (0.45 μm)	-450	Reducing - (N2-Atmosphere)	4.7	Baston et al. (1997a)	strongly reducing conditions with sodium	Np6
n.r.	granodiorite	n.r.	5	synthetic deionized water	10.1	1.0E-07	10000 MWCO	-450	Reducing - (N2-Atmosphere)	6.3	Baston et al. (1997a)	strongly reducing conditions with sodium	Np6
n.r.	hornblendite *2	n.r.	10.0	Syyry groundwater *6	9.30	1E-10	c, f (0.22 μm)	-230	reducing	0.636	Kaukonen et al. (1993)	careful, good documented experimental work	Np1
n.r.	hornblendite *2	n.r.	10.0	Syyry groundwater *6	9.70	1E-09	c, f (0.22 μm)	-216	reducing	2.547	Kaukonen et al. (1993)	Increase of HCO$_3$ decreases Kd values	Np1
n.r.	hornblendite *2	n.r.	10.0	Syyry groundwater *6	9.80	1E-07	c, f (0.22 μm)	-207	reducing	1.34	Kaukonen et al. (1993)		Np1
n.r.	hornblendite *2	n.r.	10.0	Allard water (1:10), 12 mg HCO$_3^-$ *6	n.r.	1E-09	c, f (0.22 μm)	321	oxic	0.133-0.755	Kaukonen et al. (1993)		Np1
n.r.	hornblendite *2	n.r.	10.0	Allard water (1:10), 12 mg HCO$_3^-$ *6	n.r.	1E-08	c, f (0.22 μm)	321	oxic	0.238-0.433	Kaukonen et al. (1993)		Np1
n.r.	hornblendite *2	n.r.	10.0	Allard water (1:10), 12 mg HCO$_3^-$ *6	n.r.	1E-06	c, f (0.22 μm)	321	oxic	0.057-0.079	Kaukonen et al. (1993)		Np1

Table 3: continued

redox state *1	solid phase *2	CEC *4 (meq/100g)	w/s ratio (mL/g)	water type *6	pH end *7	C init. (M)	phase sep. *9	Eh end (mV)	atm./redox condition	K_d (U) (m^3/kg)	reference	additional information, remarks	code REF
n.r.	gabbro *2	n.r.	10.0	Allard water (1:10), 12 mg HCO_3^- *6	n.r.	1E-09	c, f (0.22 µm)	321	oxic	0.017-0.021	Kaukonen et al. (1993)		Np1
n.r.	gabbro *2	n.r.	10.0	Allard water (1:10), 12 mg HCO_3^- *6	n.r.	1E-08	c, f (0.22 µm)	321	oxic	0.013-0.015	Kaukonen et al. (1993)		Np1
n.r.	gabbro *2	n.r.	10.0	Allard water (1:10), 12 mg HCO_3^- *6	n.r.	1E-06	c, f (0.22 µm)	321	oxic	0.010-0.013	Kaukonen et al. (1993)		Np1
n.r.	gabbro *2	n.r.	10.0	Allard water (1:10), 123 mg HCO_3^- *6	n.r.	1E-09	c, f (0.22 µm)	321	oxic	0.008-0.011	Kaukonen et al. (1993)		Np1
n.r.	gabbro *2	n.r.	10.0	Allard water (1:10), 12 mg HCO_3^- *6	n.r.	1E-09	c, f (0.22 µm)	321	oxic	0.021-0.026	Kaukonen et al. (1993)		Np1
n.r.	gabbro *2	n.r.	10.0	Allard water (1:10), <2 mg HCO_3^- *6	n.r.	1E-09	c, f (0.22 µm)	321	oxic	0.037-0.045	Kaukonen et al. (1993)		Np1
n.r.	granitic drill core samples *2	n.r.	n.r.	Allard water *6	n.r.	4E-06	c, f (0.22 µm)	n.r.	N_2	0.012-0.024	Suksi et al. (1989)	Conditions not very reducing (N_2), thus values for oxidising and reducing conditions similar	Np2
n.r.	granitic drill core samples *2	n.r.	n.r.	Allard water *6	n.r.	4E-06	c, f (0.22 µm)	n.r.	oxidizing	0.0005-0.001	Suksi et al. (1989)	Conversion factor from Ka to Kd values not very clear: Suksi et al. used Kd=0.37*Ka, while a factor of 370 might be more realistic.	Np2
b) volcanic rock													
n.r.	Umantum basalt *2	n.r.	n.r.	synbthetic goundwater GR-1	n.r.	2E-06	n.r.	n.r.	reducing	0.19	Pescatore and Sullivan (1985)	Experimental details recorded elsewhere	U5
n.r.	Umantum basalt *2	n.r.	n.r.	synbthetic goundwater GR-1	n.r.	1E-05	n.r.	n.r.	reducing	0.21	Pescatore and Sullivan (1985)		U5
n.r.	Umantum basalt *2	n.r.	n.r.	synbthetic goundwater GR-1	n.r.	9E-05	n.r.	n.r.	reducing	0.09	Pescatore and Sullivan (1985)		U5
n.r.	Umantum basalt *2	n.r.	n.r.	synbthetic goundwater GR-1	n.r.	3E-04	n.r.	n.r.	reducing	0.003	Pescatore and Sullivan (1985)		U5
n.r.	Umantum basalt *2	n.r.	n.r.	synbthetic goundwater GR-1	n.r.	2E-06	n.r.	n.r.	reducing	0.16	Pescatore and Sullivan (1985)		U5
n.r.	Umantum basalt *2	n.r.	n.r.	synbthetic goundwater GR-1	n.r.	9E-06	n.r.	n.r.	reducing	0.15	Pescatore and Sullivan (1985)		U5
n.r.	Umantum basalt *2	n.r.	n.r.	synbthetic goundwater GR-1	n.r.	9E-05	n.r.	n.r.	reducing	0.12	Pescatore and Sullivan (1985)		U5
n.r.	Umantum basalt *2	n.r.	n.r.	synbthetic goundwater GR-1	n.r.	6E-04	n.r.	n.r.	reducing	0.015	Pescatore and Sullivan (1985)		U5
IV	Umantum basalt *2	n.r.	n.r.	Synthetic goundwater *6	9.4	n.r.	n.r.	~-400	reducing (0.1 M hydrazine)	0.04	Salter and Jacobs (1982)	Freundlich isotherm: S=0.06*C^0.99	Am4
n.r.	Umantum basalt *2	n.r.	n.r.	Synthetic goundwater *6	9.4	n.r.	n.r.	n.r.	oxidizing	0.00	Salter and Jacobs (1982)	Dubinin-Radushkevich isotherm: S=0,000005 exp - (0.00031(RTln(1+1/C))^2)	Am4
n.r.	greenstone *2	n.r.	10.0	Syyry groundwater *6	9.50	1E-10	c, f (0.22 µm)	-203	reducing	0.789	Kaukonen et al. (1993)		Np1
n.r.	greenstone *2	n.r.	10.0	Syyry groundwater *6	10.00	1E-09	c, f (0.22 µm)	-204	reducing	1.627	Kaukonen et al. (1993)		Np1
n.r.	greenstone *2	n.r.	10.0	Syyry groundwater *6	10.00	1E-07	c, f (0.22 µm)	-226	reducing	1.191	Kaukonen et al. (1993)		Np1
n.r.	greenstone *2	n.r.	10.0	Allard water (1:10), 12 mg HCO_3^- *6	n.r.	1E-09	c, f (0.22 µm)	321	oxic	0.091-0.341	Kaukonen et al. (1993)		Np1
n.r.	greenstone *2	n.r.	10.0	Allard water (1:10), 12 mg HCO_3^- *6	n.r.	1E-08	c, f (0.22 µm)	321	oxic	0.067-0.206	Kaukonen et al. (1993)		Np1
n.r.	greenstone *2	n.r.	10.0	Allard water (1:10), 12 mg HCO_3^- *6	n.r.	1E-06	c, f (0.22 µm)	321	oxic	0.129-0.169	Kaukonen et al. (1993)		Np1
IV	tuff *2	n.r.	50	de-ionised water	9.5	1.5E-07	c (1100 g), f (0.45 µm)	-410	red. (2.5 mM Na-hydrosulphite, N_2)	62	Baston et al. (1995)	Blank experiments to monitor radionuclide behavior.	U4
IV	tuff *2	n.r.	50	de-ionised water	9.5	1.5E-07	c (1100 g), f (0.45 µm, 30000 MWCO)	-410	red. (2.5 mM Na-hydrosulphite, N_2)	28	Baston et al. (1995)	Kd values on tuff lower at a s/w = 5 g/L under strongly reducing conditions.	U4
IV	tuff *2	n.r.	50	de-ionised water	9.5	1.5E-07	c (1100 g), f (0.45 µm)	-420	red. (2.5 mM Na-hydrosulphite, N_2)	94	Baston et al. (1995)		U4
IV	tuff *2	n.r.	50	de-ionised water	9.5	1.5E-07	c (1100 g), f (0.45 µm, 30000 MWCO)	-420	red. (2.5 mM Na-hydrosulphite, N_2)	56	Baston et al. (1995)		U4
IV	tuff *2	n.r.	50	seawater	8.3	1.5E-07	c (1100 g), f (0.45 µm)	-340	red. (2.5 mM Na-hydrosulphite, N_2)	280	Baston et al. (1995)		U4
IV	tuff *2	n.r.	50	seawater	8.3	1.5E-07	c (1100 g), f (0.45 µm, 30000 MWCO)	-340	red. (2.5 mM Na-hydrosulphite, N_2)	280	Baston et al. (1995)		U4
IV	tuff *2	n.r.	50	seawater	8.1	1.5E-07	c (1100 g), f (0.45 µm)	-330	red. (2.5 mM Na-hydrosulphite, N_2)	280	Baston et al. (1995)		U4
IV	tuff *2	n.r.	50	seawater	8.1	1.5E-07	c (1100 g), f (0.45 µm, 30000 MWCO)	-330	red. (2.5 mM Na-hydrosulphite, N_2)	1200	Baston et al. (1995)		U4
VI	tuff *2	n.r.	50	de-ionised water	9.4	1.5E-07	c (1100 g), f (0.45 µm)	320	N_2 atmosphere *10	0.1	Baston et al. (1995)		U4
VI	tuff *2	n.r.	50	de-ionised water	9.4	1.5E-07	c (1100 g), f (0.45 µm, 30000 MWCO)	320	N_2 atmosphere *10	0.1	Baston et al. (1995)		U4
VI	tuff *2	n.r.	50	seawater	8.1	1.5E-07	c (1100 g), f (0.45 µm)	300	N_2 atmosphere *10	0.11	Baston et al. (1995)		U4
VI	tuff *2	n.r.	50	seawater	8.1	1.5E-07	c (1100 g), f (0.45 µm, 30000 MWCO)	300	N_2 atmosphere *10	0.11	Baston et al. (1995)		U4
n.r.	tuff	n.r.	50	seawater	8.3	1.35E-07	centrifuged	-350	strong reducing conditions	28	Baston et al. (1997b)	experimental conditions as by Baston et al. (1995)	Ac1
n.r.	tuff	n.r.	50	seawater	8.3	1.35E-07	f (0.45 µm)	-350	strong reducing conditions	63	Baston et al. (1997b)		Ac1
n.r.	tuff	n.r.	50	seawater	8.3	1.35E-07	10000 MWCO	-350	strong reducing conditions	56	Baston et al. (1997b)	partly, these seem to be the same data as reported by Baston et al., 1995 [U4]	Ac1
n.r.	tuff	n.r.	50	seawater	8.1	1.35E-07	centrifuged	-340	strong reducing conditions	11	Baston et al. (1997b)	and Baston et al., 1997a [Np6]	Ac1
n.r.	tuff	n.r.	50	seawater	8.1	1.35E-07	f (0.45 µm)	-340	strong reducing conditions	56	Baston et al. (1997b)		Ac1
n.r.	tuff	n.r.	50	seawater	8.1	1.35E-07	10000 MWCO	-340	strong reducing conditions	140	Baston et al. (1997b)		Ac1
n.r.	tuff	n.r.	50	seawater	8.3	1.35E-07	centrifuged	-340	strong reducing conditions	56	Baston et al. (1997b)		Ac1
n.r.	tuff	n.r.	50	seawater	8.3	1.35E-07	f (0.45 µm)	-340	strong reducing conditions	280	Baston et al. (1997b)		Ac1
n.r.	tuff	n.r.	50	seawater	8.3	1.35E-07	10000 MWCO	-340	strong reducing conditions	280	Baston et al. (1997b)		Ac1
n.r.	tuff	n.r.	50	seawater	8.1	1.35E-07	centrifuged	-330	strong reducing conditions	51	Baston et al. (1997b)		Ac1
n.r.	tuff	n.r.	50	seawater	8.1	1.35E-07	f (0.45 µm)	-330	strong reducing conditions	280	Baston et al. (1997b)		Ac1
n.r.	tuff	n.r.	50	seawater	8.1	1.35E-07	10000 MWCO	-330	strong reducing conditions	1200	Baston et al. (1997b)		Ac1
n.r.	tuff	n.r.	50	deionized water*6	9.4	1.35E-07	centrifuged	-410	strong reducing conditions	5.1	Baston et al. (1997b)		Ac1
n.r.	tuff	n.r.	50	deionized water*6	9.4	1.35E-07	f (0.45 µm)	-410	strong reducing conditions	19	Baston et al. (1997b)		Ac1
n.r.	tuff	n.r.	50	deionized water*6	9.4	1.35E-07	10000 MWCO	-410	strong reducing conditions	56	Baston et al. (1997b)		Ac1
n.r.	tuff	n.r.	50	deionized water*6	9.4	1.35E-07	centrifuged	-400	strong reducing conditions	9.4	Baston et al. (1997b)		Ac1
n.r.	tuff	n.r.	50	deionized water*6	9.4	1.35E-07	f (0.45 µm)	-400	strong reducing conditions	56	Baston et al. (1997b)		Ac1

Table 3: continued

redox state *1	solid phase *2	CEC *4 (meq/100g)	w/s ratio (mL/g)	water type *6	pH end *7	C init. (M)	phase sep. *9	Eh end (mV)	atm./redox condition	K_d (U) (m^3/kg)	reference	additional information, remarks	code REF
n.r.	tuff	n.r.	50	deionized water*6	9.4	1.35E-07	10000 MWCO	-400	strong reducing conditions	56	Baston et al. (1997b)		Ac1
n.r.	tuff	n.r.	50	deionized water*6	9.5	1.35E-07	centrifuged	-410	strong reducing conditions	11	Baston et al. (1997b)		Ac1
n.r.	tuff	n.r.	50	deionized water*6	9.5	1.35E-07	f (0.45 µm)	-410	strong reducing conditions	62	Baston et al. (1997b)		Ac1
n.r.	tuff	n.r.	50	deionized water*6	9.5	1.35E-07	10000 MWCO	-410	strong reducing conditions	280	Baston et al. (1997b)		Ac1
n.r.	tuff	n.r.	50	deionized water*6	9.5	1.35E-07	centrifuged	-420	strong reducing conditions	15	Baston et al. (1997b)		Ac1
n.r.	tuff	n.r.	50	deionized water*6	9.5	1.35E-07	f (0.45 µm)	-420	strong reducing conditions	94	Baston et al. (1997b)		Ac1
n.r.	tuff	n.r.	50	deionized water*6	9.5	1.35E-07	10000 MWCO	-420	strong reducing conditions	560	Baston et al. (1997b)		Ac1
n.r.	tuff	n.r.	5	synthetic deionized water	9.5	1.0E-07	f (0.45 µm)	-410	Reducing - (N2-Atmosphere)	19	Baston et al. (1997a)	strongly reducing conditions with sodium	Np6
n.r.	tuff	n.r.	5	synthetic deionized water	9.5	1.0E-07	10000 MWCO	-420	Reducing - (N2-Atmosphere)	56	Baston et al. (1997a)	strongly reducing conditions with sodium	Np6
n.r.	tuff	n.r.	5	synthetic deionized water	9.5	1.0E-07	f (0.45 µm)	-410	Reducing - (N2-Atmosphere)	56	Baston et al. (1997a)	strongly reducing conditions with sodium	Np6
n.r.	tuff	n.r.	5	synthetic deionized water	9.5	1.0E-07	10000 MWCO	-420	Reducing - (N2-Atmosphere)	56	Baston et al. (1997a)	strongly reducing conditions with sodium	Np6
VI	tuff *2	n.r.	50	synthetic groundwater *6	7-8	1E-07	f (0.45 µm, 30000 MWCO)	n.r.	N_2 atmosphere *10	0.065-0.11	Berry et al. (1995)	Blank experiments to monitor radionuclide behavior, also experiments with fractured infill materials	U3
VI	tuff *2	n.r.	50	high-pH synthetic groundwater *6	12-13	1E-07	f (0.45 µm, 30000 MWCO)	n.r.	N_2 atmosphere *10	0.018-54	Berry et al. (1995)	The Kd ranges represent several experiments with different tuff samples	U3
+VI (e)	tuff *2	2-100 *4	20	natural groundwater	≈ 8.5	n.r.	4 times c(16'000 rpm, 1h)	n.r.	atmospheric conditions	0.0015-0.0053	Vine et al. (1980a)	All experimental details taken from Wolfsberg et al. (1981)	Pu1
+VI (e)	tuff *2	2-100 *4	20	natural groundwater	≈ 8.5	n.r.	4 times c(16'000 rpm, 1h)	n.r.	N_2 atmosphere	0.00048-0.015	Vine et al. (1980a)	cf. U1 and Pu4	Pu1
n.r.	de-vitrified tuff JM-22 *2	2-3 *4	20	natural groundwater	8.68	n.r.	4 times c(16'000 rpm, 1h)	n.r.	N_2 atmosphere	0.00081	Vine et al. (1980b)	cf. Pu1 and Pu4	U1
n.r.	vitric tuff JM-38 *2	54-109 *4	20	natural groundwater	8.69	n.r.	4 times c(16'000 rpm, 1h)	n.r.	N_2 atmosphere	0.015	Vine et al. (1980b)	The presence of N_2 does not produce very reducing conditions.	U1
n.r.	de-vitrified tuff JM-54 *2	4 *4	20	natural groundwater	8.5	n.r.	4 times c(16'000 rpm, 1h)	n.r.	N_2 atmosphere	0.0017	Vine et al. (1980b)		U1
+VI	de-vitrified tuff JM-22 *2	2-3 *4	20	natural groundwater	≈ 8.5	n.r.	4 times c(16'000 rpm, 1h)	n.r.	atmospheric conditions	0.0012	Wolfsberg et al. (1981)	cf. Pu1 and U1	Pu4
+VI	vitric tuff JM-38 *2	54-109 *4	20	natural groundwater	≈ 8.5	n.r.	4 times c(16'000 rpm, 1h)	n.r.	atmospheric conditions	0.0047	Wolfsberg et al. (1981)		Pu4
+VI	de-vitrified tuff JM-54 *2	4 *4	20	natural groundwater	≈ 8.5	n.r.	4 times c(16'000 rpm, 1h)	n.r.	atmospheric conditions	0.0014	Wolfsberg et al. (1981)		Pu4
b) sedimentary rock													
IV	mudrock *2	n.r.	50	cement-equilibrated water *6	11.0	1E-07	c (1500 g/15)	-420	reducing (0.05 M $NaHSO_3$, N_2)	4.7	Baston et al. (1992b)		Th1
IV	mudrock *2	n.r.	50	cement-equilibrated water *6	11.0	1E-07	c(1500 g/15), f(0.45 µm)	-420	reducing (0.05 M $NaHSO_3$, N_2)	6.6	Baston et al. (1992b)		Th1
IV	mudrock *2	n.r.	50	cement-equilibrated water *6	11.0	1E-07	c(1500 g/15), f(30000 MWCO)	-420	reducing (0.05 M $NaHSO_3$, N_2)	6.3	Baston et al. (1992b)		Th1
IV	mudrock *2	n.r.	50	cement-equilibrated water *6	8.0	1E-07	c (1500 g/15)	-230	reducing (0.05 M $NaHSO_3$, N_2)	9	Baston et al. (1992b)		Th1
IV	mudrock *2	n.r.	50	cement-equilibrated water *6	8.0	1E-07	c(1500 g/15), f(0.45 µm)	-230	reducing (0.05 M $NaHSO_3$, N_2)	7	Baston et al. (1992b)		Th1
IV	mudrock *2	n.r.	50	cement-equilibrated water *6	8.0	1E-07	c(1500 g/15), f(30000 MWCO)	-230	reducing (0.05 M $NaHSO_3$, N_2)	4.3	Baston et al. (1992b)		Th1
n.r.	marl *2	1 - 80	1.0	groundwater	7.00	1E-07	n.r.	-244	reducing (Ar, H_2)	>2.7	Meier et al. (1994)		Pb3
n.r.	marl *2	1 - 80	1.0	groundwater	n.r.	1E-10 - 1E-7	n.r.	n.r.	aerob	0.017-0.067	Meier et al. (1994)	Langmuir isotherm (cmax = 2.8E-7 mol/g; k= 1.8E8	Pb3
n.r.	marl *2	1 - 60	1	groundwater	7.0	1E-07	n.r.	309	aerob	0	Meier et al. (1994)		Pb3
n.r.	sandstone *2	9.9	10.0	GR-2 groundwater *6	≈9	3E-09	f (0.003 µm)	-800	reducing (0.05 M hydrazine; N_2)	0.044	Barnev (1984)	Freundlich-isotherm: S=KC^N; K=0.013, N= 0.94	Ra2
n.r.	sandstone *2	9.9	10.0	GR-2 groundwater *6	≈9	3E-07	f (0.003 µm)	-800	reducing (0.05 M hydrazine; N_2)	0.034	Barnev (1984)		Ra2
n.r.	sandstone *2	9.9	10.0	GR-2 groundwater *6	≈9	3E-06	f (0.003 µm)	-800	reducing (0.05 M hydrazine; N_2)	0.029	Barnev (1984)		Ra2
n.r.	sandstone *2	9.9	10.0	GR-2 groundwater *6	≈9	3E-09	f (0.003 µm)	-800	reducing (0.05 M hydrazine; N_2)	0.314	Barnev (1984)	Freundlich-isotherm: S=KC^N; K=0.046, N= 0.91	Ra2
n.r.	sandstone *2	9.9	10.0	GR-2 groundwater *6	≈9	3E-07	f (0.003 µm)	-800	reducing (0.05 M hydrazine; N_2)	0.206	Barnev (1984)		Ra2
n.r.	sandstone *2	9.9	10.0	GR-2 groundwater *6	≈9	3E-06	f (0.003 µm)	-800	reducing (0.05 M hydrazine; N_2)	0.169	Barnev (1984)		Ra2
n.r.	sandstone *2	9.9	10.0	GR-2 groundwater *6	≈9	3E-09	f (0.003 µm)	-800	reducing (0.05 M hydrazine; N_2)	0.244	Barnev (1984)	Freundlich-isotherm: S=KC^N; K=0.0037, N= 0.79	Ra2
n.r.	sandstone *2	9.9	10.0	GR-2 groundwater *6	≈9	3E-07	f (0.003 µm)	-800	reducing (0.05 M hydrazine; N_2)	0.093	Barnev (1984)		Ra2
n.r.	sandstone *2	9.9	10.0	GR-2 groundwater *6	≈9	3E-06	f (0.003 µm)	-800	reducing (0.05 M hydrazine; N_2)	0.057	Barnev (1984)		Ra2
IV	St. Bees sandstone *2	n.r.	50	cement-equilibrated water *6	11.0	1E-07	c (1500 g/15)	-500	reducing (0.05 M $NaHSO_3$, N_2)	> 10	Baston et al. (1992b)	Better phase separation procedure increases Kd	Th1
IV	St. Bees sandstone *2	n.r.	50	cement-equilibrated water *6	11.0	1E-07	c(1500 g/15), f(0.45 µm)	-500	reducing (0.05 M $NaHSO_3$, N_2)	> 10	Baston et al. (1992b)	Kd values slightly increase with increasing pH	Th1
IV	St. Bees sandstone *2	n.r.	50	cement-equilibrated water *6	11.0	1E-07	c(1500 g/15), f(30000 MWCO)	-500	reducing (0.05 M $NaHSO_3$, N_2)	> 10	Baston et al. (1992b)		Th1
IV	St. Bees sandstone *2	n.r.	50	cement-equilibrated water *6	7.9	1E-07	c (1500 g/15)	-360	reducing (0.05 M $NaHSO_3$, N_2)	12	Baston et al. (1992b)		Th1
IV	St. Bees sandstone *2	n.r.	50	cement-equilibrated water *6	7.9	1E-07	c(1500 g/15), f(0.45 µm)	-360	reducing (0.05 M $NaHSO_3$, N_2)	12	Baston et al. (1992b)		Th1
IV	St. Bees sandstone *2	n.r.	50	cement-equilibrated water *6	7.9	1E-07	c(1500 g/15), f(30000 MWCO)	-360	reducing (0.05 M $NaHSO_3$, N_2)	>10	Baston et al. (1992b)		Th1
VI	St. Bees sandstone *2	n.r.	50	cement-equilibrated water *6	10.9	1E-07	c(1500 g/15), f(30000 MWCO)	260	N_2 atmosphere *10	21	Baston et al. (1992b)		Th1
VI	St. Bees sandstone *2	n.r.	50	cement-equilibrated water *6	8.5	1E-07	c(1500 g/15), f(30000 MWCO)	140	N_2 atmosphere *10	0.12	Baston et al. (1992b)		Th1

Table 3: continued

redox state *1	solid phase *2	CEC *4 (meq/100g)	w/s ratio (mL/g)	water type *6	pH end *7	C init. (M)	phase sep. *9	Eh end (mV)	atm./redox condition	K_d (U) (m³/kg)	reference	additional information, remarks	code REF
IV	Caithness flagstones *2	n.r.	50	cement-equilibrated water *6	11.3	1E-07	c (1500 g/15)	-500	reducing (0,05 M $NaHSO_3$, N_2)	4.7	Baston et al. (1992b)	Better phase separation procedure increases Kd values	Th1
IV	Caithness flagstones *2	n.r.	50	cement-equilibrated water *6	11.3	1E-07	c(1500 g/15), f(0.45 µm)	-500	reducing (0.05 M $NaHSO_3$, N_2)	5.3	Baston et al. (1992b)	Kd values slightly increase with increasing pH	Th1
IV	Caithness flagstones *2	n.r.	50	cement-equilibrated water *6	11.3	1E-07	c(1500 g/15), f(30000 MWCO)	-500	reducing (0.05 M $NaHSO_3$, N_2)	5.8	Baston et al. (1992b)		Th1
IV	Caithness flagstones *2	n.r.	50	cement-equilibrated water *6	8.0	1E-07	c (1500 g/15)	-310	reducing (0.05 M $NaHSO_3$, N_2)	2.3	Baston et al. (1992b)		Th1
IV	Caithness flagstones *2	n.r.	50	cement-equilibrated water *6	8.0	1E-07	c(1500 g/15), f(0.45 µm)	-310	reducing (0.05 M $NaHSO_3$, N_2)	8.4	Baston et al. (1992b)		Th1
IV	Caithness flagstones *2	n.r.	50	cement-equilibrated water *6	8.0	1E-07	c(1500 g/15), f(30000 MWCO)	-310	reducing (0.05 M $NaHSO_3$, N_2)	3.4	Baston et al. (1992b)		Th1
n.r.	sandstone/claystone *2	n.r.	10.0	GR-1A groundwater *6	≈9	3E-09	f (0.003 µm)	-800	reducing (0.05 M hydrazine: N_2)	0.151	Barney (1984)	Freundlich-isotherm: S=KC^N: K=0.013, N= 0.88	Ra2
n.r.	sandstone/claystone *2	n.r.	10.0	GR-1A groundwater *6	≈9	3E-07	f (0.003 µm)	-800	reducing (0.05 M hydrazine: N_2)	0.087	Barney (1984)		Ra2
n.r.	sandstone/claystone *2	n.r.	10.0	GR-1A groundwater *6	≈9	3E-06	f (0.003 µm)	-800	reducing (0.05 M hydrazine: N_2)	0.066	Barney (1984)		Ra2
n.r.	sandstone/claystone *2	n.r.	10.0	GR-1A groundwater *6	≈9	3E-09	f (0.003 µm)	-800	reducing (0.05 M hydrazine: N_2)	1.129	Barney (1984)	Freundlich-isotherm: S=KC^N; K=0.015, N= 0.79	Ra2
n.r.	sandstone/claystone *2	n.r.	10.0	GR-1A groundwater *6	≈9	3E-07	f (0.003 µm)	-800	reducing (0.05 M hydrazine: N_2)	0.429	Barney (1984)		Ra2
n.r.	sandstone/claystone *2	n.r.	10.0	GR-1A groundwater *6	≈9	3E-06	f (0.003 µm)	-800	reducing (0.05 M hydrazine: N_2)	0.265	Barney (1984)		Ra2
n.r.	sandstone/claystone *2	n.r.	10.0	GR-1A groundwater *6	≈9	3E-09	f (0.003 µm)	600	oxidizing (air)	0.066	Barney (1984)	Freundlich-isotherm: S=KC^N: K=0.0004, N= 0.74	Ra2
n.r.	sandstone/claystone *2	n.r.	10.0	GR-1A groundwater *6	≈9	3E-07	f (0.003 µm)	600	oxidizing (air)	0.020	Barney (1984)		Ra2
n.r.	sandstone/claystone *2	n.r.	10.0	GR-1A groundwater *6	≈9	3E-06	f (0.003 µm)	600	oxidizing (air)	0.011	Barney (1984)		Ra2
n.r.	sandstone/claystone *2	n.r.	10.0	GR-1A groundwater *6	≈9	3E-09	f (0.003 µm)	600	oxidizing (air)	0.630	Barney (1984)	Freundlich-isotherm: S=KC^N; K=0.252, N= 0.96	Ra2
n.r.	sandstone/claystone *2	n.r.	10.0	GR-1A groundwater *6	≈9	3E-07	f (0.003 µm)	600	oxidizing (air)	0.524	Barney (1984)		Ra2
n.r.	sandstone/claystone *2	n.r.	10.0	GR-1A groundwater *6	≈9	3E-06	f (0.003 µm)	600	oxidizing (air)	0.478	Barney (1984)		Ra2
IV	Interbed. sand/claystone *2	n.r.	n.r.	Synthetic goundwater *6	≈8	n.r.	n.r.	≈-400	reducing (0.1 M hydrazine)	0.10	Salter and Jacobs (1982)	Extract from extensive experimental works, experimental details are not reported.	Am4
n.r.	Interbed. sand/claystone *2	n.r.	n.r.	Synthetic goundwater *6	≈8	n.r.	n.r.	n.r.	oxidizing	0.03	Salter and Jacobs (1982)	Interbed material contains more highly sorptive clays and zeolites	Am4
d) other													
n.r.	sandy sediments *2	1 - 80	1.0	groundwater	7.00	1E-07	n.r.	-214	reducing (Ar, H_2)	0.373	Meier et al. (1994)		Pb3
n.r.	sandy sediments *2	1 - 80	1.0	groundwater	7.00	1E-07	n.r.	-271	reducing (Ar, H_2)	0.273	Meier et al. (1994)		Pb3
n.r.	sandy sediments *2	1 - 80	1.0	groundwater	7.00	1E-07	n.r.	-224	reducing (Ar, H_2)	0.403	Meier et al. (1994)		Pb3
n.r.	sandy sediments *2	1 - 80	1.0	groundwater	n.r.	1E-10 - 1E-7	n.r.	n.r.	aerob	0.0006-0.0051	Meier et al. (1994)	Langmuir Isotherm (cmax = 7.3E-8 mol/g; k= 2.8E7 ml/mol).	Pb3
n.r.	sandy sediments *2	1 - 80	3.5	groundwater	7.00	1E-07	n.r.	381	aerob	0.0026	Meier et al. (1994)	Short overview about wide range of experimental work. Lack of experimental details.	Pb3
n.r.	sandy sediments *2	1 - 80	1.4	groundwater	7.00	1E-07	n.r.	327	aerob	0.001	Meier et al. (1994)	desorption coefficients investigated	Pb3
n.r.	sandy sediments *2	1 - 80	1	groundwater	7.0	1E-07	n.r.	343	aerob	0.00	Meier et al. (1994)		Pb3

Table 4: Compilation of batch distribution coefficients for Np on rocks

redox state *1	solid phase *2	CEC *4 (meq/100g)	w/s ratio (mL/g)	water type *6	pH end *7	C init. (M)	phase sep. *9	Eh end (mV)	atm/redox condition	K_d (Np) (m^3/kg)	reference	additional information, remarks	code REF
a) plutonic rock													
IV	granite *2	n.r.	11.0	synthetic groundwater (aq293) *6	~8	≈1E-10	c(4000/50)	-150 - -210	reducing (Fe(II))	1.995262315	Allard et al. (1978)	careful experimental work	Ra1
V	granite *2	n.r.	11.0	synthetic groundwater (aq293) *6	~8	≈1E-10	c(4000/50)	n.r.	atmospheric conditions	0.063095734	Allard et al. (1978)		Ra1
IV	porphyric granite *2	n.r.	10.0	Allard water *6	8.6-8.7	n.r.	c, f (0.22 µm)	n.r.	reducing	2.67-2.76	Kaukonen et al. (1993)	careful, good documented experimental work	Np1
V	porphyritic granite *2	n.r.	10.0	Allard water *6	n.r.	n.r.	c, f (0.22 µm)	n.r.	oxic	0.043-0.046	Kaukonen et al. (1993)	several measurements under similar conditions	Np1
+IV / +V *1	Westerly granite *2	n.r.	6	PW	9.6	1.6E-08	n.r.	-200	reducing (N$_2$)	0.13	Bondietti and Francis (1979)		Np4
+IV / +V *1	Westerly granite *2	n.r.	6.0	PW	9.60	1.6E-08	n.r.	-200	reducing (N$_2$)	0.294	Bondietti and Francis (1979)		Np4
V (e)	granitic drill core samples *2	n.r.	n.r.	Allard water *6	n.r.	7.8E-05	c, f (0.22 µm)	n.r.	reducing (N$_2$)	0.007-0.015	Suksi et al. (1989)	conditions not very reducing (N$_2$), thus values for oxidising and reducing conditions similar	Np2
V (e)	granitic drill core samples *2	n.r.	n.r.	Allard water *6	n.r.	6.7E-05	c, f (0.22 µm)	n.r.	oxidizing (O$_2$)	0.003-0.16	Suksi et al. (1989)	Conversion factor from Ka to Kd values not very clear; Suksi et al. used Kd=0.37*Ka, while a factor of 370 might be more realistic.	Np2
n.r.	granodiorite	n.r.	5	de-ionised water*6	10.1	6.0E-09	centrifuged	-460	strong reducing conditions	0.2	Baston et al. (1997b)	In part, these data are also reported by Baston et al., 1997a [Np6]	Ac1
n.r.	granodiorite	n.r.	5	de-ionised water*6	10.1	6.0E-09	f (0.45 µm)	-460	strong reducing conditions	1.3	Baston et al. (1997b)		Ac1
n.r.	granodiorite	n.r.	5	de-ionised water*6	10.1	6.0E-09	10000 MWCO	-460	strong reducing conditions	3.2	Baston et al. (1997b)		Ac1
n.r.	granodiorite	n.r.	5	de-ionised water*6	9.6	6.0E-09	centrifuged	-470	strong reducing conditions	0.047	Baston et al. (1997b)		Ac1
n.r.	granodiorite	n.r.	5	de-ionised water*6	9.6	6.0E-09	f (0.45 µm)	-470	strong reducing conditions	0.79	Baston et al. (1997b)		Ac1
n.r.	granodiorite	n.r.	5	de-ionised water*6	9.6	6.0E-09	10000 MWCO	-470	strong reducing conditions	1	Baston et al. (1997b)		Ac1
n.r.	granodiorite	n.r.	5	synthetic deionized water	10.1	6.0E-09	f (0.45 µm)	-460	Reducing - (N2-Atmosphere)	1.3	Baston et al. (1997a)	strongly reducing conditions with sodium hydrosulfite	Np6
n.r.	granodiorite	n.r.	5	synthetic deionized water	10.1	6.0E-09	10000 MWCO	-460	Reducing - (N2-Atmosphere)	3.2	Baston et al. (1997a)		Np6
n.r.	granodiorite	n.r.	5	synthetic deionized water	9.6	6.0E-09	f (0.45 µm)	-470	Reducing - (N2-Atmosphere)	0.79	Baston et al. (1997a)		Np6
n.r.	granodiorite	n.r.	5	synthetic deionized water	9.6	6.0E-09	10000 MWCO	-470	Reducing - (N2-Atmosphere)	1	Baston et al. (1997a)		Np6
IV	hornblendite *2	n.r.	10.0	Syyry groundwater *6	9.40	1E-12	c, f (0.22 µm)	-169	reducing	1.342	Kaukonen et al. (1993)		Np1
IV	hornblendite *2	n.r.	10.0	Syyry groundwater *6	9.40	1E-09	c, f (0.22 µm)	-170	reducing	1.061	Kaukonen et al. (1993)		Np1
IV	hornblendite *2	n.r.	10.0	Syyry groundwater *6	9.40	1E-07	c, f (0.22 µm)	-169	reducing	1.177	Kaukonen et al. (1993)		Np1
V	hornblendite *2	n.r.	10.0	Allard water (1:10), 123 mg HCO$_3^-$ *6	n.r.	1E-13	c, f (0.22 µm)	321	oxic	0.017-0.018	Kaukonen et al. (1993)		Np1
V	hornblendite *2	n.r.	10.0	Allard water (1:10), 12.3 mg HCO$_3^-$ *6	n.r.	1E-13	c, f (0.22 µm)	321	oxic	0.043-0.049	Kaukonen et al. (1993)		Np1
V	hornblendite *2	n.r.	10.0	Allard water (1:10), <2 mg HCO$_3^-$ *6	n.r.	1E-13	c, f (0.22 µm)	321	oxic	0.061-0.156	Kaukonen et al. (1993)		Np1
V	gabbro *2	n.r.	10.0	Allard water (1:10), 123 mg HCO$_3^-$ *6	n.r.	1E-13	c, f (0.22 µm)	321	oxic	0.041-0.073	Kaukonen et al. (1993)		Np1
V	gabbro *2	n.r.	10.0	Allard water (1:10), 12.3 mg HCO$_3^-$ *6	n.r.	1E-13	c, f (0.22 µm)	321	oxic	0.083-0.125	Kaukonen et al. (1993)		Np1
V	gabbro *2	n.r.	10.0	Allard water (1:10), <2 mg HCO$_3^-$ *6	n.r.	1E-13	c, f (0.22 µm)	321	oxic	0.097-0.321	Kaukonen et al. (1993)		Np1
b) volcanic rock													
+IV/+V	McCoy basalt *2	n.r.	n.r.	synthetic groundwater GR-2	~ 10	3.2E-12	c, ultrafiltration	n.r.	reducing (0.05 M hydrazine; Ar)	6.88	Meyer et al. (1985)	Np solubility under reducing and oxic conditions > 9 E-7 M.	Np3
+IV/+V	McCoy basalt *2	n.r.	n.r.	synthetic groundwater GR-2	~ 10	1.0E-06	c, ultrafiltration	n.r.	reducing (0.05 M hydrazine; Ar)	0.195	Meyer et al. (1985)	K_d values would probabely increase with time	Np3
V	McCoy basalt *2	n.r.	n.r.	synthetic groundwater GR-2	~ 10	3.7E-12	c, ultrafiltration	n.r.	oxic	0.00098	Meyer et al. (1985)	K_d values increase with pH, no significant difference between oxic and anoxic conditions in NaCl	Np3
V	McCoy basalt *2	n.r.	n.r.	synthetic groundwater GR-3	~ 10	1.0E-06	c, ultrafiltration	n.r.	oxic	0.0037	Meyer et al. (1985)	The authors postulate that reduction to Np(IV) takes place after the adsorption.	Np3
+IV / +V *1	Sentinel Gap basalt *2	n.r.	6	PW	8.6	1.6E-08	n.r.	-140	reducing (N$_2$)	0.10	Bondietti and Francis (1979)		Np4
+IV / +V *1	Sentinel Gap basalt *2	n.r.	6	PW	8.6	1.6E-08	n.r.	-140	reducing (N$_2$)	0.21	Bondietti and Francis (1979)		Np4
+V *1	Oxidised Sentinel Gap basalt *2	n.r.	6	PW	8.6	1.6E-08	n.r.	n.r.	oxidizing	0.03	Bondietti and Francis (1979)		Np4
IV	Umantum basalt *2	n.r.	n.r.	Synthetic goundwater *6	9.4	n.r.	n.r.	~-400	reducing (0.1 M hydrazine)	0.20	Salter and Jacobs (1982)	Extract from extensive experimental works, experimental details are not reported.	Am4
n.r.	Umantum basalt *2	n.r.	n.r.	Synthetic goundwater *6	9.4	n.r.	n.r.	n.r.	oxidizing	0.02	Salter and Jacobs (1982)		Am4

Table 4: continued

redox state *1	solid phase *2	CEC *4 (meq/100g)	w/s ratio (mL/g)	water type *6	pH end *7	C init. (M)	phase sep. *9	Eh end (mV)	atm./redox condition	K_d (Np) (m³/kg)	reference	additional information, remarks	code REF
IV	greenstone *2	n.r.	10.0	Syyry groundwater *6	9.30	1E-12	c, f (0.22 µm)	-167	reducing	1.144	Kaukonen et al. (1993)		Np1
IV	greenstone *2	n.r.	10.0	Syyry groundwater *6	9.40	1E-09	c, f (0.22 µm)	-181	reducing	1.498	Kaukonen et al. (1993)		Np1
IV	greenstone *2	n.r.	10.0	Syyry groundwater *6	9.40	1E-07	c, f (0.22 µm)	-196	reducing	0.913	Kaukonen et al. (1993)		Np1
V	greenstone *2	n.r.	10.0	Allard water (1:10), 123 mg HCO_3^- *6	n.r.	1E-13	c, f (0.22 µm)	321	oxic	0.016-0.025	Kaukonen et al. (1993)		Np1
V	greenstone *2	n.r.	10.0	Allard water (1:10), 12.3 mg HCO_3^- *6	n.r.	1E-13	c, f (0.22 µm)	321	oxic	0.031-0.047	Kaukonen et al. (1993)		Np1
V	greenstone *2	n.r.	10.0	Allard water (1:10), <2 mg HCO_3^- *6	n.r.	1E-13	c, f (0.22 µm)	321	oxic	0.033-0.055	Kaukonen et al. (1993)		Np1
n.r.	tuff	n.r.	5	de-ionised water*6	9.4	6.0E-09	centrifuged	-310	strong reducing conditions	0.62	Baston et al. (1997b)	in part, these data are also reported by Baston et al., 1997a [Np6]	Ac1
n.r.	tuff	n.r.	5	de-ionised water*6	9.4	6.0E-09	f (0.45 µm)	-310	strong reducing conditions	0.81	Baston et al. (1997b)		Ac1
n.r.	tuff	n.r.	5	de-ionised water*6	9.4	6.0E-09	10000 MWCO	-310	strong reducing conditions	0.68	Baston et al. (1997b)		Ac1
n.r.	tuff	n.r.	5	de-ionised water*6	9.2	6.0E-09	centrifuged	-330	strong reducing conditions	0.32	Baston et al. (1997b)		Ac1
n.r.	tuff	n.r.	5	de-ionised water*6	9.2	6.0E-09	f (0.45 µm)	-330	strong reducing conditions	0.64	Baston et al. (1997b)		Ac1
n.r.	tuff	n.r.	5	de-ionised water*6	9.2	6.0E-09	10000 MWCO	-330	strong reducing conditions	0.21	Baston et al. (1997b)		Ac1
n.r.	tuff	n.r.	5	synthetic deionized water	9.4	6.0E-09	f (0.45 µm)	-310	Reducing - (N2-Atmosphere)	0.81	Baston et al. (1997a)	strongly reducing conditions with sodium hydrosulfite	Np6
n.r.	tuff	n.r.	5	synthetic deionized water	9.4	6.0E-09	10000 MWCO	-310	Reducing - (N2-Atmosphere)	0.68	Baston et al. (1997a)	strongly reducing conditions with sodium hydrosulfite	Np6
n.r.	tuff	n.r.	5	synthetic deionized water	9.2	6.0E-09	f (0.45 µm)	-330	Reducing - (N2-Atmosphere)	0.64	Baston et al. (1997a)	strongly reducing conditions with sodium hydrosulfite	Np6
n.r.	tuff	n.r.	5.0	synthetic deionized water	9.20	6E-09	10000 MWCO	-330	Reducing - (N2-Atmosphere)	0.21	Baston et al. (1997a)	strongly reducing conditions with sodium hydrosulfite	Np6
c) sedimentary rock													
(IV)	sandstone *2	9.9	10.0	GR-2 groundwater *6	≈9	3E-09	f (0.003 µm)	-600	reducing (0.05 M hydrazine; N_2)	1.629	Barney (1984)	Freundlich-isotherm: S=KC^N; K=3.5, N= 1.03	Ra2
(IV)	sandstone *2	9.9	10.0	GR-2 groundwater *6	≈9	3E-07	f (0.003 µm)	-600	reducing (0.05 M hydrazine; N_2)	1.871	Barney (1984)		Ra2
(IV)	sandstone *2	9.9	10.0	GR-2 groundwater *6	≈9	3E-06	f (0.003 µm)	-600	reducing (0.05 M hydrazine; N_2)	2.005	Barney (1984)		Ra2
(IV)	sandstone *2	9.9	10.0	GR-2 groundwater *6	≈9	3E-09	f (0.003 µm)	-600	reducing (0.05 M hydrazine; N_2)	0.019	Barney (1984)	Freundlich-isotherm: S=KC^N; K=1743, N= 1.36	Ra2
(IV)	sandstone *2	9.9	10.0	GR-2 groundwater *6	≈9	3E-07	f (0.003 µm)	-600	reducing (0.05 M hydrazine; N_2)	0.101	Barney (1984)		Ra2
(IV)	sandstone *2	9.9	10.0	GR-2 groundwater *6	≈9	3E-06	f (0.003 µm)	-600	reducing (0.05 M hydrazine; N_2)	0.232	Barney (1984)		Ra2
(IV)	sandstone/claystone *2	n.r.	10.0	GR-1A groundwater *6	≈9	3E-09	f (0.003 µm)	-600	reducing (0.05 M hydrazine; N_2)	2.277	Barney (1984)	Freundlich-isotherm: S=KC^N; K=0.034, N= 0.8	Ra2
(IV)	sandstone/claystone *2	n.r.	10.0	GR-1A groundwater *6	≈9	3E-07	f (0.003 µm)	-600	reducing (0.05 M hydrazine; N_2)	0.906	Barney (1984)	the increased CO_3 concentration in GR-1A groundwater	Ra2
(IV)	sandstone/claystone *2	n.r.	10.0	GR-1A groundwater *6	≈9	3E-06	f (0.003 µm)	-600	reducing (0.05 M hydrazine; N_2)	0.572	Barney (1984)	the Np sorption due to the formation of $Np(CO_3)_4^{4-}$.	Ra2
(IV)	sandstone/claystone *2	n.r.	10.0	GR-1A groundwater *6	≈9	3E-09	f (0.003 µm)	-600	reducing (0.05 M hydrazine; N_2)	0.239	Barney (1984)	Freundlich-isotherm: S=KC^N; K=0.016, N= 0.87	Ra2
(IV)	sandstone/claystone *2	n.r.	10.0	GR-1A groundwater *6	≈9	3E-07	f (0.003 µm)	-600	reducing (0.05 M hydrazine; N_2)	0.131	Barney (1984)		Ra2
(IV)	sandstone/claystone *2	n.r.	10.0	GR-1A groundwater *6	≈9	3E-06	f (0.003 µm)	-600	reducing (0.05 M hydrazine; N_2)	0.097	Barney (1984)		Ra2
(V)	sandstone/claystone *2	n.r.	10.0	GR-1A groundwater *6	≈9	3E-09	f (0.003 µm)	600	oxidizing (air)	0.125	Barney (1984)	Freundlich-isotherm: S=KC^N; K=0.0003, N= 0.69	Ra2
(V)	sandstone/claystone *2	n.r.	10.0	GR-1A groundwater *6	≈9	3E-07	f (0.003 µm)	600	oxidizing (air)	0.030	Barney (1984)		Ra2
(V)	sandstone/claystone *2	n.r.	10.0	GR-1A groundwater *6	≈9	3E-06	f (0.003 µm)	600	oxidizing (air)	0.015	Barney (1984)		Ra2
(V)	sandstone/claystone *2	n.r.	10.0	GR-1A groundwater *6	≈9	3E-09	f (0.003 µm)	600	oxidizing (air)	0.289	Barney (1984)	Freundlich-isotherm: S=KC^N; K=0.00055, N= 0.68	Ra2
(V)	sandstone/claystone *2	n.r.	10.0	GR-1A groundwater *6	≈9	3E-07	f (0.003 µm)	600	oxidizing (air)	0.068	Barney (1984)		Ra2
(V)	sandstone/claystone *2	n.r.	10.0	GR-1A groundwater *6	≈9	3E-06	f (0.003 µm)	600	oxidizing (air)	0.033	Barney (1984)		Ra2
IV	Interbed. sand/claystone *2	n.r.	n.r.	Synthetic goundwater *6	≈8	n.r.	n.r.	≈-400	reducing (0.1 M hydrazine)	0.50	Salter and Jacobs (1982)	Interbed material contains more highly sorptive clays and zeolites	Am4
n.r.	Interbed. sand/claystone *2	n.r.	n.r.	Synthetic goundwater *6	≈8	n.r.	n.r.	n.r.	oxidizing	0.04	Salter and Jacobs (1982)		Am4
d) other													
+IV / +V *1	marl & sandy sediments *2	n.r.	0.6	natural groundwater *6	n.r.	2E-04	n.r.	-146	Ar + 1% CO2	0.00000	Kim et al. (1994)	breakthrough curve, sorption low because of high organic content in groundwater (80 mg C/L).	Pa1
IV	sediments *2	n.r.	2.3 - 2.6	natural groundwater *6	7.00	4E-09	ultrafiltration	80	reducing	> 1	Lieser and Mühlenweg (1988)	During groundwater circulation, Np(V) is reduced to Np(IV). Experiments were performed for six other sediment and groundwater samples	Np5

Table 5: Compilation of batch distribution coefficients for Pu on rocks

redox state *1	solid phase *2	CEC *4 (meq/100g)	w/s ratio (mL/g)	water type *6	pH end *7	C init. (M)	phase sep. *9	Eh end (mV)	atm./redox condition	K_d (Pu) (m³/kg)	reference	additional information, remarks	code REF
a) plutonic rock													
n.r.	granite *2	n.r.	11	synthetic groundwater (aq293) *6	~8	~1E-8	c(4000/50)	-150 - -210	reducing (Fe(II))	>0.3	Allard et al. (1978)	careful experimental work	Ra1
n.r.	granite *2	n.r.	11	synthetic groundwater (aq293) *6	~8	~1E-8	c(4000/50)	n.r.	atmospheric conditions	>0.3	Allard et al. (1978)	not so clear if the values are measured in reducing or oxidizing environment	Ra1
n.r.	granitic drill core samples *2	n.r.	n.r.	Allard water *6	n.r.	4.70E-14	c, f (0.22 µm)	n.r.	N_2	0.024-0.05	Suksi et al. (1989)	conditions not very reducing (N_2), thus values for oxidising and reducing conditions similar	Np2
n.r.	granitic drill core samples *2	n.r.	n.r.	Allard water *6	n.r.	1.80E-14	c, f (0.22 µm)	n.r.	oxidizing (O_2)	0.034-0.1	Suksi et al. (1989)	Conversion factor from Ka to Kd values not very clear; Suksi et al. used Kd=0.37*Ka, while a factor of 370 might be more realistic.	Np2
n.r. *1	Climax Stock granite CS5 *2	<1 *4	20	pre-equilibrated synthetic groundwater *6	8.23	~1E-12	4 × c(12000 rpm, 1h)	n.r.	atmospheric conditions	1.4	Erdal et al. (1979)	desorption values are also recorded	U2
n.r. *1	Climax Stock granite CS5 *2	<1 *4	20	pre-equilibrated synthetic groundwater *6	8.36	~1E-12	4 × c(12000 rpm, 1h)	n.r.	atmospheric conditions	2.3	Erdal et al. (1979)		U2
n.r. *1	Climax Stock granite CS5 *2	<1 *4	20	pre-equilibrated synthetic groundwater *6	8.29	~1E-12	4 × c(12000 rpm, 1h)	n.r.	atmospheric conditions	3.5	Erdal et al. (1979)		U2
n.r. *1	Climax Stock granite CS5 *2	<1 *4	20	pre-equilibrated synthetic groundwater *6	8.38	~1E-12	4 × c(12000 rpm, 1h)	n.r.	atmospheric conditions	9.4	Erdal et al. (1979)		U2
n.r. *1	Climax Stock granite CS7 *2	<1-2 *4	20	pre-equilibrated synthetic groundwater *6	7.9	~1E-12	4 × c(12000 rpm, 1h)	n.r.	atmospheric conditions	1.1	Erdal et al. (1979)		U2
n.r. *1	Climax Stock granite CS7 *2	<1-2 *4	20	pre-equilibrated synthetic groundwater *6	8.37	~1E-12	4 × c(12000 rpm, 1h)	n.r.	atmospheric conditions	2.9	Erdal et al. (1979)		U2
n.r. *1	Climax Stock granite CS7 *2	<1-2 *4	20	pre-equilibrated synthetic groundwater *6	8.35	~1E-12	4 × c(12000 rpm, 1h)	n.r.	atmospheric conditions	3.6	Erdal et al. (1979)		U2
n.r. *1	Climax Stock granite CS7 *2	<1-2 *4	20	pre-equilibrated synthetic groundwater *6	n.r.	~1E-12	4 × c(12000 rpm, 1h)	n.r.	atmospheric conditions	25	Erdal et al. (1979)		U2
+IV	hornblendite *2	n.r.	10.0	Syyry groundwater *6	9.70	2.16E-12	c, f (0.22 µm)	-52	reducing	19	Kaukonen et al. (1993)	careful, good documented experimental work	Np1
+IV	hornblendite *2	n.r.	10.0	Syyry groundwater *6	9.70	4.19E-10	c, f (0.22 µm)	-69	reducing	14.2	Kaukonen et al. (1993)	several measurements under similar conditions	Np1
+IV	hornblendite *2	n.r.	10.0	Syyry groundwater *6	9.70	4.23E-08	c, f (0.22 µm)	-70	reducing	31.2	Kaukonen et al. (1993)		Np1
n.r.	hornblendite *2	n.r.	10.0	Allard water (1:10), 123 mg HCO_3^- *6	n.r.	1.90E-12	c, f (0.22 µm)	321	oxic	4.499	Kaukonen et al. (1993)		Np1
n.r.	hornblendite *2	n.r.	10.0	Allard water (1:10), 123 mg HCO_3^- *6	n.r.	8.80E-11	c, f (0.22 µm)	321	oxic	4.027	Kaukonen et al. (1993)		Np1
n.r.	hornblendite *2	n.r.	10.0	Allard water (1:10), 123 mg HCO_3^- *6	n.r.	8.60E-09	c, f (0.22 µm)	321	oxic	8.337	Kaukonen et al. (1993)		Np1
n.r.	hornblendite *2	n.r.	10.0	Syyry groundwater *6	n.r.	1.00E-12	c, f (0.22 µm)	328	oxic	0.931	Kaukonen et al. (1993)		Np1
n.r.	hornblendite *2	n.r.	10.0	Syyry groundwater *6	n.r.	8.10E-11	c, f (0.22 µm)	328	oxic	1.624	Kaukonen et al. (1993)		Np1
n.r.	hornblendite *2	n.r.	10.0	Syyry groundwater *6	n.r.	8.20E-09	c, f (0.22 µm)	328	oxic	1.858	Kaukonen et al. (1993)		Np1
n.r.	gabbro *2	n.r.	10.0	Allard water (1:10), 123 mg HCO_3^- *6	n.r.	1.96E-12	c, f (0.22 µm)	321	oxic	1.259	Kaukonen et al. (1993)		Np1
n.r.	gabbro *2	n.r.	10.0	Allard water (1:10), 123 mg HCO_3^- *6	n.r.	7.10E-11	c, f (0.22 µm)	321	oxic	1.629	Kaukonen et al. (1993)		Np1
n.r.	gabbro *2	n.r.	10	Allard water (1:10), 123 mg HCO_3^- *6	n.r.	9.80E-09	c, f (0.22 µm)	321	oxic	2.594	Kaukonen et al. (1993)		Np1
b) volcanic rock													
IV	Umantum basalt *2	n.r.	n.r.	Synthetic goundwater *6	9.4	n.r.	n.r.	~-400	reducing (0.1 M hydrazine)	0.02	Salter and Jacobs (1982)		Am4
n.r.	Umantum basalt *2	n.r.	n.r.	Synthetic goundwater *6	9.4	n.r.	n.r.	n.r.	oxidizing	0.02	Salter and Jacobs (1982)	Oxic:Freundlich Isotherm: S=0,98*C^1,12	Am4
+IV	Sodankylä vulcanite *2	n.r.	10.0	Syyry groundwater *6	9.30	2.24E-12	c, f (0.22 µm)	-55	reducing	18.6	Kaukonen et al. (1993)		Np1
+IV	Sodankylä vulcanite *2	n.r.	10.0	Syyry groundwater *6	8.90	4.23E-10	c, f (0.22 µm)	-60	reducing	31.2	Kaukonen et al. (1993)		Np1
+IV	Sodankylä vulcanite *2	n.r.	10.0	Syyry groundwater *6	9.20	4.22E-08	c, f (0.22 µm)	-57	reducing	18.5	Kaukonen et al. (1993)		Np1
n.r.	Sodankylä vulcanite *2	n.r.	10.0	Allard water (1:10), 123 mg HCO_3^- *6	n.r.	1.02E-12	c, f (0.22 µm)	321	oxic	6.3	Kaukonen et al. (1993)		Np1
n.r.	Sodankylä vulcanite *2	n.r.	10.0	Allard water (1:10), 123 mg HCO_3^- *6	n.r.	8.70E-11	c, f (0.22 µm)	321	oxic	123	Kaukonen et al. (1993)		Np1
n.r.	Sodankylä vulcanite *2	n.r.	10.0	Allard water (1:10), 123 mg HCO_3^- *6	n.r.	9.10E-09	c, f (0.22 µm)	321	oxic	8.506	Kaukonen et al. (1993)		Np1
n.r.	tuff *2	n.r.	50	synthetic groundwater *6	7-8	1.00E-10	f (0.45 µm, 30000 MWCO)	n.r.	N_2 atmosphere *10	1.5-250	Berry et al. (1995)	Blank experiments to monitor radionuclide behavior, also experiments with fractured infill materials	U3
n.r.	tuff *2	n.r.	50	high-pH synthetic groundwater *6	12-13	1.00E-10	f (0.45 µm, 30000 MWCO)	n.r.	N_2 atmosphere *10	1.8-77	Berry et al. (1995)	The Kd ranges represent several experiments with different tuff samples	U3
IV (e)	grey-green tuff *2	n.r.	50	synthetic groundwater *6	~8	2E-11	f (0.45 µm, 30000 MWCO)	n.r.	N_2 atmosphere *10	215	Baston et al. (1994)	Blank experiments to monitor radionuclide behavior.	Th2
IV (e)	red tuff *2	n.r.	50	synthetic groundwater *6	~8	2E-11	f (0.45 µm, 30000 MWCO)	n.r.	N_2 atmosphere *10	37	Baston et al. (1994)	Phase separation technique (no f; f(0.45 µm); f (30'000 MWCO)) had no influence on Kd values	Th2
IV (e)	grey-green tuff *2	n.r.	50	synthetic groundwater *6	~12	2E-11	f (0.45 µm, 30000 MWCO)	n.r.	N_2 atmosphere *10	90	Baston et al. (1994)		Th2
IV (e)	red tuff *2	n.r.	50	synthetic groundwater *6	~12	2E-11	f (0.45 µm, 30000 MWCO)	n.r.	N_2 atmosphere *10	2.4	Baston et al. (1994)		Th2
n.r.	tuff *2	2-100 *4	20	natural groundwater	~ 8.5	n.r.	4 times c(16'000 rpm, 1h)	n.r.	atmospheric conditions	0.084-0.25	Vine et al. (1980a)	All experimental details taken from Wolfsberg et al. (1981)	Pu1
n.r.	tuff *2	2-100 *4	20	natural groundwater	~ 8.5	n.r.	4 times c(16'000 rpm, 1h)	n.r.	N_2 atmosphere	0.12-0.8	Vine et al. (1980a)	cf. Pu2, Pu3 and Pu4	Pu1

Table 5: continued

redox state *1	solid phase *2	CEC *4 (meq/100g)	w/s ratio (mL/g)	water type *6	pH end *7	C init. (M)	phase sep. *9	Eh end (mV)	atm./redox condition	K_d (Pu) (m^3/kg)	reference	additional information, remarks	code REF
n.r.	de-vitrified tuff JM-22 *2	2-3 *4	20	natural groundwater	≈ 8.5	n.r.	4 × c(16000 rpm, 1h)	n.r.	atmospheric conditions	0.14	Wolfsberg et al. (1981)	cf. Pu1, Pu2, Pu3	Pu4
n.r.	de-vitrified tuff JM-22 *2	2-3 *4	20	natural groundwater	≈ 8.5	n.r.	4 × c(16000 rpm, 1h)	n.r.	N_2 atmosphere	0.22	Wolfsberg et al. (1981)	desorption values are also recorded	Pu4
n.r.	vitric tuff JM-38 *2	54-109 *4	20	natural groundwater	≈ 8.5	n.r.	4 × c(16000 rpm, 1h)	n.r.	atmospheric conditions	0.25	Wolfsberg et al. (1981)		Pu4
n.r.	vitric tuff JM-38 *2	54-109 *4	20	natural groundwater	≈ 8.5	n.r.	4 × c(16000 rpm, 1h)	n.r.	N_2 atmosphere	0.8	Wolfsberg et al. (1981)		Pu4
n.r.	de-vitrified tuff JM-54 *2	4 *4	20	natural groundwater	≈ 8.5	n.r.	4 × c(16000 rpm, 1h)	n.r.	atmospheric conditions	0.084	Wolfsberg et al. (1981)		Pu4
n.r.	de-vitrified tuff JM-54 *2	4 *4	20	natural groundwater	≈ 8.5	n.r.	4 × c(16000 rpm, 1h)	n.r.	N_2 atmosphere	0.12	Wolfsberg et al. (1981)		Pu4
n.r.	vitric tuff *2	44-80 *4	20	natural groundwater	≈ 8	n.r.	4 × c(16000 rpm, 1h)	n.r.	atmospheric conditions	0.17	Erdal et al. (1978)	Some experimental details taken from Wolfsberg et al. (1979)	Pu2
n.r.	de-vitrified tuff *2	2-3 *4	20	natural groundwater	≈ 8	n.r.	4 × c(16000 rpm, 1h)	n.r.	atmospheric conditions	0.11	Erdal et al. (1978)	cf. Pu1, Pu3 and Pu4	Pu2
n.r.	zeolitized tuff *2	18-30 *4	20	natural groundwater	≈ 8	n.r.	4 × c(16000 rpm, 1h)	n.r.	atmospheric conditions	0.28	Erdal et al. (1978)		Pu2
n.r.	vitric tuff JA-18 *2	44-80 *4	20	natural groundwater *6	≈ 8	n.r.	c(12'000 rpm, 1h)	n.r.	atmospheric conditions	0.14	Wolfsberg et al. (1979)	cf. Pu1, Pu2 and Pu4	Pu3
n.r.	de-vitrified tuff JA-32 *2	2-3 *4	20	natural groundwater *6	≈ 8	n.r.	c(12'000 rpm, 1h)	n.r.	atmospheric conditions	0.11	Wolfsberg et al. (1979)		Pu3
n.r.	zeolitized tuff JA-37 *2	18-30 *4	20	natural groundwater *6	≈ 8	n.r.	c(12'000 rpm, 1h)	n.r.	atmospheric conditions	0.28	Wolfsberg et al. (1979)		Pu3
c) sedimentary rock													
+IV	St. Bees sandstone *2	n.r.	50	cement-equilibrated water *6	11.7	1E-10	c (1500 g/15)	n.r.	N_2 atmosphere *10	>10	Baston et al. (1992b)		Th1
+IV	St. Bees sandstone *2	n.r.	50	cement-equilibrated water *6	11.7	1E-10	c(1500 g/15), f(0.45 µm)	n.r.	N_2 atmosphere *10	>10	Baston et al. (1992b)		Th1
+IV	St. Bees sandstone *2	n.r.	50	cement-equilibrated water *6	11.7	1E-10	c(1500 g/15), f(30000 MWCO)	n.r.	N_2 atmosphere *10	>10	Baston et al. (1992b)	Phase separation procedure has hardly an influence on Kd values	Th1
+IV	St. Bees sandstone *2	n.r.	5	cement-equilibrated water *6	11.2	1E-10	c(1500 g/15), f(30000 MWCO)	n.r.	N_2 atmosphere *10	>3	Baston et al. (1992b)	Kd values decrease with increasing s/w ratios.	Th1
+IV	St. Bees sandstone *2	n.r.	50	cement-equilibrated water *6	8.8	1E-10	c(1500 g/15), f(30000 MWCO)	n.r.	N_2 atmosphere *10	>10	Baston et al. (1992b)	Kd values slightly increase with increasing pH	Th1
+IV	St. Bees sandstone *2	n.r.	50	cement-equilibrated water *6	7.9	1E-10	c(1500 g/15), f(30000 MWCO)	n.r.	N_2 atmosphere *10	>10	Baston et al. (1992b)		Th1
+IV	St. Bees sandstone *2	n.r.	5	cement-equilibrated water *6	8.2	1E-10	c(1500 g/15), f(30000 MWCO)	n.r.	N_2 atmosphere *10	2.8	Baston et al. (1992b)		Th1
+IV	St. Bees sandstone *2	n.r.	5	cement-equilibrated water *6	8.1	1E-10	c(1500 g/15), f(30000 MWCO)	n.r.	N_2 atmosphere *10	>3	Baston et al. (1992b)		Th1
(V) or (VI)	sandstone/claystone *2	n.r.	10.0	GR-1A groundwater *6	≈9	3E-09	f (0.003 µm)	600	oxidizing (air)	1.64	Barney (1984)	Freundlich-Isotherm: S=KC^N; K=0.506, N= 0.95	Re2
(V) or (VI)	sandstone/claystone *2	n.r.	10.0	GR-1A groundwater *6	≈9	3E-07	f (0.003 µm)	600	oxidizing (air)	1.31	Barney (1984)	Presence of hydrazine greatly increases sorption.	Re2
(V) or (VI)	sandstone/claystone *2	n.r.	10.0	GR-1A groundwater *6	≈9	3E-06	f (0.003 µm)	600	oxidizing (air)	1.16	Barney (1984)		Re2
(V) or (VI)	sandstone/claystone *2	n.r.	10.0	GR-1A groundwater *6	≈9	3E-09	f (0.003 µm)	600	oxidizing (air)	1.31	Barney (1984)	Freundlich-isotherm: S=KC^N; K=0.014, N= 0.76	Re2
(V) or (VI)	sandstone/claystone *2	n.r.	10.0	GR-1A groundwater *6	≈9	3E-07	f (0.003 µm)	600	oxidizing (air)	0.48	Barney (1984)		Re2
(V) or (VI)	sandstone/claystone *2	n.r.	10.0	GR-1A groundwater *6	≈9	3E-06	f (0.003 µm)	600	oxidizing (air)	0.29	Barney (1984)		Re2
IV	Interbed. sand/claystone *2	n.r.	n.r.	Synthetic goundwater *6	≈8	n.r.	n.r.	≈ -400	red. (0.1 M hydrazine)	0.50	Salter and Jacobs (1982)	Extract from extensive experimental works, experimental details are not reported.	Am4
n.r.	Interbed. sand/claystone *2	n.r.	n.r.	Synthetic goundwater *6	≈8	n.r.	n.r.	n.r.	oxidizing	0.3	Salter and Jacobs (1982)	interbed material contains more highly sorptive clays and zeolites	Am4
d) other													
+IV	sandy sediments *2	n.r.	1.5	groundwater Gohy-1061 *6	8.20	2E-09	f(unfiltered)	n.r.	n.r. (reducing ?)	0.006	Kim et al. (1989)	Extract of many experiments, experimental details are described elsewhere.	Am2
+IV	sandy sediments *2	n.r.	1.5	groundwater Gohy-1061 *6	8.20	2E-09	f(0.45 µm)	n.r.	n.r. (reducing ?)	0.093	Kim et al. (1989)	filter size has a huge influence on Kd values, because of a relatively high colloid concentration.	Am2
+IV	sandy sediments *2	n.r.	1.5	groundwater Gohy-1061 *6	8.20	2E-09	f(0.002 µm)	n.r.	n.r. (reducing ?)	3.4	Kim et al. (1989)	Concentration of Pu has only a small influence on Kd values	Am2
+IV	sandy sediments *2	n.r.	1.5	groundwater Gohy-1061 *6	8.20	3E-07	f(unfiltered)	n.r.	n.r. (reducing ?)	0.010	Kim et al. (1989)		Am2
+IV	sandy sediments *2	n.r.	1.5	groundwater Gohy-1061 *6	8.20	3E-07	f(0.45 µm)	n.r.	n.r. (reducing ?)	0.22	Kim et al. (1989)		Am2
+IV	sandy sediments *2	n.r.	1.5	groundwater Gohy-1061 *6	8.2	2.50E-07	f(0.002 µm)	n.r.	n.r. (reducing ?)	4.28	Kim et al. (1989)		Am2

Table 6: Compilation of batch distribution coefficients for Pu on bentonite

redox state *1	solid phase *2	CEC *4 (meq/100g)	w/s ratio (mL/g)	water type *6	pH end *7	C init. (M)	phase sep. *9	Eh end (mV)	atm./redox condition	K_d (Pu) (m^3/kg)	reference	additional information, remarks	code REF
IV	bentonite	64	200	PW	6.0	8E-05	n.r.	n.r.	n.r. (reducing)	130	Billon (1982)	redox conditions not clear	Pu7
IV	bentonite	64	200	PW	7.9	8E-05	n.r.	n.r.	n.r. (reducing)	70	Billon (1982)	Kd-values for Pu(IV) are independent of pH	Pu7
IV	bentonite	64	200	PW	9.0	8E-05	n.r.	n.r.	n.r. (reducing)	130	Billon (1982)	system is probably oversaturated with respect to Pu-solid phase	Pu7
VI	bentonite	64	200	PW	5.7	6E-06	n.r.	n.r.	n.r. (oxic)	0.25	Billon (1982)	Kd-values for Pu(VI) strongly depend on pH	Pu7
VI	bentonite	64	200	PW	6.2	6E-06	n.r.	n.r.	n.r. (oxic)	0.5	Billon (1982)	system is possibly oversaturated with respect to Pu-solid phase	Pu7
VI	bentonite	64	200	PW	6.6	6E-06	n.r.	n.r.	n.r. (oxic)	6.31	Billon (1982)		Pu7
VI	bentonite	64	200	PW	7.5	6E-06	n.r.	n.r.	n.r. (oxic)	63.1	Billon (1982)		Pu7
+IV or +III	Bentonite * 2	75 - 80	100	Synthetic groundwater *6	8.5	6E-08	c (27000/60)	n.r.	inert (N_2)	3.5	Allard et al. (1982)	ambient conditions	Pu9
+IV or +III	Bentonite * 2	75 - 80	100	Synthetic groundwater *6	8.5	6E-10	c (27000/60)	n.r.	inert (N_2)	3.5	Allard et al. (1982)	ambient conditions	Pu9
n.r.	bentonite	n.r.	1000	PW	5.5	n.r.	f (0.20 µm)	n.r.	n.r.	8.0	Kudo et al. (1997)	sorption data on sulfate-reducing bacteria also available	Pu10
n.r.	bentonite	n.r.	1000	PW	8.1	n.r.	f (0.20 µm)	n.r.	n.r.	6.0	Kudo et al. (1997)		Pu10
n.r.	bentonite	n.r.	1000	PW	10.5	n.r.	f (0.20 µm)	n.r.	n.r.	7.0	Kudo et al. (1997)		Pu10
n.r.	bentonite/quartz *2	n.r.	11	synthetic groundwater (aq293) *6	≈8	≈1E-8	c(4000/50)	n.r.	atmospheric conditions	0.2	Allard et al. (1978)	not so clear if the values are measured in reducing or oxidizing environment	Ra1
IV	clay/sand (10/90) *2	8 *4	0.3	synthetic groundwater *6	8	5E-09	c, f(0.45 µm)	n.r.	mildly reducing (NO_2^-)	0.15	Sharma and Oscarson (1989)	Kd value increases with fraction of clay present (only bentonite: Kd ≈ 1.5)	Pu8
IV	clay/sand (25/75) *2	21 *4	0.3	synthetic groundwater *6	8	5E-09	c, f(0.45 µm)	n.r.	mildly reducing (NO_2^-)	0.37	Sharma and Oscarson (1989)		Pu8
IV	clay/sand (50/50) *2	41 *4	0.3	synthetic groundwater *6	8	5E-09	c, f(0.45 µm)	n.r.	mildly reducing (NO_2^-)	0.77	Sharma and Oscarson (1989)		Pu8
n.r.	boom clay *2	n.r.	1	synthetic porewater *6	n.r.	n.r.	c(25'500 g/120)	–(460-500)	anaerobic	0.32	Henrion et al. (1986)	extract from many experiments, some experimental	Pu5
n.r.	boom clay *2	n.r.	24	synthetic porewater *6	n.r.	n.r.	c(25'500 g/120)	–(460-500)	anaerobic	1.97	Henrion et al. (1986)	details not reported, careful experimental work	Pu5
n.r.	boom clay *2	n.r.	1	synthetic porewater *6	n.r.	n.r.	f(40'000 MWCO)	–(460-500)	anaerobic	2.08	Henrion et al. (1986)	Strong influence of s/w ratio and of phase separation technique	Pu5
n.r.	boom clay *2	n.r.	2	synthetic porewater *6	n.r.	n.r.	f(40'000 MWCO)	–(460-500)	anaerobic	2.73	Henrion et al. (1986)	Most of the Pu is assumed to be sorbed by the organic material.	Pu5
n.r.	boom clay *2	n.r.	5	synthetic porewater *6	n.r.	n.r.	f(40'000 MWCO)	–(460-500)	anaerobic	4.91	Henrion et al. (1986)	Oxic condition did not change the sorption significantly!	Pu5
n.r.	boom clay *2	n.r.	10	synthetic porewater *6	n.r.	n.r.	f(40'000 MWCO)	–(460-500)	anaerobic	5.26	Henrion et al. (1986)		Pu5
n.r.	boom clay *2	n.r.	12	synthetic porewater *6	n.r.	n.r.	f(40'000 MWCO)	–(460-500)	anaerobic	5.57	Henrion et al. (1986)		Pu5
n.r.	boom clay *2	n.r.	24	synthetic porewater *6	n.r.	n.r.	f(40'000 MWCO)	–(460-500)	anaerobic	8.59	Henrion et al. (1986)		Pu5
IV	kaolinite *2	14	n.r.	synthetic saline groundwater (TDS 180) *6	n.r.	n.r.	n.r.	n.r.	<0.5 ppm O_2	1.5	Ticknor et al. (1991), Ticknor (1993)	extract from many experiments, some experimental details not reported	Pu6
IV	kaolinite *2	14	n.r.	synthetic saline groundwater (TDS 11000) *6	n.r.	n.r.	n.r.	n.r.	<0.5 ppm O_2	3.7	Ticknor et al. (1991), Ticknor (1993)	Pu sorption increses with increasing surface area.	Pu6
IV	illite *2	16	n.r.	synthetic saline groundwater (TDS 180) *6	n.r.	n.r.	n.r.	n.r.	<0.5 ppm O_2	1.2	Ticknor et al. (1991), Ticknor (1993)	Conditions probabely not really reduing, O_2 still detected	Pu6
IV	chlorite *2	1.7	n.r.	synthetic saline groundwater (TDS 180) *6	n.r.	n.r.	n.r.	n.r.	<0.5 ppm O_2	0.2	Ticknor et al. (1991), Ticknor (1993)		Pu6
V, VI	kaolinite *2	14	n.r.	synthetic saline groundwater (TDS 180) *6	n.r.	n.r.	n.r.	n.r.	oxic	1.5	Ticknor et al. (1991), Ticknor (1993)	no difference between oxic and anoxic conditions	Pu6

Table 7: Compilation of batch distribution coefficients for Am on rocks

solid phase *2	CEC *4 (meq/100g)	w/s ratio (mL/g)	water type *6	pH end *7	C init. (M)	phase sep. *9	Eh end (mV)	atm./redox condition	K_d (Am) (m^3/kg)	reference	additional information, remarks	code REF
a) plutonic rock												
Climax Stock granite CS5 *2	<1 *4	20	pre-equilibrated synthetic groundwater *6	8.23	~1E-6	4 × c(12000 rpm, 1h)	n.r.	atmospheric conditions	1.2	Erdal et al. (1979)	desorption values are also recorded	U2
Climax Stock granite CS5 *2	<1 *4	20	pre-equilibrated synthetic groundwater *6	8.36	~1E-6	4 × c(12000 rpm, 1h)	n.r.	atmospheric conditions	8.7	Erdal et al. (1979)		U2
Climax Stock granite CS5 *2	<1 *4	20	pre-equilibrated synthetic groundwater *6	8.29	~1E-6	4 × c(12000 rpm, 1h)	n.r.	atmospheric conditions	6.2	Erdal et al. (1979)		U2
Climax Stock granite CS5 *2	<1 *4	20	pre-equilibrated synthetic groundwater *6	8.36	~1E-6	4 × c(12000 rpm, 1h)	n.r.	atmospheric conditions	18	Erdal et al. (1979)		U2
Climax Stock granite CS7 *2	<1-2 *4	20	pre-equilibrated synthetic groundwater *6	7.9	~1E-6	4 × c(12000 rpm, 1h)	n.r.	atmospheric conditions	2.2	Erdal et al. (1979)		U2
Climax Stock granite CS7 *2	<1-2 *4	20	pre-equilibrated synthetic groundwater *6	8.37	~1E-6	4 × c(12000 rpm, 1h)	n.r.	atmospheric conditions	3.7	Erdal et al. (1979)		U2
Climax Stock granite CS7 *2	<1-2 *4	20	pre-equilibrated synthetic groundwater *6	8.35	~1E-6	4 × c(12000 rpm, 1h)	n.r.	atmospheric conditions	2.3	Erdal et al. (1979)		U2
Climax Stock granite CS7 *2	<1-2 *4	20	pre-equilibrated synthetic groundwater *6	n.r.	~1E-6	4 × c(12000 rpm, 1h)	n.r.	atmospheric conditions	63	Erdal et al. (1979)		U2
granite *2	n.r.	11	synthetic groundwater (aq293) *6	~8	~1E-8	c(4000/50)	-150 - -210	reducing (Fe(II))	32	Allard et al. (1978)	careful experimental work	Ra1
granite *2	n.r.	11	synthetic groundwater (aq293) *6	~8	~1E-8	c(4000/50)	n.r.	atmospheric conditions	32	Allard et al. (1978)	not so clear if the values are measured in reducing or oxidizing environment	Ra1
rapavikl granite *2	n.r.	10.0	Allard water *6	n.r.	1.10E-09	n.r.	n.r.	oxidizing (air)	7.0	Pinnioja et al. (1984)		Am1
granite *2	n.r.	66	Allard water *6	8-9	1E-09	c(4000 g/60)	n.r.	n.r.	4-7	Allard and Beall (1979)	Kd values calculated from Kd values measured for rock composing minerals (cf footnote *2).	Am3
tonalite *2	n.r.	10	Allard water *6	n.r.	1.10E-09	n.r.	n.r.	oxidizing (air)	4.7	Pinnioja et al. (1984)		Am1
b) volcanic rocks												
basalt *2	n.r.	66	Allard water *6	8-9	1E-09	c(4000 g/60)	n.r.	n.r.	2-6	Allard and Beall (1979)		Am3
Umantum basalt *2	n.r.	n.r.	Synthetic goundwater *6	9.4	n.r.	n.r.	n.r.	oxidizing	0.34	Salter and Jacobs (1982)	Extract from extensive experimental works, experimental details are not reported.	Am4
tuff *2	2-100 *4	20	natural groundwater	~ 8.5	n.r.	4 × c(16000 rpm, 1h)	n.r.	atmospheric conditions	0.59-4	Vine et al. (1980a)	All experimental details taken from Wolfsberg et al. (1981)	Pu1
tuff *2	2-100 *4	20	natural groundwater	~ 8.5	n.r.	4 × c(16000 rpm, 1h) 4 × c(16000 rpm, 1h)	n.r.	N$_2$ atmosphere	1-5.6	Vine et al. (1980a)	cf. Pu2, Pu3 and Pu4	Pu1
vitric tuff *2	44-80 *4	20	natural groundwater	~ 8	n.r.	4 × c(16000 rpm, 1h)	n.r.	atmospheric conditions	0.17	Erdal et al. (1978)	Some experimental details taken from Wolfsberg et al. (1979)	Pu2
vitric tuff *2	44-80 *4	20	natural groundwater	~ 8	n.r.	4 × c(16000 rpm, 1h)	n.r.	atmospheric conditions	0.22	Erdal et al. (1978)	cf. Pu1, Pu3 and Pu4	Pu2
de-vitrified tuff *2	2-3 *4	20	natural groundwater	~ 8	n.r.	4 × c(16000 rpm, 1h)	n.r.	atmospheric conditions	0.11	Erdal et al. (1978)		Pu2
de-vitrified tuff *2	2-3 *4	20	natural groundwater	~ 8	n.r.	4 × c(16000 rpm, 1h)	n.r.	atmospheric conditions	0.1	Erdal et al. (1978)		Pu2
zeolitized tuff *2	18-30 *4	20	natural groundwater	~ 8	n.r.	4 × c(16000 rpm, 1h)	n.r.	atmospheric conditions	0.59	Erdal et al. (1978)		Pu2
zeolitized tuff *2	18-30 *4	20	natural groundwater	~ 8	n.r.	4 × c(16000 rpm, 1h)	n.r.	atmospheric conditions	0.7	Erdal et al. (1978)		Pu2
vitric tuff JA-18 *2	44-80 *4	20	natural groundwater *6	~ 8	n.r.	c(12'000 rpm, 1h)	n.r.	atmospheric conditions	0.19	Wolfsberg et al. (1979)	cf. Pu1, Pu2 and Pu4	Pu3
vitric tuff JA-18 *2	44-80 *4	20	natural groundwater *6	~ 8	n.r.	c(12'000 rpm, 1h)	n.r.	atmospheric conditions	0.22	Wolfsberg et al. (1979)		Pu3
de-vitrified tuff JA-32 *2	2-3 *4	20	natural groundwater *6	~ 8	n.r.	c(12'000 rpm, 1h)	n.r.	atmospheric conditions	0.12	Wolfsberg et al. (1979)		Pu3
de-vitrified tuff JA-32 *2	2-3 *4	20	natural groundwater *6	~ 8	n.r.	c(12'000 rpm, 1h)	n.r.	atmospheric conditions	0.11	Wolfsberg et al. (1979)		Pu3
zeolitized tuff JA-37 *2	18-30 *4	20	natural groundwater *6	~ 8	n.r.	c(12'000 rpm, 1h)	n.r.	atmospheric conditions	0.6	Wolfsberg et al. (1979)		Pu3
zeolitized tuff JA-37 *2	18-30 *4	20	natural groundwater *6	~ 8	n.r.	c(12'000 rpm, 1h)	n.r.	atmospheric conditions	0.91	Wolfsberg et al. (1979)		Pu3
de-vitrified tuff JM-22 *2	2-3 *4	20	natural groundwater	~ 8.5	n.r.	4 × c(16000 rpm, 1h)	n.r.	atmospheric conditions	4	Wolfsberg et al. (1981)	cf. Pu1, Pu2, Pu3	Pu4
de-vitrified tuff JM-22 *2	2-3 *4	20	natural groundwater	~ 8.5	n.r.	4 × c(16000 rpm, 1h)	n.r.	N$_2$ atmosphere	1.4	Wolfsberg et al. (1981)	desorption values are also recorded	Pu4
vitric tuff JM-38 *2	54-109 *4	20	natural groundwater	~ 8.5	n.r.	4 × c(16000 rpm, 1h)	n.r.	atmospheric conditions	5.5	Wolfsberg et al. (1981)		Pu4
vitric tuff JM-38 *2	54-109 *4	20	natural groundwater	~ 8.5	n.r.	4 × c(16000 rpm, 1h)	n.r.	N$_2$ atmosphere	5.6	Wolfsberg et al. (1981)		Pu4
de-vitrified tuff JM-54 *2	4 *4	20	natural groundwater	~ 8.5	n.r.	4 × c(16000 rpm, 1h)	n.r.	atmospheric conditions	0.59	Wolfsberg et al. (1981)		Pu4
de-vitrified tuff JM-54 *2	4 *4	20	natural groundwater	~ 8.5	n.r.	4 × c(16000 rpm, 1h)	n.r.	N$_2$ atmosphere	1	Wolfsberg et al. (1981)		Pu4

Table 7: continued

solid phase *2	CEC *4 (meq/100g)	w/s ratio (mL/g)	water type *6	pH end *7	C init. (M)	phase sep. *9	Eh end (mV)	atm./redox condition	K_d (Am) (m^3/kg)	reference	additional information, remarks	code REF
c) sedimentary rocks												
sandstone *2	9.9	10.0	GR-2 groundwater *6	~9	3E-09	f (0.003 µm)	600	oxidizing (air)	0.303	Barney (1984)	Freundlich-isotherm: S=KC^N; K=0.03, N= 0.89	Ra2
sandstone *2	9.9	10.0	GR-2 groundwater *6	~9	3E-07	f (0.003 µm)	600	oxidizing (air)	0.162	Barney (1984)	presence or absence of hydrazine did not exhibit a significant influence on Am sorption.	Ra2
sandstone *2	9.9	10.0	GR-2 groundwater *6	~9	3E-06	f (0.003 µm)	600	oxidizing (air)	0.142	Barney (1984)		Ra2
sandstone *2	9.9	10.0	GR-2 groundwater *6	~9	3E-09	f (0.003 µm)	600	oxidizing (air)	1.353	Barney (1984)	Freundlich-isotherm: S=KC^N; K=2.89, N= 1.03	Ra2
sandstone *2	9.9	10.0	GR-2 groundwater *6	~9	3E-07	f (0.003 µm)	600	oxidizing (air)	1.554	Barney (1984)		Ra2
sandstone *2	9.9	10.0	GR-2 groundwater *6	~9	3E-06	f (0.003 µm)	600	oxidizing (air)	1.665	Barney (1984)		Ra2
Interbed sand/claystone *2	n.r.	n.r.	Synthetic goundwater *6	~8	n.r.	n.r.	−400	reducing (0.1 M hydrazine)	>10	Salter and Jacobs (1982)	Interbed material contains more highly sorptive clays and zeolites	Am4
Interbed sand/claystone *2	n.r.	n.r.	Synthetic goundwater *6	~8	n.r.	n.r.	n.r.	oxidizing	>10	Salter and Jacobs (1982)		Am4
d) other												
marl & sandy sediments *2	n.r.	0.6	natural groundwater *6	n.r.	9E-06	n.r.	-146	Ar + 1% CO_2	0.00002	Kim et al. (1994)	breakthrough curve, sorption low because of high organic content in groundwater (80 mg C/L	Pa1
marl & sandy sediments *2	n.r.	0.6	natural groundwater *6	n.r.	2E-06	n.r.	-146	Ar + 1% CO_2	0.00001	Kim et al. (1994)		Pa1
sandy sediments *2	n.r.	13.0	groundwater Gohy-1061 *6	8.2	n.r.	f(0.45 µm)	n.r.	n.r. (reducing ?)	2.210	Kim et al. (1989)	Extract of many experiments, experimental details are described elsewhere.	Am2
sandy sediments *2	n.r.	1.9	groundwater Gohy-1061 *6	8.2	n.r.	f(0.45 µm)	n.r.	n.r. (reducing ?)	0.075	Kim et al. (1989)	Increasing s/w ratio decreases Kd values	Am2
sandy sediments *2	n.r.	1.5	groundwater Gohy-1061 *6	8.2	n.r.	f(0.45 µm)	n.r.	n.r. (reducing ?)	0.027	Kim et al. (1989)		Am2
sandy sediments *2	n.r.	1.5	groundwater Gohy-1061 *6	8.2	n.r.	f(unfiltered)	n.r.	n.r. (reducing ?)	0.005	Kim et al. (1989)	filter size has a huge influence on Kd values, because of a relatively high colloid concentration.	Am2
sandy sediments *2	n.r.	1.5	groundwater Gohy-1061 *6	8.2	n.r.	f(0.03 µm)	n.r.	n.r. (reducing ?)	1.000	Kim et al. (1989)		Am2
sandy sediments *2	n.r.	1.5	groundwater Gohy-1061 *6	8.2	n.r.	f(0.002 µm)	n.r.	n.r. (reducing ?)	3.260	Kim et al. (1989)		Am2
sandy sediments *2	n.r.	2	Gohy-1061+ 1E-3 M EDTA *6	8.2	n.r.	f(0.002 µm)	n.r.	n.r. (reducing ?)	0.00	Kim et al. (1989)	presence of EDTA drasticlly reduces Kd values	Am2

Table 8: Compilation of batch distribution coefficients for Cm on rocks

	solid phase *2	CEC *4 (meq/100g)	w/s ratio (mL/g)	water type *6	pH end *7	phase sep. *9	Eh end (mV)	atm./redox condition	K_d (Cm) (m^3/kg)	reference	additional information, remarks	code REF
a) plutonic rock												
	granodiorite	n.r.	5	de-ionised water*6	10.1	centrifuged	-430	strongly reducing conditions	0.81	Baston et al. (1997b)	in part, these data have already been published by	Ac1
	granodiorite	n.r.	5	de-ionised water*6	10.1	f (0.45 µm)	-430	strongly reducing conditions	11	Baston et al. (1997b)	Baston et al., 1997a [Np6]	Ac1
	granodiorite	n.r.	5	de-ionised water*6	10.1	10000 MWCO	-430	strongly reducing conditions	12	Baston et al. (1997b)		Ac1
	granodiorite	n.r.	5	de-ionised water*6	10.1	centrifuged	-440	strongly reducing conditions	0.54	Baston et al. (1997b)		Ac1
	granodiorite	n.r.	5	de-ionised water*6	10.1	f (0.45 µm)	-440	strongly reducing conditions	7.3	Baston et al. (1997b)		Ac1
	granodiorite	n.r.	5	de-ionised water*6	10.1	10000 MWCO	-440	strongly reducing conditions	12	Baston et al. (1997b)		Ac1
	granodiorite	n.r.	5	de-ionised water*6	9.6	centrifuged	-390	strongly reducing conditions	0.04	Baston et al. (1997b)		Ac1
	granodiorite	n.r.	5	de-ionised water*6	9.6	f (0.45 µm)	-390	strongly reducing conditions	3.2	Baston et al. (1997b)		Ac1
	granodiorite	n.r.	5	de-ionised water*6	9.6	10000 MWCO	-390	strongly reducing conditions	40	Baston et al. (1997b)		Ac1
	granodiorite	n.r.	5	de-ionised water*6	9.6	centrifuged	-400	strongly reducing conditions	0.043	Baston et al. (1997b)		Ac1
	granodiorite	n.r.	5	de-ionised water*6	9.6	f (0.45 µm)	-400	strongly reducing conditions	2.1	Baston et al. (1997b)		Ac1
	granodiorite	n.r.	5	de-ionised water*6	9.6	10000 MWCO	-400	strongly reducing conditions	23	Baston et al. (1997b)		Ac1
	granodiorite	n.r.	5	synthetic deionized water	10.1	f (0.45 µm)	-430	Reducing - (N_2-Atmosphere)	11	Baston et. al. (1997a)	strongly reducing conditions with sodium hydrosulfite	Np6
	granodiorite	n.r.	5	synthetic deionized water	10.1	10000 MWCO	-430	Reducing - (N_2-Atmosphere)	12	Baston et. al. (1997a)	strongly reducing conditions with sodium hydrosulfite	Np6
	granodiorite	n.r.	5	synthetic deionized water	9.6	f (0.45 µm)	-390	Reducing - (N_2-Atmosphere)	3.2	Baston et. al. (1997a)	strongly reducing conditions with sodium hydrosulfite	Np6
	granodiorite	n.r.	5	synthetic deionized water	9.6	10000 MWCO	-390	Reducing - (N_2-Atmosphere)	40	Baston et. al. (1997a)	strongly reducing conditions with sodium hydrosulfite	Np6
b) volcanic rocks												
	tuff	n.r.	5	synthetic deionized water	9.4	f (0.45 µm)	-430	Reducing - (N_2-Atmosphere)	30	Baston et. al. (1997a)	strongly reducing conditions with sodium hydrosulfite	Np6
	tuff	n.r.	5	synthetic deionized water	9.4	10000 MWCO	-430	Reducing - (N_2-Atmosphere)	45	Baston et. al. (1997a)	strongly reducing conditions with sodium hydrosulfite	Np6
	tuff	n.r.	5	synthetic deionized water	9.2	f (0.45 µm)	-370	Reducing - (N_2-Atmosphere)	64	Baston et. al. (1997a)	strongly reducing conditions with sodium hydrosulfite	Np6
	tuff	n.r.	5	synthetic deionized water	9.2	10000 MWCO	-370	Reducing - (N_2-Atmosphere)	130	Baston et. al. (1997a)	strongly reducing conditions with sodium hydrosulfite	Np6
	tuff	n.r.	5	de-ionised water*6	9.4	centrifuged	-430	strongly reducing conditions	7.1	Baston et al. (1997b)	in part, these data have already been published by	Ac1
	tuff	n.r.	5	de-ionised water*6	9.4	f (0.45 µm)	-430	strongly reducing conditions	30	Baston et al. (1997b)	Baston et al., 1997a [Np6]	Ac1
	tuff	n.r.	5	de-ionised water*6	9.4	10000 MWCO	-430	strongly reducing conditions	45	Baston et al. (1997b)		Ac1
	tuff	n.r.	5	de-ionised water*6	9.4	centrifuged	-440	strongly reducing conditions	5.8	Baston et al. (1997b)		Ac1
	tuff	n.r.	5	de-ionised water*6	9.4	f (0.45 µm)	-440	strongly reducing conditions	29	Baston et al. (1997b)		Ac1
	tuff	n.r.	5	de-ionised water*6	9.4	10000 MWCO	-440	strongly reducing conditions	110	Baston et al. (1997b)		Ac1
	tuff	n.r.	5	de-ionised water*6	9.2	centrifuged	-370	strongly reducing conditions	19	Baston et al. (1997b)		Ac1
	tuff	n.r.	5	de-ionised water*6	9.2	f (0.45 µm)	-370	strongly reducing conditions	64	Baston et al. (1997b)		Ac1
	tuff	n.r.	5	de-ionised water*6	9.2	10000 MWCO	-370	strongly reducing conditions	130	Baston et al. (1997b)		Ac1
	tuff	n.r.	5	de-ionised water*6	9.2	centrifuged	-370	strongly reducing conditions	17	Baston et al. (1997b)		Ac1
	tuff	n.r.	5	de-ionised water*6	9.2	f (0.45 µm)	-370	strongly reducing conditions	71	Baston et al. (1997b)		Ac1
	tuff	n.r.	5	de-ionised water*6	9.2	10000 MWCO	-370	strongly reducing conditions	210	Baston et al. (1997b)		Ac1
c) other												
	sandy sediments *2	n.r.	1.5	groundwater Gohy-1061(0.003 M NaCl) *6	8.20	f(0.45 µm)	n.r.	n.r. (reducing ?)	0.072	Kim et al. (1989)	Extract of many experiments, experimental details described elsewhere.	Am2
	sandy sediments *2	n.r.	1.5	groundwater Gohy-1061(0.003 M NaCl) *6	8.20	f(0.03 µm)	n.r.	n.r. (reducing ?)	1.580	Kim et al. (1989)	Filter size has a huge influence on K_d values,	Am2
	sandy sediments *2	n.r.	1.5	groundwater Gohy-1061(0.003 M NaCl) *6	8.20	f(0.002 µm)	n.r.	n.r. (reducing ?)	5.180	Kim et al. (1989)	as the colloid concentration is high.	Am2
	sandy sediments *2	n.r.	1.5	groundwater Gohy-1061(0.1 M NaCl) *6	8.20	f(0.002 µm)	n.r.	n.r. (reducing ?)	0.720	Kim et al. (1989)	minimum adsorption at ~ 0.1 M NaCl	Am2
	sandy sediments *2	n.r.	1.5	groundwater Gohy-1061(5 M NaCl) *6	8.20	f(0.002 µm)	n.r.	n.r. (reducing ?)	3.980	Kim et al. (1989)		Am2

Table 9: Compilation of batch distribution coefficients for Ac on rocks

solid phase *2	CEC *4 (meq/100g)	w/s ratio (mL/g)	temp. (°C)	water type *6	pH end *7	C init. (M)	phase sep. *9	Eh end (mV)	atm./redox condition	K_d (Ac) (m³/kg)	reference	additional information, remarks	code REF
a) plutonic rock													
granodiorite	n.r.	5	room	de-ionised water*6	10.1	1.4E-09	centrifuged	-550	strong reducing conditions	2	Baston et al. (1997b)		Ac1
granodiorite	n.r.	5	room	de-ionised water*6	10.1	1.4E-09	f (0.45 µm)	-550	strong reducing conditions	39	Baston et al. (1997b)		Ac1
granodiorite	n.r.	5	room	de-ionised water*6	10.1	1.4E-09	10000 MWCO	-550	strong reducing conditions	48	Baston et al. (1997b)		Ac1
granodiorite	n.r.	5	room	de-ionised water*6	10.1	1.4E-09	centrifuged	-560	strong reducing conditions	1.9	Baston et al. (1997b)		Ac1
granodiorite	n.r.	5	room	de-ionised water*6	10.1	1.4E-09	f (0.45 µm)	-560	strong reducing conditions	19	Baston et al. (1997b)		Ac1
granodiorite	n.r.	5	room	de-ionised water*6	10.1	1.4E-09	10000 MWCO	-560	strong reducing conditions	36	Baston et al. (1997b)		Ac1
granodiorite	n.r.	5	60	de-ionised water*6	9.6	2.8E-09	centrifuged	-570	strong reducing conditions	0.15	Baston et al. (1997b)		Ac1
granodiorite	n.r.	5	60	de-ionised water*6	9.6	2.8E-09	f (0.45 µm)	-570	strong reducing conditions	15	Baston et al. (1997b)		Ac1
granodiorite	n.r.	5	60	de-ionised water*6	9.6	2.8E-09	10000 MWCO	-570	strong reducing conditions	40	Baston et al. (1997b)		Ac1
granodiorite	n.r.	5	60	de-ionised water*6	9.6	2.8E-09	centrifuged	-590	strong reducing conditions	0.083	Baston et al. (1997b)		Ac1
granodiorite	n.r.	5	60	de-ionised water*6	9.6	2.8E-09	f (0.45 µm)	-590	strong reducing conditions	11	Baston et al. (1997b)		Ac1
granodiorite	n.r.	5	60	de-ionised water*6	9.6	2.8E-09	10000 MWCO	-590	strong reducing conditions	20	Baston et al. (1997b)		Ac1
b) volcanic rock													
tuff	n.r.	5	room	de-ionised water*6	9.4	2.8E-09	centrifuged	-320	strong reducing conditions	0.97	Baston et al. (1997b)		Ac1
tuff	n.r.	5	room	de-ionised water*6	9.4	2.8E-09	f (0.45 µm)	-320	strong reducing conditions	14	Baston et al. (1997b)		Ac1
tuff	n.r.	5	room	de-ionised water*6	9.4	2.8E-09	10000 MWCO	-320	strong reducing conditions	89	Baston et al. (1997b)		Ac1
tuff	n.r.	5	room	de-ionised water*6	9.4	2.8E-09	centrifuged	-320	strong reducing conditions	4.3	Baston et al. (1997b)		Ac1
tuff	n.r.	5	room	de-ionised water*6	9.4	2.8E-09	f (0.45 µm)	-320	strong reducing conditions	5.5	Baston et al. (1997b)		Ac1
tuff	n.r.	5	room	de-ionised water*6	9.4	2.8E-09	10000 MWCO	-320	strong reducing conditions	14	Baston et al. (1997b)		Ac1
tuff	n.r.	5	60	de-ionised water*6	9.4	2.4E-09	centrifuged	-110	strong reducing conditions	0.48	Baston et al. (1997b)		Ac1
tuff	n.r.	5	60	de-ionised water*6	9.4	2.4E-09	f (0.45 µm)	-110	strong reducing conditions	0.59	Baston et al. (1997b)		Ac1
tuff	n.r.	5	60	de-ionised water*6	9.4	2.4E-09	10000 MWCO	-110	strong reducing conditions	4.2	Baston et al. (1997b)		Ac1
tuff	n.r.	5	60	de-ionised water*6	9.4	2.4E-09	centrifuged	-110	strong reducing conditions	0.7	Baston et al. (1997b)		Ac1
tuff	n.r.	5	60	de-ionised water*6	9.4	2.4E-09	f (0.45 µm)	-110	strong reducing conditions	0.89	Baston et al. (1997b)		Ac1
tuff	n.r.	5	60	de-ionised water*6	9.4	2.4E-09	10000 MWCO	-110	strong reducing conditions	7.1	Baston et al. (1997b)		Ac1
c) other													
sandy sediments *2	1 - 80	n.r.	n.r.	groundwater	n.r.	n.r.	n.r.	n.r.	n.r.	1	Meier et al. (1994)	Short overview about wide range of experimental work. Lack of experimental details.	Pb3
sandy sediments *2	1 - 80	n.r.	n.r.	groundwater + 1E-3 M EDTA	n.r.	n.r.	n.r.	n.r.	n.r.	0.003	Meier et al. (1994)	EDTA decreases Ac sorption strongly.	Pb3
sandy sediments *2	1 - 80	n.r.	5.0	groundwater	n.r.	n.r.	n.r.	n.r.	n.r.	0.407	Meier et al. (1994)	desorption coefficients investigated	Pb3
sandy sediments *2	1 - 80	n.r.	20.0	groundwater	n.r.	n.r.	n.r.	n.r.	n.r.	0.655	Meier et al. (1994)	Increase of temperature increases sorption.	Pb3
sandy sediments *2	1 - 80	n.r.	35.0	groundwater	n.r.	n.r.	n.r.	n.r.	n.r.	0.71	Meier et al. (1994)	See Appendix A2, Table 1, FY95 BMG-report: Ochs and Lothenbach, 1997	Pb3
sandy sediments *2	1 - 80	n.r.	50.0	groundwater	n.r.	n.r.	n.r.	n.r.	n.r.	1.19	Meier et al. (1994)		Pb3
Weichsel glacial sediment * 2	n.r.	2.5	n.r.	Low salinity groundwater G1 *6	6.1	1.00E-09	*9	70	99% Ar, 1% CO_2	0.310	Lieser et al. (1990)	Kd is calculated from the distribution of Ac between coarse+fine particles and the molecular fraction	Pb1
Elster glacial sediment * 2	n.r.	2.5	n.r.	Medium salinity groundwater G8 *6	7.5	1.00E-09	*9	-160	99% Ar, 1% CO_2	0.164	Lieser et al. (1990)		Pb1
Elster glacial sediment * 2	n.r.	2.5	n.r.	Medium salinity groundwater G9 *6	7.7	1.00E-09	*9	-430	99% Ar, 1% CO_2	0.081	Lieser et al. (1990)	See Appendix A2, Table 1, FY95 BMG-report: Ochs and Lothenbach, 1997	Pb1

Table 10: Compilation of batch distribution coefficients for Sm on rocks

solid phase *2	CEC *4 (meq/100g)	w/s ratio (mL/g)	water type *6	pH end *7	C init. (M)	phase sep. *9	Eh end (mV)	atm./redox condition	K_d (Sm) (m^3/kg)	reference	code REF
London clay *2	n.r.	10	clay water	8.7-9.2	1.00E-07	c(1500 rpm/15)	n.r.	N_2	1.6-3.6	Baston et al. (1992a)	Nb2
London clay *2	n.r.	10	clay water	8.7-9.2	1.00E-07	f(0.45 µm)	n.r.	N_2	0.41-6.5	Baston et al. (1992a)	Nb2
London clay *2	n.r.	10	clay water	8.7-9.2	1.00E-07	f(30000 MWCO)	n.r.	N_2	5.8->10	Baston et al. (1992a)	Nb2
London clay *2	n.r.	10	clay water	7.2-8.9	1.00E-09	c(1500 rpm/15)	n.r.	N_2	0.86-0.95	Baston et al. (1992a)	Nb2
London clay *2	n.r.	10	clay water	7.2-8.9	1.00E-09	f(0.45 µm)	n.r.	N_2	0.18-0.79	Baston et al. (1992a)	Nb2
London clay *2	n.r.	10	clay water	7.2-8.9	1.00E-09	f(30000 MWCO)	n.r.	N_2	0.4-1.2	Baston et al. (1992a)	Nb2
London clay *2	n.r.	10	clay water + $Ca(OH)_2$	10.3-11.3	1.00E-09	c(1500 rpm/15)	n.r.	N_2	1.4-8.8	Baston et al. (1992a)	Nb2
London clay *2	n.r.	10	clay water + $Ca(OH)_2$	10.3-11.3	1.00E-09	f(0.45 µm)	n.r.	N_2	>10	Baston et al. (1992a)	Nb2
London clay *2	n.r.	10	clay water + $Ca(OH)_2$	10.3-11.3	1.00E-09	f(30000 MWCO)	n.r.	N_2	>10	Baston et al. (1992a)	Nb2

Table 11: Compilation of batch distribution coefficients for Ra on rocks

solid phase *2	CEC *4 (meq/100g)	w/s ratio *5 (mL/g)	water type *6	pH end *7	C init. (M)	phase sep. *9	Eh end (mV)	atm./redox condition	K_d (Ra) (m^3/kg)	reference	additional information, remarks	code REF
a) plutonic rock												
granite *2	n.r.	11	synthetic groundwater (aq293) *6	≈8	2.00E-06	c(4000/50)	-150 - -210	reducing (Fe(II))	0.5	Allard et al. (1978)	careful experimental work	Ra1
granite *2	n.r.	11	synthetic groundwater (aq293) *6	≈8	2.00E-06	c(4000/50)	n.r.	atmospheric conditions	0.5	Allard et al. (1978)	not so clear if the values are measured in reducing or oxidizing environment	Ra1
b) volcanic rock												
Umantum basalt *2	n.r.	n.r.	Synthetic goundwater *6	9.4	n.r.	n.r.	n.r.	oxidizing	0.20	Salter and Jacobs (1982)	Oxic:Freundlich Isotherm: S=356*C^1.29	Am4
tuff (haem) *2	n.r.	50	cement-equlibrated water	8	n.r.	n.r.	n.r.	N_2 atmosphere	0.08-0.16	Baston et al. (1993)		Ra4
tuff (non-haem) *2	n.r.	50	cement-equlibrated water	8	n.r.	n.r.	n.r.	N_2 atmosphere	0.03-0.07	Baston et al. (1993)		Ra4
tuff (haem) *2	n.r.	50	cement-equlibrated water	11	n.r.	n.r.	n.r.	N_2 atmosphere	0.33-0.38	Baston et al. (1993)	pH has small influence on Ra sorption	Ra4
tuff (non-haem) *2	n.r.	50	cement-equlibrated water	11	n.r.	n.r.	n.r.	N_2 atmosphere	0.10-0.32	Baston et al. (1993)		Ra4
c) sedimentary rock												
mudrock *2	20-35 *4	50	CW1 *6	12.0	1.00E-08	c (1500g/15)	n.r.	n.r.	4.0	Berry et al. (1991)	See Table 1, FY95 BMG-report: Ochs and Wanner, 1996	Ra3
mudrock *2	20-35 *4	50	CW1 *6	11.9	1.00E-08	c (1500g/15)	n.r.	n.r.	3.00	Berry et al. (1991)		Ra3
mudrock *2	20-35 *4	50	CW1 *6	11.9	1.00E-08	c (1500g/15)	n.r.	n.r.	4.00	Berry et al. (1991)		Ra3
mudrock *2	20-35 *4	50	CW1 *6	12.0	1.00E-08	c (1500g/15)/f (0.45 µm)	n.r.	n.r.	>5	Berry et al. (1991)		Ra3
mudrock *2	20-35 *4	50	CW1 *6	11.9	1.00E-08	c (1500g/15)/f (0.45 µm)	n.r.	n.r.	5.00	Berry et al. (1991)		Ra3
mudrock *2	20-35 *4	50	CW1 *6	11.9	1.00E-08	c (1500g/15)/f (0.45 µm)	n.r.	n.r.	8.00	Berry et al. (1991)		Ra3
mudrock *2	20-35 *4	50	CW1 *6	12.0	1.00E-08	c (1500g/15)/f (30000 MWCO)	n.r.	n.r.	>5	Berry et al. (1991)		Ra3
mudrock *2	20-35 *4	50	CW1 *6	11.9	1.00E-08	c (1500g/15)/f (30000 MWCO)	n.r.	n.r.	>5	Berry et al. (1991)		Ra3
mudrock *2	20-35 *4	50	CW1 *6	11.9	1.00E-08	c (1500g/15)/f (30000 MWCO)	n.r.	n.r.	>5	Berry et al. (1991)		Ra3
mudrock *2	20-35 *4	50	CW2 *6	7.8	1.00E-08	c (1500g/15)	n.r.	n.r.	0.15	Berry et al. (1991)		Ra3
mudrock *2	20-35 *4	50	CW2 *6	7.6	1.00E-08	c (1500g/15)	n.r.	n.r.	0.32	Berry et al. (1991)		Ra3
mudrock *2	20-35 *4	50	CW2 *6	7.8	1.00E-08	c (1500g/15)	n.r.	n.r.	0.17	Berry et al. (1991)		Ra3
mudrock *2	20-35 *4	50	CW2 *6	7.8	1.00E-08	c (1500g/15)/f (0.45 µm)	n.r.	n.r.	0.15	Berry et al. (1991)		Ra3
mudrock *2	20-35 *4	50	CW2 *6	7.6	1.00E-08	c (1500g/15)/f (0.45 µm)	n.r.	n.r.	0.14	Berry et al. (1991)		Ra3
mudrock *2	20-35 *4	50	CW2 *6	7.8	1.00E-08	c (1500g/15)/f (0.45 µm)	n.r.	n.r.	0.16	Berry et al. (1991)		Ra3
mudrock *2	20-35 *4	50	CW2 *6	7.8	1.00E-08	c (1500g/15)/f (30000 MWCO)	n.r.	n.r.	0.14	Berry et al. (1991)		Ra3
mudrock *2	n.r.	n.r. *5	cement-equlibrated water	n.r.	n.r.	n.r. *9	n.r.	N_2 atmosphere	0.017	Baston et al. (1993)	not reported experimental details probably equal to Ra3	Ra4
mudrock *2	n.r.	n.r. *5	porewater with 0.0002 M Ca	n.r.	n.r.	n.r. *9	n.r.	N_2 atmosphere	0.020	Baston et al. (1993)	Short overview about wide range of experimental work. Lack of experimental details.	Ra4
mudrock *2	n.r.	n.r. *5	porewater with 0.002 M Ca	n.r.	n.r.	n.r. *9	n.r.	N_2 atmosphere	0.012	Baston et al. (1993)	Increase in Ca concentration decreases Ra sorption	Ra4
mudrock *2	n.r.	n.r. *5	porewater with 0.02 M Ca	n.r.	n.r.	n.r. *9	n.r.	N_2 atmosphere	0.006	Baston et al. (1993)		Ra4
sandstone/claystone *2	n.r.	10	GR-1A groundwater *6	≈9	3E-09	f (0.003 µm)	-800	reducing (0.05 M hydrazine; N_2)	0.385	Barney (1984)	Freundlich-Isotherm: S=KC^N; K=0.056, N= 0.91	Ra2
sandstone/claystone *2	n.r.	10	GR-1A groundwater *6	≈9	3E-07	f (0.003 µm)	-800	reducing (0.05 M hydrazine; N_2)	0.254	Barney (1984)	Difference between oxidizing and reducing conditions due to ion exchange	Ra2
sandstone/claystone *2	n.r.	10	GR-1A groundwater *6	≈9	3E-06	f (0.003 µm)	-800	reducing (0.05 M hydrazine; N_2)	0.207	Barney (1984)	competition between $N_2H_5^+$ and Ra^{2+}.	Ra2
sandstone/claystone *2	n.r.	10	GR-1A groundwater *6	≈9	3E-09	f (0.003 µm)	-800	reducing (0.05 M hydrazine; N_2)	0.130	Barney (1984)	Freundlich-isotherm: S=KC^N; K=0.084, N= 0.98	Ra2
sandstone/claystone *2	n.r.	10	GR-1A groundwater *6	≈9	3E-07	f (0.003 µm)	-800	reducing (0.05 M hydrazine; N_2)	0.119	Barney (1984)		Ra2
sandstone/claystone *2	n.r.	10	GR-1A groundwater *6	≈9	3E-06	f (0.003 µm)	-800	reducing (0.05 M hydrazine; N_2)	0.113	Barney (1984)		Ra2
sandstone/claystone *2	n.r.	10	GR-1A groundwater *6	≈9	3E-09	f (0.003 µm)	600	oxidizing (air)	0.914	Barney (1984)	Freundlich-isotherm: S=KC^N; K=183, N= 1.18	Ra2
sandstone/claystone *2	n.r.	10	GR-1A groundwater *6	≈9	3E-07	f (0.003 µm)	600	oxidizing (air)	2.095	Barney (1984)		Ra2
sandstone/claystone *2	n.r.	10	GR-1A groundwater *6	≈9	3E-06	f (0.003 µm)	600	oxidizing (air)	3.170	Barney (1984)		Ra2
sandstone/claystone *2	n.r.	10	GR-1A groundwater *6	≈9	3E-09	f (0.003 µm)	600	oxidizing (air)	12.565	Barney (1984)	Freundlich-isotherm: S=KC^N; K=9.64, N= 0.99	Ra2
sandstone/claystone *2	n.r.	10	GR-1A groundwater *6	≈9	3E-07	f (0.003 µm)	600	oxidizing (air)	11.999	Barney (1984)		Ra2
sandstone/claystone *2	n.r.	10	GR-1A groundwater *6	≈9	3E-06	f (0.003 µm)	600	oxidizing (air)	11.726	Barney (1984)		Ra2

Table 11: continued

solid phase *2	CEC *4 (meq/100g)	w/s ratio *5 (mL/g)	water type *6	pH end *7	C init. (M)	phase sep. *9	Eh end (mV)	atm./redox condition	K_d (Ra) (m^3/kg)	reference	additional information, remarks	code REF
Mabton interbed material *2	n.r.	n.r.	Synthetic goundwater *6	~8	n.r.	n.r.	n.r.	oxidizing	1.50	Salter and Jacobs (1982)	Extract from extensive experimental works, experimental details are not reported.	Am4
Caithness flagstones	n.r.	50	simulated rock porewater	8.1-8.2	1E-08	c (1500 g/15)	n.r.	N_2 atmosphere	7	Berry et al. (1991)		Ra3
Caithness flagstones	n.r.	50	simulated rock porewater	8.1-8.2	1E-08	c (1500 g/15), f (30000 MWCO)	n.r.	N_2 atmosphere	7	Berry et al. (1991)		Ra3
Caithness flagstones	n.r.	50	cement-equilibrated water	8.0-8.2	1E-08	c (1500 g/15)	n.r.	N_2 atmosphere	2.3	Berry et al. (1991)	cement-equilibrated water contains one order of magnitude more Ca	Ra3
Caithness flagstones	n.r.	50	cement-equilibrated water	8.0-8.2	1E-08	c (1500 g/15), f (0.45 µm)	n.r.	N_2 atmosphere	3.5	Berry et al. (1991)	which competes with Ra for ion exchange sites	Ra3
Caithness flagstones	n.r.	50	cement-equilibrated water	8.0-8.2	1E-08	c (1500 g/15), f (30000 MWCO)	n.r.	N_2 atmosphere	2.1	Berry et al. (1991)		Ra3
Caithness flagstones	n.r.	50	cement-equilibrated water	12-12.1	1E-08	c (1500 g/15)	n.r.	N_2 atmosphere	1.8	Berry et al. (1991)		Ra3
Caithness flagstones	n.r.	50	cement-equilibrated water	12-12.1	1E-08	c (1500 g/15), f (0.45 µm)	n.r.	N_2 atmosphere	1.6	Berry et al. (1991)		Ra3
Caithness flagstones	n.r.	50	cement-equilibrated water	12-12.1	1E-08	c (1500 g/15), f (30000 MWCO)	n.r.	N_2 atmosphere	3.7	Berry et al. (1991)		Ra3
St. Bee sandstone *2	n.r.	n.r. *5	synthetic groundwater *6	n.r.	1E-08	n.r. *9	n.r.	N_2 atmosphere	0.0046	Berry et al. (1994)	not reported experimental details probabely equal to Ra3	Ra5
St. Bee sandstone *2	n.r.	n.r. *5	synthetic groundwater *6	n.r.	1E-07	n.r. *9	n.r.	N_2 atmosphere	0.0013	Berry et al. (1994)		Ra5
Calder sandstone *2	n.r.	n.r. *5	synthetic groundwater *6	n.r.	1E-08	n.r. *9	n.r.	N_2 atmosphere	0.0095	Berry et al. (1994)		Ra5
Calder sandstone *2	n.r.	n.r. *5	synthetic groundwater *6	n.r.	1E-07	n.r. *9	n.r.	N_2 atmosphere	0.0073	Berry et al. (1994)		Ra5
sandstone *2	9.9	10	GR-2 groundwater *6	~9	3E-09	f (0.003 µm)	600	oxidizing (air)	2.581	Barney (1984)	Freundlich-isotherm: S=KC^N; K=0.62, N= 0.94	Ra2
sandstone *2	9.9	10	GR-2 groundwater *6	~9	3E-07	f (0.003 µm)	600	oxidizing (air)	1.958	Barney (1984)		Ra2
sandstone *2	9.9	10	GR-2 groundwater *6	~9	3E-06	f (0.003 µm)	600	oxidizing (air)	1.705	Barney (1984)		Ra2
sandstone *2	9.9	10	GR-2 groundwater *6	~9	3E-09	f (0.003 µm)	600	oxidizing (air)	1.556	Barney (1984)	Freundlich-isotherm: S=KC^N; K=0.48, N= 0.95	Ra2
sandstone *2	9.9	10	GR-2 groundwater *6	~9	3E-07	f (0.003 µm)	600	oxidizing (air)	1.236	Barney (1984)		Ra2
sandstone *2	9.9	10	GR-2 groundwater *6	~9	3E-06	f (0.003 µm)	600	oxidizing (air)	1.101	Barney (1984)		Ra2
sandstone *2	9.9	10	GR-2 groundwater *6	~9	3E-09	f (0.003 µm)	600	oxidizing (air)	0.849	Barney (1984)	Freundlich-isotherm: S=KC^N; K=83.1, N= 1.16	Ra2
sandstone *2	9.9	10	GR-2 groundwater *6	~9	3E-07	f (0.003 µm)	600	oxidizing (air)	1.773	Barney (1984)		Ra2
sandstone *2	9.9	10	GR-2 groundwater *6	~9	3.00E-06	f (0.003 µm)	600	oxidizing (air)	2.6	Barney (1984)		Ra2
d) other												
sandy sediments *2	1 - 80	7.0	groundwater	n.r.	6E-10	n.r.	n.r.	n.r.	0.128	Meier et al. (1994)	Short overview about wide range of experimental work. Lack of experimental details.	Pb3
sandy sediments *2	1 - 80	3.5	groundwater	n.r.	6E-10	n.r.	n.r.	n.r.	0.103	Meier et al. (1994)	Increase of s/w decreases sorption.	Pb3
sandy sediments *2	1 - 80	1.4	groundwater	n.r.	6E-10	n.r.	n.r.	n.r.	0.076	Meier et al. (1994)	desorption coefficients investigated	Pb3
sandy sediments *2	1 - 80	1.0	groundwater	n.r.	6E-10	n.r.	n.r.	n.r.	0.079	Meier et al. (1994)		Pb3
sandy sediments *2	1 - 80	1.0	groundwater	6	n.r.	n.r.	n.r.	n.r.	0.0067	Meier et al. (1994)		Pb3
sandy sediments *2	1 - 80	1.0	groundwater	7	n.r.	n.r.	n.r.	n.r.	0.0126	Meier et al. (1994)		Pb3
sandy sediments *2	1 - 80	1.0	groundwater	8	n.r.	n.r.	n.r.	n.r.	0.0263	Meier et al. (1994)		Pb3
sandy sediments *2	1 - 80	1.0	groundwater	9	n.r.	n.r.	n.r.	n.r.	0.0263	Meier et al. (1994)		Pb3

Table 12: Compilation of batch distribution coefficients for Sr on rocks

solid phase *2	CEC *4 (meq/100g)	w/s ratio *5 (mL/g)	water type *6	pH end *7	C init. (M)	phase sep. *9	Eh end (mV)	atm./redox condition	K_d (Ra) (m^3/kg)	reference	additional information, remarks	code REF
a) plutonic rock												
Strongly altered tonalite	n.r.	10.0	synthetic granitic groundwater *6	n.r.	1E-5	centrifugation	n.r.	n.r.	0.04	Hölttä et al. (1997)	Batch method	Sr1
Strongly altered tonalite	n.r.	10.0	synthetic granitic groundwater *6	n.r.	1E-5	n.r.	n.r.	n.r.	0.03	Hölttä et al. (1997)	Thin section method	Sr1
Mica gneis	n.r.	10.0	synthetic granitic groundwater *6	n.r.	1E-5	centrifugation	n.r.	n.r.	0.003	Hölttä et al. (1997)	Batch method	Sr1
Mica gneis	n.r.	10.0	synthetic granitic groundwater *6	n.r.	1E-5	n.r.	n.r.	n.r.	0.003	Hölttä et al. (1997)	Thin section method	Sr1
Unaltered tonalite	n.r.	10.0	synthetic granitic groundwater *6	n.r.	1E-5	centrifugation	n.r.	n.r.	0.007	Hölttä et al. (1997)	Batch method	Sr1
Unaltered tonalite	n.r.	10.0	synthetic granitic groundwater *6	n.r.	1E-5	n.r.	n.r.	n.r.	0.007	Hölttä et al. (1997)	Thin section method	Sr1
Moderately altered tonalite	n.r.	10.0	synthetic granitic groundwater *6	n.r.	1E-5	centrifugation	n.r.	n.r.	0.04	Hölttä et al. (1997)	Batch method	Sr1
Moderately altered tonalite	n.r.	10.0	synthetic granitic groundwater *6	n.r.	1E-5	n.r.	n.r.	n.r.	0.02	Hölttä et al. (1997)	Thin section method	Sr1
fine-grained granite *2	n.r.	n.r.	synthetic groundwater *6	n.r.	n.r.	n.r.	n.r.	n.r.	8.20E-05	Johansson et al. (1997)	diffusion coefficient	Sr2
Äspö-diorite *2	n.r.	n.r.	synthetic groundwater *6	n.r.	n.r.	n.r.	n.r.	n.r.	6.90E-05	Johansson et al. (1997)	diffusion coefficient	Sr2
b) volcanic rock												
Umantum basalt *2	n.r.	n.r.	Synthetic groundwater *6	9.4	n.r.	n.r.	n.r.	oxidizing	0.17	Salter and Jacobs (1982)	Extract from extensive experimental works, experimental details are not reported.	Am4
c) sedimentary rock												
Argillite*2	10-17	20	Synthetic groundwater *6	8.88	1.20E-06	C (16'000 rpm)	n.r.	atmospheric	0.135	Erdal et. al. (1979)		Sr3
Argillite*2	10-17	20.0	Synthetic groundwater *6	8.88	0.0000012	C (16'000 rpm)	n.r.	atmospheric	0.265	Erdal et. al. (1979)		Sr3
sandstone *2	9.9	10.0	GR-2 groundwater *6	~9	3E-09	f (0.003 µm)	-800	reducing (0.05 M hydrazine; N_2)	0.483	Barnev (1984)	Freundlich-Isotherm: S=KC^N; K=0.78, N= 1.02	Ra2
sandstone *2	9.9	10.0	GR-2 groundwater *6	~9	3E-09	f (0.003 µm)	-800	reducing (0.05 M hydrazine; N_2)	0.563	Barnev (1984)	Freundlich-Isotherm: S=KC^N; K=1.17, N= 1.03	Ra2
sandstone *2	9.9	10.0	GR-2 groundwater *6	~9	3E-09	f (0.003 µm)	-800	reducing (0.05 M hydrazine; N_2)	0.151	Barnev (1984)	Freundlich-Isotherm: S=KC^N; K=12.2, N= 1.18	Ra2
d) other												
Weichsel glacial sediment * 2	n.r.	2.5	Low salinity groundwater G1 *6	6.1	1E-06	*9	70	99% Ar, 1% CO_2	0.00019	Lieser et al. (1990)	Kd is calculated from the distribution of Sr between coarse+fine particles and the molecular fraction	Pb1
Elster glacial sediment * 2	n.r.	2.5	Medium salinity groundwater G8 *6	7.5	1E-06	*9	-160	99% Ar, 1% CO_2	0.00071	Lieser et al. (1990)		Pb1
Elster glacial sediment * 2	n.r.	2.5	Medium salinity groundwater G9 *6	7.7	1E-06	*9	-430	99% Ar, 1% CO_2	0.00008	Lieser et al. (1990)		Pb1

Table 13: Compilation of batch distribution coefficients for Zr on rocks

solid phase *2	CEC *4 (meq/100g)	w/s ratio (mL/g)	water type *6	pH end *7	C init. (M)	phase sep. *9	Eh end (mV)	atm./redox condition	K_d (Zr) (m^3/kg)	reference	additional information, remarks	code REF
plutonic rock												
granite *2	n.r.	11	synthetic groundwater (aq293) *6	~8	2.00E-06	c(4000/50)	-150 - -210	reducing (Fe(II))	3.2	Allard et al. (1978)	careful experimental work	Ra1
granite *2	n.r.	11	synthetic groundwater (aq293) *6	~8	2.00E-06	c(4000/50)	n.r.	atmospheric conditions	3.2	Allard et al. (1978)	not so clear if the values are measured in reducing or oxidizing environment	Ra1
tonalite*2	n.r.	10	natural groundwater *6	n.r.	1.50E-07	c(6500 g, 30 min)	n.r.	oxic	0.437-1.000	Kulmala and Hakanen (1993)		Zr1
tonalite*2	n.r.	10	natural groundwater *6	n.r.	8.40E-06	c(6500 g, 30 min)	n.r.	oxic	0.111-0.875	Kulmala and Hakanen (1993)		Zr1

Table 14: Compilation of batch distribution coefficients for Nb on rocks

redox state *1	solid phase *2	CEC *4 (meq/100g)	w/s ratio (mL/g)	water type *6	pH end *7	C init. (M)	phase sep. *9	Eh end (mV)	atm./redox condition	K_d (Nb) (m^3/kg)	reference	additional information, remarks	code REF
a) plutonic rock													
+V	tonalite*2	n.r.	10	natural groundwater *6	n.r.	1.40E-10	c(6500 g, 30 min)	n.r.	oxic	0.479-0.973	Kulmala and Hakanen (1993)		Zr1
+V	tonalite*2	n.r.	10	natural groundwater *6	n.r.	8.60E-09	c(6500 g, 30 min)	n.r.	oxic	0.126-0.918	Kulmala and Hakanen (1993)		Zr1
b) sedimentary rock													
+V (e)	mudrock *2	n.r.	10	PW	8	2.00E-13	c(4000 rpm/30), f(0.45 µ, 30000 MWCO)	n.r.	N_2	1.32	Berry et al. (1988)	diffusion data for some elements	Nb1
+V (e)	mudrock *2	n.r.	10	clay water	8.7-9	2.00E-11	c(1500 rpm/15)	n.r.	N_2	0.24-0.38	Baston et al. (1992a)	n.r.	Nb2
+V (e)	mudrock *2	n.r.	10	clay water	8.7-9	2.00E-11	f(0.45 µm)	n.r.	N_2	>10	Baston et al. (1992a)		Nb2
+V (e)	mudrock *2	n.r.	10	clay water	8.7-9	2.00E-11	f(30000 MWCO)	n.r.	N_2	>10	Baston et al. (1992a)		Nb2
+V (e)	mudrock *2	n.r.	10	clay water	8.2-9	5.00E-11	c(1500 rpm/15)	n.r.	N_2	0.63-10	Baston et al. (1992a)		Nb2
+V (e)	mudrock *2	n.r.	10	clay water	8.2-9	5.00E-11	f(0.45 µm)	n.r.	N_2	>10	Baston et al. (1992a)		Nb2
+V (e)	mudrock *2	n.r.	10	clay water	8.2-9	5.00E-11	f(30000 MWCO)	n.r.	N_2	>10	Baston et al. (1992a)		Nb2
c) other													
+V (e)	Aquifer gravel *2	n.r.	10	PW	8	3.00E-11	c(1500 rpm/15)	n.r.	air	0.26-10	Baston et al. (1992a)		Nb2
+V (e)	Aquifer gravel *2	n.r.	10	PW	8	3.00E-11	f(0.45 µm)	n.r.	air	5.9->10	Baston et al. (1992a)		Nb2
+V (e)	Aquifer gravel *2	n.r.	10	PW	8	1.00E-11	c(1500 rpm/15)	n.r.	air	0.24-2.8	Baston et al. (1992a)		Nb2
+V (e)	Aquifer gravel *2	n.r.	10	PW	8	1.00E-11	f(0.45 µm)	n.r.	air	7.7->10	Baston et al. (1992a)		Nb2

Table 15: Compilation of batch distribution coefficients for Sb on rocks

redox state *1	solid phase *2	CEC *4 (meq/100g)	w/s ratio (mL/g)	water type *6	pH end *7	C init. (M)	phase sep. *9	Eh end (mV)	atm./redox condition	K_d (Sb) (m^3/kg)	reference	code REF
plutonic rock												
n.r.	vitric tuff JA-18 *2	44-80 *4	20	natural groundwater *6	≈ 8	n.r.	c(12'000 rpm, 1h)	n.r.	atmospheric conditions	-0.0003	Wolfsberg et al. (1979)	Pu3
n.r.	de-vitrified tuff JA-32 *2	2-3 *4	20	natural groundwater *6	≈ 8	n.r.	c(12'000 rpm, 1h)	n.r.	atmospheric conditions	-0.0004	Wolfsberg et al. (1979)	Pu3
n.r.	zeolitized tuff JA-37 *2	18-30 *4	20	natural groundwater *6	≈ 8	n.r.	c(12'000 rpm, 1h)	n.r.	atmospheric conditions	0.0003	Wolfsberg et al. (1979)	Pu3

Table 16: Compilation of batch distribution coefficients for Pb on rocks

solid phase *2	CEC *4 (meq/100g)	w/s ratio (mL/g)	water type *6	pH end *7	C init. (M)	phase sep. *9	Eh end (mV)	atm./redox condition	K_d (Pb) (m^3/kg)	reference	additional information, remarks	code REF
other												
Weichsel glacial sediment * 2	n.r.	2.5	Low salinity groundwater G1 *6	6.6	≈ 2E-9	f(0.002 µm)	163	99% Ar, 1% CO_2	1.300	Lieser and Ament (1993)		Pb2
Elster glacial sediment * 2	n.r.	2.5	Medium salinity groundwater G8 *6	7.6	≈ 4E-9	f(0.002 µm)	-50	99% Ar, 1% CO_2	> 2.5	Lieser and Ament (1993)	Sorption increases with decreasing s/w ratio.	Pb2
Elster glacial sediment * 2	n.r.	10	Medium salinity groundwater G8 *6	7.6	≈ 4E-9	f(0.002 µm)	-50	99% Ar, 1% CO_2	> 10	Lieser and Ament (1993)		Pb2
Elster glacial sediment * 2	n.r.	50	Medium salinity groundwater G8 *6	7.6	≈ 4E-9	f(0.002 µm)	-50	99% Ar, 1% CO_2	> 50	Lieser and Ament (1993)		Pb2
Elster glacial sediment * 2	n.r.	2.5	Medium salinity groundwater G9 *6	7.4	≈ 2E-9	not filtrered	-116	99% Ar, 1% CO_2	0.215	Lieser and Ament (1993)		Pb2
Elster glacial sediment * 2	n.r.	2.5	Medium salinity groundwater G9 *6	7.4	≈ 2E-9	not filtrered	-116	99% Ar, 1% CO_2	0.456	Lieser and Ament (1993)		Pb2
Elster glacial sediment * 2	n.r.	2.5	Medium salinity groundwater G9 *6	7.4	≈ 2E-9	not filtrered	-116	99% Ar, 1% CO_2	1.170	Lieser and Ament (1993)		Pb2
Elster glacial sediment * 2	n.r.	2.5	Medium salinity groundwater G9 *6	7.4	≈ 2E-9	not filtrered	-116	99% Ar, 1% CO_2	> 3	Lieser and Ament (1993)	Sorption still increasing after 4 weeks	Pb2
Elster glacial sediment * 2	n.r.	2.5	Medium salinity groundwater G9 *6	7.4	≈ 2E-9	f(0.002 µm)	-116	99% Ar, 1% CO_2	> 3	Lieser and Ament (1993)		Pb2
Elster glacial sediment * 2	n.r.	10	Medium salinity groundwater G9 *6	7.4	≈ 2E-9	f(0.002 µm)	-116	99% Ar, 1% CO_2	> 10	Lieser and Ament (1993)		Pb2
Elster glacial sediment * 2	n.r.	50.0	Medium salinity groundwater G9 *6	7.40	≈ 2E-9	f(0.002 µm)	-116	99% Ar, 1% CO_2	> 60	Lieser and Ament (1993)		Pb2

.3 Footnotes

dox state

[Np4]	Sentinel Gap basalt: 66% Np(IV), 34% Np(V) (77%, 23%). Oxidzed Sentinel Gap basalt: 3% Np(IV), 97% Np(V) (3%, 95%). Westerly granite: 71% Np(IV), 29% Np(V) (82%, 18%). Values indicate distribution in solution (in brackets: surface).
[Pa1]	The authors determined that 73% are Np(IV) and 27% are Np(V).
[U2]	In the tracer originally Pu (IV).

lid phase

[Am1]	Composition is shown in Auxiliary Table 1.
[Am2]	Sandy sediments collected near Gorleben.
[Am3]	Theoretical granite and basalt composed from quartz, feldspars, micas,amphiboles, pyroxene and olivine incl. Accessory minerals such as pyrite.
[Am4]	Umtanum basalt consists of pyroxene, plagioclase, magnetite, olivine and a silica rich glassy mesostatis. Important secondary minerals are pyrite, smectite clays, zeolites. The interbedded sandstone/claystone (Mabton) contains more clays and zeolites.
[Nb1]	London clay from Bradwell, UK, a tertiary mudrock containing 25 % smectite, 45 % illite, 20 % kaolinite, 10 % chlorite (Bloodworth and Morgan, 1989).
[Nb2]	London clay from Bradwell, UK, a tertiary mudrock containing 25 % smectite, 45 % illite, 20 % kaolinite, 10 % chlorite (Bloodworth and Morgan, 1989). Aquifer gravel from Dungness, Kent collected in 7.5 or 15 m depth.
[Np1]	The detailed compositions of ultramafic hornblendite (Syyry plutonic rock), gabbro (Mäntsälä plutonic rock), and greenstone (Sodankylä vulcanite) are given in Auxiliary Table 2. Porphyritic granite is a crushed sample from Kivetty (Finland).
[Np2]	Drill core sample is collective term for porphyric granite, granodiorite, tonalite, Rapakivi granite and mica gneiss samples that were studied by Suksi et al. (1989).
[Np4]	Sentinel Gap basalt (from Matawa, Wash.) and Westerly granite (from New Hampshire) were crushed to $\leq$ 50 mesh. Oxidized basalt was pretreated with NaOCl.
[Np3]	Basalt crushed to -70/325 mesh size.
[Np5]	Sediments covering the salt dome near Gorleben, Germany. Mainly quartz, small amounts of orthoklas, plagioklas, kaolinite, muskovite, calcite, chlorite, dolomite
[Pa1]	Sandy sediments collected at borehole Gohy 2227 near Gorleben in 130 m depth
[Pb1]	Sediments consisting mainly of quartz sand and smaller amounts of various clay minerals from layers above the Gorleben salt dome (Germany).
[Pb2]	Sediments consisting mainly of quartz sand and smaller amounts of various clay minerals from layers above the Gorleben salt dome (Germany).
[Pb3]	Sandy sediment rocks collected near Gorleben in 0 to 200 m depth (95% quartz and 5% clays mainly illite, kaolinite, montmorillonite).
[Pu1]	Crushed tuff from core samples collected on drillhole J-13 (Jackass Flats) and UE25a-1 (Yucca Mountain) at the Nevada Test Site.
[Pu2]	Crushed tuff from core samples collected on Jackass Flats at the Nevada Test Site.
[Pu3]	Crushed tuff (106-150 µm) from core samples collected on drill hole J-13 located in Jackass Flats at the Nevada Test Site. Composition see Auxiliary Table 3.
[Pu4]	Crushed tuff (106-500 µm) from core samples UE25a-1 (Yucca Mountain) at the Nevada Test Site.
[Pu5]	Boom clay posses clay minerals (illite, vermiculite), $CaCO_3$, FeS_2, 2-3% organic material.
[Pu6]	Kaolinite KGA-1 (<45 µm): Source Clay Repository, The Clay Minerals Society. Illite (< 45 µm): Ontario. Chlorite (106-180 µm): Yancey County, North Carolina.
[Pu8]	Clay from Saskatchewan, Canada: 80% montmorillonite, 10% illite and minor amounts of quartz, feldspar, gypsum, carbonate and organic matter. Na is the predominant exchangeable cation.

*2	[Pu9]	Wyoming bentonite MX-80.
*2	[Ra1]	Granite (0.063 - 0.105 mm). Bentonite:quartz mixture (10:90).
*2	[Ra2]	Sandstone from Rattlesnake Ridge Interbed above Pomona basalt flow and sandstone/claystone from Mabton Interbed located between Saddle Mountains and Wanapum Basalts (USA). Composition see Auxiliary Table 4.
*2	[Ra3]	London clay from Bradwell, UK, a tertiary mudrock: Composition see Auxiliary Table 5.
*2	[Ra4]	London clay from Bradwell, UK, a tertiary mudrock: Composition see Auxiliary Table 5. Tuff from the Borrowdale volcanics near Sellafield. haem: haematized, non-haem: not haematized (composition probably similar as given in Baston et al., 1994: C. Tweed, pers. comm)
*2	[Ra5]	St. Bees sandstone from Sellafield, UK (borehole1/1A, depth 680 m), Calder sandstone from Sellafield, UK (borehole1/1A, depth 504 m). Composition see Auxiliary Table 6.
*2	[Sr2]	fine grained granite (aplite): K-feldspar(38%), quartz (31%), plagioglase (23%), chlorite (3%), muscovite (2.5%) Äspö-diorite: plagioglase (45%), biotite (15%), K-feldspar (15%), quartz (14%), epidote (6%)
*2	[Sr3]	Detrital Quartz (25 - 32 %); other Detrital (2 - 4 %); Hematite (5 - 9 %); Clay Groundmass (60 - 64 %)
*2	[Th1]	St. Bees sandstone (Sellafield, UK: borehole1/1A, depth 680 m), Caithness flagstone (micaceous sandstone) a mudrock (tertiary London clay, Bradwell, UK) were crushed and the fraction 95% < 250 µm was used. Compositions: Auxiliary Tables 5, 6.
*2	[Th2]	Crushed tuff (< 300 µm) from Sellafield Borehole 2. Composition see Auxiliary Table 7.
*2	[Th3]	Tonalite: (quartz:35%; plagioclase:40%; biotite:20%). Mica gneiss: (quartz:30%; plagioclase:30%; biotite:30
*2	[Zr1]	Crushed tonalite (ø < 3 mm) from the Olkiluoto repository site (TVO)
*2	[U1]	Crushed tuff (75-500 µm) from core samples UE25a-1 (Yucca Mountain) at the Nevada Test Site.
*2	[U2]	Crushed granite (106-150 µm) from samples of the Piledriver tunnel at the Nevada Test Site. Composition see Auxiliary Table 8.
*2	[U3]	Crushed tuff (< 300 µm) from Sellafield Borehole 2. Tuff mineralogy dominated by quartz, feldspars and micas.
*2	[U4]	Crushed tuff and grandiorite (< 250 µm).
*2	[U5]	see *2 [Am4]

specific surface area

*3	[Pu8]	Surface area refers to the clay only (relative to the percentage present).

CEC

*4	[Ra3]	taken from Bloodworth and Morgan (1989)
*4	[Pu1]	measured with cesium and strontium.
*4	[Pu2]	measured with cesium and strontium.
*4	[Pu3]	measured with cesium and strontium.
*4	[Pu4]	measured with cesium and strontium.
*4	[Pu8]	CEC refers to the clay only (relative to the percentage present).
*4	[U1]	measured with cesium and strontium.
*4	[U2]	measured with cesium and strontium.

solid/water ratio

*5	[Ra4]	Kd values derived from through diffusion experiments with intact rocks.
*5	[Ra5]	Kd values derived from through diffusion experiments with intact rocks.

water type

*6	[Ac1]	Composition see Auxiliary Table 9.

[Am1] Groundwater composition: see Auxiliary Table 10.
[Am2] Groundwater collected at Gorleben: Gohy-2122: pH = 7, saline (2.5 M NaCl) and 0.1 mg C/L of DOC. Gohy-1061: pH = 8.1, Σ ions = 4E-3 M and 2 mg C/L of DOC.
[Am3] Composition of the Allard water see Auxiliary Table 10.
[Am4] Groundwater composition in the basalt: pH = 9.6, Eh=-0.48 V, $Na >> K \approx Ca \approx Mg > Fe(II)$; $Cl \approx SO_4 > CO_3 > F$; SiO_2 saturated. Interbed: pH≈ 8

[Np1] Groundwater composition: see Auxiliary Table 10.
[Np2] Groundwater composition: see Auxiliary Table 10.
[Np5] Groundwater composition: see Auxiliary Table 11.

[Pa1] Natural groundwater: conductivity 4550 µS/cm, Σ cations 44.3 meq/L, Σ anions 44.9 meq/L, and DOC 80 mg C/L.

[Pb1] Groundwater composition: see Auxiliary Table12.
[Pb2] Groundwater composition: see Auxiliary Table 12.

[Pu3] Groundwater composition: see Auxiliary Table 13.
[Pu5] Synthetic interstitial solution without organic material.
[Pu6] Synthetic saline groundwater (WN-1M) with 180 or 11000 mg/L total dissolved solid (TDS) in solution (corresponds to total amount of dissolved salts).
[Pu8] Synthetic groundwater with I = 0.27 (mainly Na, Ca, Cl) representing Canadian Shield groundwater.
[Pu9] Synthetic groundwater with total carbonate and salt concentration of 123 mg/L and 306 mg/L, respectively.

[Ra1] Groundwater composition: see Auxiliary Table 14.
[Ra2] Synthetic groundwater. Composition see Auxiliary Table 15.
[Ra3] CW1 is Cement-equilibrated water. Composition see Auxiliary Table 18. CW2 is CW1 adjusted with acid to the approximate far-field pH (Linklater, 1996)
[Ra5] Synthetic groundwater. Composition see Auxiliary Table 16.

[Sr1] Synthetic groundwater. Composition see Auxiliary Table 10.
[Sr2] Synthetic groundwater. Composition see Auxiliary Table 17.
[Sr3] Ca (70.8 mg/L); Mg (23.7 mg/L); K (7.6 mg/L); Si (43.4 mg/L); Na (28.5 mg/L)

[Th1] Cement-equilibrated water. Composition see Auxiliary Table 18.
[Th2] Synthetic goundwater: corresponds to groundwater in borehole 2, Sellafield. In the case of Pu, CO_2 partial pressure was controlled to prevent loss of CO_2.
[Th3] see Table 10 (Allard Water)

[U2] Synthetic groundwater prequilibrated for two weeks with granite. Composition: see Auxiliary Table19.
[U3] Synthetic goundwater: corresponds to groundwater in borehole 2, Sellafield. High-pH synthetic groundwater: corresponds to groundwater after interaction with cementious material (after soluble alkali metal hydroxides have been washed out).

[Zr1] Groundwater composition: see Auxiliary Table 20.

action time

[Ac1] These data are taken from Baston et al. (1995)

[Ra4] Kd values derived from through diffusion experiments.
[Ra5] Kd values derived from through diffusion experiments.

ase separation

[Pb1] Samples were analyzed without filtration (coarse particles), after filtration through 0.45 µm membrane filters (fine particles) and after ultrafiltration through 0.002 µm filter sets (molecular fraction).

[Ra4] Kd values derived from through diffusion experiments.

*9	[Ra5]	Kd values derived from through diffusion experiments.

atm./redox condition

*10	[Th1]	It was tried to prevent oxidation of redox-sensitive minerals in the material used.
*10	[Th2]	It was tried to prevent oxidation of redox-sensitive minerals in the material used.
*10	[U3]	It was tried to prevent oxidation of redox-sensitive minerals in the material used.

4 Auxiliary Tables

[Am1] Auxiliary Table 1: Mineral contents (in %) of the crushed rock samples used in the experiments of Pinnioja et al. (1984).

Sample name: (location)	tonalite (Olkiluoto)	rapakivi granite (Loviisa)
K-feldspar	78.6	
plagioklase	5.3	47
quartz	13	18.9
biotite	0.6	25.2
hornblende	1.5	6.8
fluorite	0.3	
apatite		0.8
chlorite	0.3	0.2
zirkon		0.4
opaques	0.4	
Fe oxides		0.7

[Np1] Auxiliary Table 2: Mineral contents (in %) of the rock samples (106-150 µm) used in the experiments of Kaukonen et al. (1993).

Sample name:	Mäntsälä plutonic rock: gabbro	Syyry plutonic rock: hornblendite	Sodankylä vulcanite: greenstone [1]
plagioklase	58.5	0.8	+++
quartz	-	-	+
K-feldspar	-	-	-
biotite	4.3	0.2	+
sericite	5	3	-
pyroxene	18.6	-	-
amphibole	8.5	90	++
olivine	1	-	-
chlorite	2.1	0.8	+(+)
carbonate	0.1	+	-
apatite	-	+	-
opaques	1.8	5.2	+

[1] The proportional abundances are depicted with + signs.

[Pu3] Auxiliary Table 3: Composition (in %) of tuff samples used in the experiments of Wolfsberg et al. (1979)

Sample name:	vitric tuff JA-18	devitrified tuff JA-32	zeolited tuff JA-37
sanidine	0.6	3.3	3
plagiclase	0.3	3	8.3
biotite	0.3	1	0.3
quartz	0.3	5	traces
opaque minerals	0.3	0.3	traces
lithic fragments	11.9	traces	11
glass	86	-	-
authigenic phases	0.3	87.3	77

[Ra2] Auxiliary Table 4: Composition of sandstone samples used in the experiments of Barney (1984).

sandstone	sandstone/ claystone
quartz	quartz
plagioclase	albite
orthoclase	anorthite
hornblende	nontronite
muscovite	biotite
biotite	orthoclase
clinopyroxene	illite

*2 [Ra4] [Th1] Auxiliary Table 5: Composition (%) of mudstone samples (Bloodworth and Morgan, 1989) used in the experiments of Baston et al. (1993) and Baston et al. (1992)

sample name:	London clay
smectite	25
illite	45
kaolinite	20
chlorite	10

*2 [Ra5] [Th1] Auxiliary Table 6: Composition (%) of sandstone and mudstone samples used in the experiments of Berry et al. (1994) and Baston et al. (1992)

sample name:	St. Bees sandstone	Calder sandstone	London clay
quartz	60	60	
K-feldspar	15	15	
plagioclase	5	10	
calcite	10	5	
clays and amorphous material	10	10	

*2 [Th2] Auxiliary Table 7: Composition of sandstone samples used in the experiments of Baston et al. (1994).

sample name:	Red eutaxitic massive tuff	Grey-green crystal-rich tuff
quartz	dominant	dominant
K-feldspar	present	minor
plagioclase	minor	major
calcite	major	present
dolomite	not detected	present ?
clays/micas	present	present
haematite	present	not detected
sample depth	577 m	723 m

*2 [U2] Auxiliary Table 8: Composition (in %) of granite samples (106-150 µm) used in the experiments of Erdal et al. (1979)

Sample name:	CS5	CS7
quartz	31	40
feldspar	48	46
plagioklas, K-feldspar	2	2
biotite, chlorite	10	5
sphene	<1	2
apatite	<1	<1
magnetite, ilmenite	8	5

*6 [Ac1] Auxiliary Table 9: Analysis of de-ionized water after equilibration for four weeks

(units in mg/L)	Temp. °C	Al	B	Ca	Fe	K	Mg	Na	Si
After equilibration with Tuff	room	0.07	0.23	10.2	0.08	0.6	0.42	75	6.8
After equilibration with Granodiorite	room	0.6	<0.1	4.1	0.2	11	2.4	29	6.2
After equilibration with Tuff	60	0.36	0.33	5	0.08	9	<0.05	97	10
After equilibration with Granodiorite	60	1.6	0.03	2.8	<.003	11	<0.05	11	14

continued:

(units in mg/L)		Sr	F-	Cl-	Br-	PO4	SO4	CO3	Final
After equilibration with Tuff		0.02	<0.1	4	<0.04	<0.1	115	37	9.
After equilibration with Granodiorite		0.02	0.41	20	0.13	ND	ND	<10	10.
After equilibration with Tuff		0.01	2.6	8.7	<0.02	<0.05	160	47	9.
After equilibration with Granodiorite		<0.002	0.78	1.2	<0.02	<0.05	0.55	<10	9.

[Am1] [Am 3] [Np1] [Np2] [Sr1] [Th3] Auxiliary Table 10: Composition of the groundwater used by Allard and Beall (1979), Pinnioja et al. (1984), Kaukonen et al. (1993) and Suksi et al. (1989) before equilibration with a solid. The composition of the solids used by Kaukonen et al. (1993) is given in Auxiliary Table

Groundwater	pH	Ca^{2+} (mg/L)	Mg^{2+} (mg/L)	K^+ (mg/L)	Na^+ (mg/L)	HCO_3^- (mg/L)	Cl^- (mg/L)	SiO_3^{2-} (mg/L)	SO_4^{2-} (mg/L)
Allard water (1:10), 123 mg/L HCO_3^-	8-8.2	1.8	0.43	0.39	47	123	4.1	1.6	0.96
Allard water (1:10), 12 mg/L HCO_3^-	8-8.2	1.8	0.43	0.39	5.6	12	4.1	1.6	0.96
Allard water (1:10), <2 mg/L HCO_3^-	8-8.2	1.8	0.43	0.39	0.95	<2	4.1	1.6	0.96
Allard water	8-8.2	18	4.3	3.9	65	123	70	12	9.6
Syvry groundwater	6.7	287	1.2	4.2	540	3.08	1338	15.3	10.16

[Np5] Auxiliary Table 11: Composition of the groundwater used by Lieser and Mühlenweg (1988)

Groundwater	pH	Na^+ (mg/L)	Mg^{2+} (mg/L)	Ca^{2+} (mg/L)	Sr^{2+} (mg/L)	$Fe^{2+/3+}$ (mg/L)	Mn^{2+} (mg/L)	Cl^- (mg/L)	Br^- (mg/L)
G7, sampled at a site near Gorleben, D	6.8 ± 0.1	57680	86	1861	2.6	0.01	4	97429	24.1

continued

	NO_3^- (mg/L)	SO_4 (mg/L)	HCO_3^- (mg/L)	SiO2 (mg/L)
	<0.01	2271	147	9.6

[Pb1] [Pb2] Auxiliary Table 12: Groundwater composition after equilibration with the sediments used in the experiments of Lieser et al. (1990) and Lieser and Ament (1993) for two weeks under anaerobic conditions (all concentrations in mmol/L).

Groundwater	Na	K	Mg	Ca	Cl	CO_3	SO_4
G1	0.75	0.028	0.12	0.45	0.54	0.87	0.22
G8	76.4	0.45	0.58	1.98	70.1	7.23	2.26
G9	162.2	0.65	2.18	6.39	160.1	8.5	5.01

[Pu3] Auxiliary Table 13: Groundwater composition after equilibration with the corresponding tuffs for two weeks under anaerobic conditions and filtration through 0.45 µm filters (Wolfsberg et al., 1979).

Groundwater	Ca (mg/L)	Fe (mg/L)	Mg (mg/L)	K (mg/L)	Na (mg/L)	CO_3 (mg/L)	Cl (mg/L)	F (mg/L)	SO_4 (mg/L)
JA-18	5.8	4.8	0.01	6.9	60	130	7.7	1.9	24
JA-32	7.2	0.5	0.8	6	60	130	7	1.7	21
JA-37	8.9	0.04	0.9	8.6	65	160	7.5	2.3	19

[Ra1] Auxiliary Table 14: Composition of the groundwater used by Allard et al. (1977, 1987), before equilibration with a solid.

Groundwater	Ca (mg/L)	Mg (mg/L)	K (mg/L)	Na (mg/L)	HCO_3 (mg/L)	Cl (mg/L)	F (mg/L)	SO_4 (mg/L)
aq1105	75	15	10	288	200	800	1.5	15
aq293	37.5	7.5	5	42	100	93	0.75	7.5

[Ra2] Auxiliary Table 15: Synthetic groundwater composition (mg/L) used in the experiments by Barney (1984).

Groundwater	Ca (mg/L)	Mg (mg/L)	K (mg/L)	Na (mg/L)	CO_3^{2-} (mg/L)	HCO_3^- (mg/L)	Cl (mg/L)	F (mg/L)	SO_4 (mg/L)
GR-1A	2	0.4	11.2	107	0	215	50 *	1.3	2.4
GR-2	1.06	0.07	2.5	225	59	75	131	29	72

* In the experiments under reducing conditions, Cl- conents increased to 479 mg/L due to addition of HCl to neutralize N_2H_4.

[Ra5] Auxiliary Table 16: Synthetic groundwater composition (M) used in the experiments by Berry et al. (1994).

Groundwater	Ca (M)	Mg (M)	Na (M)	K (M)	Al	Cl (M)	S (M)	C (M)	pH
St Bees Sandstone	0.047	0.015	1.5	0.0084	-	1.6	0.041	0.0015	7.2
Calder Sandstone	0.008	0.0053	0.072	0.00054	-	0.091	0.0029	0.00023	7.3

*6 [Sr2] Auxiliary Table 17: Synthetic groundwater composition (mg/l) used in the experiments by Johansson et al. (1997).

Li (mg/L)	Na (mg/L)	K (mg/L)	Rb (mg/L)	Cs (mg/L)	Mg (mg/L)	Ca (mg/L)	Sr (mg/L)	Ba (mg/L)	Cl (
1.3	2400	10	0.026	0.001	50	2540	35	0.14	

continued

SO_4 (mg/L)	SiO_2 (mg/L)	HCO_3 (mg/L)	pH	ionic strength
170	16	17	7.5	0.25

*6 [Th1] Auxiliary Table 18: Synthetic groundwater composition (M) used in the experiments by Baston et al. (1992).

Groundwater	Ca (M)	Mg (M)	Na (M)	K (M)	Al	Cl (M)	S (M)	C (M)	pH
cement-equilibrated water	0.011	-	0.00077	0.00071	0.000015	0.000054	-	0.00002	12.5

*6 [U2] Auxiliary Table 19: Groundwater composition after equilibration with granite for two weeks under aerobic conditions and filtration through 0.45 µm filters (Erdal et al., 1979).

Si (mg/L)	Ca (mg/L)	Fe (mg/L)	Mg (mg/L)	K (mg/L)	Na (mg/L)	CO_3 (mg/L)	Cl (mg/L)	F (mg/L)	SO_4 (mg/L
7.9	9.6	0.4	2	4.8	7.5	55	2.3	0.3	5.1

*6 [Zr1] Auxiliary Table 20: Composition of the natural groundwater (Olkiluoto) (mg/L)

NH_4	Ni	Na	Mn	Mg	K	Fe	Ca	Al	SO_4
<0.10	<0.003	190	0.018	4.97	2.48	0.066	21.7	0.097	49.7

continued

PO_4	NO_3	NO_2	F	Cl	SiO_2
0.82	<0.1	<0.1	0.63	185	14.2

Appendix B

Diffusion data tables

B.1 User's manual

B.2 Diffusion data

B.3 Footnotes

B.4 Auxiliary tables

B Diffusion database

B.1 User's manual

1) Da values are listed in an element-by-element fashion in individual spreadsheets
For each element, Da values are listed according to literature source and solid phase used.

2) Headers of columns that contain footnotes or references to auxiliary tables are tagged by an asterisk *, and a number (e. g. *3).

3) Footnotes and references to auxiliary tables can be found in the spreadsheet: footnotes
Footnotes can be found according to a code, consisting of the column header tag and the corresponding entry in the column 'code REF'.
These codes have the following format: <column header tag>[<code REF>], e.g. *2 [Pu3D], and are located in column Y.

4) Where no information on a given item could be found in the literature used, it is indicated by n.r. (not reported) in the table.

5) General informations and abbreviations for each column are given below:

column header	tag	information/abbreviations
nuclide	-	where reported, the mass of the nuclide used is given. (n.r.) = not reported, (n) = the natural isotopic composition of the respective element.
solid phase	*1	where details on the sorbents used are reported, they are given in the spreadsheets 'footnotes' and/or 'auxiliary tables'
density	*2	(d) = dry density. Other values refer to bulk (wet) density
porosity	-	-
water type	*3	details in spreadsheet 'footnotes' and/or 'auxiliary tables', PW = pure water, (p.e.) = pre-equilibrated with the sorbent
pH init	-	-
pH end	-	-
contact time	*4	(in) = in-diffusion experiment, (t) = through-diffusion experiment, (k) = kinetic data from batch sorption experiments
temp.	-	-
C init.	*5	-
stock solution	-	-
Da	*6	(c) = calculated by the corresponding authors
De	-	(c) = calculated by the corresponding authors
Dp	-	(c) = calculated by the corresponding authors
Eh init	-	-
Eh end	-	-
atm./redox condition	-	-
rock capacity factor	-	-
Reference	-	-
replicates, n	-	t = time series (i. e., individual experiments are not repeated, but there is a large number of measurements during the course of one experiment)
additional information	-	-
remarks	-	-
code REF	-	-

6) The contents of the speadsheets in this file may be sorted according to e. g. Kd value, author, or any other entry by using the Excel-functions in the menu <data - sort>.
It is recommended to copy the data into a separate file beforehand, in order to preserve the present file structure.
Note that the entries in the spreadsheets 'footnotes' and 'Auxiliary Tables' are preceded by two columns of code (e. g. column 1 = *6, column 2 = [Pb2D]),
so that both parts of the code may be used separately for sorting procedures.

B.2 Diffusion data

Table 1: Compilation of diffusion coefficients for U on rocks

nuclide	redox state	solid phase *1	density *2 g/cm³	porosity	water type *3	pH init	pH end	contact time *4 (d)	C init. *5 (M)	Da (U) *7	De (U) (1E-12 m^2/s)	Dp (U)	redox condition	K. (U) m^3/kg	α	Reference	remarks	code REF
U-233	n.r.	Rapakivi granite *1	-	n.r.	Allard water *3	8-8.2	n.r.	365 (in)	8.70E-06	0.013	n.r.	n.r.	N_2	0.015 *8	n.r.	Suksi et al. (1989)	conditions not very reducing (N_2), thus values for oxidising and reducing conditions similar	Np1D
U-233	n.r.	tonalite *1	-	n.r.	Allard water *3	8-8.2	n.r.	365 (in)	8.70E-06	0.011	n.r.	n.r.	N_2	0.015 *8	n.r.	Suksi et al. (1989)	Da calculated with rock capacity factor	Np1D
U-233	n.r.	Rapakivi granite *1	-	n.r.	Allard water *3	8-8.2	n.r.	365 (in)	8.40E-06	0.052	n.r.	n.r.	O_2	0.015 *8	n.r.	Suksi et al. (1989)		Np1D
U-233	VI	St. Bee sandstone *1	n.r.	n.r.	cement-equilibrated water *3	12.5	≈ 8	500 (t)	1E-06	0.45 (c)	6.8	n.r.	N_2	0.0068	15	Berry et al. (1994)	not reported experimental details probabely equal to Ra3	Ra1D
U-233	VI	St. Bee sandstone *1	n.r.	n.r.	cement-equilibrated water + gluconate *3	12.5	≈ 8	500 (t)	1E-06	0.65 (c)	2.6	n.r.	N_2	0.0018	4	Berry et al. (1994)	steady-state not reached, Kd values would incraese with steady state	Ra1D
U-233	VI	St. Bee sandstone *1	n.r.	n.r.	cement-equilibrated water + org. *3	12.5	≈ 8	500 (t)	1E-06	2.1 (c)	2.1	n.r.	N_2	0.0004	1	Berry et al. (1994)		Ra1D

Table 2: Compilation of diffusion coefficients for Np on rocks

nuclide	redox state	solid phase *1	density *2 g/cm³	porosity	water type *3	pH init	pH end	contact time *4 (d)	C init. *5 (M)	Da (Np) *7	De (Np) (1E-12 m^2/s)	Dp (Np)	redox condition	K. (Np) m^3/kg	α	Reference	remarks	code REF
Np-237	n.r.	Rapakivi granite *1	-	n.r.	Allard water *3	8-8.2	n.r.	365 (in)	1.60E-04	0.014	n.r.	n.r.	N_2	0.02 *8	n.r.	Suksi et al. (1989)	conditions not very reducing (N_2),	Np1D
Np-237	n.r.	tonalite *1	-	n.r.	Allard water *3	8-8.2	n.r.	365 (in)	1.60E-04	0.021	n.r.	n.r.	N_2	0.02 *8	n.r.	Suksi et al. (1989)	thus values for oxidising and	Np1D
Np-237	n.r.	tonalite *1	-	n.r.	Allard water *3	8-8.2	n.r.	365 (in)	1.30E-04	0.027	n.r.	n.r.	O_2	0.02 *8	n.r.	Suksi et al. (1989)	reducing conditions similar	Np1D
Np-237	n.r.	granodiorite (Fi8) *1	-	n.r.	synthetic GW-Fi8 *3	8.3	8.4	866 (in)	1E-08	0.0033	n.r.	n.r.	n.r. (atm)	n.r.	n.r.	Ittner et al. (1988)		Am1D
Np-237	n.r.	gneiss *1	-	n.r.	synthetic GW-Stu *3	7.3	8.4	654 (in)	1E-08	0.00	n.r.	n.r.	n.r. (atm)	n.r.	n.r.	Ittner et al. (1988)		Am1D

Table 3: Compilation of diffusion coefficients for Pu on rocks

nuclide	redox state	solid phase *1	density *2 g/cm³	porosity	water type *3	pH init	pH end	contact time *4 (d)	C init. *5 (M)	Da (Pu) *7	De (Pu)	Dp (Pu)	redox condition	K_d (Pu) m^3/kg	α	Reference	remarks	code REF
										----------	(1E-12 m^2/s)	-----------						
Pu-236	n.r.	Rapakivi granite *1	-	n.r.	Allard water *3	8-8.2	n.r.	365 (in)	9.40E-14	0.0027	n.r.	n.r.	N_2	0.02 *8	n.r.	Suksi et al. (1989)	conditions not very reducing (N_2), thus values for oxidising and reducing conditions similar	Np1D
Pu-236	n.r.	tonalite *1	-	n.r.	Allard water *3	8-8.2	n.r.	365 (in)	9.40E-14	0.0035	n.r.	n.r.	N_2	0.02 *8	n.r.	Suksi et al. (1989)		Np1D
Pu-236	n.r.	Rapakivi granite *1	-	n.r.	Allard water *3	8-8.2	n.r.	365 (in)	3.60E-14	0.0024	n.r.	n.r.	O_2	0.02 *8	n.r.	Suksi et al. (1989)		Np1D
Pu-236	n.r.	tonalite *1	-	n.r.	Allard water *3	8-8.2	n.r.	365 (in)	3.60E-14	0.0054	n.r.	n.r.	O_2	0.02 *8	n.r.	Suksi et al. (1989)		Np1D
Pu-239	n.r.	granodiorite (Fi8) *1	-	n.r.	synthetic GW-Fi8 *3	8.3	4.1	854 (in)	1E-09	0.0016	n.r.	n.r.	n.r. (atm)	n.r.	n.r.	Ittner et al. (1988)	Diffusion depends on pH	Am1D
Pu-239	n.r.	gneiss *1	-	n.r.	synthetic GW-Stu *3	7.3	2.9	858 (in)	1E-09	0.0012	n.r.	n.r.	n.r. (atm)	n.r.	n.r.	Ittner et al. (1988)		Am1D
Pu-239	n.r.	gneiss *1	-	n.r.	synthetic GW-Stu *3	8.9	3	646 (in)	1E-09	0.0015	n.r.	n.r.	n.r. (atm)	n.r.	n.r.	Ittner et al. (1988)		Am1D
Pu-238	n.r.	St. Bee sandstone *1	n.r.	n.r.	cement-equilibrated water *3	12.5	≈ 8	500 (I)	1E-10	-	< 0,01 *7	n.r.	N_2	n.r.	n.r.	Berry et al. (1994)	Kd in batch: 10	Ra1D
Pu-238	n.r.	St. Bee sandstone *1	n.r.	n.r.	cement-equil. water + gluconate *3	12.5	≈ 8	500 (I)	1E-10	0.48 (c)	1	n.r.	N_2	0.0009	2.1	Berry et al. (1994)	Kd in batch: 0,001-0,01	Ra1D
Pu-238	n.r.	St. Bee sandstone *1	n.r.	n.r.	cement-equilibrated water + org. *3	12.5	≈ 8	500 (I)	1E-10	0.83 (c)	0.33	n.r.	N_2	0.0002	0.4	Berry et al. (1994)	Kd in batch: 0,3-1,0	Ra1D
																	experimental details not reported probably equal to Ra3, steady-state not reached, Kd values would incraese with steady state	

Table 4: Compilation of diffusion coefficients for Pu on clays

nuclide	redox state	solid phase *1	density *2 g/cm³	porosity	water type *3	pH init	pH end	contact time *4 (d)	C init. *5 (M)	Da (Pu) *7	De (Pu)	Dp (Pu)	redox condition	K_d (Pu) m^3/kg	α	Reference	remarks	code REF
										----------	(1E-12 m^2/s)	-----------						
Pu-239	IV	MX-80 bentonite*1	2	n.r.	artifical groundwater (p.e.) *3	n.r.	n.r.	465 (in)	4E-10 mol *5	<0.0003	n.r.	n.r.	Fe(II)	n.r.	n.r.	Albinsson et al. (1990)	The authors assumed	Pu1D
Pu-239	n.r.	90% sand, 10% bentonite	2	n.r.	artifical groundwater (p.e.) *3	n.r.	n.r.	n.r.	n.r.	<0.002	n.r.	n.r.	atm	n.r.	n.r.	Albinsson et al. (1990)	Pu(IV) to be present	Pu1D
Pu-239	IV	MX-80 bentonite*1	2	n.r.	artifical groundwater (p.e.) *3	8.8-9	n.r.	316 (in)	3E-8 mol *5	<0.0019	n.r.	<31 (c)	atm	3.5	n.r.	Torstenfelt and Allard (1986)		Pu2D
Pu	n.r.	boom clay *1	2	0.2	synthetic porewater *3	n.r.	n.r.	1-90	n.r.	0.03 (c)	n.r.	n.r.	anaerobic	0.4	n.r.	Henrion et al. (1986)	extract from many experiments, some experimental details not reported, careful experimental work, same values for Eu, Am and Pu	Pu3D
Pu	IV	Atlantic SNAP *1	2	0.2	seawater	n.r.	n.r.	61	n.r.	n.r.	< 0,018	n.r.	N_2	n.r.	n.r.	Schreiner et al. (1985)	Experimental details not reported	Pu4D
Pu	IV	Atlantic GME *1	2	0.2	seawater	n.r.	n.r.	61	n.r.	n.r.	< 0,016	n.r.	N_2	n.r.	n.r.	Schreiner et al. (1985)		Pu4D
Pu	IV	Pacific smectite *1	2	0.2	seawater	n.r.	n.r.	61	n.r.	n.r.	< 0,010	n.r.	oxidizing	n.r.	n.r.	Schreiner et al. (1985)		Pu4D
Pu	IV	Pacific illite *1	2	0.2	seawater	n.r.	n.r.	61	n.r.	n.r.	< 0,012	n.r.	oxidizing	n.r.	n.r.	Schreiner et al. (1985)		Pu4D
Pu	VI	Pacific smectite *1	2	0.2	seawater	n.r.	n.r.	61	n.r.	n.r.	< 0,0019	n.r.	oxidizing	n.r.	n.r.	Schreiner et al. (1985)		Pu4D
Pu-239	IV	bentonite*1	2	n.r.	artifical groundwater (p.e.) *3	n.r.	n.r.	461 (in)	4E-06	< 0.0003	n.r.	n.r.	N_2	n.r.	n.r.	Albinsson et. al. (1990)	Details of experimental technique available in Torstenfeld B. et al. Soil Science 139 (6) 512 (1985)	Pu6D
Pu-239	IV	clay/sand (10/90) *1	2.09	0.22	synthetic groundwater *3	8	8	720 (in)	n.r.	0.02	n.r.	n.r.	NO_2^-	0.15	n.r.	Sharma and Oscarson (1989)	Kd value increases with fraction of clay present (only bentonite: Kd = 1,5)	Pu5D
Pu-239	IV	clay/sand (10/90) *1	2.32	0.13	synthetic groundwater *3	8	8	720 (in)	n.r.	0.02	n.r.	n.r.	NO_2^-	0.15	n.r.	Sharma and Oscarson (1989)		Pu5D
Pu-239	IV	clay/sand (25/75) *1	1.74	0.36	synthetic groundwater *3	8	8	720 (in)	n.r.	0.03	n.r.	n.r.	NO_2^-	0.37	n.r.	Sharma and Oscarson (1989)		Pu5D
Pu-239	IV	clay/sand (25/75) *1	2.13	0.21	synthetic groundwater *3	8	8	720 (in)	n.r.	0.01	n.r.	n.r.	NO_2^-	0.37	n.r.	Sharma and Oscarson (1989)		Pu5D
Pu-239	IV	clay/sand (50/50) *1	1.4	0.48	synthetic groundwater *3	8	8	720 (in)	n.r.	0.03	n.r.	n.r.	NO_2^-	0.77	n.r.	Sharma and Oscarson (1989)		Pu5D
Pu-239	IV	clay/sand (50/50) *1	1.63	0.41	synthetic groundwater *3	8	8	720 (in)	n.r.	0.02	n.r.	n.r.	NO_2^-	0.77	n.r.	Sharma and Oscarson (1989)		Pu5D

Table 5: Compilation of diffusion coefficients for Am on rocks

nuclide	solid phase *1	density g/cm³	*2porosity	water type *3	pH init	pH end	contact time *4 (d)	C init. *5 (M)	Da (Am) *7	De (Am) (1E-12 m²/s)	Dp (Am)	redox condition	K_d (Am) m³/kg	α	Reference	remarks	code REF
Am-241	granodiorite (Fi8) *1	-	n.r.	synthetic GW-Fi6 *3	7.7	n.r.	355 (in)	1E-08	0.023	n.r.	n.r.	n.r. (atm)	n.r.	n.r.	Ittner et al. (1988)	Diffusion in weathered rock seems to be larger	Am1D
Am-241	granodiorite (Fi8) *1	-	n.r.	synthetic GW-Fi7 *3	8.1	n.r.	263 (in)	1E-08	0.028	n.r.	n.r.	n.r. (atm)	n.r.	n.r.	Ittner et al. (1988)		Am1D
Am-241	granodiorite (Fi8) *1	-	n.r.	synthetic GW-Fi8 *3	8.3	8.4	877 (in)	1E-09	0.00039	n.r.	n.r.	n.r. (atm)	n.r.	n.r.	Ittner et al. (1988)		Am1D
Am-241	gneiss *1	-	n.r.	synthetic GW-Stu *3	7.3	n.r.	85 (in)	1E-08	0.00071	n.r.	n.r.	n.r. (atm)	n.r.	n.r.	Ittner et al. (1988)		Am1D
Am-241	granite *1	-	n.r.	synthetic GW-Str *3	8.9	8.6	665 (in)	1E-09	0.001	n.r.	n.r.	n.r. (atm)	n.r.	n.r.	Ittner et al. (1988)		Am1D
Am-241	granite *1	-	n.r.	synthetic GW-Str *3	8.9	8.9	1202 (in)	1E-09	0.0038	n.r.	n.r.	n.r. (atm)	n.r.	n.r.	Ittner et al. (1988)		Am1D

Table 6: Compilation of diffusion coefficients for Ra and Sr on rocks

nuclide	solid phase *1	density *2 g/cm³	porosity	water type *3	pH init	pH end	contact time *4 (d)	C init. *5 (M)	Da *7	De	Dp	redox condition	K_d m³/kg	α	Reference	remarks	code REF
									---------- (1E-12 m²/s)		----------						
Radium																	
Ra-226	St. Bee sandstone *1	n.r.	n.r.	synthetic groundwater *3	7.2	n.r.	50 (t)	1E-08	1.7	17	n.r.	N_2	0.0046	10.3	Berry et al. (1994)	experimental details not	Ra1D
Ra-226	St. Bee sandstone *1	n.r.	n.r.	synthetic groundwater *3	7.2	n.r.	50 (t)	1E-07	2.9	9.7	n.r.	N_2	0.0013	3.3	Berry et al. (1994)	reported probably equal to Ra3	Ra1D
Ra-226	Calder sandstone *1	n.r.	n.r.	synthetic groundwater *3	7.3	n.r.	50 (t)	1E-08	1.7	36	n.r.	N_2	0.0095	21.5	Berry et al. (1994)	Da calculated with	Ra1D
Ra-226	Calder sandstone *1	n.r.	n.r.	synthetic groundwater *3	7.3	n.r.	50 (t)	1E-07	2.3	37	n.r.	N_2	0.0073	16.2	Berry et al. (1994)	rock capacity factor	Ra1D
Ra	London clay *1	n.r.	n.r.	cement-equtibrated water	~12	n.r.	n.r. (t)	n.r.	1.2	49	n.r.	N_2	0.017	n.r.	Baston et al. (1993)	experimental details not	Ra2D
Ra	London clay *1	n.r.	n.r.	porewater with 0.0002 M Ca	n.r.	n.r.	n.r. (t)	n.r.	1.4	63	n.r.	N_2	0.020	n.r.	Baston et al. (1993)	reported probably equal to Ra3	Ra2D
Ra	London clay *1	n.r.	n.r.	porewater with 0.002 M Ca	n.r.	n.r.	n.r. (t)	n.r.	1.9	53	n.r.	N_2	0.012	n.r.	Baston et al. (1993)	Da calculated with	Ra2D
Ra	London clay *1	n.r.	n.r.	porewater with 0.02 M Ca	n.r.	n.r.	n.r. (t)	n.r.	3.2	45	n.r.	N_2	0.006	n.r.	Baston et al. (1993)	rho=2300 kg/m3, e=0.25)	Ra2D
Strontium																	
Sr-85	Inada granite *1	n.r.	0.8	deionized water *3	4.3	n.r.	7 (in)	2 kBq/ml	0.04	n.r.	n.r.	n.r. (atm)	n.r.	n.r.	Idemitsu et al. (1992)		Ra3D
Sr-85	Inada granite *1	n.r.	0.8	deionized water *3	6	n.r.	7 (in)	2 kBq/ml	0.04	n.r.	n.r.	n.r. (atm)	n.r.	n.r.	Idemitsu et al. (1992)		Ra3D
Sr-85	Inada granite *1	n.r.	0.8	deionized water *3	7.7	n.r.	7 (in)	2 kBq/ml	0.05	n.r.	n.r.	n.r. (atm)	n.r.	n.r.	Idemitsu et al. (1992)		Ra3D
Sr-85	Inada granite *1	n.r.	0.8	deionized water *3	9.4	n.r.	7 (in)	2 kBq/ml	0.04	n.r.	n.r.	n.r. (atm)	n.r.	n.r.	Idemitsu et al. (1992)		Ra3D
Sr-85	fine grained granite *1	n.r.	0.25	synthetic groundwater *3	7.5	n.r.	n.r. (t)	n.r.	1.4	0.035	n.r.	n.r. (atm)	8.20E-05	0.025	Johansson et. al. (1997)	Da calculated with	Sr1D
Sr-85	Äspö-diorite *1	n.r.	0.55	synthetic groundwater *3	7.5	n.r.	n.r. (t)	n.r.	2.2	0.063	n.r.	n.r. (atm)	6.90E-05	0.029	Johansson et. al. (1997)	rock capacity factor	Sr1D
Sr-90	granodiorite (Fi7) *1	n.r.	n.r.	synthetic GW-Fi7 *3	8.1	n.r.	164 (in)	1E-07	0.49	n.r.	n.r.	n.r. (atm)	n.r.	n.r.	Ittner et al. (1988)	Diffusion mainly in veins	Am1D
Sr-90	gneiss *1	n.r.	n.r.	synthetic GW-Stu *3	7.3	8.3	432 (in)	1E-07	0.027	n.r.	n.r.	n.r. (atm)	n.r.	n.r.	Ittner et al. (1988)		Am1D
Sr-90	granite *1	n.r.	n.r.	synthetic GW-Str *3	8.9	8.5	657 (in)	1E-07	0.024	n.r.	n.r.	n.r. (atm)	n.r.	n.r.	Ittner et al. (1988)		Am1D

B.3 Footnotes

solid phase

*1 [Am1D] The composition of the granites are given in Auxiliary Table 1.

*1 [Np1D] The composition is given in Auxiliary Table 2.

*1 [Pu1D] Wyoming bentonite MX-80 was compacted to a density of 2E-3 kg/m^3. Its composition is given in Auxiliary Table
*1 [Pu2D] Wyoming bentonite MX-80 was compacted to a density of 2E-3 kg/m^3. Its composition is given in Auxiliary Table
*1 [Pu3D] Boom clay consists of clay minerals (illite, vermiculite), $CaCO_3$, FeS_2, 2-3% organic material.
*1 [Pu4D] Composition of SNAP and GME see Auxiliary Table 4. Pacific smectite and Pacific illite: red clays collected in the Pacific MPG I area (31°30' N; 158° W), consisting of clay minerals, hydrous iron oxides and manganese.
*1 [Pu5D] Clay from Saskatchewan, Canada: 80% montmorillonite, 10% illite and minor amounts of quartz, feldspar, gypsum, carbonate and organic matter. Na is predominant exchangeable cation.
*1 [Pu6D] Sodium bentonite (MX-80, Wyoming bentonite) compacted to a density of 2000 kg/m^3.

*1 [Ra1D] St. Bees sandstone from Sellafield, UK (borehole1/1A, depth 680 m), Calder sandstone from Sellafield, UK (borehole1/1A, depth 504 m). Composition see Auxiliary Table 5.
*1 [Ra2D] London clay from Bradwell, UK, a tertiary mudrock containing 25 % smectite, 45 % illite, 20 % kaolinite, 10 % chlorite (Bloodworth and Morgan, 1989).

*1 [Sr1D] fine grained granite: K-feldspar(38%), quartz (31%), plagioglase (23%), chlorite (3%), muscovite (2.5%). Äspö-diorite: plagioglase (45%), biotite (15%), K-feldspar (15%), quartz (14%), epidote (6%)

water type

*3 [Am1D] The composition of the synthetic groundwaters is given in Auxiliary Table 6.

*3 [Np1D] The composition is given in Auxiliary Table 7.

*3 [Pu1D] Allard Water', see Auxiliary Table 8.
*3 [Pu2D] Allard Water', see Auxiliary Table 8.
*3 [Pu3D] Synthetic interstitial solution without organic material.
*3 [Pu5D] Synthetic groundwater with I = 0.27 (mainly Na, Ca, Cl) representing Canadian Shield groundwater.

*3 [Ra1D] Synthetic groundwater and cement water. Composition see Auxiliary Table 9. Org: authentic degradation produc from 10% cellulose in the cement.

*3 [Sr1D] Synthetic groundwater. Composition see Auxiliary Table 10.

C init

*5 [Pu1D] 4E-10 moles represents the total amount of Pu added in the experiment.
*5 [Pu2D] 3E-8 moles represents the total amount of Pu added in the experiment.

stock solution

*6 [Pu6D] First 1 mL of 1 M HCl was added and thereafter 15 mL of liquid scintillation cocktail (Pico-Fluor 30, Packard Instruments Company, USA)

*6 [Ra1D] Calibrated acidic stock solutions from the Actinide Chemistry and Analysis Department, AEA Fuel Services, Harwell, UK.

D_a

*** 7 [Ra1D]** no breakthrough was observed in the absence of organic materials.

K_d

*** 8 [Np1D]** K_a in m3/m2; $K_a = K_d$/ surface area

B.4 Auxiliary Tables

*1 [Am1D] Auxiliary Table 1: Mineral contents (in %) of the granitic drill core samples used in the experiments of Ittner et al. (1988).

Sample name:	Finnsjön granite-Fi6	Finnsjön granite-Fi7	Finnsjön granite-Fi8	Studsvik granite	Stripa granite
quartz	30	30	30	40-70	
feldspar				10-40	
microcline	18	18	18		30-40
plagioklase	32	32	32		
biotite/chlorite	9	9	9	+	5-10
hornblende	11	11	11		
rock type	granodiorite (foliated)	granodiorite (foliated)	granodiorite (foliated)	gneis [1]	granite [2]
fractures	no	no	filled with calcite	no	yes

[1] Hetergeneous gneis of sedimentary origin which strongly migmatized and veined in parts. Additionally to quartz, feldspar, biotite and chlorite it contains also andalusite, sillimanite, garnet, and corderite.

[2] Homogeneous granite containing hematite. Fractures filled with chlorite and sericite or with quartz and feldspars.

*1 [Np1D] Auxiliary Table 2: Mineral contents (in %) of the granitic drill core samples used in the experiments of Suksi et al. (1989).

Sample name:	Rapaviki granite	tonalite
quartz	28.9	15.9
K-feldspar	49.9	0.1
plagioklase	12.5	47.9
biotite	4.7	26.6
hornblende	3.3	4.9
apatite	+	0.9
epidote	+	0.1
sphene	-	0.3
carbonate	+	0.2
chlorite	0.3	0.9
muskovite	0.6	1.6
opaques	0.3	0.4

[1] The proportional abundances are depicted with + signs.

*1 [Pu1D] [Pu2D] Auxiliary Table 3: Composition of Wyoming bentonite MX-80 used in the experiments of Albinsson et al. (1990) and Torstenfelt and Allard (1986).

Parameters	MX-80	Reference
Minerals:		
smectite	88.6%	-
quartz	10.0%	van Olphen and Fripiat (1979)
calcite	1.4%	Müller-Vonmoos and Kahr (1983)
Soluble impurities:		
NaCl	0.01%	Wanner et al. (1992)
$CaSO_4$	0.34%	Wanner et al. (1992)
Surface chemical parameters:		
CEC	85 meq/100g	Wieland et al. (1994)
exchangable Na^+	81.7%	Müller-Vonmoos and Kahr (1983)
exchangable K^+	0.3%	Müller-Vonmoos and Kahr (1983)
exchangable Mg^{2+}	3.9%	Müller-Vonmoos and Kahr (1983)
exchangable Ca^{2+}	14.1%	-
SOH site density	2.8 meq/100g	Wieland et al. (1994)

*1 [Pu4D] Auxiliary Table 4: Composition (in %; proportional abundances are depicted with + or – signs) of the ocean floor sediment samples used in the experiments of Schreiner et al. (1985).

Sample name:	SNAP: Southern Nares Abyssal Plain	GME: Great Meteor Location, Atlantic Ocean
quartz	28.9	15.9
K-feldspar	49.9	0.1
plagioklase	12.5	47.9
biotite	4.7	26.6
hornblende	3.3	4.9
apatite	+	0.9
epidote	+	0.1
sphene	-	0.3
carbonate	+	0.2
chlorite	0.3	0.9
muskovite	0.6	1.6
opaques	0.3	0.4

*1 [Ra1D] Auxiliary Table 5: Composition of sandstone samples used in the experiments of Berry et al. (1994).

sample name:	St. Bees sandstone	Calder sandstone
quartz	60	60
K-feldspar	15	15
plagioclase	5	10
calcite	10	5
clays and amorphous material	10	10

*3 [Am1D] Auxiliary Table 6: The composition (mg/L) of the synthetic groundwaters representative of the groundwater compositions sampled in boreholes at Finnsjön (GW-Fi6 - GW-Fi8), Stripa (GW-Str), and Studsvik (GW-Stu) (Ittner et al., 1988).

Parameters	GW-Fi6	GW-Fi7	GW-Fi8	GW-Str	GW-Stu
Ca	1.38E-02	3.34E-03	9.23E-04	3.49E-04	7.73E-04
Mg	2.84E-03	6.58E-04	4.94E-04	9.46E-06	3.70E-04
Na	4.17E-02	1.19E-02	1.39E-02	2.13E-03	3.91E-03
K	4.09E-04	4.09E-04	3.07E-04	1.51E-05	7.16E-05
Cl	6.81E-02	1.35E-02	1.09E-02	9.90E-04	1.61E-03
SO4	2.13E-03	4.68E-04	4.37E-04	5.10E-05	3.75E-04
F	5.26E-05	9.47E-05	1.21E-04	0.00E+00	0.00E+00
CO3	2.02E-03	4.59E-03	4.31E-03	1.41E-03	3.20E-03
SiO2	2.83E-04	2.16E-04	2.00E-04	9.15E-05	1.83E-04
pH	7.7	8.1	8.3	8.9	7.3

*3 [Np1D] Auxiliary Table 7: Composition of the Allard water used by Suksi et al. (1989) before equilibration with a solid.

Groundwater	pH	Ca^{2+} (mg/L)	Mg^{2+} (mg/L)	K^{+} (mg/L)	Na^{+} (mg/L)	HCO_3^{-} (mg/L)	Cl^{-} (mg/L)	SiO_3^{2-} (mg/L)	SO_4^{2-} (mg/L)
Allard water	8-8.2	18	4.3	3.9	65	123	70	12	9.6

*3 [Pu1D] Auxiliary Table 8: Composition (mg/L) of Allard water used in the experiments of Torstenfelt and
[Pu2D] Allard (1986) and Albinsson et al. (1990).

Parameters	mg/L
Ca	6.6
Mg	1.7
Na	670
K	11
Cl	132
SO_4	870
NO_3	6.8
pH	8.8-9.0

*3 [Ra1D] Auxiliary Table 9: Synthetic groundwater composition (M) used in the experiments by Berry et al. (1994).

Groundwater	Ca (M)	Mg (M)	Na (M)	K (M)	Al	Cl (M)	S (M)	C (M)	pH
cement-equilibrated water	0.011	-	0.00077	0.00071	0.000015	0.000054	-	0.00002	12.5
St Bees Sandstone	0.047	0.015	1.5	0.0084	-	1.6	0.041	0.0015	7.2
Calder Sandstone	0.008	0.0053	0.072	0.00054	-	0.091	0.0029	0.00023	7.3

*3 [Sr1D] Auxiliary Table 10: Synthetic groundwater composition (mg/l) used in the experiments by Johansson et al. (1997).

Li (mg/L)	Na (mg/L)	K (mg/L)	Rb (mg/L)	Cs (mg/L)	Mg (mg/L)	Ca (mg/L)	Sr (mg/L)	Ba (mg/L)	Cl (mg/L)
1.3	2400	10	0.026	0.001	50	2540	35	0.14	8350

cont.

SO (mg/L)	SiO (mg/L)	HCO (mg/L)	pH	ionic strength
170	16	17	7.5	0.25

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Thermodynamic Data for Predicting Concentrations of AnO_2^+ and AnO_2^{2+} Species in Geologic Environments

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Introduction

This report supplements those on the thermodynamic databases for the trivalent and tetravalent actinides from PNNL [97RAI/RAO-1], [97RAI/RAO-2]. In this report, the stability constants compiled from a review of the literature are presented in a series of tables. In addition, available literature data on the solubility products are tabulated. Finally, an evaluation of the recommended values of log β_1 (stability constants for the 1:1 complexes) are given as a guide for the more reliable values in the tables. The project did not provide time or resources for conducting a critical evaluation comparable to the multi-year, multi-investigator projects of the OECD-NEA. We accept the NEA recommended values for U(VI), Pu(VI) and Pu(V) data as reliable and suggest use of these to determine the more reliable values for the other AnO_2^+ and AnO_2^{2+} systems.

Solubility Product Data

The solubility product values, log K_{sp} listed, for the actinide (V) oxidation state are those for NpO_2^+ from recent studies. Earlier studies do not characterize the solid state well and thus should not be used. Solid state characterization is also a problem for the values of $NpO_2(OH)$. Values for the green amorphous and white crystalline $NpO_2(OH)$ solids have been determined by [92NEC/KIM]; however the crystalline solid may not have had aged sufficiently (2-4 weeks). A recent value for the amorphous solid of log K_{sp} = -8.79 [96ROB/SIL] was determined with more data than the -8.76 value of [92NEC/KIM] and is recommended for the $NpO_2(OH)_{am}$. No values for the crystalline solid have been chosen. Recommended log K_{sp} values for $NaNpO_2CO_3$ and $Na_3NpO_2(CO_3)_2$ are -11.00 and -14.32 respectively [95NEC/RUN].

Solubility products have been determined experimentally for U(VI), Np(VI) and Pu(VI) with various inorganic ligands, i.e., CO_3^{2-}, OH^-, HPO_4^-, SO_3^{2-}, etc. The log K_{sp} values from the recent thermodynamic compilations of NEA [92GRE] and IAEA [92FUG/KHO] are recommended. No recommended values for the hydrolysis compounds of the hexavalent species can be given since for most values, the experiments did use a pure solid state which had been adequately characterized.

Pitzer Parameters for Modeling

Values for the Pitzer parameters of the important species are reported for the most for the actinides in the (V) oxidation state. As one would expect, all of these studies are for the most stable ion, NpO_2^+, obtained from solubility studies. While experimentally, the studies seem equally well done, the β parameters from [95NEC/FAN] are recommended as a consistent set. These can be augmented with the interaction parameters of [96RUN/NEU] which is a more complicated study that included hydrolysis. Values from other studies are not used since they neglect the β(1) determination for important species making the β(0) values too large.

Pitzer parameter values for the actinide (VI) oxidation state are sparse, making recommendation of values difficult. The only experimentally determined values are for UO_2^{2+} systems. The β(0) and β(1) values reported for plutonyl carbonates [97PAS/CZE] are for uranyl carbonate. These plutonyl carbonate values do work well only as a first approximation. All of the other reported Pitzer parameters are unique except for those of UO_2^{2+}-ClO_4^-. An average of the β(0), β(1), and C^Φ determinations from [73PIT/MAY] and [88KIM/FRE] are recommended for use. These estimated values are 0.6, 2.0 and 0.016 for β(0), β(1), and, C^Φ, respectively.

Recommended log $\beta_1°$

A set of values of the stability constant for the reaction

$$An^{m+} + X^{na-} = An^{n-m}$$

where An=An^{3+}, An^{4+}, AnO_2^+ and AnO_2^{2+} at I = 0 M and 25°C have been selected and listed in a separate section. The basis of selection of these values is given in the Introduction to that section.

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Tables of
Stability Constants for
NpO_2^+ and PuO_2^+

Equilibrium constants (β_{mn})[1] for formation of aqueous NpO_2^+ complexes with F^- ($mNpO_2^+ + nF^- \rightleftharpoons (NpO_2)_mF_n^{(m-n)+}$)

log β_1	log β_2	Medium	Maximum Metal/H^+/Ligand Concentration	Method	Reference
1.76		0.1M $NaClO_4$	M:3mM, H:5mM, L:2mM	pot, F^-	[85SAW/RIZ]
1.5		0.1M $NaClO_4$	M:5mM, pH=6.5, L:2mM	pot, F^-	[85SAW/RIZ]
1.26		1M $NaClO_4$	M:tr, pH=3, L:6mM	pot, F^-	[84CHO/RAO]
1.39	2.07	1M $NaClO_4$	M:tr, pH=6.6, L:0.4M	dis	[85INO/TOC2]
1.2		1M $NaClO_4$	M:5mM, pH=6.5, L:0.3mM	pot, F^-	[85SAW/RIZ]
1.35		2M $NaClO_4$		sp	[78RAO/PAT]
0.99		2M $NaClO_4$	M:tr, pH[2], L:60mM	dis	[79RAO/GUD]
0.90		[3]	[3]	nmr	[76VOD/KOL]

1) If m = 1, β_{mn} is written β_n

2) pH not mentioned in the paper

3) No experimental details are given in the paper

Equilibrium constants (β_{mn})[1] for formation of aqueous NpO_2^+ complexes with Cl^- ($mNpO_2^+ + nCl^- \rightleftharpoons (NpO_2)_mCl_n^{(m-n)+}$)

log β_1	log β_2	Medium	Maximum Metal/H⁺/Ligand Concentration	Method	Reference
-0.29	<-1	I=0[2]	M:tr, H:1mM, L:5M	dis	[95NEC/FAN]
-0.55		1M Na(ClO_4,Cl)	M:tr, H:1mM, L:1M	dis	[95NEC/FAN]
-0.30		2M H(ClO_4,Cl)	M:tr, H:2M, L:2M	cix	[64GAI/SYK]
-0.42		2M Na(ClO_4,Cl)	M:tr, pH[3], L:1M	dis	[79RAO/GUD]
-0.42		2M Na(ClO_4,Cl)	M:tr, H:1mM, L:2M	dis	[95NEC/FAN]
-0.28	-1.70	3M Na(ClO_4,Cl)	M:tr, H:1mM, L:3M	dis	[95NEC/FAN]
-2.52	-1.55	4M Na (ClO_4,NO_3)	M:tr, H:0.1M, L:4M	dis	[71DAN/CHI]
-0.05	-0.70	5M Na(ClO_4,Cl)	M:tr, H:1mM, L:5M	dis	[95NEC/FAN]

1) If m = 1, β_{mn} is written β_n

2) Etrapolated to zero ionic strength from the results of the same author at the higher ionic strengths.

2) pH not mentioned in the paper

Equilibrium constants (β_{mn})[1] for formation of aqueous NpO_2^+ complexes with NO_3^- ($mNpO_2^+ + nNO_3^- \rightleftharpoons (NpO_2)_m(NO_3)_n^{(m-n)+}$)

log β_1	log β_2	Medium	Maximum Metal/H⁺/Ligand Concentration	Method	Reference
-0..25		2M H(ClO_4,NO_3)	M:tr, H:2M, L:2M	cix	[64GAI/SYK]
-0.6		2M Na (ClO_4,NO_3)	M:tr, pH[2], L:1M	dis	[79RAO/GUD]
-1.60	-1.37	4M Na (ClO_4,NO_3)	M:tr, H:0.1M, L:4M	dis	[71DAN/CHI]
-0.28		8M H(ClO_4,NO_3)	M:tr, H:8M, L:8M	dis	[70LAH/KNO]

1) If m = 1, β_{mn} is written β_n

2) pH not mentioned in the paper

Equilibrium constants (β_{mn})^1 for formation of aqueous NpO_2^+ complexes with OH^- ($mNpO_2^+ + nH_2O$] $\rightleftharpoons$ [$(NpO_2)_mOH_n^{(m-n)+} + nH^+$

log β_1	log β_2	Medium	Maximum Metal/H^+/Ligand Concentration	Method	Reference
-10.08		dil. $HClO_4/NH_3$	M:0.025M, pH=6.6	sol	[71MOS3]
-8.7		dil. $HClO_4$/NaOH	M:0.5mM, pH=3	pr/tc	[80SCH/GOR]
-8.89		0.001M $(Na,H)NO_3$	M:tr, H:3e-8M	sp	[76SEV/KHA]
-8.89		0.002M $(Na,H)NO_3$	M:1mM, H:3e-8M	sp	[76SEV/KHA]
-8.88		0.02M $(Na,H)NO_3$	M:10mM, H:2e-7M	gl	[76SEV/KHA]
-8.85		0.1		pH	[48KRA/NEL]
-10.45	-21.95	0.1M (H,Na) (ClO_4,OH)	M:tr, pH=1	tp	[87ROS/MIL]
-9.12		1M $NaClO_4$	M:0.3mM, H:8e-8M	sol	[83MAY]

1) If m = 1, β_{mn} is written β_n

Equilibrium constants (β_{mn})[1] for formation of aqueous NpO_2^+ complexes with OH^- ($mNpO_2^+ + nOH^- \rightarrow (NpO_2)_mOH_n^{(m-n)+}$)

log β_1	log β_2	Medium	Maximum Metal/H^+/Ligand Concentration	Method	Reference
3.30	5.58	I=0[2]	M:0.3mM, pH=6	sol	[92ITA/NAK]
5.7	9.2	I=0.005[3]	M:tr, pH=4	tp	[88NAG/TAN]
5.7	8.6	0.1M HNO_3	M:0.3mM, pH=7	sol	[88NAK/ARI]
	5.16	0.012M $NaClO_4$	M:0.3mM, pH=6	sol	[92ITA/NAK]
3.31	5.74	0.05M $NaClO_4$	M:0.3mM, pH=6	sol	[92ITA/NAK]
6.0	9.9	I=0.01[3]	M:tr, pH=4	tp	[88NAG/TAN]
2.67	5.74	0.1M $NaClO_4$	M:0.3mM, pH=6	sol	[92ITA/NAK]
2.44	4.1	0.1M $NaClO_4$	M:10mM, pH=7	sol	[92NEC/KIM]
4.16		0.2M $NaClO_4$		dis	[85BID/TAN]
3.49	4.7	0.4M $NaClO_4$	M:0.3mM, pH=6	sol	[92ITA/NAK]
2.91	5.50	0.8M $NaClO_4$	M:0.3mM, pH=6	sol	[92ITA/NAK]
2.3	4.89	1M $NaClO_4$	M:10mM, pH=7	sol	[85LIE/TRE]
2.67	4.41	1M $NaClO_4$	M:10mM, pH=7	sol	[92NEC/KIM]
3.18	5.15	3M $NaClO_4$	M:1mM, pH=7	sol	[92NEC/KIM]

1) If m = 1, β_{mn} is written β_n
2) Extrapolated to zero ionic strentg using the values presented in the same paper
3) Ion medium not metioned in the paper, only ionic strength

Equilibrium constants (β_{mn})[1] for formation of aqueous NpO_2^+ complexes with CO_3^{2-} ($mNpO_2^+ + nCO_3^{2-} \rightleftharpoons (NpO_2)_m(CO_3)_n^{(m-2n)+}$

log β_1	log β_2	log β_3	Medium	Maximum Metal/H^+/Ligand Concentration	Method	Reference
5.9		16.3	0.05M $NaClO_4$		iE	[83EDE/BUC]
4.34			0.1M $NaClO_4$	M:tr, L:0.1mM	sp	[90NIT/STA]
4.58	6.60	<6.8	0.1M $NaClO_4$	M:1mM, pH=7, L:0.1M	sol	[94NEC/RUN]
4.8			0.1M NaCl	M:1mM, L:0.1M	sol	[96RUN/NEU]
4.13	7.06		0.2M $NaClO_4$	M:tr, pH=8, L:0.01M	dis	[85BID/TAN]
4.49	7.11	8.53	1M $NaClO_4$	M:3mM, L:0.1M	sol	[83MAY]
4.14	6.78		1M	M:tr, L.0.15M	dis	[85INO/TOC]
4.73[2]	7.0[2]		1M (Na,K) (ClO_4,Cl)	M:0.1mM, L:0.1M	sol	[93LEM/BOY]
5.6[3]			1M (Na,K) (ClO_4,Cl)	M:0.1mM, L:0.1M	sol	[93LEM/BOY]
5.2[4]			1M (Na,K) (ClO_4,Cl)	M:0.1mM, L:0.1M	sol	[93LEM/BOY]
4.50	6.96	8.67	1M $NaClO_4$	M:1mM, pH=7, L:0.1M	sol	[94NEC/RUN]
5.09	8.15	10.46	3M $NaClO_4$	M:1mM, pH[2], [CO_3^{2-}]=0.05M	sol	[86GRE/ROB]
4.76	7.69	10.30	3M $NaClO_4$	M:1mM, pH=7, L:0.1M	sol	[94NEC/RUN]
4.3	7.1	9.2	3M NaCl	M:1mM, L:0.1M	sol	[96RUN/NEU]
5.00	8.29	11.47	5M $NaClO_4$	M:1mM, pH=7, L:0.1M	sol	[94NEC/RUN]

1) If m = 1, β_{mn} is written β_n
2) T=303 K
3) T=323 K
4) T=348 K
5) pH not mentioned in the paper, only [CO_3^{2-}] are given

Equilibrium constants (β_{mn})[1] for formation of aqueous NpO_2^+ complexes with HCO_3^- ($mNpO_2^+ + nHCO_3^- \rightleftharpoons (NpO_2)_m(HCO_3)_n^{(m-n)+}$)

log β_1	Medium	Maximum Metal/H+/Ligand Concentration	Method	Reference
2.15	0.25M NH_4Cl	M:tr, pH=8.5, L:0.12M	cppt	[79MOS/POZ]

1) If m = 1, β_{mn} is written β_x

Equilibrium constants for formation of aqueous NpO_2^+ complexes with various CO_3^{2-}-species

Reaction	log K	Medium	Maximum Metal/H+/Ligand Concentration	Method	Reference
$CO_3^{2-} + OH^- + NpO_2^+ \rightleftharpoons NpO_2OHCO_3^-$	4.83	0.2-2M $(NH_4)_2CO_3$	M.0.1mM, pH=8.8, L:2M	sol	[71MOS2]
$CO_3^{2-} + OH^- + NpO_2^+ \rightleftharpoons NpO_2OHCO_3^-$	7.6	3M $NaClO_4$	M:1mM, OH:2M, L:1M	sp	[97NEC/FAN]
$CO_3^{2-} + 2OH^- + NpO_2^+ \rightleftharpoons NpO_2(OH)_2CO_3^{3-}$	9.56	3M $NaClO_4$	M:1mM, OH:2M, L:1M	sp	[97NEC/FAN]
$2CO_3^{2-} + OH^- + NpO_2^+ \rightleftharpoons NpO_2OH(CO_3)_2^{4-}$	4.85	0.2-2M $(NH_4)_2CO_3$	M.0.1mM, pH=8.8, L:2M	sol	[71MOS2]
$2CO_3^{2-} + OH^- + NpO_2^+ \rightleftharpoons NpO_2OH(CO_3)_2^{4-}$	10.06	3M $NaClO_4$	M:1mM, OH:2M, L:1M	sp	[97NEC/FAN]

Equilibrium constants (β_{mn})^1 for formation of aqueous NpO_2^+ complexes with PO_4^{3-} ($mNpO_2^+ + nPO_4^{3-}$) ⇀ $(NpO_2)_m(PO_4)_n^{(m-3n)+}$)

log β_1	Medium	Maximum Metal/H$^+$/Ligand Concentration	Method	Reference
6.33	0.1M $NaClO_4$	M:tr, pH=6.5, L:2.4mM	sp	[96MOR/KIM]
5.78	1M NH_4Cl	M:tr, pH=8.5, L:0.7M	cppt	[79MOS/POZ]

1) If m = 1, β_{mn} is written β_n

Equilibrium constants (β_{mn})^1 for formation of aqueous NpO_2^+ complexes with HPO_4^{2-}($mNpO_2^+ + nHPO_4^{2-}$ ⇀ $(NpO_2)_m(HPO_4)_n^{(m-2n)+}$)

log β_1	log β_2	Medium	Maximum Metal/H$^+$/Ligand Concentration	Method	Reference
3.38		I=0^2	M:tr, pH=6.5, L:0.05M	cix	[64MOS/PER]
2.36		0.1M (H,Na)ClO_4	M:tr, pH=7.5, L:0.01M	cix	[84REE/DAN]
2.06^3		0.1M (H,Na)ClO_4	M:tr, pH=7.5, L:0.01M	cix	[84REE/DAN]
3.11^4		0.1M (H,Na)ClO_4	M:tr, pH=7.5, L:0.01M	cix	[84REE/DAN]
2.54		0.1M $NaClO_4$	M:tr, pH=6.5, L:2.4mM	sp	[96MOR/KIM]
2.85		0.2M NH_4ClO_4	M:tr, pH=6.5, L:0.05M	cix	[64MOS/PER]
2.9		1M NH_4ClO_4	M:tr, pH=8.5, L:0.7M	cppt	[79MOS/POZ]
2.11	3.43	1M $NaClO_4$	M.tr, pH=1, L=1M	dis	[85INO/TOC2]
4.54	7.49	1M $NaClO_4$	M:tr, pH=2.5, L:0.01M	dis	[94MAT/CHO]

1) If m = 1, β_{mn} is written β_n
2) Extrapolated to zero Ionic strength from the experimental results in the same paper
3) T=308 K
4) T=283 K

Equilibrium constants (β_{mn})[1] for formation of aqueous NpO_2^+ complexes with $H_2PO_4^{2-}$ ($mNpO_2^+ + nH_2PO_4^{2-} \rightleftharpoons (NpO_2)_m(H_2PO_4)_n^{(m-n)+}$)

log β_1	Medium	Maximum Metal/H$^+$/Ligand Concentration	Method	Reference
0.81	0.2M NH_4ClO_4	M:tr, pH=6.5, L:0.05M	cix	[64MOS/PER]
1.04	1M $NaClO_4$	M.tr, pH=1, L=1M	dis	[85INO/TOC2]
2.52	1M $NaClO_4$	M:tr, pH=2.5, L:0.01M	dis	[94MAT/CHO]

[1] If m = 1, β_{mn} is written β_n

Equilibrium constants $(\beta_{mn})^1$ for formation of aqueous NpO_2^+ complexes with SO_4^{2-} $(mNpO_2^+ + nSO_4^{2-} \rightleftharpoons (NpO_2)_m(SO_4)_n^{(m-2n)+})$

$\log \beta_1$	Medium	Maximum Metal/H^+/Ligand Concentration	Method	Reference
2.11	$I=0^2$	M:tr, pH=8.5, L:0.6M	cppt	[79MOS/POZ]
-0.10	0.5M $NaClO_4$	M:tr, pH^5, L:0.15M	dis	[83HAL/OLI]
0.25^3	0.5M $NaClO_4$	M:tr, pH^5, L:0.15M	dis	[83HAL/OLI]
-0.43^4	0.5M $NaClO_4$	M:tr, pH^5, L:0.15M	dis	[83HAL/OLI]
0.06	1M $NaClO_4$	M:tr, pH^5, L:0.3M	dis	[83HAL/OLI]
0.34^3	1M $NaClO_4$	M:tr, pH^5, L:0.3M	dis	[83HAL/OLI]
-0.18^4	1M $NaClO_4$	M:tr, pH^5, L:0.3M	dis	[83HAL/OLI]
0.76	1M Na (ClO_4, SO_4)	M.tr, pH=7, L:1M	dis	[85INO/TOC2]
1.04	1.5M NH_4Cl	M:tr, pH=8.5, L:0.6M	cppt	[79MOS/POZ]
0.45	2M $NaClO_4$	M:tr, pH^6, L:0.25M	dis	[79RAO/GUD]
0.19	2M $NaClO_4$	M:tr, pH^5, L:0.3M	dis	[83HAL/OLI]
0.40^3	2M $NaClO_4$	M:tr, pH^5, L:0.3M	dis	[83HAL/OLI]
-0.04^4	2M $NaClO_4$	M:tr, pH^5, L:0.3M	dis	[83HAL/OLI]
0.61	2M $NaClO_4$	M:1mM, pH=3, L^7	sp	[90RIZ/NEC]

1) If m = 1, β_{mn} is written β_n
2) Extrapolated to zero Ionic strength from the experimental results in the same paper
3) T=318 K
4) T=278 K
5) pH between 4 and 7, evidence is provided that the extraction and complexation is independent of the pH in the neutral area.
6) pH not mentioned in the paper

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Equilibrium Constants (β_{mn})[1] for Formation of Aqueous PuO_2^+ complexes with Cl^- ($mPuO_2^+ + nCl^- \rightleftharpoons (PuO_2)_mCl_n^{(m-n)+}$)

log β_1	Medium	Maximum Metal/H^+/Ligand Concentration	Method	Reference
-0.17	2	2	sp	[56NEW], [57KAT/SEA]

1) If m = 1, $\beta_{1,x}$ is written β_x
2) Limited experimental details are given

Equilibrium Constants (β_{mn})[1] for Formation of Aqueous PuO_2^+ complexes with OH^- ($mPuO_2^+ + nH_2O \rightleftharpoons (PuO_2)_mOH_n^{(m-n)+} + nH^+$)

log β_1	Medium	Maximum Metal/H^+/Ligand Concentration	Method	Reference
-9.73	0.1M $NaClO_4$	M:tr, pH=3	sp	[92BEN/HOF]

1) If m = 1, $\beta_{1,x}$ is written β_x

Equilibrium Constants (β_{mn})[1] for Formation of Aqueous PuO_2^+ complexes with CO_3^{2-} ($mPuO_2^+ + nCO_3^{2-} \rightleftharpoons (PuO_2)_m(CO_3)_n^{(m-2n)+}$)

log β_1	log β_3	Medium	Maximum Metal/H^+/Ligand Concentration	Method	Reference
5.12		I=0[2]	M:tr, pH=6.25, L:3.5mM	sp	[92BEN/HOF]
4.6		0.5M $NaClO_4$	M:tr, pH=6.25, L:3.5mM	sp	[92BEN/HOF]
	10.1	I=1	[3]	red	[86LIE/KIM]

1) If m = 1, $\beta_{1,x}$ is written β_x
2) Extrapolated to zero ionic strength from the results in the same paper
3) No experimental details available

Equilibrium Constants (β_{mn})[1] for Formation of Aqueous PuO_2^+ complexes with HCO_3^- ($mPuO_2^+ + nHCO_3^- \rightleftharpoons (PuO_2)_m(HCO_3)_n^{(m-n)+}$)

log β_1	Medium	Maximum Metal/H^+/Ligand Concentration	Method	Reference
1.9	0.25M NH_4Cl	M:tr, pH=8.5, L:0.12M	cppt	[79MOS/POZ]

1) If m = 1, $\beta_{1,x}$ is written β_x

Equilibrium Constants (β_{mn})[1] for Formation of Aqueous PuO_2^+ complexes with HPO_4^{2-} ($mPuO_2^+ + nHPO_4^{2-} \rightleftharpoons (PuO_2)_m(HPO_4)_n^{(m-2n)+}$)

log β_1	Medium	Maximum Metal/H^+/Ligand Concentration	Method	Reference
2.39	0.1M NH_4Cl	M:tr, pH=8, L=0.7M	cppt	[79MOS/POZ]

1) If m = 1, $\beta_{1,x}$ is written β_x

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Tables of
Stability Constants for
UO_2^{2+}, NpO_2^{2+} and PuO_2^{2+}

Equilibrium Constants (β_{mn})[1] for Formation of Aqueous UO_2^{2+} complexes with F^- ($mUO_2^{2+} + nF^- \rightleftharpoons (UO_2)_mF_n^{(2m-n)+}$)

log β_1	log β_2	log β_3	log β_4	Medium	Maximum Metal/H^+/Ligand Concentration	Method	Reference
4.59	7.93	10.49	11.85	1.0M $(H,Na)ClO_4$	M:25mM, H:25mM, L:335mM	emf	[54AHR/LAR]
5.30				H_2O	M:0.1M, H:25mM, L:0.6M	est	[56AHR/LAR]
4.54	7.89	10.46	11.81	1.0M NaCl		qh	[56AL]
4.77				H_2O	M:0.02mM, pH=3.0, 0.35M	sp	[61KUT]
4.398				2.0M			[67AHR]
4.65				0.50M $NaClO_4$	M:16mM, H:16mM, L:16M	prx	[69VDO/STE2]
4.58				0.50M			[69VDO/STE2]
4.54	7.98	10.41	11.89	1.0M $NaCl0_4$	M:31mM, H:30mM, L:4.0mM	qh	[71AHR/KUL]
4.54				1.0M $NaCl0_4$		cal	[71AHR/KUL2]
5.37				H_2O	M:8x10^{-8}M, L:2M, H:2.0M	est	[76PAT/RAM]
4.54				1.0M			[76SMI/MAR]
4.30				0.50M			[76SMI/MAR]
4.54				1.0M			[76SMI/MAR]
4.39	7.77	9.83		1.0M NaCl		ise	[77ISH/KAO]
4.70[a]				1.0M $NaClO_4$	L:0.03M, pH=2.6	ise	[84CHO/RAO]
4.52				1.0M $NaClO_4$	L:0.03M, pH=2.6	dis	[84CHO/RAO]
5.08				H_2O		est	[84TRI]
4.56	7.99	10.34		1.0M $NaClO_4$		ise	[85SAW/CHA]

Cont.

log β_1	log β_2	log β_3	log β_4	Medium	Maximum Metal/H$^+$/Ligand Concentration	Method	Reference
4.90				3.62M			[88LEM]
4.54				1.0M			[93FER/SAL]
4.86	8.62	11.71	13.78	3.0M $NaClO_4$	M:1mM, pH=3.5	pot	[93FER/SAL]

1) If m = 1, β_{mn} is written β_n, a)296K

Equilibrium Constants (β_{mn})1 for Formation of Aqueous UO_2^{2+} complexes with F^- ($mUO_2^{2+} + nHF \rightleftharpoons (UO_2)_mF_n^{(2m-n)+} + nH^+$)

log β_1	Medium	Maximum Metal/H$^+$/Ligand Concentration	Method	Reference
1.52	H_2O		est	[54DAY/POW]
1.71	0.05M $NaClO_4$	M:1x10^{-5}M, H:0.05M, L:10mM	dis	[54DAY/POW]
1.57	0.25M $NaClO_4$	M:1x10^{-5}M, H:0.05M, L:9mM	dis	[54DAY/POW]
1.38	0.50M $NaClO_4$	M:1x10^{-5}M, H:0.05M, L:90mM	dis	[54DAY/POW]
1.43	1.0M $NaClO_4$	M:1x10^{-5}M, H:0.05M, L:10mM	dis	[54DAY/POW]
1.41	2.0M $NaClO_4$	M:1x10^{-5}M, H:0.05M, L:10mM	dis	[54DAY/POW]
1.18	0.5M	M:38.7mM, L:0.2M, H:0.5M	sp	[61CON/PAU]
1.31	2.1M $HClO_4$	M:7.6x10^{-8}M, L:82.6mM, pH=1.1	cix	[68KRY/KOM3]
1.52	1.04M $HClO_4$	M:7.6x10^{-8}M, L:132mM, pH=0.9	cix	[68KRY/KOM3]
1.54	0.51M $HClO_4$	M:7.6x10^{-8}M, L:130mM, pH=0.9	cix	[68KRY/KOM3]
1.57	0.20M $HClO_4$	M:7.6x10^{-8}M, L:80.6mM, pH=1.1	cix	[68KRY/KOM3]
1.57	2.0M $HClO_4$		cix	[68KRY/KOM3]
1.479	4.0M (H,Na)ClO_4	M:50mM, L:50mM, H:0.6M	qh	[69GRE/VAR]
1.561	2.0M $HClO_4$	M:8x10^{-5}M, L:2.0M, H:2.0M	qh	[76PAT/RAM]
1.52	1.0M			[80BON/HEF]

1) If m = 1, β_{mn} is written β_n

Equilibrium Constants (β_{mn})[1] for Formation of Aqueous UO_2^{2+} complexes with Cl^- ($mUO_2^{2+} + nCl^- \rightleftharpoons (UO_2)_mCl_n^{(2m-n)+}$)

log β_1	log β_2	log β_3	Medium	Maximum Metal/H^+/Ligand Concentration	Method	Reference
-0.3			1.0M (H,Na)ClO_4		sp	[51AHR]
-0.1			1.0M (H,Na)ClO_4		qh	[51AHR]
0.11			n/a			[51NEL/KRA]
0.38			n/a			[51NEL/KRA]
-0.24[b]			2.0M (H,Na)ClO_4	M:$1x10^{-5}$M, H:0.05M, L:1.95M	dis	[54DAY/POW]
-0.056			2.0M (H,Na)ClO_4	M:$1x10^{-5}$M, H:0.05M, L:1.95M	dis	[54DAY/POW]
-0.057[g]			2.0M (H,Na)ClO_4	M:$1x10^{-5}$M, H:0.05M, L:1.95M	dis	[54DAY/POW]
0.22			H_2O		est	[57BAL/DAV]
0.03			H_2O	L:0.8M	est	[57DAV/MON]
0.21			0.25-0.85M (H,Na)ClO_4	L:0.8M	sp	[57DAV/MON]
0.03			H_2O		est	[60HEF/AMI]
1.64			1.238M (H,Na)ClO_4		sp	[60HEF/AMI]
0.300[e]			1.0M $NaClO_4$	M:0.2M, pH=2.95	cix	[61BAN/TRI]
0.26[a]			H_2O		fp	[62FAU/CRE]
-0.27			1.06M (K,Na)(NO_3,ClO_4)		cix	[67OHA/MOR]
0.15			0.82M (K,Na)(NO_3,ClO_4)		cix	[67OHA/MOR]
0.38			0.54M (K,Na)(NO_3,ClO_4)		cix	[67OHA/MOR]
1.55			H_2O		cix	[67OHA/MOR]
1.50[f]			H_2O		cix	[67OHA/MOR2]

Cont.

log β_1	log β_2	log β_3	Medium	Maximum Metal/H^+/Ligand Concentration	Method	Reference
0.8			H_2O	M:0.3mM, L:2.0M	est	[74BUN]
0.002			0.60M $HClO_4$	M:0.3mM, L:2.0M	cix	[74BUN]
0.025			2.0M $HClO_4$	M:0.3mM, L:2.0M	cix	[74BUN]
0.303			4.0M $HClO_4$	M:0.3mM, L:2.0M	cix	[74BUN]
-0.46			6.0M $NaClO_4$		mvd	[74JED]
-0.60			1.0M $NaClO_4$		mvd	[74JED]
-0.60			2.0M $NaClO_4$		mvd	[74JED]
-0.52			4.0M $NaClO_4$		mvd	[74JED]
-0.22	-1.00		8.0M $NaClO_4$		mvd	[74JED]
1.57			0.01M HCl	M:1mM, H:0.01M:, L:0.01M	ie	[75ALY/ABD]
1.58			0.10M HCl	M:1mM, H:0.10M:, L:0.10M	ie	[75ALY/ABD]
1.59			0.50M HCl	M:1mM, H:0.5M:, L:0.5M	ie	[75ALY/ABD]
1.65			1.0M HCl	M:1mM, H:1.0M:, L:1.0M	ie	[75ALY/ABD]
-0.102			1.0M HCl?		cix	[76SOU/SHA]
0.055			2.0M HCl?		cix	[76SOU/SHA]
-0.301			1.0M HCl?		cix	[76SOU/SHA]
1.96^i			0.03M KCl		gl	[77NIK2]
2.23^j			0.03M KCl		gl	[77NIK2]

Cont.

log β_1	log β_2	log β_3	Medium	Maximum Metal/H^+/Ligand Concentration	Method	Reference
2.40[k]			0.03M KCl		gl	[77NIK2]
-0.12	-0.64		2.0M $HClO_4$		dis	[78BED/FID]
-0.30[e]			1.0M $HClO_4$	M:2mM, L:4.M	sp	[81AWA/SUN]
-0.28[f]			1.0M $HClO_4$	M:2mM, L:4.M	sp	[81AWA/SUN]
-0.26[h]			1.0M $HClO_4$	M:2mM, L:4.M	sp	[81AWA/SUN]
-0.12	-6.4		2.0M $HClO_4$	M:2mM, L:4.M	dis	[81AWA/SUN]
-0.15	-1.29		2.0M $HClO_4$	M:2mM, L:4.M	sp	[81AWA/SUN]
-0.13[f]	-1.21		2.0M $HClO_4$	M:2mM, L:4.M	sp	[81AWA/SUN]
-0.11[h]	-1.14		2.0M $HClO_4$	M:2mM, L:4.M	sp	[81AWA/SUN]
0.15	-0.46		3.5M $HClO_4$	M:2mM, L:4.M	sp	[81AWA/SUN]
0.17[f]	-0.39		3.5M $HClO_4$	M:2mM, L:4.M	sp	[81AWA/SUN]
0.19[h]	-0.32		3.5M $HClO_4$	M:2mM, L:4.M	sp	[81AWA/SUN]
0.26	-0.18	-1.5	4.0M $HClO_4$	M:2mM, L:4.M	sp	[81AWA/SUN]
0.28[f]	-0.11		4.0M $HClO_4$	M:2mM, L:4.M	sp	[81AWA/SUN]
0.32[h]	-0.04		4.0M $HClO_4$	M:2mM, L:4.M	sp	[81AWA/SUN]
0.50[h]	0.48		4.9M $HClO_4$	M:2mM, L:4.M	sp	[81AWA/SUN]
1.481			N/A		est	[87OHA/MOR]
-9.0(?)			H_2O		est	[88CRO/EWA]

Cont.

$\log \beta_1$	$\log \beta_2$	$\log \beta_3$	Medium	Maximum Metal/H^+/Ligand Concentration	Method	Reference
0.10			1.37M			[88LEM]
0.10			3.62M			[88LEM]
-0.32			0.50M			[92FUG/KHO]
-0.400			1.0M			[92FUG/KHO]
-1.00			8.0M NaCl		mvd	[74JED]
0.0			H_2O		est	[78ALL]

a) T=270 K, b) T=283 K, c) T=288 K, d) T=293 K
e) T=303 K, f) T=308 K, g) T=313 K, h) T=318 K
i) T=343 K, j) T=363 K, k) T=373 K

Equilibrium Constants (β_{mn})^1 for Formation of Aqueous UO_2^{2+} complexes with NO_3^- ($mUO_2^{2+} + nNO_3^- \rightleftharpoons (UO_2)_m(NO_3)_n^{(2m-n)+}$)

log β_1	log β_2	Medium	Maximum Metal/H^+/Ligand Concentration	Method	Reference
-0.68		5.38M(H,Na)ClO_4	M:0.61M, L:2.56M, H=2.0M	sp	[49BET/MIC]
-0.30[b]		1.00M $NaClO_4$		gh	[51AHR]
-0.52[a]		2.00M(H,Na)ClO_4	M:1x10^{-5}M, H:0.05M, L:1.95M	dis	[54DAY/POW]
-0.62		2.00M(H,Na)ClO_4	M:1x10^{-5}M, H:0.05M, L:1.95M	dis	[54DAY/POW]
-0.77[c]		2.00M(H,Na)ClO_4	M:1x10^{-5}M, H:0.05M, L:1.95M	dis	[54DAY/POW]
-1.40[d]	0.50	1.00M $NaClO_4$		cix	[61BAN/TRI]
-0.42		0.54 MNa(Cl,ClO_4)		gl	[67OHA/MOR]
-0.72		1.06 M Na(Cl,ClO_4)		gl	[67OHA/MOR]
-0.47	-1.5	8.0M $HClO_4$		dis	[70LAH/KNO]
0.699		2.0M			[76SOU/SHA]
-0.678		2.0M			[76SOU/SHA]
0.800		H_2O		est	[78ALL/BEA]
-0.82		6.25M $NaClO_4$	M:1.12M, L:4.58M	ram	[80BRO/HUA]
0.66		H_2O		est	[87BRO/WAN]
-0.20		0.71M $HClO_4$		dis	[68PUS/NIK]
-0.54		2.0M $NaClO_4$		sp	[80MAR/DEC]

1) If m = 1, β_{mn} is written β_n

a) T=283 K, b) T=293 K, c) T=305 K, d) T=313 K

Equilibrium Constants (β_{mn})^1 for Formation of Aqueous UO_2^{2+} complexes with OH^- $mUO_2^{2+} + nH_2O \rightleftharpoons (UO_2)_m(OH)_n^{(2m-n)+} + nH^+$

log β_1	log β_2	log β_3	Other log β_{mn}	Medium	Maximum Metal/H^+/Ligand Concentration	Method	Reference
-4.3				0.16M	M:40mM, pH=1.1	qh	[42HEI]
-4.09				H_2O	M:10mM, pH=3.0	pol	[47HAR/KOL]
			log $\beta_{2,2}$=-5.72^j	0.06M $Ba(NO_3)_2$		gl	[47SCH/FAU]
			log $\beta_{2,2}$=-5.94 log $\beta_{3,5}$=-16.02	0.15M $NaClO_4$	M:0.1M	gl	[49SUT]
			log $\beta_{2,2}$=-5.99 log $\beta_{3,5}$=-17.84	0.15M $NaClO_4$	M:10mM	gl	[49SUT]
			log $\beta_{2,2}$=-6.10 log $\beta_{3,5}$=-16.74	1M $NaClO_4$	M:60.7mM, pH=4.1	gl, qh	[49AHR]
			log $\beta_{2,2}$=-5.97	0.6M $Ba(NO_3)_2$		gl	[54FEA]
-4.14				H_2O	M:7.67x10^{-3}M, pH=4.0	sol	[55GAY/LEI]
-4.19				H_2O		sp	[55KOM/TRE]
-4.2				0.1M $NaClO_4$		dis	[55RYD]
			log $\beta_{2,2}$=-6.10	1M $NaClO_4$		qh	[56ROS/ROS]
			log $\beta_{2,2}$=-6.68	H_2O		qh	[56ORB/BAR]
-5.82			log $\beta_{2,2}$=-6.15	0.035M $Ba(ClO_4)_2$	M:11.6mM, pH= 3.25	gl	[57HEA/WHI]
-5.1^i			log $\beta_{2,2}$=-5.92^i	0.035M $Ba(ClO_4)_2$	M:11.6mM, pH=3.19	gl	[57HEA/WHI]
-5.40			log $\beta_{2,2}$=-5.82	0.35M $Ba(ClO_4)_2$	M:0.1158M, pH=2.45	gl	[57HEA/WHI]
			log $\beta_{2,2}$=-5.99	0.16M NaCl		gl	[58LI/DOO]
			log $\beta_{2,1}$=-3.66 log $\beta_{2,2}$=-6.02	1M $NaClO_4$	M:0.4M, 0.7<pH<3.0	gl, qh	[59HIE/SIL]

Cont.

log β_1	log β_2	log β_3	Other log β_{mn}	Medium	Maximum Metal/H$^+$/Ligand Concentration	Method	Reference
			log $\beta_{2,1}$=-3.68 log $\beta_{2,2}$=-6.31	3M $NaClO_4$	M:1.4M, 0.7<pH<2.5	gl, qh	[59HIE/SIL]
-6.10			log $\beta_{2,2}$=-5.84 log $\beta_{6,4}$=-17.6	0.1M KNO_3	M:5mM, pH=2.5	gl	[60GUS/RIC]
-5.0	-10.5	-17.1		0.1M $NaNO_3$		dis	[60STA]
			log $\beta_{2,2}$=-5.01^a	Sat. Ag_2SO_4		sol	[60LIE/STO]
			log $\beta_{2,2}$=-4.27^b	Sat. Ag_2SO_4		sol	[60LIE/STO]
			log $\beta_{2,2}$=-3.84^c	Sat. Ag_2SO_4		sol	[60LIE/STO]
			log $\beta_{2,2}$=-3.71^d	Sat. Ag_2SO_4		sol	[60LIE/STO]
			log $\beta_{2,2}$=-5.96 log $\beta_{3,4}$=-12.79 log $\beta_{3,5}$=-16.21	1.5M Na_2SO_4	M:40mM, pH=1.1	gl	[61PET]
-5.7			log $\beta_{2,2}$=-5.92 log $\beta_{3,5}$=-16.22	0.5M KNO_3	M:20mM, pH=2.0	gl	[62BAE/MEY]
-4.2^k			log $\beta_{2,2}$=-4.51 log $\beta_{3,5}$=-12.74	0.5M KNO_3	M:20mM, pH=1.6	gl	[62BAE/MEY]
			log $\beta_{2,2}$=-6.2	0.5M $NaNO_3$		sp	[62NIK/PAR]
			log $\beta_{3,5}$=-16	0.5M $NaNO_3$		cix	[62NIK/PAR]
			log $\beta_{2,2}$=-6.1	1M $Ba(NO_3)_2$		gl	[62NIK/PAR]
			log $\beta_{2,2}$=-6.3	1M $Ba(NO_3)_2$		sp	[62NIK/PAR]

Cont.

log β_1	log β_2	log β_3	Other log β_{mn}	Medium	Maximum Metal/H^+/Ligand Concentration	Method	Reference
-5.60			log $\beta_{2,2}$=-6.17 log $\beta_{3,4}$=-12.33 log $\beta_{3,5}$=-17.00	1M NaCl	M:0.1M, pH=2.7	gl	[62RUS/JOH]
			log $\beta_{2,1}$=-3.70 log $\beta_{2,2}$=-6.04 log $\beta_{3,5}$=-16.53	3M $NaClO_4$	M:0.100M	gl, qh	[62SCH]
			log $\beta_{2,2}$=-6.64 log $\beta_{3,4}$=-12.54 log $\beta_{3,5}$=-18.07 log $\beta_{4,6}$=-19.96 log $\beta_{4,7}$=-24.91	3M NaCl	M:80mM, pH=2	gl, qh	[63DUN/SIL]
			log $\beta_{2,1}$=-4.16 log $\beta_{2,2}$=-5.96 log $\beta_{3,4}$=-12.79 log $\beta_{3,5}$=-16.21	1M KNO_3	M:80mM	gl	[63DUN/HIE]
-6.0			log $\beta_{2,1}$=-3.81 log $\beta_{2,2}$=-6.25 log $\beta_{3,5}$=-17.18	3M $Mg(ClO_4)_2$	M:1.2M, pH=1.5	gl, qh	[63HIE/ROW]
			log $\beta_{2,1}$=-3.96 log $\beta_{2,2}$=-6.20 log $\beta_{3,5}$=-16.91	3M $Ca(ClO_4)_2$	M:1.2M, pH=1.5	gl, qh	[63HIE/ROW]
-6.10			log $\beta_{2,1}$=-3.70 log $\beta_{2,2}$=-6.02 log $\beta_{3,5}$=-16.54	3M $NaClO_4$	M:1.2M, pH=1.5	gl, qh	[63HIE/ROW]
			log $\beta_{2,2}$=-5.94 log $\beta_{3,5}$=-16.41	1M $NaClO_4$	M:0.1M, pH=3.3	sp	[63RUS/JOH]

Cont.

log β_1	log β_2	log β_3	Other log β_{mn}	Medium	Maximum Metal/H^+/Ligand Concentration	Method	Reference
			log $\beta_{2,2}$=-5.91 log $\beta_{3,5}$=-16.43	1M $NaClO_4$	M:0.1M, pH=3.3	gl	[63RUS/JOH]
			log $\beta_{2,1}$=-1.9 log $\beta_{2,2}$=-6.28	0.1M $NaClO_4$		sp	[64BAR/SOM]
			log $\beta_{2,2}$=-6.09	0.1M $NaClO_4$		gl	[64BAR/SOM]
-6.0				H_2O	M:0.2mM, pH=4.3	kin	[67COL/EYR]
			log $\beta_{2,2}$=-4.9^b	H_2O	M:6mM	con	[67RYZ/NAU]
			log $\beta_{2,2}$=-3.8^d	H_2O	M:6mM	con	[67RYZ/NAU]
-5.16	-11.97		log $\beta_{2,2}$=-5.83	H_2O		gl	[68NIK/ANT]
			log $\beta_{2,2}$=-6.02 log $\beta_{3,5}$=-16.54	3M $NaClO_4$	M:0.100M	cal	[68ARN/SCH]
-5.38			log $\beta_{2,2}$=-5.92 log $\beta_{3,5}$=-16.16	3M $Mg(NO_3)_2$	M:0.100M, pH=2.0	gl	[68SCH/FRY]
-5.53			log $\beta_{2,2}$=-6.52 log $\beta_{3,5}$=-17.76	5M $Mg(NO_3)_2$	M:0.100M, pH=2.5	gl	[68SCH/FRY]
			log $\beta_{2,2}$=-5.92 log $\beta_{3,5}$=-16.16	0.2M $NaClO_4$	M:6mM, pH=3.0	gl	[68OST/CAM]
-4.39			log $\beta_{2,1}$=-1.9 log $\beta_{2,2}$=-6.09 log $\beta_{3,5}$=-15.64 log $\beta_{3,7}$=-24.03	0.1M $NaClO_4$		gl	[69TSY]
-5.70			log $\beta_{2,2}$=-5.95 log $\beta_{3,5}$=-16.36	0.5M KNO_3	M:6mM, pH=2.7	gl	[69VAN/OST]

Cont.

log β_1	log β_2	log β_3	Other log β_{mn}	Medium	Maximum Metal/H$^+$/Ligand Concentration	Method	Reference
-4.47^a	-10.4^a		log $\beta_{2,2}$=-5.22^a	H_2O		gl	[71NIK]
-4.00^e	-9.38^e		log $\beta_{2,2}$=-4.80^e	H_2O		gl	[71NIK]
-4.47^f			log $\beta_{2,2}$=-4.41^f	H_2O		gl	[71NIK]
-3.38^b	-7.99^b		log $\beta_{2,2}$=-4.25^b	H_2O		gl	[71NIK]
-2.94^g	-7.00^g		log $\beta_{2,2}$=-3.85^g	H_2O		gl	[71NIK]
-2.55^c	-6.13^c		log $\beta_{2,2}$=-3.50^c	H_2O		gl	[71NIK]
			log $\beta_{2,2}$=-6.80	3M $NaClO_4$		gl	[72KAK/AMA]
-5.08	-12.32		log $\beta_{2,2}$=-5.73	H_2O		sol	[72NIK/SER]
-4.36^a	-11.3^a		log $\beta_{2,2}$=-4.97^a	H_2O		sol	[72NIK/SER]
-3.20^b	-9.77^b		log $\beta_{2,2}$=-3.26^b	H_2O		sol	[72NIK/SER]
-2.31^c	-8.57^c		log $\beta_{2,2}$=-2.84^c	H_2O		sol	[72NIK/SER]
-1.61^d	-7.62^d		log $\beta_{2,2}$=-2.11^d	H_2O		sol	[72NIK/SER]
			log $\beta_{2,2}$=-6.0 log $\beta_{3,5}$=-13	0.5M $NaClO_4$		sp, pH	[73MAV, 74MAV]
-4.00				0.5M NaClO4	M:12mM, pH=2.7	sp	[76GHO/MUK]
-4.03				H_2O	M:47.8mM, pH=3.0	gl, dis	[77VOL/BEL]
-5.2				H_2O	M:0.5mM, pH=3.14	tc	[78SCH/SUL]
			log $\beta_{2,2}$=-5.63 log $\beta_{3,5}$=-15.87	0.1M (Et_4NClO_4)		gl	[79SPI/ARN]

Cont.

$\log \beta_1$	$\log \beta_2$	$\log \beta_3$	Other $\log \beta_{mn}$	Medium	Maximum Metal/H^+/Ligand Concentration	Method	Reference
-5.50			$\log \beta_{2,2}$=-5.89 $\log \beta_{3,4}$=-12.31 $\log \beta_{3,5}$=-16.46 $\log \beta_{4,7}$=-22.76	0.1M KNO_3	M:1.853x10^{-3}M, pH = 3.2	gl	[79SYL/DAV2]
			$\log \beta_{2,1}$=-3.81 $\log \beta_{2,2}$=-6.03 $\log \beta_{3,5}$=-16.78 $\log \beta_{4,6}$=-18.91	0.5M $NaClO_4$	M:0.100M, pH=2.5	gl	[79LAJ/PAR]
			$\log \beta_{2,2}$=-6.0 $\log \beta_{3,5}$=-16.6	3M $NaClO_4$	M:10mM, pH>5, P_{CO2}=0.97atm	gl	[79CIA/FER]
			$\log \beta_{2,2}$=-6.3 $\log \beta_{3,2}$=-11.20 $\log \beta_{4,6}$=-17.85	3M KCl		gl	[79MIL/ELK]
			$\log \beta_{2,2}$=-5.83 $\log \beta_{3,5}$=-19	0.2M $NaNO_3$		gl	[80PON/DOU]
			$\log \beta_{2,2}$=-5.64 $\log \beta_{3,5}$=-15.94	0.024M $NaClO_4$	M:1.0mM	gl	[81VAI/MAK]
			$\log \beta_{2,2}$=-5.85 $\log \beta_{3,5}$=-16.32	0.105M $NaClO_4$	M:1.0mM	gl	[81VAI/MAK]
			$\log \beta_{2,2}$=-5.89 $\log \beta_{3,5}$=-16.46	0.254M $NaClO_4$	M:1.0mM	gl	[81VAI/MAK]
			$\log \beta_{2,2}$=-5.97 $\log \beta_{3,5}$=-16.51	0.506M $NaClO_4$	M:1.0mM	gl	[81VAI/MAK]

Cont.

log β_1	log β_2	log β_3	Other log β_{mn}	Medium	Maximum Metal/H$^+$/Ligand Concentration	Method	Reference
			log $\beta_{2,2}$=-6.06 log $\beta_{3,5}$=-16.67	1.005M $NaClO_4$	M:1.0mM, pH=3.5	gl	[81VAI/MAK]
			log $\beta_{2,2}$=-6.16 log $\beta_{3,5}$=-16.79	2.003M $NaClO_4$	M:1.0mM	gl	[81VAI/MAK]
			log $\beta_{2,2}$=-5.89 log $\beta_{3,5}$=-16.19	0.1M $NaClO_4$	M:2.0mM, pH=5.5, P_{CO2}=3.55atm	gl	[82MAY]
			log $\beta_{2,2}$=-5.95 log $\beta_{3,1}$=-4.5 log $\beta_{3,5}$=-16.54 log $\beta_{4,3}$=-12.5	0.1M KNO_3	pH=3.0	gl	[82OVE/LUN]
			log $\beta_{2,2}$=-6.01 log $\beta_{4,3}$=-12.24	0.5M $NaNO_3$	M:10mM, pH=2.5	gl	[82MIL/SUR]
			log $\beta_{2,2}$=-6.07 log $\beta_{4,3}$=-12.31	1M $NaNO_3$	M:10mM, pH=2.5	gl	[82MIL/SUR]
			log $\beta_{2,2}$=-6.10 log $\beta_{4,3}$=-12.40	1.5M $NaNO_3$	M:10mM, pH=2.5	gl	[82MIL/SUR]
			log $\beta_{2,2}$=-6.13 log $\beta_{4,3}$=-12.41	2M $NaNO_3$	M:10mM, pH=2.5	gl	[82MIL/SUR]
			log $\beta_{2,2}$=-6.13 log $\beta_{4,3}$=-12.48	2.5M $NaNO_3$	M:10mM, pH=2.5	gl	[82MIL/SUR]
			log $\beta_{2,2}$=-6.13 log $\beta_{3,5}$=-16.65	3M $NaNO_3$	M:0.100M, pH=1.0	gl	[82MIL/SUR]
-6.04				0.05M $NaClO_4$	pH=5.64	dis	[83CAC/CHO2]

Cont.

log β_1	log β_2	log β_3	Other log β_{mn}	Medium	Maximum Metal/H^+/Ligand Concentration	Method	Reference
-6.09				0.1M $NaClO_4$	pH=4.72	dis	[83CAC/CHO2]
-6.20				0.4M $NaClO_4$	pH=5.55	dis	[83CAC/CHO2]
-6.09				0.7M $NaClO_4$	pH=4.67	dis	[83CAC/CHO2]
-6.03				1M $NaClO_4$	pH=5.54	dis	[83CAC/CHO2]
-3.43				0.5M $NaNO_3$	M:1x10^{-5}M, pH=1.0	ix, sp	[83DAV/EFR]
-5.5			log $\beta_{2,2}$=-6.0 log $\beta_{3,5}$=-17.7	0.1M $NaClO_4$		gl	[83EDE/BUC]
-5.20				H_2O		pol	[84GEI]
-4.57[a]				H_2O		pol	[84GEI]
-4.10[h]				H_2O		pol	[84GEI]
			log $\beta_{2,2}$=-6.45 log $\beta_{3,5}$=-17.29 log $\beta_{4,7}$=-23.12	0.1M KNO_3		gl	[84KOT/EVS]
			log $\beta_{2,2}$=-6 log $\beta_{2,3}$=-10.3 log $\beta_{9,19}$=-69.7	H_2O		gl, sp	[87VIL]
			log $\beta_{1,3}$=-19.69 log $\beta_{3,3}$=-16.54 log $\beta_{3,7}$=-31.9	0.5M $NaClO_4$		sol	[89BRU/SAN]
			log $\beta_{1,3}$=-19.09	0.5M $NaClO_4$		sol	[89BRU/SAN]
			log $\beta_{2,2}$=-6.07 log $\beta_{3,5}$=-16.40	0.5M $NaClO_4$	M:1mM, 3.5<pH<5.2	gl	[91GRE/LAG]

Cont.

log β_1	log β_2	log β_3	Other log β_{mn}	Medium	Maximum Metal/H$^+$/Ligand Concentration	Method	Reference
			log $\beta_{2,2}$= -5.84[l] log $\beta_{3,5}$= -15.95[l]	0.1M $NaClO_4$	M:10mM, 4.5<pH<5.5	sol	[92KRA/BIS]
			log $\beta_{2,2}$=-5.73	0.1M		est, ave	[93MEI/KIMA]
			log $\beta_{2,2}$= -5.97 log $\beta_{3,5}$= -16.93	3.0M $NaClO_4$	M:75mM	pot	[93FER/SAL]

1) If m = 1, β_{mn} is written β_n
a) T= 323 K, b) T= 373 K, c) T= 423 K, d) T= 473 K,
e) T= 343 K, f) T= 363 K, g) T= 398 K, h) T= 347 K,
i) T= 313 K, j) T= 288 K, k) T= 367 K l) assuming log $_{kW}$=14 original log β values are 22.16 and 53.05

Equilibrium Constants (β_{mn})[1] for Formation of Aqueous UO_2^{2+} complexes with CO_3^{2-} ($mUO_2^{2+} + nCO_3^{2-} \leftrightarrow (UO_2)_m(CO_3)_n^{(m-n)+}$)

log β_1	log β_2	log β_3	Other log β_{mn}	Medium	Maximum Metal/H^+/Ligand Concentration	Method	Reference
	15.57	20.7		0.2M NH_4NO_3	M:10mM, 7.0<ph<9.0, L:1M H_2CO_3	col	[60BAB/KOD]
9.87				H_2O		sol	[72SER/NIK]
10.0[a]				H_2O		sol	[72SER/NIK]
10.55[c]				H_2O		sol	[72SER/NIK]
11.38[e]				N/A		sol	[72SER/NIK]
12.39[f]				H_2O		sol	[72SER/NIK]
13.54[g]				H_2O		sol	[72SER/NIK]
14.79[h]				H_2O		sol	[72SER/NIK]
		21.54[i]		0.1M $NaNO_3$			[75CIN/SCA]
10.09[a]				H_2O			[76PIR/NIK]
10.25[b]				H_2O			[76PIR/NIK]
10.57[c]				H_2O			[76PIR/NIK]
11.12[d]				H_2O			[76PIR/NIK]
11.62[e]				H_2O			[76PIR/NIK]
9.02				3.0 M			[76SMI/MAR]
9.00	16.22	21.70		0.1M $NaNO_3$			[77SCA]
9.90				H_2O			[82PHI]
	19.19 16.15	31.21 21.81		0.1M $NaClO_4$	M:2mM, pH=5.5, P_{CO2}=3.55atm	gl	[82MAY]
8.3	16.20	22.61	log $\beta_{3,6}$= 56.2	3.0 M $NaClO_4$	6.3<pH<3.5, L: 0.97 atm	sol	[84GRE/FER]

Cont.

log β_1	log β_2	log β_3	Other log β_{mn}	Medium	Maximum Metal/H^+/Ligand Concentration	Method	Reference
8.3	15.36	21.46	log $\beta_{3,6}$= 53.7	0.5M $NaClO_4$	6.3<pH<3.5, L: 0.98 atm	sol	[84GRE/FER]
9.86				3.0M $NaClO_4$		cal	[84GRE/SPA]
9.81				0.01M			[84PHI]
9.19				0.10M			[84PHI]
8.50				0.50M			[84PHI]
8.18				1.0M			[84PHI]
7.88				2.0M			[84PHI]
7.73				3.0M			[84PHI]
9.65				H_2O			[84TRI]
9.80				H_2O			[85GRE]
9.80				H_2O			[84TRI]
8.60				3.0M	M:10mM, pH=2.95, P_{co2}=0.97atm		[85NEW/SUL]
9.87				H_2O	M:10mM, pH=2.95, P_{co2}=0.97atm	est	[85NEW/SUL]
8.30				1.37M			[88LEM]
8.00				3.62M			[88LEM]
8.70	16.33	23.92		0.1M $NaClO_4$	M:10mM, pH<6.7, L:1x10^{-6} M	sol	[92KRA/BIS]
8.93	15.3	21.0		0.1M $NaClO_4$	M:2mM, 3.5<pH<8, P_{co2}=1atm	sol	[97PAS/CZR]

1) If m = 1, β_{mn} is written β_n

a) T=323 K, b) T=348 K, c) T=373 K, d) T=398 K,
e) T=423 K, f) T=473 K, g) T=523 K, h) T=573 K, i) T=293 K

Other Equilibrium Constants for Formation of Aqueous UO_2^{2+} Complexes with Various CO_3^{2-}-species

Reaction	log K	Medium	Maximum Metal/H^+/Ligand Concentration	Method	Reference
$UO_2\,CO_{3(c)} = UO_2\,CO_{3(aq)}$	-4.366[a]	H_2O			[72SER/NIK]
$UO_2\,CO_{3(c)} = UO_2\,CO_{3(aq)}$	-4.387	H_2O			[72SER/NIK]
$UO_2\,CO_{3(c)} = UO_2\,CO_{3(aq)}$	-4.347[c]	H_2O			[72SER/NIK]
$UO_2\,CO_{3(c)} = UO_2\,CO_{3(aq)}$	-4.337[e]	n/a			[72SER/NIK]
$UO_2\,CO_{3(c)} = UO_2\,CO_{3(aq)}$	-4.215[f]	H_2O			[72SER/NIK]
$UO_2\,CO_{3(c)} = UO_2\,CO_{3(aq)}$	-4.37[a]	H_2O			[72SER/NIK]
$UO_2\,CO_{3(c)} = UO_2\,CO_{3(aq)}$	-4.35[c]	H_2O			[72SER/NIK]
$UO_2\,CO_{3(c)} = UO_2\,CO_{3(aq)}$	-4.34[e]	H_2O			[72SER/NIK]
$UO_2\,CO_{3(c)} = UO_2\,CO_{3(aq)}$	-4.30[f]	n/a			[72SER/NIK]
$UO_2\,CO_{3(c)} = UO_2\,CO_{3(aq)}$	-4.28[g]	H_2O			[72SER/NIK]
$UO_2\,CO_{3(c)} = UO_2\,CO_{3(aq)}$	-4.23[h]	H_2O			[72SER/NIK]
$CO_{2(g)} + UO_2^{2+} + H_2O = UO_2\,CO_{3(aq)} + 2H^+$	-9.0	H_2O	M:10mM, pH>5, P_{CO2}=0.97atm	gl	[79CIA/FER]
$CO_3^{2-} + U^{4+} + 2H_2O = UO_2\,CO_{3(aq)} + 4H^+$	0.85	H_2O			[80PAR/THO]
$H_2CO_{2(g)} + UO_2^{2+} + H_2O = UO_2\,CO_{3(aq)} + 2H^+$	-6.62	0.01M			[84PHI]
$H_2CO_{2(g)} + UO_2^{2+} + H_2O = UO_2\,CO_{3(aq)} + 2H^+$	-6.78	0.10M			[84PHI]
$H_2CO_{2(g)} + UO_2^{2+} + H_2O = UO_2\,CO_{3(aq)} + 2H^+$	-6.97	0.50M			[84PHI]
$H_2CO_{2(g)} + UO_2^{2+} + H_2O = UO_2\,CO_{3(aq)} + 2H^+$	-7.07	1.0M			[84PHI]0

Cont.

Reaction	log K	Medium	Maximum Metal/H⁺/Ligand Concentration	Method	Reference
$H_2CO_{2(g)} + UO_2^{2+} + H_2O = UO_2CO_{3(aq)} + 2H^+$	-7.19	2.0M			[84PHI]
$H_2CO_{2(g)} + UO_2^{2+} + H_2O = UO_2CO_{3(aq)} + 2H^+$	-7.27	3.0M			[84PHI]
$CO_3^{2-} + U^{4+} + 2H_2O = UO_2CO_{3(aq)} + 4H^+$	0.456	H_2O			[89BRU/PUI]

a) T=323 K, b) T=348 K, c) T=373 K, d) T=398 K,
e) T=423 K, f) T=473 K, g) T=523 K, h) T=573 K

Equilibrium Constants $(\beta_{mn})^1$ for Formation of Aqueous UO_2^{2+} complexes with $H_2PO_4^-$ $(mUO_2^{2+} + nH_2PO_4^- \rightarrow (UO_2)_m(H_2PO_4)_n^{(2m-n)+})$

log β_1	Medium	Maximum Metal/H⁺/Ligand Concentration	Method	Reference
2.3	H_2O		dis	[69MOS]
1.66	0.50 M^2		dis	[69MOS]

1) If m = 1, β_{mn} is written β_n

Equilibrium Constants (β_{mn})[1] for Formation of Aqueous UO_2^{2+} complexes with SO_4^{2-}
($mUO_2^{2+} + nSO_4^{2-} \rightleftharpoons (UO_2)_m(SO_4)_n^{(m-n)+}$)

log β_1	log β_2	log β_3	Other log β_{mn}	Medium	Maximum Metal/H$^+$/Ligand Concentration	Method	Reference
1.75	2.65			1.0M $NaClO_4$	M:30mM, L:0.300M	sp	[51AHR2]
1.70	2.54	3.40	log $\beta_{1,1}$ = 3.79[j] log $\beta_{2,1}$ = 4.60[j]	1.0M $NaClO_4$	M:25mM, L:0.200M	qh	[51AHR2]
3.23				H_2O		est	[54BRO/BUN]
1.80[a]	2.76			2.0M $NaClO_4$	M:1x10^{-5}M, H:0.05M, L:0.09M	dis	[54DAY/POW]
1.90	2.80			2.0M $NaClO_4$	M:1x10^{-5}M, H:0.05M, L:0.11M	dis	[54DAY/POW]
1.98[c]	2.91			2.0M $NaClO_4$	M:1x10^{-5}M, H:0.05M, L:0.09M	dis	[54DAY/POW]
2.94	3.94			0.01-0.3M $NaClO_4$		sp	[57DAV/MON]
2.95				0.30 M $NaClO_4$		sp	[57DAV/MON]
1.53	2.30			1.0M SO_4^{2-}		dis	[58ALL]
2.76				H_2O			[58ALL]
2.93				H_2O			[58ALL]
2.98				H_2O			[58ALL]
1.81	2.29			1.0M		sp	[60MAT]
1.63	3.8			1.0M $NaClO_4$	M:0.201M, pH=3.05	cix	[61BAN/TRI]
3.85				H_2O	M:11.3mM, L:11.3mM, pH=3.27		[63POZ/STE]
2.34				0.10 M NH_4ClO_4	L:34mM, pH=5	dis	[67WAL]

Cont.

$\log \beta_1$	$\log \beta_2$	$\log \beta_3$	Other $\log \beta_{mn}$	Medium	Maximum Metal/H^+/Ligand Concentration	Method	Reference
2.47[b]				0.10 M NH_4ClO_4	pH=5	dis	[67WAL]
2.44				0.075 M NH_4ClO_4	L:25mM, pH=5	dis	[67WAL]
2.51				0.05 M NH_4ClO_4	L:16.9mM, pH=5	dis	[67WAL]
2.62[b]				0.05 M NH_4ClO_4	pH=5	dis	[67WAL]
1.77				1.0M		est	[68AHR]
1.88				2.0M		est	[68AHR]
3.48[d]				H_2O		con	[70NIK]
3.62[e]				H_2O		con	[70NIK]
3.89[f]				H_2O		con	[70NIK]
1.76	2.64	3.51		1.0M $NaClO_4$		cal	[71AHR/KUL3]
1.78	2.65			1.0M $NaClO_4$			[71AHR/KUL3]
1.78	2.71			1.0M $NaClO_4$			[71AHR/KUL3]
1.78	2.80			1.0M $NaClO_4$			[71AHR/KUL3]
1.81	2.71			1.0M $NaClO_4$		est	[71AHR/KUL3]
1.78	2.70	3.18		1.0M $NaClO_4$			[71AHR/KUL3]
1.81	2.76			1.0M $NaClO_4$			[71AHR/KUL3]
1.81	2.80			1.0M $NaClO_4$		est	[71AHR/KUL3]
1.85	2.70			1.0M $NaClO_4$			[71AHR/KUL3]

Cont.

log β_1	log β_2	log β_3	Other log β_{mn}	Medium	Maximum Metal/H^+/Ligand Concentration	Method	Reference
1.85	2.80			1.0M $NaClO_4$			[71AHR/KUL3]
1.81				1.0M $NaClO_4$			[71AHR/KUL3]
2.93				H_2O		gl	[71NIK]
1.81	2.29			1.0 M ClO_4^-			[73MAJ]
3.35				H_2O			[76NIK]
3.48[d]				H_2O			[76NIK]
3.62[e]				H_2O			[76NIK]
3.89				H_2O			[76NIK]
2.93				H_2O			[76NIK]
3.20[d]				H_2O			[76NIK]
3.68[e]				H_2O			[76NIK]
4.13[f]				H_2O			[76NIK]
4.37[g]				H_2O			[76NIK]
4.99[h]				H_2O			[76NIK]
5.63[i]				H_2O			[76NIK]
3.10				2M $HClO_4$	M:8x10^{-5}M, L:2M, H:2M		[76PAT/RAM]
1.60				N/A			[83EDE/BUC]
3.22				H_2O	M:54mM, L:1.0M, pH=2.1	cal	[86ULL/SCH]

Cont.

log β_1	log β_2	log β_3	Other log β_{mn}	Medium	Maximum Metal/H$^+$/Ligand Concentration	Method	Reference
1.80				1.37M			[88LEM]
1.60				3.62M			[88LEM]

1) If m = 1, β_{mn} is written β_n

a) T=283 K, b) T=308 K, c) T=313 K, d) T=323 K, e) T=343 K, f) T=363 K, g) T=373 K, h) T=398 K, i) T=423 K, j) T=293K

Equilibrium Constants for Formation of Aqueous UO_2^{2+} complexes with various SO_4^{2-}-species

Reaction	log K	Medium	Maximum Metal/H$^+$/Ligand Concentration	Method	Reference
$HSO_4^- + UO_2^{2+} \rightleftharpoons UO_2SO_4(aq) + H^+$	0.70	2.0M H_2SO_4	M:20mM, L:2M, H:2M		[49BET/MIC]
$HSO_4^- + UO_2^{2+} \rightleftharpoons UO_2SO_4(aq) + H^+$	0.81	2.0M $NaClO_4$	M:1x10^{-5}M, H:0.05M, L:0.11M	dis	[54DAY/POW]
$HSO_4^- + UO_2^{2+} \rightleftharpoons UO_2SO_4(aq) + H^+$	0.881	2M $HClO_4$	M:8x10^{-5}M, L:2M, H:2M	extr	[76PAT/RAM]

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Equilibrium constants (β_{mn})[1] for formation of aqueous NpO_2^{2+} complexes with F^- ($mNpO_2^{2+} + nF^- \rightleftharpoons (NpO_2)_mF_n^{(2m-n)+}$)

log β_1	log β_2	log β_3	Medium	Maximum Metal/H$^+$/Ligand Concentration	Method	Reference
4.18	6.96	9.64	0.1M $NaClO_4$	M:4.5mM, H:30mM, L:30mM	pot, F^-	[85SAW/CHA]
4.27			1M $NaClO_4$	M:tr, pH=3, L:6mM	pot, F^-	[84CHO/RAO]
3.94	6.82	8.49	1M $NaClO_4$	M:4.5mM, H:30mM, L:26mM	pot, F^-	[85SAW/CHA]
5.16			1.04M $HClO_4$	M:tr, H:1M, L:70mM	cix	[68KRY/KOM2]
5.16			2.11M $HClO_4$	M:tr, H:2M, L:70mM	cix	[68KRY/KOM2]

1) If m = 1, β_{mn} is written β_n

Equilibrium Constants (β_{mn})[1] for Formation of Aqueous NpO_2^{2+} complexes with F^- ($mNpO_2^{2+} + nHF \rightleftharpoons (NpO_2)_mF_n^{(2m-n)+} + nH^+$)

log β_1	log β_2	Medium	Maximum Metal/H$^+$/Ligand Concentration	Method	Reference
1.41	1.45	I=0[2]	M:0.4mM, H:0.5M, L:70mM	red	[70ALN/WAI2]
1.20	1.17	0.1M $HClO_4$	M:0.4mM, H:0.1M, L:70mM	red	[70ALN/WAI2]
1.16	1.19	0.2M $HClO_4$	M:0.4mM, H:0.2M, L:70mM	red	[70ALN/WAI2]
1.14	1.20	0.3M $HClO_4$	M:0.4mM, H:0.3M, L:70mM	red	[70ALN/WAI2]
1.12	1.20	0.4M $HClO_4$	M:0.4mM, H:0.4M, L:70mM	red	[70ALN/WAI2]
1.11	1.14	0.5M $HClO_4$	M:0.4mM, H:0.5M, L:70mM	red	[70ALN/WAI2]
0.93	1.11	1M $H(ClO_4,F)$	M:0.44mM, H:1M, L:0.4M	dis	[68AHR/BRA]
1.12		2M $HClO_4$	M:tr, H:2M, L:0.5M	dis	[76PAT/RAM]

1) If m = 1, β_{mn} is written β_n

2) Extrapolated to zero ionic strength from the resuls presented in the same paper

Equilibrium Constants (β_{mn})[1] for Formation of Aqueous NpO_2^{2+} complexes with NO_3^- ($mNpO_2^{2+} + nNO_3^- \leftrightarrow (NpO_2)_m(NO_3)_n^{(2m-n)+}$)

log β_1	log β_2	Medium	Maximum Metal/H$^+$/Ligand Concentration	Method	Reference
-0.98		0.4M $H(ClO_4,NO_3)$	M:0.4mM, H:0.4M, L:0.1M	red	[70ALN/WAI]
-0.89		0.5M $H(ClO_4,NO_3)$	M:0.4mM, H:0.5M, L:0.2M	red	[70ALN/WAI]
-0.96		0.6M $H(ClO_4,NO_3)$	M:0.4mM, H:0.6M, L:0.2M	red	[70ALN/WAI]
-0.94		0.8M $H(ClO_4,NO_3)$	M:0.4mM, H:0.8M, L:0.2M	red	[70ALN/WAI]
-0.4		2M $H(ClO_4,NO_3)$	M:7mM, H:2M, L:2M	kin	[66RYK/YAK]
-0.68		4M Na (ClO_4,NO_3)	M:tr, H:0.1M, L:3.5M	cix	[71DAN/CHI]
-0.57	-0.55	8M $H(ClO_4,NO_3)$	M:tr, H:8M, L:8M	dis	[70LAH/KNO]

1) If m = 1, β_{mn} is written β_n

Equilibrium Constants (β_{mn})[1] for Formation of Aqueous NpO_2^{2+} complexes with OH^- ($mNpO_2^{2+} + nH_2O \leftrightarrow (NpO_2)_mOH_n^{(2m-n)+} + nH^+$)

log β_1	log β_2	Other log β_{mn}	Medium	Maximum Metal/H$^+$/Ligand Concentration	Method	Reference
-3.37	-5.44		I=0[2]	M:9mM, pH=2.7	sol	[71MOS3]
-5.4			I=0	M:0.5mM, pH=3.95	pr/tc	[83SCH/GOR]
-5.17		log $\beta_{2,2}$=-6.68 log $\beta_{3,5}$=-18.25	1M $NaClO_4$	M.80mM, H:1mM	gl	[72CAS/MAG2]

1) If m = 1, β_{mn} is written β_n

2) No information about medium is given in the paper, the results are extrapolated to zero ionic strength

Equilibrium Constants $(\beta_{mn})^1$ for Formation of Aqueous NpO_2^{2+} complexes with OH^- $(mNpO_2^{2+} + nOH^- \rightleftharpoons (NpO_2)_mOH_n^{(2m-n)+})$

log β_2	log β_3	Medium	Maximum Metal/H^+/Ligand Concentration	Method	Reference
	19.61	0.1M $NaClO_4$	M:1mM, pH=13	sol	[95MOR/PRA]
21.41		0.3M $(NH_4)_2CO_3$	M:20mM, pH=9, L:0.3M	sol	[71MOS2]

1) If m = 1, β_{mn} is written β_n

Other Equilibrium Constants for Formation of Aqueous NpO_2^{2+} Complexes with OH^-

Reaction	log K	Medium	Maximum Metal/H^+/Ligand Concentration	Method	Reference
$NpO_2(OH)_{2(aq)} + NpO_2OH^+ \rightleftharpoons (NpO_2)_2(OH)_3^+$	-3.54	I=0¹	M:9mM, pH=2.7	sol	[71MOS3]
$NpO_2(OH)_{2(aq)} + NpO_2(OH)_3^- \rightleftharpoons (NpO_2)_2(OH)_5^-$	-4.66	I=0¹	M:9mM, pH=2.7	sol	[71MOS3]

1) No information about medium is given in the paper, the results are extrapolated to zero ionic strength

Equilibrium Constants (β_{mn})[1] for Formation of Aqueous NpO_2^{2+} complexes with CO_3^{2-} ($mNpO_2^{2+} + nCO_3^{2-} \rightarrow (NpO_2)_m(CO_3)_n^{(m-n)+}$)

log β_2	log β_3	Medium	Maximum Metal/H^+/Ligand Concentration	Method	Reference
14.2		I=0[2]	M:20mM, pH=9, L:0.3M	sol	[71MOS2]
17.95		I=0[3]	M:50mM, pH=3, L:0.5M	cal	[88ULL/SCH]
	<17.78	0.1M $NaClO_4$	M:1mM, pH=13, L:0.1M	sol	[95MOR/PRA]
13.0		0.3M $(NH_4)_2CO_3$	M:20mM, pH=9, L:0.3M	sol	[71MOS2]
	22.00	1M $Na_2(SO_4,CO_3)$	M:50mM, H[4], L:0.3M	cal	[85SCH/FRI]

1) If m = 1, β_{mn} is written β_n

2) Varying concentrations of $(NH_4)_2CO_3$ (0.1-0.3M) used as medium. The result is extrapolated to zero ionic strength.

3) Varying concentrations of Na_2CO_3 and Na_2SO_4 used as medium, giving varying ionic strength. The results are extrapolated to zero Ionic strength.

4) pH not mentioned in the paper

Other Equilibrium Constants for Formation of Aqueous NpO_2^{2+} Complexes with Various CO_3^{2-}-species

Reaction	log K	Medium	Maximum Metal/H⁺/Ligand Concentration	Method	Reference
$CO_3^{2-} + NpO_2(OH)_2CO_3^{2-} \rightleftharpoons NpO_2(CO_3)_2^{2-} + 2OH^-$	-8.82	0.3M $(NH_4)_2CO_3$	M:20mM, pH=9, L:0.3M	sol	[71MOS2]
$NpO_2^+ + 2OH^- + CO_3^{2-} \rightleftharpoons NpO_2(OH)_2CO_3^{2-}$	20.21	~0.1M $Na(ClO_4,CO_3)$	M:0.3mM, pH=9.6, L:0.17M	sol	[93PRA/MOR]
$NpO_2^+ + 2OH^- + CO_3^{2-} \rightleftharpoons NpO_2(OH)_2CO_3^{2-}$	20.11	0.1M $NaClO_4$	M:1mM, pH=13, L:0.1M	sol	[95MOR/PRA]
$2CO_2(g) + NpO_2^{2+} \rightleftharpoons NpO_2(CO_3)_2^{2-} + 2H^+$	17.71	1M $NaClO_4$	M:1mM, pH=5, pCO_2=1	gl	[84MAY]
$3CO_2(g) + NpO_2^{2+} \rightleftharpoons NpO_2(CO_3)_3^{4-} + 3H^+$	30.18	1M $NaClO_4$	M:1mM, pH=5, pCO_2=1	gl	[84MAY]
$CO_2(g) + 2NpO_2^{2+} + 3H_2O \rightleftharpoons (NpO_2)_2(OH)_2CO_3^{2-} + 4H^+$	18.60	1M $NaClO_4$	M:1mM, pH=5, pCO_2=1	gl	[84MAY]
$3NpO_2(CO_3)_3^{4-} \rightleftharpoons (NpO_2)_3(CO_3)_6^{6-} + 3CO_3^{2-}$	-10.1	3M $NaClO_4$	M:20mM, L:0.1M	sp	[86GRE/RIG]

Equilibrium Constants (β_{mn})[1] for Formation of Aqueous NpO_2^{2+} complexes with HPO_4^{2-} ($mNpO_2^{2+} + nHPO_4^{2-} \rightleftharpoons (NpO_2)_m(HPO_4)_n^{(m-n)+}$)

log β_1	Medium	Maximum Metal/H⁺/Ligand Concentration	Method	Reference
8.18	I=0[2]	[2]	dis	[69MOS]
7.18	I=0.5[2]	[2]	dis	[69MOS]

1) If m = 1, β_{mn} is written β_n

2) No details of the experiment is given in the paper.

Equilibrium Constants (β_{mn})[1] for Formation of Aqueous NpO_2^{2+} complexes with $H_2PO_4^-$ ($mNpO_2^{2+} + nH_2PO_4^- \rightleftharpoons (NpO_2)_m(H_2PO_4)_n^{(2m-n)+}$)

log β_1	Medium	Maximum Metal/H$^+$/Ligand Concentration	Method	Reference
2.3	I=0[2]	[2]	dis	[69MOS]
1.66	I=0.5[2]	[2]	dis	[69MOS]

1) If m = 1, β_{mn} is written β_n

2) No details of the experiment is given in the paper.

Equilibrium Constants (β_{mn})^1 for Formation of Aqueous NpO_2^{2+} complexes with SO_4^{2-} ($mNpO_2^{2+} + nSO_4^{2-} \rightleftharpoons (NpO_2)_m(SO_4)_n^{(m-n)+}$)

log β_1	log β_2	Medium	Maximum Metal/H^+/Ligand Concentration	Method	Reference
3.45	4.4	I=0^2	M:50mM, pH=2, L:0.25M	cal	[86ULL/SCH]
		I=0^3	M:0.4mM, H:0.5M, L:50mM	red	[70ALN/WAI2]
2.44		0.1M $HClO_4$	M:0.4mM, H:0.1M, L:8mM	red	[70ALN/WAI2]
2.27		0.2M $HClO_4$	M:0.4mM, H:0.2M, L:18mM	red	[70ALN/WAI2]
2.18		0.3M $HClO_4$	M:0.4mM, H:0.3M, L:30mM	red	[70ALN/WAI2]
2.10		0.4M $HClO_4$	M:0.4mM, H:0.4M, L:45mM	red	[70ALN/WAI2]
2.07		0.5M $HClO_4$	M:0.4mM, H:0.5M, L:50mM	red	[70ALN/WAI2]
1.11		1M $HClO_4$	^{4}	red	[58STR/PEE]
1.90	2.78	1M $(H,Na)ClO_4$	M:tr, H:1M, L:65mM	dis	[68AHR/BRA2]
1.64		2M $NaClO_4$	^{4}	sp	[62SYK/TAY]

1) If m = 1, β_{mn} is written β_n
2) Varying concentrations of Na_2SO_4 used as medium, giving varying ionic strength. The results are extrapolated to zero ionic strength
3) Extrapolated to zero ionic strength from the results given in the same paper
4) No experimental details availableEquilibrium Constants for Formation of Aqueous NpO_2^{2+} complexes with various SO_4^{2-}-species

Equilibrium Constants (β_{mn})^1 for Formation of Aqueous NpO_2^{2+} complexes with HSO_4^-

Reaction	log K	Medium	Maximum Metal/H^+/Ligand Concentration	Method	Reference
$HSO_4^- + NpO_2^{2+} \rightleftharpoons NpO_2SO_{4(aq)} + H^+$	1.07	2M $H(ClO_4,SO_4)$	M:tr, H:2M, L:0.9M	dis	[76PAT/RAM]
$2HSO_4^- + NpO_2^{2+} \rightleftharpoons NpO_2(SO_4)^{2-} + 2H^+$	0.60	2M $H(ClO_4,SO_4)$	M:tr, H:2M, L:0.9M	dis	[76PAT/RAM]

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Equilibrium Constants $(\beta_{mn})^1$ for Formation of Aqueous PuO_2^{2+} complexes with F^- ($mPuO_2^{2+} + nF^- \rightleftharpoons (PuO_2)_mF_n^{(2m-n)+}$)

log β_1	log β_2	log β_3	Medium	Maximum Metal/H^+/Ligand Concentration	Method	Reference
4.11	6.92	9.01	0.1M $NaClO_4$	M:10mM, H:28mM, L:21mM	pot, F^-	[85SAW/CHA]
4.22			1M $NaClO_4$	M:0.05mM, pH=3, L:6mM	pot, F^-	[84CHO/RAO]
3.84	6.31	7.73	1M $NaClO_4$	M:17mM, H:28mM, L:38mM	pot, F^-	[85SAW/CHA]

1) If m = 1, β_{mn} is written β_n

Equilibrium Constants $(\beta_{mn})^1$ for Formation of Aqueous PuO_2^{2+} complexes with F^- ($mPuO_2^{2+} + nHF \rightleftharpoons (PuO_2)_mF_n^{(2m-n)+} + nH^+$)

log β_1	log β_2	log β_3	log β_4	Medium	Maximum Metal/H^+/Ligand Concentration	Method	Reference
2.11	4.15	6.08	6.3	1M $HClO_4$	M:tr, H:1M, L:0.06M	cix	[68KRY/KOM]
2	3.82	5	6.68	2M $HClO_4$	M:tr, H:2M, L:0.06M	cix	[68KRY/KOM]
1.079				2M $HClO_4$	M:tr, H:2M, L:0.5M	dis	[76PAT/RAM]

1) If m = 1, β_{mn} is written β_n

Equilibrium Constants (β_{mn})[1] for Formation of Aqueous PuO_2^{2+} complexes with Cl^- ($mPuO_2^{2+} + nCl^- \rightarrow (PuO_2)_mCl_n^{(2m-n)+}$)

log β_1	log β_2	Medium	Maximum Metal/H^+/Ligand Concentration	Method	Reference
0.0969	-0.456	2M $HCl/HClO_4$	M:[7], H:2M, L:2M	sp	[57NEW/BAK]
0.085	-0.43	2M $H(Cl,ClO_4)$	M:[7], H:2M, L:2M	sp	[61RAB/MAS]
-0.04[2]	-0.68[2]	2M $H(Cl,ClO_4)$	M:[7], H:2M, L:2M	sp	[61RAB/MAS]
0.0[3]	-0.60[3]	2M $H(Cl,ClO_4)$	M:[7], H:2M, L:2M	sp	[61RAB/MAS]
0.03[4]	-0.55[4]	2M $H(Cl,ClO_4)$	M:[7], H:2M, L:2M	sp	[61RAB/MAS]
0.06[5]	-0.48[5]	2M $H(Cl,ClO_4)$	M:[7], H:2M, L:2M	sp	[61RAB/MAS]
0.11[6]	-0.37[6]	2M $H(Cl,ClO_4)$	M:[7], H:2M, L:2M	sp	[61RAB/MAS]
-0.10	-0.43	2M $H(Cl,ClO_4)$	M:tr, H:2M, L:2M	dis	[78BED/FID]
0.1	-0.8	4.1M $H(Cl,ClO_4)$	M:tr, H:4.1M, L:2M	dis	[65MAZ/SIV]

1) If m = 1, β_{mn} is written β_n
2) T=276 K
3) T=283 K
4) T=288 K
5) T=293 K
6) T=303 K

Equilibrium Constants (β_{mn})[1] for Formation of Aqueous PuO_2^{2+} complexes with NO_3^- ($mPuO_2^{2+} + nNO_3^- \rightleftharpoons (PuO_2)_m(NO_3)_n^{(2m-n)+}$)

log β_1	log β_2	Medium	Maximum Metal/H$^+$/Ligand Concentration	Method	Reference
1.86	3.41	2mM HNO_3	M:10mM, pH=2.7, L:2mM	gl	[59KRE/NIK]
-0.03		4.1M $H(Cl,NO_3)$	M:tr, H:4.1M, L:2M	dis	[65MAZ/SIV]
-0.6		I=4.6	[2]	dis	[52HEI/HIC]
-0.57	-0.55	8M $H(ClO_4,NO_3)$	M:tr, H:8M, L:8M	dis	[70LAH/KNO]
	4.65	1-15M HNO_3	M:1e-3M, H:15M, L:15M	sp	[75VAS/AND]

1) If m = 1, β_{mn} is written β_n
2) Noexperimental details avaiable

Equilibrium Constants (β_{mn})[1] for Formation of Aqueous PuO_2^{2+} complexes with OH^- ($mPuO_2^{2+} + nOH^- \rightleftharpoons (PuO_2)_mOH_n^{(2m-n)+}$)

log β_1	log β_2	Medium	Maximum Metal/H$^+$/Ligand Concentration	Method	Reference
8.84		I=0[2]	M:0.05M, pH=6	sp	[93PAS/KIM2]
8.69	17.58	1M $NaClO_4$	M:0.05M, pH=6	sp	[93PAS/KIM2]

1) If m = 1, β_{mn} is written β_n
2) Extrapolated to zero ionic strength using the results in the same paper

Equilibrium Constants (β_{mn})[1] for Formation of Aqueous PuO_2^{2+} complexes with OH^- ($mPuO_2^{2+} + nH_2O \rightleftharpoons (PuO_2)_mOH_n^{(2m-n)+} + nH^+$)

log β_1	log β_2	log β_3	Other log β_{mn}	Medium	Maximum Metal/H^+/Ligand Concentration	Method	Reference
-6.3				I=0	M:0.5mM, pH3.79	pr/tc	[83SCH/GOR]
-3.33	-4.05			2mM HNO_3	M:10mM, pH=2.74	gl	[59KRE/NIK]
-3.85	-7.4		log $\beta_{2,3}$=-10.6	0.1M $NaClO_4$	M:1.5mM, pH=0.5	sp	[73MUS/POR]
-5.5	-7.2	-19.0	log $\beta_{2,2}$=-5.6 log $\beta_{3,5}$=-12.7	0.1M $NaClO_4$		sol/sp	[86LIE/KIM]
-6.3	-7.3			0.1M $NaClO_4$	M:tr, pH=3	sp	[93OKA/REE]
-5.71				1M $NaClO_4$	M:0.13M, pcH=4.7	gl	[49KRA/DAM]
-5.97			log $\beta_{2,2}$=-8.51 log $\beta_{3,5}$=-22.16	1M $NaClO_4$		gl	[72CAS/MAG]
			log $\beta_{2,2}$=-8.01 log $\beta_{3,5}$=-21.33	1M Na(ClO_4,Cl)	M:0.1M, pH=1.62	Ram	[84MAD/BEG]
			log $\beta_{2,2}$=-8.21 log $\beta_{3,5}$=-21.72	3M $NaClO_4$	M:0.13M, pH=3	gl	[71SCH]
			log $\beta_{2,2}$=-8.23	3M $NaClO_4$	M:0.2M, pH=3	gl	[75SCH]
-3.39	-5.25			varying	M:60mM, pH=3.3	sol	[62MOS/ZAI]

1) If m = 1, β_{mn} is written β_n

Equilibrium Constants (β_{mn})[1] for Formation of Aqueous PuO_2^{2+} complexes with CO_3^{2-} ($mPuO_2^{2+} + nCO_3^{2-} \rightleftharpoons (PuO_2)_m(CO_3)_n^{(m-n)+}$)

log β_1	log β_2	log β_3	Medium	Maximum Metal/H^+/Ligand Concentration	Method	Reference
12	15.1		I=0[2]	M:tr, pH=9.5, L:0.44M	sol	[62GEL/MOS]
	15.1	18.5	I=0[3]	M:15mM, pH=2.8, L:0.2M	cal	[88ULL/SCH]
8.7	14.1	17.8	0.1M $NaClO_4$	M:1mM, pH=3.5, pCO_2=1	sol	[97PAS/CZE]
8.6	13.6	18.2	3M $NaClO_4$	M:2, pH=5, L:3mM	sp	[87ROB/VIT]

1) If m = 1, β_{mn} is written β_n

2) Varying concentrations of $(NH_4)_2CO_3$ (0-0.44M) used as medium. The results are extrapolated to zero ionic strength

3) Varying concentrations of Na_2CO_3 and Na_2SO_4 used as medium, giving varying ionic strength. The results are extrapolated to zero ionic strength

Equilibrium Constants (β_{mn})[1] for Formation of Aqueous PuO_2^{2+} complexes with HCO_3^- ($mPuO_2^{2+} + nHCO_3^- \rightleftharpoons (PuO_2)_m(HCO_3)_n^{(2m-n)+}$)

log β_1	log β_2	Medium	Maximum Metal/H^+/Ligand Concentration	Method	Reference
2.67	4.39	0.1M $NaClO_4$	M:5mM, pH=8.3, L:0.1M	sp/cal	[82SUL/WOO]

1) If m = 1, β_{mn} is written β_n

Other Equilibrium Constants for Formation of Aqueous PuO_2^{2+} Complexes with Various CO_3^{2-}-species

Reaction	log K	Medium	Maximum Metal/H$^+$/Ligand Concentration	Method	Reference
$2HCO_3^- + PuO_2(OH)_{2(aq)} \rightleftharpoons PuO_2(CO_3)_2^{2-}$	4.36	0.1M $NaClO_4$	M:0.005M, pH=8.3, L:0.1M	sp/cal	[82SUL/WOO]
$CO_3^{2-} + OH^- + PuO_2^{2+} \rightleftharpoons PuO_2OHCO_3^-$	23.85	I=0^1	M:tr, pH=9.5, L:0.44M	sol	[62GEL/MOS]
$CO_3^{2-} + 2OH^- + PuO_2^{2+} \rightleftharpoons PuO_2(OH)_2CO_3^-$	23	I=0^1	M:tr, pH=9.5, L:0.44M	sol	[62GEL/MOS]
$HCO_3^- + PuO_2(OH)_{2(aq)} \rightleftharpoons PuO_2(OH)_2HCO_3^-$	2.67	0.1M $NaClO_4$	M:5mM, pH=8.3, L:0.1M	sp/cal	[82SUL/WOO]
$3PuO_2(CO_3)_3^{4-} \rightleftharpoons (PuO_2)_3(CO_3)_6^{6-} + 3CO_3^{2-}$	-7.4	3M $NaClO_4$	M:16mM, L:0.1M	sp	[86GRE/RIG]

Equilibrium Constants $(\beta_{mn})^1$ for Formation of Aqueous PuO_2^{2+} complexes with HPO_4^{2-} $(mPuO_2^{2+} + nHPO_4^{2-} \rightleftharpoons (PuO_2)_m(HPO_4)_n^{(2m-2n)+})$

log β_1	Medium	Maximum Metal/H$^+$/Ligand Concentration	Method	Reference
8.19	I=0^2	^{2}	dis	[69MOS]

1) If m = 1, β_{mn} is written β_n
2) No experimental details are given in the paper

Equilibrium Constants $(\beta_{mn})^1$ for Formation of Aqueous PuO_2^{2+} complexes with $H_2PO_4^{2-}$ $(mPuO_2^{2+} + nH_2PO_4^{2-} \rightleftharpoons (PuO_2)_m(H_2PO_4)_n^{(2m-n)+})$

log β_1	Medium	Maximum Metal/H$^+$/Ligand Concentration	Method	Reference
2.3	I=0^2	^{2}	dis	[69MOS]
1.66	I=0.5^2	^{2}	dis	[69MOS]
3.93	0.02-0.2 M H_3PO_3	M:tr, H:0.05M, L:0.175M	sol	[67DEN/SHE]

1) If m = 1, β_{mn} is written β_n
2) no experimental details are given in the paper

Equilibrium Constants (β_{mn})[1] for Formation of Aqueous PuO_2^{2+} complexes with SO_4^{2-} ($mPuO_2^{2+} + nSO_4^{2-} \rightleftharpoons (PuO_2)_m(SO_4)_n^{(m-n)+}$)

log β_1	log β_2	Medium	Maximum Metal/H⁺/Ligand Concentration	Method	Reference
3.45	4.4	I=0[2]	M:0.05M, pH=2.1, L:0.25M	cal	[86ULL/SCH]

1) If m = 1, β_{mn} is written β_n

2) Varying concentrations of Na_2SO_4 used as medium, giving varying ionic strength. The results are, however only given for I=0; Davies equation has been used to recalculate the experimental obtained stability constants.

Equilibrium Constants for Formation of Aqueous PuO_2^{2+} complexes with various SO_4^{2-}-species

Reaction	log K	Medium	Maximum Metal/H⁺/Ligand Concentration	Method	Reference
$HSO_4^- + PuO_2^{2+} \rightleftharpoons PuO_2SO_4(aq) + H^+$	1.16	2M $HClO_4$	M:tr, H:2M, L:0.86M	dis	[76PAT/RAM]

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Tables of
Solubility Products for
NpO_2^+

Np(V) solubility product with Carbonates and Sodium:

Reaction	log Ksp	Medium	Max. Concentration	Method	Reference
$Na^+ + NpO_2^+ + CO_3^{2-} = NaNpO_2CO_{3(s)}$	-10.14	1.0 $NaClO_4$	M:3mM, L:1.0mM	sol	[83MAY]
$Na^+ + NpO_2^+ + CO_3^{2-} = NaNpO_2CO_{3(s)}$	-10.56	3.0 $NaClO_4$	M:1mM, L:0.5M	sol	[86GRE/ROB]
$Na^+ + NpO_2^+ + CO_3^{2-} = NaNpO_2CO_{3(s)}$	-9.77[a]	1.0 NaCl		sol	[94RUN/KIM]
$Na^+ + NpO_2^+ + CO_3^{2-} = NaNpO_2CO_{3(s)}$	-9.61[a]	5.0 NaCl		sol	[94RUN/KIM]
$Na^+ + NpO_2^+ + CO_3^{2-} = NaNpO_2CO_{3(s)}$	-10.28	0.1M $NaClO_4$	M:0.2mM, L:10^{-3}atm, 6.8<pH<10.5	sol	[95NEC/RUN]
$Na^+ + NpO_2^+ + CO_3^{2-} = NaNpO_2CO_{3(s)}$	-10.10	1.0M $NaClO_4$	M:0.2mM, L:10^{-3}atm, 6.8<pH<10.5	sol	[95NEC/RUN]
$Na^+ + NpO_2^+ + CO_3^{2-} = NaNpO_2CO_{3(s)}$	-10.45	3.0M $NaClO_4$	M:0.2mM, L:10^{-3}atm, 6.8<pH<10.5	sol	[95NEC/RUN]
$Na^+ + NpO_2^+ + CO_3^{2-} = NaNpO_2CO_{3(s)}$	-11.06	5.0M $NaClO_4$	M:0.2mM, L:10^{-3}atm, 6.8<pH<10.5	sol	[95NEC/RUN]
$Na^+ + NpO_2^+ + CO_3^{2-} = NaNpO_2CO_{3(s)}$	-11.00[o]	I = 0	M:0.2mM, L:10^{-3}atm, 6.8<pH<10.5	est	[95NEC/RUN]
$Na^+ + NpO_2^+ + CO_3^{2-} = NaNpO_2CO_{3(s)}$	-10.63	5.0M NaCl	M:0.2mM, L:10^{-3}atm, 6.8<pH<10.5	sol	[95NEC/RUN]
$Na^+ + NpO_2^+ + CO_3^{2-} = NaNpO_2CO_{3(s)}$	-10.4[a]	1.0M NaCl	M:10mM, L:0.1M, 7<pH<13	sol	[96RUN/NEU]
$Na^+ + NpO_2^+ + CO_3^{2-} = NaNpO_2CO_{3(s)}$	-9.4[a]	3.0M NaCl	M:10mM, L:0.1M, 7<pH<13	sol	[96RUN/NEU]

o) log Ksp°, a)296K

Np(V) solubility product with Carbonates and Sodium:

Reaction	log Ksp	Medium	Max. Concentration	Method	Reference
$3Na^+ + NpO_2^+ + 2CO_3^{2-} = Na_3NpO_2(CO_3)_{2(s)}$	-12.44	3.0M $NaClO_4$	M:1mM, L:0.5M	sol	[86GRE/ROB]
$3Na^+ + NpO_2^+ + 2CO_3^{2-} = Na_3NpO_2(CO_3)_{2(s)}$	-11.46[a]	5.0M NaCl		sol	[94RUN/KIM]
$3Na^+ + NpO_2^+ + 2CO_3^{2-} = Na_3NpO_2(CO_3)_{2(s)}$	-12.23	1.0M $NaClO_4$	M:0.2mM, L:10^{-3}atm, 6.8<pH<10.5	sol	[95NEC/RUN]
$3Na^+ + NpO_2^+ + 2CO_3^{2-} = Na_3NpO_2(CO_3)_{2(s)}$	-12.59	3.0M $NaClO_4$	M:0.2mM, L:10^{-3}atm, 6.8<pH<10.5	sol	[95NEC/RUN]
$3Na^+ + NpO_2^+ + 2CO_3^{2-} = Na_3NpO_2(CO_3)_{2(s)}$	-13.57	5.0M $NaClO_4$	M:0.2mM, L:10^{-3}atm, 6.8<pH<10.5	sol	[95NEC/RUN]
$3Na^+ + NpO_2^+ + 2CO_3^{2-} = Na_3NpO_2(CO_3)_{2(s)}$	-14.32[o]	I = 0	M:0.2mM, L:10^{-3}atm, 6.8<pH<10.5	est	[95NEC/RUN]
$3Na^+ + NpO_2^+ + 2CO_3^{2-} = Na_3NpO_2(CO_3)_{2(s)}$	-12.48	5.0M NaCl	M:0.2mM, L:1atm, 6.8<pH<10.5	sol	[95NEC/RUN]

o) log Ksp°, a)296K

Np(V) solubility product with Hydroxide:

Reaction	log Ksp	Medium	Max. Concentration	Method	Reference
$NpO_2^{2+} + 2OH^- = NpO_2(OH)_{2(s)}$	-9.20	0.1M NaCl	M:mM, 6<pH<13	titr	[48KRA/NEL]
$NpO_2^+ + OH^- + xH_2O = NpO_2(OH) \cdot xH_2O_{(s)}$	-9.02^b	dil $NaClO_4/NH_3$	M: 25mM, pH:6.6	spec	[71MOS]
$NpO_2^+ + OH^- + xH_2O = NpO_2(OH) \cdot xH_2O_{(s)}$	-9.73^a	0.02M $(Na,H)NO_3$	M: 10mM, pH:7.7	spec	[76SEV/KHA]
$NpO_2^+ + OH^- = NpO_2(OH)_{(s)}$	-8.81	1.0M $NaClO_4$	M:1x10^{-5}mM, 6<pH<13	gl	[85LIE/TRE]
$NpO_2^+ + OH^- = NpO_2(OH)_{(s)}$	-10.7	0.01M $NaNO_3$	M:0.1mM, 6<pH<13	sol	[88NAK/ARI]
$NpO_2^+ + OH^- = NpO_2(OH)_{(am)}$	-8.56	0.1M $NaClO_4$	M:30mg, 7.3<pH<13.7	ls,spec	[92NEC/KIM]
$NpO_2^+ + OH^- = NpO_2(OH)_{(am)}$	-8.76^c	I = 0	M:30mg, 7.3<pH<13.7	ls,spec	[92NEC/KIM]
$NpO_2^+ + OH^- = NpO_2(OH)_{(cr)}$	-9.30	1.0M $NaClO_4$	M:30mg, 7.3<pH<13.7	est	[92NEC/KIM]
$NpO_2^+ + OH^- = NpO_2(OH)_{(cr)}$	-9.85	3.0M $NaClO_4$	M:30mg, 7.3<pH<13.7	ls,spec	[92NEC/KIM]
$NpO_2^+ + OH^- = NpO_2(OH)_{(cr)}$	-9.44^c	I =0	M:30mg, 7.3<pH<13.7	est	[92NEC/KIM]
$NpO_2^+ + OH^- = NpO_2(OH)_{(s)}$	-10.21	0.8M $NaClO_4$	M:20mM, 7.0<pH<13.5	sol,prop	[92ITA/NAK]
$NpO_2^+ + OH^- = NpO_2(OH)_{(s)}$	-9.61	0.4M $NaClO_4$	M:20mM, 7.0<pH<13.5	sol,prop	[92ITA/NAK]
$NpO_2^+ + OH^- = NpO_2(OH)_{(s)}$	-8.94	0.1M $NaClO_4$	M:20mM, 7.0<pH<13.5	sol,prop	[92ITA/NAK]
$NpO_2^+ + OH^- = NpO_2(OH)_{(s)}$	-8.91	0.05M $NaClO_4$	M:20mM, 7.0<pH<13.5	sol,prop	[92ITA/NAK]
$NpO_2^+ + OH^- = NpO_2(OH)_{(s)}$	-8.04	0.012M $NaClO_4$	M:20mM, 7.0<pH<13.5	sol,prop	[92ITA/NAK]
$NpO_2^+ + OH^- = NpO_2(OH)_{(s)}$	-8.68^c	I = 0	M:20mM, 7.0<pH<13.5	est	[92ITA/NAK]
$NpO_2^+ + OH^- = NpO_2(OH)_{(s)}$	-9.56^a	5.0M NaCl		sol	[94RUN/KIM]
$NpO_2^+ + OH^- = NpO_2(OH)_{(am)}$	-8.61^c	0.3M NaCl	M:0.3mM, pH<10	sol	[96ROB/SIL]
$NpO_2^+ + OH^- = NpO_2(OH)_{(am)}$	-8.56^c	0.59M NaCl	M:0.3mM, pH<10	sol	[96ROB/SIL]

Cont.

Reaction	log Ksp	Medium	Max. Concentration	Method	Reference
$NpO_2^+ + OH^- = NpO_2(OH)_{(am)}$	-8.51^c	0.98 NaCl	M:0.3mM, pH<10	sol	[96ROB/SIL]
$NpO_2^+ + OH^- = NpO_2(OH)_{(am)}$	-8.56^c	1.7M NaCl	M:0.3mM, pH<10	sol	[96ROB/SIL]
$NpO_2^+ + OH^- = NpO_2(OH)_{(am)}$	-8.73^c	2.8M NaCl	M:0.3mM, pH<10	sol	[96ROB/SIL]
$NpO_2^+ + OH^- = NpO_2(OH)_{(am)}$	-9.02^c	5.0M NaCl	M:0.3mM, pH<10	sol	[96ROB/SIL]
$NpO_2^+ + OH^- = NpO_2(OH)_{(am)}$	-8.79^{oc}	I = 0	M:0.3mM, pH<10	sol	[96ROB/SIL]

o) log Ksp°, a)296K, b)293K, c)294K

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Tables of
Solubility Products for
UO_2^{2+}, NpO_2^{2+} and PuO_2^{2+}

U(VI) solubility product with Carbonates:

Reaction	log Ksp	Medium	Max. Concentration	Method	Reference
$UO_2^{2+} + CO_3^{2-} = UO_2CO_{3(s)}$	-10.73	0.2M NH_4NO_3	M:10mM, 7.0<ph<9.0, L:1M H_2CO_3	col	[60BAB/KOD]
$UO_2^{2+} + CO_3^{2-} = UO_2CO_{3(s)}$	-14.26	var	M:2.5mM, ph<7.0, L:1 atm	col	[72SER/NIK]
$UO_2^{2+} + CO_3^{2-} = UO_2CO_{3(s)}$	-14.37	var 50C	M:1.2mM, ph<7.0, L:1 atm	col	[72SER/NIK]
$UO_2^{2+} + CO_3^{2-} = UO_2CO_{3(s)}$	-14.90	H_2O 100C	M:0.4mM, ph<7.0, L:1 atm	col	[72SER/NIK]
$UO_2^{2+} + CO_3^{2-} = UO_2CO_{3(s)}$	-15.72	H_2O 150 C	M:0.5mM, ph<7.0, L:1 atm	col	[72SER/NIK]
$UO_2^{2+} + CO_3^{2-} = UO_2CO_{3(s)}$	-16.69	H_2O 200 C	M:0.6mM, ph<7.0, L:1 atm	col	[72SER/NIK]
$UO_2^{2+} + CO_3^{2-} = UO_2CO_{3(s)}$	-17.82	250 C		est	[72SER/NIK]
$UO_2^{2+} + CO_3^{2-} = UO_2CO_{3(s)}$	-19.02	300 C		est	[72SER/NIK]
$UO_2^{2+} + CO_3^{2-} = UO_2CO_{3(s)}$	-14.50° -14.15 -14.84^{d} -15.04^{f} -15.22^{g} -16.14^{h} -17.4^{i}	I = 0.01 M	4.18<ph< 3.67, L=2 atm	sol	[76NIK]
$UO_2^{2+} + CO_3^{2-} = UO_2CO_{3(s)}$	-14.46^{m}	I=0 M		est,rev	[78LAN]
$UO_2^{2+} + CO_3^{2-} = UO_2CO_{3(s)}$	-14.2^{o} -14.7^{oe} -15^{og} -17^{oi} -18^{oj}			est	[80LEM/TRE]
$UO_2^{2+} + CO_3^{2-} = UO_2CO_{3(s)}$	-14.4	I = 0 M	6.3<pH<3.5, L: 0.98 atm	est	[84GRE/FER]
$UO_2^{2+} + CO_3^{2-} = UO_2CO_{3(s)}$	-13.21	0.5M $NaClO_4$	6.3<pH<3.5, L:0.98 atm	sol	[84GRE/FER]
$UO_2^{2+} + CO_3^{2-} = UO_2CO_{3(s)}$	-13.94	3.0M $NaClO_4$	6.3<pH<3.5, L: 0.97 atm	sol	[84GRE/FER]

Cont.

Reaction	log Ksp	Medium	Max. Concentration	Method	Reference
$UO_2^{2+} + CO_3^{2-} = UO_2CO_{3(s)}$	-13.29	0.1M $NaClO_4$	M: 0.01 M, ph<6.7, L:1 atm	gl,sol	[92KRA/BIS]
$UO_2^{2+} + CO_3^{2-} = UO_2CO_{3(s)}$	-14.47^{o}			est	[92GRE]
$UO_2^{2+} + CO_3^{2-} = UO_2CO_{3(s)}$	-14.18	0.1M $NaClO_4$	L:1 atm		[93MEI/KIM]
$UO_2^{2+} + CO_3^{2-} = UO_2CO_{3(s)}$	-13.89^{c}	0.1M $NaClO_4$	M:2 mM, 2.8<ph<4.6, L:1 atm	gl, pot	[93MEI/KIMA]
$UO_2^{2+} + CO_3^{2-} = UO_2CO_{3(s)}$	-13.35^{a} -14.22^{oa}	0.1M $NaClO_4$	M:18.6 mM, pH<4.0, L: 1 atm	sp, ICP-AES, est	[93PAS/RUN]
$UO_2^{2+} + CO_3^{2-} = UO_2CO_{3(s)}$	-14.49^{o}			est	[95SIL/BID]
$UO_2^{2+} + CO_3^{2-} = UO_2CO_{3(s)}$	-14.10	0.1M $NaClO_4$	M:20 mM, ph<5.0, L:1 atm	sol,ls	[96KAT/KIM]
$UO_2^{2+} + CO_3^{2-} = UO_2CO_{3(s)}$	-13.50	0.1M $NaClO_4$	M:>10^{-5}M, ph<6.3, L:100 kPa	uv-vis,sp	[96MEI/KLE]
$UO_2^{2+} + CO_3^{2-} = UO_2CO_{3(s)}$	-14.47^{oa}	0.1M $NaClO_4$	M:0.4 mM, ph<6.0, L:1 atm	sol,est	[97PAS/CZE]

o) log Ksp°, a)295K, b)293K, c)297K, d)323K, e)333K, f)348K, g)373K, h)398K, i)423K, j)473K, k)523K, l)573K, m)calculated from fit of literature data between 25-300°C $K_{sp} = 4.54-0.03318T-2716/T$

U(VI) solubility product with Hydroxide:

Reaction	log Ksp	Medium	Max. Concentration	Method	Reference
$UO_2^{2+} + 2OH^- = UO_2(OH)_{2(s)}$	-23.5	0.1 M $NaNO_3$			[48KRA/NEL]
$UO_2^{2+} + 2OH^- = UO_2(OH)_{2(s)}$	-21.9	NH_3/HNO_3	M:4.2mM, 4.5<pH<6.2	sol	[54MIL]
$UO_2^{2+} + 2OH^- = UO_2(OH)_{2(s)}$	-21.74	0.2 M NH_4NO_3	m:150mM, 3.6<pH<5.3	sol,col	[60BAB/KOD]
$UO_2^{2+} + 2OH^- = UO_2(OH)_{2(s)}$	-22.44^{on}			est,rev	[78LAN]
$UO_2^{2+} + 2OH^- = UO_2(OH)_{2(s)}$	-22.4^{o}			est	[80ALL/KIP]
$UO_2^{2+} + 2OH^- = UO_2(OH)_{2(s)}$	-22.21	0.1M $NaClO_4$	M:0.01 M, pH<5.71	ls,gl	[92KRA/BIS]

o) log Ksp°, n)calculated from fit of literature data between 25-300°C $K_{sp} = 6.16-0.03261T-5628/T$

U(VI) solubility product with Hydroxide:

Reaction	log Ksp	Medium	Max. Concentration	Method	Reference
$UO_2^{2+} + 2OH^- = UO_3{\bullet}H_2O_{(s)}$	-21.96	$NaOH/HClO_4$	M:0.65M, 4.1<pH<5.2	sol	[55GAY/LEI]
$UO_2^{2+} + 2OH^- = UO_3{\bullet}2H_2O_{(s)}$	-22.34^{c}	0.1 M $NaClO_4$	M:2mM, 2.8<pH<4.6, 0.03 atm CO_2	gl,pot	[93MEI/KIMA]
$UO_2^{2+} + 2OH^- = UO_3{\bullet}2H_2O_{(s)}$	-22.20^{c}	0.1 M $NaClO_4$	M:2mM, 2.8<pH<4.6, 0.98 atm CO_2	gl,pot	[93MEI/KIMA]
$UO_2^{2+} + 2OH^- = UO_3{\bullet}2H_2O_{(s)}$	-22.28^{c}	0.1 M $NaClO_4$	M:2mM, 2.8<pH<4.6	ave	[93MEI/KIMA]
$UO_2^{2+} + 2OH^- = UO_3{\bullet}2H_2O_{(s)}$	-22.15	0.1 M $NaClO_4$	M:20mM, pH<5.0 0.03% CO_2	sol	[96KAT/KIM]
$UO_2^{2+} + 2OH^- = UO_3{\bullet}2H_2O_{(am)}$	-20.34	0.5 M $NaClO_4$	N_2 atm	est	[93MEI/KIM]
$UO_2^{2+} + 2OH^- = UO_3{\bullet}2H_2O_{(cr)}$	-21.26	0.5 M $NaClO_4$	N_2 atm	est	[93MEI/KIMA]

o) log Ksp°,c)297K

U(VI) solubility product with Sodium and Carboxide:

Reaction	log Ksp	Method	Reference
$4Na^+ + UO_2(CO_3)_3^{4-} = Na_4UO_2(CO_3)_{3(s)}$	-5.340^{o}	est	[92GRE]

o) log Ksp°

U(VI) solubility product with Sulphite:

Reaction	log Ksp	Medium	Max. Concentration	Method	Reference
$UO_2^{2+} + SO_3^{2-} = UO_2SO_{3(s)}$	-8.59	2 M $(NH_4)_2SO_3$	M:0.4M, L:0.2M, pH <7	sol	[59KLY/KOL]

o) log Ksp°,

U(VI) solubility product with Sulphate:

Reaction	log Ksp	Method	Reference
$UO_2^{2+} + SO_4^{2-} + 2.5H_2O = UO_2SO_4{\bullet}2.5H_2O_{(s)}$	-1.589^{om}	est	[92GRE]
$UO_2^{2+} + SO_4^{2-} + 3.5H_2O = UO_2SO_4{\bullet}3.5H_2O_{(s)}$	-1.585^{om}	est	[92GRE]

o) log Ksp°,m) calculated from $\Delta_rG°_m$

U(VI) solubility product with Iodate:

Reaction	log Ksp	Medium	Max. Concentration	Method	Reference
$UO_2^{2+} + 2IO_3^- = UO_2(IO_3)_{2(s)}$	-7.0	0.2 M NH_4Cl	M:M, L:0.2M, 2.03<pH<4.75	sol	[59KLY/SMI2]
$UO_2^{2+} + 2IO_3^- = UO_2(IO_3)_{2(s)}$	-6.65^{e}	0.2 M NH_4Cl	M:M, L:0.2M, 2.03<pH<4.75	sol	[59KLY/SMI2]
$UO_2^{2+} + 2IO_3^- = UO_2(IO_3)_{2(s)}$	-7.88^{o}			est	[92GRE]

o) log Ksp°, e) 333K

U(VI) solubility product with phosphate:

Reaction	log Ksp	Medium	Max. Concentration	Method	Reference
$4H_2O + UO_2^{2+} + HPO_4^{2-} = UO_2HPO_4{\bullet}4H_2O_{(s)}$	-12.17	0.3M var	M:7.7mM, L:81mM, 0.7<pH<2.0	sol	[65VES/PEK]
$4H_2O + UO_2^{2+} + H_3PO_4 = 2H^+ + UO_2HPO_4{\bullet}4H_2O_{(s)}$	-2.500[o]	I = 0M		est	[92GRE]
$4H_2O + 3UO_2^{2+} + 2PO_4^{3-} = (UO_2)_3(PO_4)_2{\bullet}4H_2O_{(s)}$	-49.7	0.3M var	M:56mM, L:0.37mM, 0.6<pH<2.0	sol	[65VES/PEK]
$4H_2O + 3UO_2^{2+} + 2PO_4^{3-} = (UO_2)_3(PO_4)_2{\bullet}4H_2O_{(s)}$	-48.48	0.5M $NaClO_4$	L:0.1M, 3<pH<9	sol	[91SAN]
$4H_2O + 3UO_2^{2+} + 2H_3PO_4 = 6H^+ + (UO_2)_3(PO_4)_2{\bullet}4H_2O_{(s)}$	-5.960[o]			est	[92GRE]
$Na^+ + UO_2^{2+} + PO_4^{3-} + xH_2O = UO_2PO_4{\bullet}xH_2O_{(s)}$	-24,21	0.22M var	M:7.7mM, L:81mM, pH:1.5	sol	[65VES/PEK]
$K^+ + UO_2^{2+} + PO_4^{3-} + xH_2O = UO_2PO_4{\bullet}xH_2O_{(s)}$	-25,50	0.22M var	M:7.7mM, L:81mM, pH:1.5	sol	[65VES/PEK]
$Rb^+ + UO_2^{2+} + PO_4^{3-} + xH_2O = UO_2PO_4{\bullet}xH_2O_{(s)}$	-25,72	0.22M var	M:7.7mM, L:81mM, pH:1.5	sol	[65VES/PEK]
$Cs^+ + UO_2^{2+} + PO_4^{3-} + xH_2O = UO_2PO_4{\bullet}xH_2O_{(s)}$	-25,41	0.22M var	M:7.7mM, L:81mM, pH:1.5	sol	[65VES/PEK]
$NH_4^+ + UO_2^{2+} + PO_4^{3-} + xH_2O = UO_2PO_4{\bullet}xH_2O_{(s)}$	-26,23	0.22M var	M:7.7mM, L:81mM, pH:1.5	sol	[65VES/PEK]

o) log Ksp°,

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Np(VI) solubility product with Carbonates:

Reaction	log Ksp	Medium	Max. Concentration	Method	Reference
$NpO_2^{2+} + CO_3^{2-} = NpO_2CO_{3(s)}$	-13.8	var	var	est	[83ALL]
$NpO_2^{2+} + CO_3^{2-} = NpO_2CO_{3(s)}$	-14.62	0.1M $NaClO_4$	M=20mM, pH=2.9-4.9, L=0.8atm	sol,ls	[96KAT/KIM]
$NpO_2^{2+} + CO_3^{2-} = NpO_2CO_{3(s)}$	-13.92	0.1M $NaClO_4$	M=20mM, pH=2.9-6.8, L=0.8atm	sol,ls	[97KAT/KIM]

o) log Ksp°, a)295K, b)293K

Np(VI) solubility product with Hydroxide:

Reaction	log Ksp	Medium	Max. Concentration	Method	Reference
$NpO_2^{2+} + 2OH^- = NpO_2(OH)_{2(s)}$	-22.70^{ob}	var	pH=3.5-8.5	sol,gl	[71MOS]
$NpO_2^{2+} + 2OH^- = NpO_2(OH)_{2(s)}$	-21.4^{o}			est	[76BAE/MES]
$NpO_2^{2+} + 2OH^- = NpO_2(OH)_{2(s)}$	-22.7^{o}			est	[80ALL/KIP]

o) log Ksp°,

Np(VI) solubility product with Hydroxide:

Reaction	log Ksp	Medium	Max. Concentration	Method	Reference
$NpO_2^{2+} + 2OH^- = NpO_3 \bullet H_2O_{(s)}$	-21.72	0.1M $NaClO_4$	M=20mM, pH=2.9-4.9, L=0.0003atm	sol,ls	[96KAT/KIM]
$NpO_2^{2+} + 2OH^- = NpO_3 \bullet H_2O_{(s)}$	-21.74	0.1M $NaClO_4$	M=20mM, pH=2.9-4.9, L=0.0099atm	sol,ls	[96KAT/KIM]

o) log Ksp°,

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Pu(VI) solubility product with Carbonates:

Reaction	log Ksp	Medium	Max. Concentration	Method	Reference
$PuO_2^{2+} + CO_3^{2-} = PuO_2CO_{3(s)}$	−12.8[b]	1M $(NH_4)_2CO_3$	pH=9.5, L=0.44M	sol	[62GEL/MOS]
$PuO_2^{2+} + CO_3^{2-} = PuO_2CO_{3(s)}$	−13.8[o]			est	[83ALL/RYD]
$PuO_2^{2+} + CO_3^{2-} = PuO_2CO_{3(s)}$	−13.5[b]	3.0M $NaClO_4$	M=3.0mM, pH<9.62, L=$10^{-3.5}$ atm	sol	[87ROB/VIT]
$PuO_2^{2+} + CO_3^{2-} = PuO_2CO_{3(s)}$	−13.98[a] −14.84[oa]	0.1M $NaClO_4$	M=1.5 mM, pH<7.0, L= 1 atm	spc, est	[93PAS/RUN]
$PuO_2^{2+} + CO_3^{2-} = PuO_2CO_{3(s)}$	−14.85[oa]	0.1M $NaClO_4$	M=0.4 mM, ph<6.0, L=1 atm	est	[97PAS/CZE]

o) log Ksp°, a)295K, b)293K

Pu(VI) solubility product with Hydroxide:

Reaction	log Ksp	Medium	Max. Concentration	Method	Reference
$PuO_2^{2+} + OH = PuO_2(OH)_{2(s)}$	−22.74	var		sol	[53MAN/FRA]
$PuO_2^{2+} + OH = PuO_2(OH)_{2(s)}$	−20.5	0.1 M $NaNO_3$			[56KRA/NEL]
$PuO_2^{2+} + OH = PuO_2(OH)_{2(s)}$	−22.74	var	pH=3.25	sol	[62MOS/ZAI]
$PuO_2^{2+} + OH = PuO_2(OH)_{2(s)}$	−24.52	0.186mM HNO_3	M: mM,	sol	[62GEL/MOS]
$PuO_2^{2+} + OH = PuO_2(OH)_{2(s)}$	−24.05	0.1M $NaClO_4$	M: 1.51mM, pH<7.5	abs,spc	[73MUS/POR]
$PuO_2^{2+} + OH = PuO_2(OH)_{2(s)}$	−22.8[o]			est	[80ALL/KIP]
$PuO_2^{2+} + OH = PuO_2(OH)_{2(s)}$	−23.0[o]			est	[83ALL/RYD]
$PuO_2^{2+} + OH = PuO_2(OH)_{2(s)}$	−23.0	0.1M $NaClO_4$	M: 0.22mM, 5<pH<12	sol	[86LIE/KIM]
$PuO_2^{2+} + OH = PuO_2(OH)_{2(s)}$	−21.1[a]	0.1M $NaClO_4$	M: 10mM, pH<7.0	spc,est	[95PAS/KIM]

o) log Ksp°,

Pu(VI) solubility product with Phosphate:

Reaction	log Ksp	Medium	Max. Concentration	Method	Reference
$PuO_2^{2+} + HPO_4^{2-} = PuO_2HPO_{4(s)}$	−12.5	1M $NaClO_4$	M:71mM, L:5.88M, 0.65<pH<2.2	Sol	[67DEN/SHE]
$PuO_2^{2+} + HPO_4^{2-} = PuO_2HPO_{4(s)}$	−12.6°			est	[83ALL/RYD]
$2PuO_2^{2+} + 3PO_4^{3-} = (PuO_2)_3(PO_4)_{2(s)}$	−23.5°			est	[83ALL/RYD]

o) log Ksp°,

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Values of Pitzer Parameters for NpO_2^+, UO_2^{2+} and PuO_2^{2+}

Pitzer (V)

Species	$\beta^{(0)}$	$\beta^{(1)}$	$\beta^{(2)}$	C^{ϕ}	References
NpO_2^+-ClO_4^-	0.312				[94NOV/ROB]
NpO_2^+-ClO_4^-	0.257	0.180		0.0081	[95Nec/Fan]
NpO^{2+}-ClO_4^-	0.2306	0.3474		0.0067	[96Run/Neu]
Na^+-$NpO_2(OH)_2^-$	-0.069				[96Run/Neu]
Na^+-$NpO_2(CO_3)^-$	0.161				[94NOV/ROB]
Na^+-$NpO_2(CO_3)^-$	0.128				[96Run/Neu]
Na^+-$NpO_2(CO_3)_2^{3-}$	0.407				[94NOV/ROB]
Na^+-$NpO_2(CO_3)_2^{3-}$	0.461	4.584			[96Run/Neu]
Na^+-$NpO_2(CO_3)_3^{5-}$	1.97	16			[94NOV/ROB]
Na^+-$NpO_2(CO_3)_3^{5-}$	1.691	23.981			[96Run/Neu]
K^+-$NpO_2(CO_3)_3^{5-}$	2.34	22.7	-96.0	-0.22	[97Nov/Mah]
NpO_2^+-Cl^-	0.169				[94NOV/ROB]
NpO_2^+-Cl^-	0.1415	0.281		0	[95Nec/Fan]
NpO_2^+-Cl^-	0.1467	0.2010		0	[96Run/Neu]

Species	λ_{ni}	References
Na^+-$NpO_2OH(aq)$	-0.101	[96Run/Neu]
Na^+-$NpO_2OH(aq)$	-0.21[a]	[96Run/Neu]

[a] i = Cl^-

Species	θ_{ij}	Ψ_{ijk}	References
Na^+-$NpO_2(CO_3)^-$- Cl^-	−0.206		[96Run/Neu]
Na^+-$NpO_2(CO_3)_2^{3-}$- Cl^-	−0.267		[96Run/Neu]
Na^+-$NpO_2(CO_3)_3^{5-}$- Cl^-	−0.496	0.098	[96Run/Neu]
Na^+-$NpO_2(OH)_2^-$-Cl^-	−0.18		[96Run/Neu]

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Pitzer (VI)

Species	$\beta^{(0)}$	$\beta^{(1)}$	C^{ϕ}	References
UO_2^{2+}-ClO_4^-	0.62346	1.97357	0.02084	[88Kim/Fre]
UO_2^{2+}-ClO_4^-	0.6113[a]	2.144[a]	0.01084[b]	[73Pit/May]
Na^+-$UO_2(CO_3)_2^{2-}$	0.212	2.5	0	[97Pas/Cze]
Na^+-$UO_2(CO_3)_3^{4-}$	1.25	11.6	0	[97Pas/Cze]
UO_2^{2+}-Cl^-	0.4274[a]	1.644[a]	−0.01843[b]	[73Pit/May]
UO_2^{2+}-NO_3^{2-}	0.4607[a]	1.613[a]	−0.01577[b]	[73Pit/May]
UO_2^{2+}-SO_4^{2-}	0.322	1.827	−0.0176	[91Pit]
[c]Na^+-$PuO_2(CO_3)_2^{2-}$	0.212	2.5	0	[97Pas/Cze]
[c]Na^+-$PuO_2(CO_3)_3^{4-}$	1.25	11.6	0	[97Pas/Cze]

a originally reported as $4/3\beta$

[b] originally reported as $2/3(2)^{5/2}$

[c] UO_2^{2+} values used for PuO_2^{2+}

Species	λ	References
Na^+-UO_2CO_3	0.5	[97Pas/Cze]
ClO_4^--UO_2CO_3	0.5	[97Pas/Cze]

Species	θ_{ij}	ψ_{ijk}	References
Na^+-UO_2^{2+}-ClO_4^-	0.0231	−0.0437	[88Kim/Fre]
H^+-UO_2^{2+}-ClO_4^-	0.1377	−0.0 319	[88Kim/Fre]

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Literature “Recommended” Values of log β_i°

Introduction

Values of log β_1 (the stability constant for the reaction $M + X = (MX)$ at $I = 0(M)$ have been calculated by various authors as reported in the preceding tables of "recommended" equilibrium constants and in the report for the tetravalent (97RAI/RAO-2) actinides. Since, in a number of cases, these reported values differ significantly, we have made estimates of the most reliable values to choose the set of values we recommend. The basis for our evaluation were the log β_1 values of Sm(III) and UO_2^{2+} since the complexation of these cations can be performed at macro concentrations without concern for perturbing effects due to the radioactivity of the metal ions and with no variation in metal ion redox changes.

Sm(III) has complexation very similar to Am(III). Moreover, linear correlations are found for plots of log β_1 (SmX) and log β_1 of An(IV)X. The similar linear dioxo structure of $An(V)O_2^+$ and $An(VI)O_2^{2+}$ species allow the values of log β_1 of UO_2X to be used to screen the reported values of log β_1 for NpO_2^+, NpO_2^{2+}, PuO_2^+ and PuO_2^{2+} with the ligands of interest.

The electrostatic nature of the metal-ligand bond in f-element (Ln and An) complexation with hard base donors(e.g., O and F) allow use of the Born equation to estimate values of log β_1 for An-X and An-O complexes. The form of the equation used was:

$$\log \beta_1(MX) = \log \beta_1(AnX) \bullet [Z(An)/Z(M)] \bullet [D(M)/D(An)] \bullet [R(MX)/R(AnX)] \qquad (1)$$

M=Sm(III) or $U(VI)O_2^{2+}$; An=Am(III), Pu(III), Th(IV), U(IV), Np(IV), Pu(IV), $Np(V)O_2^+$, $Pu(V)O_2^+$, $Np(VI)O_2^{2+}$ and $Pu(VI)O_2^{2+}$. The Z is the effective positive charge on the actinide metal ion, the O is the effective dielectric constant for the solution of the metal ion and R is the bond distance of the metal-donor atom bond (using Shannon radii, [76Shan]). The values used in the estimates are listed in Table 1. The estimated values from equation 1 are presented in Table 2. These values were used to screen the "recommended" values in which we have sufficient confidence to recommend their use. Only log $\beta_1°$ values were screened but it is reasonable to assume that references in which the log $\beta_1°$ values are reliable are likely to also have the more reliable log $\beta_2°$, etc values. Our recommended values from this screening analysis for log $\beta_1°$ at I=0(M), T=25.0°C are listed in Table III.

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Table 1
Parameters Used in Born Estimates

Cation	Z(An)	D(An)	R(An-F), Å	R(An-O), Å
Sm(III)	+3	57	2.63	2.40
Pu(III)	+3	57	2.40	2.45
Am(III)	+3	57	2.37	2.44
Th(IV)	+4	50	2.22	2.26
U(IV)	+4	50	2.17	2.21
Np(IV)	+4	50	2.15	2.19
Pu(IV)	+4	50	2.14	2.18
Np(V)O_2^+	+2.2	65	2.03	2.07
Pu(V)O_2^+	+2.2	65	2.02	2.06
U(VI)O_2^{2+}	+3.3	55	1.99	2.03
Np(VI)O_2^{2+}	+3.3	55	2.00	2.04
Pu(VI)O_2^{2+}	+3.3	55	1.99	2.03

Table 2
Values Estimated form Born Equation
log β_1°

	F^-	Cl^-	NO_3^-	OH^-	CO_3^{2-}	SO_4^{2-}	HPO_4^-	HPO_4^{2-}
*Sm(III)	4.2	0.3	1.2	6.1	7.3	3.7	5.23	5.35
Pu(III)	4.1	0.3	1.2	6.0	7.2	3.6	2.2	5.2
Am(III)	4.2	0.3	1.2	6.0	7.2	3.6	2.2	5.2
Th(IV)	6.8	0.5	1.9	9.9	11.8	5.9	3.6	8.6
U(IV)	6.9	0.5	2.0	10.1	12.1	6.1	3.7	8.8
Np(IV)	7.0	0.5	2.0	10.2	12.2	6.1	3.7	8.9
Pu(IV)	7.0	0.5	2.0	10.2	12.2	6.1	3.7	9.0

	F^-	Cl^-	NO_3^-	OH^-	CO_3^{2-}	SO_4^{2-}	HPO_4^-	HPO_4^{2-}	PuO_4^{3-}
*U(VI)O_2^{2+}	5.09	0.17	0.3	8.8	9.68	3.15	3.26	7.24	13.23
Np(V)O_2^+	2.8	0.09	0.17	4.9	5.4	1.8	1.8	4.0	7.4
Pu(V)O_2^+	2.8	0.09	0.17	4.9	5.4	1.8	1.8	4.0	7.4
Np(VI)O_2^{2+}	5.1	0.17	0.3	8.8	9.6	3.1	3.2	7.2	13.2
Pu(VI)O_2^{2+}	5.1	0.17	0.3	8.8	9.7	3.2	3.3	7.2	13.2

Table III
Log β_1°

“Screened” and Recommended

III Ions	Cl	F	NO_3	OH	CO_3	HPO_4	H_2PO_4	SO_4
Sm^{+3}		3.58[a]	1.2[e]	6.8[a]		5.35(a)	2.23(a)	3.67[e]
Am^{+3}	1.05[b]	3.25[b]	1.33[b]	7.6[b]	7.8[b]	5.35[a]	3[b]	3.85[b]
Pu^{+3}	(1.03)	3.3[c]	1.41[d]	7.6	(7.7)	(5.31)	2.95	(3.80)

IV Ions*	Cl	F	NO_3	OH	CO_3	HPO_4	H_2PO_4	SO_4
Th		9.28	2. 5					6.1
U	1.72	6.0	2.1	13.5			3.26	6.4
Np	1.8	5.8	2.2					7.6
Pu	2.0	5.8	2.6					5.5

V Ions	Cl	F	NO_3	OH	CO_3	HPO_4	H_2PO_4	SO_4
NpO_2^+	(0.7)	1.9[f]	1.1[e]	5[g]	5.1[f]	3.4[f]	(1.5)	2[c]
PuO_2^+	(0.7)	(1.9)	(1.1)	5[e]	5[c]	(3.4)	(1.5)	2[c]

VI Ions	Cl	F	NO_3	OH	CO_3	HPO_4	H_2PO_4	SO_4
UO_2^{2+}	0.17[f]	6.1[f]	1.47[f]	8.8[f]	9.68[f]	7.24[f]	3.26[f]	3.5[f]
NpO_2^{2+}	0.4[f]	5.7[c]	(1.5)	8.4[i]	10.1[c]	(8)	(3.3)	3.4[d]
PuO_2^{2+}	0.1[f]	5.7[c]	(1.5)	8.9[i]	(10)	(8)	(3.3)	(3.4)

a= [92MIL]
b= [95SIL/BID]
c= [86WAN]
d= [83FUG2]
e= [78ALL/BEA]
f= [92FUG/KHO]

( ) = estim.

g= [80ALL/KIP]
h= [92GRE/FUG]
i= [83ALL]
N.B. An(IV) from Rai/Felmig Report

*From 97RAI/RAO-2.

Equilibrium Constants (β_{mn})[1] for Formation of Aqueous Sm^{3+} complexes with F^- ($mSm^{3+} + nF^- \rightleftharpoons Sm_mF_n^{(3m-n)+}$)

log β_1	Ionic Strength	Reference
4.2	I=0	[78ALL/BEA]
4.17	I=0	[90WOO]
3.58	I=0	[92MIL]
3.12	I=1	[80BON/HEF]

1) If m = 1, β_{mn} is written β_n

Equilibrium Constants (β_{mn})[1] for Formation of Aqueous Sm^{3+} complexes with Cl^-, ($mSm^{3+} + nCl^- \rightleftharpoons Sm_mCl_n^{(3m-n)+}$)

log β_1	Ionic Strength	Reference
0.36	I=0	[90WOO]
0.30	I=0	[92MIL]

1) If m = 1, β_{mn} is written β_n

Equilibrium Constants (β_{mn})[1] for Formation of Aqueous Sm^{3+} complexes with NO_3^-, ($mSm^{3+} + nNO_3^- \rightleftharpoons Sm_mNO_3^{(3m-n)+}$)

log β_1	Ionic Strength	Reference
1.2	I=0	[78ALL/BEA]
0.78	I=0	[92MIL]

1) If m = 1, β_{mn} is written β_n

Equilibrium Constants (β_{mn})[1] for Formation of Aqueous Sm^{3+} complexes with OH^- ($mSm^{3+} + nH_2O \rightarrow Sm_mOH_n^{(3m-n)+} + nH^+$)

log β_1	Ionic Strength	Reference
-7.9	I=0	[81BAE/MES]
-7.9	I=0	[90WOO]
-8.19	I=0	[92MIL]

1) If m = 1, β_{mn} is written β_n

Equilibrium Constants (β_{mn})[1] for Formation of Aqueous Sm^{3+} complexes with CO_3^{2-} ($mSm^{3+} + nCO3^{2-} \rightarrow Sm_m(CO_3)_n^{(3m-2n)+}$)

log β_1	log β_2	Ionic Strength	Reference
7.3	12.11	I=0	[92MIL]

1) If m = 1, β_{mn} is written β_n

Equilibrium Constants (β_{mn})[1] for Formation of Aqueous Sm^{3+} complexes with HCO_3^- ($mSm^{3+} + nHCO_3- \rightarrow Sm_m(HCO_3)_n^{(3m-n)+}$)

log β_1	Ionic Strength	Reference
1.75	I=0	[92MIL]

1) If m = 1, β_{mn} is written β_n

Equilibrium Constants (β_{mn})[1] for Formation of Aqueous Sm^{3+} complexes with HPO_4^{2-} ($mSm^{3+} + nHPO4^{2-} \rightleftharpoons Sm_m(HPO_4)_n^{(3m-2n)+}$)

log β_1	log β_2	Ionic Strength	Reference
5.35	8.96	I=0	[92MIL]

1) If m = 1, β_{mn} is written β_n

Equilibrium Constants (β_{mn})[1] for Formation of Aqueous Sm^{3+} complexes with $H_2PO_4^-$ ($mSm^{3+} + nH_2PO4^- \rightleftharpoons Sm_m(H_2PO_4)_n^{(3m-n)+}$)

b_1	Ionic Strength	Reference
2.23	I=0	[92MIL]

1) If m = 1, β_{mn} is written β_n

Equilibrium Constants (β_{mn})[1] for Formation of Aqueous Sm^{3+} complexes with SO_4^{2-} ($mSm^{3+} + nSO4^{2-} \rightleftharpoons Sm_m(SO_4)_n^{(3m-2n)+}$)

log β_1	log β_2	Ionic Strength	Reference
3.67	5.20	I=0	[78ALL/BEA]
3.28		I=0	[92MIL]

1) If m = 1, β_{mn} is written β_n

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Recommended values

Equilibrium Constants $(\beta_{mn})^1$ for Formation of Aqueous Ac^{3+} complexes with F^- $(mAc^{3+} + nF- \rightleftharpoons Ac_mF_n^{(3m-n)+})$

log β_1	log β_2	log β_3	Medium	Reference
3.6	6.6	9.8	I=0	[78ALL/BEA]
2.69	5.18	7.78	I=0.5	[80BON/HEF]
2.7	5.2	7.9	I=0.5	[92FUG/KHO]

1) If m = 1, β_{mn} is written β_n

Equilibrium Constants $(\beta_{mn})^1$ for Formation of Aqueous Ac^{3+} complexes with Cl^-, $(mAc^{3+} + nCl^- \rightleftharpoons Ac_mCl_n^{(3m-n)+})$

log β_1	log β_2	Medium	Reference
1.1		I=0	[78ALL/BEA]
1.3		I=0	[92FUG/KHO]
-0.05	-1	I=4	[92FUG/KHO]

1) If m = 1, β_{mn} is written β_x

Equilibrium Constants $(\beta_{mn})^1$ for Formation of Aqueous Ac^{3+} complexes with NO_3^-, $(mAc^{3+} + nNO_3^- \rightleftharpoons Ac_mNO_3^{(3m-n)+})$

log β_1	Medium	Reference
0.1	I=1	[92FUG/KHO]

1) If m = 1, β_{mn} is written β_n

Equilibrium Constants (β_{mn})[1] for Formation of Aqueous Ac^{3+} complexes with OH^- ($mAc^{3+} + nH_2O \rightleftharpoons Ac_mOH_n^{(3m-n)+} + nH^+$)

log β_1	Medium	Reference
<-10.4	I=0	[76BAE/MES]

1) If m = 1, β_{mn} is written β_n

Equilibrium Constants (β_{mn})[1] for Formation of Aqueous Ac^{3+} complexes with $H_2PO_4^-$ ($mAc^{3+} + nH_2PO4^- \rightleftharpoons Ac_m(H_2PO_4)_n^{(3m-n)+}$)

log β_1	Medium	Reference
2.5	I=0	[92FUG/KHO]

1) If m = 1, β_{mn} is written β_n

Equilibrium Constants (β_{mn})[1] for Formation of Aqueous Ac^{3+} complexes with SO_4^{2-} ($mAc^{3+} + nSO4^{2-} \rightleftharpoons Ac_m(SO_4)_n^{(3m-2n)+}$)

log β_1	log β_2	Medium	Reference
3.6	5.5	I=0	[78ALL/BEA]

1) If m = 1, β_{mn} is written β_n

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Equilibrium Constants (β_{mn})^1 for Formation of Aqueous Np^{3+} complexes with OH^- ($m[Np^{3+}] + n[OH^-] \rightarrow [Np_mOH_n^{(3m-n)+}]$)

log β_1	log β_2	log β_3	log β_4	Other log β_{mn}	Ionic Strength	Reference
7	13	19	23	$b_{2,2}$=15	I=0	[78ALL/BEA]
6.6	11	15	18	$b_{2,2}$=15	I=0	[80ALL/KIP]

1) If m = 1, β_{mn} is written β_n

Equilibrium Constants (β_{mn})^1 for Formation of Aqueous Np^{3+} complexes with OH^- ($mNp^{3+} + nH_2O \rightarrow Np_mOH_n^{(3m-n)+} + nH^+$)

log β_1	log β_2	log β_3	log β_4	Other log β_{mn}	Ionic Strength	Reference
-7	-15	-25	-35	$b_{2,2}$=-14	I=0	[86WAN]
-7.43					I=0.3	[80FUG/KHO]
-7.43					n/a	[74MED/KRO]

1) If m = 1, β_{mn} is written β_n

Equilibrium Constants (β_{mn})^1 for Formation of Aqueous Np^{3+} complexes with CO_3^{2-} ($mNp^{3+} + nCO3^{2-} \rightarrow Np_m(CO_3)_n$(3m-2n)+)

log β_1	log β_2	log β_3	Ionic Strength	Reference
9.6	12.9	16.2	I=0	[86WAN]

1) If m = 1, β_{mn} is written β_n

Equilibrium Constants (β_{mn})[1] for Formation of Aqueous Np^{3+} complexes with $H_2PO_4^-$ ($mNp^{3+} + nH_2PO4^- \rightleftharpoons Np_m(H_2PO_4)_n^{(3m-n)+}$)

log β_1	Ionic Strength	Maximum Metal/H^+/Ligand Concentration	Method	Reference
2.5	I=0	n/a	est	[92FUG/KHO]

1) If m = 1, β_{mn} is written β_n

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Recommended values

Equilibrium Constants (β_{mn})[1] for Formation of Aqueous Pu^{3+} complexes with F^- ($mPu^{3-} + nF- \rightleftharpoons Pu_mF_n(3m-n)+$)

log β_1	log β_2	log β_3	Medium	Reference
3.3			I=0	[83FUG2]
4.3	7.6	10.8	I=0	[86WAN]

1) If m = 1, β_{mn} is written β_n

Equilibrium Constants (β_{mn})[1] for Formation of Aqueous Pu^{3+} complexes with Cl^-, ($mPu^{3+} + nCl^- \rightleftharpoons Pu_mCl_n^{(3m-n)+}$)

log β_1	Medium	Reference
1.1	I=0	[78ALL/BEA]
-0.1	I=0	[82JEN]
1.2	I=0	[83FUG2]
-1.9	I=0	[85COW/JEN]
0.1	I=0.5	[92FUG/KHO]
-0.15	I=1	[53CON/MCV]
-0.1	I=1	[76SMI/MAR]
0.5	I=1	[92FUG/KHO]

1) If m = 1, β_{mn} is written β_n

Equilibrium Constants (β_{mn})[1] for Formation of Aqueous Pu^{3+} complexes with Cl^-, ($mPu^{3+} + nHCl \rightleftharpoons Pu_mCl^{(3m-n)+} + nH^+$)

$\log \beta_1$	Medium	Reference
-2.40	I=0	[77RAI/SER]

[1] If m = 1, β_{mn} is written β_n

Equilibrium Constants (β_{mn})[1] for Formation of Aqueous Pu^{3+} complexes with NO_3^-, ($mPu^{3+} + nNO_3^- \rightleftharpoons Pu_mNO_3^{(3m-n)+}$)

$\log \beta_1$	$\log \beta_2$	$\log \beta_3$	Medium	Reference
1.41	2.22	2.52	I=0	[85COW/JEN]

[1] If m = 1, β_{mn} is written β_n

Equilibrium Constants (β_{mn})[1] for Formation of Aqueous Pu^{3+} complexes with OH^- $mPu^{3+} + nOH^- \rightleftharpoons Pu_mOH_n^{(3m-n)+}$

$\log \beta_1$	$\log \beta_2$	$\log \beta_3$	$\log \beta_4$	Other $\log \beta_{mn}$	Medium	Reference
7					I=0	[76SMI/MAR]
7.2	14	19	24	$\log b_{2,2}=16$	I=0	[78ALL/BEA]
7.2	12.1	16.7	20.2	$\log b_{2,2}=16$	I=0	[80ALL/KIP]
6.7					I=0	[82JEN]
6.5	11.5	15.5	19	$\log b_{2,2}=14$	I=0	[83ALL]

[1] If m = 1, β_{mn} is written β_n

Equilibrium Constants (β_{mn})[1] for Formation of Aqueous Pu^{3+} complexes with OH^- ($mPu^{3+} + nH_2O \rightleftharpoons Pu_mOH_n(3m-n)+ + nH^+$)

log β_1	log β_2	log β_3	log β_4	Other log β_{mn}	Medium	Reference
-6.95					I=0	[77RAI/SER]
-8					I=0	[80LEM/TRE]
-7.5	-16.5	-26.5	-37	$b_{2,2}$=-14	I=0	[86WAN]
-7.37					I=0.024	[80FUG/KHO]
-7.22					I=0.069	[80FUG/KHO]
-3.8					I=0.2	[80FUG/KHO]

1) If m = 1, β_{mn} is written β_n

Equilibrium Constants (β_{mn})[1] for Formation of Aqueous Pu^{3+} complexes with CO_3^{2-} ($mPu^{3+} + nCO3^{2-} \rightleftharpoons Pu_m(CO_3)_n^{(3m-2n)+}$)

log β_1	log β_2	log β_3	Medium	Reference
9.6	12.9	16.2	I=0	[82JEN]
6	10	13	I=0	[83ALL]
6	10	13	I=0	[86WAN]

1) If m = 1, β_{mn} is written β_n

Equilibrium Constants (β_{mn})[1] for Formation of Aqueous Pu^{3+} complexes with HPO_4^{2-} ($mPu^{3+} + nHPO_42- \rightleftharpoons Pu_m(HPO_4)_n^{(3m-2n)+}$)

log β_1	Medium	Reference
9.7	I=0	[80LEM/TRE]

1) If m = 1, β_{mn} is written β_n

Equilibrium Constants (β_{mn})[1] for Formation of Aqueous Pu^{3+} complexes with PO_4^{3-} ($mPu^{3+} + nPO4^{3-} + 2nH^{+} \rightleftharpoons Pu_m(H_2PO_4)_n^{(3m-n)+}$

log β_1	log β_2	Medium	Reference
21.64	42.31	I=0	[85COW/JEN]
22		I=0	[86WAN]

1) If m = 1, β_{mn} is written β_n

Equilibrium Constants (β_{mn})[1] for Formation of Aqueous Pu^{3+} complexes with PO_4^{3-}($mPu^{3+} + nPO4^{3-} + nH^{+} \rightleftharpoons Pu_m(HPO_4)_n^{(3m-2n)+}$)

log β_1	Medium	Reference
18.3	I=0	[86WAN]

1) If m = 1, β_{mn} is written β_n

Equilibrium Constants (β_{mn})[1] for Formation of Aqueous Pu^{3+} complexes with SO$_4^{2-}$ ($m\mathrm{Pu}^{3+} + n\mathrm{SO4}^{2-} \rightleftharpoons \mathrm{Pu}_m(\mathrm{SO}_4)_n^{(3m-2n)+}$

log β_1	log β_2	Medium	Reference
3.7		I=0	[78ALL/BEA]
3.5		I=0	[80LEM/TRE]
1.26		I=0	[82JEN]
3.61	5.47	I=0	[82COW/JEN]
3.5	5.2	I=0	[86WAN]
4.5	6.7	I=0	[92FUG/KHO]
1.26	3.39	I=1	[76SMI/MAR]
1.26		I=1	[77RAI/SER]
1.26		I=1	[79CLE]

1) If m = 1, β_{mn} is written β_n

Equilibrium Constants (β_{mn})[1] for Formation of Aqueous Pu^{3+} complexes with SO$_4^{2-}$ ($m\mathrm{Pu}^{3+} + n\mathrm{HSO4}^{-} \rightleftharpoons \mathrm{Pu}_m(\mathrm{SO}_4)_n^{(3m-2n)+}] + n[\mathrm{H}^+]$)

log β_1	log β_2	Medium	Reference
4.5	6.7	I=0	[92FUG/KHO]
0.34		I=2	[83NAS/CLE]

1) If m = 1, β_{mn} is written β_n

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[92FUG/KHO] Fuger, J., Khodakovsky, I.L., Sergeyeva, E.I., Medvedev, V.A., Navratil, J.D. The chemical Thermodynamics of Actinide Elements and Compounds: Part 12. The Actinide Aqueous Inorganic Complexes Vienna:International Atomic Energy Agency, 1992, 224p.

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Equilibrium Constants $(\beta_{mn})^1$ for Formation of Aqueous Am^{3+} complexes with F^- $(mAm^{3+} + nF^- \rightleftharpoons Am_mF_n^{(3m-n)+})$

log β_1	log β_2	log β_3	log β_4	Medium	Reference
3.39	6.11	9		I=0	[76SMI/MAR]
4.3	7.5	10.8	14	I=0	[78ALL/BEA]
3.39	6.11	9		I=0	[82JEN]
4.3	7.4	10.6		I=0	[82PHI]
4.3	7.6	10.8		I=0	[86WAN]
3.24				I=0	[87PHI/HAL]

1) If m = 1, β_{mn} is written β_n

Equilibrium Constants $(\beta_{mn})^1$ for Formation of Aqueous Am^{3+} complexes with **Cl^-,** $(mAm^{3+} + nCl^- \rightleftharpoons Am_mCl_n^{(3m-n)+})$

log β_1	log β_2	Medium	Reference
1	0.5	I=0	[78ALL/BEA]
-0.1		I=0	[82JEN]
1.3	1.4	I=0	[92FUG/KHO]
1.05		I=0	[95SIL/BID]
0.5		I=0.1	[92FUG/KHO]
0.1		I=0.5	[92FUG/KHO]
-0.1	-0.5	I=1	[92FUG/KHO]
-0.15	-0.7	I=4	[92FUG/KHO]

1) If m = 1, β_{mn} is written β_n

Equilibrium Constants (β_{mn})[1] for Formation of Aqueous Am^{3+} complexes with NO_3^-, ($mAm^{3+} + nNO_3^- \rightarrow Am_mNO_3^{(3m-n)+}$)

log β_1	log β_2	Medium	Reference
-1(?)	0.5	I=0	[78ALL/BEA]
1.5		I=0	[92FUG/KHO]
1.33		I=0	[95SIL/BID]
0.25		I=1	[92FUG/KHO]

1) If m = 1, β_{mn} is written β_n

Equilibrium Constants (β_{mn})[1] for Formation of Aqueous Am^{3+} complexes with OH^- ($mAm^{3+} + nOH^- \rightarrow Am_mOH_n^{(3m-n)+}$

log β_1	log β_2	log β_3	Medium	Reference
8.2	15	21	I=0	[78ALL/BEA]
7.9			I=0	[82JEN]
6.5			I=0	[83ALL]
7.9			I=0.1	[76SMI/MAR]

1) If m = 1, β_{mn} is written β_n

Equilibrium Constants (β_{mn})^1 for Formation of Aqueous Am^{3+} complexes with OH^- ($mAm^{3+} + nH_2O \rightarrow Am_mOH_n^{(3m-n)+} + nH^+$

log β_1	log β_2	log β_3	Medium	Reference
-7.5	-16.5	-26.5	I=0	[86WAN]
-8	-16.9	-29	I=0	[92EWA/SMI]
-6.4	-14.1	-25.7	I=0	[95SIL/BID]
-3.3			I=0.005	[80FUG/KHO]
-5.3			I=0.1	[80FUG/KHO]
-8.2			?	[84RAI/RYA]

1) If m = 1, β_{mn} is written β_n

Equilibrium Constants (β_{mn})^1 for Formation of Aqueous Am^{3+} complexes with CO_3^{2-} ($m[Am^{3+}] + n[CO3^{2-}] \rightarrow [Am_m(CO_3)_n^{(3m-2n)+}$)

log β_1	log β_2	log β_3	log β_4	Medium	Reference
			11	I=0	[78ALL/BEA]
6	10	13		I=0	[83ALL]
8.3				I=0	[92FUG/KHO]
6.4	14	13.38		I=0	[92EWA/SMI]
7.8	12.3	15.2		I=0	[95SIL/BID]
6.9				I=0.1	[92FUG/KHO]
5.7				I=1	[92FUG/KHO]

1) If m = 1, β_{mn} is written β_n

Equilibrium Constants (β_{mn})[1] for Formation of Aqueous Am^{3+} complexes with $H_2PO_4^-$ ($mAm^{3+} + nH_2PO4^- \rightleftharpoons Am_m(H_2PO_4)_n^{(3m-n)+}$

log β_1	Medium	Reference
2.5	I=0	[78ALL/BEA]
2.5	I=0	[92FUG/KHO]
3	I=0	[95SIL/BID]

1) If m = 1, $\beta_{1,x}$ is written β_x
2) T=314

Equilibrium Constants (β_{mn})[1] for Formation of Aqueous Am^{3+} complexes with PO_4^{3-} ($mAm^{3+} + nPO4^- + nH^+ \rightleftharpoons Am_m(HPO_4)_n^{(3m-2n)+}$)

log β_1	Medium	Reference
18.4	I=0	[86WAN]

1) If m = 1, β_{mn} is written β_n

Equilibrium Constants (β_{mn})[1] for Formation of Aqueous Am^{3+} complexes with SO_4^{2-} ($mAm^{3+} + nSO4^{2-} \rightarrow Am_m(SO_4)_n^{(3m-2n)+}$)

log β_1	log β_2	Medium	Reference
3.6	5.6	I=0	[78ALL/BEA]
1.57	2.66	I=0	[82JEN]
3.5	5.2	I=0	[86WAN]
4.2	6.1	I=0	[92FUG/KHO]
3.85	5.4	I=0	[95SIL/BID]
1.86	2.82	I=0.5	[76SMI/MAR]

1) If m = 1, β_{mn} is written β_n

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Equilibrium Constants (β_{mn})[1] for Formation of Aqueous Cm^{3+} complexes with F^- ($mCm^{3+} + nF- \rightarrow Cm_mF_n^{(3m-n)+}$

log β_1	log β_2	log β_3	Medium	Reference
4.3	7.6	10.9	I=0	[78ALL/BEA]
3.34	6.18	9.1	I=0	[82JEN]
3.34	6.17	9.07	I=0.5	[80BON/HEF]
	6.2	9.1	I=0.5	[92FUG/KHO]

1) If m = 1, β_{mn} is written β_n

Equilibrium Constants (β_{mn})[1] for Formation of Aqueous Cm^{3+} complexes with **Cl^-**, ($mCm^{3+} + nCl^- \rightarrow Cm_mCl_n^{(3m-n)+}$)

log β_1	Medium	Reference
1.3	I=0	[92FUG/KHO]

1) If m = 1, β_{mn} is written β_n

Equilibrium Constants (β_{mn})[1] for Formation of Aqueous Cm^{3+} complexes with OH^- ($mCm^{3+} + nOH^- \rightarrow Cm_mOH_n^{(3m-n)+}$)

log β_1	log β_2	Medium	Reference
8.4		I=0	[78ALL/BEA]
7.9	19	I=0	[82JEN]

1) If m = 1, β_{mn} is written β_n

Equilibrium Constants (β_{mn})[1] for Formation of Aqueous Cm^{3+} complexes with SO_4^{2-} ($mCm^{3+} + nSO4^{2-} \rightarrow Cm_m(SO_4)_n^{(3m-2n)+}$)

log β_1	log β_2	Medium	Reference
3.6	5.6	I=0	[78ALL/BEA]
1.86	2.7	I=0	[82JEN]
4.2	6.1	I=0	[92FUG/KHO]

1) If m = 1, β_{mn} is written β_n

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Equilibrium Constants $(\beta_{mn})^1$ for Formation of Aqueous NpO_2^+ complexes with OH^- ($mNpO_2^+ + nOH^- \rightarrow (NpO_2)_mOH_n^{(m-n)+}$)

$\log \beta_1$	$\log \beta_2$	Medium	Reference
5.1	10	I=0	[78ALL/BEA]
5	10	I=0	[80ALL/KIP]
4	9.9	I=0	[82JEN]
5.1		I=0	[83ALL]

1) If m = 1, β_{mn} is written β_n

Equilibrium Constants $(\beta_{mn})^1$ for Formation of Aqueous NpO_2^+ complexes with CO_3^{2-} ($mNpO_2^+ + nCO_3^{2-} \rightarrow (NpO_2)_m(CO_3)_n^{(m-2n)+}$)

$\log \beta_1$	$\log \beta_2$	$\log \beta_3$	Medium	Reference
5.9	11.1	16.3	I=0	[83ALL]
4.49	7.11		I=0	[85NEW/SUL]
5.9	11.1		I=0	[86WAN]
4.9	7.05		I=0	[92FUG/KHO]
4.4	7.1		I=0.1	[92FUG/KHO]
4.4	7.1		I=1	[92FUG/KHO]
5.1	8.1		I=3	[92FUG/KHO]

1) If m = 1, β_{mn} is written β_n

Recommended Values

Equilibrium Constants $(\beta_{mn})^1$ for Formation of Aqueous NpO_2^+ complexes with F^- $(mNpO_2^+ + nF^- \rightleftharpoons (NpO_2)_mF_n^{(m-n)+})$

$\log \beta_1$	Medium	Reference
3.7	I=0	[86WAN]
1.9	I=0	[92FUG/KHO]
1.76	I=0.1	[92FUG/KHO]
0.99	I=2	[76SMI/MAR]

1) If m = 1, β_{mn} is written β_n

Equilibrium Constants $(\beta_{mn})^1$ for Formation of Aqueous NpO_2^+ complexes with NO_3^- $(mNpO_2^+ + nNO_3^- \rightleftharpoons (NpO_2)_m(NO_3)_n^{(m-n)+})$

$\log \beta_1$	Medium	Reference
1.1	I=0	[78ALL/BEA]

1) If m = 1, β_{mn} is written β_n

Equilibrium Constants $(\beta_{mn})^1$ for Formation of Aqueous NpO_2^+ complexes with OH^- $(mNpO_2^+ + nH_2O \rightleftharpoons (NpO_2)_mOH_n^{(m-n)+} + nH^+)$

$\log \beta_1$	Medium	Reference
-8.85	I=0	[76BAE/MES]
-8.9	I=0	[86WAN]

1) If m = 1, β_{mn} is written β_n

Equilibrium Constants $(\beta_{mn})^1$ for Formation of Aqueous NpO_2^+ complexes with HPO_4^{2-} $(mNpO_2^+ + nHPO_4^{2-} \rightleftharpoons (NpO_2)_m(HPO_4)_n^{(m-2n)+})$

log β_1	Other log β_{mn}	Medium	Reference
3.4		I=0	[92FUG/KHO]

1) If m = 1, β_{mn} is written β_n

Equilibrium Constants $(\beta_{mn})^1$ for Formation of Aqueous NpO_2^+ complexes with SO_4^{2-} $(mNpO_2^+ + nSO_4^{2-} \rightleftharpoons (NpO_2)_m(SO_4)_n^{(m-2n)+}$

log β_1	Medium	Reference
2.0	I=0	[86WAN]
0.6	I=0	[92FUG/KHO]
-0.1	I=0.5	[92FUG/KHO]
-0.06	I=1	[92FUG/KHO]
0.45	I=2	[76SMI/MAR]
0.19	I=2	[92FUG/KHO]

1) If m = 1, β_{mn} is written β_n

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Recommended Values

Equilibrium Constants (β_{mn})[1] for Formation of Aqueous PuO_2^+ complexes with F^- ($mPuO_2^+ + nF^- \rightleftharpoons (PuO_2)_mF_n^{(m-n)+}$)

log β_1	Medium	Reference
3.7	H_2O	[86WAN]

1) If m = 1, β_{mn} is written β_n

Equilibrium Constants (β_{mn})[1] for Formation of Aqueous PuO_2^+ complexes with Cl^- ($mPuO_2^+ + nCl^- \rightleftharpoons (PuO_2)_mCl_n^{(m-n)+}$)

log β_1	Medium	Reference
-0.17	H_2O	[77RAI/SER]

1) If m = 1, β_{mn} is written β_n

Equilibrium Constants (β_{mn})[1] for Formation of Aqueous PuO_2^+ complexes with OH^- ($mPuO_2^+ + nOH^- \rightleftharpoons (PuO_2)_mOH_n^{(m-n)+}$)

log β_1	log β_2	Medium	Reference
5	10	H_2O	[78ALL/BEA]
4.3	9	H_2O	[80ALL/KIP]
4.3		H_2O	[82JEN]
4.3		H_2O	[83ALL]

1) If m = 1, β_{mn} is written β_n

Equilibrium Constants $(\beta_{mn})^1$ for Formation of Aqueous PuO_2^+ complexes with OH^- $(mPuO_2^+ + nH_2O \rightleftharpoons (PuO_2)_mOH_n^{(m-n)+} + nH^+)$

$\log \beta_1$	Medium	Reference
-9.7	H_2O	[76BAE/MES]
-9.7	H_2O	[77RAI/SER]
-10	H_2O	[80LEM/TRE]
-9.7	H_2O	[86WAN]
-9.49	I=0.026	[79CLE]
<-9.7	I=0.03	[49KRA/DAM]
-9.7	I=0.03	[79CLE]

1) If m = 1, β_{mn} is written β_n

Equilibrium Constants $(\beta_{mn})^1$ for Formation of Aqueous PuO_2^+ complexes with CO_3^{2-} $(mPuO_2^+ + nCO_3^{2-} \rightleftharpoons (PuO_2)_m(CO_3)_n^{(m-2n)+})$

$\log \beta_1$	$\log \beta_2$	$\log \beta_3$	Medium	Reference
5	10	15.3	H_2O	[83ALL]
5	10	15.3	H_2O	[86WAN]

1) If m = 1, β_{mn} is written β_n

Equilibrium Constants $(\beta_{mn})^1$ for Formation of Aqueous PuO_2^+ complexes with SO_4^{2-} $(mPuO_2^+ + nSO_4^{2-} \rightleftharpoons (PuO_2)_m(SO_4)_n^{(m-2n)+})$

$\log \beta_1$	Medium	Reference
2	H_2O	[86WAN]

1) If m = 1, β_{mn} is written β_n

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Equilibrium Constants (β_{mn})[1] for Formation of Aqueous UO_2^{2+} complexes with F^- ($mUO_2^{2+} + nF^- \rightleftharpoons (UO_2)_mF_n^{(2m-n)+}$)

log β_1	Medium	Method	Reference
4.80	I = 0	est	[78ALL/BEA]
5.10	I = 0	est	[80LEM/TRE]
5.16	I = 0	est	[81TUR/WHI]
4.54	I = 0	est	[82JEN]
4.70	I = 0	est	[86WAN]
4.90	I = 0	est	[87BRO/WAN]
5.41	I = 0	est	[92FUG/KHO]
5.09	I = 0	est	[92GRE/FUG]

1) If m = 1, β_{mn} is written β_n.

Equilibrium Constants (β_{mn})[1] for Formation of Aqueous UO_2^{2+} complexes with Cl^- ($mUO_2^{2+} + nCl^- \rightleftharpoons (UO_2)_mCl_n^{(2m-n)+}$)

log β_1	log β_2	log β_3	Medium	Method	Reference
1.66[a]			I = 0	est	[67OHA/MOR]
0.21			I = 0	est	[76SMI/MAR]
0.21			I = 0	est	[78ALL/BEA]
2.00			I = 0	est	[80LEM/TRE]
-0.100			I = 0	est	[82JEN]
0.21			I = 0	est	[81TUR/WHI]
1.174			I = 0	est	[86MOR/OHA]
1.517			I = 0	est	[86MOR/OHA]
0.2			I = 0	est	[86WAN]
0.45	0.600	0.57	I = 0	est	[87BRO/WAN]
0.45			I = 0	est	[92FUG/KHO]
0.17	-1.100		I = 0	est	[92GRE/FUG]

a) T=288 K,

Equilibrium Constants (β_{mn})[1] for Formation of Aqueous UO_2^{2+} complexes with NO_3^- ($mUO_2^{2+} + nNO_3^- \rightleftharpoons (UO_2)_m(NO_3)_n^{(2m-n)+}$)

log β_1	Medium	Method	Reference
0.300	I = 0	est	[92GRE/FUG]
0.100	I = 0	est	[78ALL/BEA]
0.200	I = 0	est	[87BRO/WAN]

1) If m = 1, β_{mn} is written β_n

Equilibrium Constants (β_{mn})[1] for Formation of Aqueous UO_2^{2+} complexes with OH^- ($mUO_2^{2+} + nH_2O \rightleftharpoons (UO_2)_m(OH)_n^{(2m-n)+} + nH^+$)

log β_1	Other log β_{mn}	Medium	Method	Reference
	log $\beta_{2,2}$=-5.54 log $\beta_{3,5}$=-15.64	I = 0	est	[81VAI/MAK]
-5.88		I = 0	est	[83CAC/CHO2]
-5.2	log $\beta_{2,2}$= -5.62 log $\beta_{3,5}$= -15.55	I = 0	est	[92GRE/FUG]
-5.76	log $\beta_{2,2}$= -5.54 log $\beta_{3,5}$= -15.44	I = 0	est	[92FUG/KHO]

1) If m = 1, β_{mn} is written β_n

Equilibrium Constants (β_{mn})[1] for Formation of Aqueous UO_2^{2+} complexes with CO_3^{2-} ($mUO_2^{2+} + nCO_3^{2-} \rightleftharpoons (UO_2)_m(CO_3)_n^{(m-n)+}$)

log β_1	log β_2	log β_3	Other log β_{mn}	Medium	Method	Reference
12.0				I = 0	est	[78ALL/BEA]
9.87				I = 0		[80FUG/KHO]
10.10				I = 0		[80LEM/TRE]
7.50				I = 0		[81TUR/WHI]
10.10				I = 0		[82JEN]
10.10				I = 0		[83ALL]
9.5	16.6	21.3	log $\beta_{3,6}$= 53.4	I=0	est	[84GRE/FER]
10.17				I = 0	est	[84PHI]
10.05				I = 0	est	[86WAN]
8.29				I = 0	est	[87BRO/WAN]
10.0				I = 0	est	[92FUG/KHO]
9.68				I = 0	est	[92GRE/FUG]
9.67				I = 0	est	[95SIL/BID]

1) If m = 1, β_{mn} is written β_n

Other Equilibrium Constants for Formation of Aqueous UO_2^{2+} Complexes with Various CO_3^{2-}-species

Reaction	log K	Medium	Reference
$UO_2\,CO_{3(c)} = UO_2\,CO_{3(aq)}$	-4.39	I = 0	[72SER/NIK]
$H_2CO_{2(g)} + UO_2^{2+} + H_2O = UO_2\,CO_{3(aq)} + 2H^+$	-6.53	I = 0	[84PHI]

Equilibrium Constants (β_{mn})^1 for Formation of Aqueous UO_2^{2+} complexes with PO_4^{3-} ($UO_2^{2+} + PO_4^{2-} \rightarrow (UO_2)(PO_4)^-$)

log β_1	Medium	Reference
13.65	I = 0	[87BRO/WAN]
13.23	I = 0	[92GRE/FUG]

1) If m = 1, β_{mn} is written β_n

Equilibrium Constants (β_{mn})[1] for Formation of Aqueous UO_2^{2+} complexes with SO_4^{2-} ($mUO_2^{2+} + nSO_4^{2-} \rightleftharpoons (UO_2)_m(SO_4)_n^{(m-n)+}$)

log β_1	log β_2	Medium	Maximum Metal/H^+/Ligand Concentration	Method	Reference
2.73		I = 0	Sat Ag_2SO_4.	est	[60LIE/STO]
3.14		I = 0		est	[67WAL]
2.71		I = 0		est	[68AHR]
2.95	4.0	I = 0		est	[76SMI/MAR]
2.95		I = 0		est	[78ALL/BEA]
2.90		I = 0		est	[80LEM/TRE]
2.95		I = 0		est	[81TUR/WHI]
1.81		I = 0		est	[82JEN]
3.00		I = 0		est	[86WAN]
2.65		I = 0		est	[87BRO/WAN]
3.36		I = 0		est	[92FUG/KHO]
3.15	4.14	I = 0		est	[92GRE/FUG]

1) If m = 1, β_{mn} is written β_n

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Recommended Values

Equilibrium Constants (β_{mn})[1] for Formation of Aqueous NpO_2^{2+} complexes with F^- ($mNpO_2^{2+} + nF^- \rightleftharpoons (NpO_2)_mF_n^{(2m-n)+}s$)

log β_1	log β_2	log β_3	log β_4	Medium	Reference
4.60				I=0	[76SMI/MAR]
4.6	7.5	10.0	11.0	I=0	[78ALL/BEA]
3.85	6.97			I=0	[82JEN]
5.7	11.1	15.9	18.8	I=0	[86WAN]
4.59				I=0	[88PHI/HAL]
4.66	7.8	10.4		I=0	[92FUG/KHO]
	7.01			I=0.1	[76SMI/MAR]

1) If m = 1, β_{mn} is written β_n

Equilibrium Constants (β_{mn})[1] for Formation of Aqueous NpO_2^{2+} complexes with F^- ($mNpO_2^{2+} + nHF \rightleftharpoons (NpO_2)_mF_n^{(2m-n)+} + nH^+$)

log β_1	log β_2	Medium	Reference
0.93	1.11	I=1	[80BON/HEF]

1) If m = 1, β_{mn} is written β_n

Equilibrium Constants (β_{mn})^1 for Formation of Aqueous NpO_2^{2+} complexes with Cl^- ($mNpO_2^{2+} + nCl^- \rightleftharpoons (NpO_2)_mCl_n^{(2m-n)+}$)

log β_1	log β_2	Medium	Reference
	-0.8	I=0	[76SMI/MAR]
0.2	0.0	I=0	[78ALL/BEA]
-0.1	-0.8	I=0	[82JEN]
0.4		I=0	[92FUG/KHO]
-0.3		I=0.5	[76SMI/MAR]
-0.95		I=0.5	[92FUG/KHO]
-0.45		I=1	[92FUG/KHO]
-0.35		I=2	[76SMI/MAR]
-0.46		I=2	[92FUG/KHO]
-0.37	-0.95	I=3	[92FUG/KHO]
0.10		I=4	[92FUG/KHO]

1) If m = 1, β_{mn} is written β_n

Equilibrium Constants (β_{mn})^1 for Formation of Aqueous NpO_2^{2+} complexes with NO_3^- ($mNpO_2^{2+} + nNO_3^- \rightleftharpoons (NpO_2)_m(NO_3)_n^{(2m-n)+}$)

log β_1	Medium	Reference
1.0	I=0	[78ALL/BEA]

1) If m = 1, β_{mn} is written β_n

Equilibrium Constants (β_{mn})[1] for Formation of Aqueous NpO_2^{2+} complexes with OH^- ($mNpO_2^{2+} + nOH^- \rightleftharpoons (NpO_2)_mOH_n^{(2m-n)+}$)

log β_1	log β_2	log β_3	Other log β_{mn}	Medium	Reference
8.9			log $\beta_{2,2}$=21.6 log $\beta_{3,5}$=52.5	I=0	[76SMI/MAR]
8.9	18		log $\beta_{2,1}$=10 log $\beta_{2,2}$=21.6 log $\beta_{3,5}$=52.5	I=0	[78ALL/BEA]
9.1	17.8	23	log $\beta_{2,1}$=10 log $\beta_{2,2}$=21.6 log $\beta_{3,4}$=43 log $\beta_{3,5}$=53	I=0	[80ALL/KIP]
8.6	17	21.3	log $\beta_{2,2}$=20.9 log $\beta_{3,5}$=50.7	I=0	[82JEN]
8.9	17.8	23	log $\beta_{2,2}$=21.6 log $\beta_{3,5}$=53	I=0	[83ALL]

1) If m = 1, β_{mn} is written β_n

Equilibrium Constants (β_{mn})[1] for Formation of Aqueous NpO_2^{2+} complexes with OH^- ($mNpO_2^{2+} + nH_2O \rightleftharpoons (NpO_2)_mOH_n^{(2m-n)+} + nH^+$)

log β_1	log β_2	log β_3	Other log β_{mn}	Medium	Reference
-5.15			log $\beta_{2,2}$=-6.39 log $\beta_{3,5}$=-17.49	I=0	[76BAE/MES]
-5.15	-10.2	-19	log $\beta_{2,1}$=-4.0 log $\beta_{2,2}$=-6.39 log $\beta_{3,4}$=-13 log $\beta_{3,5}$=-17.49	I=0	[82PHI]
-5.1	-10.4	-19	log $\beta_{2,2}$=-6.4 log $\beta_{3,5}$=-17	I=0	[86WAN]

1) If m = 1, β_{mn} is written β_n

Equilibrium Constants (β_{mn})[1] for Formation of Aqueous NpO_2^{2+} complexes with CO_3^{2-} ($mNpO_2^{2+} + nCO_3^{2-} \rightleftharpoons (NpO_2)_m(CO_3)_n^{(m-n)+}$)

log β_1	log β_2	log β_3	Other log β_{mn}	Medium	Reference
10.1	16.7	23.8	log β_{36}=60.1	I=0	[83ALL]
10.1	16.7	23.8	log β_{36}=60.1	I=0	[86WAN]
	13	20.2		I=0.1	[85NEW/SUL]

[1] If m = 1, β_{mn} is written β_n.

Other Equilibrium Constants for Formation of Aqueous NpO_2^{2+} Complexes with Various CO_3^{2-}-species

Reaction	log K	Medium	Reference
$CO_3^{2-} + 3OH^- + 2NpO_2^{2+} \rightleftharpoons (NpO_2)_2(OH)_3CO_3^-$	41	I=0	[83ALL]
$CO_3^{2-} + 3H_2O + 2NpO_2^{2+} \rightleftharpoons (NpO_2)_2(OH)_3CO_3^- + 3H^+$	-1	I=0	[86WAN]

Other Equilibrium Constants for Formation of Aqueous NpO_2^{2+} Complexes with Various PO_4^{3-}-species

Reaction	log K	Medium	Reference
$H^+ + PO_4^{3-} + NpO_2^{2+} \rightleftharpoons NpO_2HPO_{4(aq)}$	20.8	I=0	[86WAN]
$2H^+ + 2PO_4^{3-} + NpO_2^{2+} \rightleftharpoons NpO_2(HPO_4)_2^{2-}$	43.2	I=0	[86WAN]
$2H^+ + PO_4^{3-} + NpO_2^{2+} \rightleftharpoons NpO_2H_2PO_4^+$	22.5	I=0	[86WAN]

Equilibrium Constants (β_{mn})[1] for Formation of Aqueous NpO_2^{2+} complexes with SO_4^{2-} ($mNpO_2^{2+} + nSO_4^{2-} \rightleftharpoons (NpO_2)_m(SO_4)_n^{(m-n)+}$)

log β_1	log β_2	log β_3	Medium	Reference
3.27			I=0	[76SMI/MAR]
3.27	4.1	5	I=0	[78ALL/BEA]
1.82	2.62		I=0	[82JEN]
3.0	4.3		I=0	[86WAN]
3.4			I=0	[92FUG/KHO]
	3.8		I=0.1	[76SMI/MAR]

1) If m = 1, β_{mn} is written β_n

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Recommended Values

Equilibrium Constants (β_{mn})[1] for Formation of Aqueous PuO_2^{2+} complexes with F^- ($mPuO_2^{2+} + nF^- \rightleftharpoons (PuO_2)_mF_n^{(2m-n)+}$)

log β_1	log β_2	log β_3	log β_4	Medium	Reference
5.6	11	15.9	18.8	I=0	[80LEM/TRE]
5.7				I=0	[83FUG2]
4.03				I=0	[85COW/JEN]
5.7	11.1	15.9	18.8	I=0	[86WAN]
4.57	8.24	9.8		I=0	[92FUG/KHO]
4.21				I=0.1	[76SMI/MAR]

1) If m = 1, β_{mn} is written β_n

Equilibrium Constants (β_{mn})[1] for Formation of Aqueous PuO_2^{2+} complexes with F^- ($mPuO_2^{2+} + nHF \rightleftharpoons (PuO_2)_mF_n^{(2m-n)+} + nH^+$)

log β_1	log β_2	log β_3	log β_4	Medium	Reference
2.11	4.15	6.08	6.3	I=1	[80BON/HEF]

1) If m = 1, β_{mn} is written β_n

Equilibrium Constants (β_{mn})[1] for Formation of Aqueous PuO_2^{2+} complexes with Cl^- ($mPuO_2^{2+} + nCl^- \rightleftharpoons (PuO_2)_mCl_n^{(2m-n)+}$)

log β_1	log β_2	Medium	Reference
0.1	-0.35	I=0	[76SMI/MAR]
0.4	0	I=0	[78ALL/BEA]
-0.3		I=0	[80LEM/TRE]
0.1	-0.35	I=0	[82JEN]
0.09	-0.45	I=0	[83FUG2]
0.068	-2.07	I=0	[85COW/JEN]
0.1	-0.45	I=2	[77RAI/SER]
0.09	-0.45	I=2	[92FUG/KHO]

1) If m = 1, β_{mn} is written β_n

Equilibrium Constants (β_{mn})[1] for Formation of Aqueous PuO_2^{2+} complexes with NO_3^- ($mPuO_2^{2+} + nNO_3^- \rightleftharpoons (PuO_2)_m(NO_3)_n^{(2m-n)+}$)

log β_1	Medium	Reference
-1.14	I=0	[85COW/JEN]

1) If m = 1, β_{mn} is written β_n

Equilibrium Constants (β_{mn})[1] for Formation of Aqueous PuO_2^{2+} complexes with OH^-($mPuO_2^{2+} + nOH^- \leftrightarrow (PuO_2)_mOH_n^{(2m-n)+}$)

log β_1	log β_2	log β_3	log β_4	Other log β_{mn}	Medium	Reference
8.4				log $\beta_{2,2}$=19.6 log $\beta_{3,5}$=48.4	I=0	[76SMI/MAR]
8.4	16	22		log $\beta_{2,1}$=10 log $\beta_{2,2}$=19.6 log $\beta_{3,4}$=37 log $\beta_{3,5}$=48.4	I=0	[78ALL/BEA]
8.9	17.6	22		log $\beta_{2,1}$=10 log $\beta_{2,2}$=20.3 log $\beta_{3,4}$=41 log $\beta_{3,5}$=50	I=0	[80ALL/KIP]
7.9	17	21.3		log $\beta_{2,2}$=20.1 log $\beta_{3,5}$=49.3	I=0	[82JEN]
8.4	17.6	22		log $\beta_{2,2}$=19.7 log $\beta_{3,5}$=48.4	I=0	[83ALL]

1) If m = 1, β_{mn} is written β_n

Equilibrium Constants (β_{mn})^1 for Formation of Aqueous PuO_2^{2+} complexes with OH^- ($mPuO_2^{2+} + nH_2O \rightarrow (PuO_2)_mOH_n^{(2m-n)+} + nH^+$)

log β_1	log β_2	log β_3	Other log β_{mn}	Medium	Reference
-5.3	-11	-20.7		I=0	[54HIN]
-5.71				I=0	[54HIN]
-5.6			log $\beta_{3,5}$=-21.65	I=0	[76BAE/MES]
-5.3	-11.01	-20.71		I=0	[77RAI/SER]
--3.62	-7.98	-17.68		I=0	[79CLE]
<-5.6			log $\beta_{2,2}$=-8.3 log $\beta_{3,5}$=-21.6	I=0	[80LEM/TRE]
-9.7	-10.4	-20	log $\beta_{2,2}$=-8.36 log $\beta_{3,4}$=-15 log $\beta_{3,5}$=-21.65	I=0	[82PHI]
			log $\beta_{2,2}$=-8.2 log $\beta_{4,7}$=-29.11	I=0	[85COW/JEN]
-5.6	-10.2	-20	log $\beta_{2,2}$=-8.3 log $\beta_{3,5}$=-21.6	I=0	[86WAN]
			log $\beta_{2,2}$=-8.51 log $\beta_{3,5}$=-22.16	I=1	[77RAI/SER]

1) If m = 1, β_{mn} is written β_n

Equilibrium Constants (β_{mn})[1] for Formation of Aqueous PuO_2^{2+} complexes with CO_3^{2-} ($mPuO_2^{2+} + nCO_3^{2-} \rightleftharpoons (PuO_2)_m(CO_3)_n^{(m-n)+}$)

log β_1	log β_2	log β_3	Other log β_{mn}	Medium	Reference
	15.04			I=0	[77RAI/SER]
	15.04			I=0	[79CLE]
	15			I=0	[80LEM/TRE]
12	15	18.3		I=0	[82JEN]
9	15	22	log β_{36}=60.1	I=0	[83ALL]
9	15	22	log β_{36}=60.1	I=0	[86WAN]
	13.1			I=0.1	[85NEW/SUL]
		6.2		0.15M $NaClO_4$	[78WOO/MIT]
		20		I=0.15	[85NEW/SUL]
12				I=1	[77RAI/SER]

1) If m = 1, β_{mn} is written β_n.

Other Equilibrium Constants for Formation of Aqueous PuO_2^{2+} Complexes with Various CO_3^{2-}-species

Reaction	log K	Medium	Reference
$CO_3^{2-} + OH^- + PuO_2^{2+} \rightleftharpoons PuO_2OHCO_3^-$	23.85	I=0	[77RAI/SER]
$CO_3^{2-} + OH^- + PuO_2^{2+} \rightleftharpoons PuO_2OHCO_3^-$	23.85	I=0	[79CLE]
$CO_3^{2-} + OH^- + PuO_2^{2+} \rightleftharpoons PuO_2OHCO_3^-$	23.85	I=0	[82JEN]
$CO_3^{2-} + 2OH^- + PuO_2^{2+} \rightleftharpoons PuO_2(OH)_2CO_3^-$	23	I=0	[77RAI/SER]
$CO_3^{2-} + 2OH^- + PuO_2^{2+} \rightleftharpoons PuO_2(OH)_2CO_3^-$	23	I=0	[79CLE]
$CO_3^{2-} + 2OH^- + PuO_2^{2+} \rightleftharpoons PuO_2(OH)_2CO_3^-$	23	I=0	[82JEN]
$HCO_3^- + 2OH^- + PuO_2(OH)_{2(aq)} \rightleftharpoons PuO_2(OH)_2HCO_3^-$	20	I=0.1	[85NEW/SUL]
$CO_3^{2-} + 3OH^- + 2PuO_2^{2+} \rightleftharpoons (PuO_2)_2(OH)_3CO_3^-$	41	I=0	[83ALL]
$CO_3^{2-} + 3H_2O + 2PuO_2^{2+} \rightleftharpoons (PuO_2)_2(OH)_3CO_3^- + 3H^+$	-1	I=0	[86WAN]
$CO_3^{2-} + 3OH^- + 3PuO_2^{2+} \rightleftharpoons (PuO_2)_3(OH)_3CO_3^+$	43	I=0	[83ALL]
$CO_3^{2-} + 3H_2O + 3PuO_2^{2+} \rightleftharpoons (PuO_2)_3(OH)_3CO_3^+ + 3H^+$	1	I=0	[86WAN]

Other Equilibrium Constants for Formation of Aqueous PuO_2^{2+} Complexes with Various PO_4^{3-}-species

Reaction	log K	Medium	Reference
$H^+ + PO_4^{3-} + PuO_2^{2+} \rightleftharpoons PuO_2HPO_{4(aq)}$	20.8	I=0	[86WAN]
$2H^+ + 2PO_4^{3-} + PuO_2^{2+} \rightleftharpoons PuO_2(HPO_4)_2^{2-}$	43.2	I=0	[86WAN]
$H^+ + HPO_4^{2-} + PuO_2^{2+} \rightleftharpoons PuO_2H_2PO_4^+$	11	I=0	[80LEM/TRE]
$2H^+ + PO_4^{3-} + PuO_2^{2+} \rightleftharpoons PuO_2H_2PO_4^+$	22.5	I=0	[86WAN]

Equilibrium Constants (β_{mn})[1] for Formation of Aqueous PuO_2^{2+} complexes with SO_4^{2-} ($mPuO_2^{2+} + nSO_4^{2-} \rightleftharpoons (PuO_2)_m(SO_4)_n^{(m-n)+}$)

log β_1	log β_2	Medium	Reference
3		I=0	[80LEN/TRE]
3.374		I=0	[85COW/JEN]
3	4.3	I=0	[86WAN]
2.17		I=2	[76SMI/MAR]

1) If m = 1, β_{mn} is written β_n

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Reduction Potentials
for U, Np and Pu
at pH = 0, 8, 14

Table 1 of this section lists the reduction potentials for U, Np and Pu at pH 0, 8, and 14. The values at pH 8 and 14 include the effects of hydrolysis in such solutions.

Table I
T = 25.0°C., I = 1.0 (M)

Half-cell	Potential (V.)
pH = 0	
U(III) – U(IV) + e^-	-0.631
U(VI) – U(V)	+0.613
U(VI) – U(VI)	+0.338
U(V) – U(VI)	+0.063
Np(III) – Np(IV)	+0.155
Np(IV) – Np(V)	+0.739
Np(IV) – Np(VI)	+0.938
Np (V) – Np(VI)	+1.136
Pu(III) – Pu(IV)	+0.982
Pu(IV) – Pu(V)	+1.170
Pu(IV) – Pu(VI)	+1.043
Pu(V) – Pu(VI)	+0.916
pH = 8	
U(III) – U(IV)	-1.95±0.17
U(IV) – U(V)	+0.08±0.12
U(IV) – U(VI)	+0.07±0.08
U(V) – U(VI)	-1.13±0.14
Np(III) – Np(IV)	-1.13±0.05
Np(IV) – Np(V)	+0.15±0.13
Np(IV) – Np(VI)	+0.48±0.09
Np(V) – Np(VI)	-0.18±0.08
Pu(III) – Pu(IV)	-0.39±0.15

pH = 8	
Pu(IV) – Pu(V)	+0.70±0.12
Pu(IV) – Pu(VI)	+0.65±0.08
Pu(V) – Pu(VI)	+0.60±0.04

ph = 14	
U(III) – U(IV)	-2.78±0.34
U(IV) – U(V)	-0.03±0.24
U(IV) – U(VI)	-0.36±0.24
U(V) – U(VI)	-0.69±0.24
Np(III) – Np(IV)	-1.88±0.24
Np(IV) – Np(V)	-0.09±0.24
Np(IV) – Np(VI)	+0.15±0.12
Np(V) – Np(VI)	+0.38±0.24
Pu(III) – Pu(IV)	-1.04±0.24
Pu(IV) – Pu(V)	+0.52±0.24
Pu(IV) – Pu(VI)	+0.34±0.12
Pu(V) – Pu(VI)	+0.16±0.24

Index

2.　ベントナイトおよび岩石への収着／拡散データベースの整備

A Sorption and Diffusion Database for the Interaction of Th, Pa, U, Np, Am, Cm, Ac, Sm, Ra, Zr, Nb, Pd, Sb, Pb, Bi and Po with Plutonic, Volcanic and Sedimentary Rocks; and for the Interaction of Pu with Bentonite.

Database Development Project: Data Compilation

A Sorption and Diffusion Database for the Interaction of Th, Pa, U, Np, Pu, Am, Cm, Ac, Sm, Ra, Zr, Nb, Pd, Sb, Pb, Bi, and Po with Plutonic, Volcanic, and Sedimentary Rocks; and for the Interaction of Pu with bentonite

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Executive Summary

An extensive literature search for sorption and diffusion data for thorium, protactinium, uranium, neptunium, plutonium, americium, curium, actinium, samarium, radium, zirconium, niobium, palladium, antimony, lead, bismuth, and polonium in plutonic, volcanic, and sedimentary rocks has been conducted. In addition, a literature search for sorption and diffusion data for plutonium in bentonite was done in collaboration with T. Shibutani, PNC.

Based on these literature searches, we present a large compilation of distribution coefficients, K_d, and apparent diffusivities, D_a, for the key radionuclides listed above. Experimental sorption (SDB) and diffusion (DDB) databases and a large amount of additional information extracted from each source of experimental data are given in a condensed fashion in this report through (i) graphical overviews, and (ii) data tables that contain the most important information for every entry in the SDB and DDB. The actual databases are also made available to PNC in the form of two Excel files (SDB.FY97/March98/BMG, DDB.FY97/March98/BMG). These files contain a user's manual, a speadsheet for database identification, including updates etc., spreadsheets for each element, and all references used. In addition, a spreadsheet containing data that have been recommended in previous compilations is given.

The chemical characteristics of each element are briefly discussed in relation to its expected sorption behavior. A number of the elements treated in this report can take on different oxidation states as a function of the prevailing redox conditions. Taking into account the reducing conditions expected by PNC for its Reference Case Analysis, priority is given to data that had been obtained under reducing conditions. Experimental data obtained under oxidizing conditions are also included, because (i) such data can be used for elements that have only one oxidation state in aqueous environments, and because (ii) for redox-sensitive elements it may be necessary to cover uncertainties with respect to the expected Eh in the Reference Case Analysis.

Table of Contents

Appendix A: Sorption database

Appendix B: Diffusion database

1 Introduction

The Japanese disposal concept for high-level radioactive waste envisages deep geological storage of the vitrified waste and the use of compacted bentonite as a backfill material (PNC, 1992). To conduct a safety analysis of a high-level waste repository, the migration of the radionuclides from the waste matrix to the biosphere, including uptake by man, is simulated by a computer model. After resaturation of the repository with groundwater and container corrosion has occurred, the radionuclides will be released from the waste matrix and start to migrate through the backfill of compacted bentonite before reaching the host rock.

While the backfill is possibly the most effective and predictable barrier on the migration path of radionuclides, interactions of radionuclides with the host rock are also very important. Since no site for the disposal of high-level radioactive waste has been selected yet, it is necessary to adopt a general approach in which several candidate host rocks are considered. Candidate host rocks comprise plutonic (granite/granodiorite), volcanic (basalt, tuff), and sedimentary (mudstone, sandstone) rocks.

For bentonite, an integrated sorption-diffusion system (Wanner, 1995) has already been presented in earlier reports. This system defines links between bentonite and groundwater characteristics, thermodynamic data of key elements, and sorption and diffusion models that are required to calculate distribution coefficients and apparent diffusivities based on fundamental data. The calculation of K_d values for Ra/Sr and Pb is discussed in previous reports (Ochs and Wanner, 1996; Ochs and Lothenbach, 1997), and the use of the ISD system to arrive at apparent diffusivities for Cs is discussed in the report by Ochs et al. (1996). At present, this approach can be used only for a limited number of situations, due to a lack of data. For many elements of interest, no sorption models are available to date, and the surface chemical characteristics of rocks are much less known than those of bentonite. Therefore, the migration of radionuclides in host rock formations has to be evaluated by relying on compilations of sorption and diffusion data for key elements. The present report comprises sorption and diffusion databases for a large number of elements and the rocks listed above.

It is important to point out that a reliable thermodynamic database is needed, even if sorption and diffusion are evaluated through experimental databases only (i. e., without the use of models), since the speciation of a key element in the ground- and porewater still has to be predicted by a thermodynamic model. Further, in order to evaluate experimental results for a key element, or for using a chemical analog, the speciation of an element has to be known. It is also crucial to be able to check any calculation against literature data. This makes the compilation of well-documented sorption (SDB) and diffusion (DDB) databases also useful for the development and testing of sorption models.

2 Sorption (SDB) and diffusion (DDB) database

The migration of radionuclides in the geosphere is controlled by their interaction with the surfaces encountered along the flow path. In contrast to bentonite, clay minerals, and oxides, however, comparatively little effort has been made to understand sorption of radionuclides onto rocks. In the absence of applicable thermodynamic models, well-documented sorption and diffusion databases are necessary in order to assess the sorption and diffusion of radionuclides in relevant host rocks.

The compilation of well-documented sorption and diffusion databases is also a prerequisite in order to use the ISD bypass options developed for the bentonite engineered barrier system (Wanner, 1995) in an optimal fashion. In order to be able to use a compilation of distribution coefficients and apparent diffusivities within the ISD system, such a compilation needs to contain as much information as possible concerning the respective experimental conditions, rather than only values that are recommended based on 'expert opinion'. With proper documentation, it is possible to check the data contained in the SDB and DDB against thermodynamic models contained in the ISD system (and vice versa), if such models are available. Where such models are not available, a well-documented database can be of great help in the model development.

2.1 Distribution coefficient and apparent diffusivity

The basic data contained in the SDB and DDB are the distribution coefficient, K_d, and apparent diffusivity, D_a. Both parameters are single numbers that reflect all aspects of the behavior of a key element, often in a very complex system. This means that a number of general experimental conditions, such as methodology, temperature and redox conditions, as well as many specific informations, such as background electrolyte used, compositions and surface characteristics of the rocks and minerals used, solid/solution ratio, and porosity of rocks or bentonite, are implicitly contained in these values. The use of such data to evaluate the behavior of a radionuclide in the bentonite backfill or the host rock surrounding a repository is only fully justifiable when the sorption and diffusion mechanisms are known and can be implemented in models that have the ability to reproduce experimental findings under a range of conditions.

2.2 Background

2.2.1 Distribution coefficient, K_d

The K_d value, called distribution or sorption coefficient, of a key element is defined as the ratio of the concentration of the key element on the surface and the concentration of the key element in solution:

$$K_d\,[\mathrm{m^3/kg}] = \frac{\text{stoichiometric sum of surface species of element X [mol/kg]}}{\text{stoichiometric sum of solution species of element X [mol/m}^3\text{]}} \qquad (2.1)$$

Distribution coefficients are commonly determined in batch sorption experiments, where a known quantity of the element of interest is added to a suspension of a solid material (such as crushed rock or bentonite), or vice versa. Distribution ratios are then calculated as:

$$K_d = \left(\frac{C_{init} - C_{equil}}{C_{equil}} \right) \frac{v}{m} \tag{2.2}$$

where:
C_{init} is the initial aqueous concentration of a key element [mol/m^3]
C_{equil} is the final equilibrium aqueous concentration of this element [mol/m^3]
v is the volume of the solution used for a batch experiment [m^3]
m is the mass of the solid phase (rock, bentonite) used [kg]

The experimental conditions employed, such as redox conditions, pH, and concentration of ligands and competing ions in the background electrolyte solution, are also implicitly contained in a distribution coefficient. As a result, a K_d determined at a given solid/solution ratio is often not valid at a different solid/solution ratio, although in theory, the solid/solution ratio has no effect on K_d (cf. equation (2.2)). In addition, it is important to emphasize that changes in solution composition will affect different elements in different ways. Therefore, the chemical characteristics of an element have to be kept in mind in the evaluation of K_d values. This will be discussed for each individual element in section 3.

As pointed out before, distribution coefficients represent point values, valid only for a given set of conditions, and can be influenced by the respective experimental techniques. Therefore, a tabulation of K_d values that does not contain additional information is not very useful. The reporting of important chemical information and experimental techniques is necessary for two reasons:

- Information about the chemical conditions and experimental techniques enables the reader to evaluate the range of validity and quality of the compiled K_d values.
- The chemical conditions of an experiment need to be known in order to be able to interpret a distribution coefficient, e. g. with the help of a thermodynamic sorption model.

Therefore, the compilation of Kd values presented in section 3 and Appendix A contains mostly K_d values from literature sources that provide a reasonably detailed description of experimental conditions and techniques. Some values from literature sources that do not provide all the information considered necessary are also included; these values are clearly labeled, however. The literature sources considered were checked for a large number of items, defined in collaboration with PNC according to the respective requirements.

2.2.2 *Apparent diffusivity, D_a*

The apparent diffusivity, D_a, reflects both diffusion and sorption characteristics of a given species and is, thus, a very critical parameter for performance assessment. The derivation of D_a in bentonite using fundamental data and the sorption and diffusion models contained in the ISD system is described in detail in a previous report (Ochs et al., 1996), and will not be described here.

As mentioned above, D_a is dependent on K_d:

$$D_\mathrm{a} = \frac{\varepsilon}{(\varepsilon + K_\mathrm{d}\rho)} D_\mathrm{p} \tag{2.3}$$

Here, ε are the porosity and (dry) density of rock or compacted bentonite, respectively, and D_p is the pore diffusivity of the diffusing species. In a typical rock matrix, the total porosity ε is composed of two types of pores. The transport porosity ε_t refers to pores that are connected along a flow path and contribute to the transport of a diffusing species, the storage porosity ε_s refers to dead-end pores that do not contribute to transport but to the capacity of the rock to hold dissolved species; thus:

$$\varepsilon = \varepsilon_t + \varepsilon_s \tag{2.4}$$

Usually, the capacity of the rock to hold dissolved species is simply expressed through an experimentally accessible measure termed rock capacity factor, α:

$$\alpha = \varepsilon + \rho K_d \tag{2.5}$$

D_p is the diffusivity in the pores of a porous medium in the absence of sorption and is related to the diffusivity of a species in water, D_w, by:

$$D_\mathrm{p} = \frac{\delta}{\tau^2} D_\mathrm{w} \tag{2.6}$$

Here, δ/τ^2 is a material-dependent factor that can be determined experimentally. The constrictivity δ is usually viewed as a geometric factor, i. e., δ is supposed to be greater than 1 if the pore width increases, equal to 1 if the pore width remains constant along the diffusion path; and less than 1 if the width decreases, slowing down (constricting) diffusion (Kato et al., 1995). The average value of δ will be equal to 1 if the total length of the diffusion path is significantly greater than the length of the individual clay platelets. The tortuosity τ^2 takes into account the fact that the pores are not straight. If a diffusion path in a porous medium is τ times longer than it would be in water, then D_p has to be τ^2 times smaller than D_w (Kato et al., 1995).

While both D_p and K_d are contained in equation (2.3), one has to be aware that typically only diffusion experiments are carried out in intact rock or at high dry densities of bentonite, due to the experimental difficulties encountered in the performance of 'batch' sorption experiments with intact rock or compacted bentonite. Through D_a, the effects of both sorption and diffusion are measured for a sorbing species. However, one of the problems in calculating D_a from D_p and K_d stems from the fact that sorption data obtained with crushed rock or in dilute suspensions of bentonite are usually not valid under the conditions of diffusion experiments.

Apparent diffusivities are usually determined by in-diffusion, or non-steady-state, experiments. The result of such an experiment is a concentration profile extending from the source into the solid. Apparent diffusivities are then obtained by fitting theoretical curves to the experimental data. Depending on the initial experimental conditions, two different cases are distinguished (Crank, 1975). In experiments where a constant concentration of the key element is present at the source, an infinite and constant supply of this element is available for diffusion, and the following equation applies:

$$\frac{C}{C_0} = erfc\left(\frac{x}{2\sqrt{Dt}}\right) \qquad (2.7)$$

where C is the concentration of the key element, C_0 is the concentration of the key element at the source, and $erfc(y) = \frac{2}{\sqrt{\pi}}\int_y^\infty e^{-u^2}\,du$.

If a constant amount A of tracer is present at the source, the following equation is valid:

$$\frac{C}{A} = \frac{1}{2s\sqrt{\pi Dt}}\exp\left(-\frac{x^2}{4Dt}\right) \qquad (2.8$$

where s denotes the initial interfacial area between the bentonite and the aqueous solution.

In through-diffusion experiments, the element of interest diffuses through the sample, i. e., from a solution with a high concentration of this element through the solid phase into a solution with a very small concentration of the respective element. In such experiments, D_a can then be obtained through the following relation once a steady state has been reached:

$$D_a = \frac{Rd}{s(C_1 - C_2)} \qquad (2.9)$$

Here, R is the total transport rate of the key element (mass/time), d is the thickness of the solid sample, and C_1 and C_2 are the bulk concentrations of the key element in the sample on the high- and low-concentration side, respectively. A special case of a through-diffusion experiment is the so-called time-lag method, where the initial concentration of the key element on the low-concentration side equals zero. Then, D_a can be obtained through equation (2.10):

$$D_a = \frac{s^2}{6\,T} \qquad (2.10)$$

where T is obtained by plotting the cumulative amount of tracer diffused through the sample vs. time; extrapolating the asymptote at stationary state to the time axis gives the time lag *T*.

As was already pointed out for the distribution coefficient K_d, the apparent diffusivity D_a also combines a number of processes and experimental conditions into one single number. As a matter of fact, D_a contains all parameters already contained in K_d, plus several other, additional parameters, such as diffusion paths, relative importance of storage and transport porosity, and, at least in the case of compacted bentonite, interaction of diffusing ions with charged pore surfaces.

From this, it becomes obvious that diffusivities reported in the literature should also be interpreted with caution. For the compilation of diffusion data, the same procedures and principles were applied as already described in section 2.2.1. A condensed data compilation is given in Appendix B of this report.

3 Data compilation for key elements

3.1 General remarks

In this report, we present a large compilation of distribution coefficients, K_d, and apparent diffusivities, D_a, for key radionuclides (thorium, protactinium, uranium, neptunium, plutonium, americium, curium, actinium, samarium, radium, zirconium, niobium, palladium, antimony, lead, bismuth, and polonium). Experimental sorption (SDB) and diffusion (DDB) databases and a large amount of additional information extracted from each source of experimental data are given in a condensed fashion in this report through (i) graphical overviews (that do not include any entries labeled as 'doubtful'), and (ii) data tables that contain the most important information for every entry in the SDB and DDB.

The actual databases are also made available to PNC in the form of two Excel files (SDB.FY97/March98/BMG, DDB.FY97/March98/BMG). These files contain:

- a user's manual,
- a sheet for database identification, including updates etc.,
- spreadsheets for each element,
- all references used;
- in addition, a spreadsheet containing data recommended in existing compilations.

The chemical characteristics of each element are briefly discussed in relation to its expected sorption behavior. A number of the elements treated in this report can take on different oxidation states as a function of the prevailing redox conditions. Taking account of the reducing conditions expected by PNC for the Reference Case Analysis, priority was given to data that had been obtained under reducing conditions in preparing this compilation. Experimental data obtained under oxidizing conditions were also included, because (i) such data can be used for elements that have only one oxidation state in aqueous environments, (ii) for redox-sensitive elements, it may be necessary to cover uncertainties with respect to the expected Eh in the Reference Case Analysis.

The general precautions that should be applied to selecting distribution coefficients and apparent diffusivities reported in the literature have already been discussed in section 2. Comments that are important for an evaluation of the quality of the data compiled are given in the appendix of this report. Since most publications do not provide an explicit measure of uncertainty for the data reported, it is important that the experimental procedures are described in enough detail to allow a general evaluation of their soundness. In the compilations of sorption and diffusion data presented in this report most entries contain enough additional information, such as pH, electrolyte composition, phase separation techniques used, etc., to allow the reader to perform a check of consistency of the reported data. Where basic information is missing, the data are labeled as 'doubtful'.

3.2 *Data for key elements*

Below follows a brief discussion of the chemical characteristics and data compiled for each element. The compiled sorption and diffusion data are provided in the appendix, together with additional information. Since the amount of sorption data is very large, a graphical overview of sorption data is provided for each element.

Sorption and diffusion data were compiled for five potential host rocks relevant for a planned Japanese repository for high-level waste: granite, tuff, mudstone, sandstone, basalt. Data compilations were carried out for a large number of elements, considering the following priorities:

- 1st priority: Th, U, Np, Pu, Am, Cm, Pd, Ra
- 2nd priority: Sm, Zr, Nb, Sb, Pb, Bi, Po, Ac, Pa

For plutonium, sorption and diffusion data were also compiled for compacted bentonite, which is envisaged as backfill material.

3.2.1 *Thorium (Th)*

3.2.1.1 *Chemical characteristics*

In aqueous solutions, Th exists exclusively in the +IV state. Of all tetravalent actinide cations, the Th^{4+} ion has the smallest tendency to hydrolyze; the onset of hydrolysis is at pH ≈2-3, and above pH 5, $Th(OH)_4^0$ is the dominating species (Baes and Mesmer, 1976). Accordingly, strong sorption through the formation of surface complexes can be expected for Th, as well as other tetravalent actinides (see below). In analogy to the solution chemistry of Th, sorption can also be expected to be independent of redox conditions and pH, except in acidic solutions. Apart from OH^-, other hard ligands such as F^- show the strongest tendency to form complexes with Th^{4+}. The most important solid is the oxide ThO_2.

3.2.1.2 *Distribution and diffusion coefficients for thorium*

An overview of K_d values for thorium on granite, tuff, mudstone, and different sandstones (St. Bees sandstone, Caithness flagstones) is given in Figure 3.1, the corresponding data compilation is provided in Appendix A. For granite, K_d values were obtained under oxidizing and reducing conditions, all other compiled data refer to oxidizing conditions. No sorption data for basalt, and no diffusion data for any rock have been found. K_d values for thorium on silica and other oxides have already been collected for our FY95 report (Ochs and Wanner, 1996); for convenience, these data are summarized in Figure 3.2.

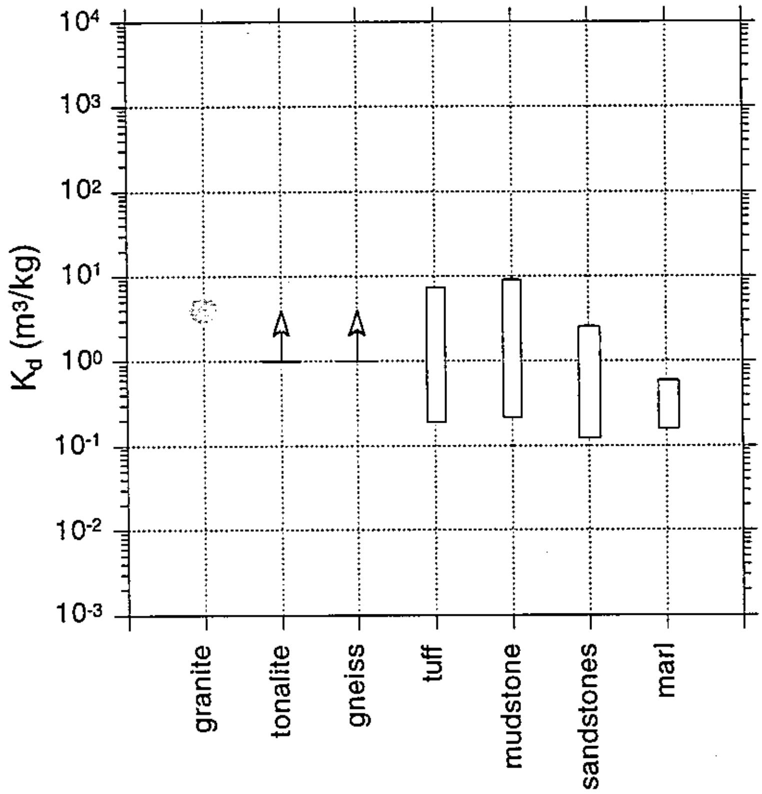

Figure 3.1: Overview of distribution coefficients for Th on rocks. Bars in the figure represent a range of data, average values are represented by a circle, minimum values are represented by arrows. Open symbols are used for data obtained under oxidizing conditions, the shaded symbol used for granite refers to data obtained under both oxidizing and reducing conditions. K_d values are listed in Appendix A.2: Table 1.

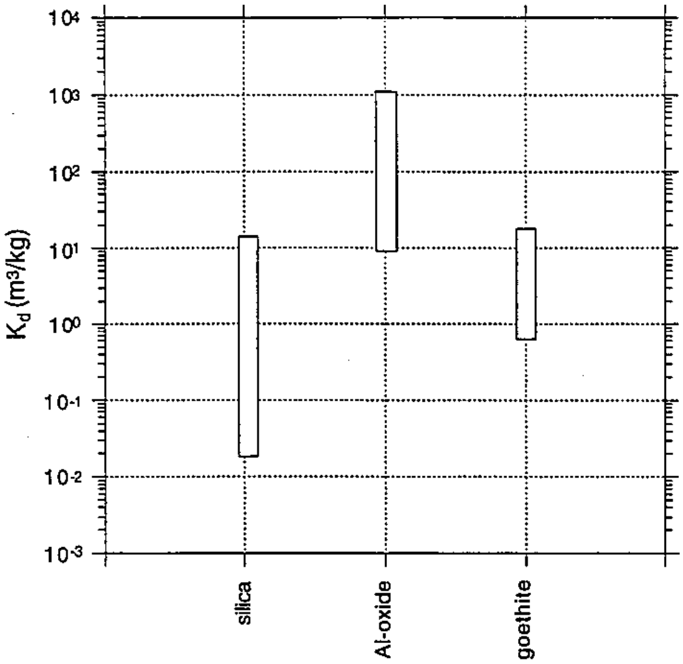

Figure 3.2: Overview of distribution coefficients for Th on oxides. Bars in the figure represent the spread of data, all measurements were carried out under oxidizing conditions. The figure is modified from Ochs and Wanner (1996), a compilation of K_d values is given in Table 15 of that report.

The K_d values obtained for Th are similar for different rocks; and all values lie within a relatively narrow range, considering the different factors that are contained in a K_d value. A comparison with Figure 3.2 shows that the K_d values for rocks shown in Figure 3.1 compare well with K_d values obtained for silica (Östhols, 1995) and goethite (Hunter et al., 1988) at low pH-values. As expected based on the redox-insensitivity of Th, no significant difference between K_d values obtained under reducing and oxidizing conditions is observed as shown by the data of Allard et al. (1978) for granite.

3.2.2 Protactinium (Pa)

3.2.2.1 Chemical characteristics

It is generally thought that Pa(V) is the most important oxidation state for protactinium, while it appears to be very difficult to prevent the oxidation of Pa(IV), except in strongly acidic or complexing solutions (Katz et al., 1986). In the reviews of Baes and Mesmer (1976) and Katz et al. (1986), estimated potentials for the Pa(IV)/Pa(V) couple of –0.1 V to –0.26 V in 1-6 M HCl are quoted. The reason for this may lie in the hydrolysis behavior of Pa(V), which appears to differ from that of Np(V) (cf. Baes and Mesmer, 1976): instead of forming an ion of the type MO_2^+, the least hydrolyzed species of Pa(V) in strongly acidic solutions is probably the

PaO(OH)$^{2+}$ ion. This species may have a stronger tendency to hydrolyze than the Pa^{4+} ion, and the species resulting from further hydrolysis seem to undergo polymerization very readily.

Overall, the aqueous chemistry of Pa is not very well known in comparison to other actinides. The uncertainties regarding the potential of the Pa(IV)/Pa/V) couple under different conditions, and the apparent tendency of Pa(V), and possibly Pa(IV), towards polymerization makes the interpretation of sorption experiments, particularly of phase separation effects, very difficult.

3.2.2.2 *Distribution and diffusion coefficients for protactinium*

K_d values for Pa on granite and granodiorite, tuff, claystone, and different marl rocks are summarized in Figure 3.3. The compiled data and supplementary information are provided in Appendix A. K_d values for Pa have already been compiled for our FY96 report (Ochs and Lothenbach, 1997), and sorption data for bentonite, Al-oxide, quartz, and sandy sediments are reproduced in Figure 3.4 for ease of comparison. The corresponding data compilation can be found in Appendix A.2, Table 4, of Ochs and Lothenbach, 1997.

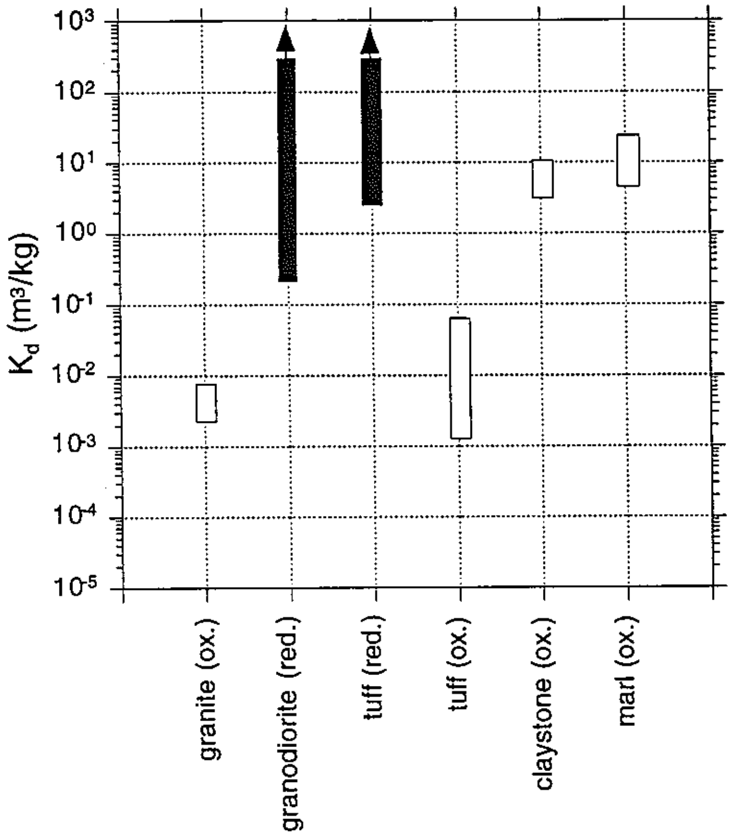

Figure 3.3: Overview of distribution coefficients for Pa on rocks. Bars in the figure represent the spread of data, minimum values are labeled by arrows. Closed symbols refer to reducing, open symbols refer to oxidizing conditions. K_d values are listed in Appendix A.2: Table 2.

There is a considerable difference between the data obtained by Baston et al. (1997b) for granodiorite and tuff under strongly reducing conditions, and the data obtained by Nakayama et al. (1986) for granite and tuff under oxidizing conditions. The K_d values obtained by Bode (1989) under oxidizing conditions for claystones and marls of different compositions are comparatively high. The K_d values for Pa measured by Baston et al. (1997b) agree well with their values for U under reducing conditions, but are higher than the corresponding data for Np. According to the measurements made by Baston et al. (1997b), K_d values for Pa on both granodiorite and tuff seem to be smaller, and more sensitive with regard to the phase separation technique employed, at 60°C than at 25°C. Interpretation of the data by Nakayama et al. (1986) is made somewhat difficult by the fact that they did not use Pa directly, but instead a stock solution of ^{237}Np. However, their measurements agree reasonably well with data for U (Figure 3.5) and Np (Figure 3.7) under oxidizing conditions.

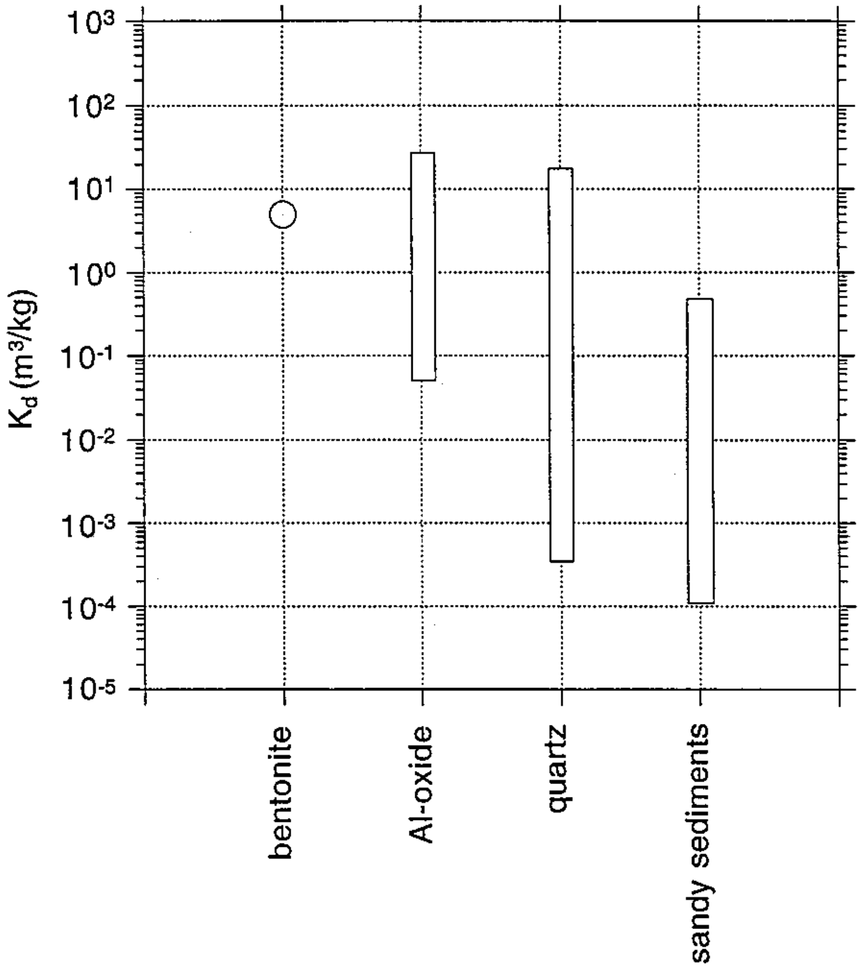

Figure 3.4: Overview of distribution coefficients for Pa on bentonite, oxides, and sediments. Bars in the figure represent a large spread of data. Single K_d values are represented by circles. All data correspond to oxidizing conditions. This figure is constructed from data that are listed in Appendix A.2, Table 4, of our FY96 report (Ochs and Lothenbach, 1997).

No diffusion data for Pa in rocks were found. As detailed in Appendix B.2, Table 2, of Ochs and Lothenbach (1997), an average D_a value for Pa in compacted bentonite (dry density ≈2 kg/m^3) under oxidizing conditions is ≈6×10^{-13} m^2/s, which would be consistent with K_d values that are approximately in the order of the values found by Nakayama et al. (1986).

3.2.3 Uranium (U)

3.2.3.1 Chemical characteristics

U can take on several different oxidation states in aqueous solution (Fuger, 1992). Under oxidizing conditions U exists in the hexavalent state as UO_2^{2+} ion. Under strongly reducing conditions, U exists in the tetravalent state as U^{4+} ion, which has a much stronger tendency to hydrolyze than the UO_2^{2+} ion and forms sparingly soluble oxides; accordingly, the solubility of U is generally lower under reducing conditions. Under intermediate redox conditions, it depends on pH and the presence of relevant ligands whether U(IV) or U(VI) are dominating. Tri- and pentavalent states of U can exist in aqueous solution, but U(III) is not stable with respect to U(IV), and U(V) is known to disproportionate into U(IV) and U(VI) (Fuger, 1992). According to the hydrolysis behavior of the U^{4+} and UO_2^{2+} ion, it can be expected that sorption of U is stronger under reducing conditions.

3.2.3.2 Distribution and diffusion coefficients for uranium

In Figure 3.5, an overview of K_d values for uranium on silicic (granite and granodiorite) and mafic plutonic rocks (hornblendite and gabbro), greenstone, tuff, and basalt is given in panel (a), data compiled for sedimentary rocks - mudstone, marl, and different sandstones (St. Bees sandstone, Caithness flagstones) - are summarized in panel (b). Supplementary data for sandy sediments are also provided in panel (b). A large number of the compiled distribution coefficients has been obtained under reducing conditions, data obtained under oxidizing conditions are provided for comparison. A compilation of K_d values is provided in Appendix A.

In case of the sedimentary rocks (panel (b)), the range of compiled K_d values is comparatively narrow. Also, the difference in K_d values obtained under reducing and oxidizing conditions is not very pronounced (except for marl and the sandy sediments, where not many data are available and other experimental conditions have not been varied appreciably).

In comparison, the range of K_d values for plutonic and volcanic rocks shown in panel (a) is much larger, which is partly due to the large differences observed between different phase separation techniques (see e. g. the data by Baston et al., 1997b; Appendix A). Clearly, however, there is a significant difference between K_d values obtained under reducing conditions and oxidizing conditions, with the latter generally being lower by at least one order of magnitude. As pointed out above, this reflects the difference in the hydrolysis behavior of U(IV) and U(VI). Sorption on plutonic rocks and tuff appears to be higher than on basalt.

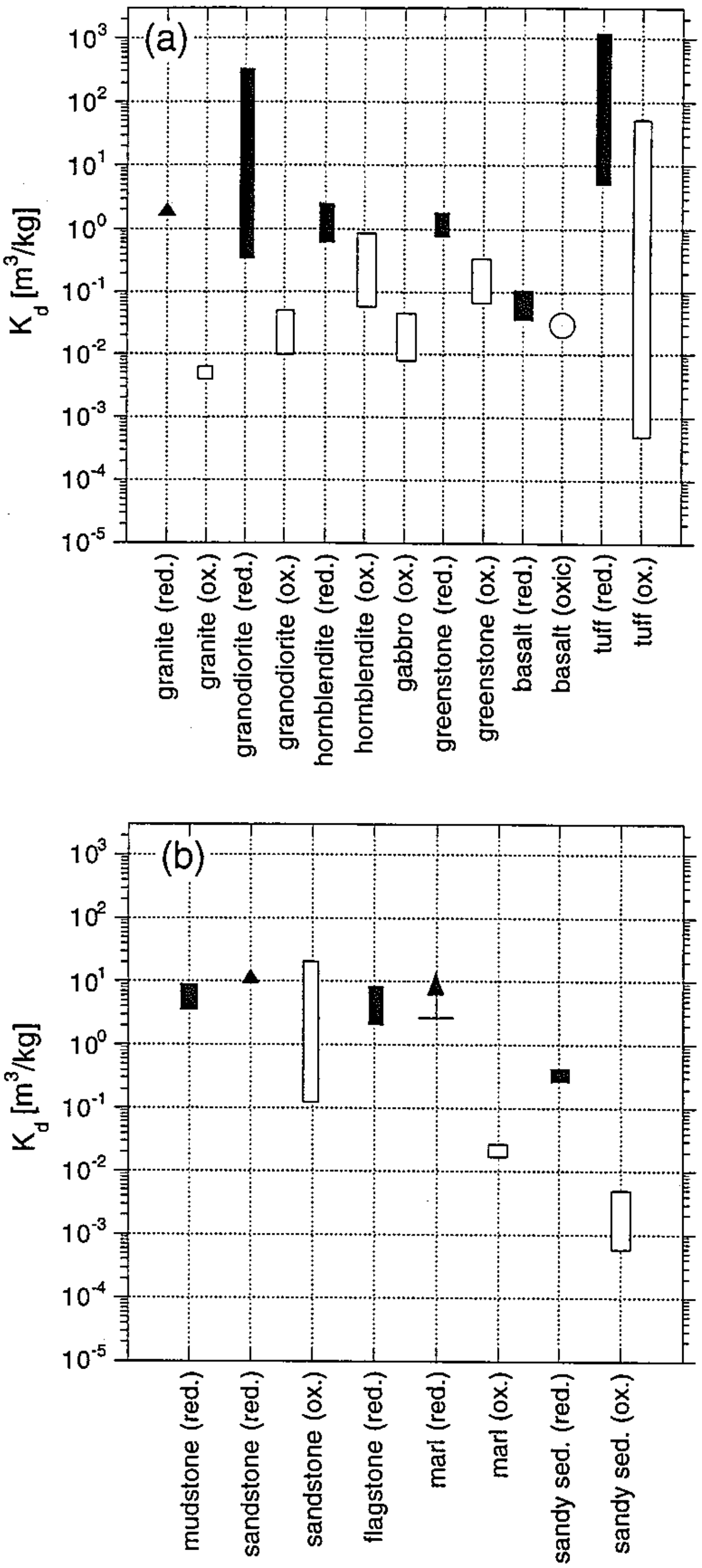

Figure 3.5: Overview of distribution coefficients for U on (a) plutonic and volcanic rocks, and (b) on sedimentary rocks. Bars in the figure represent ranges of data, circles and triangles represent single values. Closed symbols refer to reducing, open symbols refer to oxidizing conditions. K_d values are listed in Appendix A.2, Table 3.

Diffusion coefficients for silicic (Rapakivi granite) and intermediate (tonalite) plutonic rocks and for sandstone are summarized in Figure 3.6, the corresponding data compilation is provided in Appendix B. No D_a values were found for tuff, basalt, and mudstone; and no D_a values corresponding to strongly reducing conditions were found. D_a values observed by Suksi et al. (1989) in plutonic rocks are 1-2 orders of magnitude lower than the values measured by Berry et al. (1994) in St. Bees sandstone.

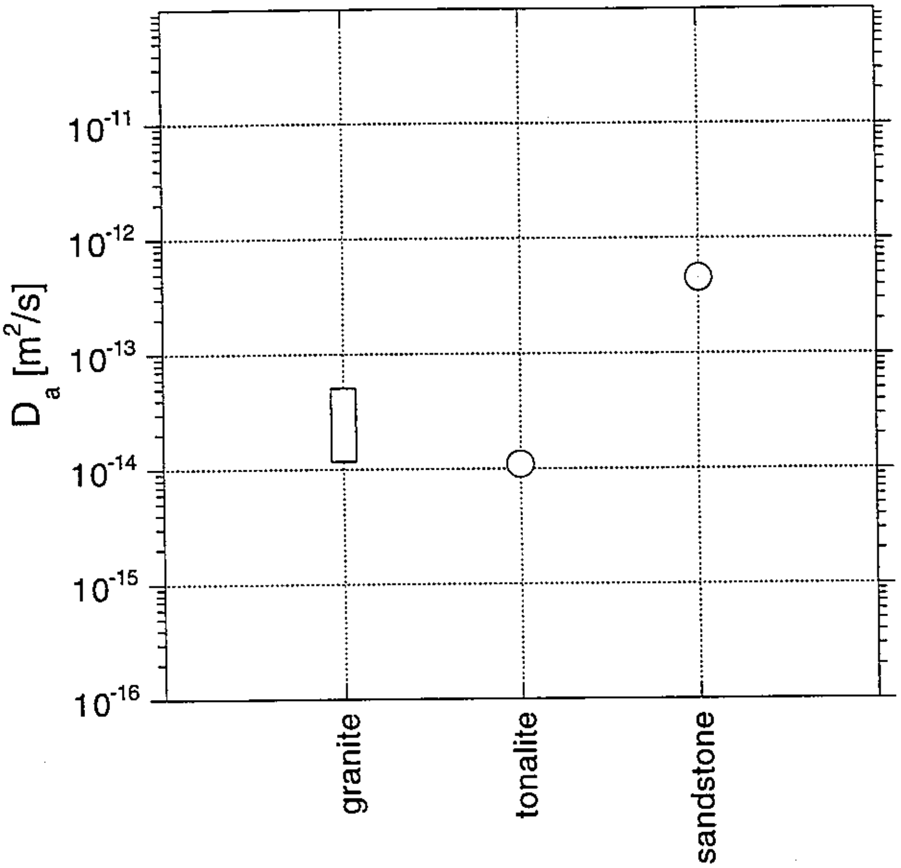

Figure 3.6: Overview of diffusion coefficients for U in rocks. Bars in the figure represent ranges of data, circles represent single values. All data were obtained under mildly (N_2 atmosphere) to strongly (air) oxidizing conditions. D_a values are listed in Appendix B.2: Table 1.

3.2.4 *Neptunium (Np)*

3.2.4.1 *Chemical characteristics*

Like U, Np can take on different oxidation states in aqueous solutions (Katz et al., 1986). Np(III) is more stable than U(III), but is not important, except in acidic solutions under reducing conditions. On the other hand, hexavalent Np (NpO_2^{2+} ion) is more readily reduced to pentavalent Np than U(VI) to U(V), and in contrast to U(V), pentavalent Np (NpO_2^+ ion) does not disproportionate in aqueous solution. Thus, Np(V) and Np(IV) are generally the relevant oxidation states under oxidizing and reducing conditions, respectively. Since the monovalent NpO_2^+ ion hydrolyzes much less readily than the Np^{4+} ion (Baes and Mesmer, 1976), it can be expected that sorption of Np is much stronger under reducing conditions.

3.2.4.2 *Distribution and diffusion coefficients for neptunium*

Figure 3.7 gives an overview of K_d values compiled for neptunium on silicic (granite and granodiorite) and mafic (hornblendite and gabbro) plutonic rocks, greenstone, tuff, basalt, and interbedded sandstone/claystone. Supplementary data for some sediments from the Gorleben site in Germany are also provided. Compiled K_d values are provided in Appendix A.

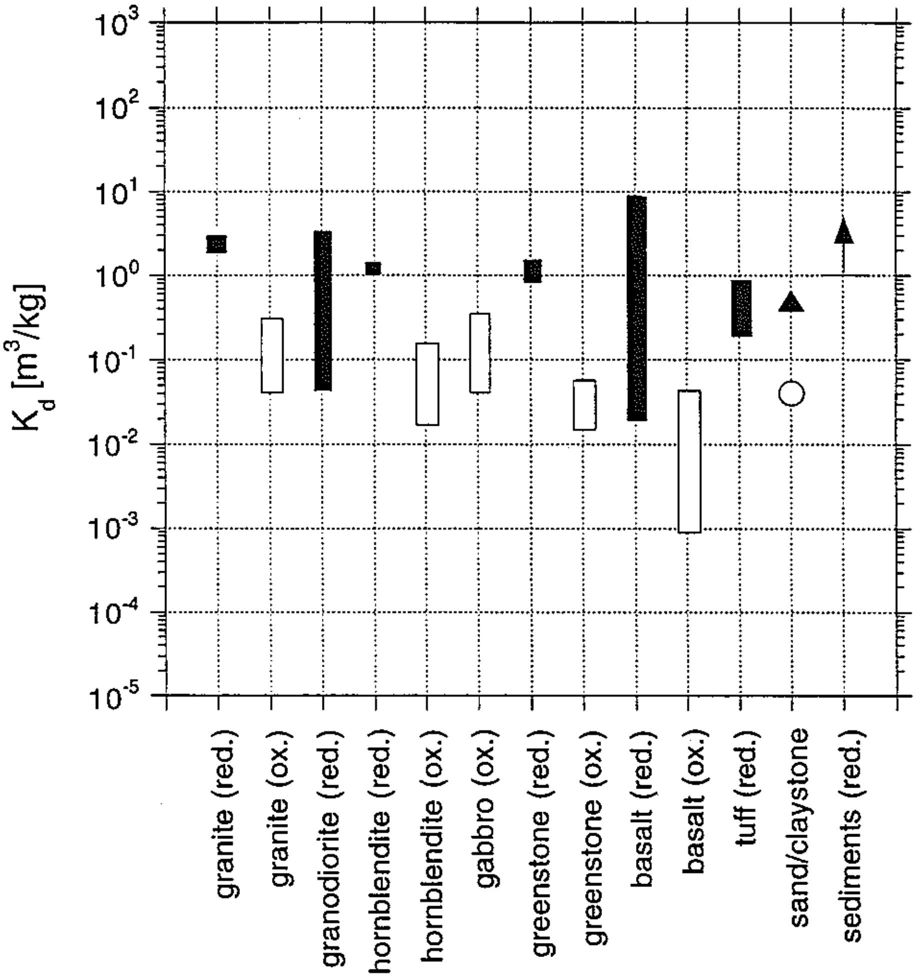

Figure 3.7: Overview of distribution coefficients for Np on different igneous and sedimentary rocks. Bars in the figure represent ranges of data, circles and triangles represent single values, arrows refer to minimum values. Closed symbols refer to reducing, open symbols refer to oxidizing conditions. K_d values are listed in Appendix A.2, Table 4.

The spread of the K_d values compiled for all rock types is not very large, and the compiled data do not point to a drastic difference between the sorptive properties of different rocks. For a given type of rock, there is a clear difference between K_d values obtained under reducing and under non-reducing or oxidizing conditions; in general, K_d values measured under reducing conditions are about one order of magnitude higher. As was already pointed out above, the stronger sorption of Np under reducing conditions reflects the stronger tendency to hydrolyze of Np(IV) in comparison with Np(V). K_d values for Np(IV) are similar to values for Th, but smaller than values for U(IV) (Figure 3.5) and values for Pa obtained under reducing conditions (Figure 3.3).

Diffusion data were found only for different granites and tonalite; and all values were obtained under air or N_2. The apparent diffusivities measured under these conditions lie all within one order of magnitude.

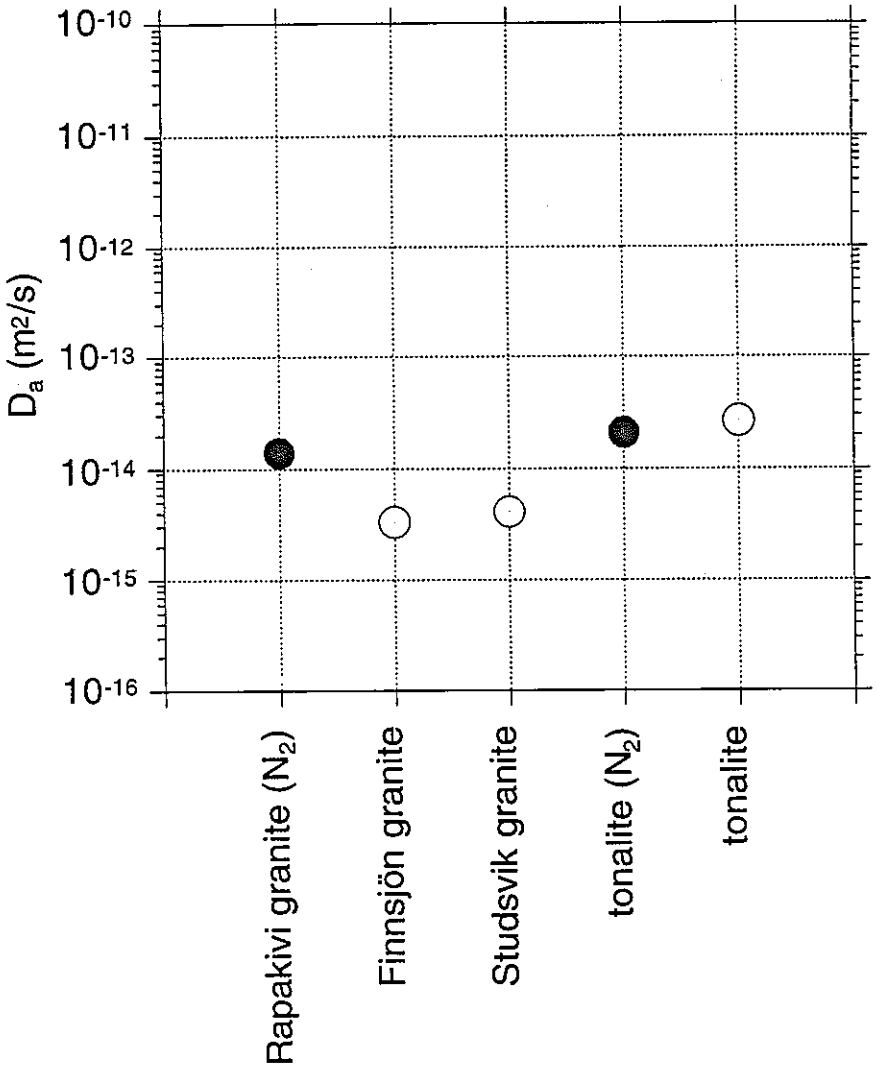

Figure 3.8: Overview of diffusion coefficients for Np on plutonic rocks. Shown are single values obtained under N_2 (shaded symbols) and under air (open symbols). D_a values are listed in Appendix B.2: Table 2.

3.2.5 Plutonium (Pu)

3.2.5.1 Chemical characteristics

The redox potentials for the different Pu-redox couples III/IV, IV/V, and V/VI all lie within a narrow range (Katz et al., 1986). Therefore, Pu species of different oxidation states may simultaneously exist in aqueous solution, with Pu(IV) being probably the most important oxidation state. In general, it can be expected that sorption is weakest for Pu(V) and strongest for Pu(III) and Pu(IV), in analogy with the hydrolysis behavior of the different oxidation states.

3.2.5.2 Distribution and diffusion coefficients for plutonium

An overview of K_d values for plutonium on granite and mafic plutonic rocks (hornblendite and gabbro), greenstone, tuff, basalt, as well as sandstone and interbedded sandstone/claystone is given in Figure 3.9. For several rock types, distribution coefficients have been obtained under reducing conditions, and corresponding data obtained under oxidizing conditions are provided for comparison. Sorption data on bentonite as well as a number of other clay minerals are summarized in Figure 3.10. K_d values compiled for Pu on rocks, as well as bentonite and other clays are provided in Appendix A.

From the data summarized in Figure 3.9, no clear difference between the sorptive characteristics of the different rock types becomes evident, except that sorption on basalt is less than on granite and tuff. Also, sorption of Pu appears to be relatively high (in comparison with Th, Np, and U) under both reducing and oxidizing conditions. Possibly, this may be explained with the simultaneous occurrence of different oxidation states of Pu already pointed out in section 3.2.5.1. The data collected for bentonite and other clays (Figure 3.10) generally agree with these findings.

Figure 3.11 gives an overview of diffusion coefficients for silicic (different granites) and intermediate (tonalite) plutonic rocks and for St. Bees sandstone, the compiled data can be found in Appendix B. All measurements had been carried out under oxidizing or slightly oxidizing conditions, and all D_a values are in the range of 1×10^{-14} to 1×10^{-15} m^2/s, corroborating the relatively high K_d values observed on rocks.

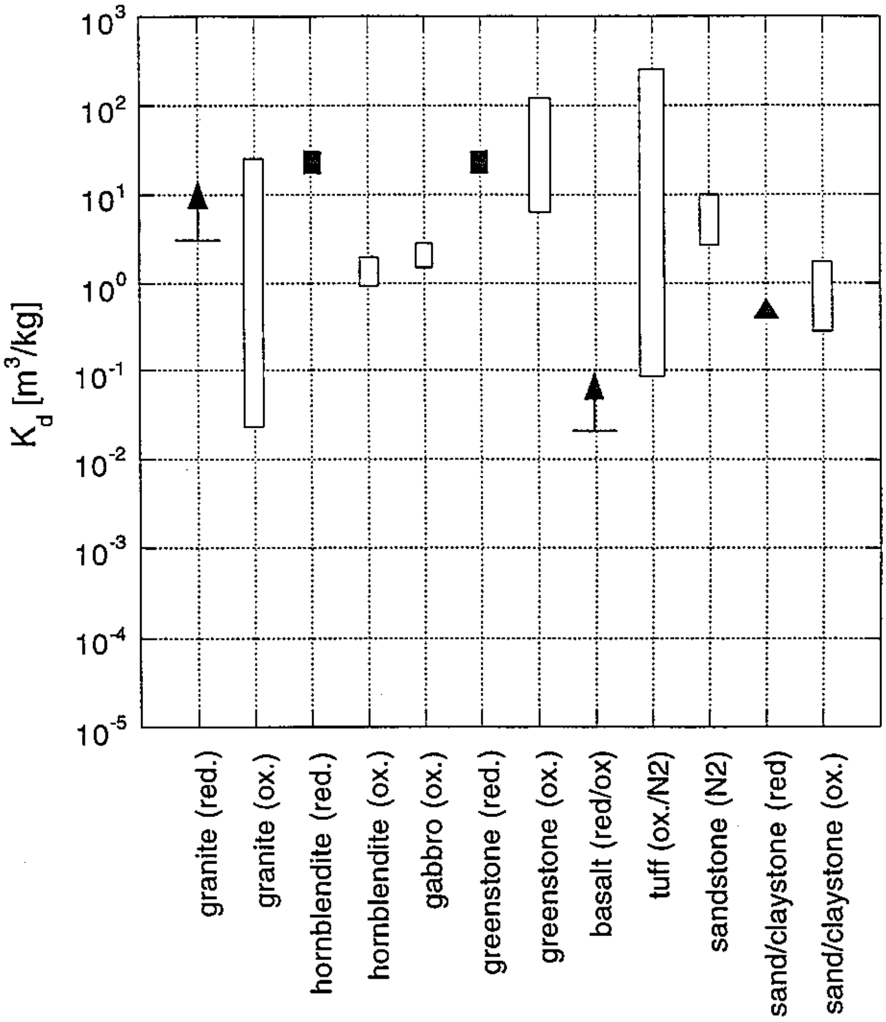

Figure 3.9: Overview of distribution coefficients for Pu on igneous and sedimentary rocks. Bars in the figure represent ranges of data, triangles refer to single values, arrows refer to minimum values. Oxidizing conditions are labeled by open symbols, reducing conditions by black symbols, the gray shading used for basalt refers to both oxidizing and reducing conditions. K_d values are listed in Appendix A.2: Table 5.

D_a values for Pu obtained in Wyoming bentonite MX-80 and Boom clay, as well as different clay/sand mixtures are summarized in Figure 3.12, the respective data compilation is provided in Appendix B. The value obtained by Albinsson et al. (1990) for MX-80 under oxic conditions agrees well with the data for plutonic rocks given in Figure 3.11, the value measured for MX-80 under reducing conditions is about one order of magnitude lower. The D_a value obtained for Boom clay (Henrion et al., 1986) is comparatively high, a possible reason could be complexation of Pu by dissolved organic matter stemming from the clay.

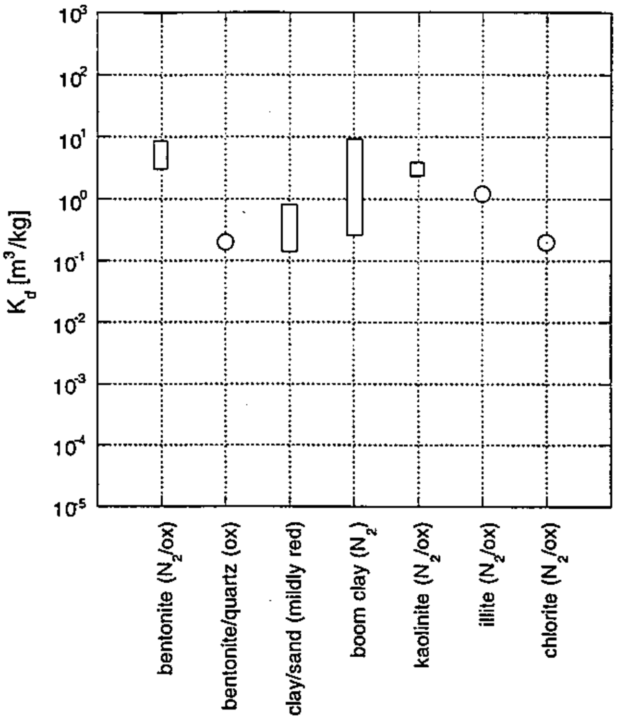

Figure 3.10: Overview of distribution coefficients for Pu on bentonite and clay minerals. Bars in the figure represent ranges of data, circles represent single values. K_d values are listed in Appendix A.2: Table 6.

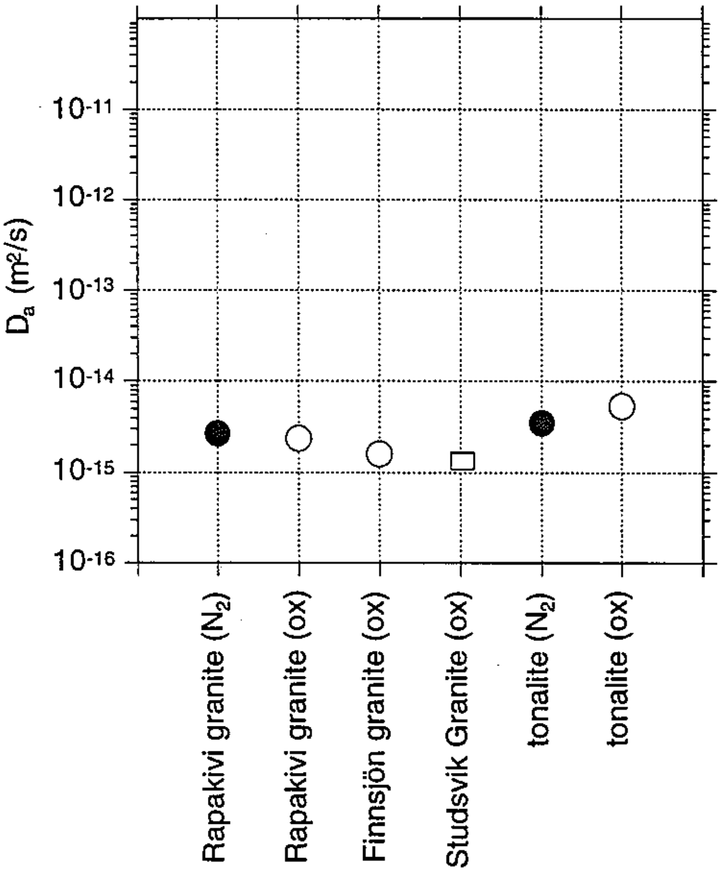

Figure 3.11: Overview of diffusion coefficients for Pu in rocks. For Studsvik granite, a range of data is shown, all other symbols refer to single values. D_a values are listed in Appendix B.2: Table 3.

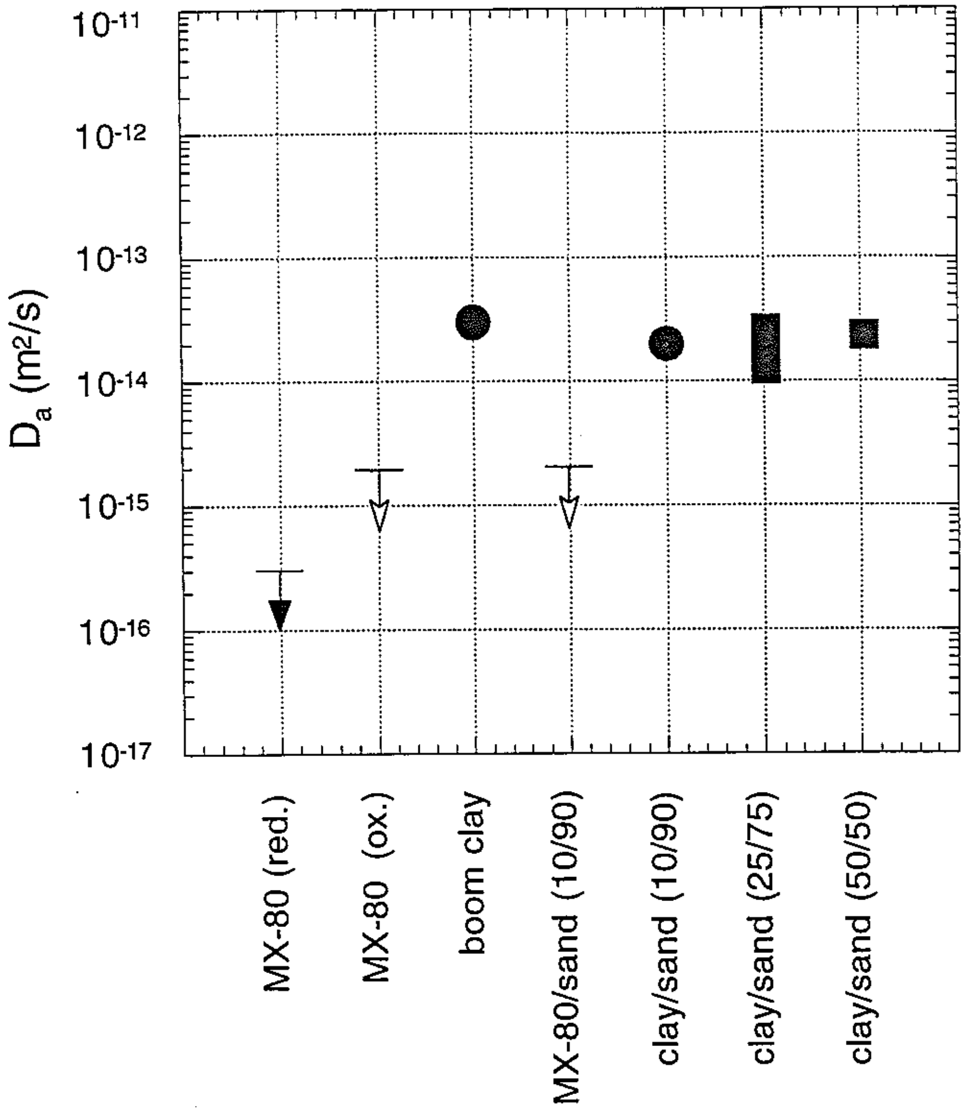

Figure 3.12: Overview of diffusion coefficients for Pu in bentonite and clay/sand mixtures. Bars in the figure represent the spread of data, circles refer to single values, and arrows refer to minimum values. Reducing, mildly reducing, and oxidizing conditions are denominated by black, gray, and open symbols, respectively. D_a values are listed in Appendix B.2: Table 4.

3.2.6 Americium (Am)

3.2.6.1 Chemical characteristics

Am occurs in aqueous solution in the +III state (Silva et al., 1995) and is chemically very similar to other trivalent actinides and lanthanides. The Am^{3+} ion hydrolyzes readily (interaction with CO_3^{2-}, SO_4^{2-}, and F^- is also important), and strong sorption through the formation of surface complexes can thus be expected.

3.2.6.2 Distribution and diffusion coefficients for americium

Figure 3.13 provides an overview of K_d values for Am on granite, tonalite, basalt, tuff, and sandstone. Practically all of the compiled distribution coefficients have been obtained under oxidizing conditions. Since the speciation of Am is not redox-sensitive, these values should also be valid under reducing conditions. The compiled data and supplementary information are provided in Appendix A. A compilation of K_d values for Am on silica and other oxides, clays, and sediments has already been carried out in our FY95 report (Ochs and Wanner, 1996); a summary of these data is provided in Figure 3.14 for convenience.

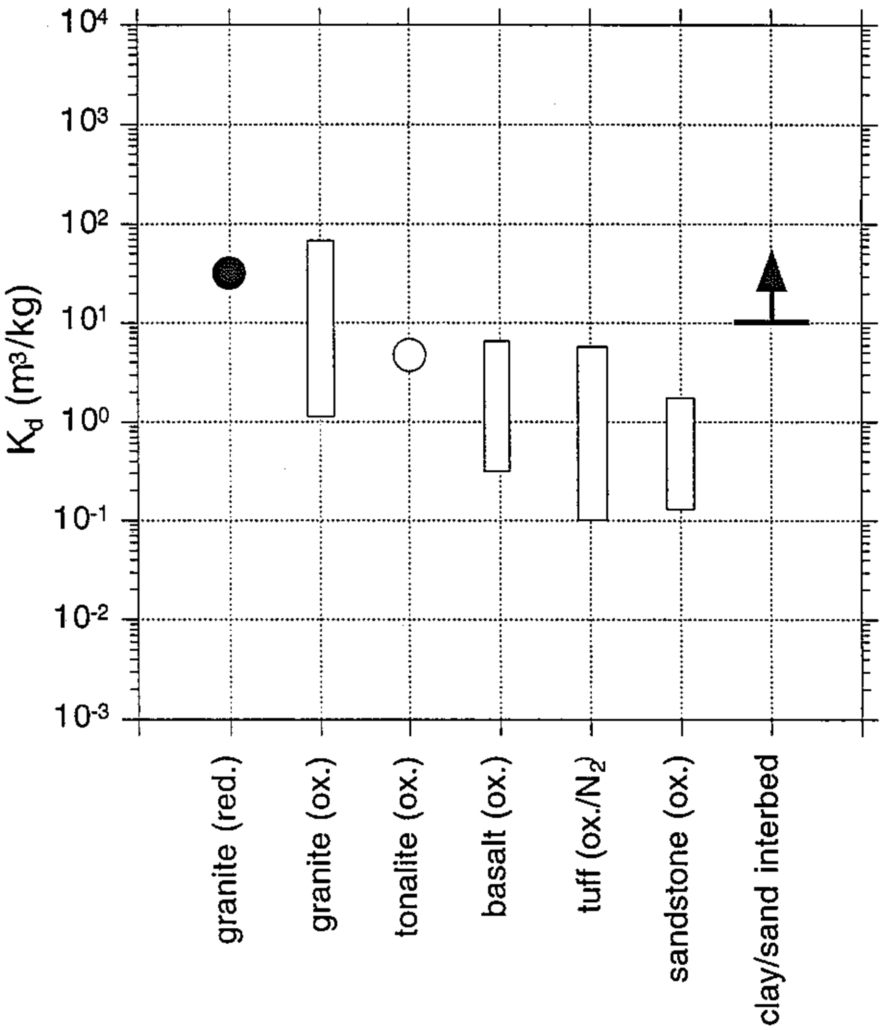

Figure 3.13: Overview of distribution coefficients for Am on igneous and sedimentary rocks. Bars in the figure represent ranges of data, circles and arrows refer to single and minimum values, respectively. Reducing and oxidizing conditions are represented by black and open symbols, gray shading refers to values obtained under both oxidizing and reducing conditions. K_d values are listed in Appendix A.2: Table 7.

K_d values for Am on rocks compare well with values for clays and silica. At pH values >7, K_d values for Am on Kunigel-V1 (Shibutani et al., 1994; Nagasaki et al., 1994) and montmorillonite (Degueldre et al., 1994) range from ≈1 m^3/kg to ≈140 m^3/kg (see Table 8 in Ochs and Wanner, 1996), and K_d values on granite and interbedded sandstone/claystone are of comparable magnitude. On the other hand, the lower K_d values observed for tuff, basalt, and sandstone probably reflect their relatively high content of silica, which is a weaker sorbent than clays and micas.

Diffusion coefficients measured for Am in different granites under oxidizing conditions are summarized in Figure 3.15. No diffusion data were found for other rock types. The apparent diffusivities observed for Am in granites compares well with D_a values obtained in Wyoming bentonite MX-80 compacted to a bulk density of 2000 kg/m^3 (1×10^{-9} - 4×10^{-9} m^2/s; Torstenfelt et al., 1983 and Torstenfelt, 1986) and in MX-80/sand mixtures (1×10^{-8} m^2/s; Albinsson and Engkvist, 1989).

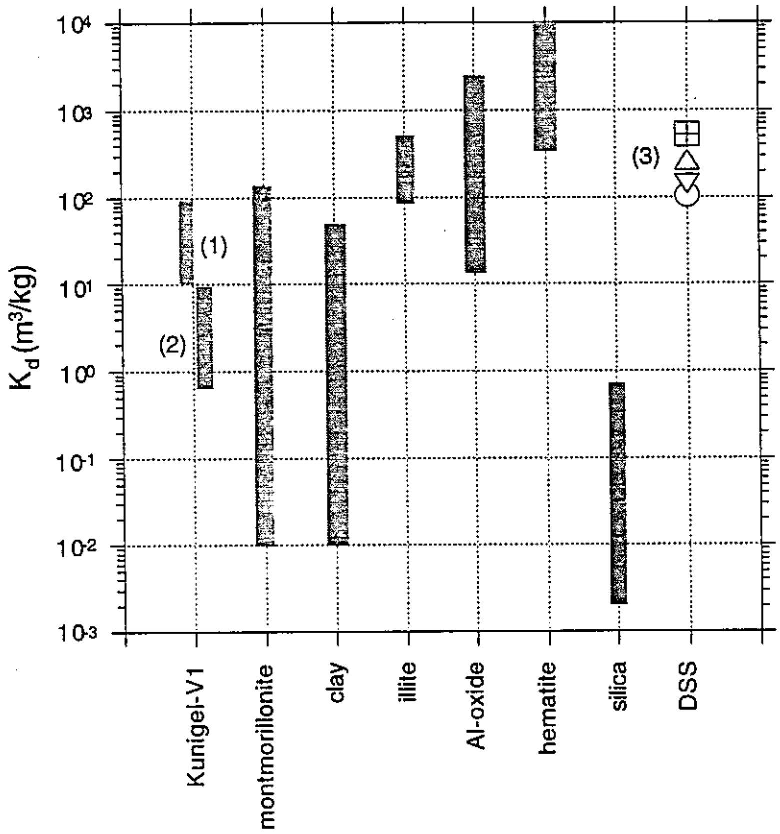

Figure 3.14: Overview of distribution coefficients for Am on clays, oxides, and sediments. Bars in the figure represent a large spread of data, symbols represent average values. No distinction is made between oxidizing and reducing conditions. The figure is taken from Ochs and Wanner (1996), a compilation of K_d values is given in Table 8 of that report. The K_d values for Kunigel-V1 were obtained by (1) Shibutani et al. (1994), and (2) Nagasaki et al. (1994). DSS (open symbols, (3)) refer to deep-sea sediment samples that are rich in oxides, smectite, illite, and calcite (top to bottom).

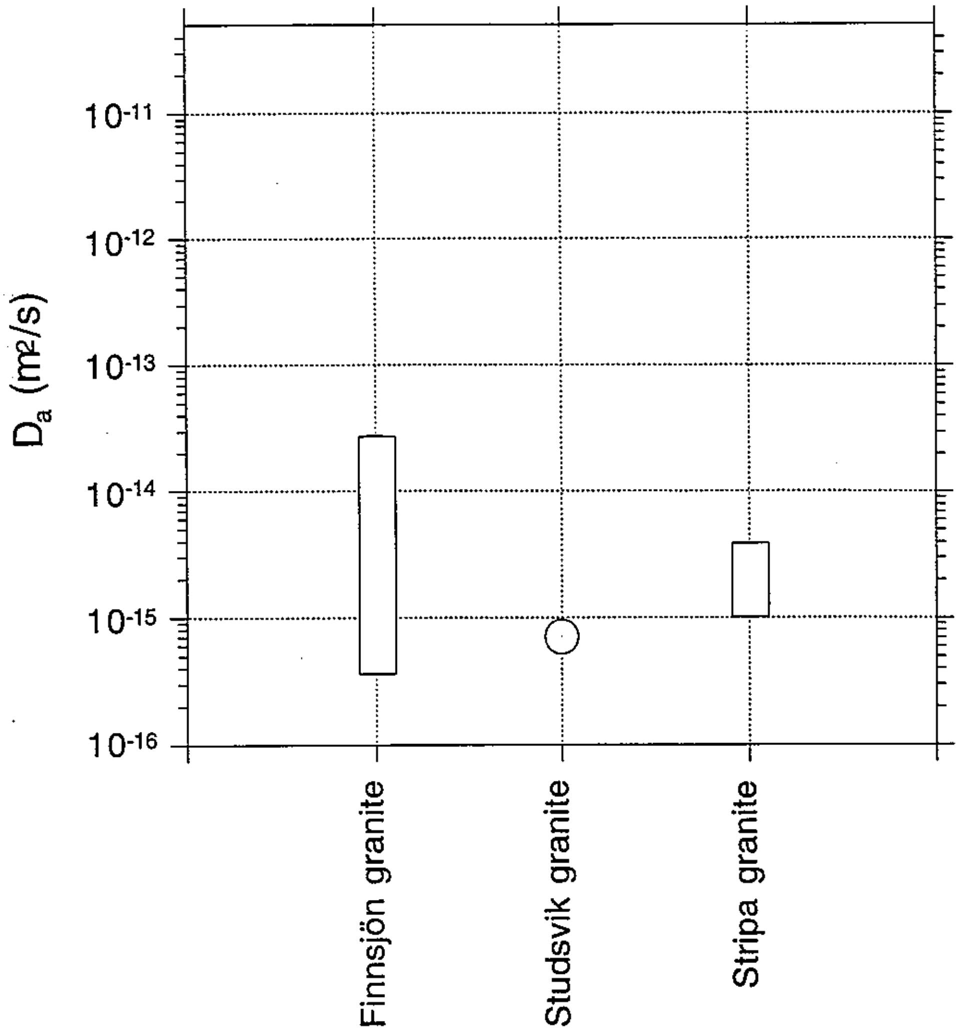

Figure 3.15: Overview of diffusion coefficients for Am in granite. Bars in the figure represent ranges of data, circles represent single values. D_a values are listed in Appendix B.2: Table 5.

3.2.7 Curium (Cm)

3.2.7.1 Chemical characteristics

As with Am, only Cm(III) occurs in aqueous solution. The hydrolysis behavior, as well as the interaction with other ligands, of the Cm^{3+} ion is very similar to that of the Am^{3+} ion, and strong sorption through the formation of surface complexes can also be expected for Cm.

3.2.7.2 Distribution and diffusion coefficients for curium

An overview of K_d values for Cm on granodiorite and tuff is given in Figure 3.16, as well as some supplementary sorption data obtained for sandy sediments from the Gorleben site in Germany. As detailed in the data compilation provided in Appendix A, the values for granodiorite and tuff had been obtained under strongly reducing conditions. No diffusion data for Cm in rocks have been found.

Considering the differences in K_d values caused by different methods of phase separation, the sorption data for Cm are in reasonable agreement with values for Am (Figure 3.15), as well as values for Ac (see section 3.2.8.2). The measurements made by Baston et al. (1997b) seem to indicate that sorption of Cm could be stronger at elevated temperatures (see also the data for Pa and Ac in Appendix A, however).

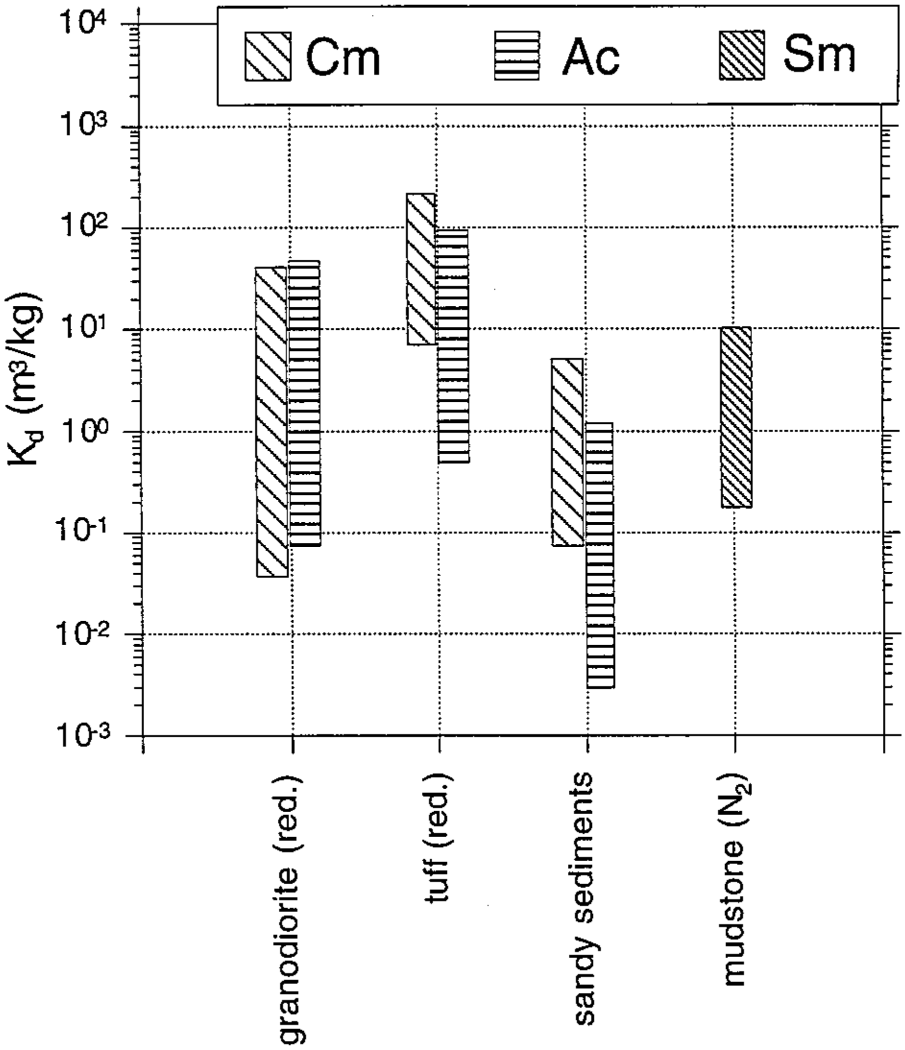

Figure 3.16: Overview of distribution coefficients for Cm, Ac, and Sm on rocks. Bars in the figure represent ranges of data. Where known, redox conditions are indicated with the types of rock. K_d values are listed in Appendix A.2: Tables 8, 9 and 10.

The apparent diffusivity (2×10^{-15} m^2/s) of Cm in compacted MX-80 bentonite (dry density = 2105 kg/m^3) measured by Albinsson et al. (1990) agrees well with D_a values of Am in compacted bentonite. By analogy, similar apparent diffusivities may then be expected for Cm and Am in rocks as well.

3.2.8 *Actinium (Ac)*

3.2.8.1 *Chemical characteristics*

Ac occurs in aqueous solution solely as Ac(III) and exhibits, thus, characteristics similar to rare earth elements and trivalent actinides (Katz, 1986). Its solution speciation and sorption behavior may be described by analogy with Am. Also, sorption and diffusion data for Am (see section 3.2.6, and the previous report by Ochs and Wanner, 1996) may be used for support.

3.2.8.2 *Distribution and diffusion coefficients for actinium*

As for Cm, K_d values for Ac on granodiorite and tuff, and supplementary sorption data for sandy sediments are summarized in Figure 3.16. The data for granodiorite and tuff have been obtained under strongly reducing conditions by Baston et al. (1997b). The respective data compilation is provided in Appendix A. No diffusion data were found for Ac, and it is suggested to rely on analogies with Am.

As already stated above, the sorption data for Ac agree reasonably well with values for Am and Cm. In contrast to Cm, however, the sorption of Ac does not appear to increase with temperature as evidenced by the data of Baston et al. (1997b). This observation is clearly unexpected and points to the lack of knowledge regarding temperature effects.

3.2.9 *Samarium (Sm)*

3.2.9.1 *Chemical characteristics*

Sm occurs in aqueous solution solely as Sm(III) and exhibits, thus, characteristics similar to other rare earth elements and trivalent actinides (Baes and Mesmer, 1976). In the absence of better data, its solution speciation and sorption behavior may be described by using the analogy with Am.

3.2.9.2 *Distribution and diffusion coefficients for samarium*

For Sm, only K_d values on mudstone were found; they are shown in Figure 3.16, the respective data compilation is given in Appendix A. In our FY96 report (Ochs and Lothenbach, 1997), a compilation of K_d values for Sm on silica and other oxides, clays, zeolites, and sediments has already been carried out; for convenience, a summary of these data is provided in Figure 3.17.

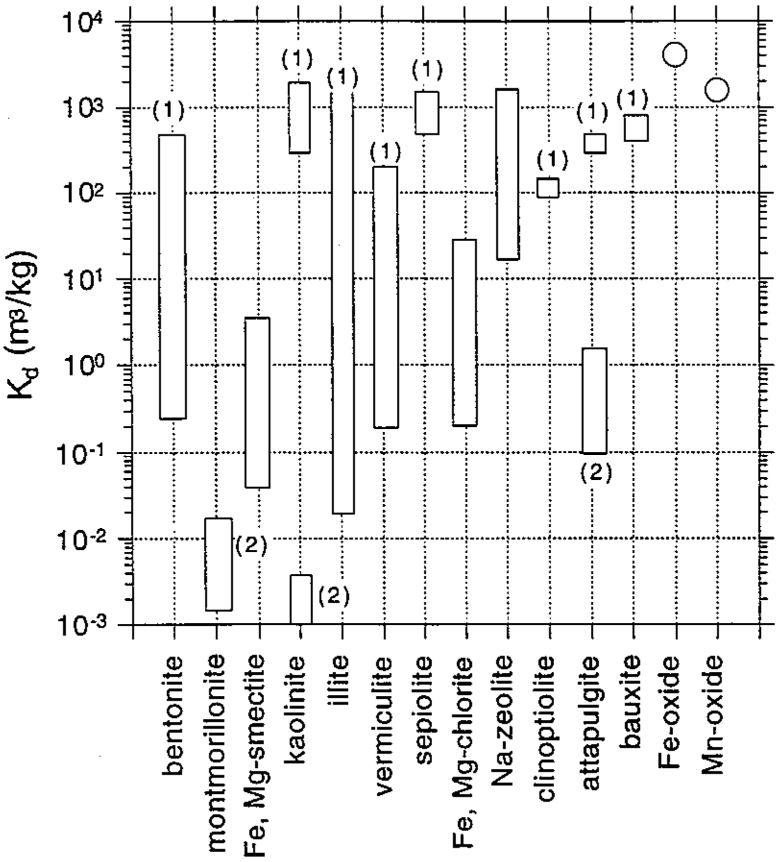

Figure 3.17: Overview of distribution coefficients for Sm on clays, oxides, zeolites, and sediments. Bars in the figure represent a large spread of data. Single K_d values are represented by circles. The figure is adapted from Ochs and Lothenbach (1997), a compilation of K_d values is given in Appendix A2, Table 8 of that report. All values were obtained under ambient or mildly oxidizing (N_2) conditions. The K_d values for the clay minerals and oxides were obtained (1) by Rancon and Rochon (1979) and Rochon et al. (1980), and (2) by Beall et al. (1979) (in Na-acetate buffer).

The K_d values for Sm on mudstone compare well with the values shown for different clays in Figure 3.17 (note that the data reported by Beall et al. (1979) are quite low due to the Na-acetate electrolyte they used). A comparison of Figure 3.17 and Figure 3.14 also shows that K_d values for Sm on a number of different minerals are in reasonable agreement with corresponding data for Am.

No diffusion data were found for Sm, and based on the above observation and the general similarity between trivalent actinides and lanthanides, Am is suggested as an analog.

3.2.10 Radium (Ra)

3.2.10.1 Chemical characteristics

Radium is an alkaline earth element that takes on an oxidation state of +II in practically all its compounds. In aqueous solution, it is expected to occur predominantly as Ra^{2+} aquo-ion with characteristics that are very similar to Sr^{2+}. Both radium and strontium do not easily hydrolyze or form complexes; therefore, they sorb mainly through ion exchange reactions involving the respective M^{2+} ions. Since Ra and Sr are chemically very similar, sorption and diffusion data were also collected for Sr.

3.2.10.2 Distribution and diffusion coefficients for radium and strontium

An overview of compiled distribution coefficients for Ra on granite, basalt, tuff, sandstone and mica-rich sandstone (Caithness flagstones), interbedded sandstone/claystone, and mudstone is given in Figure 3.18. For comparison, K_d values for Sr on tonalite, gneiss, basalt, and siltstone (Eleana argillite) are also given in Appendix A. These data are summarized in Figure 3.20, together with sorption data compiled for bentonites and other clays in our FY95 report (Ochs and Wanner, 1996). A compilation of K_d values for Ra on rock-forming minerals (silica, biotite, muscovite) and different clays has also been carried out in our FY95 report (Ochs and Wanner, 1996); a summary of these data is reproduced for convenience in Figure 3.19.

The K_d values for Ra and Sr on rocks compare reasonably well, although the values for granite by Allard et al. (1978) differ from those found by Hölttä et al. (1997) for altered tonalite and gneiss by about one order of magnitude. The highest uptake of Ra is observed for mudstone, sandstone/claystone and Caithness flagstone; K_d values on these rocks agree well with values for 2:1 clays and the mica minerals biotite and muscovite (Figure 3.19). This shows the importance of ion exchange surfaces for the sorption of Ra and Sr.

D_a values for a number of rocks (granite, sandstone, and mudstone), as well as bentonites and other clays has already been compiled for our FY95 report (Ochs and Wanner, 1996); these data are summarized in Figure 3.21. For the present project, additional data for the diffusion of Ra in mudstone (London clay) and Sr in granite and granodiorite from the Äspö site in Sweden were collected; these data are also shown in Figure 3.21.

Apparent diffusivities for both Ra and Sr in sandstone, mudstone, compacted bentonite, and some granitic rocks are in the range of 10^{-12} to 10^{-10} m^2/s. For some granites, and for the Äspö diorite, however, measured D_a values of Sr are significantly lower ($\approx 5\times10^{-14}$ m^2/s).

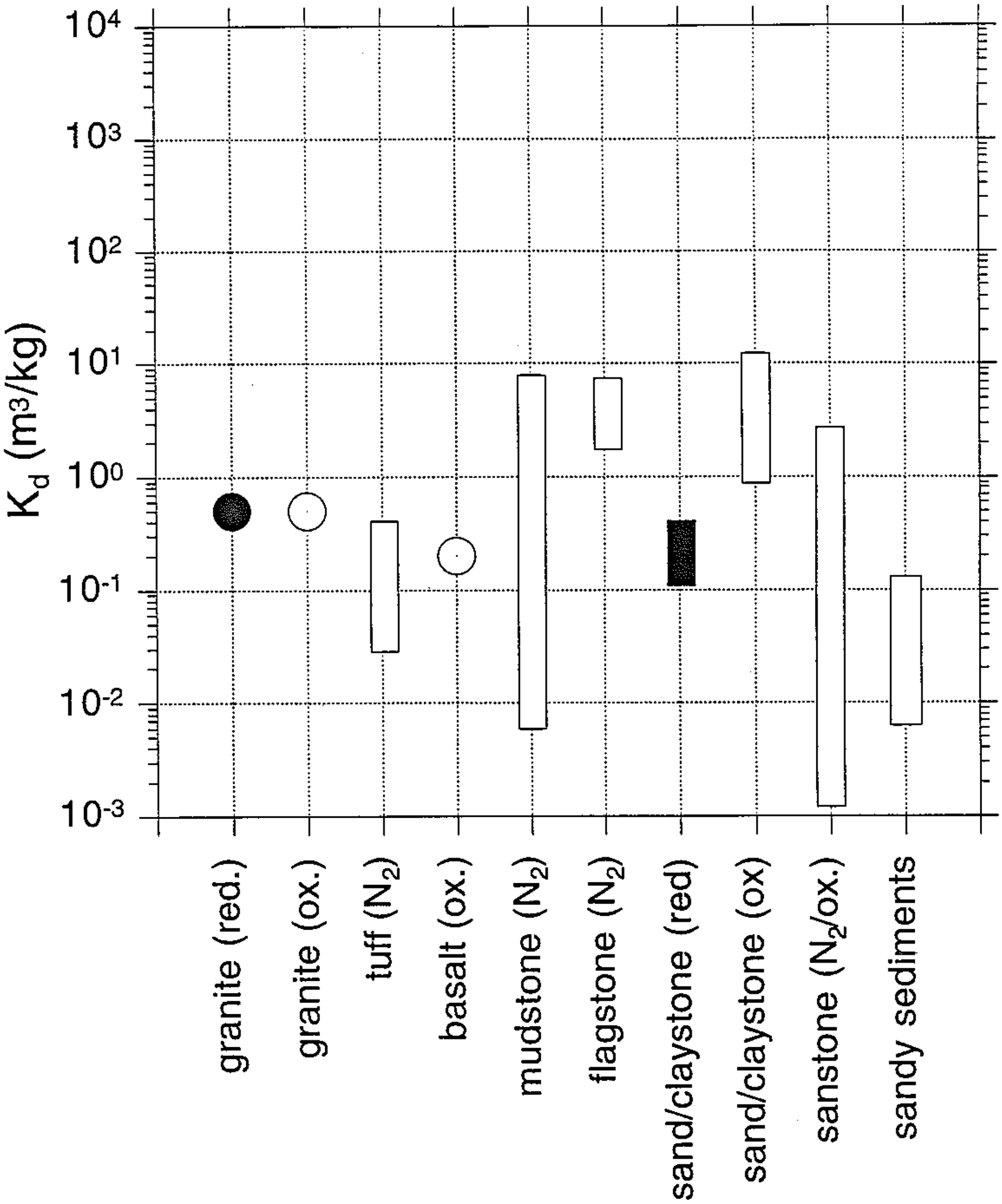

Figure 3.18: Overview of distribution coefficients for Ra on igneous and sedimentary rocks. Bars in the figure represent ranges of data, circles represent single values. Open symbols refer to oxidizing, solid symbols to reducing conditions. K_d values are listed in Appendix A.2: Table 11.

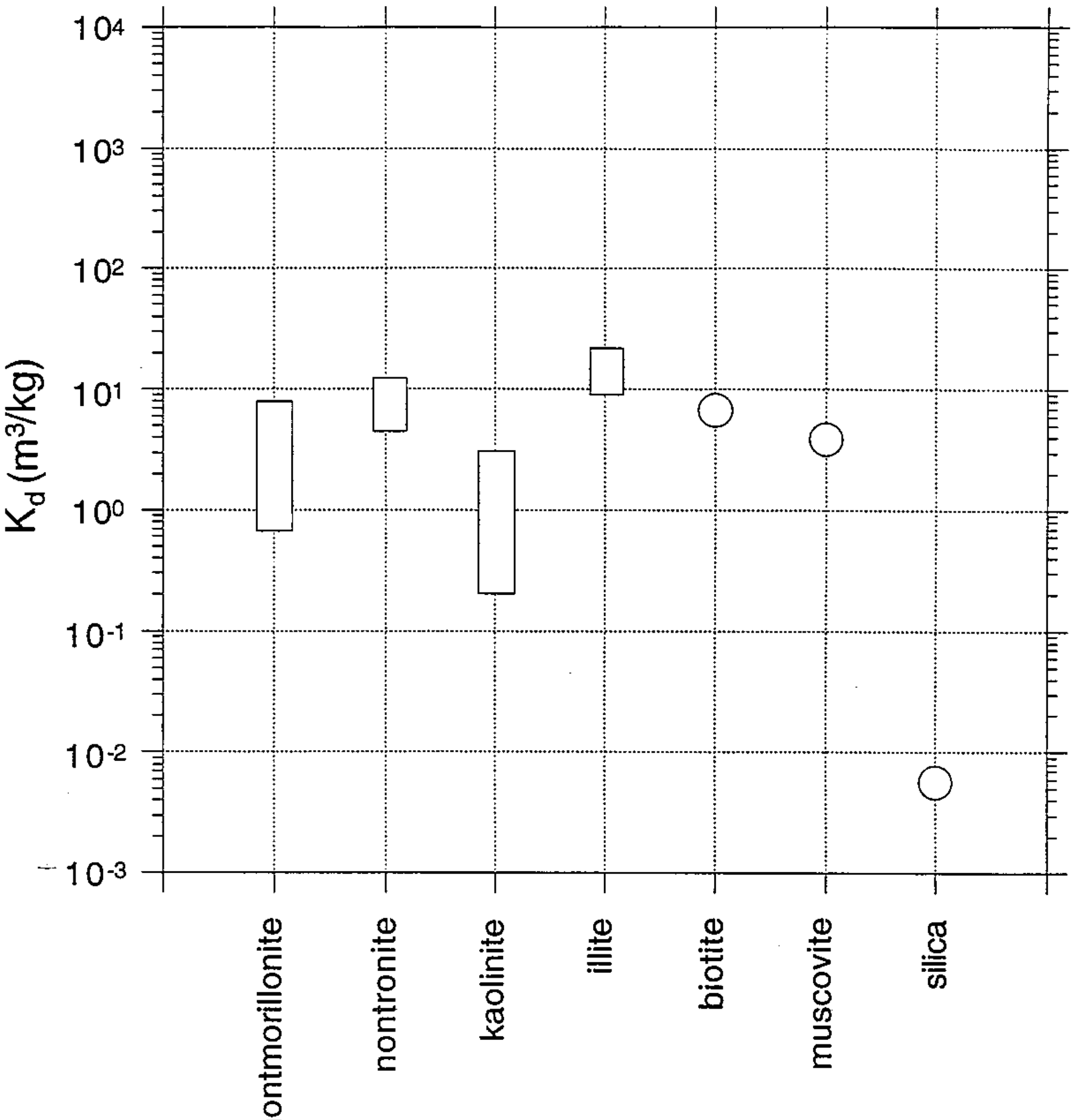

Figure 3.19: Overview of distribution coefficients for Ra on rock-forming minerals and clays. Bars in the figure represent the spread of data, average values are represented by open circles. All data correspond to oxidizing conditions. The figure is modified from Ochs and Wanner (1996), a compilation of K_d values is given in Table 1 of that report.

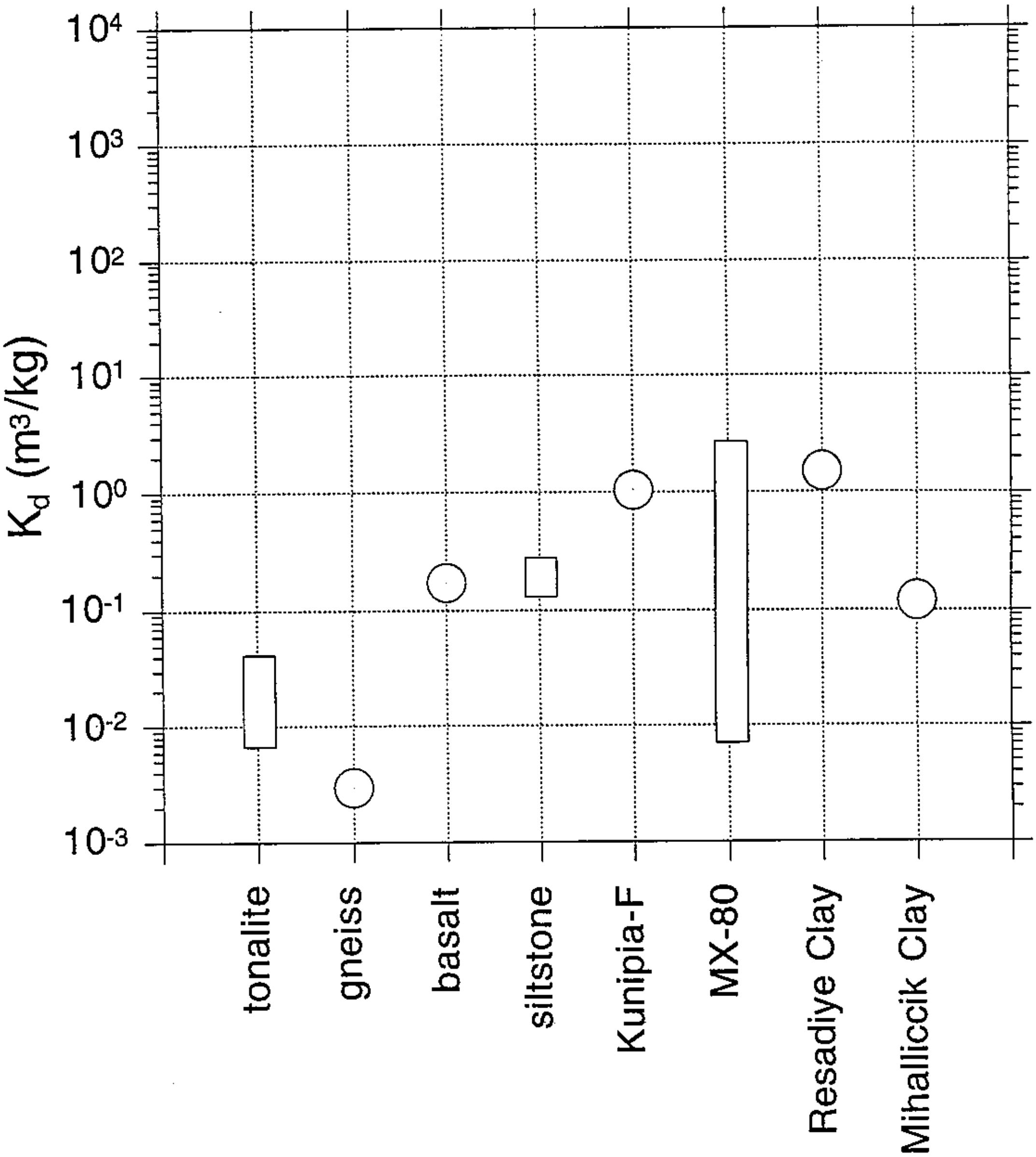

Figure 3.20: Overview of distribution coefficients for Sr on igneous and sedimentary rocks, as well as different bentonites and clays. Ranges of data and single values are represented by bars and circles, respectively. The compilation of K_d values for rocks is given in Appendix A. The data for clays are taken from Table 3 of our FY95 report (Ochs and Wanner, 1996).

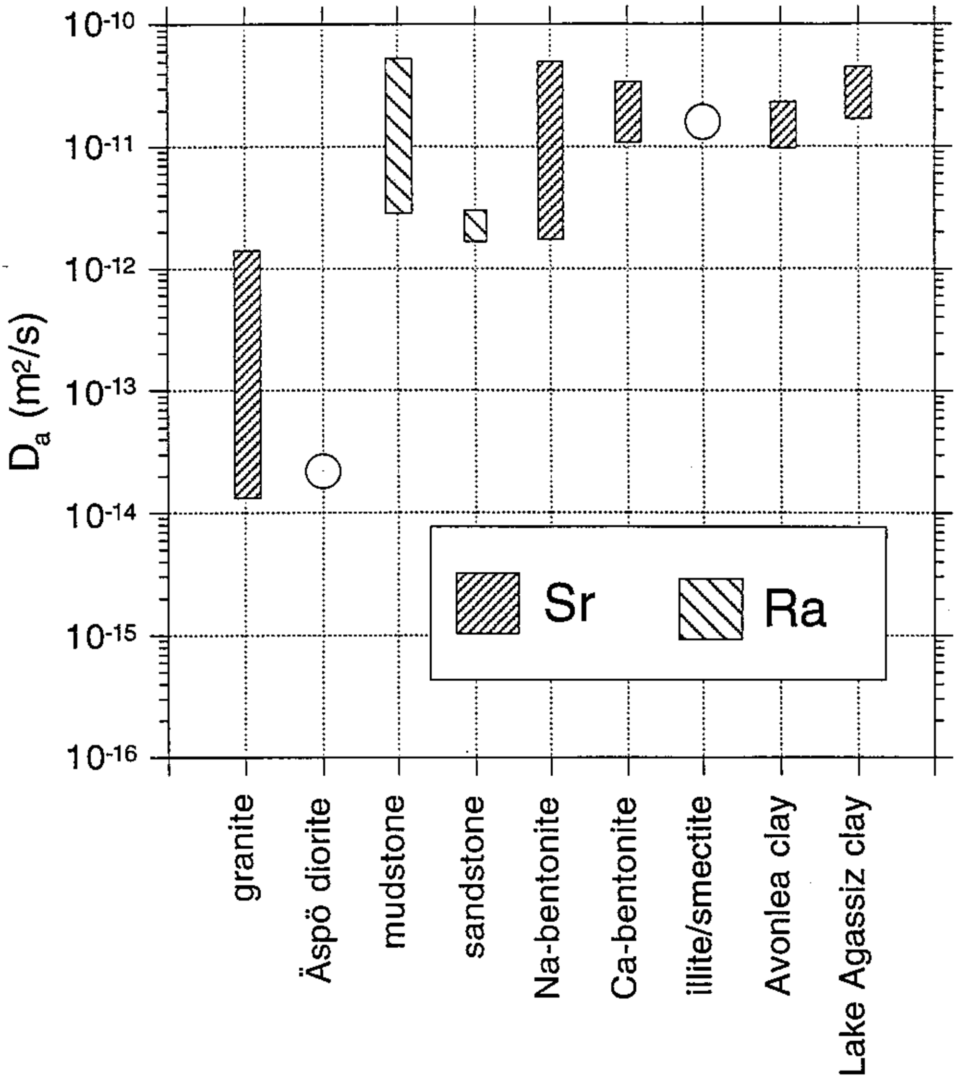

Figure 3.21: Overview of diffusion coefficients for Ra and Sr in igneous and sedimentary rocks, as well as bentonites and other clays. Compilations of D_a values can be found in Appendix B of the present report, and in Table 8 of the FY95 report by Ochs and Wanner (1996).

3.2.11 Zirconium (Zr)

3.2.11.1 Chemical characteristics

Zr occurs in aqueous solution solely as Zr(IV). In this respect, it may be compared to Th, but in contrast to Th, Zr forms a negatively charged hydroxo complex, $Zr(OH)_5^-$; and at pH values above ≈5.5-6 this species controls the solubility of Zr, which increases with increasing pH. Based on zirconium's tendency to hydrolyze, strong sorption through the formation of surface complexes may be expected, particularly at pH values between ≈ 4-8.

3.2.11.2 *Distribution and diffusion coefficients for zirconium*

K_d values for Zr on granite and tonalite are shown in Figure 3.22; no data were found for other rocks. Our FY96 report (Ochs and Lothenbach, 1997) contains a large compilation of K_d values for Zr on sediments and soils, bentonite and other clays, oxides, and a few other minerals. For comparison, these data are summarized in Figure 3.23. No diffusion data for Zr in rocks have been found.

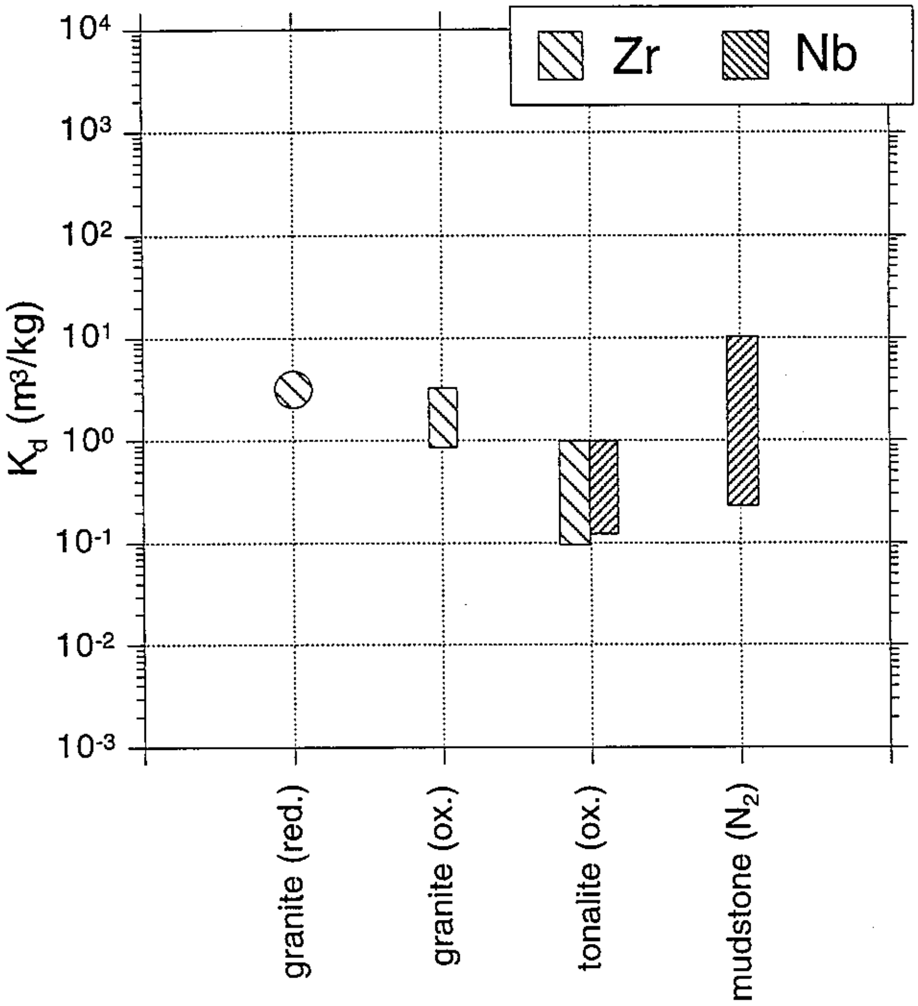

Figure 3.22: Overview of distribution coefficients for Zr and Nb on rocks. Bars in the figure represent ranges of data, circles represent single values. Redox conditions are indicated together with rock types. K_d values are listed in Appendix A.2: Tables 13 and 14.

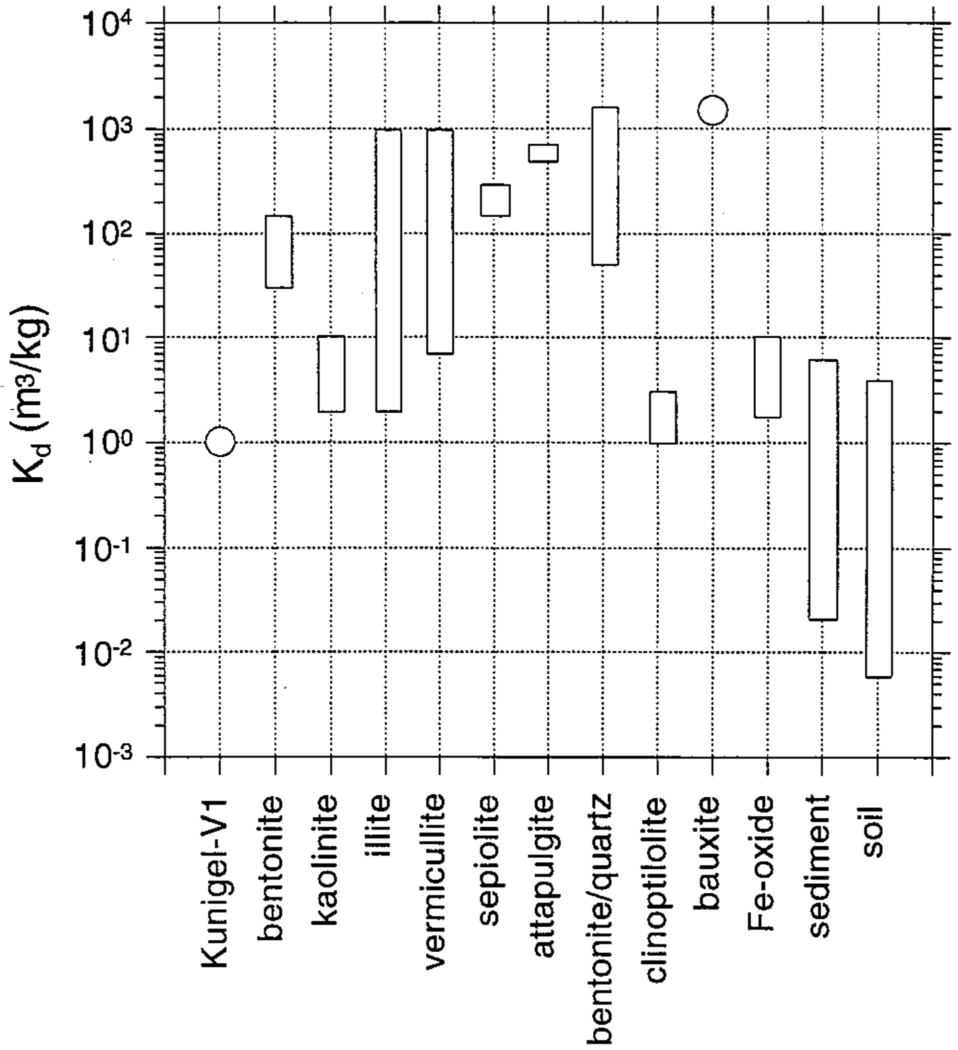

Figure 3.23: Overview of distribution coefficients for Zr on clays and other minerals. Bars in the figure represent a ranges of data. Single K_d values are represented by circles. All data correspond to oxidizing conditions. This figure is modified from the report of Ochs and Lothenbach (1997), the corresponding data compilation is given in Appendix A.2, Table 9, of that report.

3.2.12 Niobium (Nb)

3.2.12.1 Chemical characteristics

The aqueous chemistry of Nb is not well known, but the only important redox state of niobium in aqueous solutions is Nb(V), cf. Baes and Mesmer (1976) and the accompanying report by Lothenbach et al. (1998). Below pH ≈7, the solubility of Nb is very low, but increases above this pH value. Formally, this may be explained by considering two species, $Nb(OH)_5^0$ and $Nb(OH)_6^-$ (sometimes written NbO_3^-); however, it is not clear whether these species exist or whether Nb forms polynuclear species even at very low concentrations.

3.2.12.2 *Distribution and diffusion coefficients for niobium*

K_d values of Nb were found for tonalite and mudstone (Figure 3.22); some supplementary data for bentonite, sediments, sandy/clayey aquifer gravel, and soils have already been compiled for our FY96 report (Ochs and Lothenbach, 1997), they are given in Figure 3.24. These sorption data do not exhibit a very large variation, considering the different sorbents employed.

No diffusion data for Nb in rocks have been found. Some values for sediments are given in Appendix B.2, Table 1, of the previous report by Ochs and Lothenbach (1997).

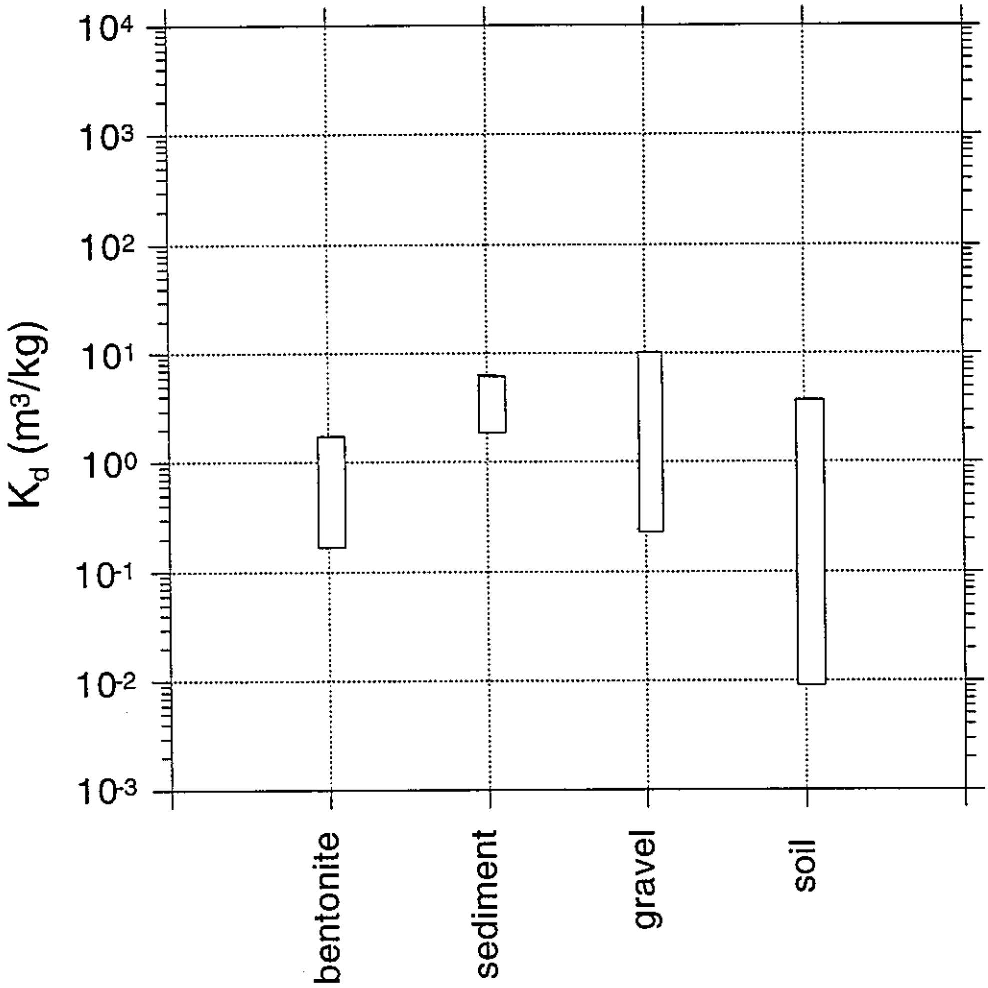

Figure 3.24: Overview of distribution coefficients for Nb on bentonite, soils, and sediments. Bars in the figure represent a ranges of data. All data correspond to oxidizing or mildly oxidizing (air or N_2 atmosphere) conditions. This figure is modified from the report of Ochs and Lothenbach (1997), the corresponding data compilation is given in Appendix A.2, Table 3, of that report.

3.2.13 *Palladium (Pd)*

No sorption or diffusion data relevant for rocks were found.

3.2.14 *Antimony (Sb)*

3.2.14.1 *Chemical characteristics*

In aqueous solution, Sb takes on the oxidation states +III and +V under reducing and oxidizing conditions, respectively (cf. Baes and Mesmer, 1976; and the section on Sb in the accompanying report by Lothenbach et al., 1998). The trivalent Sb^{3+} cation exists only in concentrated acids; in aqueous solutions, this ion is hydrolyzed and the uncharged $Sb(OH)_3^0$ is the dominant species between pH ≈ 2-11. Except in acids, Sb(V) exists as antimonic acid, $H[Sb(OH)_6]$ (or $Sb(OH)_5$), which is a weak acid and deprotonates at pH ≈ 3. At concentrations > 0.001 M, different polynuclear species are formed. Based on the hydrolysis behavior of the two oxidation states, significantly stronger sorption can be expected for Sb(III).

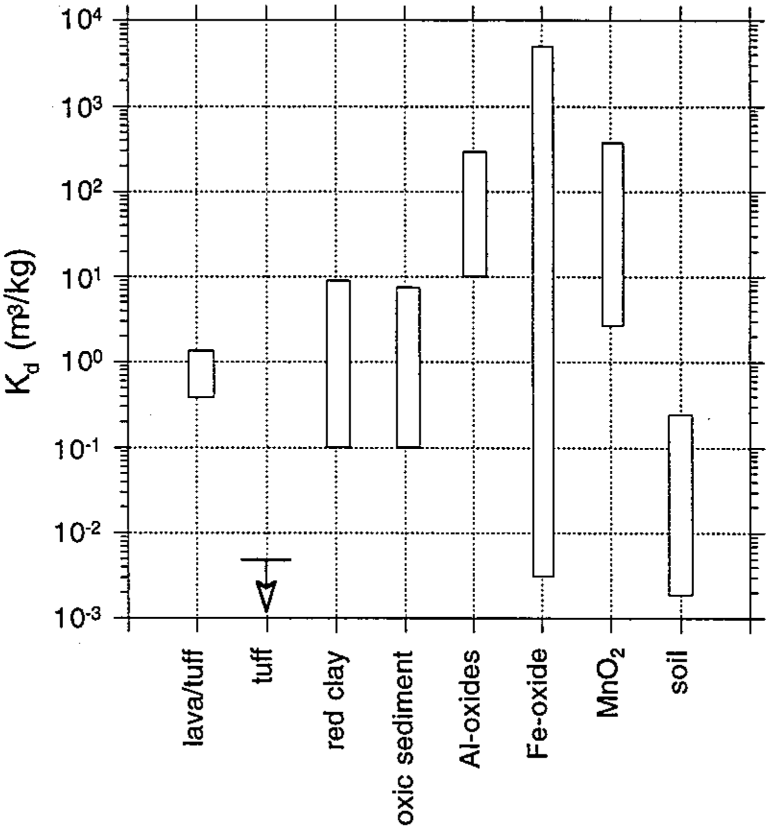

Figure 3.25: Overview of distribution coefficients for Sb. Bars in the figure represent ranges of data. Modified from the report of Ochs and Lothenbach (1997), the corresponding data compilation is given in Appendix A.2, Table 7, of that report. In most cases, redox conditions were not well documented, but all data probably correspond to oxidizing conditions, with the possible exception of data for Fe-oxides.

3.2.14.2 Distribution and diffusion coefficients for antimony

In our FY96 report (Ochs and Lothenbach, 1997), K_d values of Sb were found for tuff and colloids from a tuff/lava aquifer that consist mostly of feldspars and quartz; these values were obtained under oxidizing conditions (Figure 3.25). No data for other rocks or for reducing conditions were found. A number of sorption data for Sb have been compiled for oxides, sediments, and soils in our FY96 report (Ochs and Lothenbach, 1997) and are also given in Figure 3.25. The large K_d values measured for Fe-oxides by Bagby and West (1993) probably correspond to Sb(III) which was used for the preparation of stock solutions, although their experiments were probably carried out under ambient conditions. No diffusion data were found.

3.2.15 Lead (Pb)

3.2.15.1 Chemical characteristics

Lead occurs only as Pb(II) in aqueous solutions, except under extremely oxidizing conditions. In addition to hydrolysis, Pb forms complexes with a number of inorganic and organic ligands. The Pb^{2+} ion starts to hydrolyze at pH ≈ 6, forming 1:1, 1:2, and 1:3 hydroxo complexes with increasing pH. At higher concentrations, polynuclear species are also formed (cf. Baes and Mesmer, 1976; and the accompanying report by Lothenbach et al., 1998). As indicated by its hydrolysis characteristics, Pb may sorb via ion exchange involving the Pb^{2+} ion in the neutral to acidic pH-range, as well as through surface complexation at pH-values above ≈6 (Lothenbach et al., 1997). A thermodynamic model for the sorption of Pb on clays and bentonite that is based on both ion exchange and surface complexation has been presented earlier (Ochs and Lothenbach, 1997; Ochs et al., 1998).

3.2.15.2 Distribution and diffusion coefficients for lead

For Pb, no sorption or diffusion data for rocks were found. A very large number of sorption data could be retrieved for our FY96 report (Ochs and Lothenbach, 1997), they are summarized in Figure 3.26 for convenience. Some new sorption data for glacial sediments were found (see Appendix A), which are included in this figure.

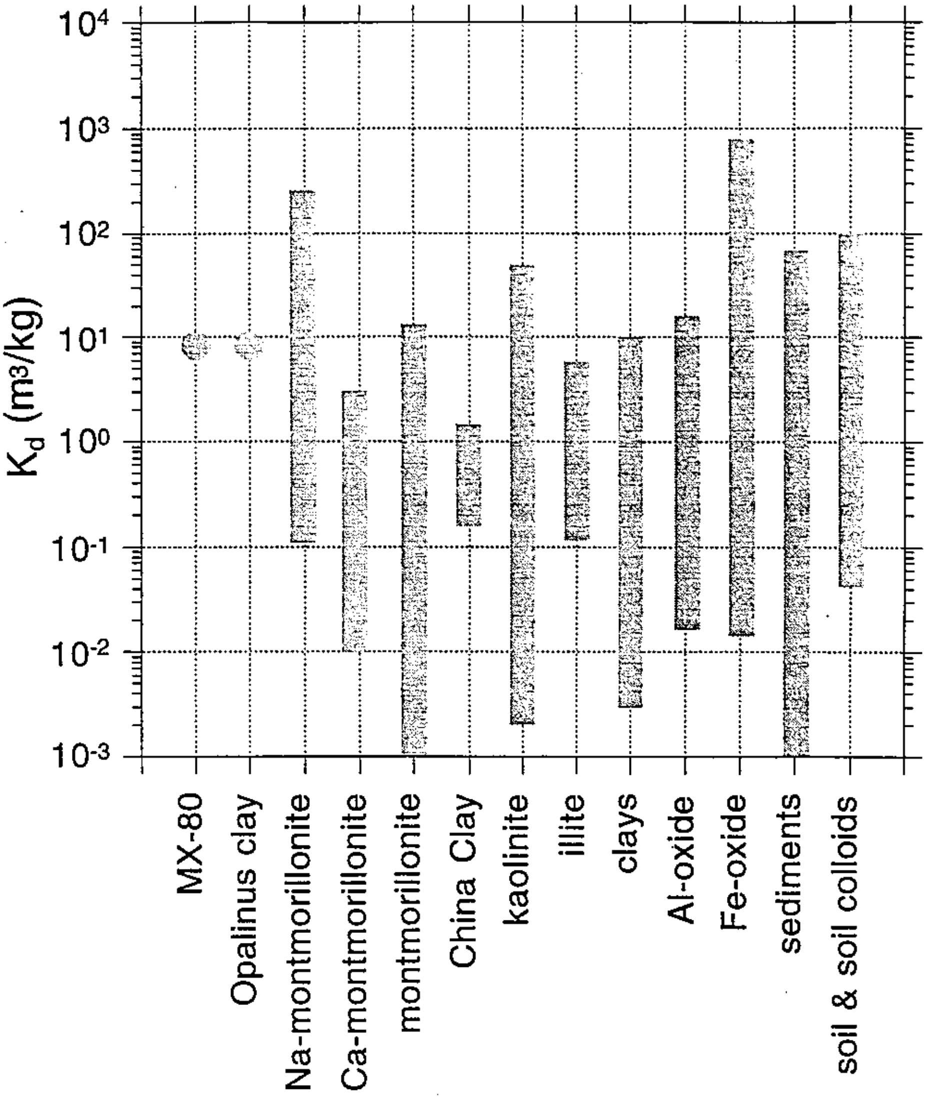

Figure 3.26: Overview of distribution coefficients for Pb on clays, oxides, and sediments. Bars in the figure represent ranges of data. Single K_d values are represented by circles. This figure is modified from the report of Ochs and Lothenbach (1997), the corresponding data compilation is given in Appendix A.2, Table 5, of that report.

3.2.16 Bismuth (Bi)

3.2.16.1 Chemical characteristics

In aqueous solutions, bismuth occurs as Bi(III). Under relevant conditions, Bi exists mainly as $Bi(OH)_3^0$ (neutral to basic pH) or polynuclear, positively charged hydroxo complex (acid to neutral pH); cf. Baes and Mesmer, 1976, and the accompanying report by Lothenbach et al. (1998). Accordingly, strong sorption through surface complex formation can be expected.

3.2.16.2 Distribution and diffusion coefficients for bismuth

No new sorption or diffusion data were found. As detailed in Appendix A.2, Table 2, of Ochs and Lothenbach, 1997, K_d values of 12.6 m^3/kg to 1000 m^3/kg were observed on different clays and colloids at pH 6 to ≈8 (Santschi et al., 1984; Ulrich and Degueldre, 1993; Smith and Degueldre, 1993).

3.2.17 Polonium (Po)

3.2.17.1 Chemical characteristics

Depending on the pH, Po may possibly exist in the divalent and tetravalent state under oxidizing to mildly reducing conditions, although Po(IV) would presumably be more important in the neutral-to-alkaline pH range. Under strongly reducing conditions, Po(0) may be important (cf. Brookins, 1988).

3.2.17.2 Distribution and diffusion coefficients for polonium

No new sorption or diffusion data were found. The sorption data by Ulrich and Degueldre (1993) on montmorillonite and Smith and Degueldre (1993) on groundwater colloids show generally a similar picture for Po and Bi, although the K_d values for Po on montmorillonite are definitely lower than the values for Bi at pH 6 - 7 (cf. Ochs and Lothenbach, 1997, Appendix A.2, Table 6).

4 References

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