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核種移行に関する基盤データ構築手法の検討
および個別モデルの高度化に関する研究(II)

－研究報告書－

(核燃料サイクル開発機構 業務委託報告書)

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(核燃料サイクル開発機構 業務委託報告書)

辻本 恵一*、三浦 房恵*、諸岡 幸一*、上田 真三*

要 旨

現象理解に基づいた信頼性が高く性能評価と密接に関連したデータベースの整備方策を検討すると共に、地層処分システムの安全評価における核種移行の個別モデルとしてコロイド影響に関する実験、及び評価コードの改良及び開発を行った。

核種移行データベースに関しては、データベースの信頼性向上を図るための基礎データ構築手法を検討した。

コロイドに関する評価コードの改良及び開発では、昨年度改良したコロイドの影響を考慮した核種移行計算コード(COLFRAC-mrl)を基にして、コードのユーザーインターフェイスの開発を行った。また、COLFRAC-mrlによるコロイドの影響を考慮した核種移行解析に基づく被曝線量評価を行い、コロイド-核種の吸着反応を、平衡論及び速度論的に扱った場合の線量への影響を検討した。

コロイドに関する実験では、安全評価上の重要パラメータである核種-コロイドの分配係数に関する標準的測定手法の検討とデータ取得を行った。

本報告書は、三菱マテリアル株式会社が核燃料サイクル開発機構との委託研究契約により実施した研究成果に関するものである。

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処分バリア性能研究グループ

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Studies on Data Base Management for Nuclide Migration and Improvement of
Individual Models (II)

(Document Prepared by Other Organization, Based on the Trust Contract)

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Abstract

Reliable database management methods, which is based on understanding of phenomena, and closely related with performance assessment, were studied as well as researches for individual model improvement like column experiment, and analysis code development for colloids.

For nuclide migration database, the basic data development method was examined in order to improve the credibility of the data stored in the database.

For the analysis and code development for colloid transport, the user interface of the colloid transport analysis code, COLFRAC-mrl code, which was developed in the last year, was developed. The dose analyses based on the nuclide transport analysis with considering colloids are executed by using COLFRAC-mrl code. The effects of chemical equilibrium and kinetics model for nuclide sorption on colloids are evaluated in the analysis.

The standard measurement method was examined and data was obtained by the experiments for distribution coefficient between nuclide and colloids, which is the important parameter for safety performance assessment of high-level radioactive waste.

This Work was performed by Mitsubishi Materials Corporation under contract with Japan Nuclear Cycle Development Institute.

JNC Liaison : Barrier Performance Group, Waste Isolation Research Division, Waste Management and Fuel Cycle Research Center, Tokai Works.

* Mitsubishi Materials Corporation

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-----付-1 (1)

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1. はじめに

サイクル機構は、高レベル放射性廃棄物地層処分の技術的信頼性を示す「第2次取りまとめ」を1999年11月に国に提出した。「第2次取りまとめ」にあたり、サイクル機構は、地層処分システムの安全評価で必要となる核種移行データベース（放射性元素の熱力学データベース：放射性元素の溶解度や化学種を推定するもの、核種のベントナイトおよび岩石に対する収着データベース：放射性元素のベントナイトおよび岩石への収着の度合いを示すもの）を開発・整備した。これら放射性元素の溶解度、化学種や収着の度合いを推定する上で基盤となるデータは、第2次取りまとめでの課題を踏まえ、より現象理解に基づいた信頼性の高いデータベースとして整備してゆく必要がある。また、天然環境において放射性元素がコロイドに収着して移行する可能性があり、地層処分システムの安全評価における核種移行の個別モデルを高度化する上では、放射性元素の化学種や収着の度合いを踏まえた現象理解に基づくコロイド影響も考慮した評価が必要である。

そこで、本件では、国内外における最新の専門家による研究内容の調査を通じて、基盤データ構築手法を検討する。また、収着データベース（JNC-SDB）を用いて、収着係数の信頼度を付与するための手法を改良する。さらに、コロイドに対する核種収着の可逆・不可逆性評価、コロイドの影響を考慮したモデル（コード）に基づく核種移行モデルの高度化を図るためのデータ・コードの整備を行う。最後に、コロイドの影響を考慮したモデル（コード）に基づいて、コロイドの影響を考慮した核種移行解析に基づく被曝線量評価を行う。これらにより、より現象理解に基づいた信頼性の高い核種移行評価を可能にし、地層処分システムの安全評価手法の高度化に資する。

2. 実施項目

- ① 熱力学データベースの利用環境整備
- ② 核種の溶解度設定における固溶体モデルの適用性に関するデータ整備
- ③ JNC-SDBを用いた収着係数の信頼度付与のための手法改良
- ④ COLFRAC-mrlのユーザーインターフェイスの開発
- ⑤ COLFRAC-mrlによるコロイドの影響を考慮した核種移行解析に基づく被曝線量評価
- ⑥ 核種-コロイドの分配係数に関する標準的測定手法の検討とデータ取得

3. 熱力学データベースの利用環境整備

サイクル機構殿では、「第 2 次取りまとめ」にあたり放射性元素の熱力学データベースを開発したが、データは 25°C の条件でのみ適用可能であり、温度依存に関わるデータ（エンタルピー）は、ほとんど整備されていない。しかしながら、想定される処分環境は、25°C よりも高い温度条件であるため、現実的な溶解度設定にあたっては、エンタルピーデータを整備する必要がある。本項では、国際的にデータベース開発が進められている OECD/NEA-TDB プロジェクト等を中心に、最新のデータベースを調査し、エンタルピーデータの整備状況を検討した。また、OECD/NEA で整備されているデータベースを地球化学コード PHREEQE のフォーマットに変換するプログラムの開発状況について調査し、適切なプログラムが存在する場合、プログラムの導入を検討した。

なお本節はスイス BMG 社の協力により実施したものである。そのオリジナルの成果は付録 1 として添付した。

4. 核種の溶解度設定における固溶体モデルの適用性に関するデータ整備

地層処分の性能評価において放射性核種の溶解度は重要な入力パラメータである。放射性核種の溶解度は、多くの場合、単純な組成を有する固相の溶解度により設定されている。しかしながら核種の種類によっては、複雑な組成を有する固溶体を形成するため、単純な組成を有する固相の場合に比べて溶解度が低くなると考えられる。そこで現実的な核種の溶解度設定にあたっては、固溶体モデルの適用性を検討する必要がある。

本項では、評価に関連する様々な種類の固溶体を検討した。様々な種類の固溶体モデルの作成方法を分析して、要求されるデータとの関連を検討した。コフィン石及び Fe-Se-S 系を対象に、放射性核種を含んだ固溶体を形成する可能性、利用可能な鉱物学的及び熱力学的データ、及びデータベースのデータのデータ欠落部を補間する方法、を分析、検討した。

なお本節はスイス BMG 社の協力により実施したものである。そのオリジナルの成果は付録 1 として添付した。

5. JNC-SDB を用いた収着係数の信頼度付与のための手法改良

JNC-SDB に取り込まれている核種のベントナイトおよび岩石に対する収着データは 20,000 件以上に及ぶ。この様な膨大なデータベースには、様々な実験条件・手法で得られ

たデータが含まれており、全てのデータを同一の条件や信頼度で評価することはできない。そのため、個々のデータに対し、データの信頼度を付与し、信頼度に応じた評価を行う必要がある。

昨年度は、収着データの信頼度として、どのような実験条件等を考慮すれば良いか、各パラメータの信頼度レベルをどう考慮すれば良いか等を検討し、個々の収着データに対し信頼度を付与するための予備的なクライテリアを設定した。また、実際に JNC-SDB に取り込まれているデータの一部を用い、クライテリアの適用性も検討し、データの信頼度付与を与える上での課題を抽出した。

今年度は、信頼度の判定に当たり、専門家の判断の必要性を低減して、再現性を改善するようにガイドラインを見直した。ガイドラインを確定した後、JNC-SDB から選定されたデータ（Np/ベントナイト、及び Pu/ベントナイトの収着データ）を用いた適用性試験の結果を比較して、ガイドラインを文書化した。さらに JNC-SDB から選定されたデータの最終的な分類結果を整理した。

なお本節はスイス BMG 社の協力により実施したものである。そのオリジナルの成果は付録 1 として添付した。

6. COLFRAC-mrl のユーザーインターフェイスの開発

昨年度改良したコロイドの影響を考慮した核種移行計算コード COLFRAC-mrl は、亀裂および多孔質媒体の両媒体中での核種移行を解くことが可能であるが、その利用にあたっては、計算機に関する高い専門知識が要求されるため、簡易に利用することが困難である。そこで、COLFRAC-mrl の汎用性を高めるため、COLFRAC-mrl の利用を簡易にするためのユーザーインターフェイスの開発を行う。

以下の項目について、ユーザーインターフェイスの開発を行った。

- ① フラックス境界条件取り入れ
- ② 核種の崩壊（1核種のみ）
- ③ 入出力修正

6.1 COLFRAC-mrl の計算方法

6.1.1 計算方法の概略

COLFRAC-mrl は二次元の亀裂の入った多孔質媒体中でのコロイドによって促進される溶質の移行を解析する目的でオハイオ州立大学 Dr.Ibaraki らによって開発された数値解析コードである (Ibaraki and Sudicky, 1995a, b)。この数値解析コードは、多孔質媒体の間隙の大きさがコロイドよりも小さく、そのためコロイドの移行は亀裂の中のみで起こるということを前提としており、多孔質媒体中でのコロイドの移行は考慮されていなかった。

COLFRAC-mrl は COLFRAC を基にして Dr.Ibaraki により開発された、亀裂中並びに多孔質媒体中での両方においてコロイドの移行を取り扱えるように改良された数値解析コードである。そのため、コロイドによって促進される溶質の移行現象を亀裂中だけでなく多孔質媒体中においても取り扱うことが可能となっている。

以下にコード改良に関連する、COLFRAC-mrl で使われた溶質に関する支配方程式を説明する。COLFRAC では解析手法としてガラーキン法を基にした有限要素法が使われている。COLFRAC-mrl は前述のように COLFRAC を基としており、数値解析手法自体は同じ手法を使っている。数値解析手法は、Ibaraki and Sudicky (1995a) に詳細が記されている。

なお COLFRAC-mrl のユーザーズガイドは付録 2 として巻末に添付した。

6.1.2 コロイドによって促進される溶質移行の支配方程式

亀裂の入った多孔質媒体中におけるコロイドによって促進される溶質移行を表現するためには、(1)溶質移行、(2)亀裂中、多孔質媒体中の地下水流におけるコロイドの移行、(3)コロイド、亀裂壁面、また多孔質媒体への溶質吸着の3つのプロセスが考慮されなければならない。また、溶解した溶質の移行を表現するには、(1)亀裂中、(2)多孔質媒体中の溶質の移動を表す2つの移行方程式が必要となる。

不連続に亀裂の入った多孔質媒体における溶質移行を表すには多孔質媒体ならびに亀裂中のそれぞれにおける移行を表す支配方程式が必要となる。溶質移行においては、その移流、拡散、また亀裂壁面や媒体への収着、さらにコロイドへの収着が起きていることが考えられる。地下水流の流れが遅いため、多孔質媒体への収着においては平衡状態が成り立っていると仮定できる。一方、亀裂壁面とコロイドへの収着は、平衡状態、または速度論が成り立っていると仮定される。

COLFRAC では、コロイドが多孔質媒体の間隙よりも大きいので多孔質媒体中に拡散しないと仮定されていたため、媒体中における溶質移行においてコロイドの影響は考慮されなかった。しかし COLFRAC-mrl では亀裂から多孔質媒体へのコロイドの移行が考慮されている。従って、多孔質媒体中においてもコロイドにより促進される溶質移行を考慮されなければならない。また、溶質のコロイドへの収着は平衡状態にあると仮定する。これらの条件における媒体中での溶質移行をあらわす移流拡散方程式は以下のように表される (Bear, 1972)。

$$\theta R \frac{\partial c_m}{\partial t} + q_i \frac{\partial c_m}{\partial x_i} - \frac{\partial}{\partial x_i} D_{ij} \frac{\partial c_m}{\partial x_j} + \theta R \lambda_d c_m + \frac{\partial}{\partial t} R_{c_m-s_m} = 0, \quad \text{式(6.1.2-1)}$$

θ は媒体の間隙率 [L³L⁻³]、 c_m は多孔質媒体中の溶質濃度 [ML⁻³]、 q_i はダルシーフラックス [LT⁻¹]、 D_{ij} は媒体の拡散係数 [L²/T]、 λ_d は放射性崩壊の係数 [T⁻¹]、 R は遅延係数である。 $R_{c_m-s_m}$ [M/L³] は移動性コロイドまたはフィルターされたコロイドに収着した溶質量と放射性崩壊の溶質濃度を示す。さらに拡散係数 D_{ij} は以下のように表される (Bear, 1972)。

$$\theta D_{ij} = (\alpha_L - \alpha_T) \frac{q_i q_j}{|q|} + \alpha_T |q| \delta_{ij} + \theta \tau D_{aq} \delta_{ij}, \quad \text{式(6.1.2-2)}$$

α_L は媒体における流れ方向の拡散係数 [L]、 α_T は媒体における横断方向の拡散係

数 [L] , δ_{ij} は Kronecker delta である。

Freundlich の収着等温一次式は溶解している溶質と媒体に収着する溶質間の可逆的な平衡状態を表す。遅延係数 R_{im} は分配係数 K_d と次式で関係が表される (Freeze and Cherry, 1979)。

$$R = 1 + \frac{\rho_b}{\theta} K_d \quad \text{式(6.1.2-3)}$$

ρ_b は媒体のかさ密度 [ML⁻³] である。

亀裂においては、溶解している溶質は (1) 移動する地下水中、(2) 亀裂壁面、(3) 亀裂壁面に位置するフィルターされたコロイド中、(4) 地下水における移動性のコロイド中の4種のフェーズに分かれている。従って、溶解している溶質移行とそれぞれのフェーズ間での交換を表す式は以下ようになる (Ibaraki and Sudicky, 1995a)。

$$2b \left[\frac{\partial c_m}{\partial t} + q_f \frac{\partial c_m}{\partial l} - \frac{\partial}{\partial l} D_f \frac{\partial c_m}{\partial l} + \lambda_d c_m + \frac{\partial}{\partial t} R_{c_m-\tilde{c}_n} \right] + 2 \left[\frac{\partial}{\partial t} R_{c_m-\tilde{c}} + \frac{\partial}{\partial t} R_{c_m-\tilde{c}_n} \pm q_{fc} \right] = 0, \quad \text{式(6.1.2-4)}$$

D_f は溶質の拡散係数 [L²/T] , q_{fc} は媒体—亀裂境界面での溶質の移流拡散を表すフラックス [M/L²T] である。

多孔質媒体における地下水流動式と亀裂における地下水流動式が連結されたと同様に、溶質のフラックスと濃度が媒体—亀裂境界面で連続していることから、7.2-5式と7.2-8式を連結することができる。

$R_{c_m-\tilde{c}}$ [ML⁻²] , $R_{c_m-\tilde{c}_n}$ [ML⁻³] , $R_{c_m-\tilde{c}_n}$ [ML⁻³] は、溶液中の溶質と亀裂壁面、移動性コロイド、フィルターされたコロイドとの間に起こる収着によって交換される溶質量をそれぞれ表している(チルダ記号(~)は収着した溶質を示す)。亀裂壁面へ収着した溶質 \tilde{c} [M/L²] は以下のように表される (Ibaraki and Sudicky, 1995a)。

$$2b \left[\frac{1}{b} \frac{\partial \tilde{c}}{\partial t} + \frac{1}{b} \lambda_d \tilde{c} - \frac{1}{b} \frac{\partial}{\partial t} R_{c_m-\tilde{c}} \right] = 0. \quad \text{式(6.1.2-5)}$$

フィルターされたコロイドへの収着した溶質 \tilde{c}_n [M/L³] はコロイドのフィルトレーション速度 λq_n と、フィルターされた移動性のコロイドにおける溶質の濃度 \tilde{c}_n [M/L³] で関係付けられる (Ibaraki and Sudicky, 1995a)。

$$2b \left[\frac{1}{b} \frac{\partial \tilde{c}_n}{\partial t} + \frac{1}{b} \lambda_d \tilde{c}_n - \frac{1}{b} \frac{\partial}{\partial t} R_{c_m - \tilde{c}_n} - \lambda q_n \tilde{c}_n \right] = 0. \quad \text{式(6.1.2-6)}$$

亀裂内の移動性のコロイド濃度は、移流拡散プロセスと亀裂壁面にフィルターされるプロセスに影響される。それゆえコロイドに収着する溶質量も同様の影響を受けることとなる。移動性のコロイドへの溶質の収着と、それらの溶質を収着したコロイドが亀裂壁面へフィルターされる過程を考慮すると、 \tilde{c} に関する物質収支式は以下のように表される (Ibaraki and Sudicky, 1995a)。

$$2b \left[\frac{\partial \tilde{c}_n}{\partial t} + q_n \frac{\partial \tilde{c}_n}{\partial l} - \frac{\partial}{\partial l} D_n \frac{\partial \tilde{c}_n}{\partial l} + \lambda_d \tilde{c}_n - \frac{\partial}{\partial t} R_{c_m - \tilde{c}_n} + \lambda q_n \tilde{c}_n \right] = 0. \quad \text{式(6.1.2-7)}$$

拡散係数 D_f , D_n は一般的に以下のように表される。

$$\begin{aligned} D_f &= \alpha_{Lf} q_f + D_{aq}, \\ D_n &= \alpha_{Lc} q_n + D_{dm}, \end{aligned} \quad \text{式(6.1.2-8)}$$

α_{Lf} は溶質の縦分散長 [L] , α_{Lc} はコロイドの縦分散長 [L] である。

6.2 フラックス境界条件取り入れ

溶質の移行に関する支配方程式を数値計算により解く際、昨年度開発した COLFRAC-mrl の亀裂上流の核種移行計算の境界条件は、第1種境界条件のみ取り入れることが可能である。

一方、本年度研究の被曝線量解析の目的は、コロイドが JNC 第2次取りまとめの性能評価体系に与える影響を評価することである。第2次取りまとめでは、人工バリアから放出される核種はフラックスとして与えられている。そこで、天然バリアの亀裂内の核種移行計算では核種フラックスが第2種境界条件として、与えられ解析が実施されている。

そこで、COLFRAC-mrl の亀裂上流の核種移行計算の境界条件に、第2種境界条件を取り入れることが可能なように、プログラムの修正を行った。

6.3 核種の崩壊（1核種のみ）

昨年度開発した COLFRAC-mrl では、核種移行に放射性崩壊を考慮することができない。

そこで、COLFRAC-mrl を、核種移行で放射性崩壊を取り入れることが可能なように、プログラムの修正を行った。同時にプログラム検証も実施した。

なお、1核種の放射性崩壊を考慮することは可能となったが、複数の核種から構成され

る崩壊連鎖を考慮することはできない事は、昨年度と同じである。

6.4 入出力修正

昨年度開発された COLFRAC-mr1 では、プログラムへの入力ユーザが1個のファイルに全ての入力変数を書き込み、それをプログラムが読み込んで解析を行うように、入力変数の読み込みが処理されていた。

この形式では、必要な入力変数がインプットされていない場合、及び不必要な入力変数をファイルに書き込んだ場合には、ファイルに書かれているデータをすべて確認して、入力エラーを起こす問題点を探して修正することが必要であった。

そこで COLFRAC-mr1 の入力変数の読み込みを、GUI を用いてウィンドウの画面の空欄に1個ずつ入力データを書き込んでいく形式に変更した。

この形式では、必要な入力変数に抜けがある場合には、入力ウィンドウを見るだけで入力に抜けがある変数をすぐ見つけることが可能である。さらに不必要な入力変数を書き込む心配もない。このように GUI を用いたユーザインターフェースを開発することにより、コードの入力変数の書き込み作業が効率化し、又コードの運用が昨年度と比べて非常に簡単、かつ低コストで可能となった。

(1)COLFRAC-mr1 データインプット

COLFRAC-mr1 は2次元の亀裂岩盤中におけるコロイドによって促進される溶質移行をシュミレーションする数値解析プログラムである。そのデータファイルは下図で示されるように 24 個のデータインプットセクション、200 行を越えるアスキー形式のテキストから構成されている。

データファイルを編集するには、ワードパッド等のエディターを使う必要があり、また、入力されたパラメータが、COLFRAC-mr1 の入力フォーマットに正確に従っている必要があるなど制約がある。さらに、①データ編集、②プリプロセッサ (前処理)、③メインプログラムである COLFRAC-mr1、④ポストプロセッサ (後処理)、⑤結果表示のための tecplot (可視化ツール)、の一連の5個のプログラムを、シミュレーションを実施する度に実行する必要がある。これらのデータファイル作成の制約や煩雑さのため、COLFRAC-mr1 を使った事の無いユーザが COLFRAC-mr1 を効率的に使う事が可能となるためには相当のトレーニングが必要である。従って現段階のコードは、すぐに誰もが使い始めることはでき

ない。

数値解析は、吸着速度係数や分散長などの物理、及び化学特性を示すパラメータによって表される各プロセスが溶質移行にどのような影響を与えるかを検証する事が目的である。その目的を達成し易くするために、シミュレーションを実施する際に必要な作業を軽減することが必要であり、効率的かつ円滑な一連の数値解析を行うためのユーザーインターフェースツールが必要である。



図 6.4-1 COLFRAC-mr1 データファイル

(2) グラフィックユーザーインターフェース

現状より効率的な数値解析を行うためのツールとして、グラフィックインターフェースを使用したデータファイル作成ツール **PyFracEd** を開発した。このツールはオブジェクト指向のプログラム言語である **python** で作られており、そのグラフィックライブラリーとして開発されている **wxpython** を使用している。これらの言語、ライブラリーを使う最大のメリットとして、以下が挙げられる。

ウィンドウズ、**Linux**、マッキントッシュ等全てのオペレーションシステム (**OS**) に対応しており、パソコンからサーバーまでソースコードを全く変更することなく使用できるなど、汎用性が高い

COLFRAC-mrl や **Tecplot** などを **PyFracEd** 内で実行することができ、他のアプリケーションとの連携性が高い

データファイルフォーマットの変更などが生じても比較的簡単にプログラムを対応させることが可能であるなど、拡張性が高い

python、**wxpython** とともにフリーソフトウェアであり、特別なソフトウェアを購入することなく使用できる

pyFracEd は図 6.4-2 に示すように 12 のタブと 7 メニューを持つフレームから構成されている。多孔質媒体、亀裂、シミュレーション時間設定等に分類データは、分類毎のタブをクリックして、また、初期条件、境界条件などはメニューを使って指定することができる。

多孔質媒体や亀裂等、幾つかの異なる物理的、化学的特性を持つ区画をドメイン内に持つことができる特性を指定する場合は、区画数を指定すると新しいウィンドウが現れ、各パラメータを新しいウィンドウにより指定する事が可能である (図 6.4-3)。濃度指定の境界条件等も、その有無を指定すると新しいウィンドウが現れ、同様にして特性を指定することができる (図 6.4-4)。

また、ヘルプメニューをクリックすることによってユーザズガイドが表示される (図 6.4-5)。

実行メニューバーから、プリプロセッサ、**COLFRAC-mrl**、ポストプロセッサ、及び **tecplot** (可視化ツール) の外部プログラムが実行できるようになっているため、ユーザ

一は PyFracEd を終了することなく、一連の数値解析を実行することが可能である。



図 6.4-2 PyFracEd メインフレーム

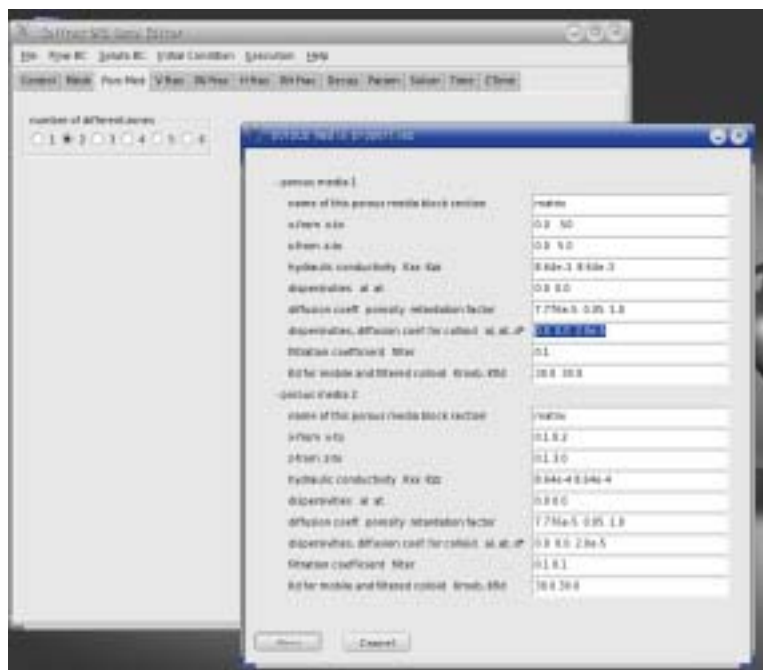


図 6.4-3 多孔質媒体特性指定ウィンドウ



図 6.4-4 初期条件設定ウィンドウ

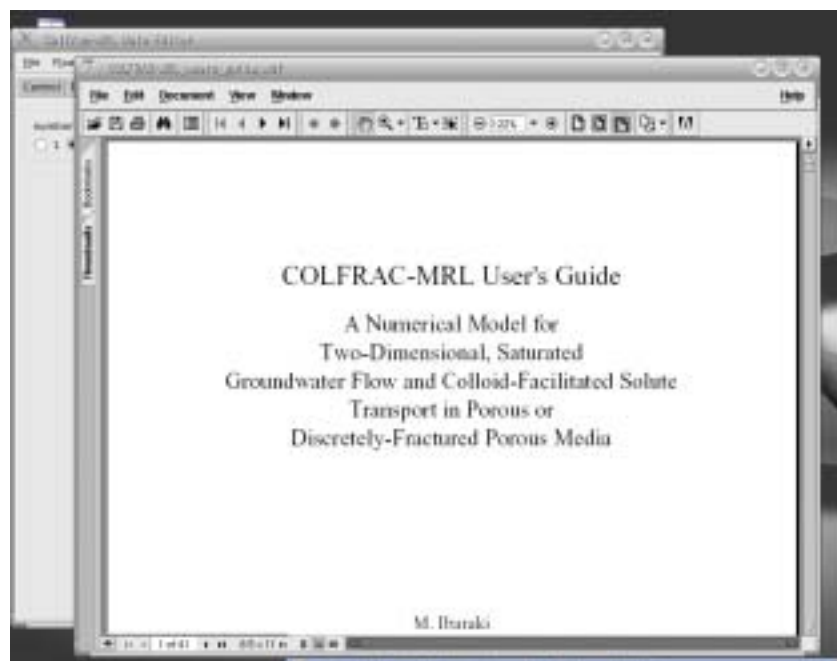


図 6.4-5 ヘルプウィンドウ

7. COLFRAC-mrl によるコロイドの影響を考慮した核種移行解析に基づく被曝線量評価

コロイドの影響を考慮した核種移行評価に関しては、「第 2 次取りまとめ」では、サイクル機構は核種-コロイド-岩盤間の収着反応を平衡論により扱う簡易な解析を実施した。「第 2 次取りまとめ」以降は、評価結果に関する信頼性向上を目的として、核種-コロイド-岩盤間の収着反応について速度論（不可逆的収着反応も含めて）も扱い得るようモデルの高度化を実施してきた。今後、サイクル機構では核種移行に及ぼすコロイドの影響を体系的に取りまとめるにあたり、収着反応を速度論により扱い核種移行評価を行い、「第 2 次取りまとめ」での結果と比較するとともに、コロイド影響の度合いを定量的に言及することが必須であると考えられる。ここでは、核種移行に及ぼすコロイド影響評価に関する体系的取りまとめに資することを目的として、COLFRAC-mrl により核種-コロイド-岩盤間の 3 相間の収着反応速度等をパラメータに核種移行率に関する感度解析を行い、その結果に基づき被曝線量評価を実施した。

7.1 解析ケース

コロイドが JNC 第 2 次取りまとめの性能評価体系に与える影響を評価するため、天然バリアモデルについて、コロイドを取り入れないモデル（コロイド無しケース）、及び、コロイドを取り入れたモデルの両方を考慮に入れて解析を実施した。

また、コロイドを取り入れたモデルに関しては、コロイドへの収着量に関する速度定数をパラメータとして、感度解析を行った。具体的には、コロイドへの収着量に関する順方向速度定数 α 、逆方向速度定数 β に関して、以下のように設定した場合の評価結果を比較した。

- ① コロイド無しケース
- ② 平衡状態にあると考えられるほど速度定数 α 、 β の値を大きく設定（平衡ケース）
- ③ コロイド収着実験結果からヘンリー型吸着等温線を仮定したときに現実的と考えられる速度定数 α 、 β の値を導出して設定（現実的設定ケース）
- ④ 速度定数 β を小さく設定（ β 小ケース）（ α は②と同じ）
- ⑤ 速度定数 α 、 β を共に小さく設定（ α β 小ケース）（ α と β の比は②と同じ）
- ⑥ 速度定数 α 、 β を共に変更（Am-243 核種の α β 変更ケース）（ α と β の比は固定）

- ⑦ コロイド濃度を 1ppm、5ppm、10ppm に設定 (Cs-135 核種の濃度依存性ケース)

7.2 解析条件

第2次取りまとめ中、コロイドの影響を考慮したケースで取り扱われている天然バリア条件を基本として、解析条件を設定した。人工バリアからの核種移行率に関しては、一律に第2次取りまとめコロイドケースの結果を用いた。解析は、母岩と断層についてのみ実施した。母岩及び断層の核種移行解析に用いた具体的な天然バリア条件を表 7.2-1 に示す。

表 7.2-1 天然バリア条件

	名称	設定値
地質環境条件	岩種	花崗岩（酸性結晶質岩）
	地下水	降水系地下水
	動水勾配[-]	0.01
境界条件	入力とした核種移行率	第 2 次取りまとめコロイドケースの人工バリアからの核種フラックス（コロイド濃度 1ppm、核種のコロイドへの分配係数 1000m ³ /kg 相当のコロイド影響を想定）
亀裂パラメータ	移行距離[m]	100（母岩）、800（断層）
	透水量係数[m ² /s]	10 ⁻⁷ （流速：50m/y）～10 ⁻¹³ （流速：0.05m/y）（母岩） 10 ⁻⁷ （流速：50m/y）（断層）
	開口幅[m]	経験則 $2b = 2\sqrt{T}$
核種移行パラメータ	分散長[m]	縦方向分散長 10（=1/10×移行距離）（母岩） 縦方向分散長 80（=1/10×移行距離）（断層）
	マトリクス拡散寄与面積率[%]	50
	マトリクス拡散深さ[m]	0.1
	有効間隙率[%]	2
	乾燥密度[Mg/m ³]	2.64
	実効拡散係数[m ² /s]	3×10 ⁻¹²
	分配係数[m ³ /kg]	1(Np,U,Pu), 5(Am), 0.05(Cs)

7.2.1 モデル

本報告書で利用した計算モデルは、人工バリアからの核種の放出フラックスを入力として、母岩、断層中の核種移行を計算して、断層から放出されるフラックスを線量に変換したものを、最終的な出力としている。計算モデルの概略を図 7.2-1 に示す。母岩に

関しては、第2次とりまとめと同様、透水量係数 $10^{-13} \sim 10^{-7} \text{m}^2/\text{s}$ の対数正規分布（対数平均-9.99、標準偏差 1.07）の 48 分割区間の各中央値についてフラックスの計算を行い、各分割区間の確率を掛けて足し合わせたものを母岩からのフラックスとした。断層に関しては、第2次取りまとめと同様、母岩からのフラックスを用いて透水量係数 $10^{-7} \text{m}^2/\text{s}$ （流速 50m/y）の場合の断層中の移行を解析し、断層出口におけるフラックスを算出した。

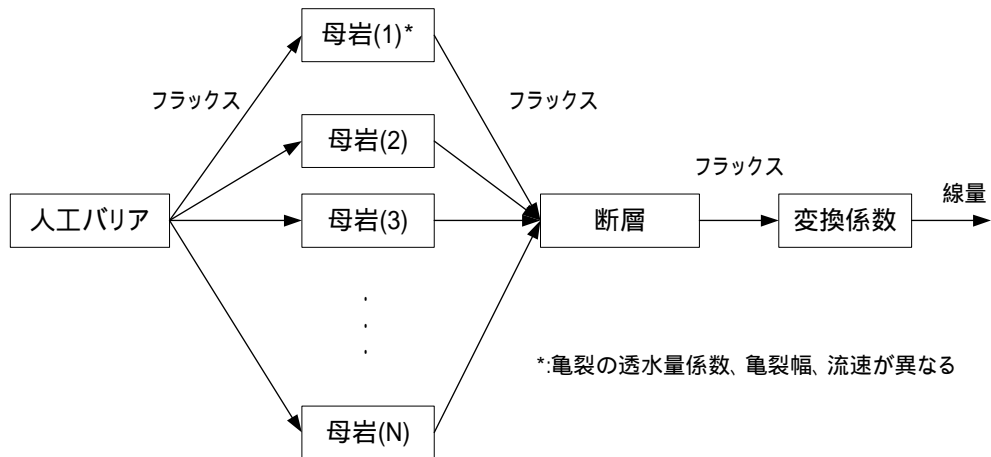


図 7.2-1 フラックス及び線量の計算の方法

7.2.2 評価距離

COLFRAC-mrl の解析に際しては、下図に示すとおり、境界条件を 0 濃度に設定した場合、モデルの端の濃度が急激に低下し、フラックスの値が 0 濃度近傍で増大する傾向が認められた。そこで、境界部の 0 濃度近傍での影響を除外するため、評価地点よりも遠方の 111m 地点を 0 濃度とし、111m の評価体系について、100m 相当地点のフラックスを評価に用いることとした。長さ 800m の断層の評価に際しては、評価地点よりも 89m 遠方の地点を 0 濃度とし、889m の評価体系について、800m 相当地点のフラックスを評価に用いた。

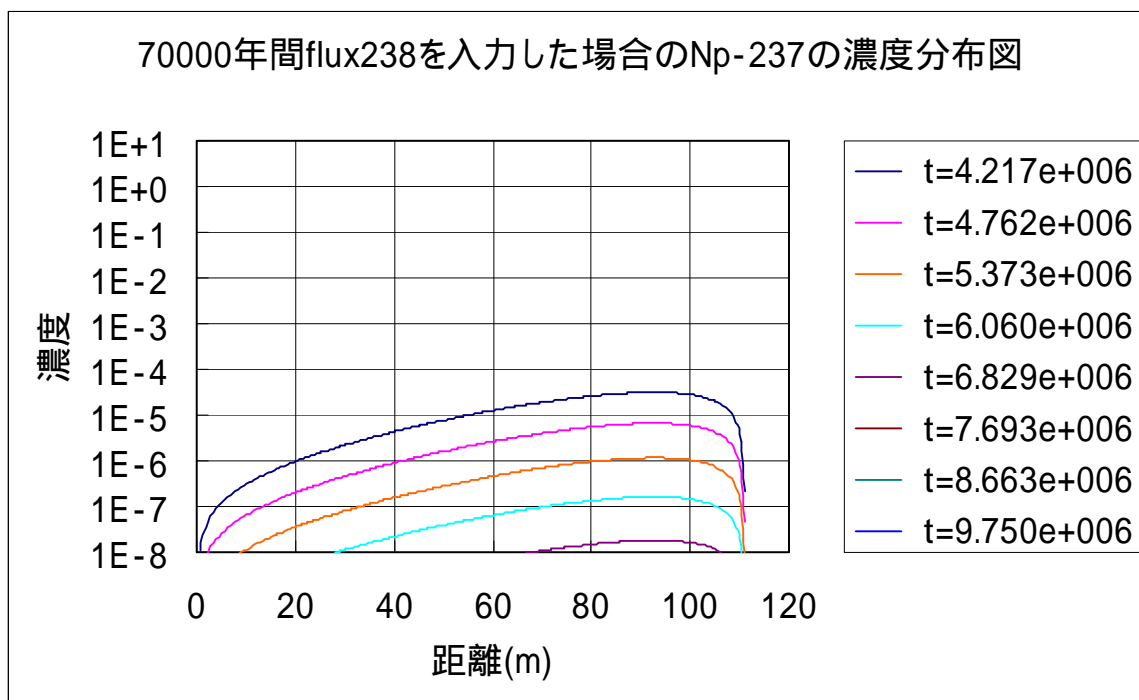


図 7.2-2 Np-237 核種濃度の空間分布図

(亀裂の上流側境界条件として、Np のフラックス[$2.5E+5 \sim 3.2E+5$ y の期間中、 $238Bq/y$ で一定]を入力)

7.2.3 解析の条件

本解析における前提条件を以下に示す。

- (ア) 崩壊連鎖 (例えば $Pu-240 \rightarrow U-236$ 、 $Cm-245 \rightarrow Pu-241 \rightarrow Am-241 \rightarrow Np-237$) は考慮していない。
- (イ) コロイドフィルトレーションは考慮していない。
- (ウ) 入力フラックスとしては、各核種のコロイドケースについての人工バリアからの放出率を用いた。
- (エ) 各核種の半減期は考慮している。

7.2.4 半減期

解析に利用した各核種の半減期を下表に示す。

表 7.2-2 各核種の半減期

核種	半減期 (年)
Np-237	2.14×10^6
Am-243	7380
Pu-240	6540
U-236	2.34×10^7
Cs-135	2.30×10^6

7.2.5 線量換算係数

断層からの核種放出率に関しては、第2次取りまとめ中に記載の河川水平野モデルを用いて算出された線量への換算係数を用い、ガラス固化体が4万本あることを考慮して線量に換算した。各評価核種に関する換算係数を下表に示す。

表 7.2-3 各核種の線量換算係数 (河川水平野モデル)

核種	線量換算係数 (mSv/Bq)
Np-237	1×10^{-11}
Am-243	2×10^{-11}
Pu-240	1×10^{-11}
U-236	1×10^{-12}
Cs-135	1×10^{-13}

7.2.6 現実的速度定数

Np、Am、Pu に関しては、地下水コロイドへの収着試験結果より、U に関しては、ベントナイトコロイドへの収着試験結果より、現実的速度定数を導出した。(NAGRA, 2003)

Cs に関しては、花崗閃緑岩への分配係数に関する実験で現実的速度定数が得られてい

る(黒澤他、2004) ので、そのデータを利用した。

(1) バッチ式収着試験の解析に利用する方程式

本項では、バッチ式収着試験の結果から速度定数を求めるために利用した方程式について説明する。

コロイドへの分配係数 K_d (ml/g) は以下の式で表される。

$$K_d = \frac{C_0 - C}{C} \frac{V}{M} \quad \text{式(7.2.6-1)}$$

K_d : コロイドへの分配係数 (ml/g)

C : 収着平衡後の液相中の核種濃度(mol/ml)

C_0 : ブランク試験における液相中の核種濃度 (mol /ml)

V : 液量 (ml)

M : コロイドないしケイ砂の重量 (g)

収着反応に関する式は、コロイドへの収着量を変数にするものと、液相中の核種濃度を変数にするものの2種がある。コロイドへの収着量を変数にする式は以下である。

$$\frac{\partial S}{\partial t} = \beta(KdC - S) \quad \text{式(7.2.6-2)}$$

S : コロイドまたは砂への収着量 (mol /g)

β : 収着量を基準としたときの速度定数(1/day)

C : 液相での濃度(mol /ml)

t : 時間(day)

実際の収着試験ではコロイドへの収着量ではなく、液相中の核種濃度が測定される。そこで実験の解析に利用する、液相中の核種濃度を変数にする式は以下である。

$$\frac{dc}{dt} = -\beta^*(KdC - S) \quad \text{式(7.2.6-3)}$$

β^* : 液相を基準としたときの速度定数(g/ml/day)

初期条件として、 $t=0$ の場合に $C=C_0$ と設定すると、式(3)の解は以下となる。

$$C = \frac{C_0}{Y} \left\{ Kd \exp(-Y\beta^* t) + \frac{V}{M} \right\} \quad \text{式(7.2.6-4)}$$

ただし、

$$Y = Kd + \frac{V}{M} \quad \text{式(7.2.6-5)}$$

また、収着量 S と濃度 C との関係は以下の式で表される。

$$S = \frac{(C_0 - C)V}{M} \quad \text{式(7.2.6-6)}$$

(2) バッチ試験結果、及び速度定数の算出

a. Np,Am,及びPu

地下水コロイドへの収着試験を Np,Am, 及び Pu の3核種について実施した結果 (NAGRA,2003) からデータを引用した。(図 7.2-3)

収着試験より得られた液相濃度の結果を表 7.2-4、試験条件を表 7.2-5 に示す。また、地下水コロイドへの収着試験では核種濃度は(mol/l)で与えられているため、表 7.2-4 に濃度の単位を(kg/m³)に変換した結果も示す。

速度定数は、式(7.2.6-4)を使って、バッチ試験結果に対してパラメータフィッティングを行って求めた。パラメータフィッティングに利用した式中の係数を表 7.2-6 に示す。パラメータフィッティングの結果を図 7.2-4～図 7.2-6 に示す。

パラメータフィッティングから得られた速度定数の単位は、(kg/m³/hr)であるので、それを(kg/m³/yr)に変換した。

また、得られた速度定数は液相基準であるので、収着量を基準とした定数に変換した。収着量を基準とした速度定数への変換には、以下の式を利用した。

$$\beta = \beta^* \frac{V}{M} \quad \text{式(7.2.6-7)}$$

β : 収着量を基準とした速度定数(1/yr)

β^* : 液相を基準とした速度定数(kg/m³/yr)

さらに、得られた速度定数より以下の式を用いて、逆方向の速度定数を求めた。

$$Kd = \frac{\beta^f}{\beta^b} \quad \text{式(7.2.6-8)}$$

β^f : 順方向速度定数(1/yr)

β^b : 逆方向速度定数(kg/m³/yr)

速度定数の計算結果を表 7.2-7 に示す。

表 7.2-4 ベントナイトコロイドへの収着試験結果 (Np, Am 及び Pu)

経過時間 (hours)	溶液中の核種濃度					
	Np		Am		Pu	
	(mol/l)	(kg/m ³)	(mol/l)	(kg/m ³)	(mol/l)	(kg/m ³)
0	1.4×10^{-8}	3.40×10^{-6}	1.3×10^{-9}	3.16×10^{-7}	8.0×10^{-10}	1.94×10^{-7}
1	1.0×10^{-8}	2.43×10^{-8}	3.0×10^{-10}	7.29×10^{-8}	6.3×10^{-10}	1.53×10^{-7}
24	1.3×10^{-8}	3.16×10^{-8}	6.0×10^{-11}	1.46×10^{-8}	4.8×10^{-10}	1.17×10^{-7}
336	1.4×10^{-8}	3.40×10^{-8}	7.0×10^{-11}	1.70×10^{-8}	2.0×10^{-11}	4.86×10^{-9}

表 7.2-5 試験条件 (Np, Am 及び Pu)

項目	データ
ベントナイトコロイドの濃度	$1.0 \times 10^{-4}(\text{g/l})$

表 7.2-6 パラメータフィッティング式の係数 (Np, Am 及び Pu)

係数	核種		
	Np	Am	Pu
C_0 (kg/m ³)	3.4×10^{-6}	3.16×10^{-7}	1.94×10^{-7}
K_a (m ³ /kg)	5.0	1.76×10^5	3.9×10^5
Y (m ³ /kg)	1.0×10^4	1.86×10^4	4.0×10^5
V/M (m ³ /kg)	1.0×10^4	1.0×10^4	1.0×10^4

表 7.2-7 速度定数の計算結果 (Np, Am 及び Pu)

速度定数の種類	核種		
	Np	Am	Pu
フィッティングにより求めた液相を基準とした場合の速度定数(β^*) (kg/m ³ /hour)	5.0×10^{-4}	5.0×10^{-5}	5.0×10^{-6}
フィッティングにより求めた液相を基準とした場合の速度定数(β^*) (kg/m ³ /yr)	4.83	4.38×10^{-1}	4.38×10^{-2}
収着量を基準とした場合の順方向速度定数(β) (1/yr)	4.83×10^4	4.38×10^3	4.38×10^2
収着量を基準とした場合の逆方向速度定数 (kg/m ³ /yr)	8.76×10^3	2.49×10^{-2}	1.12×10^{-3}

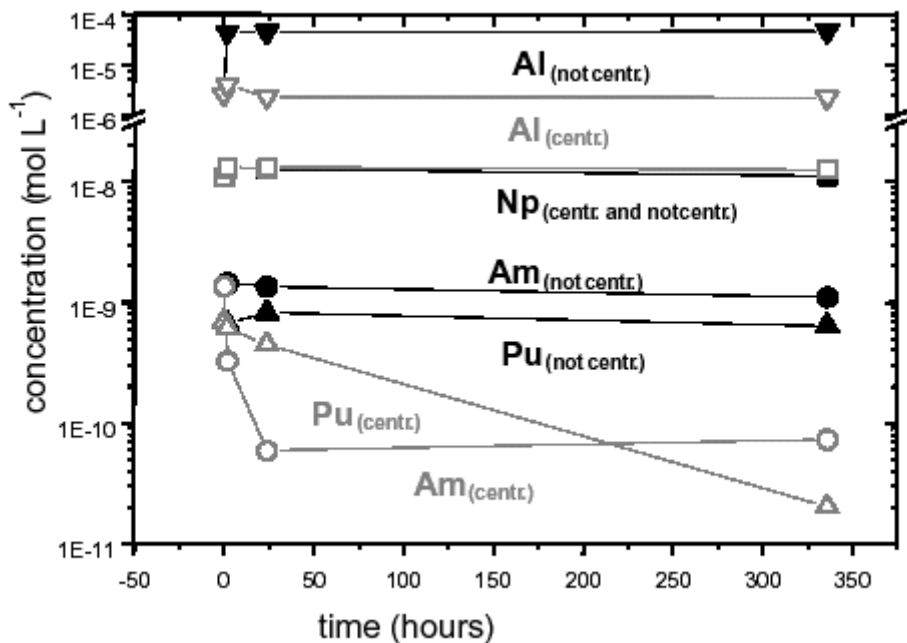


図 7.2-3 地下水コロイドのバッチ試験結果 (Np,Am 及び Pu)

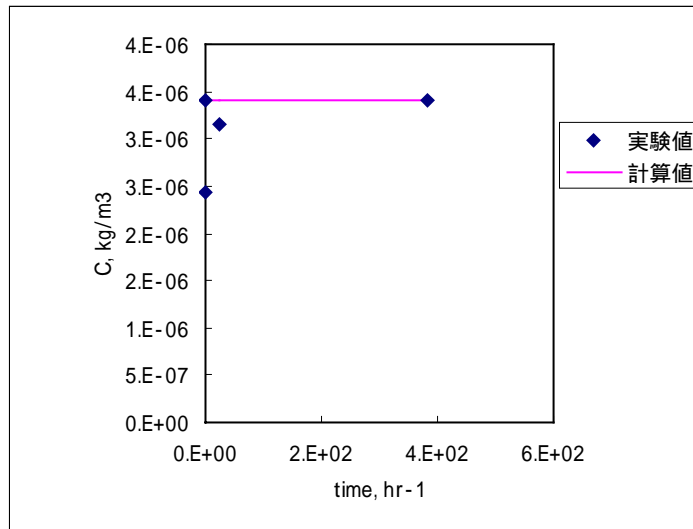


図 7.2-4 Np の速度定数のパラメータフィッティング

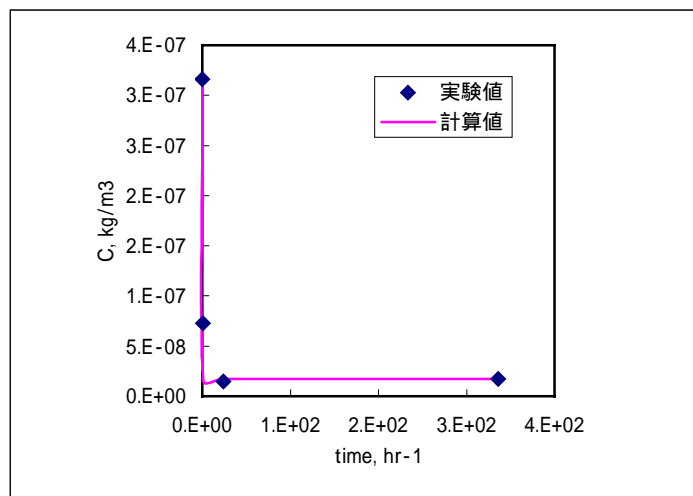


図 7.2-5 Am の速度定数のパラメータフィッティング

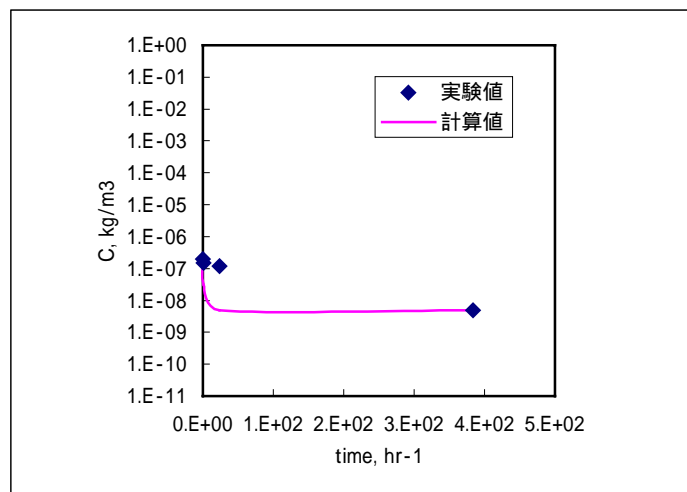


図 7.2-6 Pu の速度定数のパラメータフィッティング

b. U

速度定数を求めるために必要なデータは、ベントナイトコロイドへの収着試験の結果 (NAGRA, 2003) から試験結果を引用した。(表 7.2-12)

ベントナイトコロイドへの収着試験では、 K_d の値のみが報告されている。そこで、 K_d より液相濃度を求めた結果を表 7.2-8 に示す。試験条件を表 7.2-9 に示す。

速度定数は、式(7.2.6-4)を使って、バッチ試験結果に対してパラメータフィッティングを行って求めた。パラメータフィッティングに利用した式中の係数を表 7.2-10 に示す。パラメータフィッティングの結果を図 7.2-7 に示す。

パラメータフィッティングから得られた速度定数の単位は、 $(\text{kg}/\text{m}^3/\text{hr})$ であるので、それを $(\text{kg}/\text{m}^3/\text{yr})$ に変換した。また、得られた速度定数は液相基準であるので、収着量を基準とした定数に変換した。速度定数の変換に当たっては、 N_p, A_m , 及び Pu の場合と同じく式(7.2.6-7)を利用した。さらに、得られた速度定数より逆方向の速度定数を求めた。逆方向の速度定数の計算に当たっては、 N_p, A_m , 及び Pu の場合と同じく式(7.2.6-8)を利用した。速度定数の計算結果を表 7.2-11 に示す。

表 7.2-8 ベントナイトコロイドへの収着試験結果 (U)

経過時間 (hours)	分配係数 (kg/m ³)
0	-
168	3.25×10^{-5}
336	2.76×10^{-5}
672	2.21×10^{-5}
2016	2.11×10^{-5}

表 7.2-9 試験条件 (U)

項目	データ
V/M (m ³ /kg)	435(ml/g)

表 7.2-10 パラメータフィッティング式の係数 (U)

係数	フィッティングデータ
C ₀ (kg/m ³)	9.41×10^{-5}
K _d (m ³ /kg)	1.51
Y(m ³ /kg)	1.94
V/M(m ³ /kg)	4.35×10^{-1}

表 7.2-11 速度定数の計算結果 (U)

速度定数の種類	データ
フィッティングにより求めた液相を基準としたときの速度定数(β^*) (kg/m ³ /hour)	1.0×10 ⁻²
フィッティングにより求めた液相を基準としたときの速度定数(β^*) (kg/m ³ /yr)	8.76×10 ¹
収着量を基準としたときの順方向速度定数(β) (1/yr)	3.81×10 ¹
収着量を基準としたときの逆方向速度定数 (kg/m ³ /yr)	2.53×10 ¹

表 7.2-12 ベントナイトコロイドのバッチ試験結果 (U)

Table 4.12: K_d values for bentonite colloid dispersions (values in brackets stand for sorption onto bulk bentonite)

Radionuclide	Contact Time						
	1 hour (mL g ⁻¹)	1 day (mL g ⁻¹)	1 week (mL g ⁻¹)	2 weeks (mL g ⁻¹)	3 weeks (mL g ⁻¹)	4 weeks (mL g ⁻¹)	12 weeks (mL g ⁻¹)
²³⁷ Np ($c_0=1.410^{-6}$ M) $c_{col}: 20 \text{ mg L}^{-1}; \text{SL}: 150000$	< 5·10 ³	< 5·10 ²	< 5·10 ¹	—	< 5·10 ¹	—	—
²⁴¹ Am ($c_0=9\cdot 10^{-13}$ M) $c_{col}: 20 \text{ mg L}^{-1}; \text{SL}: 150000$	2.7·10 ⁶	2.6·10 ⁵	2.1·10 ⁵	—	1.2·10 ⁵	—	—
²⁴⁴ Pu ($c_0=3.8\cdot 10^{-15}$ M) $c_{col}: 20 \text{ mg L}^{-1}; \text{SL}: 150000$	9.9·10 ⁴	1.1·10 ⁵	1.3·10 ⁵	—	8·10 ⁵	—	—
⁹⁹ Tc (VII) ($c_0=5.33\cdot 10^{-7}$ M) $c_{col}: 2 \text{ g L}^{-1}; \text{SL}: 1485$	—	—	0 [0]	0 [0]	—	0 [0]	6.5 [1]
⁷⁵ Se ($c_0=1.36\cdot 10^{-7}$ M) $c_{col}: 2 \text{ g L}^{-1}; \text{SL}: 1485$	—	—	7 [2.7]	14 [4.3]	—	11 [49]	45 [82]
¹³⁷ Cs ($c_0=1.10\cdot 10^{-7}$ M) $c_{col}: 2 \text{ g L}^{-1}; \text{SL}: 1485$	—	—	8742 [4532]	6422 [4072]	—	6549 [4449]	8492 [4700]
²³⁵ U ($c_0=4.04\cdot 10^{-7}$ M) $c_{col}: 2 \text{ g L}^{-1}; \text{SL}: 1485$	—	—	824 [32]	1050 [44]	—	1420 [52]	1508 [36]

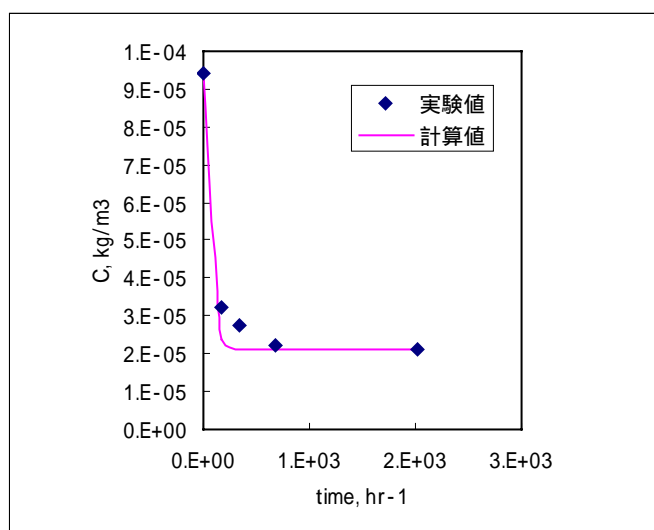


図 7.2-7 U の速度定数のパラメータフィッティング

(3)まとめ

以上よりまとめた、各評価核種のコロイドへの分配係数を以下の表に示す。

表 7.2-13 核種のコロイドへの分配係数

核種	分配係数(m ³ /kg)
Np	5.0
Am	1.76 × 10 ⁵
Pu	3.9 × 10 ⁵
U	1.51
Cs	150

7.2.7 パラメータの設定

上記の文献等を参考に、コロイド影響を考慮した各解析ケースに関するパラメータを表 7.2-14 のとおり設定した。

コロイド濃度を 0 に設定した場合（コロイド無しケース）、コロイド濃度を 1ppm とし、平衡と考えられるほど速度定数（ α 、 β ）を大きく設定した場合（平衡ケース）、及

び速度定数 (α 、 β) をコロイドの核種への収着実験から得られた値に設定した場合 (現実的設定ケース) の3種にパラメータを設定した。以降、コロイドへの核種の収着の順方向速度定数を α 、逆方向速度定数を β とする。

表 7.2-14 各解析ケースのパラメータ (現実的設定)

解析条件、核種		コロイド濃度 [ppm]	順方向速度定数 α [1/y]	逆方向速度定数 β [kg/m ³ /y]	α / β [m ³ /kg]
コロイド無しケース	Np	0	0	1	0
	U	0	0	1	0
	Am	0	0	1	0
	Pu	0	0	1	0
	Cs	0	0	1	0
平衡ケース	Np	1	5×10^{10}	1×10^{10}	5
	U	1	1.51×10^{10}	1×10^{10}	1.51
	Am	1	1.76×10^{15}	1×10^{10}	176000
	Pu	1	3.9×10^{15}	1×10^{10}	390000
	Cs	1	1.5×10^{12}	1×10^{10}	150
現実的設定ケース	Np	1	43800	8760	5
	U	1	38.1	25.3	1.51
	Am	1	4380	2.49×10^{-2}	176000
	Pu	1	438	1.12×10^{-3}	390000
	Cs	1	182500	1220	150
	Cs	5	182500	1220	150
	Cs	10	182500	1220	150

また、パラメータ変更ケースとして、速度定数 α 、 β に関して以下のような設定を行った場合の検討を行った。

① β 小ケース

逆方向速度定数 β の値を現実的な値よりも小さく設定し、感度解析的に逆方向速

度定数 β を現実的設定値よりも小さい範囲で変化させて物質移行計算を行った (β 小ケース)。全評価核種について、逆方向速度定数 β が現実的設定値よりも一桁小さい場合の評価を行った。これはコロイドから核種の脱離速度が十分の一となる場合に相当する。逆方向速度定数 β を一桁小さく設定しても変化が認められない場合には、さらに β の値を小さく設定した場合の検討を行った。 β 小ケースでコロイド影響が認められた核種 Cs-135 に関して、感度解析的にコロイド濃度が 0.1ppm の場合の解析を実施した。海外で実施された地下深部の結晶質岩（花崗岩）中での測定結果について、天然コロイドの濃度は 0.1ppm 以下との報告がある（核燃料サイクル開発機構、1999）ので、コロイド濃度が 0.1ppm を設定した。

② α β 小ケース

α 、及び β の比を変えずに α 、及び β の値を共に小さく設定した場合の評価も行った (α β 小ケース)。これは、分配係数に相当する α/β の値を一定に保ったまま、速度定数だけを小さく設定した場合の解析である。また、このパラメータ設定は、収着が遅いプロセス又、は核種とコロイドの間の相互作用が弱いプロセスに相当する。

③ Am-243 核種の α β 変更ケース

核種のコロイドに対する分配係数が大きく、コロイド影響が大きく認められた核種 Am-243 に関して、速度定数を平衡状態と考えられるほど大きな値から、 α と β の比を変えずに ($\alpha/\beta=1.76 \times 10^5 \text{ m}^3/\text{kg}$ に固定した。これは K_d の現実的設定値である) 段階的により小さな値に変化させて解析を行った。また、 α/β 値を現実的設定値よりも一桁小さく設定した場合 ($\alpha/\beta=1.76 \times 10^4 \text{ m}^3/\text{kg}$ に固定) について、同様の解析を行った。

COLFRAC-mrl を使った解析では、Am-243 核種のように核種のコロイドに対する分配係数 K_d が大きい核種の場合には、解が不安定になる傾向が認められたため、コロイド濃度を 0.1ppm と小さく設定して解析を行った。

④ Cs-135 核種の濃度依存性ケース

Cs-135 核種について、コロイド濃度を 1ppm、5ppm、10ppm に設定した場合の解析を実施した。

第 2 次取りまとめでは、地下深部のコロイド濃度として、1ppm を設定している（核燃料サイクル開発機構、1999）。また、東濃鉾山における堆積岩層での地下水

の測定結果によると、コロイド濃度は約 1～5ppm と報告されている（核燃料サイクル開発機構、1999）。以上を考慮して、コロイド濃度を 1,5,及び 10ppm に設定した。

パラメータ変更ケースに関する設定値を表 7.2-15 に、Am-243 核種の α β 変更ケースに関する設定値を表 7.2-16 に、Cs-135 核種の濃度依存性ケースに関する設定値を表 7.2-17 に示す。

表 7.2-15 各解析ケースのパラメータ（パラメータ変更ケース）

解析条件、核種		コロイド濃度 [ppm]	順方向速度定数 α [1/y]	逆方向速度定数 β [kg/m ³ /y]	α / β [m ³ /kg]
β 小ケース	Np	1	43800	8.76	5000
	Np	1	43800	876	50
	U	1	38.1	2.53	15.1
	U	1	38.1	5.06	7.53
	Am	1	4380	2.49×10^{-3}	1760000
	Am	1	4380	1.245×10^{-3}	3520000
	Pu	1	438	1.12×10^{-4}	3900000
	Pu	1	438	5.6×10^{-5}	7820000
	Cs	1	182500	122	1500
	Cs	1	182500	61	3000
	Cs	0.1	182500	122	1500
	α β 小ケース	Np	1	43.8	8.76
U		1	3.81	2.53	1.51
Am		1	438	2.49×10^{-3}	176000
Pu		1	43.8	1.12×10^{-4}	390000
Cs		1	18250	122	150

表 7.2-16 各解析ケースのパラメータ (Am-243 核種の α β 変更ケース)

解析条件、核種		コロイド濃度 [ppm]	順方向速度定数 α [1/y]	逆方向速度定数 β [kg/m ³ /y]	α / β [m ³ /kg]	$1 + \chi$ Kd
α β 変更 ケース (α $/ \beta = 1.76$ $\times 10^5$)	Am	0.1	438	2.49×10^{-3}	176000	18.6
	Am	0.1	4380	2.49×10^{-2}	176000	18.6
	Am	0.1	21900	1.245×10^{-1}	176000	18.6
	Am	0.1	43800	2.49×10^{-1}	176000	18.6
	Am	0.1	438000	2.49	176000	18.6
	Am	0.1	4380000	24.9	176000	18.6
	Am	0.1	43800000	249	176000	18.6
	Am	0.1	1.76×10^{15}	1.0×10^{10}	176000	18.6
	α β 変更 ケース (α $/ \beta = 1.76$ $\times 10^4$)	Am	0.1	43.8	0.00249	17600
Am		0.1	438	0.0249	17600	2.76
Am		0.1	2190	0.1245	17600	2.76
Am		0.1	4380	0.249	17600	2.76
Am		0.1	43800	2.49	17600	2.76
Am		0.1	438000	24.9	17600	2.76
Am		0.1	4380000	249	17600	2.76
Am		0.1	1.76×10^{14}	1×10^{10}	17600	2.76

注) $1 + \chi$ Kd はみかけの掘削影響領域通過流量 (7.3.4 項を参照)

表 7.2-17 各解析ケースのパラメータ (Cs-135 核種の濃度依存性ケース)

解析条件、核種		コロイド濃度 [ppm]	順方向速度定数 α [1/y]	逆方向速度定数 β [kg/m ³ /y]	α / β [m ³ /kg]
濃度依存性ケース	Cs	1	182500	1220	150
	Cs	5	182500	1220	150
	Cs	10	182500	1220	150

7.3 評価結果

以上のデータに基づいて、コロイドの影響を評価した物質移行解析を実施した。解析結果は、現実的なパラメータ設定（文献値から想定される速度定数 α 、 β を設定）に関する評価、及びパラメータ変更ケースに関する評価の二種類に分けて説明する。

7.3.1 現実的設定に関する評価結果

(1)解析の方法

現実的設定に関する評価では、コロイドが無い場合（コロイド無しケース）、及び、コロイドが存在する場合の解析を行った。また、コロイドに対する核種の収着量に関する速度定数 α 、 β に関しては、平衡と考えられるほど大きく設定した場合、及び、実験結果から現実的と考えられる速度定数 α 、 β 値を設定した場合の両方について解析を行った。

母岩、及び断層中の核種移行を COLFRAC-mrl を用いて解析した。人工バリアからの核種移行率に関しては、コロイド濃度 1ppm、核種のコロイドへの分配係数 1000m³/kg の場合のコロイド影響を想定して第 2 次取りまとめ中のコロイドケースの結果を入力として用いた。

各核種に関して、「第 2 次取りまとめ」と同様の解析ケースとして、ガラス固化体 1 本あたりの母岩からの核種放出率、断層からの核種放出率を Np-237、U-236、Am-243、Pu-240、Cs-135 について解析した。また、生物圏モデルとして河川水シナリオを想定した場合の線量換算係数を用いて、断層からの核種放出率を線量に換算した。ガラス固化体 4 万本についての線量を求めるために、断層からの核種放出率の線量換算値を 4 万倍して、ガラス固化体 4 万本についての線量とした。

(2)Np-237、U-236 の考察

核種のコロイドへの分配係数が 5m³/kg である核種 Np-237、及び 1.51m³/kg である核種 U-236 については、コロイド無しケースと、コロイド濃度 1ppm の平衡ケース、及び現実的速度定数ケースの解析結果はグラフ上で重なっている（図 7.3-1～図 7.3-6）。したがって、コロイド影響は無いことが示された。

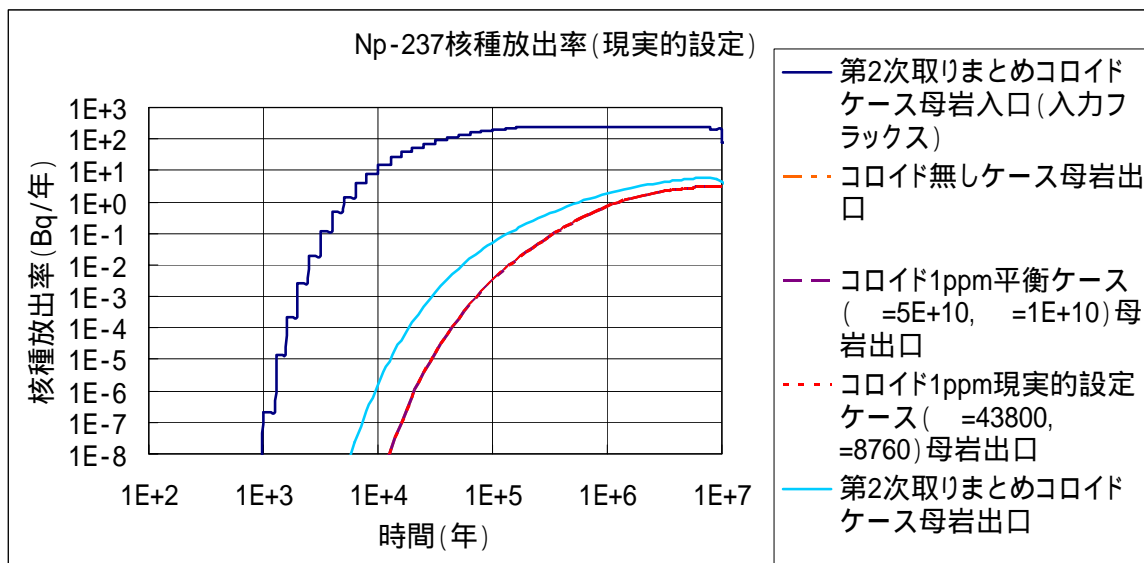


図 7.3-1 母岩からの Np-237 核種放出率 (現実的な設定ケース)

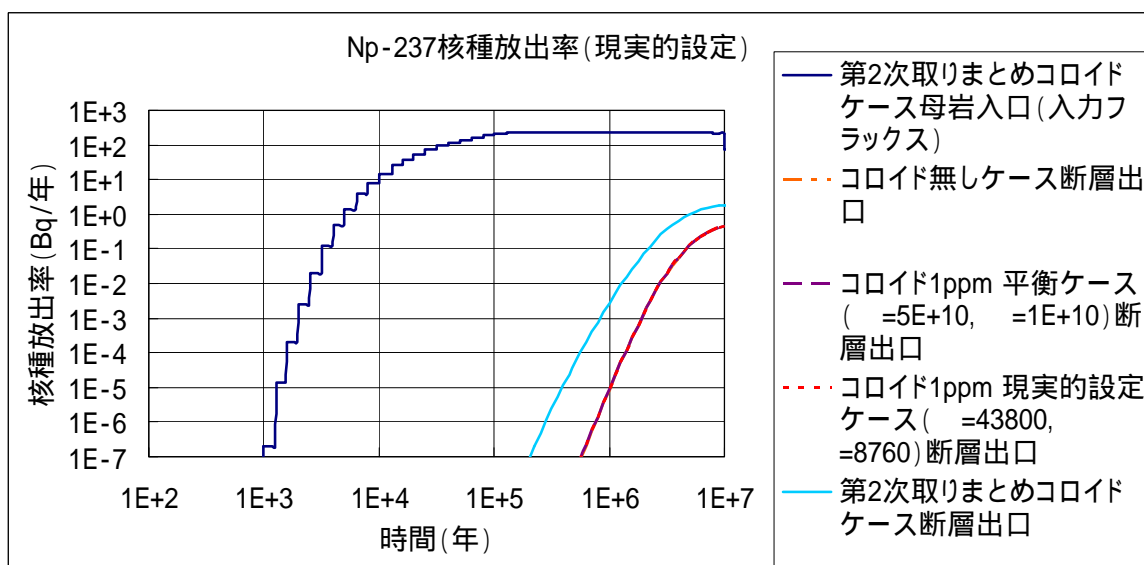


図 7.3-2 断層からの Np-237 核種放出率 (現実的な設定ケース)

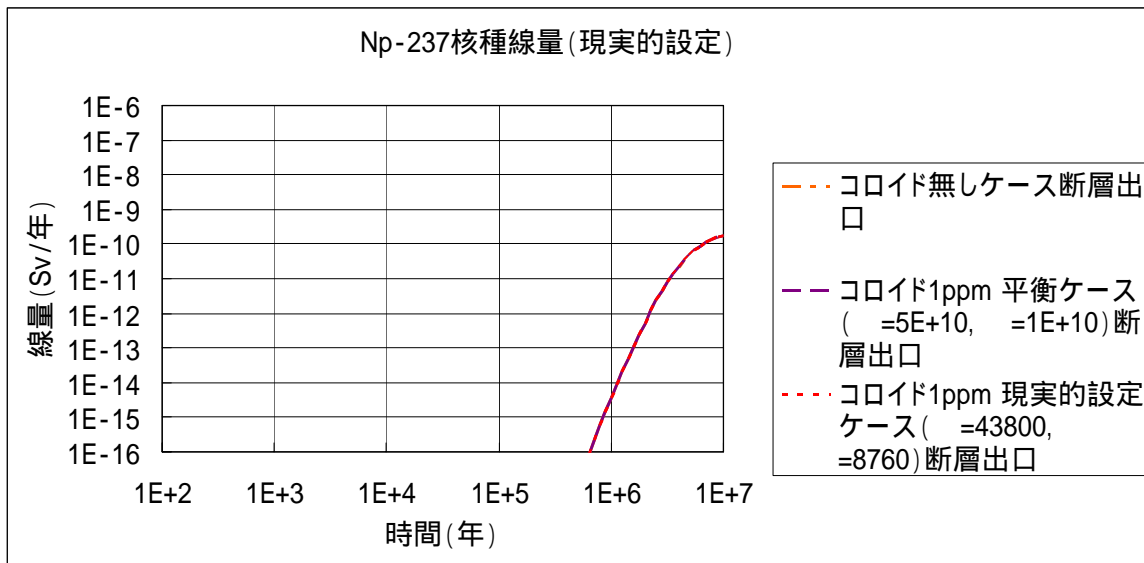


図 7.3-3 ガラス固化体 4 万本についての Np-237 核種線量 (現実的な設定ケース)

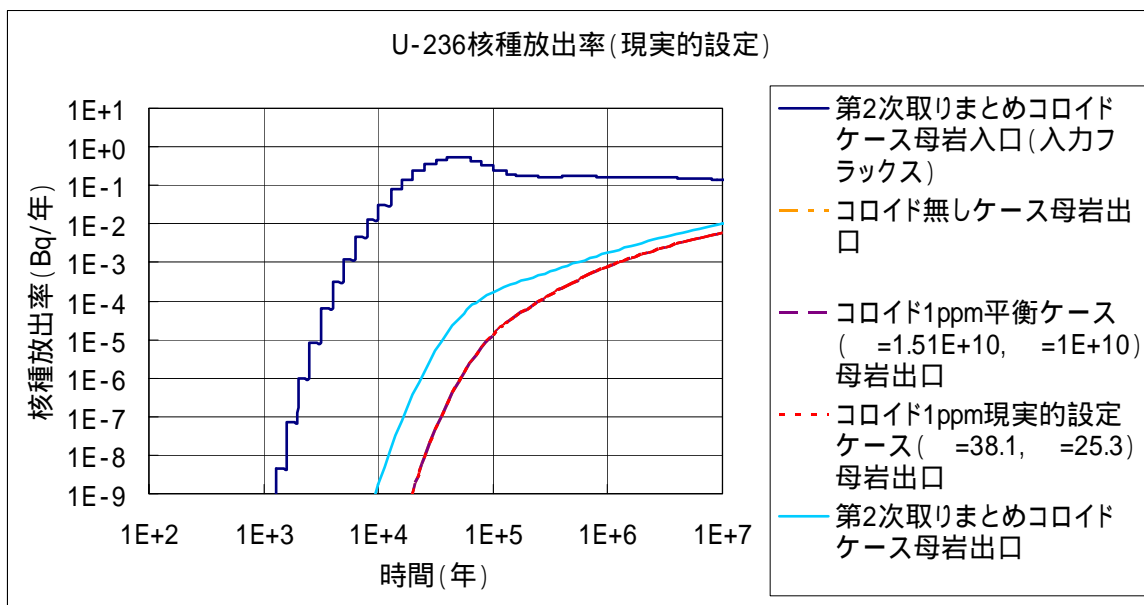


図 7.3-4 母岩からの U-236 核種放出率 (現実的な設定ケース)

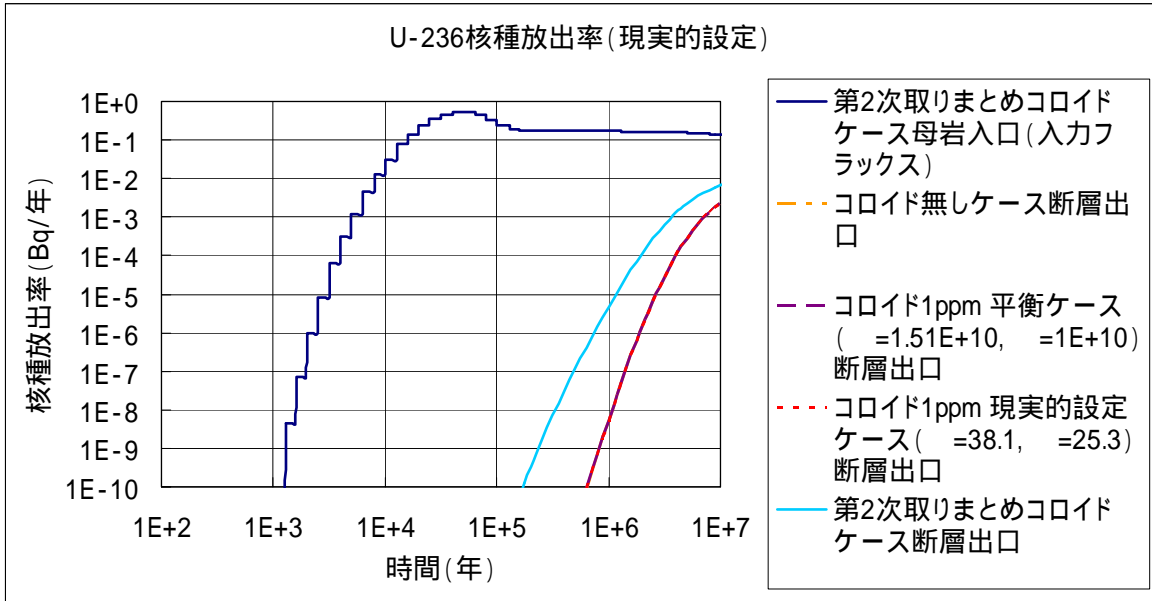


図 7.3-5 断層からの U-236 核種放出率 (現実的な設定ケース)

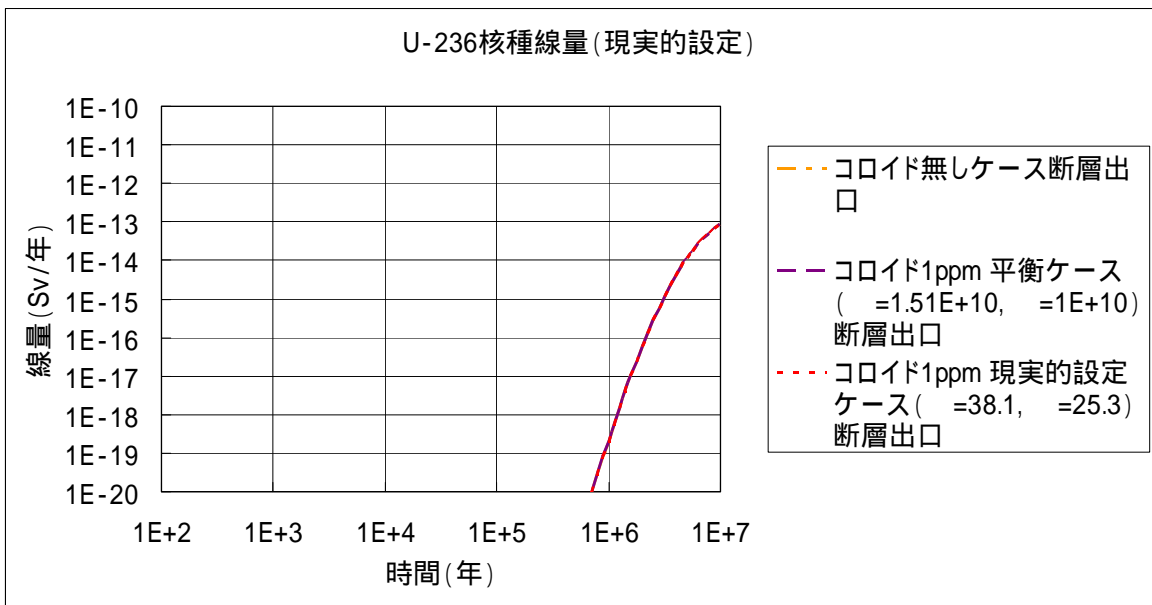


図 7.3-6 ガラス固化体 4 万本についての U-236 核種線量 (現実的な設定ケース)

(3)Cs-135 の考察

核種のコロイドへの分配係数が $150 \text{ m}^3/\text{kg}$ である核種 Cs-135 では、コロイド濃度が 1ppm の場合には、コロイド無しケース、平衡ケース、及び現実的設定ケースの解析結果が核種放出率及び線量のグラフ上で重なっており、コロイド影響は認められなかった。

コロイド濃度が 5ppm の現実的設定ケースの結果は、コロイド濃度が 1ppm の現実的設定ケースに比べて、コロイド影響による線量の増加が認められた。(図 7.3-7～図 7.3-9) 線量値は約 $8 \times 10^{-9} \text{Sv/y}$ であった。コロイド濃度が 10ppm の現実的設定ケースの結果は、コロイド濃度が 5ppm の現実的設定ケースの結果よりもさらに線量が増加して線量値は約 $1 \times 10^{-8} \text{Sv/y}$ であった。線量値とコロイド濃度をプロットして、図 7.3-10 に示した。

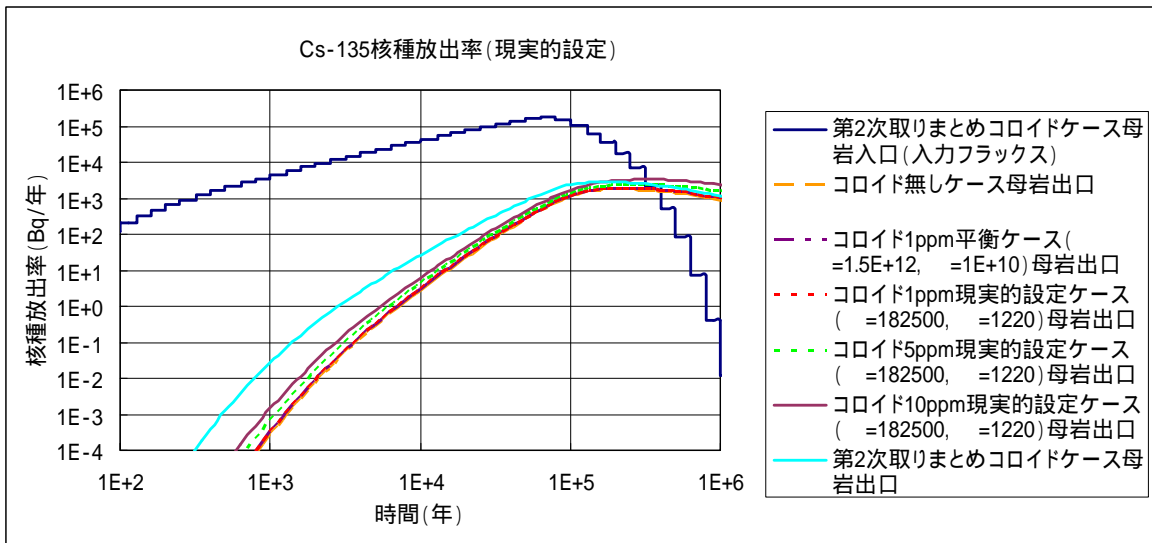


図 7.3-7 母岩からの Cs-135 核種放出率 (現実的な設定ケース)

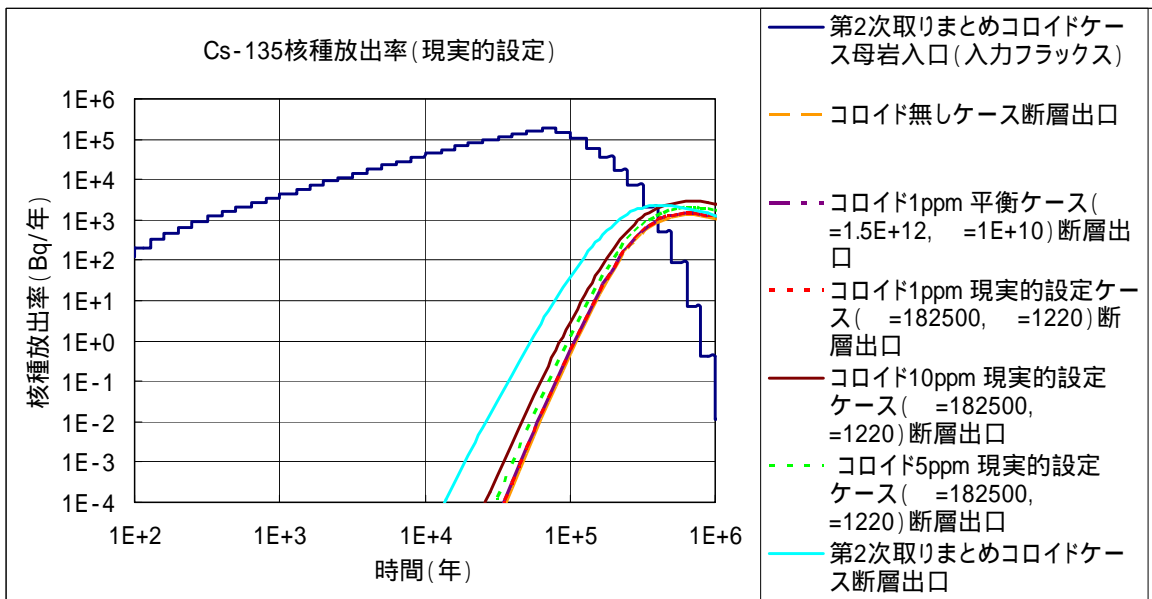


図 7.3-8 断層からの Cs-135 核種放出率 (現実的な設定ケース)

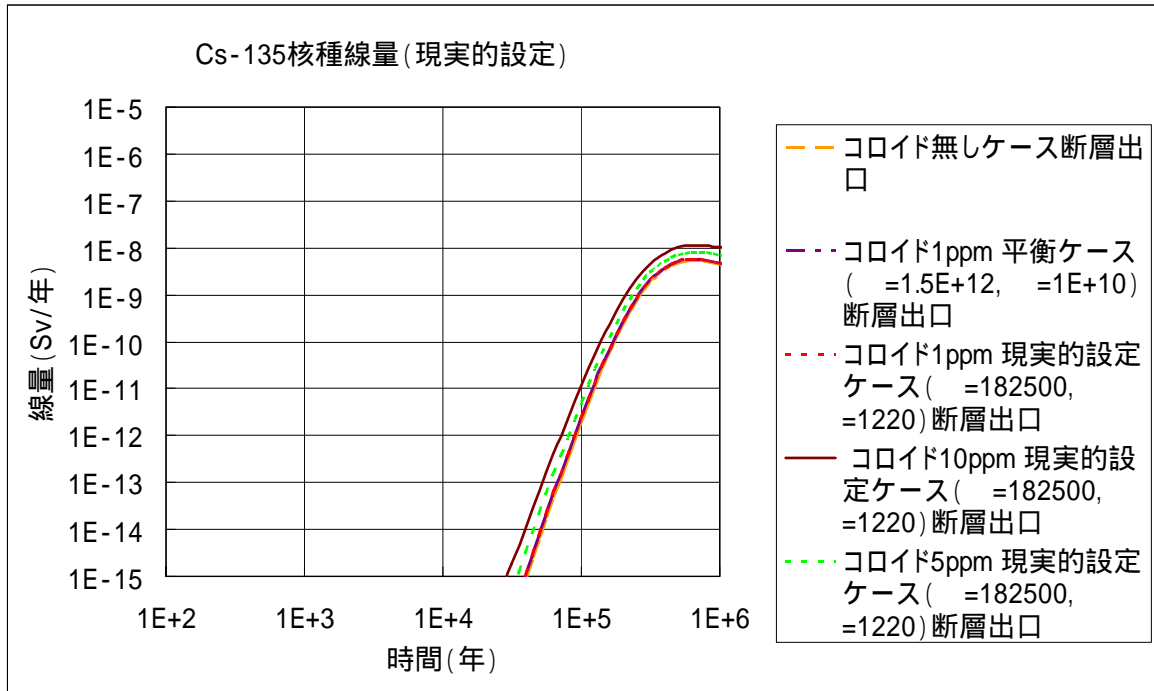


図 7.3-9 ガラス固化体 4 万本についての Cs-135 核種線量 (現実的な設定ケース)

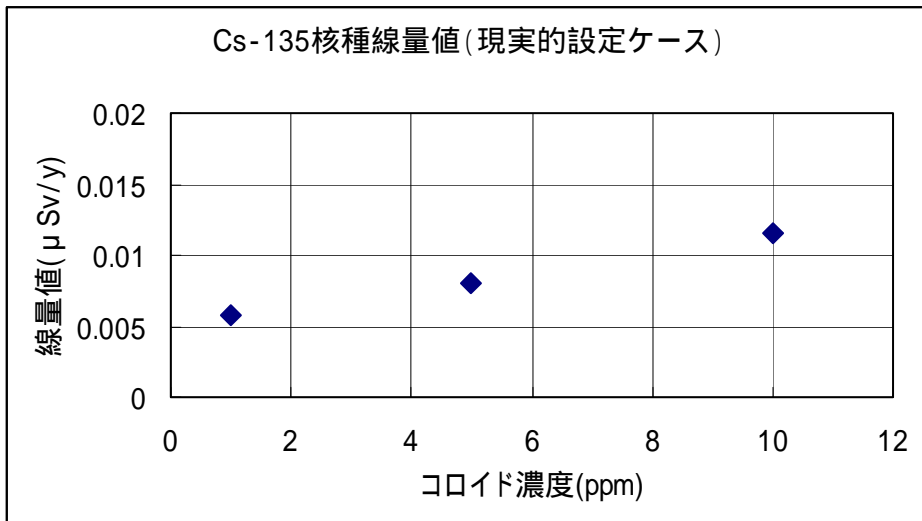


図 7.3-10 Cs-135 核種の線量値 (現実的な設定ケース)

(4)Am-243 及び Pu-240 の考察

核種のコロイドへの分配係数が $1.76 \times 10^5 \text{ m}^3/\text{kg}$ である核種 Am-243、及び $3.9 \times 10^5 \text{ m}^3/\text{kg}$ である核種 Pu-240 に関しては、コロイド濃度が 1ppm の場合、平衡ケース、及び現実的設定ケース共にコロイド無しケースよりも移行が促進され、ピーク値が高く、顕著なコロイド影響が認められた (図 7.3-11 及び図 7.3-14)。

コロイド無しケースの母岩出口におけるピーク時間は、Am-243 核種の場合に 1.1×10^5 年 (図 7.3-11)、Pu-240 核種の場合に 8.9×10^4 年 (図 7.3-14) であり、平衡ケースでは、Am-243 核種の場合に 7.1×10^4 年 (図 7.3-11)、Pu-240 核種の場合に 6.3×10^4 年であった (図 7.3-14)。平衡ケースでは、コロイド無しケースに比べて移行が促進され、かつ半減期が 7380 年 (Am-243 核種) あるいは 6540 年 (Pu-240 核種) と短いため、母岩出口における放出率の最大値がコロイド無しケースよりも大きくなったものと考えられる。

現実的な速度定数を設定した場合にも、コロイド無しケースに比べて、核種移行の促進が認められた。現実的な速度定数ケースの母岩出口におけるピーク時間は、Am-243 核種では 6.3×10^4 年 (図 7.3-11)、Pu-240 核種では 6.3×10^4 年であった (図 7.3-14)。コロイド無しケースに比べて移行が促進され、かつ半減期が短いため、母岩出口における放出率の最大値はコロイド無しケースと比べて大きくなり、顕著なコロイド影響が認められた。亀裂性媒体において、コロイドに対する収着が遅いプロセスである場合には、流動性のコロイドが溶質の移行を著しく促進しうることの評価の重要性に関して、(M.Ibaraki 他,1995) の文献で指摘されている。

Pu-240 及び Am-243 核種の母岩からの核種放出率は、透水量係数及び地下水流速が異なる複数の亀裂モデルからの核種放出率に確率を掛けて合計して求めている。(図 7.2-1) 5 個の異なる地下水流速について、亀裂モデルの核種放出率の分布を以下に示した。(図 7.3-17、図 7.3-18、図 7.3-19、図 7.3-20、及び図 7.3-21)

平衡ケースでは、母岩からの核種放出率のピーク値が、流速の低下とともに減少していく傾向が図より認められた。しかし、現実的設定ケースでは、流速が低下してもピーク値が平衡ケースほど減少しない傾向が認められた。このため、流速が速い亀裂の物質移行では、平衡ケースの方が核種放出率のピーク値は高くなっている。母岩からの放出

率は、透水量係数の異なる亀裂からの放出率を確率で荷重平均した結果であり、放出率と確率分布の両方から影響を受けている。Am-243 核種に関して、母岩からの核種放出率を透水量係数の全分割区間について確率を掛けて合計すると、現実的設定ケースの方が平衡ケースよりも放出率が大きくなっている（図 7.3-11）。これは確率分布の高い亀裂（透水量係数の分布の中間点付近、流速が 1.47m/y 付近）では、平衡ケースの核種放出率のピーク値が、現実的設定ケースのピーク値よりも小さいためと考えられる。（図 7.3-21）

現実的設定ケースで、コロイド濃度が 0.1ppm の場合には、母岩からの核種放出率の絶対値がコロイド濃度 1ppm の場合の十分の一程度となった。核種放出率と地下水流速の関係を調べると、コロイド濃度が 1ppm の場合と同様に、流速が低下しても、ピーク値がほとんど減少しない傾向が認められた（図 7.3-17～図 7.3-21）。

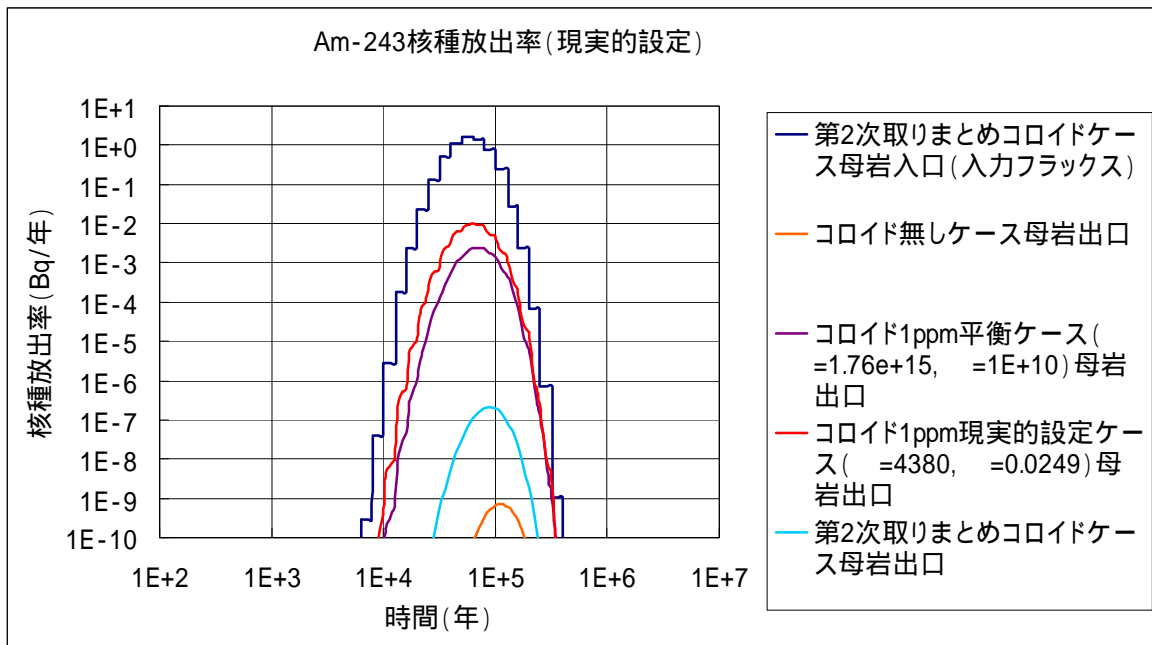


図 7.3-11 母岩からの Am-243 核種放出率（現実的な設定ケース）

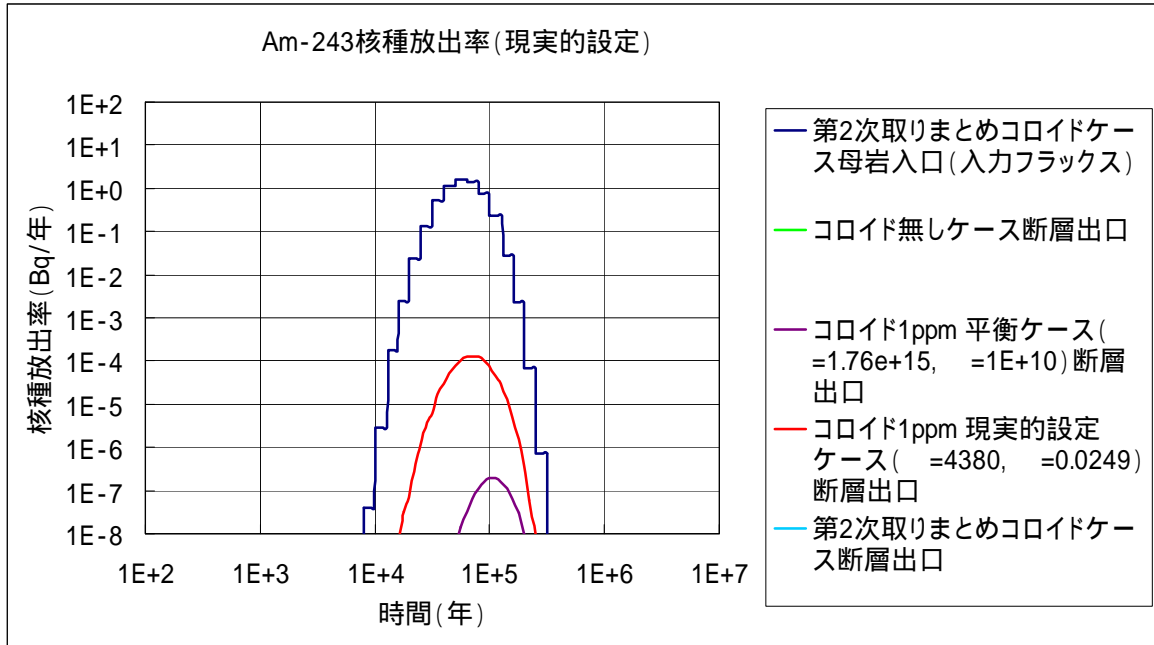


図 7.3-12 断層からの Am-243 核種放出率 (現実的な設定ケース)

(注：コロイド無しケースの断層出口における線量のピーク値は $1 \times 10^{-25} \text{Sv/y}$ 以下であり、平衡ケース、現実的設定ケースのいずれに比べても著しく低い)

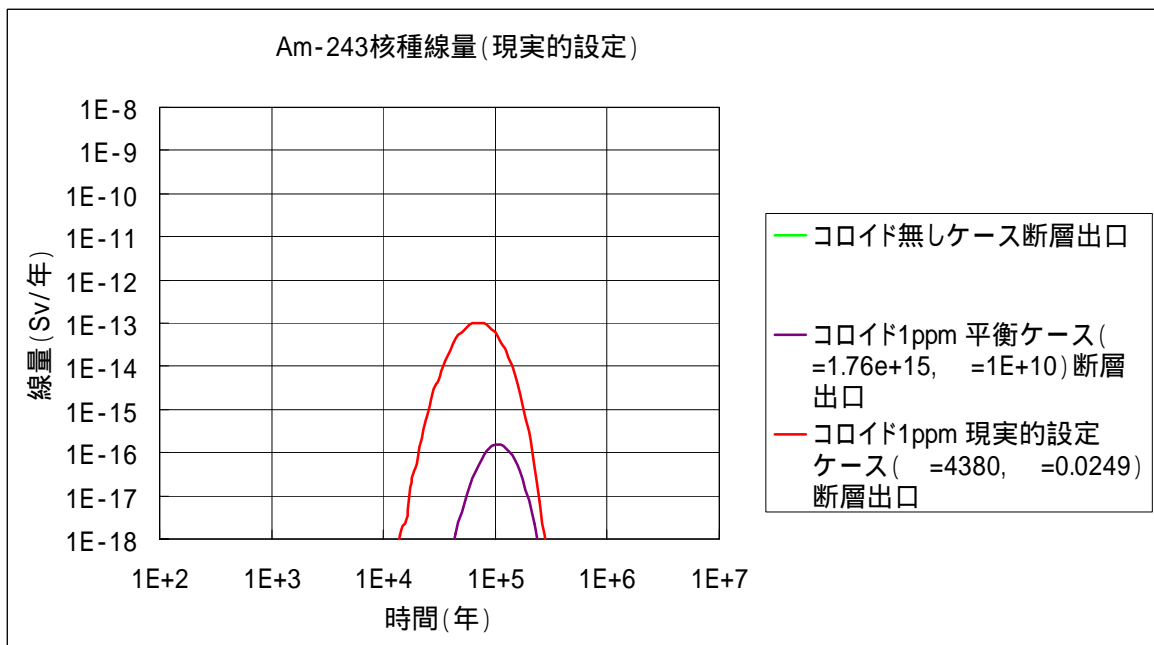


図 7.3-13 ガラス固化体 4 万本についての Am-243 核種線量 (現実的な設定ケース)

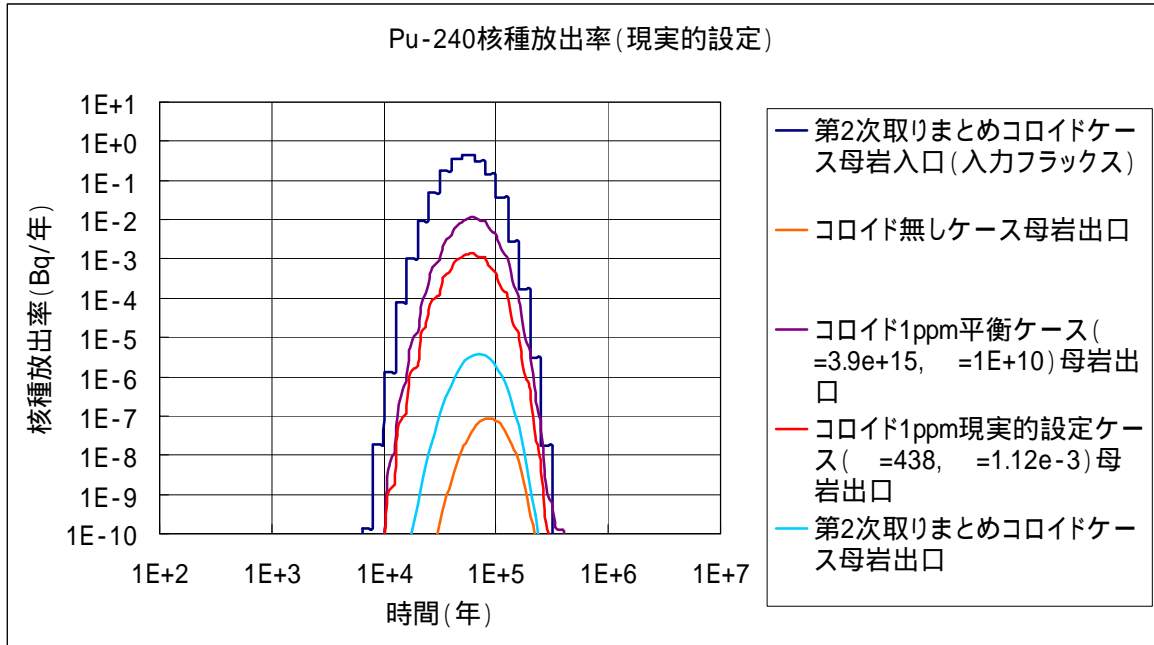


図 7.3-14 母岩からの Pu-240 核種放出率 (現実的な設定ケース)

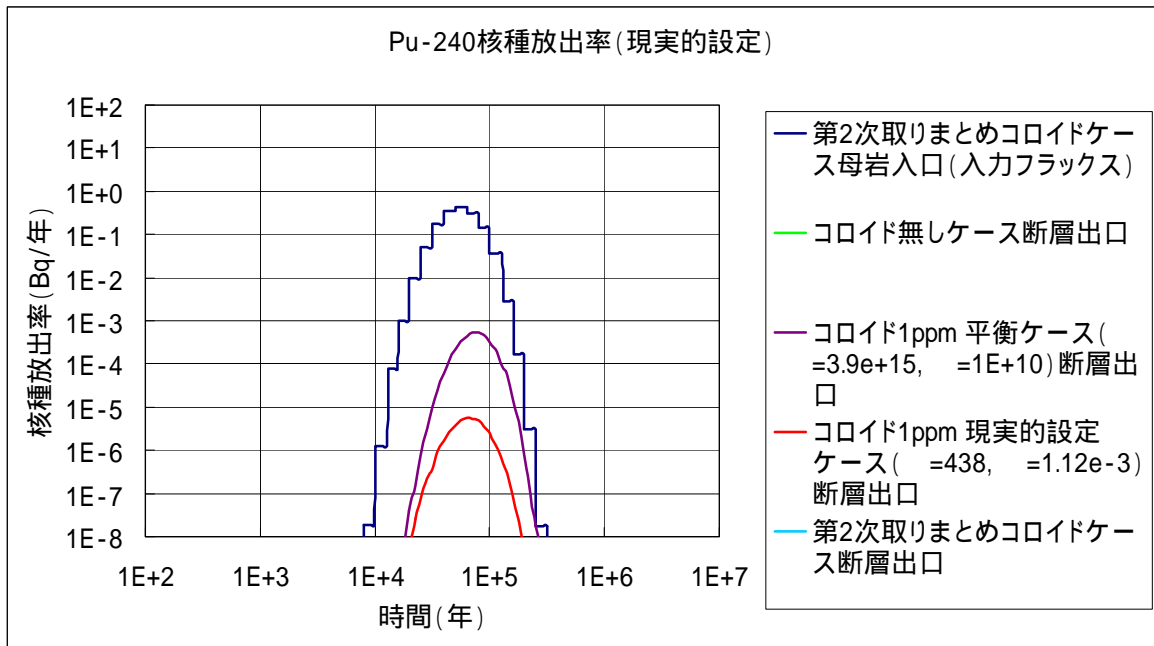


図 7.3-15 断層からの Pu-240 核種放出率 (現実的な設定ケース)

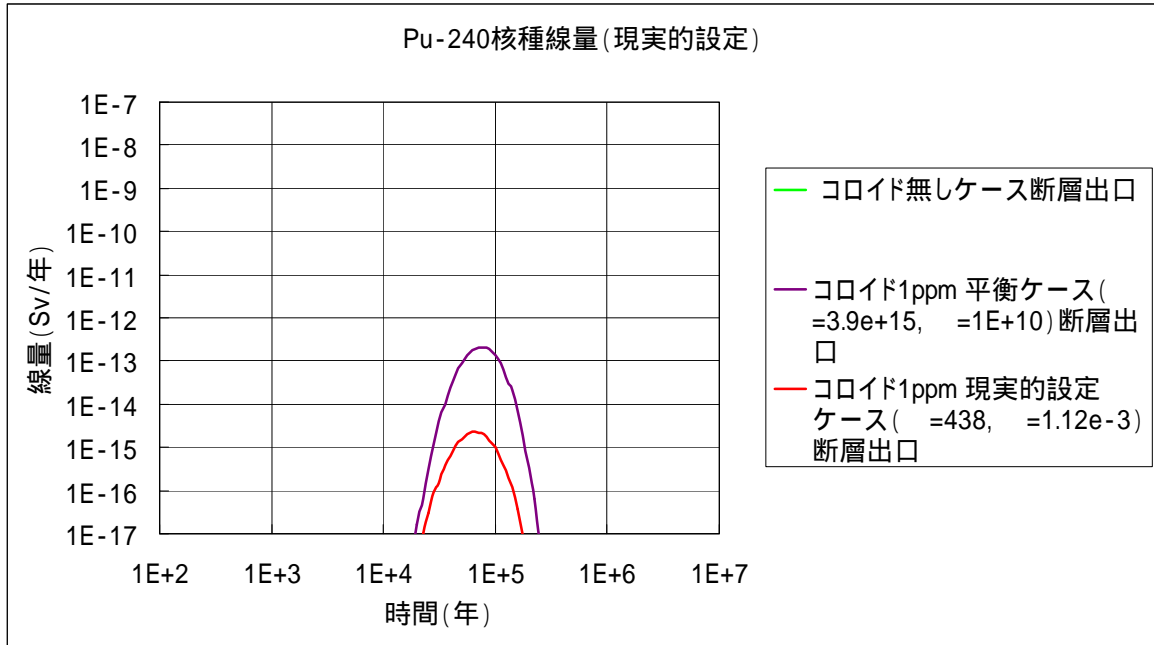


図 7.3-16 ガラス固化体 4 万本についての Pu-240 核種線量 (現実的な設定ケース)

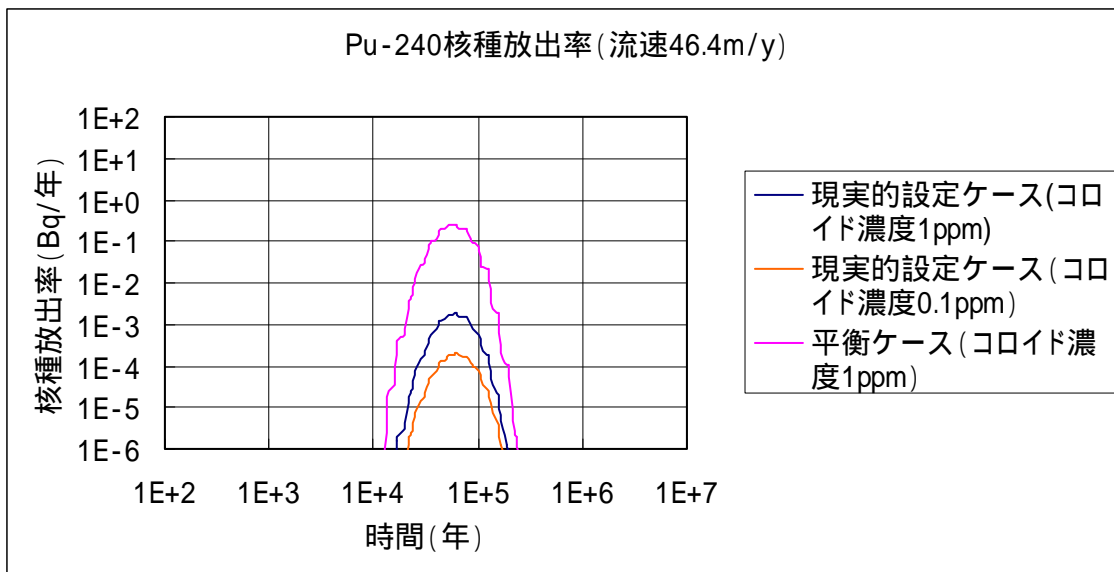


図 7.3-17 平衡ケースと現実的設定ケースの比較 (流速 46.4m/y)

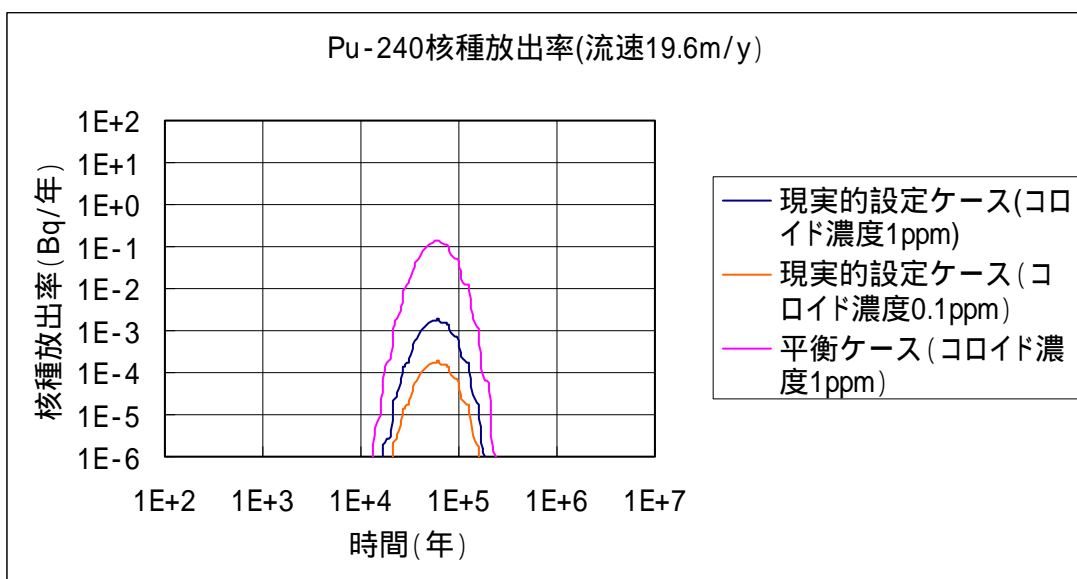


図 7.3-18 平衡ケースと現実的設定ケースの比較 (流速 19.6m/y)

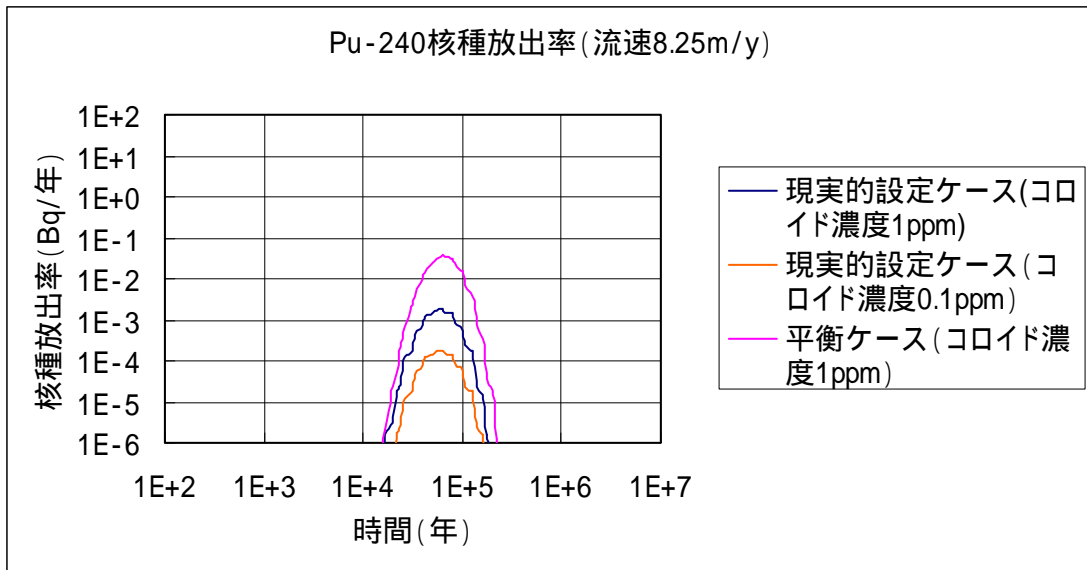


図 7.3-19 平衡ケースと現実的設定ケースの比較 (流速 8.25m/y)

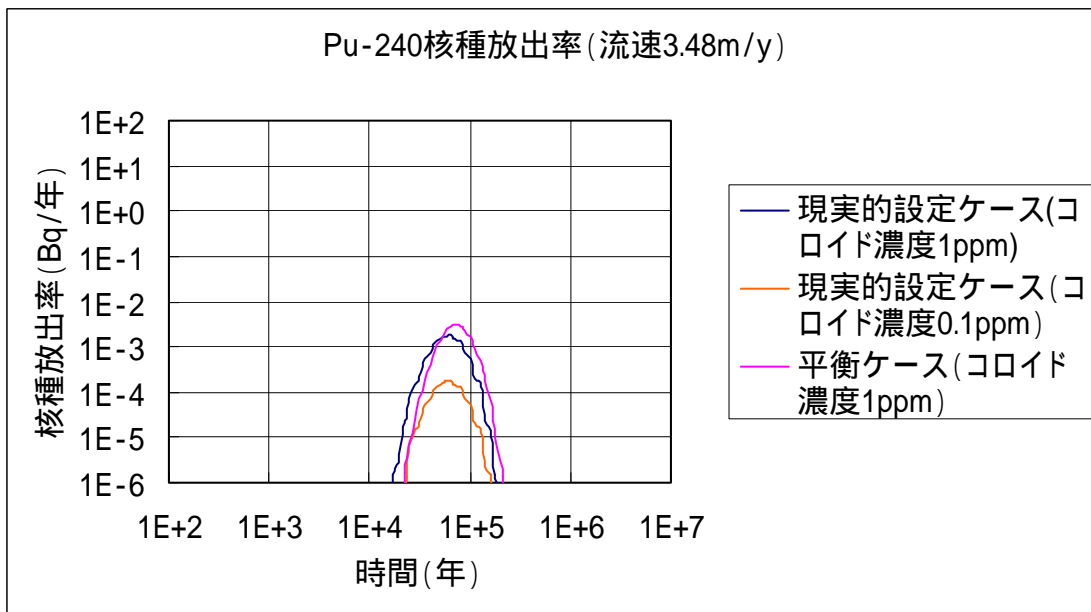


図 7.3-20 平衡ケースと現実的設定ケースの比較 (流速 3.48m/y)

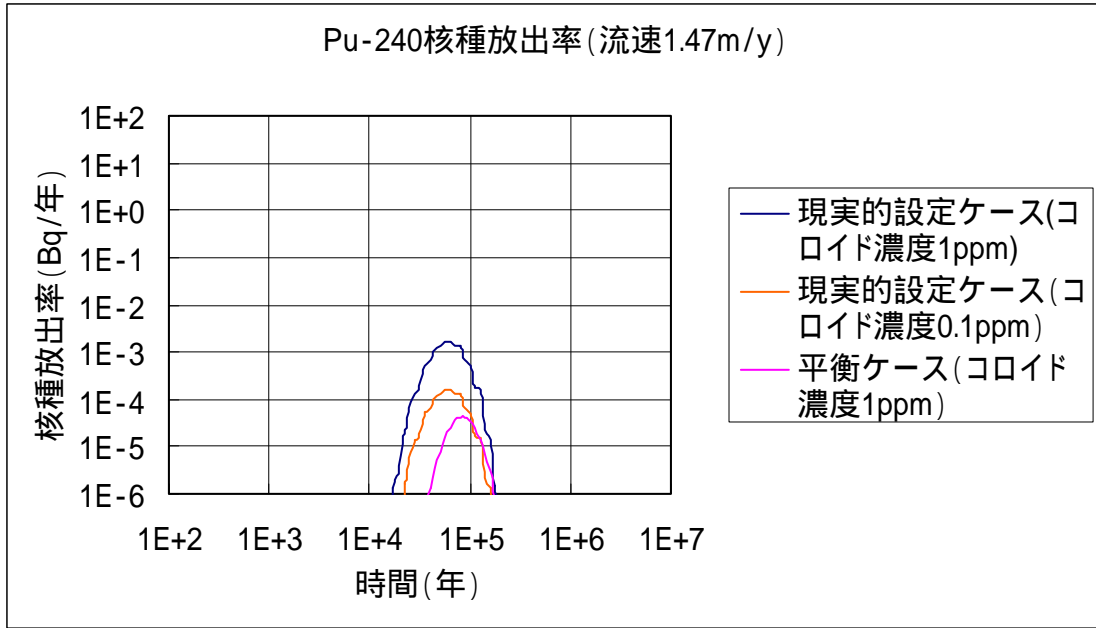


図 7.3-21 平衡ケースと現実的設定ケースの比較 (流速 1.47m/y)

(5)線量値

線量値は、Am-243 核種の現実的設定ケースでは $1 \times 10^{-13} \text{Sv/y}$ (図 7.3-13)、Pu-240 核種の現実的設定ケースでは $2 \times 10^{-15} \text{Sv/y}$ (図 7.3-16) である。

Cs-135 核種の断層からの線量値は、コロイド濃度が 1ppm の場合に $6 \times 10^{-9} \text{Sv/y}$ であり、同じコロイド濃度の Am-243 核種、Pu-240 核種に比べて何桁も高く、今回の評価核種 Np-237、U-236、Am-243、Pu-240、Cs-135 の中で、線量値が最も高いことが示された。Cs-135 核種について、コロイド濃度が 5ppm、10ppm と高くなると、線量値はさらに高くなり、 $8 \times 10^{-9} \text{Sv/y}$ 、 $1 \times 10^{-8} \text{Sv/y}$ と上昇することが示された (図 7.3-10)。

(6)まとめ

母岩及び断層からの核種放出率のピーク値の大小関係をまとめたものを、以下の表に示す。

表 7.3-1 現実的なパラメータ設定ケースのまとめ

	母岩からの核種放出率のピーク	断層からの核種放出率のピーク
Np-237(1ppm)	現実＝平衡＝コロイド無し	現実＝平衡＝コロイド無し
U-236(1ppm)	現実＝平衡＝コロイド無し	現実＝平衡＝コロイド無し
Am-243(1ppm)	現実＞平衡＞コロイド無し	現実＞平衡＞コロイド無し
Pu-240(1ppm)	平衡＞現実＞コロイド無し	平衡＞現実＞コロイド無し
Cs-135(1ppm)	現実＝平衡＝コロイド無し	現実＝平衡＝コロイド無し
Cs-135 (1,5,10ppm)	現実(10ppm)>現実(5ppm)>現実 (1ppm)	現実(10ppm)>現実(5ppm)>現 実(1ppm)

7.3.2 パラメータ変更ケースに関する評価結果

(1)解析内容

速度定数 β の値を現実的な値よりも小さく設定し、感度解析的に、速度定数 β の値を変化させて解析を行った。また、 α β 比を変えずに、 α 、 β の値を共に小さくした場合の評価も行った。

人工バリアからの核種フラックスとしては、第2次取りまとめコロイドケースの結果を入力として用い、母岩、断層中の核種移行を COLFRAC-mrl を用いて解析した。核種 Np-237、U-236、Am-243、Pu-240、及び Cs-135 について解析した。各核種のガラス固化体1本あたりの母岩からの核種放出率、及び断層からの核種放出率を解析した。さらに、断層からの核種放出率を生物圏モデルとして河川水シナリオを想定した場合の線量換算係数を用いてガラス固化体4万本についての線量に換算した。

(2)Np-237 核種についての評価結果

Np-237 核種について、パラメータ変更ケースの解析結果を以下に示す。

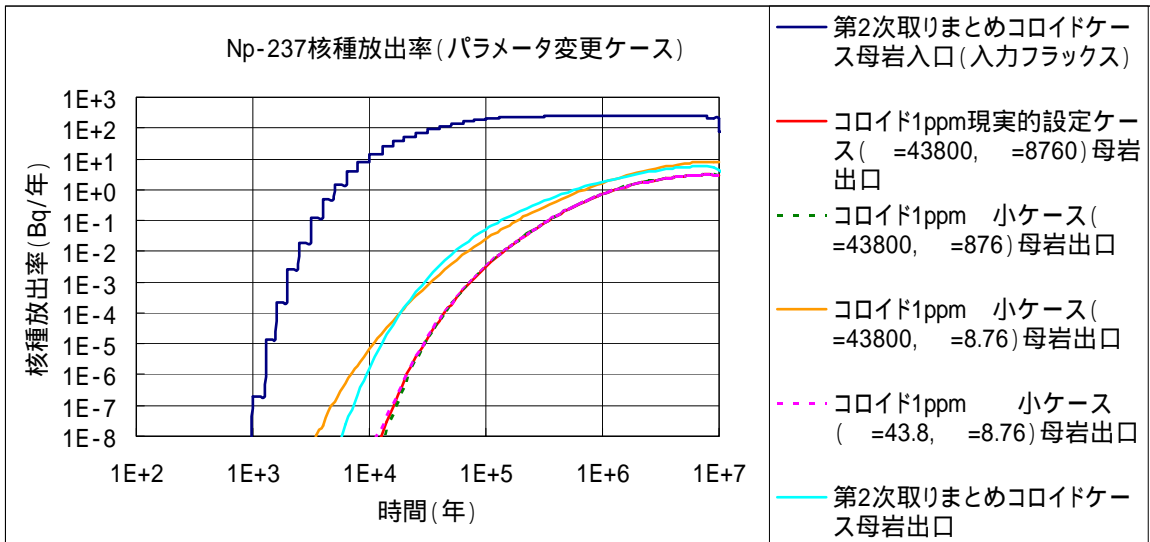


図 7.3-22 母岩からの Np-237 核種放出率 (パラメータ変更ケース)

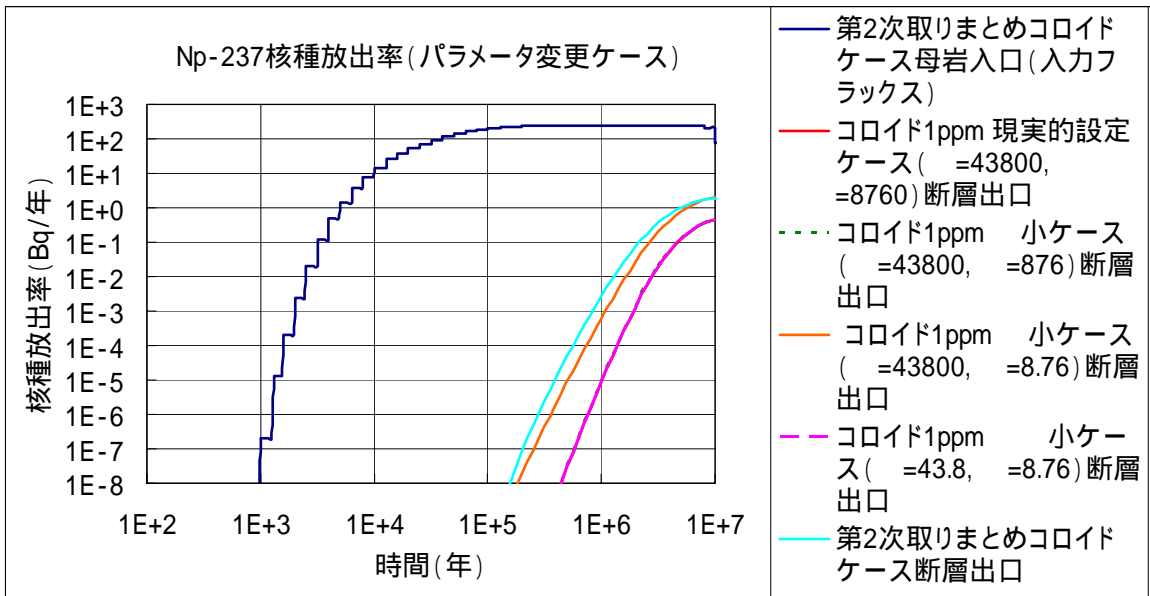


図 7.3-23 断層からの Np-237 核種放出率 (パラメータ変更ケース)

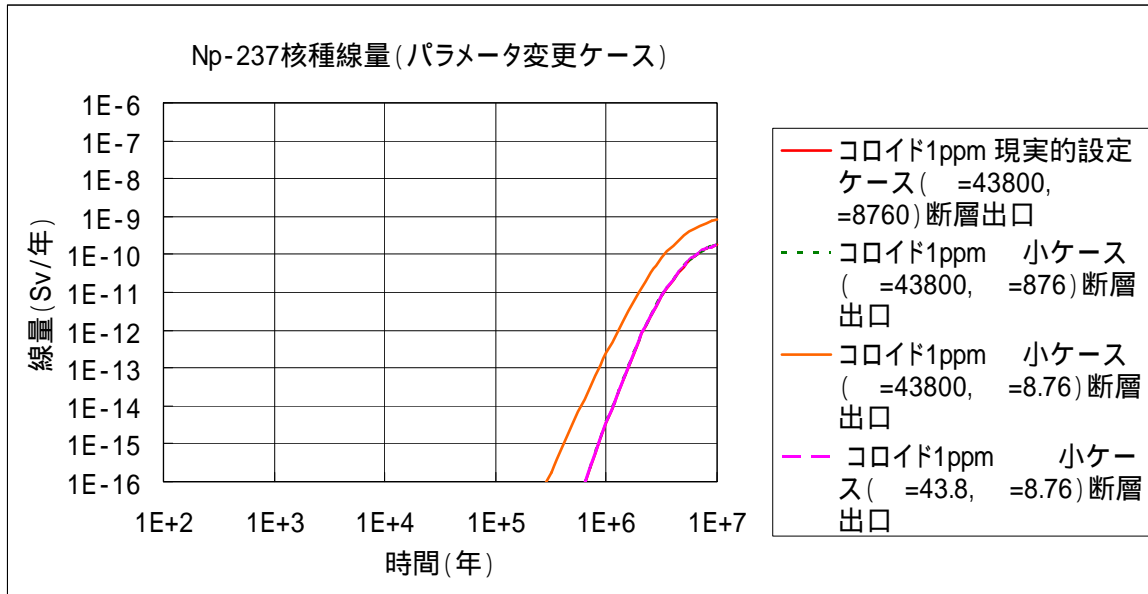


図 7.3-24 ガラス固化体 4 万本についての Np-237 核種線量 (パラメータ変更ケース)

Np-237 の場合、コロイドへの収着量に関する逆方向速度定数 β を現実的な値よりも十分の一程度に小さく設定した場合には変化は認められず、千分の一程度に小さく設定した場合に、核種移行の促進が認められた (β 小ケース)。

速度定数 α と β の値を、速度定数比 (α/β) を変えないように千分の一に設定した場合 ($\alpha \beta$ 小ケース) には、現実的設定ケースの解析結果との違いは認められなかった。

(3)U-236 核種についての評価結果

U-236 核種について、パラメータ変更ケースの解析結果を以下に示す。

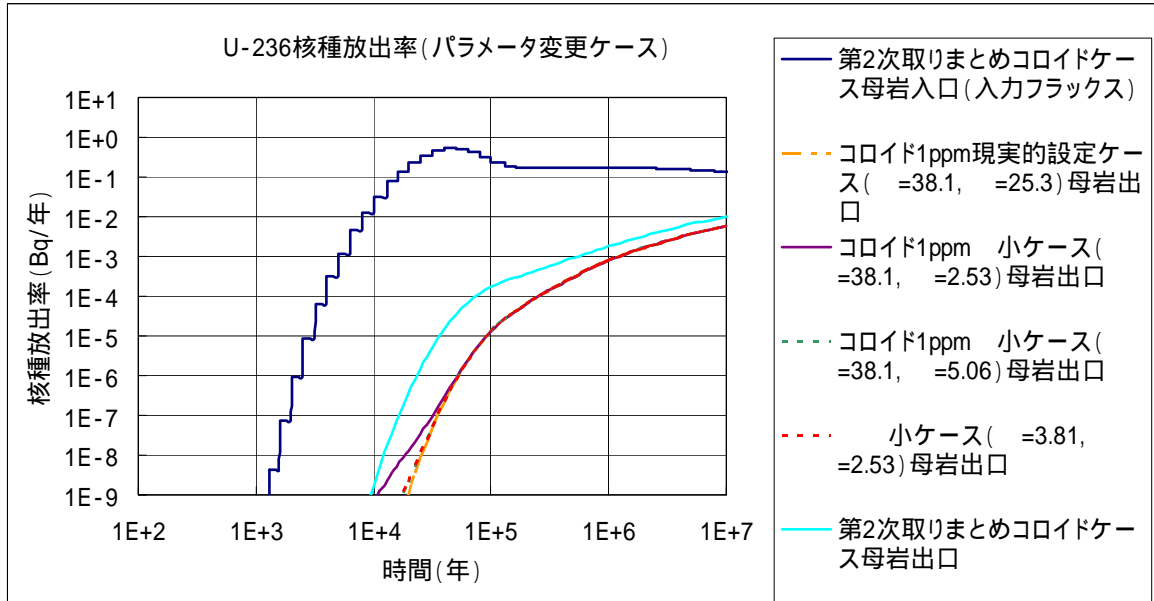


図 7.3-25 母岩からの U-236 核種放出率 (パラメータ変更ケース)

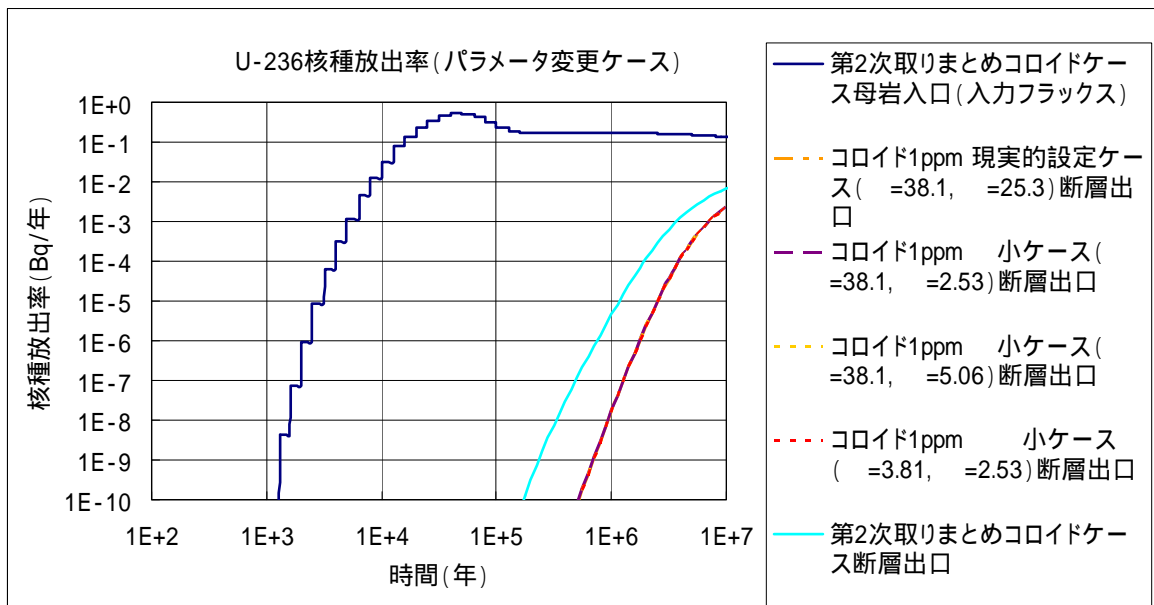


図 7.3-26 断層からの U-236 核種放出率 (パラメータ変更ケース)

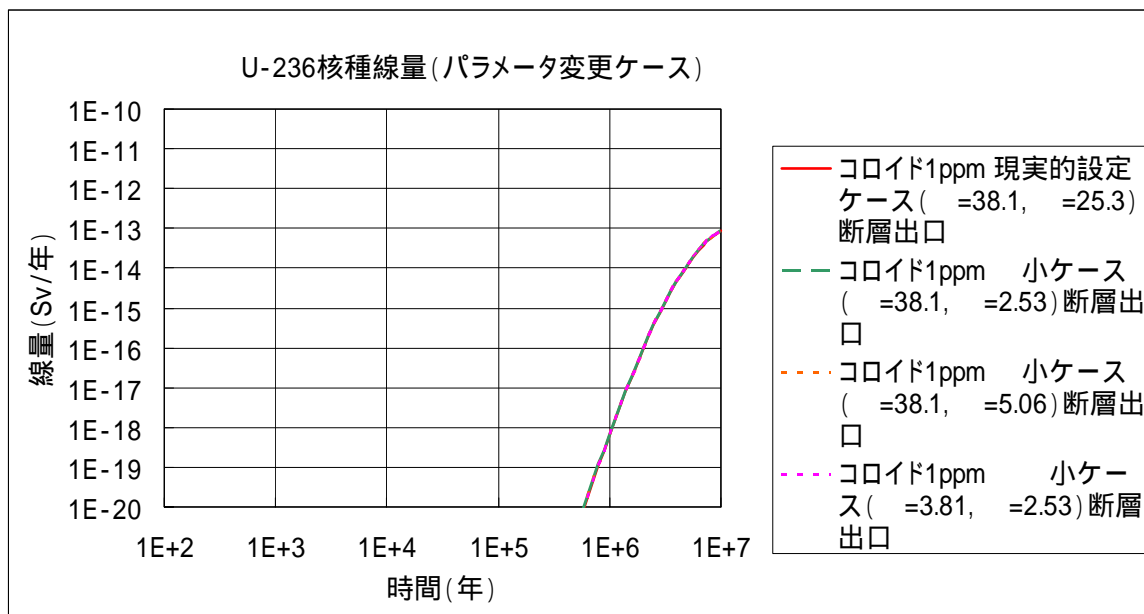


図 7.3-27 ガラス固化体 4 万本についての U-236 核種線量 (パラメータ変更ケース)

U-236 に関しては、逆方向速度定数 β を現実的な値よりも五分の一程度に小さく設定しても変化は認められず、十分の一程度に小さく設定した場合には、母岩からの核種放出率に関して、短期的に多少移行が促進される傾向が認められた (図 7.3-25)。しかし、長期的なふるまいは現実的な設定ケースと同じであった (β 小ケース)。

速度定数 α と β の値を、速度定数比 (α/β) を変えないように共に十分の一に設定した場合 ($\alpha \beta$ 小ケース) には、母岩及び断層出口の放出率、及び線量の評価結果は、現実的な速度定数を設定した場合の結果と大きな違いは認められなかった。(図 7.3-26 及び図 7.3-27)

(4)Am-243 核種に関する評価結果

Am-243 核種について、パラメータ変更ケースの解析結果を以下に示す。

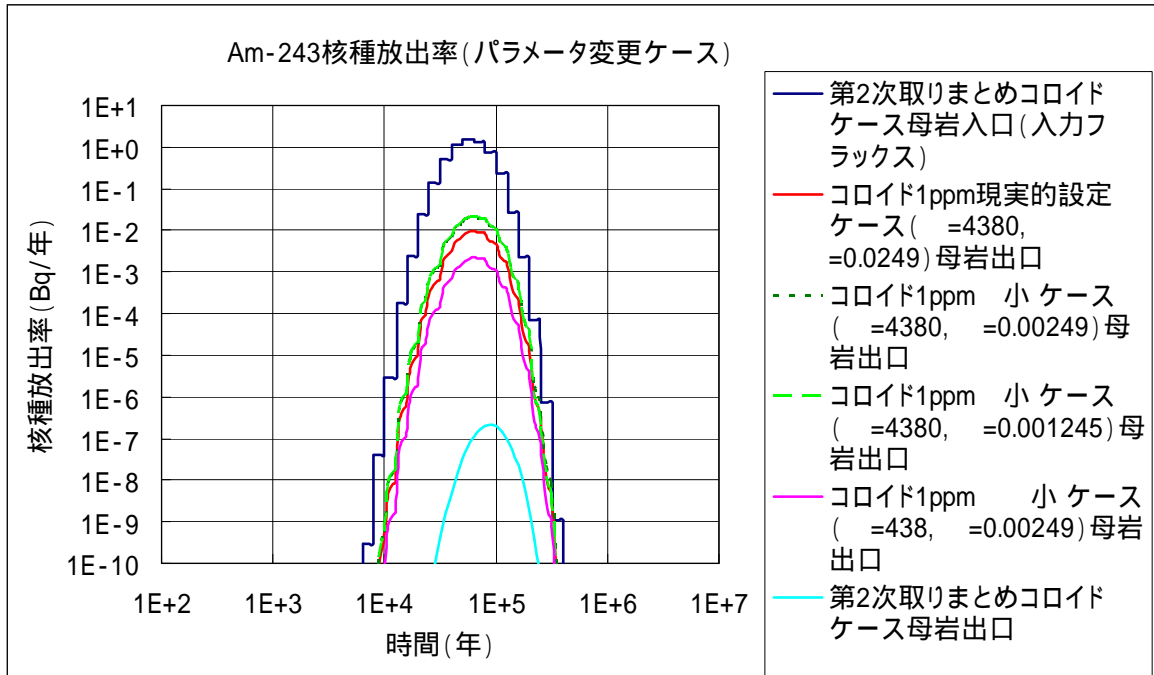


図 7.3-28 母岩からの Am-243 核種放出率 (パラメータ変更ケース)

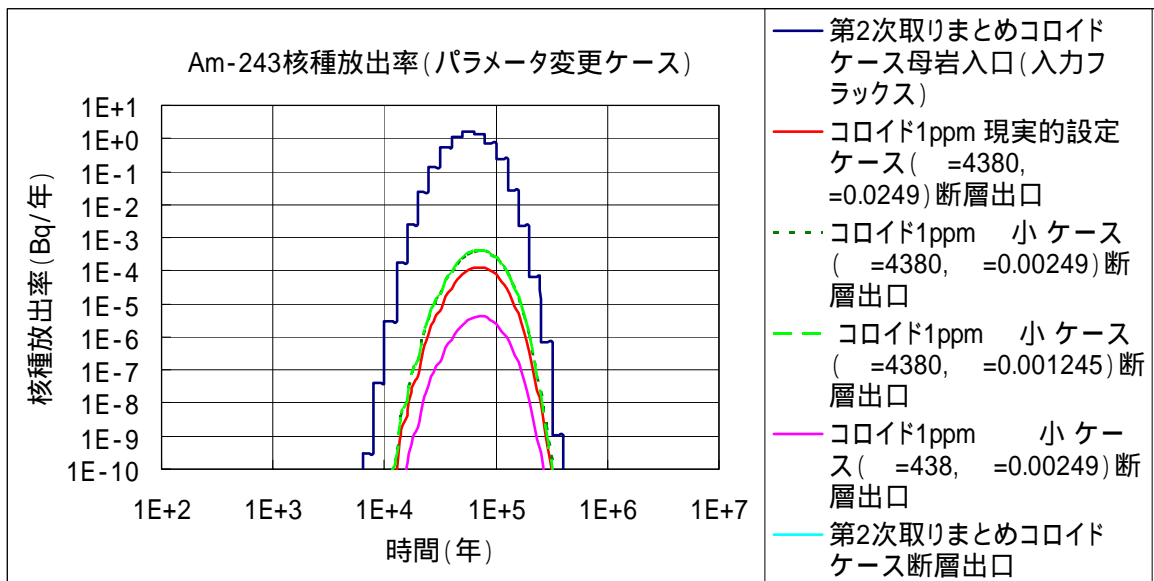


図 7.3-29 断層からの Am-243 核種放出率 (パラメータ変更ケース)

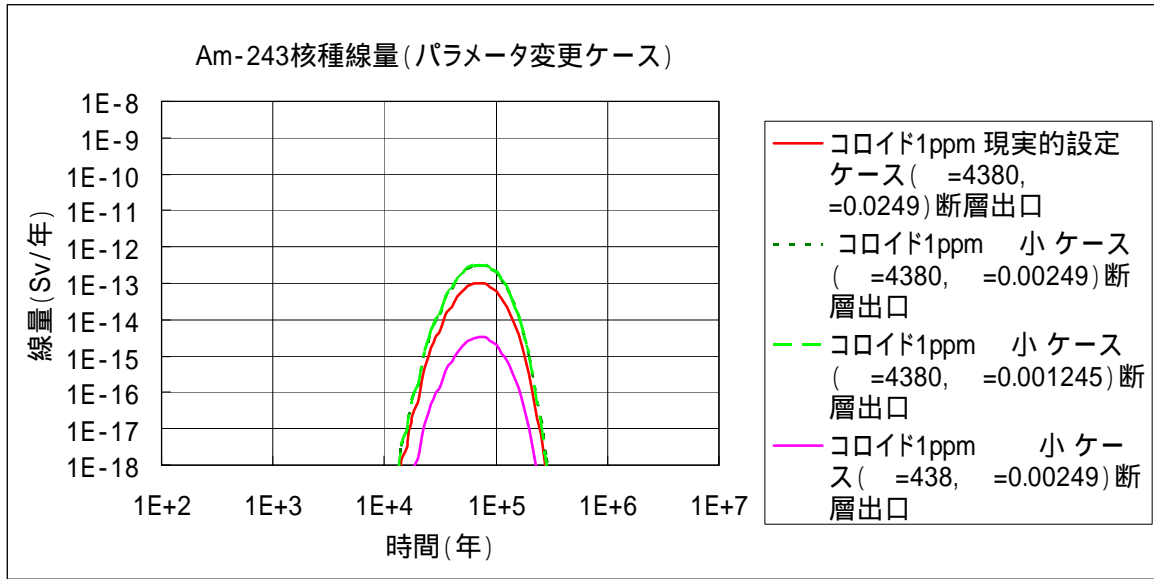


図 7.3-30 ガラス固化体 4 万本についての Am-243 核種線量 (パラメータ変更ケース)

Am-243 核種に関しては、速度定数 β の値を一桁小さくすると、分配係数に相当する速度定数の比 (α/β) が大きくなるため、現実的設定ケースよりもピーク値が高くなり、コロイド影響がより顕著になる傾向が示された。 β の値を二十分の一に小さく設定した場合 ($\beta=0.001245$) の計算結果は、 β の値を十分の一に小さく設定した ($\beta=0.00249$) 結果と重なった (β 小ケース) (図 7.3-28、図 7.3-29、及び図 7.3-30)。

速度定数 α 、及び β の値を共に一桁小さくした場合には、現実的設定ケースよりもピーク値は低くなり、コロイド影響は小さくなった ($\alpha\beta$ 小ケース)。これは、 $\alpha\beta$ 小ケースでは速度定数 α 、及び β の値が小さく設定され、コロイドとの相互作用が小さくなるためと考えられる。

(5)Pu-240 核種に関する評価結果

Pu-240 核種について、パラメータ変更ケースの解析結果を以下に示す。

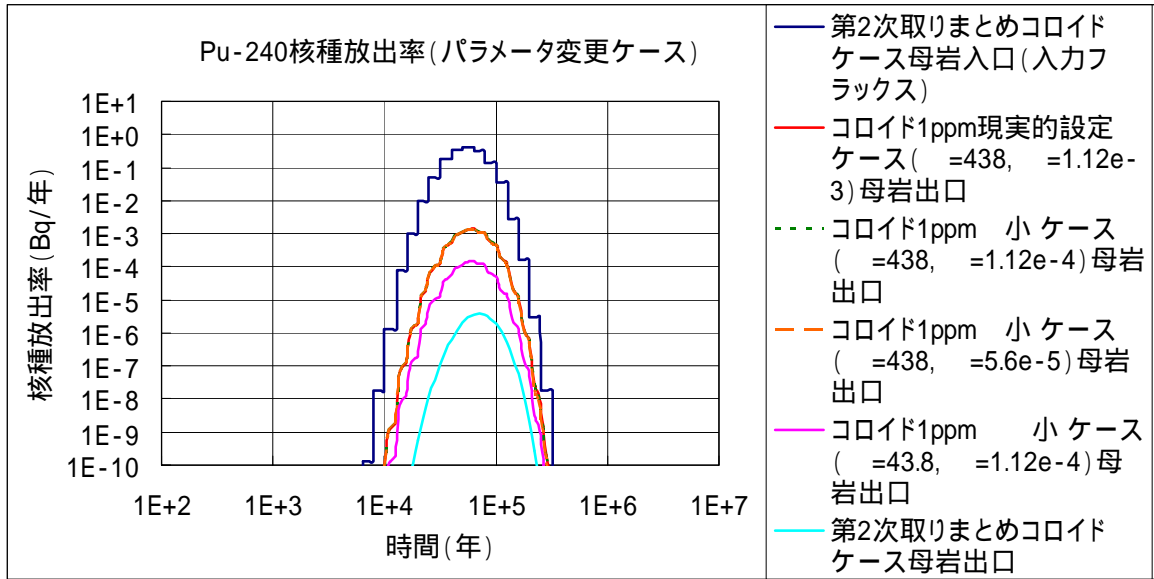


図 7.3-31 母岩からの Pu-240 核種放出率 (パラメータ変更ケース)

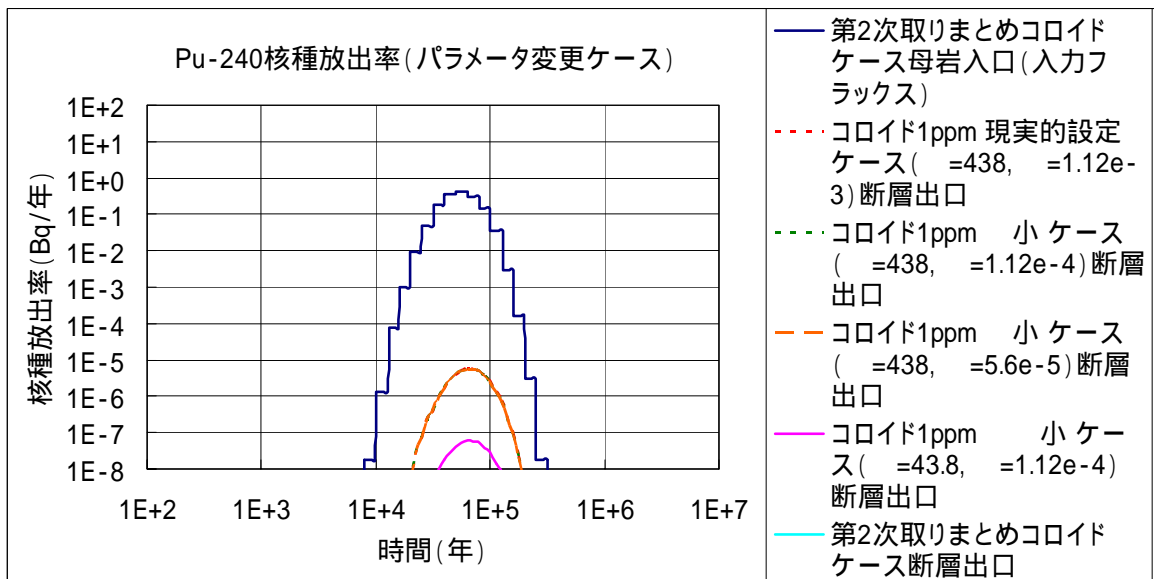


図 7.3-32 断層からの Pu-240 核種放出率 (パラメータ変更ケース)

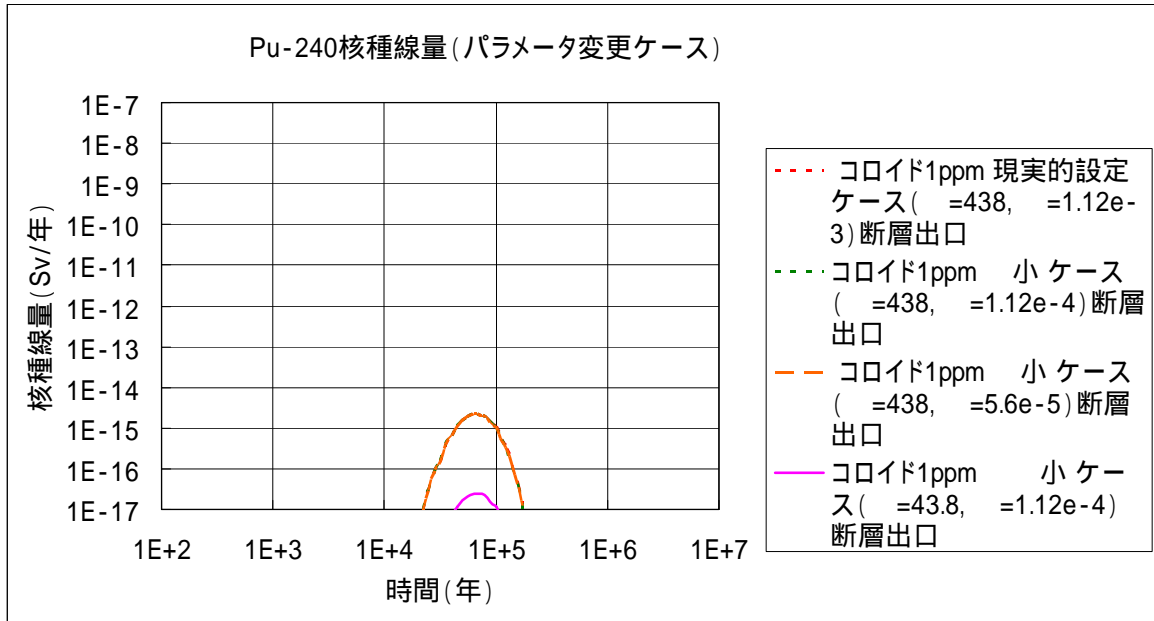


図 7.3-33 ガラス固化体 4 万本についての Pu-240 核種線量 (パラメータ変更ケース)

核種のコロイドに対する分配係数が大きく、コロイド影響が顕著であり、速度定数 β の絶対値が小さい核種 Pu-240 に関して、 β の値を一桁小さく設定、又は二十分の一に設定した場合には、現実的設定ケースと結果が変わらないことが示された (β 小ケース)。これは、速度定数 β が小さいため、速度定数 α によりコロイドへの核種の収着反応が支配されているためと考えられる。

また、速度定数 α 、及び β の値を共に一桁小さくした場合には、現実的設定ケースよりもピーク値は低くなり、コロイド影響は小さくなった ($\alpha \beta$ 小ケース)。これは、 $\alpha \beta$ 小ケースでは速度定数 α 、及び β の値が小さく設定され、コロイドとの相互作用が小さくなるためと考えられる。(図 7.3-31、図 7.3-32、及び図 7.3-33)

(6)Cs-135 核種に関する評価結果

Cs-135 核種について、パラメータ変更ケースの解析結果を以下に示す。

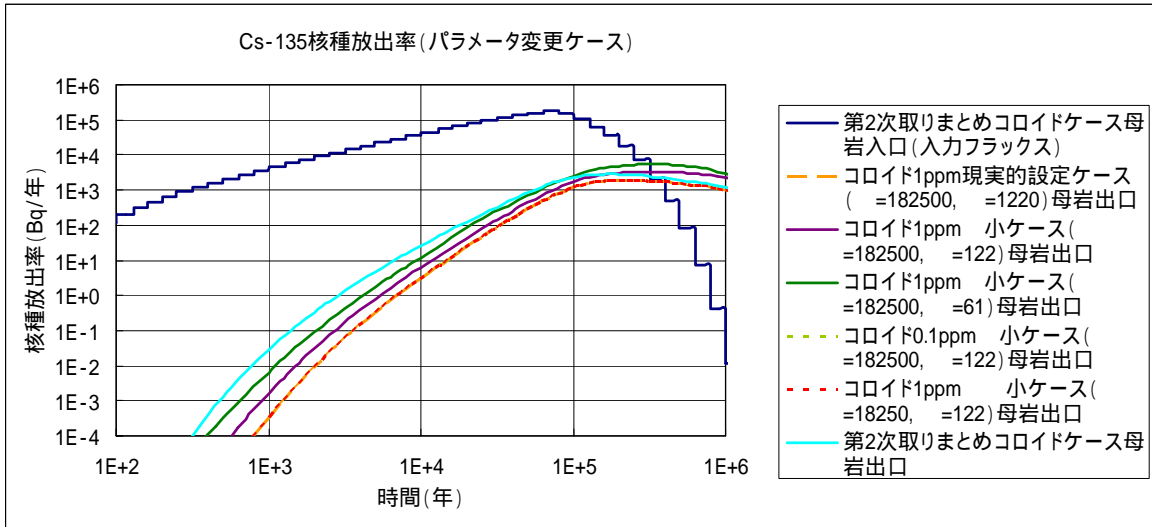


図 7.3-34 母岩からの Cs-135 核種放出率 (パラメータ変更ケース)

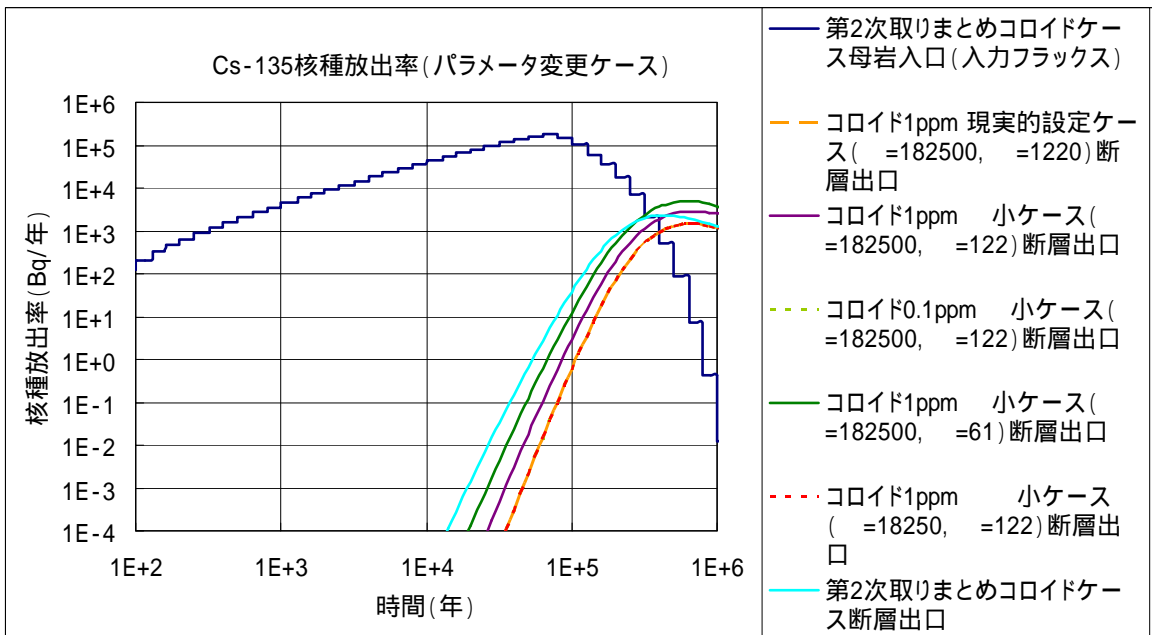


図 7.3-35 断層からの Cs-135 核種放出率 (パラメータ変更ケース)

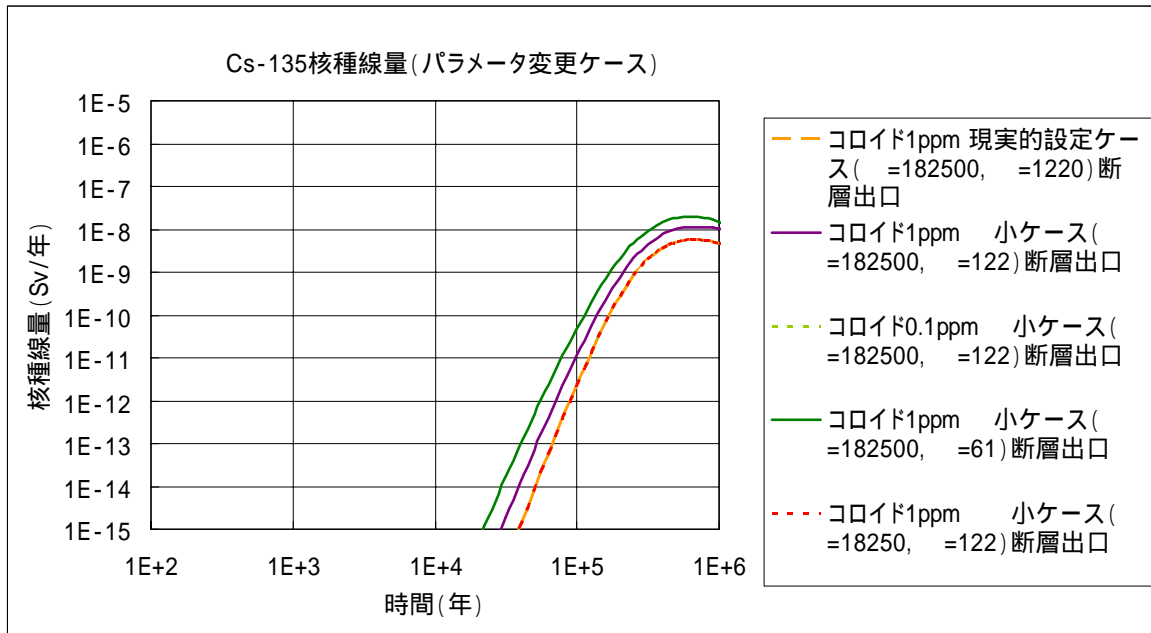


図 7.3-36 ガラス固化体 4 万本についての Cs-135 核種線量 (パラメータ変更ケース)

コロイド濃度 1ppm の場合に、 β を十分の一、又は二十分の一に設定すると、核種移行が促進する傾向が認められた (図 7.3-34～図 7.3-36) (β 小ケース)。

コロイド濃度 1ppm の β 小ケースで認められた核種移行の促進の原因としては、逆方向速度定数 β を一桁小さく設定したことにより、速度定数 α 、及び β の比が変わり、核種のコロイドに対する分配係数が現実的設定ケースよりも一桁大きい 1500kg/m^3 に設定された事が考えられる。 β 値を二十分の一に設定した場合には、核種のコロイドに対数分配係数がさらに大きく 3000kg/m^3 に設定されるため、コロイド影響が増加して核種移行の促進及び線量値の増大が認められた。

β を十分の一に設定 (β 小ケース) した場合でも、コロイド濃度を 0.1ppm に設定すると、放出率及び線量は現実的設定ケースと完全に重なり、核種移行の促進は認められなかった (図 7.3-34～図 7.3-36)。

Cs-135 核種に関して、速度定数 α 、及び β の値を、速度定数比 (α/β) を変えないように、共に十分の一に設定した場合、現実的設定ケースと結果に大きな違いは認められなかった (α/β 小ケース)。

Cs-135 核種に関する各流速についてのコロイド濃度依存性に関しては、7.3.3 で検討する。

以上より、パラメータ変更ケース（ β 小ケース、 $\alpha\beta$ 小ケース）の母岩及び断層からの核種放出率ピーク値の大小関係についてまとめたものを以下の表に示す。核種移行計算では、人工バリアからの核種フラックスは、全核種について第2次取りまとめコロイドケースの結果を用いた。

表 7.3-2 パラメータ変更ケースのまとめ（コロイド濃度 1ppm）

	母岩からの核種放出率のピーク	断層からの核種放出率のピーク
Np-237	β 小(1/10)=現実= $\alpha\beta$ 小	β 小(1/10)=現実= $\alpha\beta$ 小
U-236	β 小(1/10)=現実= $\alpha\beta$ 小	β 小(1/10)=現実= $\alpha\beta$ 小
Am-243	β 小(1/10)>現実> $\alpha\beta$ 小	β 小(1/10)>現実> $\alpha\beta$ 小
Pu-240	β 小(1/10)=現実> $\alpha\beta$ 小	β 小(1/10)=現実> $\alpha\beta$ 小
Cs-135	β 小(1/10)>現実= $\alpha\beta$ 小	β 小(1/10)>現実= $\alpha\beta$ 小

7.3.3 Cs-135 核種の濃度依存性に関する解析

母岩からの核種放出率を、3種の地下水流速について図 7.3-37～図 7.3-39 に示す。これらの図から、コロイド濃度が 10ppm の場合に最も核種移行が促進されており、コロイド濃度が 5ppm、1ppm と低下するに伴い核種移行の促進効果が弱くなる傾向が示されている。さらに、流速の低下と共に核種放出率のピーク時間が遅くなり、コロイド濃度の違いによる核種放出率のピーク高さの差がより大きくなる傾向が認められた。

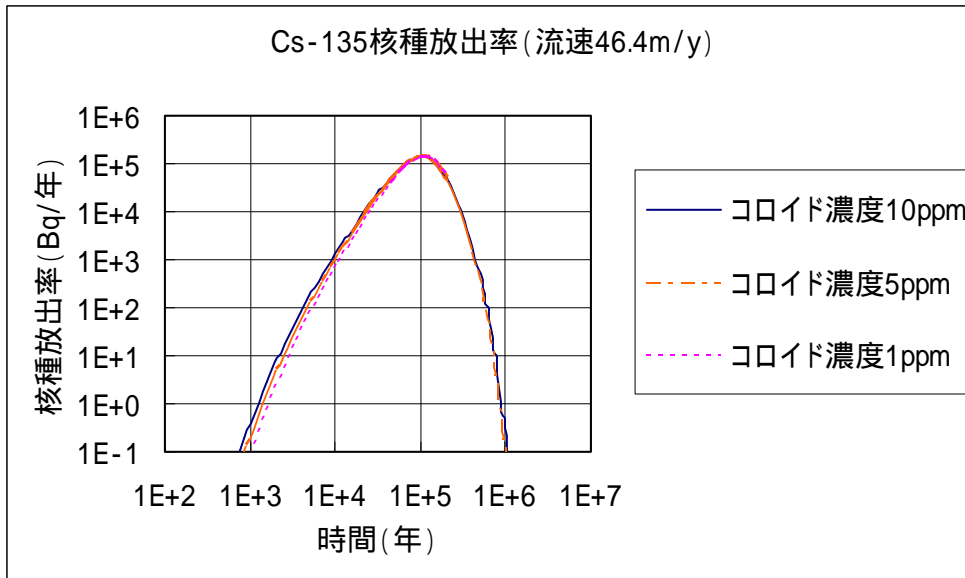


図 7.3-37 母岩からの Cs-135 核種放出率 (流速 46.4m/y)

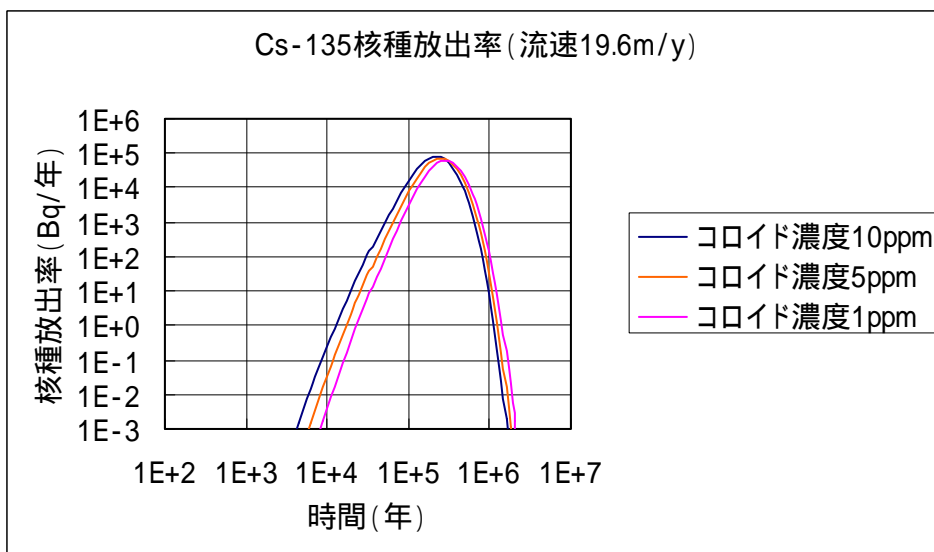


図 7.3-38 母岩からの Cs-135 核種放出率 (流速 19.6m/y)

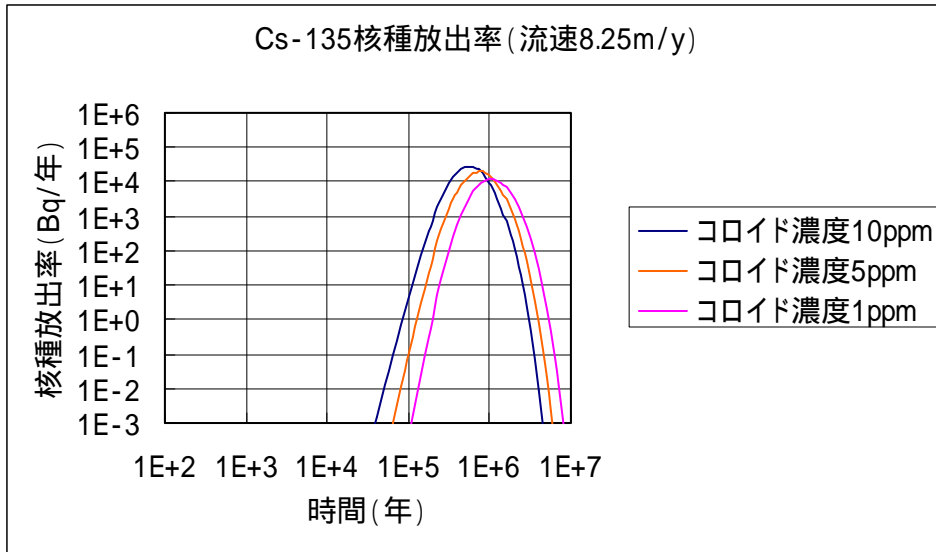


図 7.3-39 母岩からの Cs-135 核種放出率 (流速 8.25m/y)

7.3.4 Am-243 核種に関する α/β 変更ケースの解析

核種のコロイドに対する分配係数が大きく、コロイド影響が大きく認められた核種 Am-243 に関して、速度定数を平衡状態と考えられるほど大きな値から、速度定数比を変えずに ($\alpha/\beta=1.76 \times 10^5 \text{ m}^3/\text{kg}$ に固定) 段階的に値を減少させて解析を行った。また、速度定数比を現実的な値よりも一桁小さく設定した場合 ($\alpha/\beta=1.76 \times 10^4 \text{ m}^3/\text{kg}$ に固定) についても、同様の感度解析を行った。

(1)人工バリアからの核種フラックスの設定

前項までの解析では、人工バリアからの核種フラックスとして、第2次取りまとめのコロイドケースのデータ (コロイド濃度 χ が 1ppm、核種のコロイドに対する分配係数 Kd が $1000 \text{ m}^3/\text{kg}$ 程度のコロイド影響を想定) を利用して解析を行った。しかし、コロイド濃度、核種のコロイドに対する分配係数 Kd が第2次取りまとめの値と異なる場合には、コロイド濃度 χ 、及び核種のコロイドに対する分配係数 Kd を評価して線量を解析する必要がある。コロイド濃度を χ 、核種のコロイドに対する分配係数を Kd 、掘削影響領域通過流量を Q とすると、みかけの掘削影響領域通過流量 Q' は、次式に示すように Q に比べて $(1 + \chi Kd)$ 倍に変化する。(核燃料サイクル開発機構,1999)

$$Q' = (1 + \chi Kd)Q \quad \text{式(7.3.4-1)}$$

ここで、

Q' : みかけの掘削影響領域通過流量[m³/y]

χ : コロイド濃度[kg/m³]

K_d : 核種のコロイドへの分配係数[m³/kg]

Q : 掘削影響領域通過流量[m³/s]

である。

Am-243 核種では、コロイド濃度が 1ppm の場合にはみかけの掘削影響領域通過流量が、掘削影響領域通過流量の 177 倍大きくなる。このような条件で核種を解析すると COLFRAC-mrl の数値計算結果が不安定になる傾向が認められたため、コロイド濃度を 0.1ppm と小さく設定して解析を行った。前項までの解析では、第 2 次取りまとめ中のコロイドケースのデータを利用しているため、みかけの掘削影響領域通過流量は、掘削影響領域通過流量の 2 倍程度であった。従って、コロイド濃度が 1ppm の場合でも COLFRAC-mrl の解析が不安定になることなく実施できたと考えられる。

(2) 解析内容

Am-243 核種についてコロイド濃度が 0.1ppm の場合に、現実的な K_d 値 ($1.76 \times 10^5 \text{m}^3/\text{kg}$) を設定した場合の人工バリアからの核種放出率、及び現実的 K_d 値よりも K_d 値が一桁小さい場合 ($K_d=1.76 \times 10^4 \text{m}^3/\text{kg}$) の人工バリアからの核種放出率を、一次元核種移行解析コード FRONT (動力炉・核燃料開発事業団、1996) を用いて解析した (図 7.3-40)。

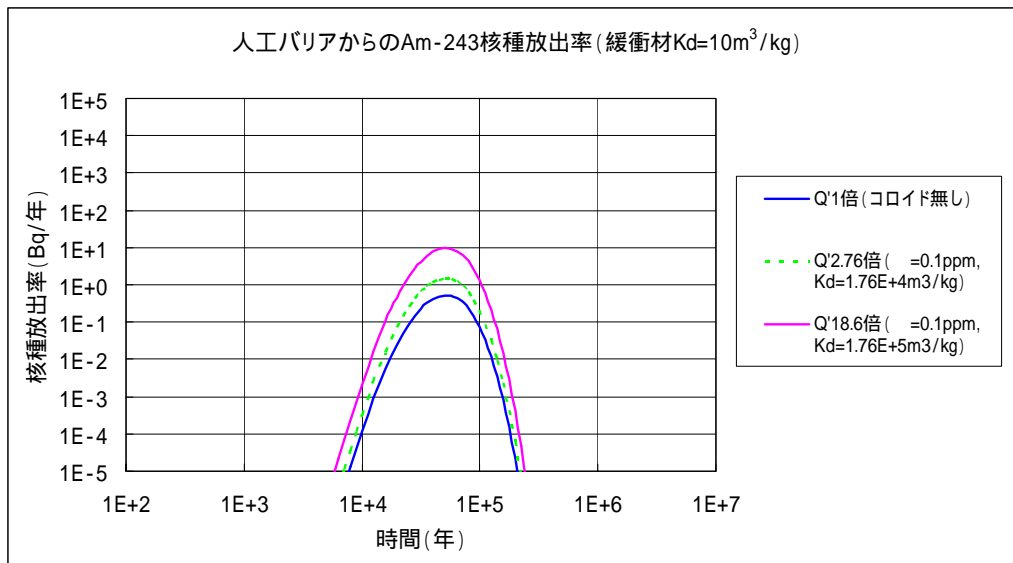


図 7.3-40 人工バリアからの Am-243 核種フラックス (FRONT による解析結果)

人工バリアからの Am-243 核種のフラックスとして図 7.3-40 の 18.6Q (みかけの掘削影響領域通過流量が、掘削影響領域通過流量の 18.6 倍) のデータを用いて、コロイド濃度 0.1ppm、及び $\alpha/\beta=1.76 \times 10^5 \text{ m}^3/\text{kg}$ の場合の、 α/β 変更ケースの解析を行った。速度定数比 (α/β) を $1.76 \times 10^5 \text{ m}^3/\text{kg}$ に固定して、 α 及び β の値を平衡状態と考えられるほど大きな値から段階的に減少させて解析を行った。

次に、人工バリアからの Am-243 核種のフラックスとして図 7.3-40 の 2.76Q の結果を用いてコロイド濃度 0.1ppm、及び $\alpha/\beta=1.76 \times 10^4 \text{ m}^3/\text{kg}$ の α/β 変更ケースの解析を行った。速度定数比 (α/β) を $1.76 \times 10^4 \text{ m}^3/\text{kg}$ に固定して、 α 及び β の値を平衡状態と考えられるほど大きな値から段階的に減少させて解析を行った。

(3) 解析結果 (Am-243 の α/β 変更ケース)

人工バリアからの Am-243 核種のフラックスとして図 7.3-40 の 18.6Q のデータを用いて、コロイド濃度 0.1ppm、及び $\alpha/\beta=1.76 \times 10^5 \text{ m}^3/\text{kg}$ に設定した場合の、母岩からの核種フラックスの解析結果を図 7.3-41 に、断層からの線量の解析結果を図 7.3-42 に示す。

次に、人工バリアからの Am-243 核種のフラックスとして図 7.3-40 の 2.76Q の結果を用いてコロイド濃度 0.1ppm、及び $\alpha/\beta=1.76 \times 10^4 \text{ m}^3/\text{kg}$ に設定した場合の、母岩からの核種フラックスの解析結果を図 7.3-43 に、断層からの線量の解析結果を図 7.3-44

に示す。

速度定数 α 、及び β の値を大きく設定した場合 ($\alpha=43800000$, $\beta=249$) には、平衡ケース ($\alpha=1.76 \times 10^{15}$, $\beta=1.0 \times 10^{10}$) と放出率、及び線量値の結果共にカーブが重なる。速度定数比 (α/β) を固定したまま、速度定数 α 、及び β の値を減少させて、核種のコロイドへの収着速度を小さくすると核種移行が促進されて放出率、及び線量値のピーク値が上昇し、速度定数 α 、及び β の値を ($\alpha=21900$, $\beta=0.1245$) と設定した場合にピーク値が最大となる。さらに速度定数 α 、 β の値を共に減少させると、核種とコロイドとの相互作用が弱くなるため、逆に放出率及び線量値のピーク値が減少していく様子が認められた。(図 7.3-41、及び図 7.3-42)

コロイドに対する核種の分配係数が一桁小さいケース (コロイド濃度 0.1ppm、核種のコロイドに対する分配係数が $1.76 \times 10^4 \text{ m}^3/\text{kg}$) についても、同じ傾向が認められた。

速度定数 α 、及び β の値を大きく設定した場合 ($\alpha=43800000$, $\beta=249$) には平衡ケースと放出率及び線量値のグラフがほぼ重なるが、速度定数比 (α/β) を固定したまま、速度定数 α 及び β の値を共に減少させると放出率及び線量値のピーク値が上昇し、速度定数 α 、 β の値が ($\alpha=2190$, $\beta=0.1245$) でピーク値が最大となる。その後速度定数 α 、 β の値が小さくなると、逆にピーク値が減少した。(図 7.3-43、及び図 7.3-43)

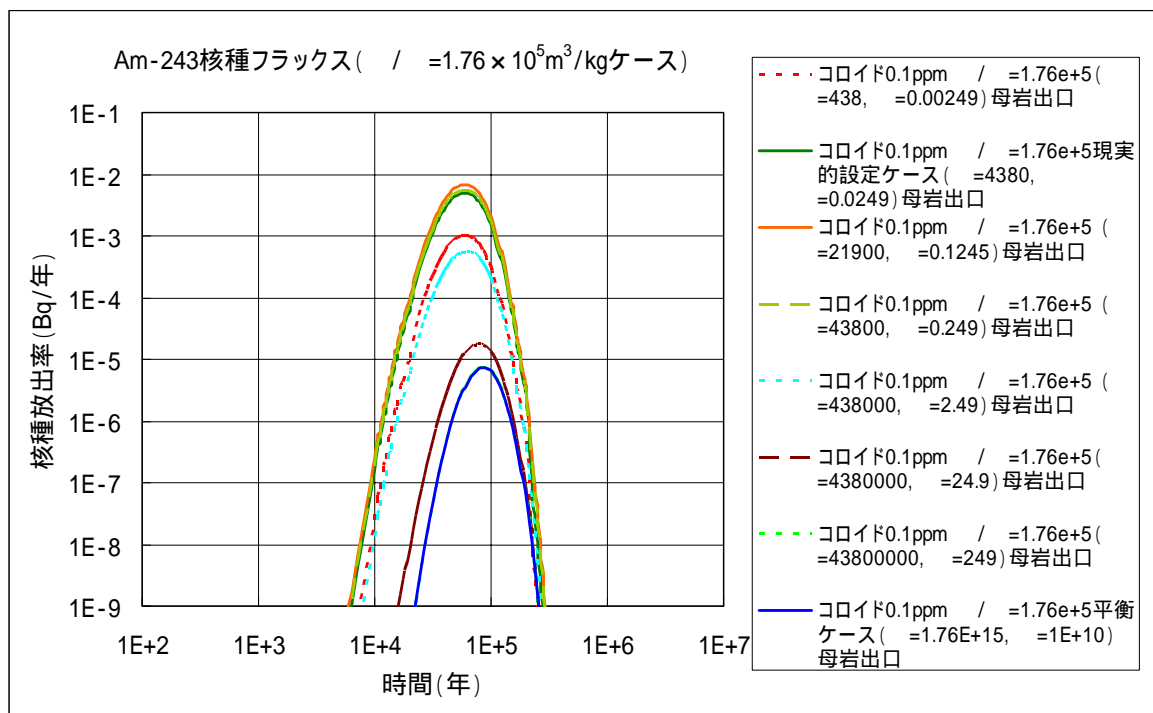


図 7.3-41 母岩からの Am-243 核種放出率 ($\alpha/\beta=1.76 \times 10^5 \text{ m}^3/\text{kg}$)

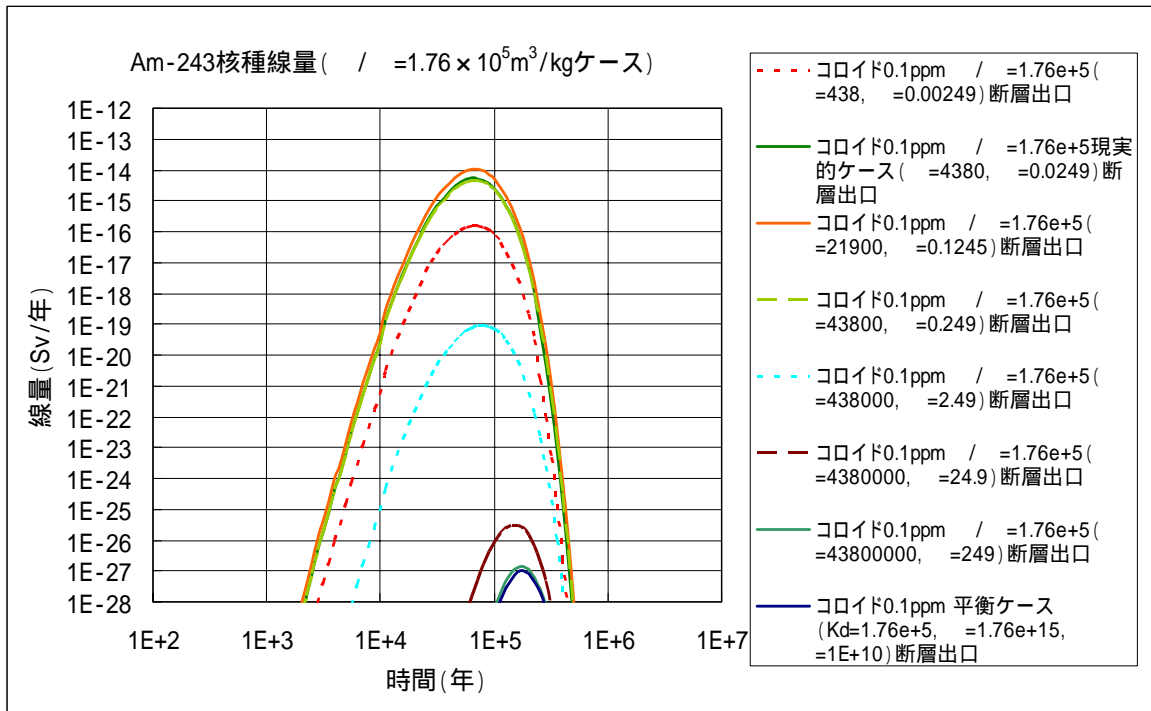


図 7.3-42 断層からの Am-243 核種線量 ($\alpha/\beta=1.76 \times 10^5 \text{ m}^3/\text{kg}$)

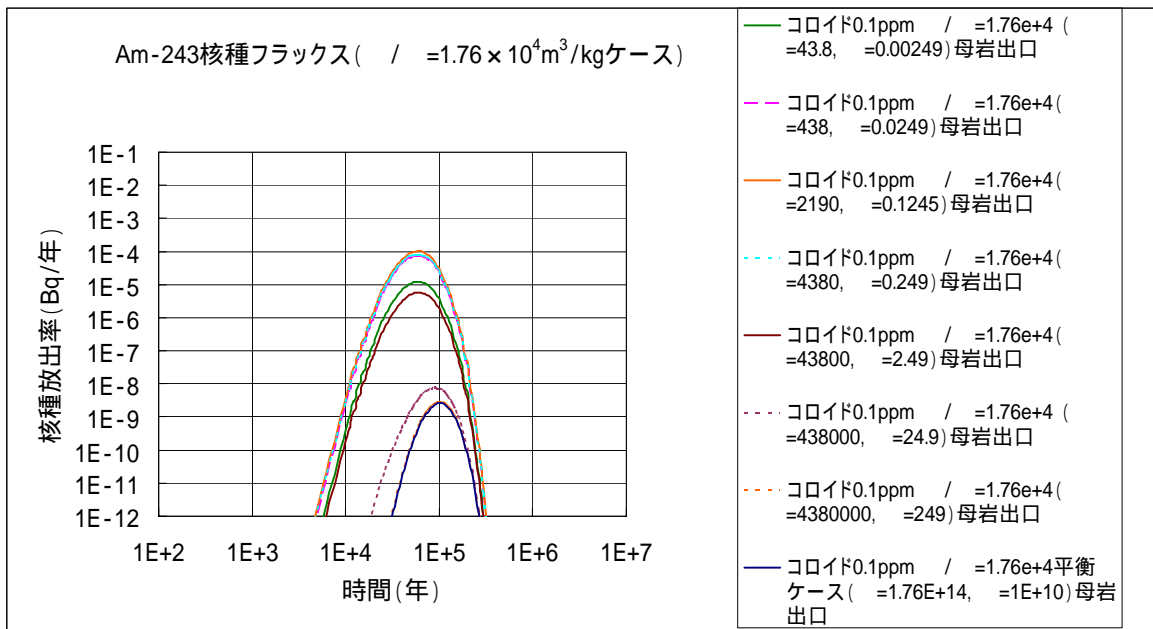


図 7.3-43 母岩からの Am-243 核種放出率 ($\alpha/\beta=1.76 \times 10^4 \text{ m}^3/\text{kg}$)

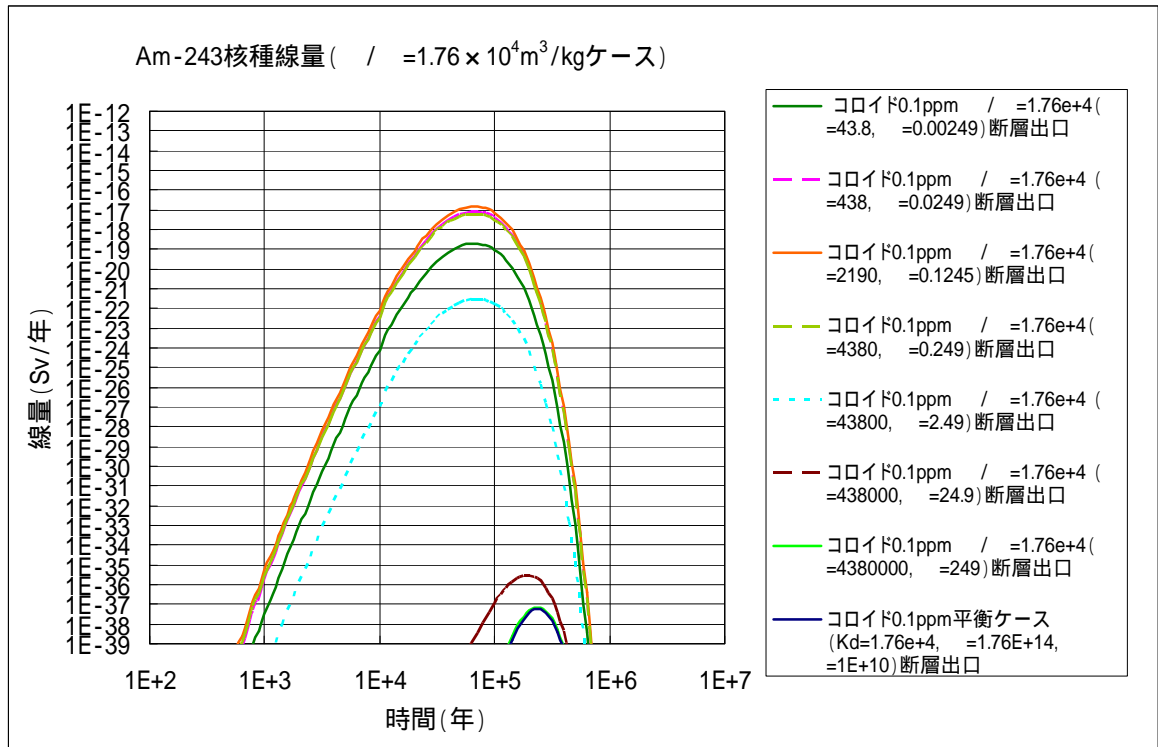


図 7.3-44 断層からの Am-243 核種線量 ($\alpha/\beta=1.76 \times 10^4 \text{m}^3/\text{kg}$)

(4)母岩からの核種放出率のピーク

母岩からの核種放出率（ガラス固化体 1 本あたり）、及び断層からの線量のピーク値の解析結果をまとめたものを、表 7.3-3 に示す。また、断層からの核種線量のピーク値について、速度定数比 (α/β) を 2 種類設定して、逆方向速度定数 β を変化させた結果をプロットしたものを図 7.3-45、及び図 7.3-46 に示す。

コロイド濃度 0.1ppm、核種のコロイドに対する分配係数が $1.76 \times 10^5 \text{m}^3/\text{kg}$ の場合の線量ピーク値の最大値は $1.0 \times 10^{-14} \text{Sv/y}$ であった。コロイドに対する核種の分配係数が一桁小さいケース（コロイド濃度 0.1ppm、核種のコロイドに対する分配係数が $1.76 \times 10^4 \text{m}^3/\text{kg}$ ）の線量のピーク値の最大値は $1.5 \times 10^{-17} \text{Sv/y}$ であり、核種とコロイド間の相互作用が小さいことを反映して、線量値は約 3 桁小さかった。人工バリア出口では、両ケースのピーク値の差は 7 倍程度であったが（図 7.3-40）、核種が母岩及び断層中を移行した結果、両ケースの差が大きくなったと考えられる。

速度定数 α 及び β を大きく設定した場合 ($\beta=249 \text{kg}/\text{m}^3/\text{年}$) には、断層からの線量の

ピーク値は平衡ケースの結果と一致する。速度定数の比 (α/β) を固定したまま、速度定数 α 及び β を減少させて核種のコロイドへの収着速度を減少させると、核種移行が促進されて線量値のピーク値が上昇して、速度定数 α 及び β が ($\alpha=21900$, $\beta=0.1245$) の場合に線量値のピーク値が最大となる。その後、さらに速度定数 α 及び β の値を減少させると逆に線量値のピーク値が減少していく様子が認められた。(図 7.3-45、及び図 7.3-46)

表 7.3-3 Am-243 核種の α β 変更ケースの各解析のピーク値とピークの時間

解析ケース		母岩からの核種放出率		断層からの核種線量	
		ピーク時間(y)	ピーク値(Bq/y)	ピーク時間(y)	ピーク値(Sv/y)
α / β = 1.76×10^5	$\alpha = 438, \beta = 0.00249$	5.96×10^4 y	9.92×10^{-4} Bq/y	6.3×10^4 y ~ 7.1×10^4 y	1.5×10^{-16} Sv/y
	$\alpha = 4380, \beta = 0.0249$ (現実的設定ケース)	5.96×10^4 y	4.88×10^{-3} Bq/y	6.3×10^4 y ~ 7.1×10^4 y	5.3×10^{-15} Sv/y
	$\alpha = 21900, \beta = 0.1245$	5.96×10^4 y	6.78×10^{-3} Bq/y	6.3×10^4 y ~ 7.1×10^4 y	1.0×10^{-14} Sv/y
	$\alpha = 43800, \beta = 0.249$	5.96×10^4 y	5.46×10^{-3} Bq/y	6.3×10^4 y ~ 7.1×10^4 y	4.4×10^{-15} Sv/y
	$\alpha = 438000, \beta = 2.49$	6.31×10^4 y	5.47×10^{-4} Bq/y	7.9×10^4 y	9.2×10^{-20} Sv/y
	$\alpha = 4380000, \beta = 24.9$	7.94×10^4 y	1.76×10^{-5} Bq/y	1.4×10^5 y ~ 1.6×10^5 y	3.0×10^{-26} Sv/y
	$\alpha = 43800000, \beta = 249$	8.41×10^4 y	7.37×10^{-6} Bq/y	1.8×10^5 y	1.4×10^{-27} Sv/y
	$\alpha = 1.76 \times 10^{15}, \beta = 1.0 \times 10^{10}$ (平衡ケース)	8.41×10^4 y	7.37×10^{-6} Bq/y	1.8×10^5 y	1.0×10^{-27} Sv/y
α / β = 1.76×10^4	$\alpha = 43.8, \beta = 0.00249$	5.96×10^4 y	1.23×10^{-5} Bq/y	6.3×10^4 y	2.0×10^{-19} Sv/y
	$\alpha = 438, \beta = 0.0249$	5.96×10^4 y	7.44×10^{-5} Bq/y	6.3×10^4 y ~ 7.1×10^4 y	8.1×10^{-18} Sv/y
	$\alpha = 2190, \beta = 0.1245$	5.96×10^4 y	1.02×10^{-4} Bq/y	6.3×10^4 y ~ 7.1×10^4 y	1.5×10^{-17} Sv/y
	$\alpha = 4380, \beta = 0.249$	5.96×10^4 y	8.10×10^{-5} Bq/y	6.3×10^4 y ~ 7.1×10^4 y	6.3×10^{-18} Sv/y
	$\alpha = 43800, \beta = 2.49$	6.31×10^4 y	5.75×10^{-6} Bq/y	7.1×10^4 y	3.1×10^{-22} Sv/y
	$\alpha = 438000, \beta = 24.9$	8.91×10^4 y	7.56×10^{-9} Bq/y	2.0×10^5 y	3.1×10^{-36} Sv/y
	$\alpha = 4380000, \beta = 249$	1.00×10^5 y	2.78×10^{-9} Bq/y	2.2×10^5 y	7.2×10^{-38} Sv/y
	$\alpha = 1.76 \times 10^{14}, \beta = 1.0 \times 10^{10}$ (平衡ケース)	1.00×10^5 y	2.58×10^{-9} Bq/y	2.2×10^5 y ~ 2.5×10^5 y	5.5×10^{-38} Sv/y

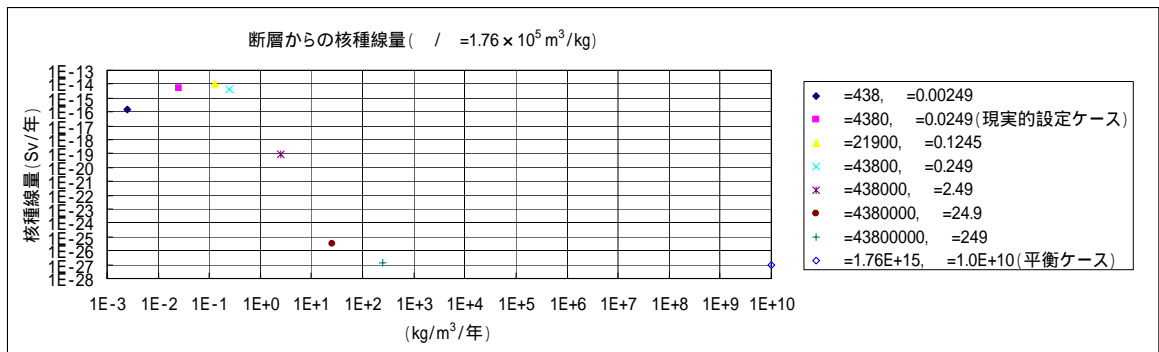


図 7.3-45 α β 変更ケース (α/β=1.76×10⁵ m³/kg) の断層からの核種線量のピーク値の逆方向速度定数 β に対するプロット (コロイド濃度 0.1ppm)

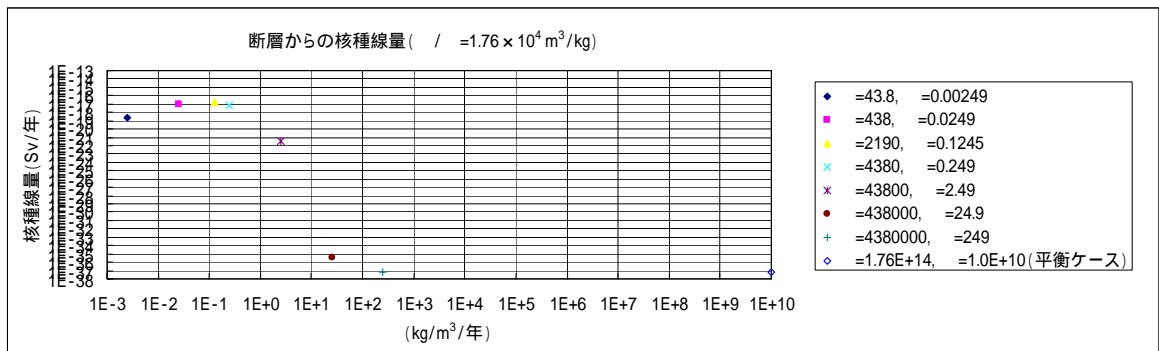


図 7.3-46 α β 変更ケース (α/β=1.76×10⁴ m³/kg) の断層からの核種線量のピーク値の逆方向速度定数 β に対するプロット (コロイド濃度 0.1ppm)

7.4 まとめ

7.4.1 実験結果から現実的と考えられる速度定数 α、β 値を設定した場合 (現実的設定ケース)

コロイドへの分配係数が小さな核種である Np-237 (分配係数: 5 m³/kg 以下)、U-236 (1.51 m³/kg) では、コロイド濃度が 1ppm の場合に、平衡状態、及び現実的な速度定数を設定した場合共に、コロイドによる核種移行の促進は認められなかった。

コロイドへの分配係数が 150 m³/kg の核種 Cs-135 で、コロイド濃度が 1ppm の場合にはコロイド影響は認められなかった。コロイド濃度が 5ppm、10ppm において、現実

的な速度定数を設定した場合には、コロイド影響による核種移行促進、及び線量の増加の傾向が認められた。この傾向は、母岩の流速が遅い方がより顕著に認められた。断層からの線量値は今回の評価核種の中で最も高かった。

他方、コロイドへの分配係数が大きな核種である Am-243 (1.76×10^5 m³/kg)、及び Pu-240 (3.9×10^5 m³/kg) に関して、コロイド濃度が 1ppm の場合について、平衡ケースにおいても現実的設定ケースにおいてもコロイド影響による核種移行の促進が認められた。分配係数が大きい場合にはコロイドへの収着量が大きくなるため、コロイド影響が顕著に現れたものと考えられる。しかし、Am-243 及び Pu-240 の線量値は Cs-135 や Np-237 に比べて何桁も低く、線量への寄与は小さいと考えられる。

7.4.2 パラメータ変更ケース

(1) β の値を現実的設定ケースよりも小さく設定した場合 (β 小ケース)

逆方向速度定数 β を現実的な値よりも小さく設定した場合は、現実的な速度定数を設定した場合に比べて、コロイドによる核種移行の促進が認められた。現実的な設定に比べて β 値を一桁小さく設定した場合、Am-243、Cs-135 核種について、コロイドによる核種移行の促進が認められた。Np-237 核種は、 β 値をさらに小さく設定すると、同様の傾向が確認された。

(2) α 及び β の値を共に現実的設定ケースよりも一桁小さく設定した場合 ($\alpha \beta$ 小ケース)

コロイド影響が顕著に認められた核種 Am-243 及び Pu-240 に関して、順方向速度定数 α 、及び逆方向速度定数 β の値を共に現実的な速度定数設定ケースよりも一桁小さく設定した場合には、核種移行へのコロイド影響が小さくなった。これはコロイドと核種の相互作用が小さい場合に相当すると考えられる。Np-237、Cs-135、U-236 核種についてはこのような現象は認められなかった。

(3) Am-243 核種の $\alpha \beta$ の比を変えずに α と β の両方を変化させた場合 ($\alpha \beta$ 変更ケース)

コロイド影響が顕著に認められた核種 Am-243 で、速度定数を $\alpha \beta$ の比を一定に保持して (K_d を一定)、平衡状態から段階的に速度定数 α 及び β の値を減少させた。その結果、 α 及び β の値が小さくなるに従い、段階的に核種移行が促進されて核種放出率のピ

ーク値が上昇したが、その後核種コロイド間の相互作用が弱くなり、核種放出率のピーク値が減少していく傾向が認められた。

7.4.3 まとめ

パラメータスタディ計算より、核種のコロイドに対する分配係数が大きい核種 Am-243、Pu-240 について、順方向速度定数 α と逆方向速度定数 β の設定値により、核種移行に対するコロイド影響は大きく変化することが示された。これから核種のコロイドに対する分配係数が大きい核種に関して、速度定数 α 、 β に関するデータ整備、及び検討の重要性が示された。しかし、その線量値は Cs-135 や Np-237 に比べて何桁も低く、線量への寄与は小さいと考えられる。

線量が最大である核種 Cs-135 に関しては、コロイド濃度が 1ppm の場合には順方向速度定数 α と逆方向速度定数 β を変化させても核種移行に対するコロイド影響は認められなかった。したがってコロイド濃度 1ppm では、核種移行へのコロイド寄与はないことが示された。

しかし、Cs-135 のコロイド濃度を 5ppm、10ppm と増加させた場合には、線量値が増加し、核種移行に対するコロイド影響が認められた。今後、母岩入り口におけるコロイド濃度が核種移行に与える影響の評価を行うことが望ましいと考えられる。

8. 核種のコロイドの分配係数に関する標準的手法の検討とデータ取得

8.1 背景及び目的

現在、日本原子力学会標準委員会（以後、「学会標準委員会」と称す）の深地層分配係数分科会では、深地中処分のバリア材を対象とした分配係数測定方法の標準的手法を検討している（例えば、油井他、2004）。同検討において、分配係数（Kd）へのコロイド影響に関する取扱いについても検討が進められており、その検討に資する基礎データの取得が望まれる。本検討では、バッチ法収着試験において、固相処理方法、振とう方法、固液分離方法などがコロイド影響とどう関係するかを調べる。

分配係数取得試験におけるコロイド影響としては、地下水などの実験水にもともと含まれているコロイドによる影響と、試験期間中に固相（岩石試料）から発生したコロイドによる影響が考えられる。実験水の取扱い方法として、地下水を使用する場合には、一般的な化学分析における液体試料の前処理と同様に懸濁物質等の影響を避けるために公称孔径 $0.45 \mu\text{m}$ のメンブランフィルタによるろ過を行うことがすでに標準化されている。そのため、実験水の取扱い方法については本検討では扱わない。

一方、固相起源のコロイド(+実験水中の $<0.45 \mu\text{m}$ のコロイド)の取扱い方法としては、収着試験終了後の固液分離の際に $0.45 \mu\text{m}$ ろ過を基本とし、分画分子量 10,000 の限外ろ過も実施し、それぞれのろ液を用いて測定した Kd を比較することによりコロイド影響を調べることが考えられている。そして、コロイド影響が認められた場合には、次式によりコロイド影響を排除した Kd を求めることが提案されている（油井他、2004）。

$$\text{分配係数 } Kd(\text{ml/g}) = \frac{C_0 - C_1}{C_2} \times \frac{V}{M} \quad (\text{式 8.1-1})$$

C_0 : 液相の初期濃度、 C_1 : 平衡後の濃度($0.45 \mu\text{m}$ ろ過後)、 C_2 : 平衡後の濃度(分画分子量 10,000 ろ過後)、 V : 液相の体積(ml)、 M : 固相の質量(g)

本検討では、バッチ法収着試験を実施し、固相の取扱い方法によるコロイド影響の度合いを検討する。さらに、上記、提案の分配係数を算出し、従来の式（8.2.2 にて後述）を用いて算出した分配係数と比較検討を行う。

8.2 方法

8.2.1 試験条件

収着試験は Kd 測定の標準化法に準じた条件で実施した。試験条件を下表に示す。

表 8.2-1 収着試験の条件

項目	内容
試験方法	バッチ法
・容器（容量）	・ポリプロピレン製容器（50mL）
対象元素	Cs
・初期濃度	1E-4 mol/L
試験溶液	幌延サイトの地下水（2種類；降水系、海水系）
・pH	・pH：降水系地下水 約7、海水系地下水 約8
固相	幌延サイトの泥岩（2種類）
・粒径	・<850 μ m
液固比（液固量）	10（50mL／5g）
試験温度	室温
試験雰囲気	大気雰囲気
試験期間	1週間
振とう	回転式機械振とう（10 r p m）、1回／1日程度の手による振とう
繰り返し数	2回または1回
固液分離方法	①※ 0.8 μ mメンブラン；フィルタユニット法 ② 0.45 μ mメンブラン；フィルタユニット法 ③ 分画分子量 10,000 の限外ろ過；フィルタユニット法
分析項目	pH および Eh；ガラス電極法 元素濃度；誘導結合プラズマ質量分析法（ICP-MS）

※：標準化法では 0.8 μ m ろ過は実施しないが、0.45 μ m ろ過との比較のために実施

(1) 試験方法

岩石に対する分配係数取得試験の方法として、最も一般的なバッチ法を用いた。容器については、学会標準委員会では廃棄物の低減化の目的から可燃物として処理可能なポリプロピレン製を推奨しており（日本原子力学会、2002、以後、浅地標準化法と記す）、本試験においてもポリプロピレン製を用いた。

(2) 対象元素

対象元素は、高レベル放射性廃棄物処分の重要核種で、コロイド影響が現れやすいと期待されることから Cs とした。

初期濃度については、サイクル機構収着データベース（渋谷他、1999）において、泥質岩に対する Cs の初期濃度として多くのデータが存在する濃度を考慮して、 $1\text{E-}4$ mol/L とした。

(3) 試験溶液

サイクル機構殿より提供された以下の幌延サイトの地下水を用いた。

- ・ 降水系地下水 HDB-9-45（採取深度約 40～50m）
- ・ 塩水系地下水 HDB-6-400（採取深度約 400m）

(4) 固相

サイクル機構殿より提供された幌延サイトの 2 種類の岩石を用いた（下図）。

- ・ 泥岩（HDB-9 孔深度約 47m）
- ・ 泥岩（HDB-6 孔深度約 417m）

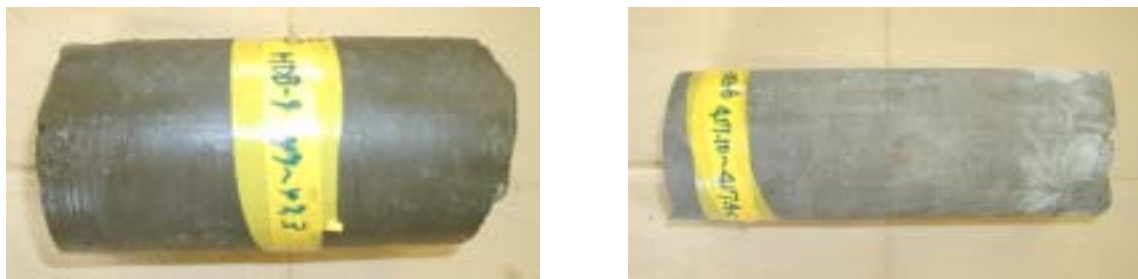


図 8.2-1 泥岩試料 HDB-9-47 (左) および泥岩試料 HDB-6-417 (右)

(5)液固比

浅地標準化法が基本条件としている 10mL/g とした。容器容量については、同標準化法では、概ね 10~50mL が安全に取り扱える作業容量であると述べており、本試験では 50mL とした。

(6) 試験温度

測定における設定温度として、浅地標準化法では、20~25℃と記されており、実験室の室温は、その温度と大きな差がなかったことから試験温度を室温とした。

(7)試験雰囲気

Cs の価数は酸化還元条件の影響を受けないこと、および地下水試料と岩石試料が採取された段階で、大気との接触を避けるための処置は特に採られていないことから、大気条件にて試験を行った。

(8)試験期間

浅地標準化法が基本条件としている 1 週間とした。

(9)振とう

浅地標準化法が標準化している機械振とうを基本とした。ただし、回転振とう機による振とうにおいて、回転軸が鉛直方向にある振とうでは、容器底の固相中の上部を液相が回転するだけで、固液の混合が十分になされない可能性があるため、回転軸が水平方向にある振とう方法とした (下図)。

深地中処分のバリア材を対象とした分配係数測定では、グローブボックス中にて試験することが多いため、試験スペースの制約から、比較的安定した分配係数が得られる（例えば、高橋他、1997）とされているハンドシェイクによる振とうも有効であるとの指摘がある。本試験では、固相からのコロイドの発生に及ぼす振とう方法の影響をみるためにハンドシェイクによる振とうも比較のために実施した。



図 8.2-2 機械振とうの状況

(10) 繰り返し数

機械振とうによる試験の繰り返し数を 2 とし、比較のためのハンドシェイクによる試験を 1 とする。

(11) 固液分離方法

固液分離の方法として、目開き $0.8\mu\text{m}$ メンブランフィルタ、目開き $0.45\mu\text{m}$ メンブランフィルタ及び分画分子量 10,000 の限外ろ過フィルタの 3 つの方法を用いた。

一般的にコロイドの大きさとして、おおよそ $1\text{nm}\sim 1\mu\text{m}$ と定義されていることから、コロイド以上の粒径をもつ固相を分離するという目的から目開き $1\mu\text{m}$ のろ過が考えられる。目開き $1\mu\text{m}$ のメンブランフィルタは市販されていないこ

とから、目開き $0.8\mu\text{m}$ のメンブランフィルタを用いた。また、深地層分配係数測定における標準的な固液分離方法として、コロイド影響を調べるために公称孔径 $0.45\mu\text{m}$ フィルタ及び分画分子量 10,000 の限外ろ過フィルタを採用することが提案されており（例えば、油井他、2004）、本試験でもそれらのろ過方法を実施した。

(12)分析項目

試験開始時及び試験終了時の pH、Eh、温度、及び試験終了時のトレーサ濃度を測定した。

以上の試験条件に係るマトリクスを下表に示す。

表 8.2-2 試験条件マトリクス

試料 No.	液相	固相	固相洗浄回数	振とう方法	固液分離方法
F-1	降水系地下水 HDB-9-45 (深度約 40 ~50m)	泥岩	0回	機械振とう	<ul style="list-style-type: none"> ・ $0.45\mu\text{m}$ろ過 ・ $0.8\mu\text{m}$ろ過 ・ 限外ろ過
F-2			0回	機械振とう	
F-3			0回	手振とう	
F-4			1回	機械振とう	
F-5			1回	機械振とう	
F-6			1回	手振とう	
F-7			2回	機械振とう	
F-8			2回	機械振とう	
F-9			2回	手振とう	
F-10		ブランク	—	機械振とう	
F-11		(固相なし)	—	手振とう	
S-1	海水系地下水	泥岩	0回	機械振とう	
S-2	HDB-6-400		0回	機械振とう	
S-3	(深度約		0回	手振とう	

S-4	400m)		1回	機械振とう		
S-5			1回	機械振とう		
S-6			1回	手振とう		
S-7			2回	機械振とう		
S-8			2回	機械振とう		
S-9			2回	手振とう		
S-10			ブランク	—		機械振とう
S-11			(固相なし)	—		手振とう

8.2.2 試験手順

収着試験は学会標準委員会が検討している深地中処分のバリア材を対象とした分配係数測定方法を基本とする。試験フローを下図に示す。

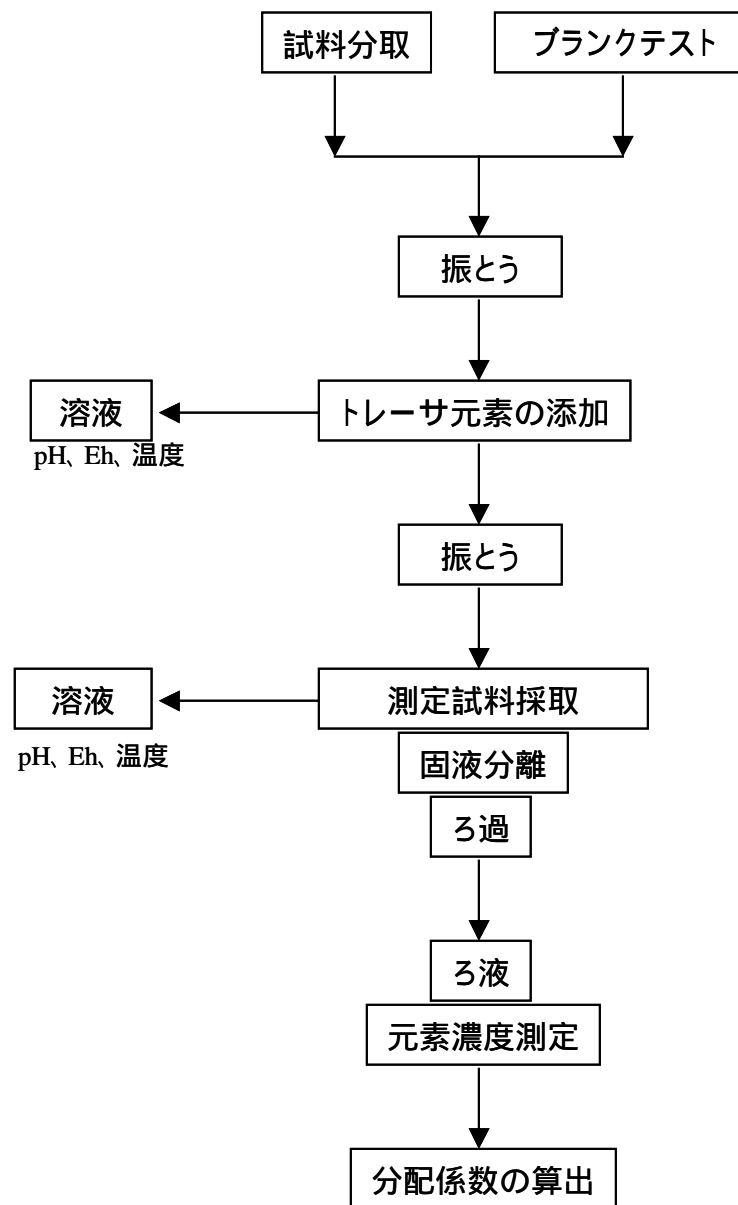


図 8.2-3 バッチ法による分配係数の測定フロー

(1)試験溶液の分析

幌延の地下水中にもともと含まれているコロイドを把握するために試験に供する前に元素組成分析を実施した。地下水を $0.8\mu\text{m}$ ろ過及び限外ろ過を行い、それぞれのろ過後の元素組成の差異をコロイドによるものとした。ここで、 $0.8\mu\text{m}$

孔径のフィルタを使用する理由は、一般のコロイドの定義から $1\mu\text{m}$ 以上の径の粒子は水中で分散・移行することが難しいために固相とみなされていることによる。 $1\mu\text{m}$ に近く、且つ一般的に用いられている $0.8\mu\text{m}$ の孔径のフィルタを用いた。

上記のろ過後の地下水分析の他に、ろ過を全くしない地下水組成分析も実施した。この場合には分析機器に係る制約から、地下水中のコロイド成分を酸により分解したうえで分析した。この処理において蒸発乾固、希釈過程を含むことから濃度測定値に比較的大きな誤差を含んでいると考えられ、参考的な扱いとした。

(2)試験溶液の調整

浅地標準化法が標準化している方法に従い、幌延の地下水は試験に用いる前に $0.45\mu\text{m}$ ろ過を実施した。なお、降水系地下水 HDB-9-45 については、地下水中の浮遊物量のため、数 mL のろ過でもフィルタ目詰まりを起こしたため、ろ過前に 18000rpm、30 分の遠心分離を行った。

(3)固相処理

固相は粉碎処理及び洗浄処理を行った。固相の粒径については、浅地標準化法では、 $2000\mu\text{m}$ 以下全量を使用することが記載されている。泥岩の構成粒子のサイズはかなり微細で、地下水と接触する個々の粒子レベルの粒径は $2000\mu\text{m}$ よりも大幅に小さいと考えられる。そこで本試験では、全固相を目開き $850\mu\text{m}$ の篩を通過させて試験に用いた。

粒径 $< 850\mu\text{m}$ の固相試料について、粉碎過程で生じる微粒子を除去する目的で固相洗浄を実施した。洗浄液として 99.5%エタノールを用い、液固比 30mL/30g で 5 分間の超音波振とうを行った。この洗浄処理による K_d への影響をみるために、洗浄を行わないもの、1 回および 2 回実施した試料を準備した。

(4)浸漬

固相試料と液相試料を混合した後、一昼夜、固相と液相を反応させた。その後、トレーサ元素を添加し収着試験を開始した。

浸漬期間中は機械振とうまたは手による振とうを行った。振とう機の回転速度

は 10rpm とし、手による振とうの頻度は 1 回/1 日程度とした。

(5) 固液分離

浸漬期間終了後の試料は、溶液の pH、Eh 測定および固液分離を行った。固液分離は 0.8 μm ろ過、0.45 μm ろ過および分画分子量 10,000 限外ろ過を別々に並行して行った。

(6) トレーサ濃度の分析

ろ過後のろ液中の Cs 濃度を誘導結合プラズマ質量分析法 (ICP-MS) にて分析した。

(7) 分配係数算出

分配係数は次式から算出した。

$$\text{分配係数 } Kd \quad (ml/g) = \frac{C_0 - C}{C} \times \frac{V}{M} \quad \begin{array}{l} \text{式 (8.2.2-1)} \\ \text{(式 (8.1-1) の再掲)} \end{array}$$

C_0 : 液相の初期濃度、 C : 平衡後の液相濃度、 V : 液相の体積(ml)、 M : 固相の質量(g)

本試験は固相起源のコロイド生成の影響を見ることを目的としているため、 C_0 は固相を添加しないブランク試料について、限外ろ過後のろ液中の核種濃度を測定し求めた。

また、前述したように、コロイドの影響が見られる場合の Kd の算出式として提案されている以下の式 (油井、他、2004) についても算出した。なお、本試験では C_1 として、0.45 μm ろ過の他に 0.8 μm ろ過後のデータも取得している。

$$\text{分配係数 } Kd' \quad (ml/g) = \frac{C_0 - C_1}{C_2} \times \frac{V}{M} \quad \text{式 (8.2.2-2)}$$

C₁ : 平衡後の濃度 (0.45 μ m ろ過後)、C₂ : 平衡後の濃度 (分画分子量 10,000 限外ろ過後)

(8) 収着試験後の液相分析 (コロイド量評価)

収着試験の結果、コロイド影響がみられた試料について、液相を分取し、0.8 μ m ろ過及び限外ろ過を実施した後、それぞれについて元素組成分析を行った。0.8 μ m ろ過後及び限外ろ過後の元素組成の差異をコロイド量として評価した。

(9) 収着試験後の固相分析

収着試験の結果、コロイド影響がみられた試料について、固相を分取し、XRD 分析及び粒度分布測定を行った。

8.3 試験結果

収着試験前の地下水中の濃度分析の結果を表 8.3-1 に示す。0.8 μ m ろ過後と限外ろ過後の元素濃度を比較すると、降水系地下水の HDB9-45 については、Al、Si、Fe の差異が比較的大きく、これらを成分とするコロイドが存在している可能性がある。ただし、コロイド量としては多くはないと考えられる。海水系地下水の HDB6-400 については、Ca と TIC の差異が比較的大きい。

収着試験開始時および終了時の pH、Eh を表 8.3-2 に示す。また、収着試験終了時のトレーサ濃度測定結果を表 8.3-3 に示す。同表には、従来の式から算出した Kd とコロイド影響がある場合の Kd' の 2 通りの分配係数を算出した。

収着試験に及ぼすコロイドの影響度合いについては、8.4 節にて後述するが、表 8.3-3 から降水系地下水試料のうち、固相洗浄回数 2 回の試料が特にコロイド影響が認められた。そのため、コロイド量評価のための収着試験後の液相分析は同試料について実施し、さらに比較のために固相洗浄回数 0 回及び 1 回の降水系地下水試料についても分析を行った。その結果を表 8.3-4 に示す。なお、収着試験前の地下水の 0.45 μ m ろ過に際して、降水系地下水の HDB9-45 については、地下水中の浮遊物によるフィルタ目詰まりのため、ろ過前に遠心分離（18,000rpm、30 分）を実施している。遠心分離により除去された固相の粒径は以下の式（白水、1988）から計算される。

$$t = \frac{63 \times \eta \times \log(R/S)}{N^2(\sigma - \rho)D^2}$$

ここで、**t**：粒子の沈降に要する遠心分離機の回転時間（分）、**R**：回転軸から沈降粒子表面までの距離(cm)、**S**：回転軸から懸濁液表面までの距離(cm)、**N**：回転数(=18000rpm)、 η ：水の粘度(=0.01 at 20°C)、 σ ：粒子の比重、 ρ ：水の比重(=1.0)、**D**：粒子の直径 (cm)

上式において、懸濁物質の比重として幌延の泥岩の値約 2.0 を用い、R/S=2.33、回転時間 t=30 とすると、D=0.05 μ m となる。すなわち、18000rpm、30 分の条件での遠心分離により、表 8.3-1 において認められたコロイド成分のうち 0.05 μ m 以上のコロイド粒子は取り除かれたと計算される。

また、収着試験後の液相分析と同様に、降水系地下水試料の洗浄回数 0 回、1 回及び 2 回の試料について、XRD 分析及び粒度分布測定を実施した。それらの結果をそれぞれ、図 8.3-1 及び図 8.3-2 に示す。

表 8.3-1 収着試験前の地下水組成分析結果

	Na	Mg	Al	Si	K	Ca	Mn	Fe	Sr	Cl	SO ₄	NO ₃	Br	B	TOC	TIC
HDB9-45 ろ過なし	9.13E-04	5.64E-05	2.48E-05	2.20E-04	< 1.28E-04	1.16E-04	< 4.55E-06	9.24E-05	< 2.85E-06	-	-	-	-	5.55E-05	1.75E-04	6.74E-04
HDB9-45 0.8 μmろ過	9.92E-04	7.08E-05	1.09E-04	1.03E-03	7.26E-05	1.07E-04	7.28E-06	1.11E-04	< 1.14E-06	3.69E-04	9.34E-05	< 4.84E-06	< 6.26E-06	< 9.25E-06	1.83E-04	6.41E-04
HDB9-45 MWCO10,000 限外ろ過	1.02E-03	4.81E-05	< 7.41E-06	7.62E-04	8.95E-05	9.86E-05	6.55E-06	< 1.79E-06	< 1.14E-06	3.79E-04	9.38E-05	< 4.84E-06	< 6.26E-06	< 9.25E-06	2.83E-04	6.91E-04
HDB6-400 ろ過なし	1.98E-01	4.85E-03	< 1.85E-05	8.12E-04	2.42E-03	3.97E-03	< 4.55E-06	1.61E-05	2.60E-05	-	-	-	-	8.22E-03	1.29E-03	4.26E-02
HDB6-400 0.8 μmろ過	5.09E-03	5.47E-03	< 7.41E-06	8.83E-04	3.02E-03	1.51E-03	< 1.82E-06	< 1.79E-06	2.10E-05	2.04E-01	< 1.04E-05	8.02E-05	5.53E-04	8.61E-03	1.39E-03	4.71E-02
HDB6-400 MWCO10,000 限外ろ過	4.92E-03	5.35E-03	< 7.41E-06	9.04E-04	3.27E-03	1.11E-03	< 1.82E-06	< 1.79E-06	1.95E-05	2.00E-01	< 1.04E-05	8.53E-05	5.70E-04	8.79E-03	1.42E-03	3.65E-02

単位: mol/L

表 8.3-2 収着試験開始時および終了時の pH、Eh

試料No.	地下水種類- 洗浄回数	振とう方法	試験開始前 (17)		試験終了後 (20)	
			pH	Eh(v.s. SHE)	pH	Eh(v.s. SHE)
F-1	降水系-0回	機械振とう	7.12	402	5.61	244
F-2	降水系-0回	機械振とう	-	-	5.90	220
F-3	降水系-0回	手振とう	-	-	6.25	253
F-4	降水系-1回	機械振とう	7.65	384	6.32	219
F-5	降水系-1回	機械振とう	-	-	6.70	194
F-6	降水系-1回	手振とう	-	-	6.69	254
F-7	降水系-2回	機械振とう	7.65	393	6.34	190
F-8	降水系-2回	機械振とう	-	-	6.49	184
F-9	降水系-2回	手振とう	-	-	6.78	254
F-10	降水系ブランク	機械振とう	6.87	411	7.01	286
F-11	降水系ブランク	手振とう	-	-	7.02	294
S-1	海水系-0回	機械振とう	7.79	251	7.92	122
S-2	海水系-0回	機械振とう	-	-	7.84	121
S-3	海水系-0回	手振とう	-	-	7.97	121
S-4	海水系-1回	機械振とう	7.53	255	7.63	140
S-5	海水系-1回	機械振とう	-	-	7.63	129
S-6	海水系-1回	手振とう	-	-	7.82	126
S-7	海水系-2回	機械振とう	7.54	253	7.71	124
S-8	海水系-2回	機械振とう	-	-	7.68	122
S-9	海水系-2回	手振とう	-	-	7.82	122
S-10	海水系ブランク	機械振とう	7.72	258	8.11	122
S-11	海水系ブランク	手振とう	-	-	8.08	121

表 8.3-3 収着試験終了時のトレーサ濃度測定結果および Cs の泥岩に対する分配係数

試料No.	地下水種類・洗浄回数	振とう方法	0.8μmメンブランろ過後						0.45μmメンブランろ過後						限外ろ過後		
			定量値 (ppb)	Kd (ml/g)	Kd (平均)	Kd' (ml/g)	Kd' (平均)	変化率 (%)	定量値 (ppb)	Kd (ml/g)	Kd (平均)	Kd' (ml/g)	Kd' (平均)	変化率 (%)	定量値 (ppb)	Kd (ml/g)	Kd (平均)
F-1	降水系-0回	機械振とう	119.4	912.5	915.4	921.8	931.9	1.8	116.2	937.5	935.9	922.0	932.1	-0.4	118.2	921.9	932.0
F-2	降水系-0回	機械振とう	118.7	918.3		941.9			116.6	934.2		942.1			115.7	942.2	
F-3	降水系-0回	手振とう	121.4	938.2	938.2	947.1	947.1	1.0	118.2	964.0	964.0	947.4	947.4	-1.7	120.3	947.2	947.2
F-4	降水系-1回	機械振とう	91.4	1195.0	1193.2	1154.5	1217.8	2.1	98.4	1109.3	1190.0	1153.7	1217.7	2.4	94.6	1154.1	1218.0
F-5	降水系-1回	機械振とう	91.7	1191.3		1281.1			86.0	1270.6		1281.7			85.3	1281.8	
F-6	降水系-1回	手振とう	110.4	1032.3	1032.3	1039.3	1039.3	0.7	112.7	1011.0	1011.0	1039.1	1039.1	2.8	109.7	1039.3	1039.3
F-7	降水系-2回	機械振とう	93.3	1169.9	1182.5	1317.2	1330.3	12.5	89.4	1222.1	1226.1	1317.7	1330.7	8.5	82.9	1318.5	1331.6
F-8	降水系-2回	機械振とう	91.4	1195.0		1343.5			88.8	1230.1		1343.8			81.3	1344.7	
F-9	降水系-2回	手振とう	125.8	904.9	904.9	1072.7	1072.7	18.5	109.9	1037.7	1037.7	1074.2	1074.2	3.5	106.1	1074.5	1074.5
F-10	降水系ブランク	機械振とう													11013.9		
F-11	降水系ブランク	手振とう													11511.4		
S-1	海水系-0回	機械振とう	1281.2	81.5	81.2	80.9	80.6	-0.8	1252.5	83.6	85.8	81.2	81.1	-5.4	1290.4	80.9	80.5
S-2	海水系-0回	機械振とう	1289.8	80.9		80.3			1196.8	88.0		81.0			1300.1	80.2	
S-3	海水系-0回	手振とう	1349.5	76.8	76.8	76.6	76.6	-0.2	1308.7	79.5	79.5	76.9	76.9	-3.2	1352.3	76.6	76.6
S-4	海水系-1回	機械振とう	1194.0	88.2	88.3	93.6	91.5	3.6	1095.3	97.0	93.9	94.5	92.1	-2.0	1124.6	94.3	91.9
S-5	海水系-1回	機械振とう	1191.7	88.4		89.4			1163.0	90.8		89.6			1178.5	89.5	
S-6	海水系-1回	手振とう	1281.8	81.4	81.4	80.4	80.4	-1.2	1246.2	84.0	84.0	80.6	80.6	-4.0	1297.8	80.2	80.2
S-7	海水系-2回	機械振とう	1123.4	94.4	93.7	91.7	93.2	-0.6	1096.4	96.9	97.1	91.9	93.5	-3.7	1156.7	91.4	93.1
S-8	海水系-2回	機械振とう	1137.7	93.1		94.7			1093.6	97.2		95.1			1118.2	94.9	
S-9	海水系-2回	手振とう	1326.5	78.3	78.3	81.2	81.2	3.8	1246.8	83.9	83.9	81.9	81.9	-2.5	1278.3	81.6	81.6
S-10	海水系ブランク	機械振とう													11725.0		
S-11	海水系ブランク	手振とう													11710.4		

表 8.3-4 収着試験後の液相分析結果

試料No.	地下水種類 -洗浄回数	振とう方法	固液分離方法	Al	Si	Fe	Na	K	Ca	Mg	TOC	TIC
				mol/L	mol/L	mol/L	mol/L	mol/L	mol/L	mol/L	mol/L	mol/L
F-1	降水系-0回	機械振とう	0.8 μmろ過	2.72E-05	1.17E-03	1.28E-04	3.02E-03	6.10E-04	2.33E-03	3.15E-03	1.82E-04	1.55E-04
			限外ろ過	3.15E-05	1.24E-03	1.41E-04	3.08E-03	6.13E-04	2.29E-03	3.16E-03	5.75E-04	0.00E+00
F-2	降水系-0回	機械振とう	0.8 μmろ過	2.37E-05	1.27E-03	2.18E-05	3.64E-03	1.24E-03	3.44E-03	5.97E-03	1.87E-04	2.23E-05
			限外ろ過	2.75E-05	1.24E-03	2.22E-05	3.65E-03	1.27E-03	3.47E-03	5.97E-03	6.89E-04	0.00E+00
F-3	降水系-0回	手振とう	0.8 μmろ過	1.18E-05	1.07E-03	4.01E-05	2.91E-03	5.16E-04	1.83E-03	2.44E-03	1.70E-04	1.70E-04
			限外ろ過	1.29E-05	1.09E-03	4.37E-05	2.95E-03	4.98E-04	1.77E-04	2.46E-03	5.20E-04	0.00E+00
F-4	降水系-1回	機械振とう	0.8 μmろ過	3.80E-06	7.74E-04	< 1.79E-06	2.83E-03	4.06E-04	1.08E-03	1.54E-03	4.54E-04	4.08E-04
			限外ろ過	5.79E-06	8.55E-04	3.22E-06	2.85E-03	4.00E-04	1.12E-03	1.60E-03	6.37E-04	3.52E-05
F-5	降水系-1回	機械振とう	0.8 μmろ過	1.96E-06	7.43E-04	< 1.79E-06	3.23E-03	4.05E-04	9.97E-04	1.48E-03	4.03E-04	1.63E-04
			限外ろ過	1.64E-06	7.44E-04	< 1.79E-06	1.07E-04	< 5.12E-05	1.00E-03	1.50E-03	1.15E-03	1.07E-04
F-6	降水系-1回	手振とう	0.8 μmろ過	2.16E-06	8.71E-04	3.94E-06	2.75E-03	2.85E-04	8.41E-04	1.20E-03	1.51E-04	7.03E-04
			限外ろ過	1.59E-06	8.25E-04	2.69E-06	2.86E-03	3.19E-04	9.21E-04	1.32E-03	6.29E-04	0.00E+00
F-7	降水系-2回	機械振とう	0.8 μmろ過	5.35E-06	8.06E-04	< 1.79E-06	3.40E-03	6.89E-04	1.75E-03	2.77E-03	2.76E-04	9.09E-05
			限外ろ過	5.21E-06	8.09E-04	< 1.79E-06	3.32E-03	6.86E-04	1.74E-03	2.78E-03	6.04E-04	7.10E-05
F-8	降水系-2回	機械振とう	0.8 μmろ過	4.17E-06	8.26E-04	< 1.79E-06	2.84E-03	3.92E-04	1.32E-03	1.97E-03	2.99E-04	3.23E-04
			限外ろ過	4.55E-06	9.02E-04	< 1.79E-06	2.88E-03	4.07E-04	1.33E-03	2.01E-03	4.00E-04	1.14E-05
F-9	降水系-2回	手振とう	0.8 μmろ過	1.62E-06	7.79E-04	< 1.79E-06	2.82E-03	3.03E-04	8.48E-04	1.21E-03	2.99E-04	3.69E-04
			限外ろ過	1.81E-06	8.55E-04	3.22E-06	2.84E-03	3.43E-04	8.68E-04	1.22E-03	5.26E-04	4.65E-05

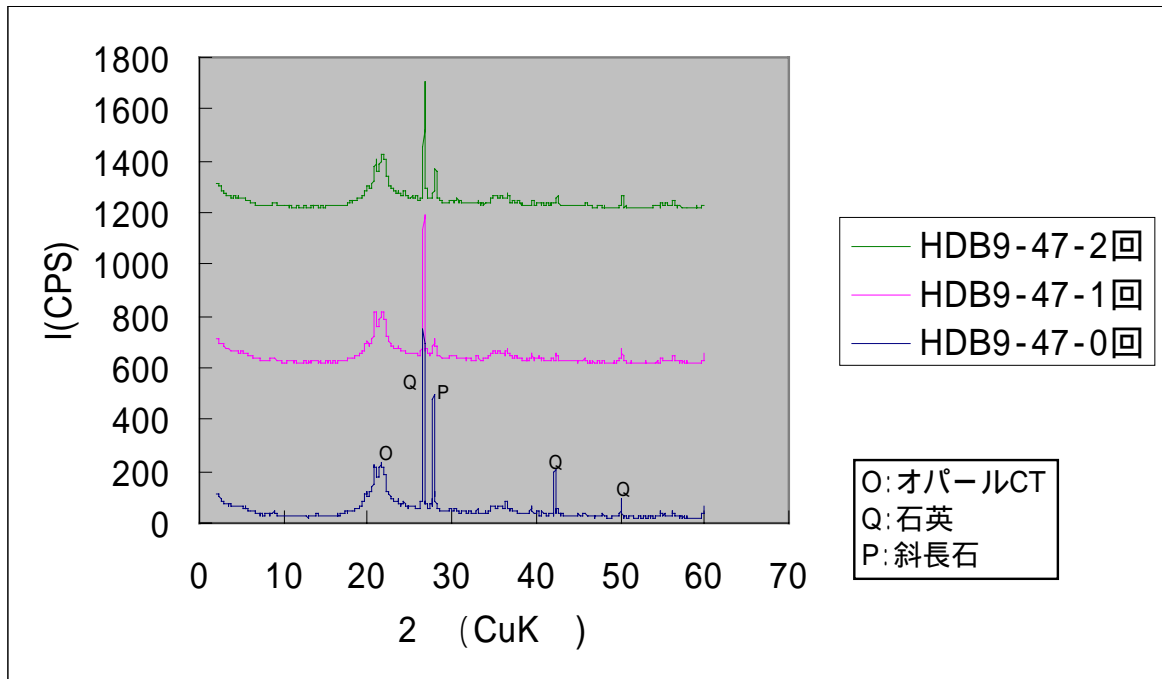
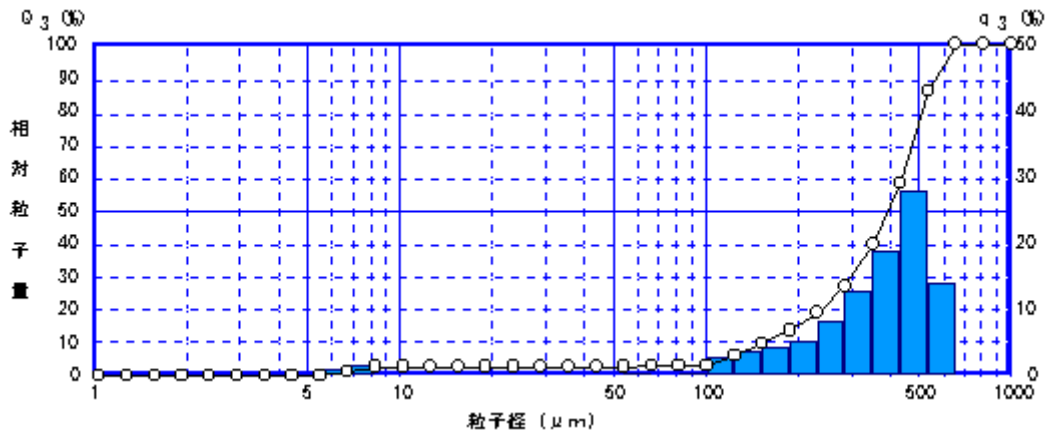
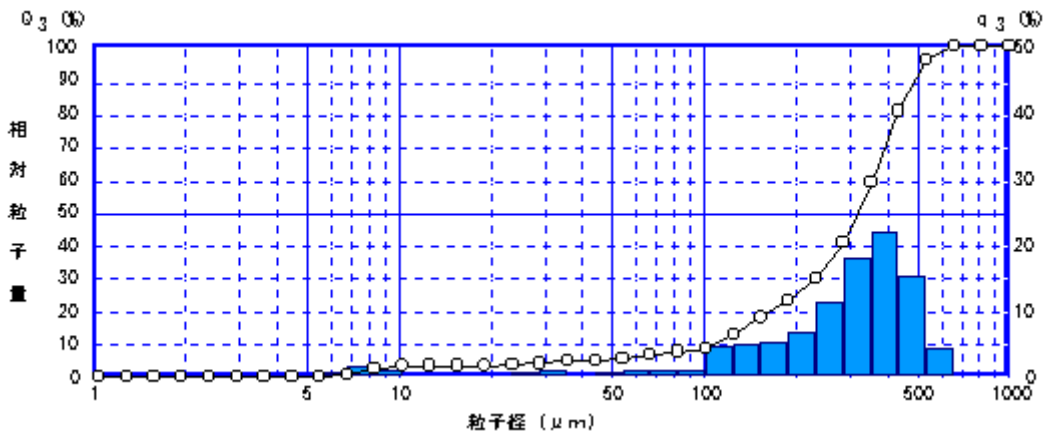


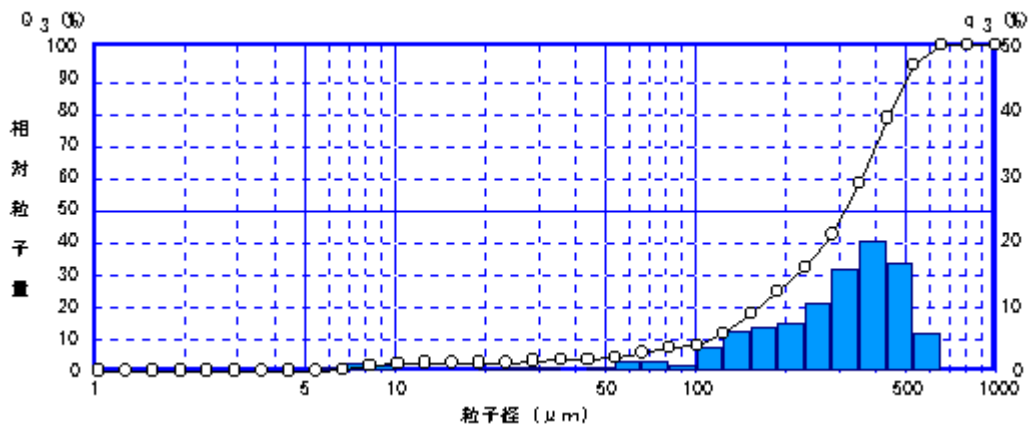
図 8.3-1 収着試験後の固相に対する XRD 分析結果



(a) 洗浄回数 0 回



(b) 洗浄回数 1 回



(c) 洗浄回数 2 回

図 8.3-2 収着試験後の固相の粒度分布測定結果

8.4 分配係数に及ぼすコロイド影響の検討

8.4.1 降水系地下水試料

従来の式 (8.2.2-1) から算出した K_d を下図に示す。

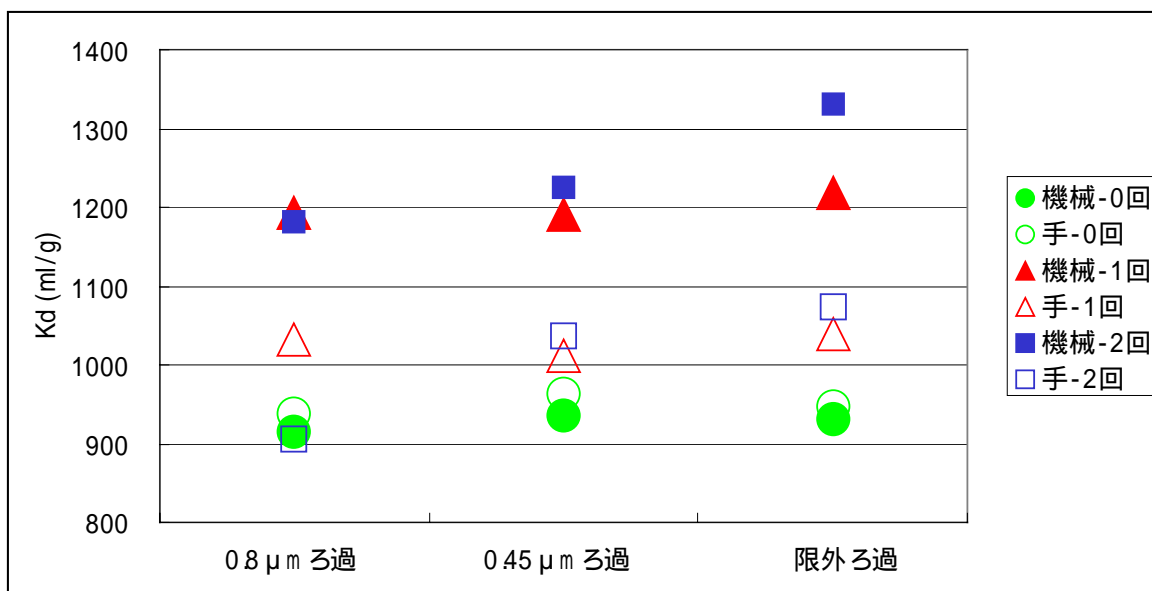


図 8.4-1 降水系地下水の K_d

上の図から、固相洗浄回数が 0 回の場合、機械振とう、手による振とう共に、ろ過方法による K_d の相違がほとんどなく、コロイド影響はほとんどないと考えられる。

洗浄回数 1 回の場合についても、ろ過方法による K_d の相違は大きなものではなく、コロイドの影響はほとんどないと考えられる。しかしながら、機械振とうのほうが手による振とうよりも高い K_d 値をとる傾向が認められる。

洗浄回数 2 回の場合、機械振とう、手による振とう共に、 K_d が $0.8 \mu\text{m}$ ろ過 < $0.45 \mu\text{m}$ ろ過 < 限外ろ過の順に増加しており、 K_d がコロイド影響を受けていると考えられる。また、手による振とうよりも機械振とうのほうが高い K_d をとっている。

次に、 $0.8 \mu\text{m}$ ろ過後及び $0.45 \mu\text{m}$ ろ過後のデータについて、コロイド影響を考慮した算出式から K_d' を導出し、上記の K_d とともに下図にプロットした。

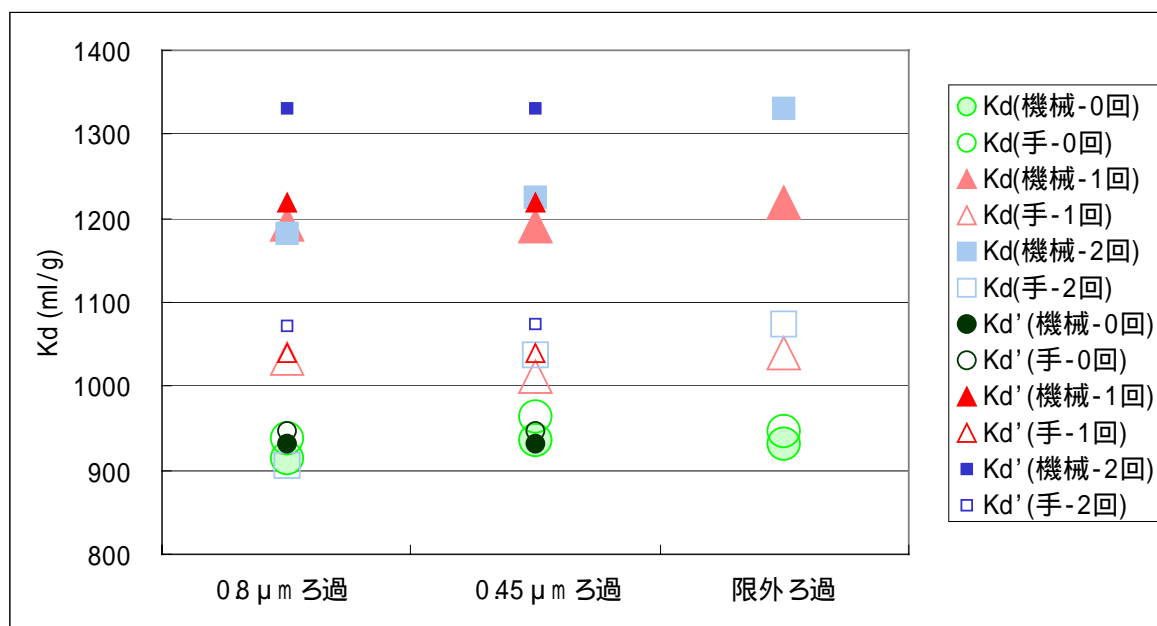


図 8.4-2 降水系地下水の K_d' と K_d の比較

上図から、図 8.4-1 においてコロイド影響があると考えられた 2 回洗浄した試料（機械振とうおよび手による振とう）については K_d と K_d' の相違が大きく、コロイド影響が少ないと考えられた固相洗浄回数 0 回または 1 回の試料については相違が小さいことがわかる。表 8.3-3 には、 K_d と K_d' の相違について、変化率 (%) = $100 \times (K_d' - K_d) / K_d$ として算出した。洗浄回数 0 回または 1 回の場合には、3% 以下の変化率であるが、2 回洗浄することにより、変化率は上昇し、特に $0.8 \mu\text{m}$ ろ過後のデータでは 10~20% 近い相違が生じることがわかる。

コロイド影響の認められた 2 回洗浄試料に関して、 K_d' は $0.8 \mu\text{m}$ ろ過後と $0.45 \mu\text{m}$ ろ過後でほぼ同じ値を示した。従来式(8.2.2-1)ではコロイドに収着した C_s が有意に存在する場合、それを固相側と液相側のどちらとみなすかにより K_d が有意に変化を示すが、算出式(8.2.2-2)では、コロイドに収着した C_s を計算に入れていないため、すなわちコロイド影響を除外しているためと考えられる。

K_d' はコロイド影響を除外した岩盤-核種間の分配係数であるので、洗浄回数によらず同様な K_d' 値をとるはずである。しかしながら、図 8.4-2 では、洗浄回数の増加とともに K_d' も増加している。収着試験後の固相の XRD 分析の結果を示した図 8.3-1 をみると洗浄回数によらず、構成鉱物の種類は変化がない。しかしながら、洗浄なしの試料に

比べて、洗浄を行った試料は構成鉱物の量比が変化しているように見える。例えば、オパール CT の強度と比較すると洗浄なしの試料は石英や斜長石のピークは比較的高いが、洗浄回数を 1 回、2 回と増やすことにより、それらの相対ピークは低下している。したがって、洗浄を行うことにより、構成鉱物の量比が変化し、それが洗浄回数による Kd' の相違をもたらした可能性がある。

図 8.3-2 をみると、洗浄回数の増加とともに、構成粒子の粒径の頻度分布が細粒側にシフトしている。洗浄の過程で粒子が粉碎され、細粒化したため Kd' の上昇をもたらしたと考えられる。今回の試験では、泥岩の構成粒子が微細であることを考慮し、浅地標準化法が標準化している「 $2000\mu\text{m}$ 以下全量」よりもさらに細粒の「 $850\mu\text{m}$ 以下全量」としたが、より細粒化し、実際の岩石の構成粒子に近い粒径にする必要があると考えられる。

次に、コロイド影響の度合いが比較的大きかった、洗浄回数 2 回の $0.8\mu\text{m}$ ろ過後の液相試料について、発生したコロイドの種類及び量を評価するために表 8.3-4 の液相分析の結果を用いた。同表から、 $0.8\mu\text{m}$ ろ過後の濃度から限外ろ過後の濃度を引いた差が最も大きくなるのは無機炭素であることがわかる。無機炭素の濃度差が液相中のコロイドに起因しているとした場合、そのコロイドは炭酸塩の形で存在していると考えられる。Fe や Ca の濃度に差がみられないが、Fe については検出下限以下であること、Ca についてはバックグラウンドが高いことが原因になっている可能性がある。ここでは、コロイドが CaCO_3 として存在すると仮定して、液相中のコロイド量を計算した。さらに、核種-コロイド間の分配係数 (Kd'' とする) を以下の式(8.4.1-1)により算出した。その結果を表 8.4-1 に示す。

$$\text{分配係数 } Kd'' \quad (\text{ml/g}) = \frac{C_1 - C_2}{C_2} \times \frac{V}{M'} \quad \text{式 (8.4.1-1)}$$

C_1 : 平衡後の濃度 ($0.8\mu\text{m}$ ろ過後)、 C_2 : 平衡後の濃度 (分画分子量 10,000 限外ろ過後)、 M' : コロイド量(g)、 V : 液相の体積 (mL)

表 8.4-1 核種-コロイド間の分配係数 (K_d'')

試料No.	地下水種類 -洗浄回数	振とう方法	液相体積 (mL)	コロイド量 (CaCO_3) (g)	C_1 ($0.8\mu\text{m}$ 過後) (ppm)	C_2 (限外ろ過後) (ppm)	K_d'' (mL/g)
F-7	降水系-2回	機械振とう	50	9.96E-05	1.19E-01	1.18E-01	5119
F-8	降水系-2回	機械振とう	50	1.56E-03	1.19E-01	1.16E-01	826
F-9	降水系-2回	手振とう	50	1.61E-03	1.21E-01	1.20E-01	296

算出された核種-コロイド間の分配係数 K_d'' を核種-岩盤間の分配係数 K_d' と比較すると、 K_d' はいずれも約 900mL/g であるので、試料 F-8 については、比較的 K_d'' と近い値をとることがわかる。しかしながら、コロイドが主としてカルサイトであるならば、既存の C_s のカルサイトへの分配係数（例えば、降水系模擬地下水条件でおよそ 8mL/g 程度[図からの読み取り]、加藤他、2001）と比較した場合には、有意に高い値となる。原因としては、トレーサ濃度や競合イオンなどの試験条件の違いの他、岩盤の構成粒子とコロイド粒子の粒径の違いが考えられる。例えば、粉末状ベントナイトがコロイドになるとシート状粒子になり収着サイトの密度が変化して K_d が上昇する（飯島他、2004）という既存の研究例もあり、カルサイトのように C_s が主として固相粒子表面に収着すると考えられる場合には、比表面積の増加が K_d の上昇要因になり得ると考えられる。コロイド粒子の径として、2種類のフィルタ孔径の中央値の $0.4\mu\text{m}$ と仮定し、 C_s - CaCO_3 収着試験に用いた鉱物の粒径 ($<250\mu\text{m}$) を $250\mu\text{m}$ として両者を比較すると、コロイドの比表面積はおよそ 600 倍程度となることから、比表面積（サイト密度）の相違が K_d に影響を与えていると仮定した場合には矛盾がない。

しかしながら、実際にはコロイドの種類は上記で仮定したカルサイト 1 種類とは限らず、コロイド粒径も一定範囲内で分布したものとなっていたと考えられる。したがって、収着試験後の液相中のコロイドについて、電子顕微鏡等を用いて種類、量、粒径等のデータを今後、取得することが望まれる。

8.4.2 海水系地下水試料

従来の式から算出した K_d を下図に示す。

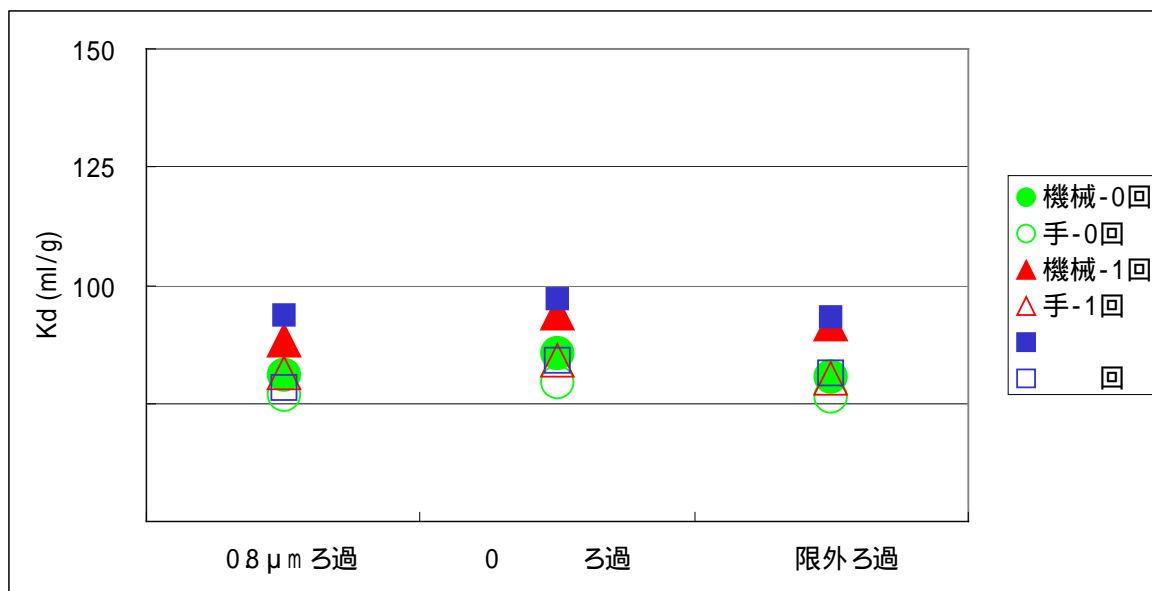


図 8.4-3 海水系地下水の K_d

上図から、いずれの試料についてもろ過方法の違いによる K_d の相違はほとんどないことがわかる。図 8.4-1 と比較して、縦軸がより詳細なスケールとなっており、同じスケールで比較するとろ過方法による相違が降水系の試料よりもかなり小さくなっている。そのためコロイド影響についても降水系試料よりもかなり小さいものと考えられる。

機械振とう試料に関して、降水系試料と同様に固相洗浄の回数が 0 回、1 回、2 回と増加するに従いわずかながら K_d の上昇が認められる。しかし、手による振とうの試料についてはそのような傾向はみられない。

次に、0.8 μm ろ過後及び 0.45 μm ろ過後のデータについて、コロイド影響を考慮した算出式から K_d' を導出し、上記の K_d とともに下図にプロットした。

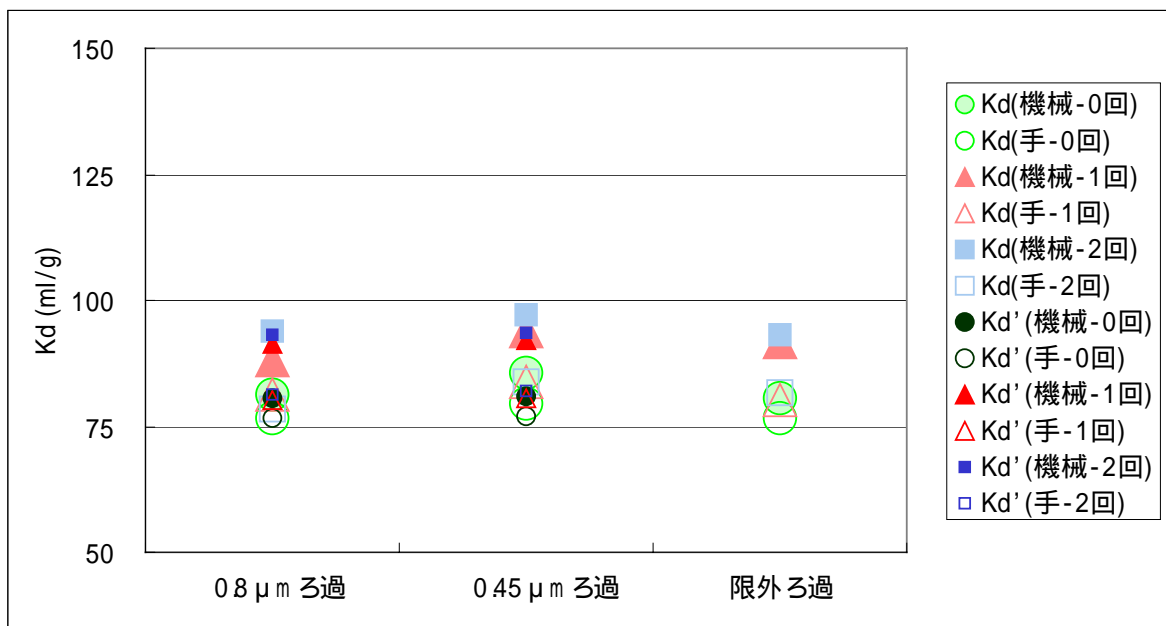


図 8.4-4 海水系地下水の K_d' と K_d の比較

上図から、 $0.8\mu\text{m}$ ろ過後および $0.45\mu\text{m}$ ろ過のいずれの試料についても、 K_d と K_d' の相違がほとんどなく、こちらの図からもコロイド影響はほとんどないことがわかる。海水系地下水のイオン強度（約 0.2M ）は降水系地下水よりもかなり高く、そのためコロイドが安定に存在できないために上記のような試験結果となったと考えられる。

8.5 まとめ

バッチ法による分配係数取得試験におけるコロイド影響を調べるためのデータ取得試験を実施した。降水系地下水を用いた試験については、事前に遠心分離を実施したため、地下水中にもともと含まれていた $0.05\ \mu\text{m}$ 以上の粒径のコロイドは除去されたと考えられる。したがって、試験においてみられたコロイド影響は、主として固相起源のコロイドによるものと考えられる。本試験の結果、以下のことがわかった。

- **Kd** 測定の標準化法では扱われていないが、固相の粉碎の際に生じる微粒子を取り除く目的で一般的に実施される場合がある固相洗浄に関して、洗浄条件によっては固相からのコロイドを発生させ、それが **Kd** に影響を与える場合があることがわかった。したがって、岩種によっては固相の洗浄処理は実施しないほうがよい。
- 分配係数の算出式(8.2.2-2)及び算出式(8.4.1-1)から、それぞれ岩盤-核種間及びコロイド-核種間の **Kd** を求められる可能性が示された。しかしながら、それらの **Kd** 値の妥当性を直接示すデータは現状では得られていない。今後、岩盤-コロイド-核種の3元系及びコロイド-核種の2元系で試験を実施し、液相中のコロイドについて種類、量、粒径等のデータを取得することが望まれる。

9. おわりに

現象理解に基づいた信頼性が高く性能評価と密接に関連したデータベースの整備方策を検討すると共に、地層処分システムの安全評価における核種移行の個別モデルとしてコロイド影響に関する実験及び評価コードの開発、及び解析を行った。

その結果、データベース基盤データ構築手法を検討した。また、収着データベース（JNC-SDB）を用いて、収着係数の信頼度を付与するための手法を改良した。

さらに、コロイドに対する核種収着の可逆・不可逆性評価、コロイドの影響を考慮したモデル（コード）に基づく核種移行モデルの高度化を図るためのデータ・コードの整備を行った。さらに、コロイドの影響を考慮したモデル（コード）に基づいて、コロイドの影響を考慮した核種移行解析に基づく被曝線量評価を行った。

今後はこれらの情報を十分に活用し、より現象に忠実なデータの取得、整備、及び現象理解を進めていく。

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付録 1

熱力学データベースの利用環境整備、
核種の溶解度設定における固溶体モデルの適用性に関するデータ整備、及び
JNC-SDB を用いた収着係数の信頼度付与のための手法改良
(スイス BMG 社による成果報告)

Technical Report

Classification of K_d values in the JNC-SDB – Revision 2

Evaluation of solid-solution modeling

Michael Ochs

January 2005

Efficiency- & Risk-Engineering

Executive Summary

JNC is developing databases and methodology that are important keystones for the performance assessment of nuclear waste repositories in Japan. Within this general framework, the present project addresses two specific tasks related to assessing the potential radionuclide migration out of a deep geological repository for vitrified high-level waste:

- Revision, testing, and finalization of a classification guideline for defining the reliability of K_d values included in the JNC Sorption Database (JNC-SDB).
- Evaluation of the state of the art and applicability of solid-solution modeling for defining radionuclide solubility limits, as well as the respective data needs, with focus on the coffinite- and Fe-S-Se-systems.

1. Reliability of entries in the JNC-SDB

As a QA measure related to making the JNC-SDB, or parts of it, available to the larger public, JNC needs to classify the relevant entries in the SDB according to their technical and scientific reliability. A procedure for the evaluation and categorization of the reliability of K_d values in the JNC-SDB had been developed and subjected to a first test previously (Ochs and Talerico, 2004). Based on these results, the guideline was revised in the present project to decrease the need for expert decisions by an operator and to improve reproducibility. The guideline was finalized and documented based on a comparison of detailed test results produced by JNC and BMG for selected datasets (K_d values for the sorption of Np and Pu on bentonite). The final classification results for these datasets are also given in this report.

2. Evaluation of solid solution modeling

Maximum concentrations of radionuclides constitute important input parameters to performance assessment calculations. Typically, such values are derived through thermodynamic speciation calculations, based on solubility products for pure radionuclide solid phases. However, there are indications that the formation of solid solutions may substantially lower the effective solubility limit of various radionuclides.

For the present report, relevant types of solid solutions are described. The modeling approaches available for addressing the different cases are analyzed and related to the corresponding data requirements. In the light of this information, the coffinite and Fe-S-Se systems are analyzed in terms of i) their potential for forming solid solutions involving radionuclides, ii) the available mineralogical and thermodynamic data, and iii) possible approaches for filling some of the gaps in the database.

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Appendices

Appendix I: Revision 2 of the classification guideline

Appendix II: Classification of the selected entries of the JNC-SDB based on Revision 3 of the classification guideline

Appendix III: Availability of enthalpy data in relevant databases

1 Introduction

JNC is developing a number of databases that form a critical part of the performance assessment of nuclear waste repositories in Japan, including databases of selected retention and transport parameters. For the H12 milestone (2000), key parameters for describing radionuclide retention and migration had been selected and listed for each relevant radioelement in a comprehensive documentation (JNC, 2000). In view of the next milestone, JNC has been and is continuing to improve and update its PA-related databases and underlying methodology.

The present project encompasses two specific issues related to radionuclide migration in the buffer and host rock:

- Revision, testing and finalization of a classification scheme regarding the reliability of K_d values for the bentonite buffer and host rock contained in the JNC-SDB
- Evaluation of approaches for solid-solution modeling and data needs, with focus on the coffinite- and Fe-S-Se-systems.

2 Reliability of entries in the JNC-SDB

For the H12 milestone (2000), JNC has been developing a number of basic and applied databases to support the performance assessment of high-level radioactive waste repositories in Japan. These databases include a sorption database (JNC-SDB) that contains a very large compilation of K_d values for all relevant radionuclides from data available in the open literature as well as in reports from various organizations. In addition to the actual K_d values, the JNC-SDB contains a large number of additional key information describing the experimental conditions and procedures pertinent to each K_d value. Following the initial establishment of the JNC-TDB, several additions have been made to this database.

Because of the potential usefulness of the JNC-SDB for waste disposal and environmental sciences in general, JNC is planning to make this database, or parts of it, available to the larger public. In this context, JNC needs to classify the relevant entries in the SDB according to their technical and scientific reliability. To this end, a procedure for the evaluation and categorization of the reliability of K_d values in the JNC-SDB has been developed in a previous project.

For the present project, the following tasks were carried out:

- The test results documented in our previous report (Ochs and Talerico, 2004) as well as in JNC internal reports showed that several parts of the guideline could be modified to decrease the need for expert decisions and to improve reproducibility. An outline of planned modifications was presented to JNC in May, 2004.
- These modifications were implemented by BMG in Revision 1 of the guideline (June 14, 2004).
- Following a detailed review of Revision 1 by JNC and BMG, Revision 2 (November 4, 2004) was prepared by BMG. Revision 2 is reproduced in Appendix I.

- Revision 2 of the guideline was subjected to extensive testing by JNC and BMG. The test datasets were selected from entries in the JNC-SDB containing data for the sorption of Pu and Np on bentonite and related minerals (Np/bentonite, Pu/bentonite). BMG's test results are documented in the present report (chapter 2.2), the results of JNC are given in internal documents.
- The classification scheme was finalized based on a comparison of the test results obtained by JNC and BMG. The definite guideline is labeled Revision 3 (March 15, 2005) and is presented in the following sections.
- The final rating of the selected entries of the JNC-SDB according to Revision 3 (March 15, 2005) is given in Appendix II.

2.1 Classification Guideline, Revision 3, March 15, 2005

2.1.1 Introduction, general description of main criteria

The reliability of K_d values in the JNC-SDB can be assessed using the following three main criteria. The three main criteria are listed in the expected sequence of application during a classification of entries in the SDB. Criteria Ia and Ib are related to documentation and data entry, whereas the technical and scientific quality of an entry is addressed by criteria II and III.

I Completeness of documentation and type of K_d information:

- a) It needs to be verified that the documentation of each entry is detailed enough to allow further examination according to the main criteria II-III. At this point, only the completeness of the documentation is examined; the appropriateness of the reported data and approaches is evaluated under criterion II below.
- b) This point takes also into account that the reliability of data input to the SDB will be substantially higher if K_d values are directly available in table format in comparison to literature that reports e.g. %-adsorbed values in a graph. The latter way of reporting requires the operator to i) manually read values off a graph and ii) to calculate K_d from the %-adsorbed and s/w ratio values given, which significantly increases the likelihood of an operator error during data input.

II Quality of reported data

This is the most important issue from a technical and scientific point of view. This criterion encompasses an evaluation of the appropriateness of the experimental system to produce reliable K_d data. The methods used (or lacking) for determining experimental uncertainty are also examined for each literature source. Further, it is considered whether the data represent single-point measurements or are part of e.g. an isotherm, which would provide additional support for their reliability.

III Consistency of data:

While the previous two main criteria address the reliability of each K_d entry in the SDB, criterion No. III requires an examination of the level of support that other K_d values in similar systems can lend to the entry under consideration. Any disagreement with data from related systems will have to be evaluated as well. It could be argued that this kind of data examination may be left to the user of the SDB. However, the classification of data entries in the JNC-SDB in terms of reliability adds an aspect of quality that is above that for a pure compilation, and users may expect that the listed K_d values passed some kind of check regarding consistency.

In this context, consistency means that data from different sources should not be in obvious disagreement. An example would be the dependency on pH of K_d values for a certain radionuclide, which should be approximately similar in all studies. Similarly, if many studies indicate e.g. stronger sorption of U(IV) than of Th(IV), for any study that indicates the opposite an appropriate explanation should be given. If no good reason can be found, such deviations make a study less reliable. These types of considerations will only be possible for sufficiently well researched elements.

2.1.2 Description of checkpoints within each main criterion

General

Each entry in the JNC-SDB (each K_d value identified in the SDB by a unique ID) should be evaluated and classified individually. Because many studies report K_d values under different experimental conditions, it is not sufficient to evaluate all data based on a given reference globally. Depending on conditions, different entries related to a given study may receive a different rating.

I Completeness of documentation and type of K_d information

The checkpoints under I-a are used for a screening prior to a further classification. Failure to satisfy these checkpoints will always result in the lowest rating (unreliable, not to be used).

I-a.1 Are all mandatory fields completed? Here it is only verified that all fields have been completed by the operator; an entry "not reported" is counted, therefore. The following entries are considered mandatory:

- element
- solid phase
- solution composition
- atmosphere composition

- pH (or other information that allows to derive pH, e.g. portlandite equilibrium)
 - pe/redox condition (only in case of redox-sensitive systems)
 - method of pe control (only in case of redox sensitive systems and imposed reducing conditions)
 - initial RN concentration (except for RN that are not solubility controlled)
 - method for phase separation (in case of batch experiments)
 - type of experiment, if different from batch
- In case of missing entries, the corresponding K_d is excluded from further evaluation and classified as unreliable (until remedied by operator). If all fields are completed, proceed to I-a.2.

I-a.2 Is all mandatory information provided? Here it is evaluated whether critical information is provided or lacking completely. The quality of the information provided is evaluated under criterion II. In addition to the information listed under Ia.1, further mandatory information includes:

- units need to be reported where relevant
- In case of missing mandatory information, the corresponding K_d is excluded from further evaluation and classified as unreliable. If all fields are completed, proceed to I-b.

I-b Does the type of K_d information provided require manipulation by the operator?

→ The following levels are distinguished:

- class 1: table with K_d values given
- class 2: table with % sorbed given
table with residual concentration given
- class 3: linear graph K_d
- class 4: linear graph % sorbed
linear graph residual concentration
- class 5: log graph K_d
- class 6: log graph % sorbed
log graph residual concentration

II Technical and scientific quality of reported data

It is generally assumed that the entries presently contained in the JNC-SDB correspond to a minimum quality standard; i.e. are assumed to be basically reliable. The different checkpoints regarding experimental quality are designed to distinguish different levels of reliability. However, if in case of critical checkpoints even the requirements leading to the lowest rating are not met, the respective entry should be classified as unreliable (indicated for each checkpoint).

II-a Solid phase (substrate)

It is evaluated whether the solid phase has been sufficiently characterized. This is equally important for properly designing experiments, as well as for using the measured K_d values. In general, three types of key information are required:

- Information about major mineral composition.
- Information about accessory minerals or impurities.
- Information about surface characteristics: Minimum is a measure of sorption capacity per mass of sorbent, such as CEC or a different measure of site density per mass.

However, the amount of information required to sufficiently characterize a given solid phase also depends on the complexity of the substrate:

1. It needs to be known whether a substrate consists of a single pure mineral phase, or whether it contains impurities or additional minerals. In general, some measure of site density per mass (e.g. CEC) needs to be known to properly design experiments, in particular with respect to achieving reasonable surface loading.
2. In case of simple substrates (pure minerals), no further information is necessary.
3. In case of complex substrates (i.e., where significant impurities are present, or where a substrate is composed of several minerals), and in particular in case of natural samples, detailed information on composition has to be provided in addition.
4. In cases where sample treatment (such as crushing or sieving) had been performed, the respective information on particle size also needs to be provided (see II-f). Where any chemical treatments (e.g. acid washing to remove calcite; but also change of redox conditions in case of redox-sensitive substrates, see II-c) had been applied, the applied method and resulting mineralogy should be given as well.
5. In case of many commercially available substrates (e.g., MX-80 or Kunigel-V1 bentonite; standard clay minerals from the Clay Minerals Society, such as SWy-1; Min-U-Sil SiO₂, etc.) detailed solid phase information is widely known and can be retrieved from a large number of publications. Therefore,

characterization of such solids is not required for each entry in the SDB; i.e., level A or B can be reached even if such information is not reported. Note that this holds only when such solids have been used as received. Where washing procedures etc. have been applied, the procedures and resulting changes still need to be documented.

→ Three levels of reliability:

- A) Major and minor mineralogy as well as surface characteristics are known. For example: The substrate is a single, well-defined mineral; or comprehensively characterized complex mineral assemblage. Either no sample treatment has been carried out, or it is described in detail and the result are documented.
- B) Major mineralogy as well as surface characteristics are known. For example: The substrate is a single mineral that may contain impurities (such as a non-purified clay mineral) or a complex mineral assemblage where additional impurities could be present. Sample treatment may have led to minor changes in mineralogy.
- C/D) Information on both major mineralogy or surface characteristics is lacking. For example: There is no information on CEC (or another measure of sorption capacity); or the substrate is a natural clay sample where it is not clear whether it is smectite, kaolinite, or illite; or a non-characterized soil or crushed rock. Sample treatment may have led to major changes in mineralogy that are not documented.

II-b Adjustment and control of pH

One of the most important solution parameters controlling RN sorption is pH. It needs to be known to interpret K_d values, but also for proper experimentation: The pH needs to be known to evaluate the solubility limits of radionuclides and some major ions, as well as the stability of certain mineral phases (in particular carbonates). Further, pH has to be approximately constant during a sorption experiment in order to reach equilibrium of sorption reactions. There are two basically different approaches in sorption experiments with regard to pH control:

1. The pH is not controlled, but allowed to reach an equilibrium value according to the experimental conditions and is then measured at the end of the experiment. In this case, it is important that the pH has been verified after experimentation, in order to know its equilibrium value and to demonstrate that it is not significantly different from the initial value.
2. The pH is controlled during the experiment by acid-base addition and/or buffers. Where it is desired to determine K_d values as a function of pH, this cannot be avoided. In this case, it needs to be shown (or known from the literature) that the added acids, bases, or buffers do not interfere with RN reactions at the surface (which obviously influence sorption) or with RN

reactions in solution (which influence sorption through changing the RN speciation). Therefore, use of a non-inert pH buffer at unspecified concentration levels leads to a classification as unreliable.

- Four levels of reliability:
- A) To achieve rating A it is sufficient, but required, that the pH is verified at the end of the experiment. This is based on the assumption that equilibrium or at least a stable state of near-equilibrium conditions has been achieved (see also II-a, II-d, and II-j). In such systems, a determination of the experimental end pH will represent an adequate measure of the actual equilibrium pH. Second, rating A is given where the successful use of inert buffers has been demonstrated (e.g. by measuring K_d in the presence and absence of buffers at some pH, or by showing through speciation calculations that the buffer does not influence RN behavior). In some cases, level A may also apply if a non-inert buffer is part of the experimental setup (see the example of K_d determination as a function of carbonate concentration under level C)
- B) The final pH is reported, but only a pH range (within 1 pH unit) is given instead of a discrete pH value. Rating B also applies in cases where only the initial pH is provided, but the experimental system is well buffered (for example, because a inert buffer is used, or because of the presence of a natural buffer system, such as carbonate).
- C) Only the initial pH is provided, no attempt is made to control final pH. All cases where non-inert pH-buffers are being added. Note that this refers to the addition of an additional complexing ligand, such as acetate, for the control of pH. On the other hand, if a sorption experiment is carried out where K_d is measured as a function of carbonate concentration and this is simultaneously used to control pH, level A applies (given that the effect of carbonate on K_d is documented).
- D) Only a range (within 1 pH unit) of initial pH is provided, no information on final pH is given.
- If a lower quality than required for level D is evident, the respective entry is excluded from further evaluation as unreliable. If a non-inert buffer (e.g. acetate or carbonate) is used at unspecified concentration levels, the entry also has to be classified as unreliable. The same applies if initial and final pH differ by more than 1.5 pH units.

II-c Redox conditions

Here it needs to be differentiated between systems that are not redox-sensitive and systems that are. Within the redox-sensitive systems, it needs to be further taken into account whether only the sorbing RN is redox-sensitive or whether other

components of the system (such as solid phase or groundwater components) are redox-sensitive as well.

In this sense, checkpoint II-c deals with the redox control of the sorbing RN, not with redox control of an overall redox-sensitive system. If the experimental system comprises a range of redox-sensitive dissolved (e.g. organics) and solid (e.g. Fe- and Mn-phases) components, imposing redox conditions different from the original level may influence many redox-equilibria simultaneously. In such a case it can be very difficult to ascertain equilibrium or to know which solid phases are present. Such effects on solution and solid phase chemistry are addressed by checkpoints II-a and II-d. It also needs to be pointed out in this context that "imposed redox condition" does not necessarily refer only to imposing reducing conditions by adding a reducing agent, it also includes imposing oxidizing conditions by e.g. transferring a reduced natural sediment to the laboratory and exposing it to O₂ (as a matter of fact, the latter may be the more common problem).

Given the focus of this checkpoint on redox control of sorbing radionuclides explained above, two different requirements on data quality can be distinguished. Levels of reliability reflect the degree to which these two requirements are met:

1. Reliability regarding control and confirmation of the redox status of the sorbing RN.
2. Reliability regarding the absence of unwanted side effects, such as changes in RN speciation induced by the addition of a reducing agent.

→ Two levels of reliability:

A/B) Level A/B applies to entries in the SDB where it is demonstrated that both of the above requirements are met. This includes the following cases:

- Systems which are not redox-sensitive in terms of sorption and where no reducing agents needed to be added (i.e., where the sorbing RN can take on only one oxidation state in aqueous solutions).
- Redox-sensitive systems that have been pre-equilibrated with and are being kept at ambient conditions.
- Experiments where reducing conditions are imposed on redox-sensitive RN (in otherwise stable systems) and where similar results are obtained using several reducing agents.

C/D) Level C/D applies to entries in the SDB where meeting the above requirements may not have been demonstrated, but can be assumed with high certainty. This includes the following cases:

- Reducing conditions imposed on redox-sensitive RN (in otherwise stable systems) using one reducing agent that can be estimated (e.g. from experience or from the literature) to be effective and to be sufficiently inert with respect to influencing RN behavior.

- In cases where a complexing reducing has been used, level C/D still can be achieved if the influence of the reducing agent on RN speciation has been estimated.
 - All cases where it can be assumed that no significant artifacts regarding RN behavior are introduced and where the oxidation state of RNs has been measured independently. Evaluating the reliability of such measurements may require an expert decision by the operator.
- If a lower quality than required for level C/D is evident, the respective entry is excluded from further evaluation as unreliable. For example, cases where it has been attempted to achieve reducing conditions only by minimizing the level of O₂ (e.g., by performing experiments in a N₂ atmosphere) generally should be labeled "unreliable" (except where the oxidation state of a RN somehow has been confirmed, see description of level B). Also, if a strongly complexing reducing agent (such as many organic acids) is used at unspecified concentration levels, the entry has to be classified as unreliable. Further, if there is clear evidence, e.g. from comparisons with more reliable studies (see Criterion III, consistency) that the reported RN oxidation state is erroneous, the entry may be classified as unreliable.

II-d Final solution composition

Note that solution composition includes dissolved carbonate concentration, which may be controlled through, or expressed as pCO₂. Added pH-buffers or reducing agents are also included, and are addressed in checkpoints II-b and II-c.

→ Two levels of reliability:

- A/B) The final solution composition is known (either from direct measurements or from the initial experimental setup and speciation calculations) and corresponds to equilibrium or is otherwise well constrained. All major components are included in the analysis. Relevant minor components (e.g. traces of carbonate or of other complexing ligands) may only be estimated. Some minor components may be unknown. In case of natural water samples, solutions are (or can be) shown to be charge balanced (within 5 %).
- C/D) The critical major solution components are known, or can be estimated approximately. There may be unknown minor components and/or less critical major components. In case of natural water samples, solutions are approximately charge balanced (within 10 %).
- If a lower quality than required for level C/D is evident, the respective entry is excluded from further evaluation as unreliable.

II-e Temperature

Here, it is evaluated whether temperature is specified and kept constant.

→ Two levels of reliability:

A/B) Temperature is approximately specified (e.g. room temperature) and constant, or varied in a controlled fashion.

C/D) Temperature is not specified at all (i.e., it is not clear whether the experiments had been performed at room temperature or not).

II-f Solid/water ratio (S/W) and grain size

It is evaluated whether enough solid had been added to avoid a significant influence by the vessel walls (see II-m), and to ensure sample homogeneity in case of complex substrates, especially in case of large grain sizes: It is estimated that in cases where less than ca. 100 mg of solid (this value depends on grain size) has been added to each experimental vessel, sample homogeneity and representativeness becomes difficult to achieve in case of complex or crushed samples.

→ Two levels of reliability:

A/B) Enough solid had been used to assume that

a) [surface area sorbent] \gg [surface area vessel], i.e. that at least 5 m² of sorbent surface had been added to each vessel, and to assume that

b) samples are homogeneous and representative; i.e. that enough substrate had been added to each vessel. Enough substrate may mean at least ca. 100 mg in case of relatively homogeneous sorbents (such as bentonite), but may mean at least one to several grams in case of rocks (depending on grain size and complexity).

C/D) Any other than the above.

II-g Sorption value

It is evaluated whether an appropriate experimental design had been employed to avoid sorption values near 0% or 100%, which can lead to higher experimental uncertainty. This problem can be addressed by choosing an appropriate S/W ratio (see II-f) or/and an appropriate initial [RN] (see II-h). However, the choice of [RN] is more restricted by solubility and analytical detection limits.

A) The sorption value is in the range of 5% - 95% sorbed.

B) The sorption value is inside the range of 2% - 98% sorbed.

C/D) Any other than the above.

II-h Initial RN concentration [RN]

This parameter is used to evaluate the likelihood of a possible supersaturation of RN-phases:

- Three levels of reliability:
- A) RN is not solubility limited, or initial [RN] was clearly (at least a factor of 5) below the solubility limit. Note that factor 5 does not take into account uncertainties in RN solubility; i.e., if the solubility of a given RN cannot be estimated with more certainty than e.g. 10^{-6} to 10^{-8} M, then initial [RN] has to be $\leq 2 \times 10^{-9}$ M for rating A to apply.
- B) Initial [RN] was clearly below the solubility limit, but maybe less than a factor of 5 (see above).
- C/D) [RN] was very small, and in all likelihood below their maximum solubility, but the solubility limit cannot be established clearly due to missing information (solution composition) or lacking thermodynamic data.
- If initial RN concentration had been clearly above the respective solubility limit, the respective entry is excluded from further evaluation as unreliable.

II-i Phase separation

Here, the appropriateness of phase separation is evaluated: Note that in cases where colloids or other artifacts are important, different phase separation methods will not lead to the same results. Identical or very similar results with different efficient methods are probably the best direct proof of absence of important colloid effects; hence such studies are rated A. Rating B would be given for methods that can be presumed to remove colloids, but where no direct proof as in A is given.

- Three levels of reliability:
- A) Identical (very similar) results are obtained with different methods of phase separation, where at least one method needs to be efficient in terms of colloids removal (ultrafiltration or high-speed centrifugation). Accordingly, the best comparison would be between two efficient methods, such as ultrafiltration and high-speed centrifugation.

Note that such a comparison of phase separation methods is not required for each individual K_d value: For example: If the absence of artifacts has been demonstrated for some representative samples of a study by comparing an efficient and a standard method of phase separation, the rating A may be given to all datapoints of this study, even if they correspond to the standard method only. Further, cases where a very low colloid concentration and stability can be expected (such as experiments involving rock samples and solutions of high ionic strength) may be rated A even if only standard phase separation methods had been used.
- B) Only one, but efficient method (high-speed centrifugation, ultrafiltration) is used, and there is no evidence for artifacts such as colloid effects or significant sorption to the filter.

- C/D) Only one standard method (normal centrifugation, membrane filtration with nominal pore sizes of 0.01-0.45 μm) is used, and there is no evidence for artifacts such as colloid effects or significant sorption to the filter.
- If no phase separation is used, or in case of obvious evidence for artifacts (colloid effect, adsorption on filter) the data should be labeled as unreliable.

II-j Reaction time

- Two levels of reliability:
- A/B) Identical (similar) results are obtained with different reaction times, or some other demonstration of near-equilibrium is provided (e.g. separate kinetic experiments).
- C/D) Only one, but reasonably long reaction time is used. What is “reasonably long” is highly dependent on the experimental system: In general, the time needed to reach equilibrium will increase with the complexity of the sorbing substrate and the strength of sorption. Sorption of Sr onto a pure clay mineral through ion exchange can be assumed to be complete within a day; sorption of a trivalent actinide onto a complex substrate may need several days to weeks for completion. In the absence of kinetic information, operator expert decisions will be required to assess this point. If possible, reaction times reported for similar systems included in the JNC-SDB could be used to evaluate what is reasonably long. Further, even for the most simple systems a reaction time of 1 day is considered as minimum requirement.
- If the requirement for level C/D is not met (i.e., if the reaction time cannot be assumed to be reasonably long), the data should be labeled as unreliable.

II-k Agitation method

- Two levels of reliability:
- A/B) Appropriate agitation is required in all cases, except where enough kinetic information is provided to show that equilibrium has been reached. Shaking is the preferred method, as use of stir bars can lead to abrasion of samples. In case of simple and well crystallized substrates (such as Al-oxide) or of substrates with very small grain size that are easily suspended, stir bars can also be accepted.
- C/D) Agitation has been carried out, but one or more of the above requirements regarding agitation methods is not satisfied.

- If it is clear that no agitation has been used, the data should be labeled as unreliable (except where enough kinetic information is provided to show that equilibrium has been reached, see level A/B).

II-1 RN loading

Ideal are values as a function of RN loading (i.e., K_d values that form part of an isotherm), otherwise low loading is preferred. RN loading (e.g. in moles RN/kg substrate) refers to the amount of RN adsorbed in relation to the amount of different surface sites available. It is known from classical isotherms (e.g. Langmuir) that a linear sorption can only be assumed if sufficient unoccupied sites are present. In case of simple substrates (including some bentonites), the linear portion of an isotherm extends to fairly high RN loading. There are other cases where K_d depends significantly on RN loading over many orders of RN concentration.

→ Three levels of reliability:

- A) At least one isotherm has been determined (for a constant solution composition and S/W), and at least some experiments have been carried out using trace level RN concentration (i.e., at least some data are included within a linear sorption region).
- B) No isotherm is available, but at least a limited variation of initial [RN] or S/W has been carried out, and some experiments have been carried out using trace level RN concentration (i.e., some data are included within a linear sorption region).
- C/D) No variation as in A or B has been carried out.

II-m Reaction vessels

High-density polyethylene (HDPE) or Teflon are preferred over normal PE, which is preferred over glass, which may lead to sorption of radionuclides by the vessel walls. Especially at high or very low pH, glass dissolution and release of dissolved or colloidal silica may also occur. On the other hand, glass is more gas-tight (especially than PE); if that is of experimental relevance. Corrections for sorption on vessel walls should not be necessary if blank tests show that it can be neglected.

Correction for sorption on vessel walls may be needed to estimate K_d values correctly in some cases, but only in cases where a) sorption on the vessel is much stronger than on the solid sorbent, or b) if the vessel offers a significant surface area in comparison to the sorbent (see II-f). If that is not the case, the sorption on the added solid will be much greater than on the vessel in a system where both solid and vessel are present. It is further an erroneous assumption that sorption on the vessel will be same in i) the absence of the solid (no competition for RN by solid) as ii) in the presence of the solid (strong competition for RN by solid). The sorption on the walls is typically much smaller in ii) than in i). Therefore, the

overall mistake is often bigger if sorption on the vessel wall is accounted for than if it is neglected.

If effects of vessel walls are corrected for, it has to be done by extracting any RN sorbed to vessel walls after experimentation (e.g. by acid washing) and establishing a complete mass balance.

→ Two levels of reliability:

- A) An appropriate vessel has been used (taking into account sorption as well as tightness with respect to CO₂ or O₂, where required), and corrections for sorption on vessel wall have been performed or no sorption on vessel wall has been observed by blank tests. If effects of vessel walls are corrected for, it has to be done by extracting any RN sorbed to vessel walls after experimentation (e.g. by acid washing) and establishing a complete mass balance. If the sorption on vessel wall has been determined as significantly lower (at least two orders of magnitude in terms of K_d) than the actual K_d value and thus corrections for sorption on vessel wall have not been performed, such a case would also correspond to level A
- B) An appropriate vessel has been used, and corrections for sorption on vessel walls have not been performed.
- C/D) The vessel used may have been not appropriate, or corrections for sorption on vessel wall have been performed based on a blank test only (i.e., without verifying that sorption on vessel walls is relevant in the presence of a solid added, thus possibly leading to overcorrection).

II-n Uncertainty estimates

In general, uncertainties based on repeated experiments (i.e., actual observations of K_d) are preferred over uncertainties based on error propagation, as the latter is an estimate based on a type of extrapolation. Thus, the difference between levels of reliability is mainly based on the amount of actual information gained by repetitions: For level A, the entire experiment is repeated; for level B, only sampling and analysis are repeated; for C, no repetitions are carried out.

Values that are based on repetitive experiments are preferred over single experimental data points. Note, however, that this checkpoint refers to single-point K_d values and may be overruled by data being part of e.g. pH-edge, isotherm, kinetic experiment, etc., which may provide independent evidence of good reproducibility or systematic errors (see checkpoint II-o).

→ Four levels of reliability:

- A) Uncertainties in K_d are derived based on entire, replicated sorption experiments (i.e., at least duplicate experiments).

- B) Uncertainties in K_d are derived based on single sorption experiments that are sampled and analyzed repeatedly. This may be supplemented by error propagation.
- C) Uncertainties in K_d are based on error propagation of estimated analytical and/or procedural uncertainties.
- D) No error estimate is given, no repeated sampling is done.

II-o Parameter variation

Studies with a systematic variation of key parameters are much more valuable and reliable than single K_d measurements. In this context, key parameters are those that influence sorption (for example, chemical parameters such as RN concentration, pH, pCO_2 , but also temperature, S/W, or grain size in case of crushed substrates), but not parameters that only help to determine the experimental framework (such as vessel type or reaction time). In particular, variation of key parameters allows improved detection of experimental problems and systematic errors. Especially the latter are not detected by repeating experiments under identical conditions. In the application of this checkpoint, care has to be taken to take into account the characteristics of the particular system studied. For example, more parameter variation may be required to show clear trends in a complicated system in comparison to a simpler one. On the other hand, the pH and carbonate concentration in experiments with calcite are quite constrained by the solid itself, and only limited variations are possible.

→ Four levels of reliability:

- A) Both RN surface loading (isotherm) as well as a chemical parameter, such as pH or pCO_2 (edge), or e.g. [Na] in case of ion exchange, are varied systematically.
- B) Either RN concentration (isotherm) and/or chemical parameters, such as pH or pCO_2 (edge), or e.g. [Na] in case of ion exchange (i.e., at least two parameters in total), are varied. These variations are less systematic than in A, but still allow to observe trends.
- C) As B, but only one parameter in total is varied.
- D) No parameter variation is done.

III Consistency of data

Here it will be evaluated whether data from a particular study can be supported by other studies. Comparisons should only be made with studies that are at least as (or more) reliable than the study under investigation, based on criteria I and II. In many cases, only approximate consistencies or inconsistencies may be apparent, because of different conditions used in the different studies.

- Therefore, the evaluation of criterion III will only be reported in the form of a comment. Any such comments will be included both in a classification report as well as in the corresponding rating summary sheets.
- If the K_d values under investigation are *clearly* inconsistent with the majority of related reliable studies, and if the reason for this observation cannot be explained, they may also be labeled unreliable based on criterion III. As this requires an expert decision by the operator, the underlying reasoning needs to be clearly documented.

2.1.3 Overall classification and recommended procedures

The above criteria are applied to an overall classification system as follows:

- The three criteria I-III are evaluated separately, the respective results are reported separately as well.
- Criterion I: The checkpoints under I-a are used in a yes/no screening fashion, entries not fulfilling I-a are labeled as unreliable and are not evaluated further. Criterion I-b is then used to assign classes 1-6 for documentation.
- Criterion II:
 - a) The datasets that pass Criterion I are again classified according to a 6-level system, where classes 1-6 represent the highest and lowest levels of reliability. To ensure a minimum quality level, certain checkpoints are regarded as critical (marked with * in Table 1) If the quality of the data does not correspond to the respective minimum requirements, the entries are not to be used and are classified as unreliable.
 - b) To facilitate transparent averaging of all checkpoints, the following numerical system is used: A=3, B=2, C=1, D=0 (A/B=3 and C/D=0 in some cases).
 - c) Initially, checkpoints II-b, II-c, II-d, and II-h are evaluated (indicated in bold letters below). If an entry is rated unreliable for any of these or other checkpoints marked as critical in Table 1 below, it is excluded from further evaluation.
 - d) Weighting of individual checkpoints at this level is done according to the factors given in Table 1 below.

Table 1: Weighting of individual checkpoints under Criterion II.

checkpoint	description	weighting factor
II-a	solid phase (substrate)	A-C/D × 2
* II-b	pH	A-D × 8
* II-c	redox conditions	A/B-C/D × 8
* II-d	final solution composition	A/B-C/D × 8
II-e	temperature	A/B-C/D × 1
II-f	S/W, grain size	A/B-D/D × 2
* II-g	sorption value	A-C/D × 2
* II-h	initial RN concentration	A-/CD × 8
* II-i	phase separation	A-C/D × 8
* II-j	reaction time	A/B-C/D × 2
* II-k	agitation	A/B-C/D × 1
II-l	RN loading	A-C/D × 2
II-m	reaction vessel	A-C/D × 1
II-n	uncertainty estimates	A-D × 2
II-o	parameter variation	A-D × 8

* critical checkpoints with minimum requirements; bold letters indicate the checkpoints to be evaluated initially

- d) The total sum of points obtained for Criterion II is then used to indicate the level of reliability. With the present system, the maximum number of points would be 183, leading to an overall classification as follows (Table 2):

Table 2: Overall classes of reliability for Criterion II

points	rating
183-151	class 1
150-121	class 2
120-91	class 3
90-61	class 4
60-31	class 5
30-0	class 6

- Criterion III: Criterion III is used to qualitatively assess consistency with other studies. In case of clear inconsistencies, an entry may be labeled as unreliable.
- Overall, the following classification system is used, with Criterion II as the main basis for assessing the reliability of entries in the JNC-SDB

Criterion	classification
I-a	accept/reject
I-b	6 classes of K_d information
II	6 classes of data quality and reliability
III	qualitative level of consistency with other studies

2.2 *Testing of the guideline: Classification of selected entries in the JNC-SDB*

Before finally accepting the revised guideline, it was tested against selected entries in the JNC-SDB containing data for the sorption of Np and Pu on bentonite. This chapter contains the classification results for these entries as obtained by BMG Engineering, based on Revision 2 (November 4, 2004) of the classification guideline. The results for criteria I, II, and III are described in detail in case of each entry. A summary of the results and the resulting overall numerical rating can be found in Appendix II.

2.2.1 *Criteria I and II: Documentation and quality of data*

2.2.1.1 *Test case Pu/bentonite*

REF: Allard et al. (1982)

I-a.1

SDB All mandatory fields are completed.

→ Yes

I-a.2

SDB Eh is not given, but both the oxidation state of Pu as well as the atmosphere and redox conditions are indicated. Overall, all mandatory information is provided.

→ Yes

I-b.1

SDB K_d values are taken from a table.

REF: It is reported that the K_d values given in the table are not actual experimental data, but values that were extrapolated to pH 8.5 based on the experimental values shown in Figure 1 in the REF.

→ class 1

Note: The above rating is retained for the moment, and the data are further evaluated illustrative purposes. However, the present entries need to be deleted or replaced with actual experimental data.

→ *To better evaluate the quality of some of the entries below it was necessary to consult the original reference (REF).*

II-a Solid phase

SDB: The solid phase is characterized as Wyoming bentonite MX-80 (in the additional Excel files). The CEC is reported, while the surface area is not reported.

Despite the fact that the surface area is not specified, MX-80 bentonite is well defined based on the open literature. Therefore the quality of information about the solid phase may be considered as complete.

→ A

II-b Adjustment and control of pH

SDB: Both initial as well as final pH are given. They agree within 0.5 units.

→ A

II-c Redox condition

SDB: The initial oxidation state of Pu is specified (IV, III). The experiments were carried out in N₂.

REF: No reducing agent was used. It is reported that Pu existed most likely as a mix of oxidation states (III/IV/V).

→ unreliable

II-d Final solution composition

SDB: A synthetic groundwater with total carbonate and salt concentration of 123 mg/L and 306 mg/L was used.

REF: The initial pH was 8.2.

→ C/D

II-e Temperature

SDB: A temperature of 25°C is specified.

→ A/B

II-f Solid/water ratio, grain size

SDB: A solution/solid ratio of 100 mL/g is given.

REF: 0.2 g solid were added to 20 mL solution.

Assuming a BET (outer) surface area of ca. 35 m²/g, this would result in ca. 7 m² bentonite surface per 20 mL vessel.

→ A/B

II-g Sorption value

According to the sorption values calculated based on the information given in the SDB, the following rating is given:

→ B: Datapoints 42536 and 42537

II-h Initial RN concentration

SDB: Initial Pu concentrations of 6×10⁻⁸ M for datapoint 42536 and of 6×10⁻¹⁰ M for datapoint 42537 are given.

The exact solution composition is not known, but at least the important parameters pH and carbonate concentration can be estimated. A bigger problem is the lack of information regarding the oxidation state of Pu. Assuming that a significant fraction of Pu was in the +IV state, with a solubility in the order of 10⁻⁹ M under the given conditions (see e.g. Rai et al., 1999), the following rating is given:

→ unreliable: Datapoint 42536

→ C/D: Datapoint 42537

II-i Phase separation

SDB: Centrifugation at 27000 g for 1 hour is indicated

→ B

II-j Reaction time

SDB: A contact time of 6 days is indicated.

REF: A range of reaction times (6 hours-6 weeks) was used, but only one dataset (for 6 days) is reported.

It can only be assumed that the kinetic experiments showed that 6 days is a reasonable reaction time.

→ A/B

II-k Agitation method

SDB: No information is available.

REF: No information is available. For the experimental technique, reference is made to a report that has not been available for the present evaluation.

It can only be assumed that the kinetic experiments showed appropriate equilibration.

→ A/B

II-l RN loading

SDB: No isotherm is reported, but two different initial Pu concentrations were used.

→ B

II-m Reaction vessels

SDB: No information is available.

REF The experiments were carried out in polypropylene vessels. No correction for sorption on vessel walls was done.

→ B

II-n Uncertainty estimates

SDB: No information is reported.

→ D

II-n Parameter variation

SDB: Only the initial Pu concentration was varied in a very limited way

→ C

REF: Barney (1981)

I-a.1

All mandatory fields are completed.

→ Yes

I-a.2

All mandatory information is provided.

→ Yes

I-b.1

K_d values are taken from a table.

→ class 1

→ *To better evaluate the quality of some of the entries below it was necessary to consult the original reference (REF).*

II-a Solid phase

SDB: The solid phase is characterized. The requested information such as CEC, surface area, grain size, and major mineralogical composition are given in the Excel file "solid phase", but not in the Access-based database.

REF: The sample had blue-green color

→ B (see note below, as well as II-c and section 2.2.2.1)

Note: Typically, natural smectites contain a number of minor auxiliary minerals, which are not reported in this case. The smectite sample used in this study is reported to have a blue-green color, which often indicates the presence of Fe(II).

While rating B is given for II-a, according to the description for this particular checkpoint, it is important to keep in mind that the experiments are carried out with a highly redox-sensitive element whose behavior could be strongly influenced by the presence of Fe(II).

→ Based on criterion III, it can be concluded that in this case, the solid phase characterization had not been sufficient to allow appropriate experimental planning.

- Considering all evidence, the data points reported for Pu(VI) are labeled unreliable in II-c because their reported oxidation state is considered to be in error due to shortcomings in the solid phase characterization.

II-b Adjustment and control of pH

SDB: Only the initial pH values are specified. The use of buffers is not specified.

REF: To investigate the dissolution behavior of the solids used, additional kinetic experiments were carried out, but apparently with groundwater #2 only. It is reported that pH leveled out at a value of about 8.4 in experiments with the secondary mineral sample (smectite). Figure 6 in the REF shows that Ca concentrations had been significantly increased after one week, and it is estimated that the change in pH occurred within the same timeframe.

Based on the above evidence, it is suggested that the equilibrium pH values could be about 2-2.5 units lower than the initial ones. However, this information seems to be available only for one groundwater type and oxidizing conditions, and it cannot be estimated whether the pH varied less or more in the case of the other groundwater compositions and/or reducing conditions.

→ unreliable

II-c Redox condition

SDB: Redox conditions are reported. The experiments were conducted with Pu(IV) and Pu(VI). All experiments were conducted in pre-equilibrated systems. The oxidation state of Pu is specified for each experiment. For the Pu(IV) experiments the authors used hydrazine as reducing agent, while the experiments carried out for Pu(VI) were conducted in air atmosphere, and in the absence of hydrazine. Final Eh values are given in the SDB.

REF: The hydrazine concentration was 0.05 M. It is reported that this hydrazine concentration lowered the redox potential from about +200 mV in an air-saturated solution to about -800 mV at pH \approx 10. While the reporting in the REF is not very specific with regard to this issue, it appears that these Eh measurements were done in separate solutions as a preliminary test of the effect of the hydrazine addition, and that they do not represent the final Eh values measured in actual sorption experiments. It is estimated that Pu exists in the +III state at -800 mV and pH \approx 10.

Note: Based on the above, it is recommended to remove the Eh data from the field "Eh end" in the SDB and to list this information in the appropriate additional Excel file instead.

→ Based on the above discussion, the Pu(IV) results are evaluated separately from those of Pu(VI), as follows:

C/D: Data for reducing conditions (44647, 44650, 44652, 44654, 44659, 44660, 44663, 44664, 44665, 44666)

Unreliable: Data for oxidizing conditions (44648, 44649, 44651, 44653, 44655, 44656, 44657, 44658, 44661, 44662):

If II-c were to be evaluated individually, the data for oxidizing conditions would receive rating A/B according to the description of this checkpoint in revision 2 of the classification guideline. However, the similarity of K_d values obtained under reducing and oxidizing conditions (see Figure 2.2.2) strongly suggests that the oxidation state of Pu had been the same in both sets of experiments. Based on the discussion of the uncertainties in the mineralogical composition of the solid phase sample, the most likely explanation is that the solid contained Fe(II) that was able to act as a reducing agent towards Pu (see II-a). It is not clear whether the reduction may have occurred only during the actual sorption reaction, leaving the dissolved Pu in an oxidized state. An alternative explanation would be to assume that Pu was oxidized in the presence of the high concentrations of hydrazine, but this seems less likely (see Figure 2.2.2).

Considering all evidence, the data points reported for Pu(VI) are labeled unreliable because the oxidation state reported for the sorbing RN is considered to be in error.

→ *Note: The following evaluation is restricted to the data obtained under reducing conditions:*

II-d Final solution composition

SDB: The experiments were conducted with different synthetic water compositions. All components of these solutions are known (see Excel file "solution composition"). The experiments were conducted both in air atmosphere and under reducing conditions.

REF: The solids were pre-equilibrated overnight with the appropriate solutions prior to the sorption experiments. However, as already noted in II-b, there is evidence that the pH and possibly other solution components changed significantly during the solid-water interaction. It is not clear whether these changes were accounted for by the brief pre-equilibration.

→ C/D

II-e Temperature

SDB: The temperature is not specified.

REF: Experiments were carried out at 23 ± 2 °C.

→ A/B

II-f Solid/water ratio, grain size

SDB: The experiments were carried out with 1 g solid and 30 mL solution. The grain size was smaller than 2 μm (at least in case of the BAS_MINER sample considered here. The amount of solid (1 g) may be considered as sufficient to achieve sample homogeneity and representativeness.

→ A/B

II-g Sorption value

According to the sorption values calculated based on the information given in the SDB, the following rating is given:

→ A: Datapoints 44647 and 44648

→ B: Datapoint 44649

→ C/D: Datapoints 44650-44666

II-h Initial RN concentration

SDB: The initial Pu concentrations were between 1.8×10^{-10} M and 8.6×10^{-12} M.

The concentrations can be considered lower than the expected solubility limits for Pu (IV) based on solubility data for $\text{ThO}_2(\text{am})$ taken from Rai et al., (1999), but not necessarily by a factor of 5 or more.

→ B

II-i Phase separation

SDB: All samples were filtered by ultra-filtration, no other technique was used for comparison.

→ B

II-j Reaction time

SDB: The experiments were sampled after a reaction time of 14 days.

REF: Separate kinetic experiments suggest that the sorption of Pu on the secondary mineral sample may not have reached equilibrium after 2 weeks.

→ unreliable

II-k Agitation method

SDB: No information is available.

REF: All samples were gently shaken during the entire experiment.

→ A/B

II-l RN loading

SDB: For any constant solution composition or S/W ratio, no isotherm was determined, and no variation of initial Pu concentration was carried out.

→ C/D

II-m Reaction vessels

SDB: No information is available.

REF The experiments were carried out in polycarbonate centrifuge tubes.

→ B

II-n Uncertainty estimates

SDB/REF: Error estimates were not determined.

→ D

II-n Parameter variation

SDB: The Pu concentration was varied while applying a constant S/W ratio and different water compositions.

REF: A statistical experimental screening design was applied, where each particular combination of parameters occurs only once.

The applied experimental design does allow to observe trends as a function of parameter variation, but only in a statistical sense. Presumably, this design will not yield useful results in cases where different parameters have compensating influences on sorption because the variation of each parameter is quite limited.

→ D

REF: Billon (1982)

I-a.1

All mandatory fields are completed.

→ Yes

To better evaluate the quality of some of the entries below it was necessary to consult the original reference (REF).

I-a.2

SDB: The following mandatory information is missing:

- The method used for phase separation is not reported in the SDB.
- The reducing agent used in the experiments with Pu(IV) is not reported.

REF: Billon (1982) carried out the sorption experiments for Pu on bentonite. The bentonite is characterized by its CEC and its major elemental composition, but the surface area and the particle size are not specified. Also not specified are the final solution composition in the sorption experiments (indicated as porewater) and how (or if) reducing conditions were imposed to the experimental system. All samples were filtered through a 0.22 µm millipore filter and their Pu concentration was measured by scintillation liquid technique. All experiments were carried out with high initial [Pu] concentrations (8×10^{-5} M) and it is not possible to verify if the experiments were solubility limited because the solution concentration of the porewater is not given. At such high initial Pu concentration, the total amount of dissolved [Pu] in the system is expected to be controlled by the Pu solubility.

→ Several mandatory pieces of information are not given in the SDB, and this situation would lead to the classification "unreliable". Even in the REF, the method used to impose reducing conditions is not reported. Therefore, only the values referring to Pu(VI) are evaluated further. The values referring to Pu(IV) are labeled "unreliable" and are not evaluated further.

The following evaluation is done only for the values referring to Pu(VI); i.e., data points 48877-48880.

I-b

SDB: Type of information is reported as " K_d "

REF: This information is not given in the copy available to BMG.

→ class 1 for the data referring to Pu(VI), following the judgment by JNC

II-a Solid phase

SDB: Solid phase is bentonite

REF: Information on major elemental composition and mineralogy as well as CED is provided, but information on minor mineralogy and impurities is not given

→ B

II-b Adjustment and control of pH

SDB: Final pH is given

REF: The initial pH is not given, but it is reported that the final pH was adjusted using additions of acid or base that had been determined based on preliminary titration experiments. Based on this information, it is assumed that the pH was controlled well in the experiments.

→ A

II-c Redox conditions

SDB: Eh is not reported. The entry in the field atm/redox condition is "n.r.", but oxidizing (or reducing) conditions are indicated by the operator. There is no information regarding the specific conditions.

REF: No additional information appears to be available.

→ The data referring to Pu(VI) are labeled C/D, based on the following distinction between A/B and C/D (see revision 2 of the guideline, November 4, 2004): Level C/D applies to entries in the SDB where meeting the requirements for A/B may not have been demonstrated, but can be assumed with high certainty.

II-d Final solution composition

SDB: The water type is given as porewater ("PW")

REF: Only the initial solution composition is given (de-ionized water).

→ Because the solid composition is not reported in any detail, it is not possible to estimate the final solution composition with enough certainty. Therefore, the study is labeled as "unreliable".

II-e Temperature

SDB: A temperature of 20°C is specified.

→ A/B

II-f Solid/water ratio, grain size

SDB: A solution/solid ratio of 200 mL/g is given.

REF: 0.1 g solid were added to 20 mL solution.

Assuming a BET (outer) surface area of ca. 35 m²/g for bentonite, this would result in ca. 3.5 m² bentonite surface per 20 mL vessel; i.e. a value which is not much above the required minimum.

→ C/D

II-g Sorption value

According to the sorption values calculated based on the information given in the SDB, the following rating is given:

→ A: Datapoints 48877 (55.6 % sorbed) and 48878 (71.4 % sorbed)

→ B: Datapoint 48879 (96.9 % sorbed)

→ C/D Datapoint 48880 (99.7 % sorbed)

II-h Initial RN concentration

SDB: An initial Pu(VI) concentration of 6×10^{-6} M is given.

REF: No further information is available.

Based on the information on U(VI) solubility in Grenthe et al. (1992), and on the solubility of Pu(VI) in Lemire et al. (2001), the initial Pu(VI) concentration may have been above the solubility limit of hydrated Pu(VI)-oxide (at least at pH > 6).

→ unreliable

II-i Phase separation

SDB: Not reported

REF: Filtration through 0.22 μm membranes was done.

→ C/D

II-j Reaction time

SDB: A contact time of 1 day is indicated.

REF: No further information is available.

Considering the information on pH control and agitation, 1 day may be sufficient.

→ C/D

II-k Agitation method

SDB: No information is available.

REF: Some automatic agitation device was used.

It can only be assumed that the agitation method was appropriate.

→ A/B

II-l RN loading

SDB: No variation of the relevant parameters is reported.

→ C/D

II-m Reaction vessels

SDB/REF: No information is available.

→ C/D

II-n Uncertainty estimates

SDB: In the field "error", it is indicated that no information is reported. On the other hand, 4 replicates are indicated for the datapoints 48877 and 48878, no repetition is indicated for datapoints 48879 and 48880.

REF: No further information is available in the incomplete copy available to BMG.

→ A Datapoints 48877 and 48878 (accepting JNC's judgment that the replicates were indeed used to determine uncertainties)

→ D Datapoints 48879 and 48880

II-n Parameter variation

SDB: Only the pH was varied.

→ C

REF: Sharma and Oscarson (1989)

I-a.1

All mandatory fields are completed.

→ Yes

I-a.2

All mandatory information is provided (the oxidation state of Pu (IV) was verified with the 2-thenoyltrifluoroacetone method and only Pu(IV) was detected, but this was probably done for the stock solution only; see II-c).

→ Yes

I-b.1

K_d values are taken from a table.

→ class 1

To better evaluate the quality of some of the entries below it was necessary to consult the original reference (REF).

II-a Solid phase

SDB: The solid phase consists of a mix of clay and sand (50/50 wt.%). Both CEC (meq/100 g) and surface area (m^2/g) of the clay are given. The approximate mineralogical composition of the clay is given. Minor impurities and the composition of the sand is not reported.

REF: For the composition of the sand the authors refer to Robin et al. (1988).

Nevertheless, the major information can be considered as complete, because the minerals important for sorption are presumably contained in the clay.

→ B

II-b Adjustment and control of pH

SDB: The pH conditions were verified at the beginning and at the end of the experiment.

→ A

II-c Redox condition

SDB: Redox conditions are reported.

REF: The actual oxidation state of Pu can not be clearly identified based on the information given in this publication. It seems that the addition of nitrite, as well as the measurement of the oxidation state of Pu refers to the stock solution rather than the actual experimental system.

Based on the lack of information regarding the oxidation state of Pu, this entry is classified as unreliable.

→ unreliable

Note: The entry on redox condition in the SDB should be verified and corrected, if necessary.

II-d Final solution composition

SDB: A synthetic groundwater was used. According to the additional information in Excel files, it represents Canadian Shield groundwater with I = 0.27 (mainly Na, Ca, Cl) .

REF: It is reported that in some cases, a small amount of distilled water had to be added to the samples to obtain enough liquid volume for analysis.

It should be possible to obtain the exact input groundwater composition. However, because of the high S/W and the addition of distilled water to some samples, it is deemed impossible to calculate a final solution composition with sufficient certainty.

→ unreliable

II-e Temperature

SDB: Not reported

REF: A temperature of 25°C is specified for the diffusion measurements. No information is given for the sorption measurements.

→ A/B (assuming that the same temperature had been used in all experiments)

II-f Solid/water ratio, grain size

SDB: A solution/solid ratio of 0.3 mL/g is given.

REF: No further information is available.

→ C/D

II-g Sorption value

According to the sorption value calculated based on the information given in the SDB, the following rating is given:

→ C/D (datapoint 59026)

II-h Initial RN concentration

SDB: The initial Pu concentration was 5×10^{-9} M.

The uncertainty in terms of solution composition does not allow to assess solubility limits with certainty.

→ C/D

II-i Phase separation

SDB: Centrifugation (with un-specified settings) and filtration through 0.45 µm membranes is indicated.

REF: Ultracentrifugation was used.

→ B

II-j Reaction time

SDB: A contact time of 90 days is indicated.

This is a very long equilibration time for a normal sorption experiment, but no kinetic data are provided. However, considering the very high S/W and the uncertainty regarding agitation (II-k), it is not clear that 90 days were enough to reach equilibrium.

→ unreliable

II-k Agitation method

SDB/REF: No information is available.

It is not clear whether normal agitation was even possible at this high S/W.

→ unreliable

II-l RN loading

SDB/REF: No variation of relevant parameters is reported.

→ C/D

II-m Reaction vessels

SDB/REF: No information is available.

→ C/D

II-n Uncertainty estimates

SDB: Experiments were duplicated, but no error estimate is reported.

REF: It is reported that replicate values agree within 20 %.

→ A

II-n Parameter variation

SDB/REF: No parameter variation is reported

→ D

REF: Shibutani et al. (1998)

I-a.1

All mandatory fields are completed.

→ Yes

I-a.2

To evaluate the mandatory information of this study it was necessary to consult the original reference (REF). An estimated oxidation state of Pu could be given in the SDB.

SDB: The end Eh and reducing agent used are given in the JNC-SDB, but the oxidation state of Pu is not directly reported.

REF: The oxidation state of Pu was estimated as +IV by the 0.5 M TTA-xylene extraction method. To control the Eh of the system, the authors used $\text{Na}_2\text{S}_2\text{O}_4$ and, based on the reported Eh measurements between -501 mV and -101 mV, it can be expected that the system is dominated by a mix of Pu(III) and Pu(IV).

→ Yes

I-b

SDB: The K_d values are derived from a scan (scanned).

REF: The K_d values are reported in a graph.

→ class 5 (accepting JNC's judgment that the graph is logarithmic)

II-a Solid phase

SDB: The experiments were carried out using as solid phase Kunigel-V1 bentonite with a surface area of $10 \text{ m}^2/\text{g}$. CEC is not reported.

However, Kunigel-V1 bentonite is well defined in the literature.

→ A

II-b Adjustment and control of pH

SDB: The pH conditions were measured at the end of the experiments.

→ A

II-c Redox condition

SDB: Redox conditions are not reported, but Eh values are available for each experiment.

Based on the measured Eh values the dissolved Pu is probably a mix of Pu(III) and Pu(IV) (see I-a.2).

→ C/D

II-d Final solution composition

SDB: The experiments were performed with 0.1 M NaClO₄ and 0.01 M NaClO₄. The pCO₂ conditions are not reported.

REF: All experiments were carried out under Ar atmosphere (O₂ < 3 ppm).

The pCO₂ was not directly specified but under the reported experimental conditions it can be considered negligibly small. Except for pH, the final solution composition is not reported, but can be obtained, if needed, from similar published experiments involving Kunigel-V1. As the L/S is reported, the final solution composition can also be estimated based on the known composition of Kunigel-V1.

→ C/D

II-e Temperature

SDB: The experiments were carried out at 25 °C.

→ A/B

II-f Solid/water ratio, grain size

SDB: The experiments were carried out at a constant solution/solid ratio of 50 mL/g, but the exact volume and weight values as well as the grain size of the solid phase are not reported. Because Kunigel-V1 is dominated by clay, a very small grain size can be assumed, however. Assuming that the experiments had been performed using at least 5 mL of volume (corresponding to at least 100 mg of sample), these entries are rated

→ A/B

II-g Sorption value

Based on the information in the SDB, the following rating is given:

datapoint	% sorbed	rating
59256	96.9	B
59257	28.9	A
59258	29.3	A
59259	97.8	B
59260	98.1	C/D
59261	99.8	C/D
59262	98.5	C/D
59263	100.0	C/D
59264	98.8	C/D
59265	98.8	C/D
59266	99.0	C/D
59267	52.3	A
59268	99.2	C/D
59269	99.2	C/D
59270	99.9	C/D
59271	99.4	C/D
59272	63.7	A
59273	99.9	C/D

II-h Initial RN concentration

SDB: The initial Pu concentration is reported as 1×10^{-8} M.

REF: The range of 1.3×10^{-12} M to 2.19×10^{-8} M is reported for initial Pu concentration

The initial [Pu] of 2.19×10^{-8} M may be close to the solubility limit based on solubility data for ThO₂(am) taken from Rai et al., (1999). Based on the available information, the following rating is given:

→ C/D

II-i Phase separation

SDB: All samples were filtered through a 10000 MWCO filter.

REF: No evidence of artefacts is reported.

The following evaluation is made on the basis of the information reported in the SDB.

→ B

II-j Reaction time

SDB: The reaction time is not reported.

REF: The reaction time was between 65 and 104 days. This is assumed to be reasonably long, even for the fairly complex system under consideration:

→ C/D

II-k Agitation method

SDB/REF: No information concerning the agitation method is given. Further, no kinetic information is available.

Following version 2 of the classification guideline, the study therefore would have to be labeled as "unreliable".

→ According to a personal communication quoted by JNC, the vessels were shaken by hand. Given that this was done repeatedly (e.g every few days), the study is labeled C/D.

II-l RN loading

SDB: No isotherms or variation in L/S or initial RN concentration are reported.

REF: Based on the reported range of initial RN concentrations, it can be expected that a limited variation of initial RN concentration has been carried out. Also, at least a few data have been measured using trace initial RN concentrations.

→ B

II-m Reaction vessels

SDB: No information concerning the reaction vessels is reported.

REF: The experiments were carried out in Teflon vessels. Furthermore blind test were performed to estimate the adsorption on the vessel wall.

→ B (Accepting JNC's rating. Based on the information available to BMG in the SDB or REF, no definite rating can be carried out.

II-n Uncertainty estimates

SDB/REF: Error estimates are not reported, the experiments were not replicated.

→ D

II-o Parameter variation

SDB: Experiments were performed in two different electrolyte solutions using a constant initial RN concentration and solid/water ratio. For both solutions the pH value was varied between about 6 and 11, yielding in both cases similar K_d trends.

REF: It seems that the initial RN concentration had been varied as well.

→ B, taking into account the information from SDB only.

REF: Sato & Shibutani (1994)

Only an incomplete copy of this report was available for the present evaluation.

I-a.1

All mandatory fields are completed.

→ Yes

I-a.2

To evaluate some of the mandatory entries it was necessary to consult the original reference (REF). For the present report, only an incomplete copy of the original reference had been available.

SDB: The oxidation state of Pu as well as Eh are not given. The experiments were done in air atmosphere.

REF: The authors investigated the sorption of ^{239}Pu isotope onto bentonite without verifying the oxidation state. The experiments were carried out in air atmosphere; i.e., in the presence of oxygen. It is not clear in which form the Pu had been added to the system originally. Consequently, it can only be supposed that all Pu had been present in an oxidized form in these experiments.

→ Yes (based on the information under atmosphere/redox condition; strictly, the oxidation state of the RN or the Eh should be reported).

I-b

SDB: The K_d values are derived from a graph (scanned)

REF: This information is not available in the summary that is available to BMG..

→ class 5 (accepting the rating given by JNC).

II-a Solid phase

SDB: The experiments were carried out with Kunigel-V1 bentonite

REF: No additional information is available in the summary that is available to BMG. However, Kunigel-V1 bentonite is well defined in the literature. Assuming that Kunigel-V1 was used without any significant sample treatment, the following rating is given:

→ A

II-b Adjustment and control of pH

SDB: The final pH is given

REF: The pH was varied from 5.2 to 8.85, using additions of NaOH and HCl and determined at the end of the experiments.

→ A

II-c Redox condition

Based on the missing information already discussed under I-a.2, this study is labeled unreliable for the moment.

→ unreliable

II-d Final solution composition

SDB: Only "equilibrated water" is indicated.

REF: The initial solution composition was 0.1 M NaCl.

Based on the known composition of Kunigel-V1 and the equilibrium with air, the final solution composition can be estimated.

→ C/D

II-e Temperature

SDB: Not reported.

REF: Room temperature is specified.

→ A/B

II-f Solid/water ratio, grain size

SDB: A solution/solid ratio of 500 mL/g is given.

REF: No further information is available.

Assuming a BET (outer) surface area of ca. 35 m²/g, this would result in ca. 3.5 m² bentonite surface per 50 mL vessel. This value would be significantly higher if the entire surface area of bentonite is considered.

→ C/D

II-g Sorption value

According to the sorption values calculated based on the information given in the SDB, the following rating is given:

datapoint	% sorbed	rating
58937	95.4	B
58938	70.6	A
58939	74.1	A
58940	96.6	B
58941	96.7	B
58942	82.2	A
58943	84.5	A
58944	98.2	C/D
58945	98.2	C/D
58946	98.4	C/D
58947	91.1	A
58948	61.3	A

II-h Initial RN concentration

SDB: The initial Pu concentration is reported as 1×10^{-7} M.

REF: It is reported that the solubility of Pu had been evaluated using an unspecified version of the HARWELL TDB, but no results are available.

Based on the information given in Lemire et al. (2001) for the solubility of Pu(VI), it is estimated that the above initial concentration was in all likelihood below the solubility limit for the data referring to $\text{pH} \leq 8$. Data referring to higher pH are evaluated as "unreliable".

→ C/D: Datapoints 58939-58942 and 58945-58948.

→ unreliable: Datapoints 58937, 58938, 58943, 58944.

II-i Phase separation

SDB: All samples were filtered through a 10000 MWCO filter.

→ B

II-j Reaction time

SDB: The reaction time is reported as 30 days.

This is evaluated as sufficient for the present experimental system.

→ C/D

II-k Agitation method

SDB/REF: No information concerning the agitation method is given. Further, no kinetic information is available.

→ unreliable

II-l RN loading

SDB/REF: No isotherms or variation in L/S or initial RN concentration are reported.

→ C/D

II-m Reaction vessels

SDB/REF: No information concerning the reaction vessels is reported.

→ C/D

II-n Uncertainty estimates

SDB: Error estimates are not reported, the experiments were not replicated.

→ D

II-o Parameter variation

SDB: Experiments were performed at variable pH, using a constant initial RN concentration and solid/water ratio.

→ C

REF: Ticknor (1993)

Note: Based on the mineral composition used in this reference (which does not include smectite), it should not be included in the "bentonite" group. "Clays" would be better.

I-a.1

All mandatory fields are completed.

→ Yes

To evaluate the pieces of information required in the following checkpoints, it was necessary to consult the original reference (REF).

I-a.2

SDB: The pe/redox condition of Pu is not reported, only the oxygen levels are indicated.

REF: The author used a thenoyltrifluoroacetone (TTA) xylene solution to extract the (IV) oxidation state for the stock solutions. Prior to initiating sorption, aliquots of the radiotracer stock solution used for the experiments were also subjected to liquid-liquid extraction to verify the oxidation state. This was repeated at the end of the sorption experiments.

Based on the information from the original reference (REF), the mandatory information satisfies the requirements.

→ Yes

I-b

SDB: A table with R_d values in mL/kg is given.

→ class 1

II-a Solid phase

SDB: The reported results refer to two different minerals, illite and kaolinite. Further information such as CEC, surface area are given in the additional Excel files only

REF: Additional information on accessory minerals and particle size is available, but there is no information on the composition of exchangeable ions or minor soluble impurities. Both samples of kaolinite and illite represent non-purified clay minerals.

→ B

II-b Adjustment and control of pH

SDB: In the Access-based SDB (version 2), only the initial pH is listed.

REF: Both initial as well as final pH are reported in the form of ranges of values that encompass ca. 0.5-1 unit. The ranges for initial and final pH differ by about 0.5-1.5 units.

→ B

Note: The final pH values should be included in the Access-based version of the SDB.

II-c Redox condition

SDB: The oxidation state of Pu as well as Eh are not reported. O₂-levels are indicated in the field "atm/redox conditions".

REF: The original paper indicates that the oxidation states of Pu were verified at the beginning and at the end of all the experiments. While it seems that all experiments were carried out with Pu in the +IV-state initially, no reducing agent was used in the experiments. This resulted in a mix of oxidation states (see Table 8 in the REF). Pu(IV) is reported to dominate in the experiments conducted at low O₂ conditions and with the synthetic groundwater 6 (60872, 60879). This is also the case for the experiments conducted with the synthetic groundwater 2 (60873, 60877, 60880, 60881) in both atmospheric conditions. The experiments performed with groundwater 6 (normal O₂) (60874, 60878) contained substantially more Pu(V) and Pu(VI). After the experiments, the ratio of reduced to oxidized Pu in solution was verified through liquid-liquid extraction and reportedly remained similar to the ratio determined in the starting solution. The experiments carried out with groundwater 1 appeared to have nearly equal distributions between reduced and oxidized states of Pu (60882, 60883, 60875, 60876).

→ Overall, the following assessment is made:

The data referring to low-O₂ conditions (60872, 60873, 60875, 60879, 60881, 60883) are labeled unreliable.

On the other hand, the data referring to normal-O₂ conditions (60874, 60876, 60877, 60878, 60880, 60882) could be expected to be reliable, because oxidizing conditions should clearly prevail. However, Table 8 in the REF indicates that Pu existed as a mixture of different oxidation states under all conditions. Figure 2.2.4 illustrates further that there is no clear difference between the data obtained under low and normal O₂ conditions

Based on the above, all data are labeled "unreliable".

II-d Final solution composition

SDB: Specific synthetic groundwaters are indicated in the field "water type". The respective compositions are given in an additional Excel file.

REF: Reported are initial compositions. It is pointed out that e.g. final carbonate levels depend on the actual pCO₂ applied in each experiment. The pCO₂ conditions are not reported, but they can be estimated. For the experiments conducted under air atmosphere the pCO₂ can be estimated, for the experiments conducted under low O₂ conditions, pCO₂ can be considered as negligibly small.

Because only ranges are provided for final pH and because some details on the solid composition are missing, the final solution composition can only be estimated approximately.

→ Therefore, all data are rated C/D.

II-e Temperature

SDB/REF: The temperature conditions are not reported.

→ C/D

II-f Solid/water ratio, grain size

SDB: The experiments were carried out at a constant solution/solid ratio of 4 mL/g.

REF: Specifically, 4 ml of solution of and 1 g of solid were used.

The amount of solid (1 g) may be considered as sufficient to achieve sample homogeneity and representativeness and to result in a sufficiently large surface area.

→ A/B

II-g Sorption value

SDB: Datapoint 60880 corresponds to a sorption value of 97.4 % sorbed, all other datapoints correspond to sorption values > 99 % sorbed.

→ Datapoint 60880 is rated B, all other datapoints are rated C/D.

II-h Initial RN concentration

SDB: Initial Pu concentrations are given for each datapoint, they vary between 7.62×10^{-11} M and 3.58×10^{-10} M.

REF: The above concentrations represent values that were determined analytically after keeping the RN-containing solutions in the reaction vessels for the same amount of time as was used for the sorption experiments. Thus, these values would include any

loss of RN due to precipitation or sorption to vessel walls. The initially added amounts of RN are not reported.

Calculations at pH 6.5 and 9.5 in the absence of atmospheric $p\text{CO}_2$ (using the thermodynamic data in Lemire et al., 2001) indicate that the solubility of Pu(IV) was about 4×10^{-11} M. Considering further the uncertainty in solution composition, all data are rated as

→ unreliable

II-i Phase separation

SDB: The solution samples were separated from the solid phase through centrifugation

REF: Centrifugation was carried out at 2800 g for 15-20 minutes. The presence of obvious artifacts is not reported.

→ C/D

II-j Reaction time

SDB: The experimental reaction time was between 27 and 30 days.

The reaction time can be considered as sufficiently long.

→ C/D

II-k Agitation method

SDB/REF: It is not clear whether any agitation has been carried out.

→ unreliable

II-l RN loading

SDB: No isotherm is reported. Initial Pu concentrations after pre-equilibration with the initial solutions and vessels varied somewhat, but it is not clear whether this represents normal experimental scatter (as the solutions were presumably saturated).

→ C/D

II-m Reaction vessels

SDB: No information is available.

REF The experiments were carried out in polypropylene vessels. No blank tests or correction for sorption on vessel walls are reported.

→ B

II-n Uncertainty estimates

SDB: Uncertainty estimates are given, based on 3 replicates.

→ A

II-o Parameter variation

SDB: The only parameter that was varied to a significant degree was pH. However, this was done in combination with other groundwater components. Further, two solid substrates were used. Therefore, these variations are viewed as individual experiments, rather than parameter variations done on a specific experimental system.

→ D

2.2.1.2 *Test case Np/bentonite*

REF: Yamaguchi et al. (1991)

I-a.1

All mandatory fields are completed.

→ Yes

To better evaluate the entries below it was necessary to consult the original reference (REF).

I-a.2

SDB: Not all mandatory information is provided: Neither the oxidation state of Np nor the Eh is reported. In the field atm/redox condition it is indicated that the experiments had been conducted under argon, but this does not allow any judgement regarding the oxidation state of Np. As neither O₂ nor any reducing agent appear to be present, the oxidation state of Np in the experiments will depend on its initial oxidation state, which is not given.

REF: It is reported that the experiments had been done with Np(V).

→ (Yes)

Notes:

- 1) *This checkpoint can only be answered "yes" when the REF is consulted. The entry in the SDB should be updated accordingly.*
- 2) *The experiments represented by datapoints 62217-62222 were not carried out under an argon atmosphere. This should be corrected in the SDB.*

I-b.1

SDB: K_d values are taken from a figure (scanned)

REF: K_d values are taken from a logarithmic figure

→ class 5

II-a Solid phase

SDB: The solid phase is identified as Kunibond, but no further information is given

REF: Kunibond is a commercially available Ca-bentonite. The REF also reports the major and minor elemental composition, but gives no further information.

→ C/D (if Kunibond is well known in Japan, this may be changed to A)

II-b Adjustment and control of pH

SDB: The final pH values are given

REF: The pH was adjusted (using acid or base) to reach the desired values, monitored every 2 days, and determined again at the end of the experiment.

→ A

Note: The SDB (Access version) contains the entry "8-160" in the field pH init, this should be corrected.

II-c Redox condition

SDB: The oxidation state of Np is not reported.

REF: The experiments were done with Np(V), and no reducing agent was used, which would clearly indicate oxidizing conditions. On the other hand, Figure 6 in the REF shows some measured Eh data from the systems with carbonate, which indicate values between 0 mV and +100 mV. According to the thermodynamic data used to construct Figure 6 in the REF, this potential would be low enough to allow the formation of Np(IV)-hydroxo-carbonato complexes. This finding may be questionable, for the following reasons: First, Eh measurements in the presence of traces of oxygen are extremely difficult and tend to underestimate the actual oxygen concentration. Second, there is no firm evidence for the existence of any soluble Np(IV)-hydroxo-carbonato species, according to Lemire et al. (2001).

Based on the above discussion, it is assumed that oxidizing conditions prevailed throughout the experiments, and that only Np(V) was present.

→ A (Note that this rating is based on the correctness of the above evaluation, not on direct evidence from the REF)

II-d Final solution composition

SDB: NaClO₄ (NaClO₄/Na₂CO₃ for some experiments) is given as the initial solution composition, but the concentrations are not listed.

REF: NaClO₄ was 1 M, the concentration of Na₂CO₃ in some sorption experiments was 3×10⁻¹ M. Table 1 in the REF gives a "porewater" composition, but it is not clear how the data relate to the sorption experiments. The information provided does not allow to calculate the final solution composition exactly.

→ C/D

II-e Temperature

SDB: All experiments were carried out at room temperature.

→ A/B

II-f Solid/water ratio, grain size

SDB: A range of 8-160 mL/g is given as liquid/solid ratio.

→ A/B (based on the typically large surface area of bentonite)

II-g Sorption value

SDB/REF: Only the initial RN concentration is known. The corresponding dissolved equilibrium concentration, and, therefore, the sorption value can not be calculated because the different K_d values cannot be connected to a specific S/W ratio. However, even if the lowest liquid/solid ratio (8 mL/g) is used, sorption values well below 95% are calculated for data points 62194-62208, and sorption values between 95% and 98% are calculated for data points 62209 and 62219-62222. Therefore, the following minimum levels can be assigned:

→ A: data points 62194-62208

B: data points 62209 and 62219-62222

C/D: data points 62210-62218

II-h Initial RN concentration

SDB: Initial Np concentration is given as 1×10^{-6} M.

REF: According to the solubility data shown in Figure 4 of the REF, the initial Np concentration exceeds the solubility limit at pH 10. Figure 5 indicates that the solubility of Np increases with increasing carbonate concentration. However, the highest carbonate concentration indicated in Figure 5 is 4×10^{-3} M, whereas 3×10^{-1} M has been used in the sorption experiments.

→ A: data points 62194-62209

B: data points 62210, 62211, and 62217-62222

unreliable: data points 62212-62216

II-i Phase separation

SDB: Filtration with a nominal porewidth of 3 nm is indicated.

REF: Centrifugation with 5000 g was also used, but probably only as a preliminary separation step, as no comparisons are shown.

→ B

II-j Reaction time

SDB/REF: Reaction time was 2 weeks.

→ C/D

II-k Agitation method

REF: Non information on agitation method is available. However, pH was monitored every two days; this is taken to resemble light shaking by hand.

→ C/D

II-l RN loading

REF: No isotherm data are available, but the liquid/solid ratio was varied between 8-160 mL/g. It can be assumed that some data would fall within the linear sorption region.

→ B

II-m Reaction vessels

REF: Polypropylene tubes were used. No corrections for sorption on vessel walls are reported.

→ B

II-n Uncertainty estimates

SDB/REF: No information given.

→ D

II-o Parameter variation

SDB/REF: S/W, pH, and carbonate concentration (only 2 levels) were varied. It appears that only pH was varied systematically.

→ B

REF: Ashida et al. (1999)

I-a.1

All mandatory fields are completed.

→ Yes

I-a.2

SDB: All mandatory information is provided.

→ Yes

Note: It seems that several pieces of information, such as a clear assignment of pH and total carbonate level to each K_d value is missing in the SDB. If possible, it is strongly suggested to update the SDB with such information.

I-b

SDB: K_d values are taken from a figure (scanned)

REF: From the summary available to BMG, it is not clear whether the figure has a logarithmic or linear scale.

→ class 5 (accepting JNC's rating)

To better evaluate some of the entries below it was necessary to consult the summary of the original reference which was made available to BMG through JNC (REF).

II-a Solid phase

SDB: The solid phase is smectite

REF: The smectite is identified as Kunipia-F. CEC, grain size, and BET-surface area are also given

→ A

II-b Adjustment and control of pH

SDB: A range of pH 8-10 is indicated for initial as well as final pH.

REF: The pH was adjusted using NaOH or HCl.

- Because the pH range reported is very large, it would fall below the requirements given in revision 2 of the classification guideline and lead to the evaluation "unreliable".

II-c Redox condition

SDB: The oxidation state of Np is reported as +IV, and Na₂S₂O₄ was used as reducing agent (N₂-atmosphere).

REF: The oxidation state of Np was identified by TTA extraction. It is not possible to say whether this was done before or after completion of the sorption experiments.

→ C/D

II-d Final solution composition

SDB: The input solution was 1 M NaCl

REF: Ten different levels of carbonate concentration were used, ranging from 0.04-0.15 M. Unfortunately, it is not possible to say which K_d value corresponds to which carbonate concentration. The final solution composition is not reported.

→ C/D

II-e Temperature

SDB: All experiments were carried out at room temperature.

→ A/B

II-f Solid/water ratio, grain size

SDB: For all experiments, 1000 mL/g is given as liquid/solid ratio.

REF: 20 mg of solid were added to each experimental vessel.

→ C/D

II-g Sorption value

SDB: Except for one datapoint with a sorption value of 2.2% sorbed, all sorption values are between 5-95% sorbed:

→ A: data points 62869-62890

B: data point 62868

II-h Initial RN concentration

SDB: Initial Np concentration is given as 1×10^{-6} M.

REF: The carbonate concentration and pH can not be clearly related, which makes an assessment of Np solubility difficult.

→ B (accepting JNC's evaluation, which is based on solubility calculations reportedly done in the REF that are not available to BMG)

II-i Phase separation

SDB/REF: Filtration with 10'000 MWCO is indicated.

→ B

II-j Reaction time

SDB/REF: Reaction time is indicated for each K_d value and ranges from 7-32 days. Because pH and carbonate level cannot be related to specific datapoints, it is not possible to assess kinetics for each condition. A rough overview indicates that the data for 7 and 14 days do not correspond to equilibrium

→ A/B: 62876-62890

unreliable: 62868-62875

II-k Agitation method

REF: It seems that some automatic shaker was used.

→ A/B

II-l RN loading

SDB/REF: No isotherm data are available, all experiments have been done at the same S/W and using the same initial RN concentration.

→ C/D

II-m Reaction vessels

SDB: No information given

REF: Polypropylene vessels were used.

→ A (accepting JNC's evaluation, which is based on information about desorption experiments that is not available to BMG)

II-n Uncertainty estimates

SDB/REF: Two replications are indicated for each experiment.

→ A

II-o Parameter variation

SDB/REF: It seems that carbonate concentration was varied systematically, possibly also pH (unclear).

→ C

REF: Ticknor (1993)

Note: Based on the mineral composition used in this reference (which does not include smectite), it should not be included in the "bentonite" group. "Clays" would be better.

I-a.1

All mandatory fields are completed.

→ Yes

To evaluate the pieces of information required in the following checkpoints, it was necessary to consult the original reference (REF).

I-a.2

SDB: The pe/redox condition of Np is not reported, only the oxygen levels are indicated.

REF: The author used a thenoyltrifluoroacetone (TTA)-xylene solution to extract the (IV) oxidation state for the stock solutions. Prior to initiating sorption, aliquots of the radiotracer stock solution used for the experiments were also subjected to liquid-liquid extraction to verify the oxidation state. This was repeated at the end of the sorption experiments.

Based on the information from the original reference (REF), the mandatory information satisfies the requirements.

→ Yes

I-b

SDB: A table with R_d values in mL/kg is given.

→ class 1

II-a Solid phase

SDB: The reported results refer to two different minerals, illite and kaolinite. Further information such as CEC, surface area are given in the additional Excel files only

REF: Additional information on accessory minerals and particle size is available, but there is no information on the composition of exchangeable ions or minor soluble impurities. Both samples of kaolinite and illite represent non-purified clay minerals.

→ B

II-b Adjustment and control of pH

SDB: In the Access-based SDB (version 2), only the initial pH is listed.

REF: Both initial as well as final pH are reported in the form of ranges of values that encompass ca. 0.5-1 unit. The ranges for initial and final pH differ by about 0.5-1.5 units.

→ B

II-c Redox condition

SDB: The oxidation state of Np as well as Eh are not reported. O₂-levels are indicated in the field "atm/redox conditions".

REF: The original paper indicates that the oxidation states of Np were verified at the beginning and at the end of all the experiments. While it seems that all experiments were carried out with Np in the +IV-state initially, no reducing agent was used in the experiments. This may be expected to result in at least partial oxidation of Np. The performed liquid-liquid extractions at the end of the experiments even suggest that +V was the predominant oxidation state of Np under all conditions. Considering the small difference between low O₂ and normal O₂ conditions and the overall small sorption (e.g., in comparison to Np(V) sorption on montmorillonite, see Figure 2.2.4), these results are accepted.

→ Therefore, all data are rated A/B.

II-d Final solution composition

SDB: Specific synthetic groundwaters are indicated in the field "water type". The respective compositions are given in an additional Excel file.

REF: Reported are initial compositions. It is pointed out that e.g. final carbonate levels depend on the actual pCO₂ applied in each experiment. The pCO₂ conditions are not reported, but they can be estimated. For the experiments conducted under air atmosphere the pCO₂ can be estimated, for the experiments conducted under low O₂ conditions, pCO₂ can be considered as negligibly small.

Because only ranges are provided for final pH and because some details on the solid composition are missing, the final solution composition can only be estimated approximately.

→ Therefore, all data are rated C/D.

II-e Temperature

SDB/REF: The temperature conditions are not reported.

→ C/D

II-f Solid/water ratio, grain size

SDB: The experiments were carried out at a constant solution/solid ratio of 4 mL/g.

REF: Specifically, 4 ml of solution of and 1 g of solid were used.

The amount of solid (1 g) may be considered as sufficient to achieve sample homogeneity and representativeness and to result in a sufficiently large surface area.

→ A/B

II-g Sorption value

SDB: Datapoint 60817 corresponds to a sorption value of 95.2%, all other datapoints correspond to sorption values of 25.9-93.4%

→ Datapoint 60817 is rated B, all other datapoints are rated A.

II-h Initial RN concentration

SDB: Initial Np concentrations are given for each datapoint, they vary between 8.84×10^{-6} M and 9.54×10^{-6} M.

REF: The above concentrations represent values that were determined analytically after keeping the RN-containing solutions in the reaction vessels for the same amount of time as was used for the sorption experiments. Thus, these values would include any loss of RN due to precipitation or sorption to vessel walls. The initially added amounts of RN are not reported.

In comparison to the solubility measurements by Yamaguchi et al.(1991) in the absence and presence of carbonate, it appears that the experiments at pH 9.5 may have been very close to the solubility limit, whereas the Np concentration in the experiments at pH 8.25 and especially at pH 6.5 should have been clearly below the solubility limit. Calculations at pH 6.5, 8.25, and 9.5 in the presence and absence of atmospheric $p\text{CO}_2$ (using the thermodynamic data in Lemire et al., 2001) also indicate that the solubility of Np(V) was higher than 10^{-5} M under all conditions.

→ The following rating is given:

datapoint	pH	rating
60818	6.75	A
60819	6.75	A
60822	6.75	A
60813	8.25	A
60814	8.25	A
60816	8.25	A
60812	9.5	B
60815	9.5	B
60817	9.5	B
60820	9.5	B
60821	9.5	B
60823	9.5	B

II-i Phase separation

SDB: The solution samples were separated from the solid phase through centrifugation

REF: Centrifugation was carried out at 2800 g for 15-20 minutes. The presence of obvious artifacts is not reported.

→ C/D

II-j Reaction time

SDB: The experimental reaction time was between 27 and 30 days.

The reaction time can be considered as sufficiently long.

→ C/D

II-k Agitation method

SDB/REF: It is not clear whether any agitation has been carried out.

Based on this information, the rating "unreliable" should be given. However, based on the evaluation made under checkpoint III (section 2.2.2.2), it seems reasonable to assume that (i) either some kind of agitation had been performed, or (ii) that a near-equilibrium state had been reached in the absence of agitation. Therefore, the following rating is given:

→ C/D

I-I RN loading

SDB: No isotherm is reported. Initial N_p concentrations after pre-equilibration with the initial solutions and vessels varied somewhat, but it is not clear whether this represents normal experimental scatter (as the solutions could have been initially saturated).

→ C/D

II-m Reaction vessels

SDB: No information is available.

REF The experiments were carried out in polypropylene vessels. No blank tests or correction for sorption on vessel walls are reported.

→ B

II-n Uncertainty estimates

SDB: Uncertainty estimates are given, based on 3 replicates.

→ A

II-o Parameter variation

SDB: The only parameter that was varied to a significant degree was pH. However, this was done in combination with other groundwater components. Further, two solid substrates were used. Therefore, these variations are viewed as individual experiments, rather than parameter variations done on a specific experimental system.

→ D

REF: Allard et al. (1979b)

I-a.1

SDB All mandatory fields are completed.

→ Yes

I-a.2

SDB All mandatory information is provided.

→ Yes

I-b.1

SDB Log K_d values are taken from a table.

→ class 1

II-a Solid phase

SDB: The solid phase is given as a mixture of bentonite and quartz (10:90)

REF: No further information is available

→ C/D

II-b Adjustment and control of pH

SDB: Initial pH is given.

REF: The synthetic groundwaters used contained carbonate. It can be assumed that the bentonite contained some CaCO_3 as well.

The initial pH of 8.2 corresponds to the equilibrium pH of atmospheric CO_2 in contact with CaCO_3 -saturated water. Since the experiments were carried out in normal atmosphere conditions (see II-c), it can be expected that the initial pH was relatively well buffered. Making these assumptions, the following rating is given:

→ B

II-c Redox condition

SDB: All experiments were carried out under aerobic conditions. The initial oxidation state of Np is not given.

REF: The experimental systems were aerated.

Because of the presence of oxygen and because similar results were obtained after 7 days and 6 months, it is assumed that Np was present in the +V state throughout the sorption experiments.

→ A/B

II-d Final solution composition

SDB: The composition of the synthetic input solutions are given in an additional Excel file. All experiments were carried out under aerated conditions.

REF: No further information is available.

Some solution components, such as carbonate concentration and pH, can probably be estimated reasonably well. On the other hand, it is not known which, and how much, soluble impurities were contained in the bentonite; and whether the sand contained any impurities. While the final solution composition cannot be estimated with certainty, it is estimated that enough information is available to give rating

→ C/D

II-e Temperature

SDB: A temperature of 25°C or of 65°C is specified for different datapoints.

→ A/B

II-f Solid/water ratio, grain size

SDB: A solution/solid ratio of 10-50 mL/g is indicated.

REF: 1-3 g solid were added to 30-50 mL solution.

Assuming a BET (outer) surface area of ca. 35 m²/g for bentonite, this would result in ca. 3.5-10.5 m² bentonite surface per vessel.

→ C/D

II-g Sorption value

Based on the information given in the SDB, and on a solution/solid ratio of 10-50 mL/g, sorption values between 16.7-66.7 % sorbed can be calculated.

→ A

II-h Initial RN concentration

SDB: The initial Np concentration was < 1×10⁻⁸ M.

In comparison with the measurements of Yamacuchi et al. (1991), this concentration is at least a factor of 5 below the solubility limit.

→ A

II-i Phase separation

SDB: Centrifugation at an unspecified setting, and filtration through 0.5 µm membranes is indicated.

REF: Centrifugation was done at 7000 rpm for 50 minutes. This was compared to filtration through 0.2 µm membranes: It is not clear whether filtration was done on centrifuged or on original samples, but it is reported that it did not influence the values.

Two methods were used, but none of them is considered to be very efficient for removal of colloids.

→ C/D

II-j Reaction time

SDB: Contact time was 180 days for datapoints 42377 and 42380, and 7 days for all other datapoints.

The K_d values seem to be slightly higher after 180 days, but not by a significant factor.

→ A/B

II-k Agitation method

SDB: No information is available.

REF: Samples were shaken for 8-12 hours.

→ A/B

II-l RN loading

SDB: All experiments were conducted at the same S/W and initial RN concentration.

→ C/D

II-m Reaction vessels

SDB: No information is available.

REF The experiments were carried out in glass vessels. No correction for sorption on vessel walls is reported.

Because glass surfaces may sorb RN to a limited degree, the following rating is given:

→ C/D

II-n Uncertainty estimates

SDB/REF: No information is reported.

→ D

II-o Parameter variation

SDB: Only the temperature was varied in a limited way.

While only 2 different temperatures were used, the data suggest that Np sorption is not changed significantly between 25 °C and 65 °C. Therefore, the following rating is given:

→ C

REF: Barney (1981)

I-a.1

All mandatory fields are completed.

→ Yes

I-a.2

All mandatory information is provided.

→ Yes

I-b.1

K_d values are taken from a table.

→ class 1

II-a Solid phase

SDB: The solid phase is characterized. The requested information such as CEC, surface area, grain size, and major mineralogical composition are given in the Excel file "solid phase", but not in the Access-based database.

REF: The sample had blue-green color

→ B (see note below)

Note: Typically, natural smectites contain a number of minor auxiliary minerals, which are not reported in this case. The smectite sample used in this study is reported to have a blue-green color, which often indicates the presence of Fe(II).

While rating B is given for II-a, according to the description for this particular checkpoint, it is important to keep in mind that the experiments are carried out with a highly redox-sensitive element whose behavior could be strongly influenced by the presence of Fe(II).

II-b Adjustment and control of pH

SDB: Only the initial pH values are specified. The use of buffers is not specified.

REF: To investigate the dissolution behavior of the solids used, additional kinetic experiments were carried out, but apparently with groundwater #2 only. It is reported that pH leveled out at a value of about 8.4 in experiments with the secondary mineral sample (smectite). Figure 6 in the REF shows that Ca concentrations had been

significantly increased after one week, and it is estimated that the change in pH occurred within the same timeframe.

Based on the above evidence, it is suggested that the equilibrium pH values are about 2-2.5 units lower than the initial ones. However, this information is available only for one groundwater type, and it cannot be estimated whether the pH varied less or more in the case of the other groundwater compositions.

→ unreliable

II-c Redox condition

SDB: Redox conditions are reported for each experiment. The experiments were conducted with Np(IV) and Np(V). All experiments were conducted in pre-equilibrated systems. For the experiments with Np(IV) the authors used hydrazine as reducing agent, while the experiments carried out with Np(V) were conducted in air atmosphere, and in the absence of hydrazine. Final Eh values are given in the SDB.

REF: The hydrazine concentration was 0.05 M. It is reported that this hydrazine concentration lowered the redox potential from about +200 mV in an air-saturated solution to about -800 mV at pH \approx 10. While the reporting in the REF is not very specific with regard to this issue, it appears that these Eh measurements were done in separate solutions as a preliminary test of the effect of the hydrazine addition, and that they do not represent the final Eh values measured in actual sorption experiments.

Note: Based on the above, it is recommended to remove the Eh data from the field "Eh end" in the SDB and to list this information in the appropriate additional Excel file instead.

→ Based on the above discussion, the Np results obtained under reducing conditions are evaluated separately from those obtained under oxidizing conditions, as follows:

C/D: Data for reducing conditions (44596, 44598-44606)

A/B: Data for Np(V) (44587-44595, 44597)

Note that the similarity of K_d values obtained under reducing and oxidizing conditions (see Figure 2.2.2) suggests that the oxidation state of Np may have been the same in both sets of experiments. In contrast to the data for Pu by this REF, the Np data are more consistent with other data for Np(V) than with data for Th(IV), which could indicate that Np had not been reduced quantitatively. It is also possible that the low K_d for Np under reducing conditions (in comparison to the values for Th) can be attributed to solubility limitation of Np(IV) in case of the reducing conditions.

Despite these reservations, the rating given above is retained for this particular checkpoint.

II-d Final solution composition

SDB: The experiments were conducted with different synthetic water compositions. All components of these solutions are known (see Excel file "solution composition"). The experiments were conducted both in air atmosphere and under reducing conditions.

sorption experiments. However, as already noted in II-b, there is evidence that the pH and possibly other solution components changed significantly during the solid-water interaction. It is not clear whether these changes were accounted for by the brief pre-equilibration.

→ C/D

II-e Temperature

SDB: The temperature is not specified.

REF: Experiments were carried out at 23 ± 2 °C.

→ A/B

II-f Solid/water ratio, grain size

SDB: The experiments were carried out with 1 g solid and 30 mL solution. The grain size was smaller than 2 µm (at least in case of the BAS_MINER sample considered here). The amount of solid (1 g) may be considered as sufficient to achieve sample homogeneity and representativeness.

→ A/B

II-g Sorption value

Based on the information given in the SDB, calculated sorption values for all datapoints are between 43-88 %sorbed.

→ A

II-h Initial RN concentration

SDB: The initial Np concentrations were between 4.2×10^{-6} M and 6.6×10^{-6} M.

REF: It is reported that initial concentrations represent analytical measurements performed after the input solutions had been spiked with a solid tracer and filtered (0.3 µm membrane). No clear information is provided on the redox situation of the spiked solutions. In particular, it is not clear at which point of the experimental procedure the hydrazine had been added.

For Np(V), the initial concentrations are by more than a factor of 5 below the solubility limit, given that the assumed carbonate concentrations are approximately correct. Once reducing conditions are established, the solubility limit of Np(IV) will be exceeded, however.

→ A: Data referring to oxidizing conditions (44587-44595, 44597)

→ unreliable: Data referring to reducing conditions (44596, 44598-44606).

II-i Phase separation

SDB: All samples were filtered by ultra-filtration, no other technique was used for comparison.

→ B

II-j Reaction time

SDB: The experiments were sampled after a reaction time of 14 days.

REF: Separate kinetic experiments suggest that the sorption of Pu on the secondary mineral sample may not have reached equilibrium after 2 weeks. In the same set of experiments, it appears that the sorption of Np reached a near-equilibrium state after two weeks. However, this information is available for one solid-groundwater combination only, and it is not possible to judge whether kinetics were slower or faster in other situations.

Based on the above, it is judged that the experimental system is complex and may need more than two weeks to equilibrate.

→ unreliable

II-k Agitation method

SDB: No information is available.

REF: All samples were gently shaken during the entire experiment.

→ A/B

II-l RN loading

SDB: For any constant solution composition or S/W ratio, no isotherm was determined, and no variation of initial Np concentration was carried out.

→ C/D

II-m Reaction vessels

SDB: No information is available.

REF The experiments were carried out in polycarbonate centrifuge tubes.

→ B

II-n Uncertainty estimates

SDB/REF: Error estimates were not determined.

→ D

II-o Parameter variation

SDB: The Pu concentration was varied while applying a constant S/W ratio and different water compositions.

REF: A statistical experimental screening design was applied, where each particular combination of parameters occurs only once.

The applied experimental design does allow to observe trends as a function of parameter variation, but only in a statistical sense. Presumably, this design will not yield useful results in cases where different parameters have compensating influences on sorption because the variation of each parameter is quite limited.

→ D

REF: Baston et al. (1997)

I-a.1

All mandatory fields are completed.

→ Yes

I-a.2

SDB All mandatory information is provided.

→ Yes

I-b.1

SDB K_d values are taken from a table.

→ class 1

II-a Solid phase

SDB: The experiments were carried out using Kunigel-V1 bentonite. No further information is given.

REF: No further information is given.

Kunigel-V1 bentonite is well defined in the literature.

→ A

II-b Adjustment and control of pH

SDB: Final pH values are given.

REF: It is reported that pH was maintained at the value of solid-equilibrated de-ionized water. It is not specified how this was done, but no use of buffers is mentioned.

It is assumed that the final pH corresponds to equilibrium and no buffers had been used.

→ A

II-c Redox condition

SDB: The initial oxidation state of Np is not given. Final Eh values are given, and the experiments were reportedly performed under nitrogen.

REF: It is reported that strongly reducing conditions were achieved by an initial addition of 2×10^{-3} M $\text{Na}_2\text{S}_2\text{O}_4$ and maintained by adding additional $\text{Na}_2\text{S}_2\text{O}_4$.

→ C/D

II-d Final solution composition

SDB: The input solution was de-ionized water.

REF: Synthetic solutions were prepared. Their composition was based on the final solution composition obtained after equilibrating de-ionized water with the solid samples for one month.

Since S/W as well as the composition of Kunigel-V1 are known, the final solution composition can be estimated. Based on the information given in the REF, it is also very likely that the solution composition corresponds to equilibrium.

→ A/B

II-e Temperature

SDB: The experiments were carried out at 21 and 60 °C..

→ A/B

II-f Solid/water ratio, grain size

SDB: A solution/solid ratio of 20 mL/g is given for all experiments.

REF: It is reported that Np data could only be obtained from large-scale experiments, due to analytical limitations.

While "large-scale" is not specified further, it is assumed that enough solid had been used to achieve sample homogeneity and representativeness and to result in a sufficiently large surface area (considering the large surface area and relative homogeneity of Kunigel-V1).

→ A/B

II-g Sorption value

SDB: Based on the information in the SDB, the sorption values for all datapoints are > 99 %sorbed (using an initial Np concentration of 6×10^{-9} M).

→ C/D

II-h Initial RN concentration

SDB: Initial Np concentrations are given as $< 6 \times 10^{-9}$ M.

REF: Initial Np concentrations are given as approximately 6×10^{-9} M.

Preliminary speciation calculations using the thermodynamic data for Np(IV) given in Lemire et al. (2001) for 25 °C, a pH range of 9.4-10.4, and in the presence and absence of calcite or gypsum (from bentonite) indicate that the initial Np concentration may have been at or slightly above the solubility limit for NpO₂ (hyd, am). Figure 2.2.3 shows that the K_d values reported in Bradbury and Baeyens (2003) for Th with an initial concentration $< 10^{-9}$ M are substantially higher than the values given in this REF. This difference would also be consistent with a solubility limitation in the present case.

→ C/D (tentative)

Note: It can be considered that the initial Np concentration is within the uncertainty of the respective solubility limit. If one assumes thermodynamic equilibrium (i.e., complete reversibility), the residual dissolved Np concentrations would be significantly below the solubility limit. On the other hand, the difference to the data reported by Bradbury and Baeyens (2003) for Th under comparable conditions is significant. On the other hand, there is a discrepancy between the way the initial Np concentration is reported in the SDB and in the REF. It is suggested to re-examine the initial Np concentration, if possible, and to re-calculate the solubility limit in order to do the final rating.

II-i Phase separation

SDB: Filtration with 0.45 μm and 10'000 MWCO membranes was done. The resulting K_d values are similar.

REF: Samples were centrifuged at 1100 g prior to filtration. Filtration with 0.45 μm and 10'000 MWCO membranes was done in sequence, and the filters were washed and pre-conditioned. The presence of obvious artifacts is not reported.

→ A

II-j Reaction time

SDB: An experimental reaction time of 120 days is given.

The reaction time can be considered as sufficiently long.

→ C/D

II-k Agitation method

SDB: No information given

REF: Continuous, gentle agitation is reported.

→ A/B

II-l RN loading

SDB: All experiments have been done at the same S/W and using the same initial RN concentration.

→ C/D

II-m Reaction vessels

SDB: No information given

REF: It is stated that it was verified that sorption occurred onto the solid and not onto the vessel walls, but no details are given.

→ A

II-n Uncertainty estimates

SDB: Error estimates are given

REF: It is reported that samples were set up in duplicate. However, the reported error estimates represent only analytical uncertainties (2σ).

→ C

II-o Parameter variation

SDB: Experiments were done at two temperatures. No other parameter variation has been performed.

→ C

REF: Stammose et al. (1992)

I-a.1

SDB All mandatory fields are completed.

→ Yes

I-a.2

SDB All mandatory information is provided.

→ Yes

I-b.1

SDB K_d values are taken from a figure (scanned).

REF: The figure is logarithmic.

→ class 5

II-a Solid phase

SDB: The solid phase is identified as clay. In the additional Excel file, CEC and specific surface area are given. This file actually contains an entry "clay" and an entry "FoCa 7 (clay)" for this REF, but it is not clear whether both entries refer to the same material.

REF: FoCa7 clay was purified following a method described in a different publication (Stammose and Dolo, 1990). It is reported that all non-clay minerals were eliminated by the purification, without altering the clays itself. The clay fraction reportedly consisted of 7% kaolinite and a mixed-layer 53 % kaolinite/47 % smectite component. However, the proportion of the latter with regard to the total clay mass is not clearly reported. Na is reported as the main exchangeable cation.

Stammose and Dolo (1990, see also the respective entries in the SDB) report that the mixed-layer kaolinite/smectite component makes up 93 % of the total mass. They also report that goethite, calcite, and gypsum had been quantitatively removed by the applied washing procedure.

→ A (taking into account the additional information given in Stammose and Dolo, 1990)

II-b Adjustment and control of pH

SDB: Final pH values are given.

REF: The experiments were well buffered ($p\text{CO}_2 = 10^{-3.5}$ atm) and pre-equilibrated.

→ A

II-c Redox condition

SDB: Np is reported to be in the +V oxidation state. The experiments were reportedly performed under air.

REF: It appears that the initial oxidation state of Np was also +V. Experiments were pre-equilibrated.

→ A/B

II-d Final solution composition

SDB: NaClO₄ solutions with concentrations between 0.01-1 M are indicated in the field "water type". Experiments were carried out under air.

REF: Solid and solutions were pre-equilibrated. At least some analyses (Al, Si) were carried out on the solutions used for pre-equilibration, but all concentrations were below detection.

Based on the information available on initial solution and solids composition, as well as atmosphere conditions, the final solution composition can be estimated.

→ C/D

II-e Temperature

SDB: The experiments were carried out at 22 °C..

→ A/B

II-f Solid/water ratio, grain size

SDB: A solution/solid ratio of 200 mL/g is given for all experiments.

REF: Solution volume was 20 mL, solid weight was 0.1 g.

The solid can be considered to be fairly homogeneous, and 0.1 g corresponds to 12 m² according to the specific surface area reported.

→ A/B

II-g Sorption value

SDB: Based on the information in the SDB, the following rating can be given:.

→ A: datapoints 59329-59330, 59332-59354, 59356-59357

B: datapoints 59331, 59355, 59358.

II-h Initial RN concentration

SDB: Initial Np concentrations are given as 4.5×10^{-7} M.

Following the solubility measurements given in Yamaguchi et al. (1991), the initial RN concentration can be considered to be by more than a factor of 5 below the solubility limit in the considered pH range.

→ A

II-i Phase separation

SDB: Centrifugation is indicated as method used for phase separation, but no details are given

REF: Samples were centrifuged at 30'000 rpm for 30 min, no other method was used.

→ B

II-j Reaction time

SDB: An experimental reaction time of 1 day is indicated.

REF: This reaction time of 1 day was determined as sufficient in separate kinetic experiments. However, this reaction time is reported as being probably too short in case of the desorption experiments.

Kinetic data for Am are provided in Stammose and Dolo (1990). The reaction time can be considered as sufficiently long in case of the sorption experiments, but not in case of the desorption experiments.

→ A/B

II-k Agitation method

SDB: No information given

REF: Continuous shaking is reported.

Separate kinetic experiments (data not shown) reportedly show attainment of equilibrium.

→ A/B

II-l RN loading

SDB: All experiments have been done at the same S/W and using the same initial RN concentration.

→ C/D

II-m Reaction vessels

SDB: No information given

REF: No information given regarding experimental vessels. No corrections for sorption on vessel walls are reported.

→ C/D

II-n Uncertainty estimates

SDB/REF: No estimates of uncertainty are given

→ D

II-o Parameter variation

SDB: Ionic strength of the initial solution as well as pH were varied systematically, at a constant RN surface loading.

→ B

2.2.2 *Criterion III: Consistency of data for Np/bentonite and Pu/bentonite datasets*

2.2.2.1 *Overview and discussion of trends*

In this section, data from the various entries in the JNC-SDB are compared to each other as well as to data obtained from additional independent studies. Where possible, comparisons are also made with studies involving different actinides that can be used as analogs. Entries of the JNC-SDB are discussed individually below in sections .

In order to evaluate the consistency of the selected Pu and Np data, the K_d values contained in the JNC-SDB are compared (i) among each other, and (ii) with the results of independent sorption studies carried out for other actinides, such as Am(+III), Th(+IV), and U(+VI). For these actinides, the variation of K_d as a function of pH has been studied in some detail, and their respective oxidation state is known with more certainty than in the case of Pu.

The comparison of all results is given in Figure 2.2.1 to Figure 2.2.4, where K_d values are plotted as a function of pH. In order to facilitate viewing, selected information is shown in different plots. Figure 2.2.1 shows trends of K_d values obtained for the sorption of different actinides on clay minerals as a function of pH and carbonate concentration for III- to VI-valent actinides.

Data for Pu(III/IV) and Np(IV) are compared with data for Am(+III) published by Gorgeon (1994), and with data for Th(+IV) published by Bradbury & Baeyens (2003). For the +V and +VI oxidation states, the comparison was carried out considering various datasets for (i) Np(V) by Gorgeon (1994) and Turner et al. (1998) and (ii) for U(VI) by Pabalan and Turner (1997), Turner et al. (1996), Zachara and McKinley (1993), and Stammose et al. (1992). These studies provide sorption data obtained as a function of relevant conditions, covering a fairly wide range of pH, carbonate levels, and ionic strength:

- For the V- and VI-valent elements, the trend of sorption as a function of pH is well established in the absence and presence of dissolved carbonate. Especially at elevated pH values, the interaction of actinide ions with dissolved and surface-bound OH-groups and with carbonate ions is important. The sorption behavior of both U(VI) and Np(V) in the absence vs. in the presence of carbonate is consistent with the formation of mixed hydroxide-carbonate complexes in solution (see Guillaumont et al., 2003). The formation of ternary U(VI) surface-carbonate complexes has also been shown spectroscopically (Bargar et al., 2001).
- In comparison, data for III- and IV-valent actinides are much more sparse. At the same time, the importance of ternary hydroxide-carbonate complexes is less clear. While Lemire et al. (2001) conclude that no firm evidence exists for the formation of mixed hydroxide-carbonate complexes in solution, Guillaumont et al. (2003) suggest that there is strong evidence for the formation of such complexes (however, no data are selected). In the case of Am(III) it seems clear that the formation of mixed hydroxide-carbonate complexes in solution can be ruled out (see Guillaumont et al., 2003).

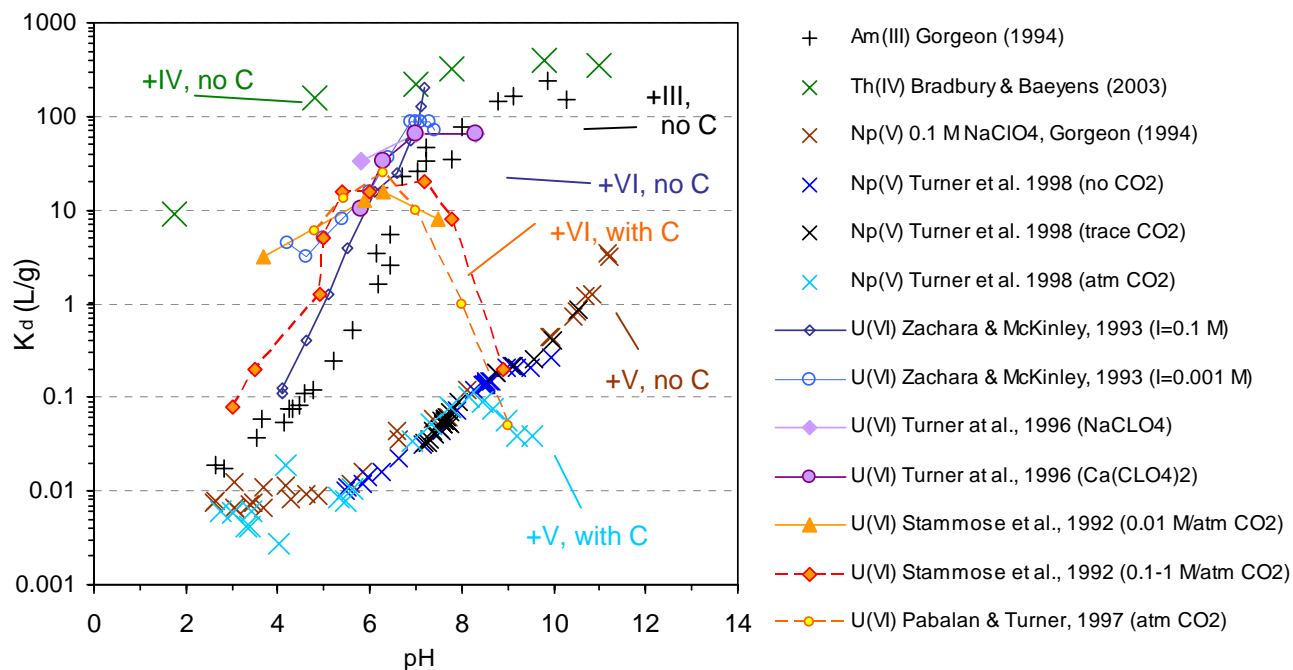


Figure 2.2.1: Overview of data on the sorption of different actinides on clay minerals used for comparison with the entries evaluated in the present report. The oxidation state of the different actinides is shown, "no C" and "with C" indicates the absence and presence of significant levels of dissolved carbonate, respectively.

2.2.2.2 Examination of data in the JNC-SDB

The studies of Billon (1982), Sharma and Oscarson (1989), Sato and Shibutani (1994), and Ashida et al. (1999) are not evaluated under criterion III, based on the results obtained for criteria I-II..

Data for Pu and Np by Barney (1981)

Checkpoint III is not conclusive. The uncertainty with regard to pH, final carbonate concentration, and redox conditions makes it difficult to compare the values of Barney (1981) with other data and renders his study unreliable in the end:

- Assuming the final pH reported for one kinetic experiment to be correct, the data measured by Barney (1981) for both reducing and oxidizing conditions would not be completely inconsistent with the sorption of U(VI) in the presence of carbonate or with the sorption behavior of Np(V). Unfortunately, it is not possible to say whether the assumed pH is correct, and to know the actual dissolved carbonate concentration. On the other hand, Barney's (1981) data for both reducing and oxidizing conditions

could also be interpreted as lying between other data for Th(IV) and Np(V); which could also point to the simultaneous existence of reduced and oxidized forms of Pu.

- On the other hand, if the initial pH is assumed, the data measured by Barney (1981) for both reducing and oxidizing conditions would not be inconsistent with the values observed by Shibutani et al. under reducing conditions (which follow the trend of Am(III))
- Overall, the data by Barney (1981) could be consistent with independent data for the +V/VI or the +III oxidation state. There is no agreement with the data for Th(IV) by Bradbury and Baeyens (2003). The biggest problem is actually the uncertainty in pH.

Data by Allard et al. (1982) and Baston et al. (1997)

In both the studies of Baston et al. (1997) and Allard et al. (1982) the initial RN concentration was low, but may have been close to or slightly above the respective solubility limit. Figure 2.2.3 suggests that this may indeed be the case:

The K_d values from both studies are significantly lower than the data for Th by Bradbury and Baeyens (2003). While this could be explained in case of Allard et al. (1982) by uncertainties in the oxidation state of Pu, the +IV oxidation state is well established in the study of Baston et al. (1997). Thus, a possible apparent consistency with the sorption behavior of (1) Pu(VI) in the presence of carbonate, (2) Np(V), or (3) possibly Pu/Am(III) is evaluated as meaningless. A possible explanation is that the respective RN solubility had been exceeded in both studies.

→ The data from both studies are rated as "not conclusive" under checkpoint III.

Data by Shibutani et al., (1998)

The Pu (+III) and Pu(IV) K_d values of Shibutani et al., (1998) were obtained from experiments carried out over a relatively large pH interval. From pH 6 to pH 8, the K_d values rapidly increase, marking a clear ascendant trend, whereas at higher pH values, the K_d values drastically decrease with pH (Figure 2.2.2).

The rising portion of the pH-edge described by the data of Shibutani et al. (1998) is in very good agreement with the Am(+III) data of Gorgeon (1994). At pH 8-10, the K_d values by Shibutani et al. (1998) also agree with the data of Gorgeon (1994) as well as the data for Th(+IV) by Bradbury and Baeyens (2003). Overall, the agreement is clearly better with the data for Am(III).

Unfortunately, comparisons are very difficult in the higher pH range. However, it seems that the steep decrease of the K_d values by Shibutani et al., (1998) is not entirely consistent with the sorption behavior of either Am or Th.

→ Tentatively, the following assessment is made:

A: Datapoints 59256, 59260, 59261, 59263, 59270, 59272, 59273

B. Datapoints 59257-59259, 59262, 59264-59269, 59271

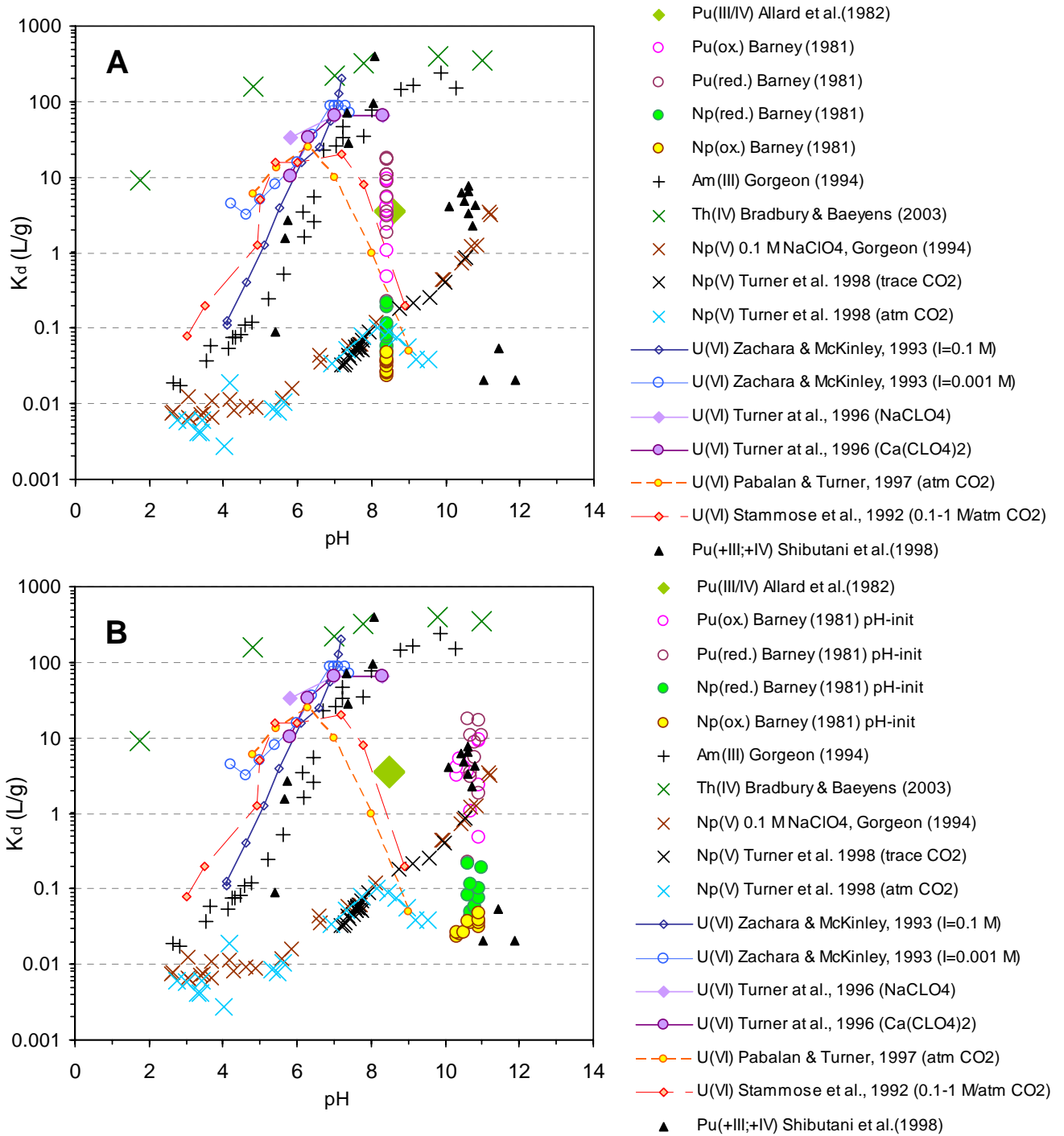


Figure 2.2.2: Overview of data for Pu and Np by Barney (1981) and Allard et al. (1982). The data by Barney (1981) are plotted vs. the presumed equilibrium pH in panel A, and vs. the initial pH in panel B. In addition to data from Figure 2.2.1, results by Shibutani et al. are also shown for comparison.

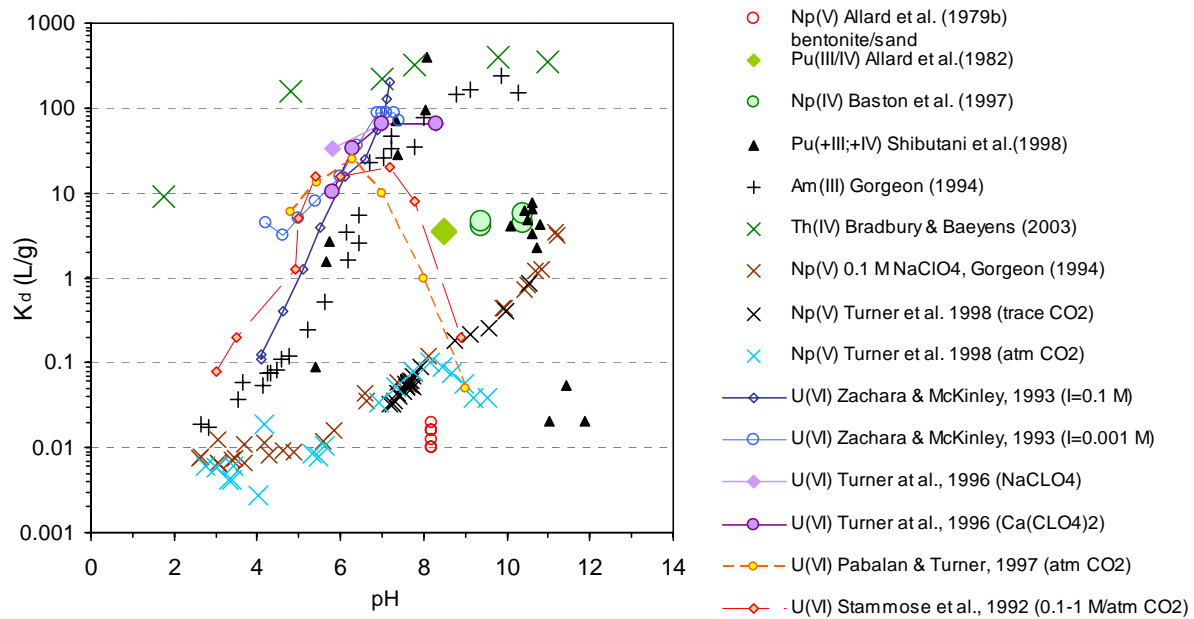


Figure 2.2.3: Overview of data for Pu and Np by Baston (1987) and Allard et al. (1979b). In addition to data from Figure 2.2.1, results by Shibutani et al. are also shown for comparison.

Data by Ticknor (1993)

In this study, experiments with Pu and Np were carried out at different pH values under reducing and oxidizing conditions.

- The K_d values reported for Np are basically consistent with independent data for Np(V), if it is considered that the sorption site density (\sim CEC) of the used minerals illite and especially kaolinite is smaller than that of montmorillonite. It should be noted in this context that the data by Allard et al. (1979b) for the sorption of Np(V) by a 10:90 bentonite/sand mixture fall in the same range as the data for illite by Ticknor (1993). This confirms the assessment that Np existed in the +V oxidation state in these experiments.

→ A rating of A is given for all datapoints.

- The K_d values reported for Pu are more difficult to evaluate. The data obtained under low- O_2 conditions seem to be fairly consistent with independent data for Np(V). However, it is impossible to say whether this is due to (i) Pu being in the +V oxidation state, or (ii) due to Pu existing as a mixture of oxidation states. Therefore, the following rating from checkpoint II-c is retained:

→ The data referring to low- O_2 conditions (60872, 60873, 60875, 60879, 60881, 60883) are labeled "unreliable".

- The K_d values reported for Pu under normal- O_2 conditions seem to be fairly consistent with independent data for U(VI) in the case of illite. On the other hand, the data for kaolinite do not correspond to any of the observed trends. It can also be noted that all K_d values for Pu by Ticknor (1993) show a similar upper limit. An alternative explanation, therefore, could be that a significant fraction of Pu existed in the +IV oxidation state even under normal- O_2 conditions, and that the observed K_d values represent solubility effects. Therefore, the rating from checkpoint II-c is retained and all data are labeled:

→ "unreliable"

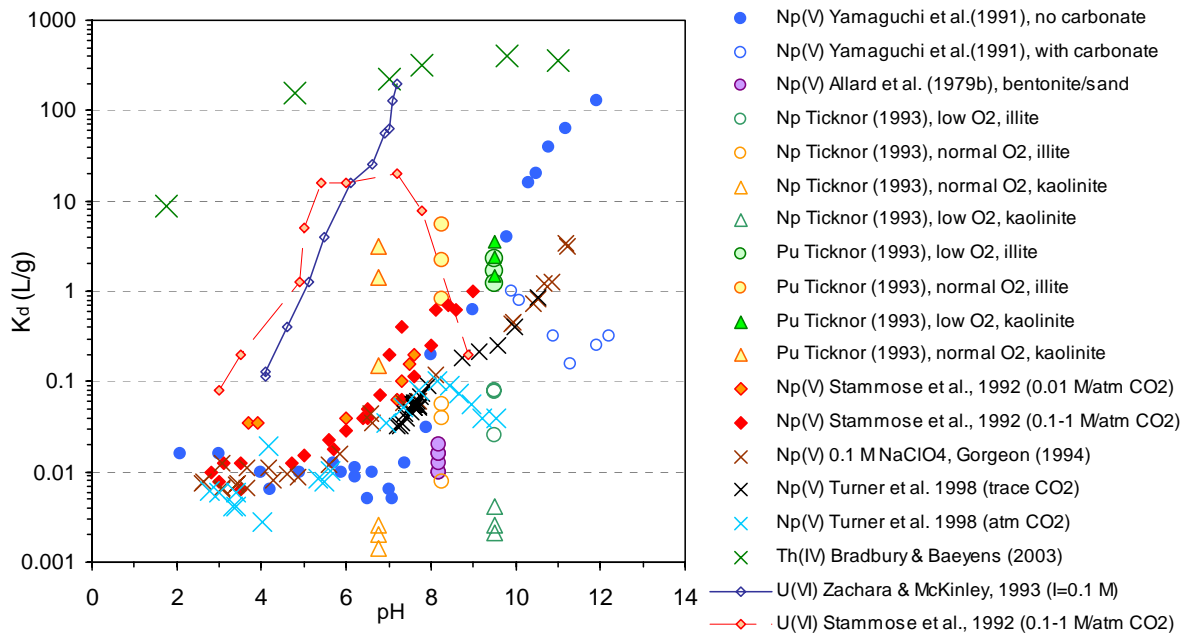


Figure 2.2.4: Overview of data for Pu and Np by Ticknor (1993) Data from Figure 2.2.1 are also shown for comparison.

Data for Np(V) by Allard et al. (1979b), Yamaguchi et al. (1991), Stammose et al. (1992)

Generally, all of these data agree well with each other, as well as with independent data by Turner et al. (1998) and Gorgeon (1994).

The slightly lower values measured by Allard et al. (1979b) are consistent with the respective solid used (10:90 bentonite/sand mixture):

→ A

All data for Np(V) by Stammose et al. (1992) agree very well with independent data and are labeled:

→ A

In the case of Yamaguchi et al. 1991), the data in the high pH range had been labeled "unreliable" under checkpoint II-h; this rating is retained. At the same time, the K_d values in the pH-range 6-8 are lower than expected. No good explanation (except experimental uncertainties) can be offered at the moment. The effect of carbonate shows the same trend as in the data by Turner et al. (1998), but occurs only at higher pH. The reason for this may be differences in the solution composition. Overall, the following rating is given:

→ Datapoints 62194-62200, 62210, 62211, and 62217-62222 are labeled A

→ Datapoints 62201-62209 are labeled B

→ Datapoints 62212-62216: rating "unreliable" is retained from checkpoint II-h

2.3 *Evaluation of the classification procedure*

Based on the results of the test runs using Revision 2 (November 4, 2004) of the classification guideline, some conclusions can be drawn 1) with respect to the suitability of the guideline for classifying the entries in the JNC-SDB, and 2) with respect to procedures that should be followed in the actual classification project:

Suitability of the guideline for classifying the entries in the JNC-SDB

- The proposed classification scheme allows a suitable classification of the K_d values on the basis of the quality of the underlying experiments.
- The use of minimum requirements for certain checkpoints to exclude unreliable data is reasonable.
- The updated classification procedure allows a finer differentiation of data quality than the previous version documented in Ochs and Talerico (2004). The proposed distribution of basically reliable data into six classes of different quality is adequate.
- The present report documents the results of BMG. The results by JNC are documented in internal JNC reports. A comparison showed that the results of JNC and BMG are consistent in most cases, and observed discrepancies can be traced to a particular reason.
- Based on the results of the test runs by JNC and BMG, Revision 2 was slightly amended to yield the final version documented in section 2.1: Revision 3 (March 15, 2005).

Recommended procedures for the actual data classification

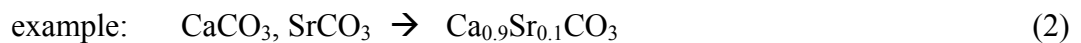
- To evaluate the quality of some of the data in the JNC-SDB or to verify some of the checkpoints listed under criterion II (which are not necessarily reported in the JNC-SDB) it was in most cases necessary to consult the original reference. Thus, the need to rely on the original reference has to be expected for classification of any part of the JNC-SDB.
- If information from the original reference contradicts information in the SDB, the situation has to be assessed and the SDB corrected, if necessary.
- The test runs showed that the rating "unreliable" is typically due to shortcomings in a few checkpoints, namely II-b, II-c, II-d, and II-h. It is therefore recommended to start evaluation of Criterion II by considering these checkpoints (see section 2.1.3).
- Once an entry is rated unreliable for these or any of the other checkpoints marked as critical in Table 1 (section 2.1.3), it is excluded from further evaluation.

3 Evaluation of the state of the art and applicability of solid-solution modeling for defining radionuclide solubility limits

Solubility limits (maximum concentrations) of radionuclides constitute important input parameters to performance assessment calculations. Typically, such values are derived through thermodynamic speciation calculations, based on solubility products for pure radionuclide solid phases. There are indications that the formation of solid solutions may substantially lower the effective solubility limit of various radionuclides. However, effects of solid solution formation are typically only being considered for the "classical" cases of Ra or Sr (see e.g. JNC, 2000, H-12 report). Because of the potential relevance of this topic for future PA exercises, JNC retained BMG with a first evaluation of the state of the art and applicability of solid solution modeling for the definition of radionuclide solubility limits to be used in PA. The scope of this task is limited to the coffinite- and Fe-S-Se-systems

3.1 Introduction and terminology

By a strict definition only those solids are termed solid-solutions that are the result of isomorphous replacement, i.e. where crystal lattice sites of a major ion of the solid are occupied by a foreign ion. A solid-solution of the end-member solids AC and BC can then be written as $A_xB_{1-x}C$, where for example A and B are cationic species and C is the corresponding anion:



Similarly mixed solid phases, which are not solid solutions in a strict sense, can also result from a co-precipitation of more than one pair of ionic species from aqueous solution, or from other (non-isomorphous) types of incorporation of foreign ions in the crystal lattice of a solid. For example, co-precipitation resulting in mixed crystals where incorporation of foreign ions in lattice defects occurs (Figure 3.1.1) or trapping of discrete particles in a growing solid (Figure 3.1.2) are not referred to as solid-solutions in a strict sense. Also, the result of a sorption-related uptake of dissolved species in a solid or on a solid surface is not a solid-solution in the strict sense (Curti 1997).

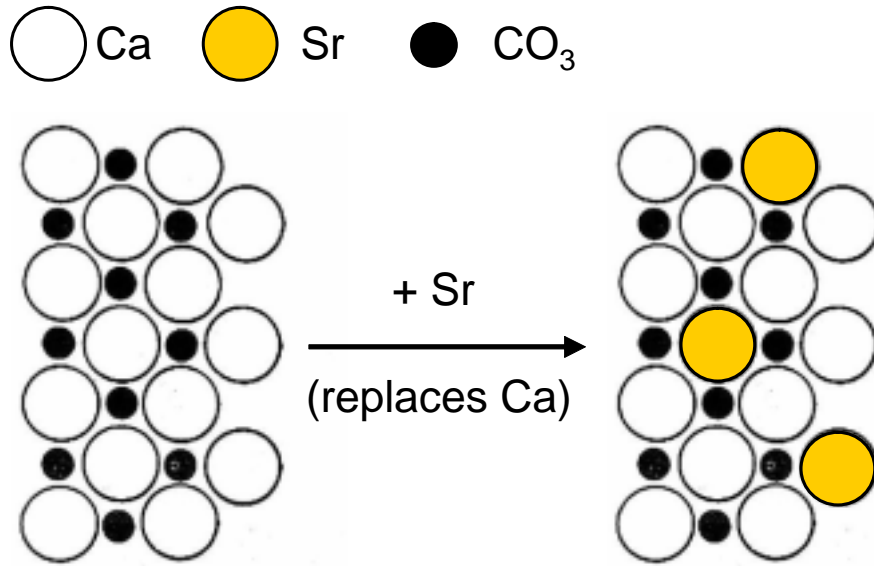


Figure 3.1.1: Example of the formation of a true solid solution of the type $A_xB_{1-x}C$ through isomorphous replacement of Ca^{2+} ions in a calcite crystal lattice by Sr^{2+} ions.

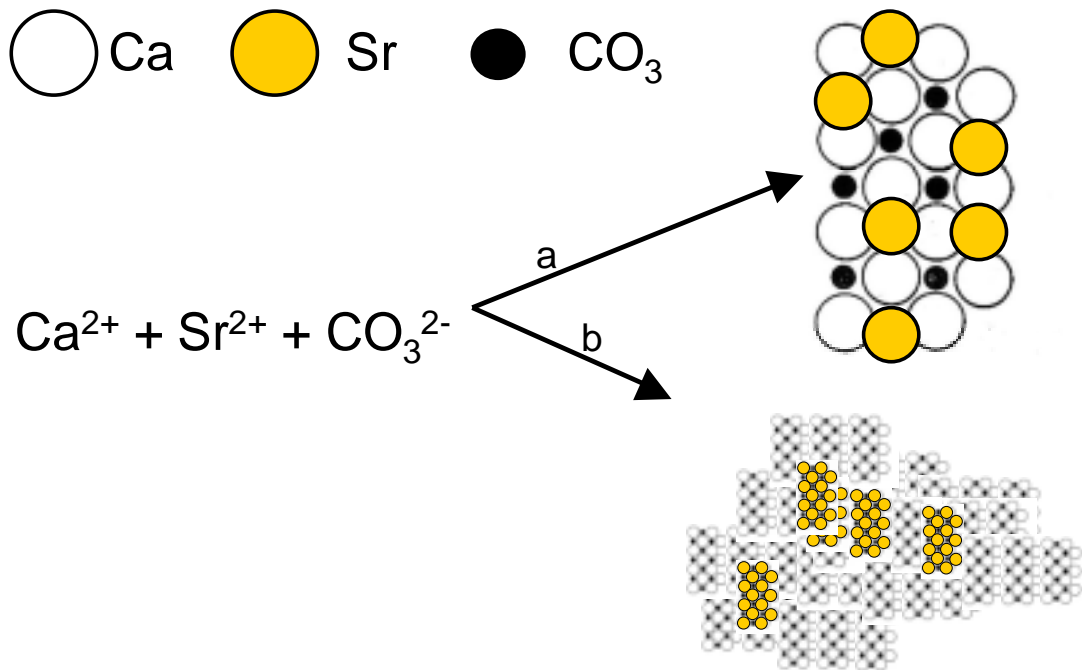


Figure 3.1.2: Example of the formation of co-precipitates of the type $A_xB_{1-x}C$ through non-isomorphous replacement (incorporation in lattice defect sites) of Ca^{2+} ions in calcite by Sr^{2+} ions (a), and through the incorporation of individual $SrCO_3(s)$ particles in a larger calcite crystal (b).

Following the above argumentation, the following prerequisites for the formation of true solid-solutions can be identified:

- Pure end-members of a solid-solution must crystallize in the same lattice type
- The ionic diameter of the foreign ion must not differ greatly from the major ion

3.2 *Approaches to modeling solid-solutions*

A key issue for solid solution modeling is knowledge of the solid-phase activity coefficients of the relevant components (for example, the cations A and B), as this parameter allows to connect composition and solubility product of a solid solution phase. Whether these solid-phase activity coefficients can be predicted or easily determined depends on the ideal/non-ideal behavior of a given solid solution. Solid-solutions can be distinguished as ideal or as non-ideal by their behavior in dissolution experiments. In the following, we distinguish the following cases:

- *Ideal solid solutions*

The solid phase activity coefficient of each component is equal to unity, and the solubility product can be calculated based on the mole-fraction of the components in the solid solution phase.

- *Non-ideal solid solutions*

In contrast to ideal cases, the solid-phase activity coefficients, and thus the solubility product of the solid cannot be estimated independently but have to be determined or approximated based on careful experiments.

3.2.1 *Ideal solid-solutions*

An ideal solid-solution behaves like a one-component solid with unit activity. It shows stoichiometric dissolution and the resulting aqueous solution attains a stoichiometric saturation state (Glynn & Reardon 1990). One of the few published examples for ideal behavior of a solid-solution¹ can be found in the system U(VI)-Fe(OH)₃ (Bruno et al. 1995).

In case of solid-phase activity coefficients of unity, the equilibrium ion activity product of the solid-solution (IAP_{SS}) is equal to its solubility product (K_{SS}):

$$\text{IAP}_{\text{SS}} = \text{K}_{\text{SS}} \quad (3)$$

¹ An alternative explanation for the ideal behavior in this case could be that the underlying process was adsorption, rather than solid solution formation.

The IAP_{SS} of the solid-solution $A_xB_{1-x}C$ can be calculated from the mass action law of the dissolution reaction



$$IAP_{SS} = \{A^+\}^x \{B^+\}^{1-x} \{C^-\} \quad (5)$$

where $\{A^+\}$, $\{B^+\}$, and $\{C^-\}$ denote the activities of the ions in the aqueous phase. For ideal solid-solutions a plot of $\log K_{SS}$ versus the mole fraction of one of the components A or B in the solid leads to a straight line connecting K_{AC} and K_{BC} , the solubility products of the pure end-members AC and BC. Hence, the solubility product of an ideal solid-solution is given by its end-member solubilities (see Figure 3.2.1).

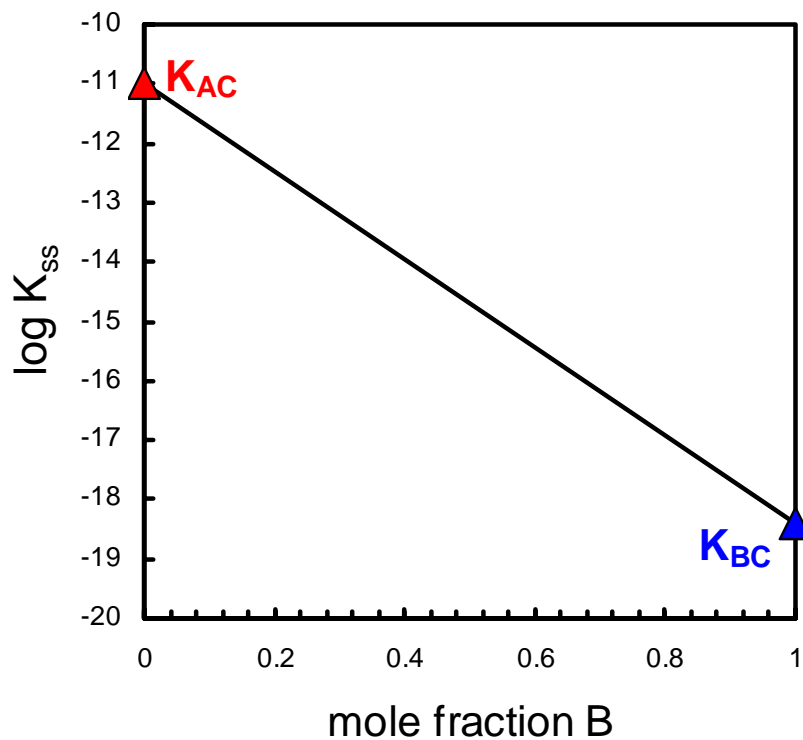


Figure 3.2.1 Log K_{SS} values as a function of the mole fraction of B in the solid. In an ideal solid-solution, K_{SS} can be calculated from the solubility products of the pure end-members, K_{AC} and K_{BC} .

3.2.2 *Non-ideal solid-solutions*

In non-ideal solid-solutions the activities of the components in the solid are not equal to unity and may differ from each other, therefore, a plot of $\log K_{SS}$ vs. mole fraction as shown in Figure 3.2.1 shows a deviation from the straight line behavior. In this case, the solubility

product of the solid-solution cannot be predicted from the K_{SP} values of the pure end-members, but needs to be evaluated based on solubility measurements as a function of solid phase composition. In terms of modeling approaches, two cases of non-ideality can be distinguished:

3.2.2.1 Non-ideal solid-solutions with stoichiometric dissolution

If the solid dissolves stoichiometrically, the mole fractions of A and B in the solid-solution remain constant and are identical to those in the aqueous solution. The dependency of K_{SS} on the composition of the solid-solution can be described by an expression for the solid-phase activity coefficients derived in the following (see Glynn and Reardon, 1990; Glynn, 2000):

Given that a non-ideal solid-solution dissolves stoichiometrically, one can calculate the excess free energy of mixing by

$$G^E = RT(\ln K_{SS} - x(\ln K_{AC} + \ln x) - (1-x)(\ln K_{BC} + \ln(1-x))) \quad (6)$$

where G^E is the free energy of mixing, x and $1-x$ are the mole fractions of AC and BC, respectively, in the solid solution, and K_{AC} and K_{BC} are the solubility products of the pure end-members.

Using a Guggenheim expansion series for the free energy of mixing

$$G^E = x(1-x)RT(a_0 + a_1(x - (1-x)) + a_2(x - (1-x))^2 - \dots) \quad (7)$$

where a_0 , a_1 , a_2 etc. denote the dimensionless Guggenheim parameters, and combining this with eq. (6), a general expression for K_{SS} can be written.

For the simple case of a regular solution model where G^E is independent of the temperature and equals the mixing enthalpy (Lippmann 1980) there is only a single coefficient left in the Guggenheim expansion: a_0 . This leads to

$$\ln K_{SS} = x(1-x)a_0 + (1-x)\ln(K_{AC}(1-x)) + x\ln(K_{BC}x) \quad (8)$$

The slope of this curve depends only on the value of a_0 , see Figure 3.2.2.

From the dimensionless Guggenheim parameter a_0 one can calculate the activity coefficients γ_{AC} and γ_{BC} of the components A and B in the solid-solution,

$$\ln \gamma_{AC} = a_0 x^2 \quad (9)$$

$$\ln \gamma_{BC} = a_0 (1-x)^2 \quad (10)$$

leading to a general expression for K_{SS} :

$$K_{SS} = a_{AC}^x \cdot K_{AC}^x \cdot a_{BC}^{1-x} \cdot K_{BC}^{1-x} \quad (11)$$

where a_{AC} and a_{BC} denote the activity of the components of the solid-solution at a given composition.

For a solid-solution of type $A_xB_{1-x}C$ these activities can be calculated as (Glynn & Reardon 1990)

$$a_{AC} = x \gamma_{AC} \quad (12)$$

$$a_{BC} = (1 - x) \gamma_{BC} \tag{13}$$

Estimation of the solid-phase activity coefficients may also be possible through semi-empirical mixing models (e.g. models by Margules, etc., see also Parkhurst and Appelo, 1999) based on a good knowledge of the solid-phase characteristics.

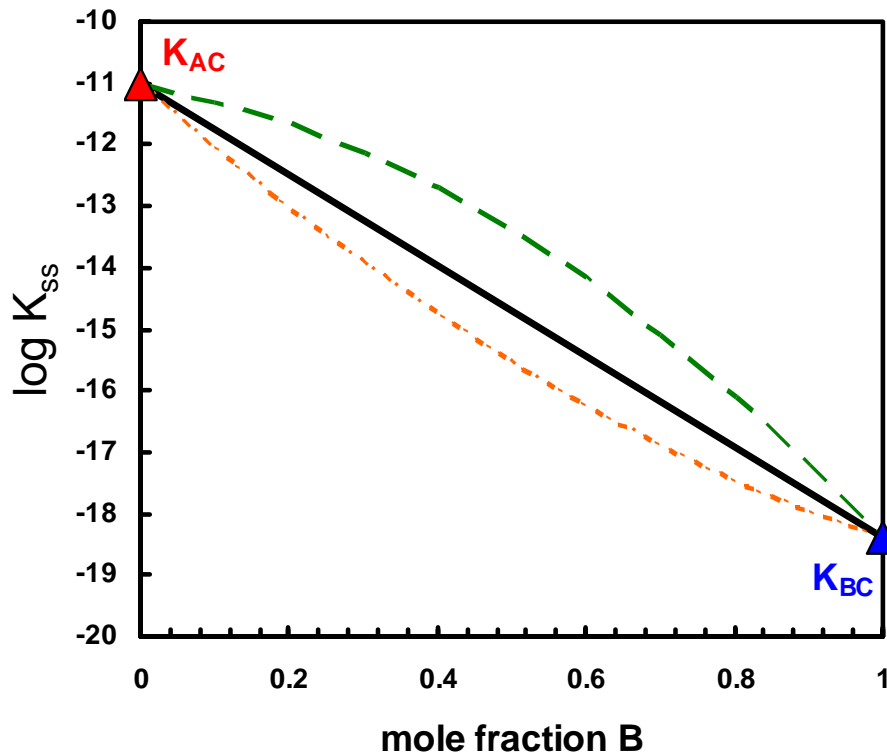


Figure 3.2.2 The dashed and dotted lines represent the deviation of K_{SS} from ideality (solid line) calculated with a Guggenheim parameter of value $a_0=-4.9$ (dotted) and $a_0=20$ (dashed).

3.2.2.2 Non-ideal solid-solutions with non-stoichiometric dissolution

If the solid does not dissolve stoichiometrically, the mole fractions of A and B in the solid-solution do not remain constant during dissolution and are not identical to those in the aqueous solution. In this case, the relations discussed above are not valid anymore, but one can apply the concept of the “total solubility product” (Lippmann 1980)

$$\Sigma \Pi = (\{A^+\} + \{B^+\}) \{C^-\} \tag{14}$$

In thermodynamic equilibrium the deviation from the straight-line behavior shown in Figure 3.2.1 is given by the so-called “solidus curve” defined as follows (see Figure 3.2.3):

$$\Sigma \Pi_{eq} = a_{AC} K_{AC} + a_{BC} K_{BC} \tag{15}$$

For ideal solid-solutions ($\gamma_{AC}=\gamma_{BC}=1$ leading to $a_{AC}=x$ and $a_{BC}=1-x$) this curve is identical to the straight line in Figure 3.2.1.

The composition of the saturated aqueous solution for any given composition of the solid-solution is defined by the so-called “solutus curve”. For the general case of a non-ideal solid-solution “solutus curve” is defined in eq. (16) by expressing the solid phase activities in terms of aqueous phase mole fractions and solid phase activity coefficients:

$$\Sigma\Pi_{\text{eq}} = 1 / \left(\frac{\chi_{A,\text{aq}}}{K_{AC}\gamma_{AC}} + \frac{\chi_{B,\text{aq}}}{K_{BC}\gamma_{BC}} \right) \tag{16}$$

where

$$\chi_{A,\text{aq}} = \frac{\{A^+\}}{\{A^+\} + \{B^+\}} \quad \text{and} \quad \chi_{B,\text{aq}} = \frac{\{B^+\}}{\{A^+\} + \{B^+\}} \tag{17,18}$$

are the activity fractions of the ions A and B in the aqueous phase.

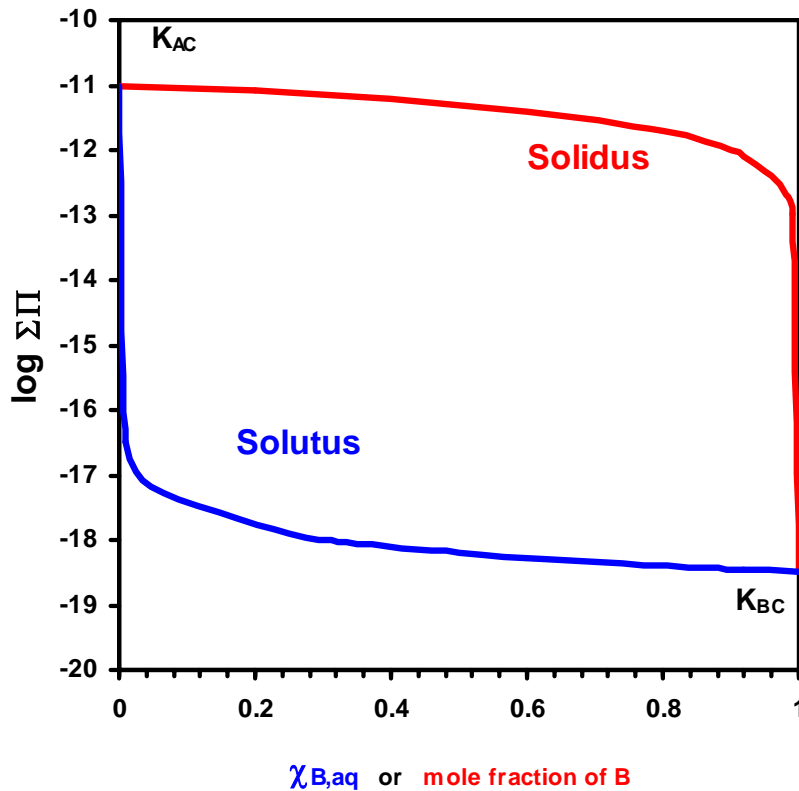


Figure 3.2.3 Lippmann phase diagram for a binary solid-solution, where the solidus curve is plotted against x_{BC} and the solutus curve is plotted against $\chi_{B,\text{aq}}$.

Different combinations of $\chi_{A,\text{aq}}$ and $\chi_{B,\text{aq}}$ lead to different solutus lines corresponding to different solubility products. These activity fractions can only be determined by measuring the equilibrium concentrations of the respective ions in the aqueous solution. The solid phase

activity coefficients γ_{AC} and γ_{BC} cannot be determined directly or by a direct measurement, but a great variety of semi-empirical mixing models have been developed and parameterized (e.g. models by Margules, Redlich-Kister, van Laar, Wilson etc., see also Parkhurst and Appelo, 1999).

3.3 Overview Coffinite- and F-S-Se-system

3.3.1 Literature research on solid solutions of coffinite

Searching for “coffinite” in GeoRef (recommended for geochemical literature searches by library experts of Swiss Federal Institute of Technology¹) returned 332 hits containing key words like “coffinite”, “coffinite bearing”, “coffinite localities”, “coffinite occurrence”, “coffinite uraninite”, “coffinitization”, and “coffinitisation”. Searching for “solid solution” returned 3610 hits, whereas the combined search only returned one single article (Pointer et al., 1988). No references were found that contained the key words “coffinite” and “precipitation” simultaneously.

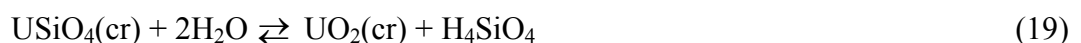
A first review of the literature on coffinite revealed information and data of varying quality for the following relevant aspects of solid solution chemistry of coffinite:

1. Stability regime of coffinite
2. Occurrence and conditions of coffinitization of uraninite
3. Miscibility gap in the zircon/coffinite-system
4. Substitution of U^{4+} with other ions like Zr^{4+} , Th^{4+} , Hf^{4+} in the coffinite lattice
5. Zircon as a host phase for actinides

However, no data were found regarding the solubility limitation of uranium by coffinite-like material, i.e. by partially substituted coffinite.

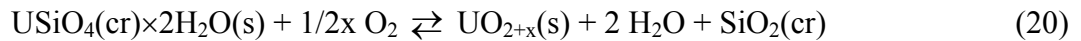
3.3.1.1 Stability regime of coffinite ($USiO_4(cr)$)

The solubility of $USiO_4(cr)$ in pure water amounts to 4.9×10^{-6} mol/L whereas, at pH 8.2 and $E_h = -275$ mV a value of 1.4×10^{-9} mol/L is found (Delécaut et al., 2002). Similarly, Yajima and co-workers found the solubility of UO_2 under reducing conditions to be in the order of 10^{-9} mol/L for pH values above 4 (Yajima et al., 1995). The equilibrium between coffinite and uraninite in aqueous solutions can be written as follows:



¹ GeoRef provides access to over 2.3 million references to articles, books, maps, conference papers, reports, and theses. GeoRef includes more than 3,500 journals in 40 languages and references to all publications of the U.S. Geological Survey (from <http://georef.cos.com>).

To account for the formation of mixed oxides and the hydration of coffinite, eq. (19) was written by Janeczek and Ewing (1992) as follows:



Equilibrium for eq. (16) is found at a H_4SiO_4 concentration of 10^{-3} mol/L (60 ppm as SiO_2) (Langmuir 1978) or at a silica activity of $10^{-3.59}$ (Hemingway 1982). The equilibrium constant for eq. (19) is found to be $\log K = 0.5 \pm 0.03$, based on a Gibbs free energy for eq. (19) of $\Delta G_f^0 = -1885.98$ kJ/mol (Langmuir 1997). This value is well in agreement with $\Delta G_f^0 = -1883.6 \pm 4.0$ kJ/mol as published by NEA (Guillaumont et al., 2003).

From natural sources with groundwater showing silica concentrations close to or even exceeding the value given above (Palmottu/Finland, Cigar Lake/Canada) it is known that uraninite is partially replaced by coffinite (Janeczek and Ewing, 1992). Naturally occurring coffinite specimen also always show incorporation of other minerals (e.g. Cigar Lake/Canada: PbO , CaO , SiO_2 ; Oklo/Gabon: CaO , PbO , Ce_2O_3 ; Caribou Mine/USA: Y_2O_3 ; Grants Mineral Belt/USA: Y_2O_3 , P_2O_5 , CaO , Witwatersrand/South Africa: ThO_2 , PbO , Y_2O_3 ; Ririwai/Nigeria: ZrO_2 , ThO_2 , Y_2O_3).

3.3.1.2 Occurrence and conditions of coffinitization of uraninite

Natural deposits of coffinite are believed to be alteration products of other uranium ores, typically formed by coffinitization of uraninite (Janeczek and Ewing, 1992). Conditions must include silicate rich water and low E_h for coffinitization to occur, hence, close associations of sulfides and bitumen are mostly found with coffinite. In contrast, presence of oxygen favors uraninite-like phases which are stable towards higher E_h -values than coffinite, see eq. (17) (Janeczek and Ewing, 1992).

3.3.1.3 Miscibility gap in the zircon/coffinite-system

Coffinite is iso-structural with zircon (ZrSiO_4), thorite (ThSiO_4) and hafnon (HfSiO_4). There is evidence for solid solutions with each of these minerals (De Vivo et al., 1984). Because of the similar ionic radii of Zr and Hf there is complete miscibility in the System ZrSiO_4 - HfSiO_4 but miscibility gaps seem to occur in the systems ZrSiO_4 - USiO_4 , ZrSiO_4 - ThSiO_4 , and ThSiO_4 - USiO_4 (ionic radii: $\text{Hf}^{4+} = 83$ pm, $\text{Zr}^{4+} = 84$ pm, $\text{U}^{4+} = 100$ pm, $\text{Th}^{4+} = 105$ pm) (Speer and Cooper, 1982).

3.3.1.4 Substitution of uranium in coffinite with other elements

In naturally occurring uranium ore from Oklo-Okélobondo not only coffinite was found, but also an (U,Zr)-silicate with a ZrO_2 -content of 28 wt%. This phase also included zircon with uranium content of up to 8.6 wt% (Jensen and Ewing, 2001). In a biotite granite from Ririwai, Nigeria, Pointer et al. found coffinite with a ZrO_2 -content of 11.9 wt% and Y_2O_3 -content of up to 15.9 wt% (Pointer et al., 1988).

3.3.1.5 *Zircon and thorite as a host phase for U(IV)*

Mumpton and Roy concluded from analyses of zircon and thorite in the literature that the solubility limit of USiO_4 in ZrSiO_4 is 5 mole%, and of USiO_4 in ThSiO_4 is 35 mole% (Mumpton and Roy, 1961). Ushakov et al. (1999) found a slightly lower maximum solubility of 4 ± 1 mole% U in synthesized samples of ZrSiO_4 (Ushakov et al., 1999). Kurepin (1988) suggests a theoretical approach for the determination of the solubility limits of zircon solid solutions with actinides and lanthanides. This approach is based on inter-atomic distances in iso-structural compounds and predicts complete miscibility of U and Zr in zircon at very elevated temperatures (>1000 K) (Kurepin, 1998). Keller synthesized orthosilicates (MSiO_4) with zircon-like structure of the following elements: M = Pa, Np, Pu, and Am (Keller, 1963).

3.3.2 *Solid solutions in the system Fe-S-Se*

A literature search was carried out in a similar way as documented for the coffinite system. Solid solutions in the system Iron-Sulphur-Selenium may exist between the isomorphic solids Pyrite¹ (isometric FeS_2) and Dzharkenite (isometric FeSe_2), between Marcasite (orthorhombic FeS_2) and Ferroselite (orthorhombic FeSe_2) and between Troilite (hexagonal FeS) and Achavalite² (hexagonal FeSe).

Since dzharkenite is polymorphous with ferroselite and was only discovered in 1995 there is some uncertainty regarding the crystallographic nature of the solid FeSe_2 -species under investigation in the literature before 1995.

Another uncertainty lies in the possible difference in solubility of the different crystal structures of the pure end-members of these solid solutions.

3.3.2.1 *Fe-S-Se composition in naturally occurring minerals*

In natural sulphides from uranium deposits in Wyoming, USA, Coleman and Delevaux (1957) found large amounts of selenium. The maximum amount of Se substituting for S in pyrite was found to be 3 wt%. Pyrites from other sites also contained varying amounts of Se (Simon et al., 1997).

Yakovleva et al. (2003) found even higher selenium content in pyrites from copper-zinc deposits in South Urals, Russia. In contrast to Franz (1983), who found a miscibility gap between 10 and 68 mol% (corresponding to $\text{Fe}(\text{S}_{1.8}\text{Se}_{0.2})$ and $\text{Fe}(\text{S}_{1.36}\text{Se}_{0.64})$) for synthetic $\text{Fe}(\text{S},\text{Se})_{\Sigma=2}$ crystals, Yakovleva et al. (2003) found FeSe_2 with higher S-content, thus

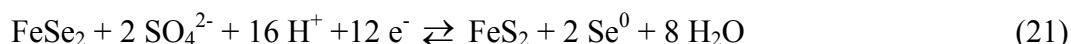
¹ All mineral names are according to the “Commission on New Minerals and Mineral Names” (CNMMN) of the “International Mineralogical Association” (IMA). A comprehensive website can be found at <http://www.mindat.org>

² Achavalite is not an approved IMA mineral name, but used throughout the literature.

reducing this miscibility gap to 10-40 mol%. They also could show that the FeSe₂ was indeed dzharkenite and not ferroselite. According to the close ionic radii and electro-negativities of S²⁻ and Se²⁻ Yakovleva et al. (2003) finally speculate about the existence of a completely miscible solid solution series in the system Fe(S,Se)_{Σ=2}.

3.3.2.2 *Fe-S-Se in aqueous solution, thermodynamic data*

Howard (1977) constructed complete Eh-pH-diagrams from some 20 reactions of the system Fe-S-Se in aqueous solution, stating that FeS and FeSe only coexist when the [H₂Se]/[H₂S] ratio exceeds 10^{-2.87}. The stability region of FeSe lies below an Eh of -100 mV at a pH of 2 to 5. On the other hand, the coexistence of FeS₂ and FeSe₂ given by the equilibrium



spans a pH-region of 2 to 10 at Eh values ranging from 200 mV to -300 mV.

Masscheleyn et al. (1991) calculated stability fields for solid-solutions of Fe(S,Se)_{Σ=1} for different activities of Fe, S, and Se. They overlay the phase diagrams of Fe-S and Fe-Se and predict stability for the solid solution at pH>4 and a redox potential smaller than -2pe. Underlying thermodynamical data was later adopted for the Nagra/PSI data base by Hummel et al. (2002).

Seby et al. (2001) revisited published thermodynamical data on selenium compounds: equilibrium constants, standard potentials, solubilities, and dissociation constants. All these are also part of the selenium chapter of the Nagra/PSI data base (Hummel et al., 2002). Based on a preliminary evaluation, the data used by Howard (1977) appear to be not inconsistent with these more recently selected data.

Recently, Kitamura et al. (2004) carried out solubility measurements of FeSe₂ under different conditions (Eh, pH) and found that values in standard thermodynamic databases may overestimate the solubility of pure Se-phases under reducing conditions.

3.3.2.3 *Concluding remarks*

The literature review produced data on possible solid solutions of Fe-S-Se. From naturally occurring species it is known that these solid solutions exist and there is evidence that at least for the system Fe(S,Se)_{Σ=2} there might be no miscibility gap. The thermodynamic basis for the calculation of the stability regions of these solid solutions as well as their quantitative composition is still not adequately treated. No data was found for solubilities of the individual constituents Fe, S, and Se in presence of these solid solutions.

3.4 *Data situation for modeling solid-solution - aqueous solution equilibria*

There are different data needs for modeling the different types of solid-solution - aqueous-solution equilibria as described in the preceding sections.

- In case of ideal solid-solutions, knowledge of solubility products (K_{SP}) of the pure end-members is sufficient to calculate solubility products for the entire solid-solution series (K_{SS}).
- In case of non-ideal solid-solutions, additional knowledge for the determination of the solid phase activity coefficients γ_{AC} and γ_{BC} is needed. These can be calculated from model fits to experimental data from e.g. dissolution experiments of solid-solutions with different composition. If data of good quality are available on analog systems or solid-phase characteristics, such models may also include direct input of Guggenheim expansion parameters, Margules parameters, etc. (Parkhurst and Appelo, 1999).

3.4.1 *Fe-S-Se system*

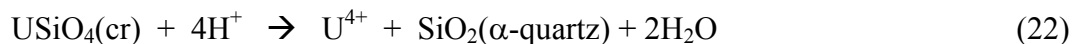
Solubility products are available for the solid end-members $FeS_2/FeSe_2$ and $FeS/FeSe$, and it may be possible to model ideal solid-solutions. However, the database for the Fe-selenides appears to be of questionable quality, and there are some doubts regarding the crystal structure in the $FeS_2/FeSe_2$ -type solids. No data on the solid solution - aqueous solution behavior could be found.

3.4.2 *Coffinite system and other actinide silicates*

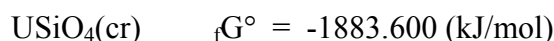
In general, the thermodynamic database for actinide-silica reactions is very incomplete. At least in part, this is probably due to experimental difficulties, such as the strong tendency of dissolved silica towards polymerization (Grenthe et al., 1992). In case of IV-valent actinides, the solid silicates (such as coffinite) will always occur together with solid SiO_2 and AnO_2 to some degree, as illustrated by equations (19-20).

3.4.2.1 *Coffinite, U(IV)-silicates*

No thermodynamic data on the solid solution - aqueous solution behavior could be found. Data for pure coffinite is available for the dissolution reaction



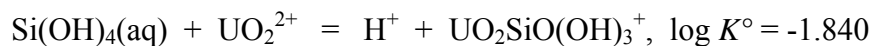
Guillaumont et al. (2003) give ΔG as well as ΔH values for all species, allowing to calculate K_{SP} as a function of temperature. The value for ΔG is (Guillaumont et al., 2003):



Langmuir (1997) gives a ΔG for amorphous coffinite as well, but this value is not accepted in the review of Guillaumont et al. (2003). No data for dissolved species could be found.

3.4.2.2 *U(VI)-silicates*

The only dissolved species considered by Guillaumont et al. (2003) is $\text{UO}_2\text{SiO}(\text{OH})_3^+$; the following data are given in their review:



Guillaumont et al. (2003) discuss data for several solid U(VI)-silicates (soddyite, uranophane, Na-boltwoodite, Na-weeksite). While the data are actually not selected in their review, Guillaumont et al. (2003) estimate the quality as sufficient for scoping calculations.

3.4.2.3 *Other actinide(IV,III)-silicates, zircon*

Of the other potential end-members, the data situation for $\text{ZrSiO}_4(\text{s})$ could be sufficient (a $\text{}^{\circ}G^{\circ}$ value is given in Babushkin et al., 1985), but no relevant data were found for ThSiO_4 and other actinide(IV) silicates (" PuSiO_4 , NpSiO_4 ").

For Am, Guillaumont et al. (2003) recommend data for one aqueous species, but no information on solid Am-silicates appears to be available.

3.5 *Approaches for filling data gaps*

3.5.1 *Investigation of actinide solubility control through silicates*

The relevant conditions for any experimental investigation aimed at this question would be those considered to be representative for the dissolution of waste glass in a deep repository. It is assumed that the system Eh under such conditions would be low enough to keep U and Np in the IV-valent state. In case of Pu, the oxidation state is less clear, but it is assumed that only reduced species would be relevant. Therefore, the formation of actinide(V/VI)-silicates is not considered in the following.

For tetravalent actinides, the only important solid silicates are coffinite-like compounds ($\text{An}^{\text{IV}}\text{SiO}_4$) according to present knowledge. From work on coffinite it is known that two requirements need to be met (apart from maintaining reducing conditions) in order to favor the formation of this mineral:

- the pH needs to be in the range ≈ 7 -10;
- the concentration of dissolved silica needs to be sufficiently high.

Because of the experimental difficulties discussed above, the synthesis of coffinite minerals has been notably difficult (cf. Hummel et al., 2002). Note in this respect that the thermodynamic data for coffinite given in the NEA-TDB were determined by Langmuir

(1978) through an estimation based on naturally occurring coffinite and corresponding concentrations of dissolved silica, and are not based on experimental results (the estimation by Langmuir, 1978, was accepted by Grenthe et al., 1992; this was retained by Guillaumont et al., 2003).

Because of the great number of parameters that can be varied in experiments performed under approximated repository conditions, it is not possible to suggest a detailed experimental design (without detailed knowledge of the envisaged conditions). However, the following general recommendations can be given:

- Taking into account the complexities already inherent in the coffinite system, it is recommended to keep the experimental system initially as simple as possible.
- Considering the lack of data regarding solid silicate compounds of reduced actinides, the uranium-coffinite system would offer the advantage of being able to use at least some reference data for scoping calculations, mineral identification, etc.
- Solubility control by solid silicates obviously means that the resulting solubilities have to be lower than those above e.g. $\text{UO}_2(\text{s})$, and in a pH range $\approx 7-10$. This shows that the analytical detection limit has to be evaluated carefully.
- In a first step, the potential importance of solid silicates could be investigated by considering several similar model systems containing different levels of dissolved silicate:
 - Initially, the simplest system could only contain U(IV) at the desired levels; e.g., to achieve different degrees of over- and undersaturation with respect to $\text{UO}_2(\text{s})$ in the relevant pH range of about 7-10. If possible, the nature of the resulting solids in oversaturated samples should be examined by XRD or spectroscopic methods.
 - Each of the above systems could then be extended by introducing different levels of dissolved silica. Given that the detection limit is sufficiently low, this should allow to detect whether the solubility of U is actually lowered by the addition of silica.
 - This would be a critical result. Therefore, this first set of experiments should be kept as simple as possible. Planning of further experimental details will become important only if such an effect can be observed. The solid phases formed should be examined by XRD or spectroscopic methods.
 - Eq. (19) shows that a large excess of silica will be needed (the estimation procedure by Langmuir, 1978, is based on $\text{USiO}_4(\text{s}) \Leftrightarrow \text{UO}_2(\text{s})$ equilibrium at a dissolved silica concentration of 10^{-3} M). This also shows that it will be very difficult to obtain only pure coffinite as solid phase.
 - Some attention should be paid regarding the expected speciation of dissolved silica under repository conditions. As pointed out above, dissolved silica has a fairly strong tendency towards polymerization, but mainly at $\text{pH} > 10$ (Eikenberg, 1990; Grenthe et al., 1992).

- As the information on the kinetics of the formation of pure coffinite or related solid solutions is very poor, the experimental setup should allow to maintain constant conditions over extended reaction times.
- It may also be good to keep at least some samples (presumably the ones with elevated silica concentrations) at elevated temperatures, if this is relevant under Japanese deep repository conditions.

3.5.2 *Solid solutions*

The first task will be an investigation of the basic solid solution - aqueous solution behavior; i.e. to determine if the system follows ideal or non-ideal behavior. This can either be done by measuring equilibrium ion concentrations in solubility experiments of solid solutions with different compositions or by structure determination of synthesized solid-solutions with different compositions. It is for example reasonable to assume ideal behavior when the lattice parameter changes linearly with increasing content of the foreign ion (Wu et al., 2000).

If ideal behavior can be observed, it should be possible, in principle, to model the behavior of solid solutions based on the properties of the corresponding end-members. As pointed out above, there are still uncertainties related to the underlying thermodynamic data, however.

For the case of non-ideal solid-solutions aqueous solutions it could be sufficient to study the solubility behavior of selected solid-solution compositions to describe the complete system by fitting a solid-phase activity coefficient model to the measured data. For example, Baron and Palmer (2002) used only seven different compositions of the system $\text{KFe}_3(\text{Cr}_x\text{S}_{1-x}\text{O}_4)_2(\text{OH})_6$ to prove non-ideal behavior of the system and plot complete Lippmann phase diagrams. Similarly, Wu et al. (2000) synthesized eight different compositions of the system $\text{Pb}_x\text{Sr}_{1-x}(\text{NO}_3)_2$ and could show ideal behavior (Wu et al., 2000).

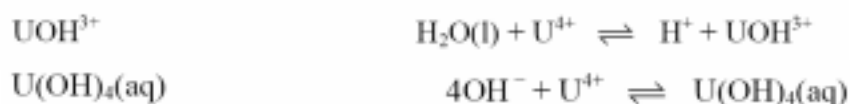
As an alternative approach, direct determination of the solid phase activity coefficients from first principles calculations (molecular modeling) also have been demonstrated, e.g. for the system $(\text{Ba,Sr})\text{SO}_4 \cdot \text{H}_2\text{O}$ (Prieto et al., 2000).

4 TDB issues

4.1 Conversion of NEA-TDB data files into other database formats

Within the NEA-TDB program, thermodynamic data of very high quality have been critically selected for a number of actinide and other elements (Guillaumont et al., 2003). The NEA makes these data also available in electronic file format. However, the selected data format is not directly compatible with the formats of input files for common speciation codes, such as the PHREEQE family. While the data can of course be transferred manually, this is time-consuming and also opens up the possibility of operator errors. Therefore, the availability of computer programs for automatic conversion of the NEA-TDB format to other data formats would be desirable. However, no such program is available at the moment, according to the NEA-TDB secretariat (F. Mompean, pers. comm. to M. Ochs, February 7/8, 2005). Based on our information, there are also no other organizations to date that have developed such a conversion program.

One of the likely reasons for this situation is the incompatibility between many data as represented in the NEA-TDB on one hand with the chemical master species used by common speciation codes on the other hand (F. Mompean, pers. comm. to M. Ochs, February 7/8, 2005). A typical example would be ligands that are represented in their de-protonated form in one case vs. their protonated form in the other. It also needs to be pointed out that not all of the reaction-specific data (log K values) in the NEA-TDB are based on the same formulation. For example, both OH^- as well as H_2O is used to define chemical equilibria. The following examples are taken from Guillaumont et al. (2003):



In principle, it would be preferable to use species-specific data (ΔG values), which could then be converted to log K values. However, the recommended auxiliary data provided by the NEA do actually not contain all the data that would be needed to formulate the relevant equilibria involving ligands and other major species. Therefore, each user would have to fill in some values, which would be a potential source of inconsistencies.

In summary, it appears that many of the chemical reactions given in the NEA-TDB would have to be re-formulated to render the corresponding log K values compatible with a particular data format. At the same time, additional data for auxiliary species would have to be included in the NEA-TDB, to avoid the need for users to select data on their own. The NEA-TDB secretariat is aware of this situation (F. Mompean, pers. comm. to M. Ochs, February 7/8, 2005).

4.2 *Availability of enthalpy data in the NEA-TDB: Update*

In order to calculate radionuclide speciation for the assessment of solubilities or sorption behavior at elevated temperatures, $\log K$ values valid at the standard state need to be corrected to correspond to the relevant temperature. Many speciation codes use a van't Hoff-type expression. This method, as well as other temperature extrapolation methods, requires enthalpy data at standard conditions (species-specific molar enthalpy of formation $\Delta_f H^\circ$ or reaction-specific molar enthalpy of formation $\Delta_r H^\circ$ [kJ/mol]).

In an earlier report (Ochs et al., 2002), an overview of the availability of enthalpy data in several databases (NEA-TDB, PHREEQE, Nagra-TDB, SPRONS, HATCHES) was presented, considering each specific reaction given in the JNC-TDB. However, in case of the NEA-TDB, only the data given in Grenthe et al. (1992) had been considered at the time. Further, several updates of the NEA-TDB have taken place in the meantime. Therefore, an update of the availability of enthalpy data in the NEA-TDB for the reactions given in the JNC-TDB has been done for the present report. The result is presented in Appendix III.

5 References (excluding the references given in the SDB)

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Appendix I: Revision 2 of the classification guideline

Evaluation and categorization of the reliability of K_d values in the JNC-SDB

Revision 2, November 4, 2004

Introduction, description of main criteria

The reliability of K_d values in the JNC-SDB can be assessed using the following three main criteria. The three main criteria are listed in the expected sequence of application during a classification of entries in the SDB. Criteria Ia and Ib are related to documentation and data entry, whereas the technical and scientific quality of an entry is addressed by criteria II and III.

I Completeness of documentation and type of K_d information:

- a) It needs to be verified that the documentation of each entry is detailed enough to allow further examination according to the main criteria II-III. At this point, only the completeness of the documentation is examined; the appropriateness of the reported data and approaches is evaluated under criterion II below.
- b) This point takes also into account that the reliability of data input to the SDB will be substantially higher if K_d values are directly available in table format in comparison to literature that reports e.g. %-adsorbed values in a graph. The latter way of reporting requires the operator to i) manually read values off a graph and ii) to calculate K_d from the %-adsorbed and s/w ratio values given, which significantly increases the likelihood of an operator error during data input.

II Quality of reported data

This is the most important issue from a technical and scientific point of view. This criterion encompasses an evaluation of the appropriateness of the experimental system to produce reliable K_d data. The methods used (or lacking) for determining experimental uncertainty are also examined for each literature source. Further, it is considered whether the data represent single-point measurements or are part of e.g. an isotherm, which would provide additional support for their reliability.

III Consistency of data:

While the previous two main criteria address the reliability of each K_d entry in the SDB, criterion No. III requires an examination of the level of support that other K_d values in similar systems can lend to the entry under consideration. Any disagreement with data from related systems will have to be evaluated as well. It

could be argued that this kind of data examination may be left to the user of the SDB. However, the classification of data entries in the JNC-SDB in terms of reliability adds an aspect of quality that is above that for a pure compilation, and users may expect that the listed K_d values passed some kind of check for internal consistency.

Internal consistency means that data from different sources should not be in obvious disagreement. An example would be the dependency on pH of K_d values for a certain radionuclide, which should be approximately similar in all studies. Similarly, if many studies indicate e.g. stronger sorption of U(IV) than of Th(IV), for any study that indicates the opposite an appropriate explanation should be given. If no good reason can be found, such deviations make a study less reliable. These types of considerations will only be possible for sufficiently well researched elements.

Description of checkpoints within each main criterion

General

Each entry in the JNC-SDB (each K_d value identified in the SDB by a unique ID) should be evaluated and classified individually. Because many studies report K_d values under different experimental conditions, it is not sufficient to evaluate all data based on a given reference globally. Depending on conditions, different entries related to a given study may receive a different rating.

I Completeness of documentation and type of K_d information

The checkpoints under I-a are used for a screening prior to a further classification. Failure to satisfy these checkpoints will always result in the lowest rating (unreliable, not to be used).

I-a.1 Are all mandatory fields completed? Here it is only verified that all fields have been completed by the operator; an entry "not reported" is counted, therefore. The following entries are considered mandatory:

- element
- solid phase
- solution composition
- atmosphere composition
- pH (or other information that allows to derive pH, e.g. portlandite equilibrium)
- pe/redox condition (only in case of redox-sensitive systems)

- method of pe control (only in case of redox sensitive systems and imposed reducing conditions)
- initial RN concentration (except for RN that are not solubility controlled)
- method for phase separation (in case of batch experiments)
- type of experiment, if different from batch
- In case of missing entries, the corresponding K_d is excluded from further evaluation and classified as unreliable (until remedied by operator). If all fields are completed, proceed to Ia.2.

I-a.2 Is all mandatory information provided? Here it is evaluated whether critical information is provided or lacking completely. The quality of the information provided is evaluated under criterion II. In addition to the information listed under Ia.1, further mandatory information includes:

- units
- In case of missing mandatory information, the corresponding K_d is excluded from further evaluation and classified as unreliable. If all fields are completed, proceed to Ib.

I-b Does the type of K_d information provided require manipulation by the operator?

→ The following levels are distinguished:

- class 1: table with K_d values given
- class 2: table with % sorbed given
table with residual concentration given
- class 3: linear graph K_d
- class 4: linear graph % sorbed
linear graph residual concentration
- class 5: log graph K_d
- class 6: log graph % sorbed
log graph residual concentration

II Technical and scientific quality of reported data

It is generally assumed that the entries presently contained in the JNC-SDB correspond to a minimum quality standard; i.e. are assumed to be basically reliable. The different checkpoints regarding experimental quality are designed to distinguish different levels of reliability.

However, if in case of critical checkpoints even the requirements leading to the lowest rating are not met, the respective entry should be classified as unreliable (indicated for each checkpoint).

II-a Solid phase (substrate)

It is evaluated whether the solid phase has been sufficiently characterized. This is equally important for properly designing experiments, as well as for using the measured K_d values. In general, three types of key information are required:

- Information about major mineral composition.
- Information about accessory minerals or impurities.
- Information about surface characteristics: Minimum is a measure of sorption capacity per mass of sorbent, such as CEC or a different measure of site density per mass.

However, the amount of information required to sufficiently characterize a given solid phase also depends on the complexity of the substrate:

6. It needs to be known whether a substrate consists of a single pure mineral phase, or whether it contains impurities or additional minerals. In general, some measure of site density per mass (e.g. CEC) needs to be known to properly design experiments, in particular with respect to achieving reasonable surface loading.
7. In case of simple substrates (pure minerals), no further information is necessary.
8. In case of complex substrates (i.e., where significant impurities are present, or where a substrate is composed of several minerals), and in particular in case of natural samples, detailed information on composition has to be provided in addition.
9. In cases where sample treatment (such as crushing or sieving) had been performed, the respective information on particle size also needs to be provided (see II-f). Where any chemical treatments (e.g. acid washing to remove calcite; but also change of redox conditions in case of redox-sensitive substrates, see II-c) had been applied, the applied method and resulting mineralogy should be given as well.
10. In case of many commercially available substrates (e.g., MX-80 or Kunigel-V1 bentonite; standard clay minerals from the Clay Minerals Society, such as SWy-1; Min-U-Sil SiO₂, etc.) detailed solid phase information is widely known and can be retrieved from a large number of publications. Therefore, characterization of such solids is not required for each entry in the SDB; i.e., level A or B can be reached even if such information is not reported. Note that this holds only when such solids have been used as received. Where

washing procedures etc. have been applied, the procedures and resulting changes still need to be documented.

- Three levels of reliability:
- A) Major and minor mineralogy as well as surface characteristics are known. For example: The substrate is a single, well-defined mineral; or comprehensively characterized complex mineral assemblage. Either no sample treatment has been carried out, or it is described in detail and the result are documented.
 - B) Major mineralogy as well as surface characteristics are known. For example: The substrate is a single, well-defined mineral that may contain impurities (such as a non-purified clay mineral) or a complex mineral assemblage where additional impurities could be present. Sample treatment may have led to minor changes in mineralogy.
 - C/D) Information on both major mineralogy and surface characteristics is lacking. For example: There is no information on CEC (or another measure of sorption capacity); or the substrate is a natural clay sample where it is not clear whether it is smectite, kaolinite, or illite; or a non-characterized soil or crushed rock. Sample treatment may have led to major changes in mineralogy that are not documented.

II-b Adjustment and control of pH

One of the most important solution parameters controlling RN sorption is pH. It needs to be known to interpret K_d values, but also for proper experimentation: The pH needs to be known to evaluate the solubility limits of radionuclides and some major ions, as well as the stability of certain mineral phases (in particular carbonates). Further, pH has to be approximately constant during a sorption experiment in order to reach equilibrium of sorption reactions. There are two basically different approaches in sorption experiments with regard to pH control:

3. The pH is not controlled, but allowed to reach an equilibrium value according to the experimental conditions and is then measured at the end of the experiment. In this case, it is important that the pH has been verified after experimentation, in order to know its equilibrium value and to demonstrate that it is not significantly different from the initial value.
4. The pH is controlled during the experiment by acid-base addition and/or buffers. Where it is desired to determine K_d values as a function of pH, this cannot be avoided. In this case, it needs to be shown (or known from the literature) that the added acids, bases, or buffers do not interfere with RN reactions at the surface (which obviously influence sorption) or with RN reactions in solution (which influence sorption through changing the RN speciation). Therefore, use of a non-inert pH buffer at unspecified concentration levels leads to a classification as unreliable.

- Four levels of reliability:
- A) The pH is verified at the end of the experiment and is not significantly different from initial pH (± 0.5 pH units); or the successful use of inert buffers has been demonstrated (e.g. by measuring K_d in the presence and absence of buffers at some pH, or by showing through speciation calculations that the buffer does not influence RN behavior). In some cases, level A may also apply if a non-inert buffer is part of the experimental setup (see the example of K_d determination as a function of carbonate concentration under point C)
 - B) Both initial and final pH are reported, but in both cases only a pH range (within 1 pH unit) is reported instead of a discrete pH value. Initial and final pH ranges do not differ significantly (within 1 to maximum 1.5 pH units). Only the initial pH is provided, but the experimental system is well buffered (for example, because a inert buffer is used, or because of the presence of a natural buffer system, such as carbonate).
 - C) Only the initial pH is provided, no attempt is made to control final pH. All cases where non-inert pH-buffers are being added. Note that this refers to the addition of an additional complexing ligand, such as acetate, for the control of pH. On the other hand, if a sorption experiment is carried out where K_d is measured as a function of carbonate concentration and this is simultaneously used to control pH, level A applies (given that the effect of carbonate on K_d is documented).
 - D) Only a range (within 1 pH unit) of initial pH is provided, no information on final pH is given.
- If a lower quality than required for level D is evident, the respective entry is excluded from further evaluation as unreliable. If a non-inert buffer (e.g. acetate or carbonate) is used at unspecified concentration levels, the entry also has to be classified as unreliable. The same applies if initial and final pH differ by more than 1.5 pH units.

II-c Redox conditions

Here it needs to be differentiated between systems that are not redox-sensitive and systems that are. Within the redox-sensitive systems, it needs to be further taken into account whether only the sorbing RN is redox-sensitive or whether other components of the system (such as solid phase or groundwater components) are redox-sensitive as well.

In this sense, checkpoint II-c deals with the redox control of the sorbing RN, not with redox control of an overall redox-sensitive system. If the experimental system comprises a range of redox-sensitive dissolved (e.g. organics) and solid (e.g. Fe-

and Mn-phases) components, imposing redox conditions different from the original level may influence many redox-equilibria simultaneously. In such a case it can be very difficult to ascertain equilibrium or to know which solid phases are present. Such effects on solution and solid phase chemistry are addressed by checkpoints II-a and II-d. It also needs to be pointed out in this context that "imposed redox condition" does not necessarily refer only to imposing reducing conditions by adding a reducing agent, it also includes imposing oxidizing conditions by e.g. transferring a reduced natural sediment to the laboratory and exposing it to O₂ (as a matter of fact, the latter may be the more common problem).

Given the focus of this checkpoint on redox control of sorbing radionuclides explained above, two different requirements on data quality can be distinguished. Levels of reliability reflect the degree to which these two requirements are met:

3. Reliability regarding control and confirmation of the redox status of the sorbing RN.
4. Reliability regarding the absence of unwanted side effects, such as changes in RN speciation induced by the addition of a reducing agent.

→ Three levels of reliability:

A/B) Level A/B applies to entries in the SDB where it is demonstrated that both of the above requirements are met: This includes the following cases:

- Systems which are not redox-sensitive in terms of sorption and where no reducing agents needed to be added (i.e., where the sorbing RN can take on only one oxidation state in aqueous solutions).
- Redox-sensitive systems that have been pre-equilibrated with and are being kept at ambient conditions.
- Experiments where reducing conditions are imposed on redox-sensitive RN (in otherwise stable systems) and where similar results are obtained using several reducing agents; or where it is otherwise demonstrated that the desired redox conditions are achieved and that the added reducing agent does not interfere with RN sorption.

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C/D) Level C/D applies to entries in the SDB where meeting the above requirements may not have been demonstrated, but can be assumed with high certainty. This includes the following cases:

- Reducing conditions imposed on redox-sensitive RN (in otherwise stable systems) using one reducing agent that is known (e.g. from experience or from the literature) to be effective and to be sufficiently inert with respect to influencing RN behavior.
- In cases where a complexing reducing has been used, level C/D still can be achieved if the influence of the reducing agent on RN speciation has been estimated.

- All cases where it can be assumed that no significant artifacts regarding RN behavior are introduced and where the oxidation state of RNs has been measured independently. The reliability of such measurements will in most cases require a detailed evaluation, depending on the particular RN in question and analytical technique used.
- If a lower quality than required for level C/D is evident, the respective entry is excluded from further evaluation as unreliable. For example, if a strongly complexing reducing agent (such as many organic acids) is used at unspecified concentration levels, the entry has to be classified as unreliable. Further, if there is clear evidence, e.g. from comparisons with more reliable studies (see Criterion III, consistency) that the reported RN oxidation state is erroneous, the entry should be classified as unreliable.

II-d Final solution composition

Note that solution composition includes dissolved carbonate concentration, which may be controlled through, or expressed as $p\text{CO}_2$. Added pH-buffers or reducing agents are also included, and are addressed in checkpoints II-b and II-c.

→ Two levels of reliability:

A/B) The final solution composition is known (either from direct measurements or from the initial experimental setup and speciation calculations) and corresponds to equilibrium or is otherwise well constrained. All major components are included in the analysis. Relevant minor components (e.g. traces of carbonate or another complexing ligand) may be estimated. Some minor components may be unknown. In case of natural water samples, solutions are (or can be) shown to be charge balanced (within 5 %).

C/D) The critical major solution components are known, or are estimated approximately. There may be unknown minor components and/or less critical major components. In case of natural water samples, solutions are approximately charge balanced (within 10 %).

→ If a lower quality than required for level C/D is evident, the respective entry is excluded from further evaluation as unreliable.

II-e Temperature

Here, it is evaluated whether temperature is specified and kept constant.

→ Two levels of reliability:

A/B) Temperature is approximately specified (e.g. room temperature) and constant, or varied in a controlled fashion.

C/D) Temperature is not specified at all (i.e., it is not clear whether the experiments had been performed at room temperature or not).

II-f Solid/water ratio (S/W) and grain size

It is evaluated whether enough solid had been added to avoid a significant influence by the vessel walls (see II-m), and to ensure sample homogeneity in case of complex substrates, especially in case of large grain sizes: It is estimated that in cases where less than ca. 100 mg of solid (this value depends on grain size) has been added to each experimental vessel, sample homogeneity and representativeness becomes difficult to achieve in case of complex or crushed samples.

→ Two levels of reliability:

A/B) Enough solid had been used to assume that

- a) [surface area sorbent] » [surface area vessel], i.e. that at least 5 m³ of sorbent surface had been added to each vessel, and to assume that
- b) samples are homogeneous and representative; i.e. that at least ca. 100 mg (depending on grain size and complexity) of substrate had been added to each vessel.

C/D) Any other than the above.

II-g Sorption value

It is evaluated whether an appropriate experimental design had been employed to avoid sorption values near 0% or 100%, which can lead to higher experimental uncertainty. This problem can be addressed by choosing an appropriate S/W ratio (see II-f) or/and an appropriate initial [RN] (see II-h). However, the choice of [RN] is more restricted by solubility and analytical detection limits.

A) The sorption value is in the range of 5% - 95% sorbed.

B) The sorption value is inside the range of 2% - 98% sorbed.

C/D) Any other than the above.

II-h Initial RN concentration [RN]

This parameter is used to evaluate the likelihood of a possible supersaturation of RN-phases:

→ Three levels of reliability:

- A) RN is not solubility limited, or initial [RN] was clearly (at least a factor of 5) below the solubility limit. Note that factor 5 does not take into account uncertainties in RN solubility; i.e., if the solubility of a given RN cannot be estimated with more certainty than e.g. 10⁻⁶ to 10⁻⁸ M, then initial [RN] has to be $\leq 5 \times 10^{-9}$ M for rating A to apply.

- B) Initial [RN] was clearly below the solubility limit, but maybe less than a factor of 5 (see above).
- C/D) [RN] was very small, and in all likelihood below their maximum solubility, but the solubility limit cannot be established clearly due to missing information (solution composition) or lacking thermodynamic data.
- If initial RN concentration had been clearly above the respective solubility limit, the respective entry is excluded from further evaluation as unreliable.

II-i Phase separation

Here, the appropriateness of phase separation is evaluated: Note that in cases where colloids or other artifacts are important, different phase separation methods will not lead to the same results. Identical or very similar results with different efficient methods are probably the best direct proof of absence of important colloid effects; hence such studies are rated A. Rating B would be given for methods that can be presumed to remove colloids, but where no direct proof as in A is given.

→ Three levels of reliability:

- A) Identical (very similar) results are obtained with different methods of phase separation, where at least one method needs to be efficient in terms of colloids removal (ultrafiltration or high-speed centrifugation). Accordingly, the best comparison would be between two efficient methods, such as ultrafiltration and high-speed centrifugation.

Note that such a comparison of phase separation methods is not required for each individual K_d value: For example: If the absence of artifacts has been demonstrated for some representative samples of a study by comparing an efficient and a standard method of phase separation, the rating A may be given to all datapoints of this study, even if they correspond to the standard method only.

- B) Only one, but efficient method (high-speed centrifugation, ultrafiltration) is used, and there is no evidence for artifacts such as colloid effects or significant sorption to the filter.
- C/D) Only one standard method (normal centrifugation, membrane filtration with nominal pore sizes of 0.01-0.45 μm) is used, and there is no evidence for artifacts such as colloid effects or significant sorption to the filter.
- If no phase separation is used, or in case of obvious evidence for artifacts (colloid effect, adsorption on filter) the data should be labeled as unreliable.

II-j Reaction time

→ Two levels of reliability:

- A/B) Identical (similar) results are obtained with different reaction times, or some other demonstration of near-equilibrium is provided (e.g. separate kinetic experiments).
 - C/D) Only one, but reasonably long reaction time is used. What is “reasonably long” is highly dependent on the experimental system: In general, the time needed to reach equilibrium will increase with the complexity of the sorbing substrate and the strength of sorption. Sorption of Sr onto a pure clay mineral through ion exchange can be assumed to be complete within a day; sorption of a trivalent actinide onto a complex substrate may need several days to weeks for completion. In the absence of kinetic information, operator expert decisions will be required to assess this point. If possible, reaction times reported for similar systems included in the JNC-SDB could be used to evaluate what is reasonably long. Further, even for the most simple systems a reaction time of 1 day is considered as minimum requirement.
- If the requirement for level C/D is not met (i.e., if the reaction time cannot be assumed to be reasonably long), the data should be labeled as unreliable.

II-k Agitation method

- Two levels of reliability:
- A/B) Appropriate agitation is required in all cases, except where enough kinetic information is provided to show that equilibrium has been reached. Shaking is the preferred method, as use of stir bars can lead to abrasion of samples. In case of simple and well crystallized substrates (such as Al-oxide) or of substrates with very small grain size that are easily suspended, stir bars can also be accepted. Other methods of stirring make it difficult to keep out air. (In case of column or diffusion experiments, it has to be shown or must be presumed that the dimensions of the column or diffusion cell are sufficient.)
 - C/D) Agitation has been carried out, but one or more of the above requirements regarding agitation methods is not satisfied.
- If no agitation has been used, the data should be labeled as unreliable (except where enough kinetic information is provided to show that equilibrium has been reached, see level A/B).

II-l RN loading

Ideal are values as a function of RN loading (i.e., K_d values that form part of an isotherm), otherwise low loading is preferred. RN loading (e.g. in moles RN/kg substrate) refers to the amount of RN adsorbed in relation to the amount of different surface sites available. It is known from classical isotherms (e.g. Langmuir) that a linear sorption can only be assumed if sufficient unoccupied sites

are present. In case of simple substrates (including some bentonites), the linear portion of an isotherm extends to fairly high RN loading. There are other cases where K_d depends significantly on RN loading over many orders of RN concentration.

→ Four levels of reliability:

- A) At least one isotherm has been determined (for a constant solution composition and S/W), and at least some experiments have been carried out using trace level RN concentration (i.e., at least some data are included within a linear sorption region).
- B) No isotherm is available, but at least a limited variation of initial [RN] or S/W has been carried out, and some experiments have been carried out using trace level RN concentration (i.e., some data are included within a linear sorption region).
- C/D) No variation as in A or B has been carried out.

II-m Reaction vessels

High-density polyethylene (HDPE) or Teflon are preferred over normal PE, which is preferred over glass, especially at high or very low pH (glass dissolution). On the other hand, glass is more gas-tight (especially than PE); if that is of experimental relevance. Corrections for sorption on vessel walls should not be necessary if blank tests show that it can be neglected.

Correction for sorption on vessel walls may be needed to estimate K_d values correctly in some cases, but only in cases where a) sorption on the vessel is much stronger than on the solid sorbent, or b) if the vessel offers a significant surface area in comparison to the sorbent (see II-f). If that is not the case, the sorption on the added solid will be much greater than on the vessel in a system where both solid and vessel are present. It is further an erroneous assumption that sorption on the vessel will be same in i) the absence of the solid (no competition for RN by solid) as ii) in the presence of the solid (strong competition for RN by solid). The sorption on the walls is typically much smaller in ii) than in i). Therefore, the overall mistake is often bigger if sorption on the vessel wall is accounted for than if it is neglected.

If effects of vessel walls are corrected for, it has to be done by extracting any RN sorbed to vessel walls after experimentation (e.g. by acid washing) and establishing a complete mass balance.

→ Two levels of reliability:

- A) An appropriate vessel has been used (taking into account sorption as well as tightness with respect to CO_2 or O_2 , where required), and corrections for sorption on vessel wall have been performed or no sorption on vessel wall has been observed by blank tests. If effects of vessel walls are corrected for,

it has to be done by extracting any RN sorbed to vessel walls after experimentation (e.g. by acid washing) and establishing a complete mass balance. If the sorption on vessel wall has been determined as significantly lower (at least two orders of magnitude in terms of K_d) than the actual K_d value and thus corrections for sorption on vessel wall have not been performed, such a case would also correspond to level A

- B) An appropriate vessel has been used, and corrections for sorption on vessel walls have not been performed.
- C/D) The vessel used may have been not appropriate, or corrections for sorption on vessel wall have been performed based on a blank test only (i.e., without verifying that sorption on vessel walls is relevant in the presence of a solid added, thus possibly leading to overcorrection).

II-n Uncertainty estimates

In general, uncertainties based on repeated experiments (i.e., actual observations of K_d) are preferred over uncertainties based on error propagation, as the latter is an estimate based on a type of extrapolation. Thus, the difference between levels of reliability is mainly based on the amount of actual information gained by repetitions: For level A, the entire experiment is repeated; for level B, only sampling and analysis are repeated; for C, no repetitions are carried out.

Values that are based on repetitive experiments are preferred over single experimental data points. Note, however, that this checkpoint refers to single-point K_d values and may be overruled by data being part of e.g. pH-edge, isotherm, kinetic experiment, etc., which may provide independent evidence of good reproducibility or systematic errors (see checkpoint II-o).

→ Four levels of reliability:

- A) Uncertainties in K_d are derived based on entire, replicated sorption experiments (i.e., at least duplicate experiments).
- B) Uncertainties in K_d are derived based on single sorption experiments that are sampled and analyzed repeatedly. This may be supplemented by error propagation.
- C) Uncertainties in K_d are based on error propagation of estimated analytical and/or procedural uncertainties.
- D) No error estimate is given, no repeated sampling is done.

II-o Parameter variation

Studies with a systematic variation of key parameters (for example, RN concentration, pH, $p\text{CO}_2$, S/W, grain size in case of crushed substrates) are much more valuable and reliable than single K_d measurements. In particular, variation of

key parameters allows improved detection of experimental problems and systematic errors. Especially the latter are not detected by repeating experiments under identical conditions. In the application of this checkpoint, care has to be taken to take into account the characteristics of the particular system studied. For example, more parameter variation may be required to show clear trends in a complicated system in comparison to a simpler one. On the other hand, the pH and carbonate concentration in experiments with calcite are quite constrained by the solid itself, and only limited variations are possible.

→ Four levels of reliability:

- A) Both RN surface loading (isotherm) as well as a chemical parameter, such as pH or pCO₂ (edge), or e.g. [Na] in case of ion exchange, are varied systematically.
- B) Either RN concentration (isotherm) and/or chemical parameters, such as pH or pCO₂ (edge), or e.g. [Na] in case of ion exchange (i.e., at least two parameters in total), are varied. These variations are less systematic than in A, but still allow to observe trends.
- C) As B, but only one parameter in total is varied.
- D) No parameter variation is done.

III Consistency of data

Here it will be evaluated whether data from a particular study can be supported by other studies. Comparisons should only be made with studies that are at least as (or more) reliable than the study under investigation, based on criteria I and II. In many cases, only approximate consistencies or inconsistencies may be apparent, because of different conditions used in the different studies. To be simple enough and to correspond at the same time to the classifications system used for Criterion II, which uses 6 classes (see Table 1 and Table 2), the following levels are distinguished:

- A) class 1/2 Data are consistent with isotherms or pH-edges etc. from other studies.
 - B) class 3/4 Data are consistent with single K_d values from other studies.
 - C/D) class 5/6 The overall database is not comprehensive enough to allow any clear conclusions as regards consistency.
- If the K_d values under investigation are clearly inconsistent with the majority of related reliable studies, and if the reason for this observation cannot be explained, they may also be labeled unreliable.

Overall classification

The above criteria are applied to an overall classification system as follows:

- The three criteria I-III are evaluated separately, the respective results are reported separately as well.
- Criterion I: The checkpoints under I-a are used in a yes/no screening fashion, entries not fulfilling I-a are labeled as unreliable and are not evaluated further. Criterion I-b is then used to assign classes 1-6 for documentation.
- Criterion II:
 - a) The datasets that pass Criterion I are again classified according to a 6-level system, where classes 1-6 represent the highest and lowest levels of reliability. To ensure a minimum quality level, certain checkpoints are regarded as critical (marked with * in Table 1) If the quality of the data does not correspond to the respective minimum requirements, the entries are not to be used and are classified as unreliable.
 - b) To facilitate transparent averaging of all checkpoints, the following numerical system is suggested: A=3, B=2, C=1, D=0 (A/B=3 and C/D=0 in some cases).
 - c) Weighting of individual checkpoints at this level is done according to the factors given in Table 1 below.

Table 1: Weighting of individual checkpoints under Criterion II.

checkpoint	description	weighting factor
II-a	solid phase (substrate)	$A-C/D \times 2$
* II-b	pH	$A-D \times 8$
* II-c	redox conditions	$A/B-C/D \times 8$
* II-d	final solution composition	$A/B-C/D \times 8$
II-e	temperature	$A/B-C/D \times 1$
II-f	S/W, grain size	$A/B-D/D \times 2$
* II-g	sorption value	$A-C/D \times 2$
* II-h	initial RN concentration	$A-/CD \times 8$
* II-i	phase separation	$A-C/D \times 8$
* II-j	reaction time	$A/B-C/D \times 2$
* II-k	agitation	$A/B-C/D \times 1$
II-l	RN loading	$A-C/D \times 2$
II-m	reaction vessel	$A-C/D \times 1$
II-n	uncertainty estimates	$A-D \times 2$
II-o	parameter variation	$A-D \times 8$

* critical checkpoints with minimum requirements

d) The total sum of points obtained for Criterion II is then used to indicate the level of reliability. With the present system, the maximum number of points would be 183, leading to an overall classification as follows (Table 2):

Table 2: Overall classes of reliability for Criterion II

points	rating
183-151	class 1
150-121	class 2
120-91	class 3
90-61	class 4
60-31	class 5
30-0	class 6

- Criterion III: Criterion III is used to assign classes for consistency with other studies.
- Overall, the following classification system is used, with Criterion II as the main basis for assessing the reliability of entries in the JNC-SDB

Criterion	classification
I-a	accept/reject
I-b	6 classes of Kd information
II	6 classes of data quality and reliability
III	3 levels* of consistency with other studies

* nominally corresponding to 6 classes

Appendix II: Classification of the selected entries of the JNC-SDB based on Revision 3 of the classification guideline.

N.C. = not conclusive, N.E. = not evaluated, m.i. = missing information

Np	Reference	I - Completeness of documentation and type of K_d				II - Technical and scientific quality of reported data																	
		I-a.1	I-a.2	Rating I-a	Rating I-b	checkpoints \Rightarrow level: A-D (numerical value: 3-0) / unreliable Rating II \Rightarrow class 1-6 / unreliable																	
Datapoint	Reference					II.a solid phase	II.b pH	II.c redox conditions	II.d solution composition	II.e temperature	II.f S/W	II.g sorption value											
42375	Allard et al. (1979b)	yes	yes	yes (can be used)	class 1	C/D	0	B	2	A/B	3	C/D	0	A/B	3	C/D	0	A	3				
42376	Allard et al. (1979b)	yes	yes	yes (can be used)	class 1	C/D	0	B	2	A/B	3	C/D	0	A/B	3	C/D	0	A	3				
42377	Allard et al. (1979b)	yes	yes	yes (can be used)	class 1	C/D	0	B	2	A/B	3	C/D	0	A/B	3	C/D	0	A	3				
42378	Allard et al. (1979b)	yes	yes	yes (can be used)	class 1	C/D	0	B	2	A/B	3	C/D	0	A/B	3	C/D	0	A	3				
42379	Allard et al. (1979b)	yes	yes	yes (can be used)	class 1	C/D	0	B	2	A/B	3	C/D	0	A/B	3	C/D	0	A	3				
42380	Allard et al. (1979b)	yes	yes	yes (can be used)	class 1	C/D	0	B	2	A/B	3	C/D	0	A/B	3	C/D	0	A	3				
44587	Barney(1981)	yes	yes	yes (can be used)	class 1	C/D	0	unreliable	A/B	3	C/D	0	A/B	3	A/B	3	A	3					
44588	Barney(1981)	yes	yes	yes (can be used)	class 1	C/D	0	unreliable	A/B	3	C/D	0	A/B	3	A/B	3	A	3					
44589	Barney(1981)	yes	yes	yes (can be used)	class 1	C/D	0	unreliable	A/B	3	C/D	0	A/B	3	A/B	3	A	3					
44590	Barney(1981)	yes	yes	yes (can be used)	class 1	C/D	0	unreliable	A/B	3	C/D	0	A/B	3	A/B	3	A	3					
44591	Barney(1981)	yes	yes	yes (can be used)	class 1	C/D	0	unreliable	A/B	3	C/D	0	A/B	3	A/B	3	A	3					
44592	Barney(1981)	yes	yes	yes (can be used)	class 1	C/D	0	unreliable	A/B	3	C/D	0	A/B	3	A/B	3	A	3					
44593	Barney(1981)	yes	yes	yes (can be used)	class 1	C/D	0	unreliable	A/B	3	C/D	0	A/B	3	A/B	3	A	3					
44594	Barney(1981)	yes	yes	yes (can be used)	class 1	C/D	0	unreliable	A/B	3	C/D	0	A/B	3	A/B	3	A	3					
44595	Barney(1981)	yes	yes	yes (can be used)	class 1	C/D	0	unreliable	A/B	3	C/D	0	A/B	3	A/B	3	A	3					
44596	Barney(1981)	yes	yes	yes (can be used)	class 1	C/D	0	unreliable	C/D	0	C/D	0	A/B	3	A/B	3	A	3					
44597	Barney(1981)	yes	yes	yes (can be used)	class 1	C/D	0	unreliable	A/B	3	C/D	0	A/B	3	A/B	3	A	3					
44598	Barney(1981)	yes	yes	yes (can be used)	class 1	C/D	0	unreliable	C/D	0	C/D	0	A/B	3	A/B	3	A	3					
44599	Barney(1981)	yes	yes	yes (can be used)	class 1	C/D	0	unreliable	C/D	0	C/D	0	A/B	3	A/B	3	A	3					
44600	Barney(1981)	yes	yes	yes (can be used)	class 1	C/D	0	unreliable	C/D	0	C/D	0	A/B	3	A/B	3	A	3					
44601	Barney(1981)	yes	yes	yes (can be used)	class 1	C/D	0	unreliable	C/D	0	C/D	0	A/B	3	A/B	3	A	3					
44602	Barney(1981)	yes	yes	yes (can be used)	class 1	C/D	0	unreliable	C/D	0	C/D	0	A/B	3	A/B	3	A	3					
44603	Barney(1981)	yes	yes	yes (can be used)	class 1	C/D	0	unreliable	C/D	0	C/D	0	A/B	3	A/B	3	A	3					
44604	Barney(1981)	yes	yes	yes (can be used)	class 1	C/D	0	unreliable	C/D	0	C/D	0	A/B	3	A/B	3	A	3					
44605	Barney(1981)	yes	yes	yes (can be used)	class 1	C/D	0	unreliable	C/D	0	C/D	0	A/B	3	A/B	3	A	3					
44606	Barney(1981)	yes	yes	yes (can be used)	class 1	C/D	0	unreliable	C/D	0	C/D	0	A/B	3	A/B	3	A	3					
46820	Baston et al. (1997)	yes	yes	yes (can be used)	class 1	A	3	A	3	C/D	0	A/B	3	A/B	3	A/B	3	C/D	0				
46821	Baston et al. (1997)	yes	yes	yes (can be used)	class 1	A	3	A	3	C/D	0	A/B	3	A/B	3	A/B	3	C/D	0				
46822	Baston et al. (1997)	yes	yes	yes (can be used)	class 1	A	3	A	3	C/D	0	A/B	3	A/B	3	A/B	3	C/D	0				
46823	Baston et al. (1997)	yes	yes	yes (can be used)	class 1	A	3	A	3	C/D	0	A/B	3	A/B	3	A/B	3	C/D	0				
59329	Stammose et al. (1992)	yes	yes	yes (can be used)	class 5	A	3	A	3	A/B	3	C/D	0	A/B	3	A/B	3	A	3				
59330	Stammose et al. (1992)	yes	yes	yes (can be used)	class 5	A	3	A	3	A/B	3	C/D	0	A/B	3	A/B	3	A	3				
59331	Stammose et al. (1992)	yes	yes	yes (can be used)	class 5	A	3	A	3	A/B	3	C/D	0	A/B	3	A/B	3	B	2				
59332	Stammose et al. (1992)	yes	yes	yes (can be used)	class 5	A	3	A	3	A/B	3	C/D	0	A/B	3	A/B	3	A	3				
59333	Stammose et al. (1992)	yes	yes	yes (can be used)	class 5	A	3	A	3	A/B	3	C/D	0	A/B	3	A/B	3	A	3				
59334	Stammose et al. (1992)	yes	yes	yes (can be used)	class 5	A	3	A	3	A/B	3	C/D	0	A/B	3	A/B	3	A	3				
59335	Stammose et al. (1992)	yes	yes	yes (can be used)	class 5	A	3	A	3	A/B	3	C/D	0	A/B	3	A/B	3	A	3				
59336	Stammose et al. (1992)	yes	yes	yes (can be used)	class 5	A	3	A	3	A/B	3	C/D	0	A/B	3	A/B	3	A	3				
59337	Stammose et al. (1992)	yes	yes	yes (can be used)	class 5	A	3	A	3	A/B	3	C/D	0	A/B	3	A/B	3	A	3				
59338	Stammose et al. (1992)	yes	yes	yes (can be used)	class 5	A	3	A	3	A/B	3	C/D	0	A/B	3	A/B	3	A	3				
59339	Stammose et al. (1992)	yes	yes	yes (can be used)	class 5	A	3	A	3	A/B	3	C/D	0	A/B	3	A/B	3	A	3				
59340	Stammose et al. (1992)	yes	yes	yes (can be used)	class 5	A	3	A	3	A/B	3	C/D	0	A/B	3	A/B	3	A	3				
59341	Stammose et al. (1992)	yes	yes	yes (can be used)	class 5	A	3	A	3	A/B	3	C/D	0	A/B	3	A/B	3	A	3				
59342	Stammose et al. (1992)	yes	yes	yes (can be used)	class 5	A	3	A	3	A/B	3	C/D	0	A/B	3	A/B	3	A	3				
59343	Stammose et al. (1992)	yes	yes	yes (can be used)	class 5	A	3	A	3	A/B	3	C/D	0	A/B	3	A/B	3	A	3				
59344	Stammose et al. (1992)	yes	yes	yes (can be used)	class 5	A	3	A	3	A/B	3	C/D	0	A/B	3	A/B	3	A	3				
59345	Stammose et al. (1992)	yes	yes	yes (can be used)	class 5	A	3	A	3	A/B	3	C/D	0	A/B	3	A/B	3	A	3				
59346	Stammose et al. (1992)	yes	yes	yes (can be used)	class 5	A	3	A	3	A/B	3	C/D	0	A/B	3	A/B	3	A	3				
59347	Stammose et al. (1992)	yes	yes	yes (can be used)	class 5	A	3	A	3	A/B	3	C/D	0	A/B	3	A/B	3	A	3				
59348	Stammose et al. (1992)	yes	yes	yes (can be used)	class 5	A	3	A	3	A/B	3	C/D	0	A/B	3	A/B	3	A	3				
59349	Stammose et al. (1992)	yes	yes	yes (can be used)	class 5	A	3	A	3	A/B	3	C/D	0	A/B	3	A/B	3	A	3				
59350	Stammose et al. (1992)	yes	yes	yes (can be used)	class 5	A	3	A	3	A/B	3	C/D	0	A/B	3	A/B	3	A	3				
59351	Stammose et al. (1992)	yes	yes	yes (can be used)	class 5	A	3	A	3	A/B	3	C/D	0	A/B	3	A/B	3	A	3				
59352	Stammose et al. (1992)	yes	yes	yes (can be used)	class 5	A	3	A	3	A/B	3	C/D	0	A/B	3	A/B	3	A	3				
59353	Stammose et al. (1992)	yes	yes	yes (can be used)	class 5	A	3	A	3	A/B	3	C/D	0	A/B	3	A/B	3	A	3				
59354	Stammose et al. (1992)	yes	yes	yes (can be used)	class 5	A	3	A	3	A/B	3	C/D	0	A/B	3	A/B	3	A	3				
59355	Stammose et al. (1992)	yes	yes	yes (can be used)	class 5	A	3	A	3	A/B	3	C/D	0	A/B	3	A/B	3	B	2				
59356	Stammose et al. (1992)	yes	yes	yes (can be used)	class 5	A	3	A	3	A/B	3	C/D	0	A/B	3	A/B	3	A	3				
59357	Stammose et al. (1992)	yes	yes	yes (can be used)	class 5	A	3	A	3	A/B	3	C/D	0	A/B	3	A/B	3	A	3				
59358	Stammose et al. (1992)	yes	yes	yes (can be used)	class 5	A	3	A	3	A/B	3	C/D	0	A/B	3	A/B	3	B	2				

Appendix II, cont.

Np	II - Technical and scientific quality of reported data														III - Consistency		comment/rating		
	Checkpoints P level: A-D (numerical value: 3-0) / unreliable Rating II P class 1-6 / unreliable														total value	class			
	Datapoint	II.h initial [RN]	II.i phase separation	II.j reaction time	II.k agitation	II.l RN loading	II.m reaction vessels	II.n error estimates	II.o parameter variation	Rating II									
42375	A	3	C/D	0	A/B	3	A/B	3	C/D	0	C/D	0	D	0	C	1	90	class 4	consistent with solid used
42376	A	3	C/D	0	A/B	3	A/B	3	C/D	0	C/D	0	D	0	C	1	90	class 4	consistent with solid used
42377	A	3	C/D	0	A/B	3	A/B	3	C/D	0	C/D	0	D	0	C	1	90	class 4	consistent with solid used
42378	A	3	C/D	0	A/B	3	A/B	3	C/D	0	C/D	0	D	0	C	1	90	class 4	consistent with solid used
42379	A	3	C/D	0	A/B	3	A/B	3	C/D	0	C/D	0	D	0	C	1	90	class 4	consistent with solid used
42380	A	3	C/D	0	A/B	3	A/B	3	C/D	0	C/D	0	D	0	C	1	90	class 4	consistent with solid used
44587	A	3	B	2	A/B	3	A/B	3	C/D	0	B	2	D	0	D	0		unreliable	
44588	A	3	B	2	A/B	3	A/B	3	C/D	0	B	2	D	0	D	0		unreliable	
44589	A	3	B	2	A/B	3	A/B	3	C/D	0	B	2	D	0	D	0		unreliable	
44590	A	3	B	2	A/B	3	A/B	3	C/D	0	B	2	D	0	D	0		unreliable	
44591	A	3	B	2	A/B	3	A/B	3	C/D	0	B	2	D	0	D	0		unreliable	
44592	A	3	B	2	A/B	3	A/B	3	C/D	0	B	2	D	0	D	0		unreliable	
44593	A	3	B	2	A/B	3	A/B	3	C/D	0	B	2	D	0	D	0		unreliable	
44594	A	3	B	2	A/B	3	A/B	3	C/D	0	B	2	D	0	D	0		unreliable	
44595	A	3	B	2	A/B	3	A/B	3	C/D	0	B	2	D	0	D	0		unreliable	
44596	unreliable		B	2	A/B	3	A/B	3	C/D	0	B	2	D	0	D	0		unreliable	
44597	A	3	B	2	A/B	3	A/B	3	C/D	0	B	2	D	0	D	0		unreliable	
44598	unreliable		B	2	A/B	3	A/B	3	C/D	0	B	2	D	0	D	0		unreliable	
44599	unreliable		B	2	A/B	3	A/B	3	C/D	0	B	2	D	0	D	0		unreliable	
44600	unreliable		B	2	A/B	3	A/B	3	C/D	0	B	2	D	0	D	0		unreliable	
44601	unreliable		B	2	A/B	3	A/B	3	C/D	0	B	2	D	0	D	0		unreliable	
44602	unreliable		B	2	A/B	3	A/B	3	C/D	0	B	2	D	0	D	0		unreliable	
44603	unreliable		B	2	A/B	3	A/B	3	C/D	0	B	2	D	0	D	0		unreliable	
44604	unreliable		B	2	A/B	3	A/B	3	C/D	0	B	2	D	0	D	0		unreliable	
44605	unreliable		B	2	A/B	3	A/B	3	C/D	0	B	2	D	0	D	0		unreliable	
44606	unreliable		B	2	A/B	3	A/B	3	C/D	0	B	2	D	0	D	0		unreliable	
46820	C/D	0	A	3	C/D	0	A/B	3	C/D	0	A	3	C	1	C	1	103	class 3	inconsistent with Th, not conclusive
46821	C/D	0	A	3	C/D	0	A/B	3	C/D	0	A	3	C	1	C	1	103	class 3	inconsistent with Th, not conclusive
46822	C/D	0	A	3	C/D	0	A/B	3	C/D	0	A	3	C	1	C	1	103	class 3	inconsistent with Th, not conclusive
46823	C/D	0	A	3	C/D	0	A/B	3	C/D	0	A	3	C	1	C	1	103	class 3	inconsistent with Th, not conclusive
59329	A	3	B	2	A/B	3	A/B	3	C/D	0	C/D	0	D	0	B	2	134	class 2	agrees well with other studies
59330	A	3	B	2	A/B	3	A/B	3	C/D	0	C/D	0	D	0	B	2	134	class 2	agrees well with other studies
59331	A	3	B	2	A/B	3	A/B	3	C/D	0	C/D	0	D	0	B	2	132	class 2	agrees well with other studies
59332	A	3	B	2	A/B	3	A/B	3	C/D	0	C/D	0	D	0	B	2	134	class 2	agrees well with other studies
59333	A	3	B	2	A/B	3	A/B	3	C/D	0	C/D	0	D	0	B	2	134	class 2	agrees well with other studies
59334	A	3	B	2	A/B	3	A/B	3	C/D	0	C/D	0	D	0	B	2	134	class 2	agrees well with other studies
59335	A	3	B	2	A/B	3	A/B	3	C/D	0	C/D	0	D	0	B	2	134	class 2	agrees well with other studies
59336	A	3	B	2	A/B	3	A/B	3	C/D	0	C/D	0	D	0	B	2	134	class 2	agrees well with other studies
59337	A	3	B	2	A/B	3	A/B	3	C/D	0	C/D	0	D	0	B	2	134	class 2	agrees well with other studies
59338	A	3	B	2	A/B	3	A/B	3	C/D	0	C/D	0	D	0	B	2	134	class 2	agrees well with other studies
59339	A	3	B	2	A/B	3	A/B	3	C/D	0	C/D	0	D	0	B	2	134	class 2	agrees well with other studies
59340	A	3	B	2	A/B	3	A/B	3	C/D	0	C/D	0	D	0	B	2	134	class 2	agrees well with other studies
59341	A	3	B	2	A/B	3	A/B	3	C/D	0	C/D	0	D	0	B	2	134	class 2	agrees well with other studies
59342	A	3	B	2	A/B	3	A/B	3	C/D	0	C/D	0	D	0	B	2	134	class 2	agrees well with other studies
59343	A	3	B	2	A/B	3	A/B	3	C/D	0	C/D	0	D	0	B	2	134	class 2	agrees well with other studies
59344	A	3	B	2	A/B	3	A/B	3	C/D	0	C/D	0	D	0	B	2	134	class 2	agrees well with other studies
59345	A	3	B	2	A/B	3	A/B	3	C/D	0	C/D	0	D	0	B	2	134	class 2	agrees well with other studies
59346	A	3	B	2	A/B	3	A/B	3	C/D	0	C/D	0	D	0	B	2	134	class 2	agrees well with other studies
59347	A	3	B	2	A/B	3	A/B	3	C/D	0	C/D	0	D	0	B	2	134	class 2	agrees well with other studies
59348	A	3	B	2	A/B	3	A/B	3	C/D	0	C/D	0	D	0	B	2	134	class 2	agrees well with other studies
59349	A	3	B	2	A/B	3	A/B	3	C/D	0	C/D	0	D	0	B	2	134	class 2	agrees well with other studies
59350	A	3	B	2	A/B	3	A/B	3	C/D	0	C/D	0	D	0	B	2	134	class 2	agrees well with other studies
59351	A	3	B	2	A/B	3	A/B	3	C/D	0	C/D	0	D	0	B	2	134	class 2	agrees well with other studies
59352	A	3	B	2	A/B	3	A/B	3	C/D	0	C/D	0	D	0	B	2	134	class 2	agrees well with other studies
59353	A	3	B	2	A/B	3	A/B	3	C/D	0	C/D	0	D	0	B	2	134	class 2	agrees well with other studies
59354	A	3	B	2	A/B	3	A/B	3	C/D	0	C/D	0	D	0	B	2	134	class 2	agrees well with other studies
59355	A	3	B	2	A/B	3	A/B	3	C/D	0	C/D	0	D	0	B	2	132	class 2	agrees well with other studies
59356	A	3	B	2	A/B	3	A/B	3	C/D	0	C/D	0	D	0	B	2	134	class 2	agrees well with other studies
59357	A	3	B	2	A/B	3	A/B	3	C/D	0	C/D	0	D	0	B	2	134	class 2	agrees well with other studies
59358	A	3	B	2	A/B	3	A/B	3	C/D	0	C/D	0	D	0	B	2	132	class 2	agrees well with other studies

Appendix II, cont.

Np	II - Technical and scientific quality of reported data										III - Consistency		comment/rating					
	Checkpoints P level: A-D (numerical value: 3-0) / unreliable Rating II P class 1-6 / unreliable										total value	class						
Datapoint	II.h initial [RN]	II.i phase separation	II.j reaction time	II.k agitation	II.l RN loading	II.m reaction vessels	II.n error estimates	II.o parameter variation	Rating II									
60812	B	2	C/D	0	C/D	0	C/D	0	B	2	A	3	D	0	80	class 4	basically consistent with other data for Np(V)	
60813	A	3	C/D	0	C/D	0	C/D	0	B	2	A	3	D	0	88	class 4	basically consistent with other data for Np(V)	
60814	A	3	C/D	0	C/D	0	C/D	0	B	2	A	3	D	0	88	class 4	basically consistent with other data for Np(V)	
60815	B	2	C/D	0	C/D	0	C/D	0	B	2	A	3	D	0	80	class 4	basically consistent with other data for Np(V)	
60816	A	3	C/D	0	C/D	0	C/D	0	B	2	A	3	D	0	88	class 4	basically consistent with other data for Np(V)	
60817	B	2	C/D	0	C/D	0	C/D	0	B	2	A	3	D	0	78	class 4	basically consistent with other data for Np(V)	
60818	A	3	C/D	0	C/D	0	C/D	0	B	2	A	3	D	0	88	class 4	basically consistent with other data for Np(V)	
60819	A	3	C/D	0	C/D	0	C/D	0	B	2	A	3	D	0	88	class 4	basically consistent with other data for Np(V)	
60820	B	2	C/D	0	C/D	0	C/D	0	B	2	A	3	D	0	80	class 4	basically consistent with other data for Np(V)	
60821	B	2	C/D	0	C/D	0	C/D	0	B	2	A	3	D	0	80	class 4	basically consistent with other data for Np(V)	
60822	A	3	C/D	0	C/D	0	C/D	0	B	2	A	3	D	0	88	class 4	basically consistent with other data for Np(V)	
60823	B	2	C/D	0	C/D	0	C/D	0	B	2	A	3	D	0	80	class 4	basically consistent with other data for Np(V)	
62194	A	3	B	2	C/D	0	C/D	0	B	2	B	2	D	0	125	class 2	basically consistent with other data for Np(V)	
62195	A	3	B	2	C/D	0	C/D	0	B	2	B	2	D	0	125	class 2	basically consistent with other data for Np(V)	
62196	A	3	B	2	C/D	0	C/D	0	B	2	B	2	D	0	125	class 2	basically consistent with other data for Np(V)	
62197	A	3	B	2	C/D	0	C/D	0	B	2	B	2	D	0	125	class 2	basically consistent with other data for Np(V)	
62198	A	3	B	2	C/D	0	C/D	0	B	2	B	2	D	0	125	class 2	basically consistent with other data for Np(V)	
62199	A	3	B	2	C/D	0	C/D	0	B	2	B	2	D	0	125	class 2	basically consistent with other data for Np(V)	
62200	A	3	B	2	C/D	0	C/D	0	B	2	B	2	D	0	125	class 2	basically consistent with other data for Np(V)	
62201	A	3	B	2	C/D	0	C/D	0	B	2	B	2	D	0	125	class 2	not conclusive	
62202	A	3	B	2	C/D	0	C/D	0	B	2	B	2	D	0	125	class 2	not conclusive	
62203	A	3	B	2	C/D	0	C/D	0	B	2	B	2	D	0	125	class 2	not conclusive	
62204	A	3	B	2	C/D	0	C/D	0	B	2	B	2	D	0	125	class 2	not conclusive	
62205	A	3	B	2	C/D	0	C/D	0	B	2	B	2	D	0	125	class 2	not conclusive	
62206	A	3	B	2	C/D	0	C/D	0	B	2	B	2	D	0	125	class 2	not conclusive	
62207	A	3	B	2	C/D	0	C/D	0	B	2	B	2	D	0	125	class 2	not conclusive	
62208	A	3	B	2	C/D	0	C/D	0	B	2	B	2	D	0	125	class 2	not conclusive	
62209	A	3	B	2	C/D	0	C/D	0	B	2	B	2	D	0	123	class 2	not conclusive	
62210	B	2	B	2	C/D	0	C/D	0	B	2	B	2	D	0	111	class 3	basically consistent with other data for Np(V)	
62211	B	2	B	2	C/D	0	C/D	0	B	2	B	2	D	0	111	class 3	basically consistent with other data for Np(V)	
62212	unreliable	B	2	C/D	0	C/D	0	B	2	B	2	D	0	B	2	unreliable		
62213	unreliable	B	2	C/D	0	C/D	0	B	2	B	2	D	0	B	2	unreliable		
62214	unreliable	B	2	C/D	0	C/D	0	B	2	B	2	D	0	B	2	unreliable		
62215	unreliable	B	2	C/D	0	C/D	0	B	2	B	2	D	0	B	2	unreliable		
62216	unreliable	B	2	C/D	0	C/D	0	B	2	B	2	D	0	B	2	unreliable		
62217	B	2	B	2	C/D	0	C/D	0	B	2	B	2	D	0	111	class 3	basically consistent with other data for Np(V)	
62218	B	2	B	2	C/D	0	C/D	0	B	2	B	2	D	0	111	class 3	basically consistent with other data for Np(V)	
62219	B	2	B	2	C/D	0	C/D	0	B	2	B	2	D	0	115	class 3	basically consistent with other data for Np(V)	
62220	B	2	B	2	C/D	0	C/D	0	B	2	B	2	D	0	115	class 3	basically consistent with other data for Np(V)	
62221	B	2	B	2	C/D	0	C/D	0	B	2	B	2	D	0	115	class 3	basically consistent with other data for Np(V)	
62222	B	2	B	2	C/D	0	C/D	0	B	2	B	2	D	0	115	class 3	basically consistent with other data for Np(V)	
62868	B	2	B	2	unreliable	A/B	3	C/D	0	A	3	A	3	C	1	unreliable		
62869	B	2	B	2	unreliable	A/B	3	C/D	0	A	3	A	3	C	1	unreliable		
62870	B	2	B	2	unreliable	A/B	3	C/D	0	A	3	A	3	C	1	unreliable		
62871	B	2	B	2	unreliable	A/B	3	C/D	0	A	3	A	3	C	1	unreliable		
62872	B	2	B	2	unreliable	A/B	3	C/D	0	A	3	A	3	C	1	unreliable		
62873	B	2	B	2	unreliable	A/B	3	C/D	0	A	3	A	3	C	1	unreliable		
62874	B	2	B	2	unreliable	A/B	3	C/D	0	A	3	A	3	C	1	unreliable		
62875	B	2	B	2	unreliable	A/B	3	C/D	0	A	3	A	3	C	1	unreliable		
62876	B	2	B	2	A/B	3	A/B	3	C/D	0	A	3	A	3	C	1	N.E.	N.E.
62877	B	2	B	2	A/B	3	A/B	3	C/D	0	A	3	A	3	C	1	N.E.	N.E.
62878	B	2	B	2	A/B	3	A/B	3	C/D	0	A	3	A	3	C	1	N.E.	N.E.
62879	B	2	B	2	A/B	3	A/B	3	C/D	0	A	3	A	3	C	1	N.E.	N.E.
62880	B	2	B	2	A/B	3	A/B	3	C/D	0	A	3	A	3	C	1	N.E.	N.E.
62881	B	2	B	2	A/B	3	A/B	3	C/D	0	A	3	A	3	C	1	N.E.	N.E.
62882	B	2	B	2	A/B	3	A/B	3	C/D	0	A	3	A	3	C	1	N.E.	N.E.
62883	B	2	B	2	A/B	3	A/B	3	C/D	0	A	3	A	3	C	1	N.E.	N.E.
62884	B	2	B	2	A/B	3	A/B	3	C/D	0	A	3	A	3	C	1	N.E.	N.E.
62885	B	2	B	2	A/B	3	A/B	3	C/D	0	A	3	A	3	C	1	N.E.	N.E.
62886	B	2	B	2	A/B	3	A/B	3	C/D	0	A	3	A	3	C	1	N.E.	N.E.
62887	B	2	B	2	A/B	3	A/B	3	C/D	0	A	3	A	3	C	1	N.E.	N.E.
62888	B	2	B	2	A/B	3	A/B	3	C/D	0	A	3	A	3	C	1	N.E.	N.E.
62889	B	2	B	2	A/B	3	A/B	3	C/D	0	A	3	A	3	C	1	N.E.	N.E.
62890	B	2	B	2	A/B	3	A/B	3	C/D	0	A	3	A	3	C	1	N.E.	N.E.

Appendix II, cont.

Pu		I - Completeness of documentation and type of K_d				II - Technical and scientific quality of reported data														
		Rating \Rightarrow I-a: yes/no, I-b: class 1-6				Checkpoints \Rightarrow level: A-D (numerical value: 3-0) / unreliable Rating II \Rightarrow class 1-6 / unreliable														
Datapoint	Reference	I-a.1	I-a.2	Rating I-a	Rating I-b	II.a solid phase	II.b pH	II.c redox conditions	II.d solution composition	II.e temperature	II.f S/W	II.g sorption value								
42536	Allard et al.(1982)	yes	yes	yes (can be used)	class 1	A	3	A	3	unreliable	C/D	0	A/B	3	A/B	3	B	2		
42537	Allard et al.(1982)	yes	yes	yes (can be used)	class 1	A	3	A	3	unreliable	C/D	0	A/B	3	A/B	3	B	2		
44647	Barney(1981)	yes	yes	yes (can be used)	class 1	B	2	unreliable	C/D	0	C/D	0	A/B	3	A/B	3	A	3		
44650	Barney(1981)	yes	yes	yes (can be used)	class 1	B	2	unreliable	C/D	0	C/D	0	A/B	3	A/B	3	C/D	0		
44652	Barney(1981)	yes	yes	yes (can be used)	class 1	B	2	unreliable	C/D	0	C/D	0	A/B	3	A/B	3	C/D	0		
44654	Barney(1981)	yes	yes	yes (can be used)	class 1	B	2	unreliable	C/D	0	C/D	0	A/B	3	A/B	3	C/D	0		
44659	Barney(1981)	yes	yes	yes (can be used)	class 1	B	2	unreliable	C/D	0	C/D	0	A/B	3	A/B	3	C/D	0		
44660	Barney(1981)	yes	yes	yes (can be used)	class 1	B	2	unreliable	C/D	0	C/D	0	A/B	3	A/B	3	C/D	0		
44663	Barney(1981)	yes	yes	yes (can be used)	class 1	B	2	unreliable	C/D	0	C/D	0	A/B	3	A/B	3	C/D	0		
44664	Barney(1981)	yes	yes	yes (can be used)	class 1	B	2	unreliable	C/D	0	C/D	0	A/B	3	A/B	3	C/D	0		
44665	Barney(1981)	yes	yes	yes (can be used)	class 1	B	2	unreliable	C/D	0	C/D	0	A/B	3	A/B	3	C/D	0		
44666	Barney(1981)	yes	yes	yes (can be used)	class 1	B	2	unreliable	C/D	0	C/D	0	A/B	3	A/B	3	C/D	0		
44648	Barney(1981)	yes	yes	yes (can be used)	class 1	B	2	unreliable	N.C.*		C/D	0	A/B	3	A/B	3	A	3		
44649	Barney(1981)	yes	yes	yes (can be used)	class 1	B	2	unreliable	N.C.*		C/D	0	A/B	3	A/B	3	B	2		
44651	Barney(1981)	yes	yes	yes (can be used)	class 1	B	2	unreliable	N.C.*		C/D	0	A/B	3	A/B	3	C/D	0		
44653	Barney(1981)	yes	yes	yes (can be used)	class 1	B	2	unreliable	N.C.*		C/D	0	A/B	3	A/B	3	C/D	0		
44655	Barney(1981)	yes	yes	yes (can be used)	class 1	B	2	unreliable	N.C.*		C/D	0	A/B	3	A/B	3	C/D	0		
44656	Barney(1981)	yes	yes	yes (can be used)	class 1	B	2	unreliable	N.C.*		C/D	0	A/B	3	A/B	3	C/D	0		
44657	Barney(1981)	yes	yes	yes (can be used)	class 1	B	2	unreliable	N.C.*		C/D	0	A/B	3	A/B	3	C/D	0		
44658	Barney(1981)	yes	yes	yes (can be used)	class 1	B	2	unreliable	N.C.*		C/D	0	A/B	3	A/B	3	C/D	0		
44661	Barney(1981)	yes	yes	yes (can be used)	class 1	B	2	unreliable	N.C.*		C/D	0	A/B	3	A/B	3	C/D	0		
44662	Barney(1981)	yes	yes	yes (can be used)	class 1	B	2	unreliable	N.C.*		C/D	0	A/B	3	A/B	3	C/D	0		
48874	Billon(1982)	yes	no	no (can not be used)																
48875	Billon(1982)	yes	no	no (can not be used)																
48876	Billon(1982)	yes	no	no (can not be used)																
48877	Billon(1982)	yes	yes	yes (can be used)	class 1	B	2	A	3	A/B	3	unreliable	A/B	3	C/D	0	A	3		
48878	Billon(1982)	yes	yes	yes (can be used)	class 1	B	2	A	3	A/B	3	unreliable	A/B	3	C/D	0	A	3		
48879	Billon(1982)	yes	yes	yes (can be used)	class 1	B	2	A	3	A/B	3	unreliable	A/B	3	C/D	0	B	2		
48880	Billon(1982)	yes	yes	yes (can be used)	class 1	B	2	A	3	A/B	3	unreliable	A/B	3	C/D	0	C/D	0		
59026	Sharma and Oscarson(1989)	yes	yes	yes (can be used)	class 1	B	2	A	3	C/D	0	unreliable	A/B	3	C/D	0	C/D	0		
59256	Shibutani et al.(1998)	yes	yes	yes (can be used)	class 5	A	3	A	3	C/D	0	C/D	0	A/B	3	A/B	3	B	2	
59257	Shibutani et al.(1998)	yes	yes	yes (can be used)	class 5	A	3	A	3	C/D	0	C/D	0	A/B	3	A/B	3	A	3	
59258	Shibutani et al.(1998)	yes	yes	yes (can be used)	class 5	A	3	A	3	C/D	0	C/D	0	A/B	3	A/B	3	A	3	
59259	Shibutani et al.(1998)	yes	yes	yes (can be used)	class 5	A	3	A	3	C/D	0	C/D	0	A/B	3	A/B	3	B	2	
59260	Shibutani et al.(1998)	yes	yes	yes (can be used)	class 5	A	3	A	3	C/D	0	C/D	0	A/B	3	A/B	3	C/D	0	
59261	Shibutani et al.(1998)	yes	yes	yes (can be used)	class 5	A	3	A	3	C/D	0	C/D	0	A/B	3	A/B	3	C/D	0	
59262	Shibutani et al.(1998)	yes	yes	yes (can be used)	class 5	A	3	A	3	C/D	0	C/D	0	A/B	3	A/B	3	C/D	0	
59263	Shibutani et al.(1998)	yes	yes	yes (can be used)	class 5	A	3	A	3	C/D	0	C/D	0	A/B	3	A/B	3	C/D	0	
59264	Shibutani et al.(1998)	yes	yes	yes (can be used)	class 5	A	3	A	3	C/D	0	C/D	0	A/B	3	A/B	3	C/D	0	
59265	Shibutani et al.(1998)	yes	yes	yes (can be used)	class 5	A	3	A	3	C/D	0	C/D	0	A/B	3	A/B	3	C/D	0	
59266	Shibutani et al.(1998)	yes	yes	yes (can be used)	class 5	A	3	A	3	C/D	0	C/D	0	A/B	3	A/B	3	C/D	0	
59267	Shibutani et al.(1998)	yes	yes	yes (can be used)	class 5	A	3	A	3	C/D	0	C/D	0	A/B	3	A/B	3	A	3	
59268	Shibutani et al.(1998)	yes	yes	yes (can be used)	class 5	A	3	A	3	C/D	0	C/D	0	A/B	3	A/B	3	C/D	0	
59269	Shibutani et al.(1998)	yes	yes	yes (can be used)	class 5	A	3	A	3	C/D	0	C/D	0	A/B	3	A/B	3	C/D	0	
59270	Shibutani et al.(1998)	yes	yes	yes (can be used)	class 5	A	3	A	3	C/D	0	C/D	0	A/B	3	A/B	3	C/D	0	
59271	Shibutani et al.(1998)	yes	yes	yes (can be used)	class 5	A	3	A	3	C/D	0	C/D	0	A/B	3	A/B	3	C/D	0	
59272	Shibutani et al.(1998)	yes	yes	yes (can be used)	class 5	A	3	A	3	C/D	0	C/D	0	A/B	3	A/B	3	A	3	
59273	Shibutani et al.(1998)	yes	yes	yes (can be used)	class 5	A	3	A	3	C/D	0	C/D	0	A/B	3	A/B	3	C/D	0	
58937	Sato and Shibutani(1994)	yes	yes	yes (can be used)	class 5	A	3	A	3	unreliable	C/D	0	A/B	3	C/D	0	B	2		
58938	Sato and Shibutani(1994)	yes	yes	yes (can be used)	class 5	A	3	A	3	unreliable	C/D	0	A/B	3	C/D	0	A	3		
58939	Sato and Shibutani(1994)	yes	yes	yes (can be used)	class 5	A	3	A	3	unreliable	C/D	0	A/B	3	C/D	0	A	3		
58940	Sato and Shibutani(1994)	yes	yes	yes (can be used)	class 5	A	3	A	3	unreliable	C/D	0	A/B	3	C/D	0	B	2		
58941	Sato and Shibutani(1994)	yes	yes	yes (can be used)	class 5	A	3	A	3	unreliable	C/D	0	A/B	3	C/D	0	B	2		
58942	Sato and Shibutani(1994)	yes	yes	yes (can be used)	class 5	A	3	A	3	unreliable	C/D	0	A/B	3	C/D	0	A	3		
58943	Sato and Shibutani(1994)	yes	yes	yes (can be used)	class 5	A	3	A	3	unreliable	C/D	0	A/B	3	C/D	0	A	3		
58944	Sato and Shibutani(1994)	yes	yes	yes (can be used)	class 5	A	3	A	3	unreliable	C/D	0	A/B	3	C/D	0	C/D	0		
58945	Sato and Shibutani(1994)	yes	yes	yes (can be used)	class 5	A	3	A	3	unreliable	C/D	0	A/B	3	C/D	0	C/D	0		
58946	Sato and Shibutani(1994)	yes	yes	yes (can be used)	class 5	A	3	A	3	unreliable	C/D	0	A/B	3	C/D	0	C/D	0		
58947	Sato and Shibutani(1994)	yes	yes	yes (can be used)	class 5	A	3	A	3	unreliable	C/D	0	A/B	3	C/D	0	A	3		
58948	Sato and Shibutani(1994)	yes	yes	yes (can be used)	class 5	A	3	A	3	unreliable	C/D	0	A/B	3	C/D	0	A	3		
60872	Ticknor(1993)	yes	yes	yes (can be used)	class 1	B	2	B	2	unreliable	C/D	0	C/D	0	A/B	3	C/D	0		
60873	Ticknor(1993)	yes	yes	yes (can be used)	class 1	B	2	B	2	unreliable	C/D	0	C/D	0	A/B	3	C/D	0		
60874	Ticknor(1993)	yes	yes	yes (can be used)	class 1	B	2	B	2	A/B	3	C/D	0	C/D	0	A/B	3	C/D	0	
60875	Ticknor(1993)	yes	yes	yes (can be used)	class 1	B	2	B	2	unreliable	C/D	0	C/D	0	A/B	3	C/D	0		
60876	Ticknor(1993)	yes	yes	yes (can be used)	class 1	B	2	B	2	A/B	3	C/D	0	C/D	0	A/B	3	C/D	0	
60877	Ticknor(1993)	yes	yes	yes (can be used)	class 1	B	2	B	2	A/B	3	C/D	0	C/D	0	A/B	3	C/D	0	
60878	Ticknor(1993)	yes	yes	yes (can be used)	class 1	B	2	B	2	A/B	3	C/D	0	C/D	0	A/B	3	C/D	0	
60879	Ticknor(1993)	yes	yes	yes (can be used)	class 1	B	2	B	2	unreliable	C/D	0	C/D	0	A/B	3	C/D	0		
60880	Ticknor(1993)	yes	yes	yes (can be used)	class 1	B	2	B	2	A/B	3	C/D	0	C/D	0	A/B	3	B	2	
60881	Ticknor(1993)	yes	yes	yes (can be used)	class 1	B	2	B	2	unreliable	C/D	0	C/D	0	A/B	3	C/D	0		
60882	Ticknor(1993)	yes	yes	yes (can be used)	class 1	B	2	B	2	A/B	3	C/D	0	C/D	0	A/B	3	C/D	0	
60883	Ticknor(1993)	yes	yes	yes (can be used)	class 1	B	2	B	2	unreliable										

Appendix II, cont.

Pu	II - Technical and scientific quality of reported data														III - Consistency				
	Checkpoints ⇒ level: A-D (numerical value: 3-0) / unreliable Rating II ⇒ class 1-6 / unreliable																		
Datapoint	II.h initial [RN]		II.i phase separation		II.j reaction time		II.k agitation		II.l RN loading		II.m reaction vessels		II.n error estimates		II.o parameter variation		Rating II		comment/rating
	total value	class																	
42536	unreliable		B	2	A/B	3	A/B	3	B	2	B	2	D	0	C	1		unreliable	
42537	C/D	0	B	2	A/B	3	A/B	3	B	2	B	2	D	0	C	1		unreliable	
44647	B	2	B	2	C/D	0	A/B	3	C/D	0	B	2	D	0	D	0		unreliable	
44650	B	2	B	2	C/D	0	A/B	3	C/D	0	B	2	D	0	D	0		unreliable	
44652	B	2	B	2	C/D	0	A/B	3	C/D	0	B	2	D	0	D	0		unreliable	
44654	B	2	B	2	C/D	0	A/B	3	C/D	0	B	2	D	0	D	0		unreliable	
44659	B	2	B	2	C/D	0	A/B	3	C/D	0	B	2	D	0	D	0		unreliable	
44660	B	2	B	2	C/D	0	A/B	3	C/D	0	B	2	D	0	D	0		unreliable	
44663	B	2	B	2	C/D	0	A/B	3	C/D	0	B	2	D	0	D	0		unreliable	
44664	B	2	B	2	C/D	0	A/B	3	C/D	0	B	2	D	0	D	0		unreliable	
44665	B	2	B	2	C/D	0	A/B	3	C/D	0	B	2	D	0	D	0		unreliable	
44666	B	2	B	2	C/D	0	A/B	3	C/D	0	B	2	D	0	D	0		unreliable	
44648	B	2	B	2	C/D	0	A/B	3	C/D	0	B	2	D	0	D	0		unreliable	
44649	B	2	B	2	C/D	0	A/B	3	C/D	0	B	2	D	0	D	0		unreliable	
44651	B	2	B	2	C/D	0	A/B	3	C/D	0	B	2	D	0	D	0		unreliable	
44653	B	2	B	2	C/D	0	A/B	3	C/D	0	B	2	D	0	D	0		unreliable	
44655	B	2	B	2	C/D	0	A/B	3	C/D	0	B	2	D	0	D	0		unreliable	
44656	B	2	B	2	C/D	0	A/B	3	C/D	0	B	2	D	0	D	0		unreliable	
44657	B	2	B	2	C/D	0	A/B	3	C/D	0	B	2	D	0	D	0		unreliable	
44658	B	2	B	2	C/D	0	A/B	3	C/D	0	B	2	D	0	D	0		unreliable	
44661	B	2	B	2	C/D	0	A/B	3	C/D	0	B	2	D	0	D	0		unreliable	
44662	B	2	B	2	C/D	0	A/B	3	C/D	0	B	2	D	0	D	0		unreliable	
48874																			
48875																			
48876																			
48877	unreliable		C/D	0	C/D	0	A/B	3	C/D	0	C/D	0	A	3	C	1		unreliable	
48878	unreliable		C/D	0	C/D	0	A/B	3	C/D	0	C/D	0	A	3	C	1		unreliable	
48879	unreliable		C/D	0	C/D	0	A/B	3	C/D	0	C/D	0	D	0	C	1		unreliable	
48880	unreliable		C/D	0	C/D	0	A/B	3	C/D	0	C/D	0	D	0	C	1		unreliable	
59026	C/D	0	B	2	unreliable	unreliable	C/D	0	C/D	0	A	3	D	0			unreliable		
59256	C/D	0	B	2	C/D	0	C/D	0	B	2	B	2	D	0	B	2	#REF!	#REF!	consistent with data for Am
59257	C/D	0	B	2	C/D	0	C/D	0	B	2	B	2	D	0	B	2	#REF!	#REF!	not conclusive
59258	C/D	0	B	2	C/D	0	C/D	0	B	2	B	2	D	0	B	2	#REF!	#REF!	not conclusive
59259	C/D	0	B	2	C/D	0	C/D	0	B	2	B	2	D	0	B	2	#REF!	#REF!	not conclusive
59260	C/D	0	B	2	C/D	0	C/D	0	B	2	B	2	D	0	B	2	#REF!	#REF!	consistent with data for Am
59261	C/D	0	B	2	C/D	0	C/D	0	B	2	B	2	D	0	B	2	#REF!	#REF!	consistent with data for Am
59262	C/D	0	B	2	C/D	0	C/D	0	B	2	B	2	D	0	B	2	#REF!	#REF!	not conclusive
59263	C/D	0	B	2	C/D	0	C/D	0	B	2	B	2	D	0	B	2	#REF!	#REF!	consistent with data for Am
59264	C/D	0	B	2	C/D	0	C/D	0	B	2	B	2	D	0	B	2	#REF!	#REF!	not conclusive
59265	C/D	0	B	2	C/D	0	C/D	0	B	2	B	2	D	0	B	2	#REF!	#REF!	not conclusive
59266	C/D	0	B	2	C/D	0	C/D	0	B	2	B	2	D	0	B	2	#REF!	#REF!	not conclusive
59267	C/D	0	B	2	C/D	0	C/D	0	B	2	B	2	D	0	B	2	#REF!	#REF!	not conclusive
59268	C/D	0	B	2	C/D	0	C/D	0	B	2	B	2	D	0	B	2	#REF!	#REF!	not conclusive
59269	C/D	0	B	2	C/D	0	C/D	0	B	2	B	2	D	0	B	2	#REF!	#REF!	not conclusive
59270	C/D	0	B	2	C/D	0	C/D	0	B	2	B	2	D	0	B	2	#REF!	#REF!	consistent with data for Am
59271	C/D	0	B	2	C/D	0	C/D	0	B	2	B	2	D	0	B	2	#REF!	#REF!	not conclusive
59272	C/D	0	B	2	C/D	0	C/D	0	B	2	B	2	D	0	B	2	#REF!	#REF!	consistent with data for Am
59273	C/D	0	B	2	C/D	0	C/D	0	B	2	B	2	D	0	B	2	#REF!	#REF!	consistent with data for Am
58937	unreliable		B	2	C/D	0	C/D	0	C/D	0	C/D	0	D	0	C	1			
58938	unreliable		B	2	C/D	0	C/D	0	C/D	0	C/D	0	D	0	C	1			
58939	C/D	0	B	2	C/D	0	C/D	0	C/D	0	C/D	0	D	0	C	1			
58940	C/D	0	B	2	C/D	0	C/D	0	C/D	0	C/D	0	D	0	C	1			
58941	C/D	0	B	2	C/D	0	C/D	0	C/D	0	C/D	0	D	0	C	1			
58942	C/D	0	B	2	C/D	0	C/D	0	C/D	0	C/D	0	D	0	C	1			
58943	unreliable		B	2	C/D	0	C/D	0	C/D	0	C/D	0	D	0	C	1			
58944	unreliable		B	2	C/D	0	C/D	0	C/D	0	C/D	0	D	0	C	1			
58945	C/D	0	B	2	C/D	0	C/D	0	C/D	0	C/D	0	D	0	C	1			
58946	C/D	0	B	2	C/D	0	C/D	0	C/D	0	C/D	0	D	0	C	1			
58947	C/D	0	B	2	C/D	0	C/D	0	C/D	0	C/D	0	D	0	C	1			
58948	C/D	0	B	2	C/D	0	C/D	0	C/D	0	C/D	0	D	0	C	1			
60872	unreliable		C/D	0	C/D	0	C/D	0	C/D	0	B	2	A	3	D	0			
60873	unreliable		C/D	0	C/D	0	C/D	0	C/D	0	B	2	A	3	D	0			
60874	unreliable		C/D	0	C/D	0	C/D	0	C/D	0	B	2	A	3	D	0			
60875	unreliable		C/D	0	C/D	0	C/D	0	C/D	0	B	2	A	3	D	0			
60876	unreliable		C/D	0	C/D	0	C/D	0	C/D	0	B	2	A	3	D	0			
60877	unreliable		C/D	0	C/D	0	C/D	0	C/D	0	B	2	A	3	D	0			
60878	unreliable		C/D	0	C/D	0	C/D	0	C/D	0	B	2	A	3	D	0			
60879	unreliable		C/D	0	C/D	0	C/D	0	C/D	0	B	2	A	3	D	0			
60880	unreliable		C/D	0	C/D	0	C/D	0	C/D	0	B	2	A	3	D	0			
60881	unreliable		C/D	0	C/D	0	C/D	0	C/D	0	B	2	A	3	D	0			
60882	unreliable		C/D	0	C/D	0	C/D	0	C/D	0	B	2	A	3	D	0			
60883	unreliable		C/D	0	C/D	0	C/D	0	C/D	0	B	2	A	3	D	0			

Appendix III: Availability of enthalpy data in relevant databases

date: March 18, 2005

Reactions	JNC-TDB (Yui et al., 1999)		NEA		remark
	log K	Reference	$\Delta_f H^\circ$	$\Delta_f H^\circ$	
Am					
Reaction Involving Solid Compounds					
Am(OH)3(am) \leftrightarrow Am+3 +3OH-	-25	Silva et al. (1995)	-	(\ddot{u})	the solid in the NEA-TDB is Am(OH)3(cr)
Am(OH)3(cr) \leftrightarrow Am+3 +3OH-	-26.8	Silva et al. (1995)	-	\ddot{u}	
Am2(CO3)3(cr) \leftrightarrow 2Am+3 +3CO3-2	-33.4	Silva et al. (1995)	-	-	
AmOHCO3(cr) \leftrightarrow Am+3 +OH- +CO3-2	-22.5	Felmy et al. (1990)	-	-	
NaAm(CO3)2*6H2O (cr) \leftrightarrow Na+ +Am+3 +2CO3-2 +6H2O	-21.4	Rai et al. (1999a)	-	-	
AmPO4*xH2O (am) \leftrightarrow Am+3 +PO4-3 +xH2O	-24.8	Rai et al. (1999a)	-	-	
AmF3(cr) \leftrightarrow Am+3 +3F-	-19.5	Rai et al. (1999a)	-	\ddot{u}	
Reaction Involving Solution Species					
Am+3 +H2O \leftrightarrow AmOH+2 +H+	-6.4	Silva et al. (1995)	-	-	
Am+3 +2 H2O \leftrightarrow Am(OH)2+ +2H+	-14.1	Silva et al. (1995)	-	-	
Am+3 +3 H2O \leftrightarrow Am(OH)3(aq) +3H+	< -28.6*1	Felmy et al. (1990)	-	-	
Am+3 +F- \leftrightarrow AmF+2	3.4	Silva et al. (1995)	-	-	
Am+3 +2F- \leftrightarrow AmF2+	5.8	Silva et al. (1995)	-	-	
Am+3 +3F- \leftrightarrow AmF3(aq)	< 11.2*1	Rai et al. (1999a)	-	-	
Am+3 + CO3-2 \leftrightarrow Am(CO3)+	7.6	Felmy et al. (1990)	-	-	
Am+3 + 2CO3-2 \leftrightarrow Am(CO3)2-	12.3	Felmy et al. (1990)	-	-	
Am+3 + 3CO3-2 \leftrightarrow Am(CO3)3-3	15.2	Felmy et al. (1990)	-	-	
Am+3 + H2PO4- \leftrightarrow AmH2PO4+2	2.74	Rai et al. (1999a)	-	-	
Th					
Reaction Involving Solid Compounds					
ThO2(am) + 2H2O \leftrightarrow Th+4 + 4OH-	-45.5	Felmy et al. (1991)	na	na	
ThO2(cr) + 2H2O \leftrightarrow Th+4 + 4OH-	-54.2	Rai et al. (1987)	na	na	
ThO2(am) + H+ + H2O +CO3-2 \leftrightarrow Th(OH)3CO3-	6.78	Oesthols et al. (1994)	na	na	
ThO2(am) + 4H+ +5CO3-2 \leftrightarrow Th(CO3)5-6 + 2H2O	37.6	Felmy et al. (1997)	na	na	
ThF4onH2O(s) +4H+ \leftrightarrow Th+4 + 4HF + nH2O	-16.29	Felmy et al. (1993)	na	na	
ThF4onNaFoh2O(cr) +4H+ \leftrightarrow Th+4+ Na+ +5HF + H2O	-18.23	Felmy et al. (1993)	na	na	
ThF4onNH4F(s) +5H+ \leftrightarrow Th+4 + NH4+ + 5HF	-18.09	Felmy et al. (1993)	na	na	
Reaction Involving Solution Species					
Th+4 + 4H2O \leftrightarrow Th(OH)4(aq) + H+	\leq -19.7	Ryan and Rai (1987)	na	na	
Th+4 +3SO4-2 \leftrightarrow Th(SO4)3-2	12.42	Felmy and Rai (1992)	na	na	
Th+4 +3F- \leftrightarrow ThF3+	18.89	Felmy et al. (1993)	na	na	
Th+4 + 4F- \leftrightarrow ThF4(aq)	22.33	Felmy et al. (1993)	na	na	
Th+4 + 5F- \leftrightarrow ThF5-	24.76	Felmy et al. (1993)	na	na	
Th+4 + 6F- \leftrightarrow ThF6-2	25.56	Felmy et al. (1993)	na	na	
Th+4 + NO3- \leftrightarrow ThNO3+3	2.5 *2	Rai et al. (1999b)	na	na	
Pa					
Reaction Involving Solid Compounds					
PaO2(cr) +4H+ \leftrightarrow Pa+4 +2H2O	0.6	Baes and Mesmer (1976)	na	na	
Pa2O5(s) + 10H+ +2e- \leftrightarrow 2Pa+4 +5H2O	-8.72	Shibutani and Shibutani (1998)	na	na	
PaCl4(cr) \leftrightarrow Pa+4 +4Cl-	24.01	Shibutani and Shibutani (1998)	na	na	
PaCl5(cr) \leftrightarrow Pa+4 +5Cl- +e-	32.85	Shibutani and Shibutani (1998)	na	na	
Reaction Involving Solution Species					
Pa+4 +H2O \leftrightarrow PaOH+3 +H+	0.84	Baes and Mesmer (1976)	na	na	
Pa+4 + 2H2O \leftrightarrow Pa(OH)2+2 +2H+	-0.02	Baes and Mesmer (1976)	na	na	
Pa+4 + 3H2O \leftrightarrow Pa(OH)3+ +3H+	-1.5	Baes and Mesmer (1976)	na	na	
Pa+4 +2H2O \leftrightarrow PaOOH+2 +3H+ +e-	1.86	Fuger and Oetting (1976)	na	na	
Pa+4 +3H2O \leftrightarrow PaO(OH)2+ +4H+ +e-	0.85	Shibutani and Shibutani (1998a)	na	na	
Pa+4 +4H2O \leftrightarrow PaO(OH)3(aq) +5H+ +e-	-3.6	Shibutani and Shibutani (1998a)	na	na	
U					
Redox Reaction					
UO2+2 + 2e- +4H+ \leftrightarrow U+4 +2H2O	9.038	Grenthe et al. (1992)	-	\ddot{u}	
UIV					
Reaction Involving Solid Compounds					
UO2(am) +2H2O \leftrightarrow U+4 +4OH-	-53.45	Rai et al. (1997)	-	(\ddot{u})	the solid in the NEA-TDB is UO2(cr)
UO2(am) +2HCO3- \leftrightarrow U(OH)2(CO3)2-2	-4.8	Rai et al. (1998a)	-	-	
UO2(am) +2H2O \leftrightarrow U(OH)4(aq)	< -8.7 *1	Yajima et al. (1995)	-	(\ddot{u})	the solid in the NEA-TDB is UO2(cr)
UO2(am) +4H+ +5CO3-2 \leftrightarrow U(CO3)5-6 +2H2O	33.8	Rai et al. (1998a)	-	(\ddot{u})	
*1 This value is the detection limit in literature					
Reaction Involving Solution Species					
U+4 + H2O \leftrightarrow UOH+3 + H+	-0.5	Rai et al. (1990)	\ddot{u}	\ddot{u}	
U+4 +SO4-2 \leftrightarrow USO4+2	9	Rai et al. (1999b)	\ddot{u}	\ddot{u}	

Appendix III: Availability of enthalpy data in relevant databases(cont.)

Reactions	JNC-TDB (Yui et al., 1999)		NEA		remark
	log K	Reference	$\Delta_r H^\circ$	$\Delta_f H^\circ$	
U+4 + NO ⁻³ <=> UNO ₃ +3	1.47	Grenthe et al. (1992)	-	-	
U+4 + 2NO ₃ ⁻ <=> U(NO ₃) ₂ +2	2.3	Grenthe et al. (1992)	-	-	
U+4 + F ⁻ <=> UF+3	9.28	Grenthe et al. (1992)	Ü	Ü	
U+4 + 2F ⁻ <=> UF ₂ +2	16.23	Grenthe et al. (1992)	Ü	Ü	
U+4 + 3F ⁻ <=> UF ₃ +3	21.6	Grenthe et al. (1992)	Ü	Ü	
U+4 + 4F ⁻ <=> UF ₄ (aq)	25.6	Grenthe et al. (1992)	Ü	Ü	
U+4 + 5F ⁻ <=> UF ₅ ⁻	27.01	Grenthe et al. (1992)	-	-	
U+4 + 6F ⁻ <=> UF ₆ -2	29.08	Grenthe et al. (1992)	-	-	
UVI					
Reaction Involving Solid Compounds					
α -UO ₃ <=> UO ₂ +2 -2H ⁺ +H ₂ O	8.632*	Grenthe et al. (1992)	-	Ü	
β -UO ₃ <=> UO ₂ +2 -2H ⁺ +H ₂ O	8.302*	Grenthe et al. (1992)	-	Ü	
γ -UO ₃ <=> UO ₂ +2 -2H ⁺ +H ₂ O	7.702*	Grenthe et al. (1992)	-	Ü	
α -UO ₃ *0.9H ₂ O <=> UO ₂ +2 -2H ⁺ +1.9H ₂ O	5.002*	Grenthe et al. (1992)	-	Ü	
β -UO ₂ (OH) ₂ <=> UO ₂ +2 -2H ⁺ +2H ₂ O	4.932*	Grenthe et al. (1992)	-	Ü	
UO ₃ *2H ₂ O(cr) + 2H ⁺ <=> UO ₂ +2 +3H ₂ O	4.812*	Grenthe et al. (1992)	-	Ü	
UF ₆ (cr) <=> UO ₂ +2 -4H ⁺ -2H ₂ O +6F ⁻	17.202*	Grenthe et al. (1992)	-	Ü	
UO ₂ (IO ₃) ₂ (cr) <=> UO ₂ +2 + 2IO ₃ ⁻	-7.88	Grenthe et al. (1992)	-	Ü	
UO ₂ SO ₄ *3.5H ₂ O(cr) +2H ⁺ <=> UO ₂ +2 +SO ₄ -2 + 3.5H ₂ O	-1.585	Grenthe et al. (1992)	-	Ü	
UO ₂ SO ₄ *2.5H ₂ O(cr) +2H ⁺ <=> UO ₂ +2 +SO ₄ -2 + 2.5H ₂ O	-1.589	Grenthe et al. (1992)	-	Ü	
UO ₂ CO ₃ (cr) <=> UO ₂ +2 +CO ₃ -2	-14.49	Silva et al. (1995)	-	Ü	
Na ₄ UO ₂ (CO ₃) ₃ (cr) <=> 4Na ⁺ +UO ₂ (CO ₃) ₃ -4	-5.34	Grenthe et al. (1992)	-	-	
*log K value of the reaction based on Gibbs free energy $\Delta_r G^\circ$ in Grenth et al. (1992)					
Reaction Involving Solution Species					
UO ₂ +2 + H ₂ O <=> UO ₂ OH ⁺ + H ⁺	-5.2	Grenthe et al. (1992)	-	Ü	
UO ₂ +2 + 2H ₂ O <=> UO ₂ (OH) ₂ (aq) + 2H ⁺	< -10.300 *	Grenthe et al. (1992)	-	-	
UO ₂ +2 + 3H ₂ O <=> UO ₂ (OH) ₃ +3H ⁺	-19.2	Grenthe et al. (1992)	-	-	
UO ₂ +2 + 4H ₂ O <=> UO ₂ (OH) ₄ -2 +4H ⁺	-33	Grenthe et al. (1992)	-	-	
2UO ₂ +2 + H ₂ O <=> (UO ₂) ₂ OH ⁺ +H ⁺	-2.7	Grenthe et al. (1992)	-	-	
2UO ₂ +2 + 2H ₂ O <=> (UO ₂) ₂ (OH) ₂ +2 +2H ⁺	-5.62	Grenthe et al. (1992)	-	Ü	
3UO ₂ +2 + 4H ₂ O <=> (UO ₂) ₃ (OH) ₄ +2 +4H ⁺	-11.9	Grenthe et al. (1992)	-	-	
3UO ₂ +2 + 5H ₂ O <=> (UO ₂) ₃ (OH) ₅ + +5H ⁺	-15.55	Grenthe et al. (1992)	-	Ü	
3UO ₂ +2 + 7H ₂ O <=> (UO ₂) ₃ (OH) ₇ - +7H ⁺	-31	Grenthe et al. (1992)	-	-	
4UO ₂ +2 + 7H ₂ O <=> (UO ₂) ₄ (OH) ₇ + +7H ⁺	-21.9	Grenthe et al. (1992)	-	-	
UO ₂ +2 + F ⁻ <=> UO ₂ F ⁺	5.09	Grenthe et al. (1992)	Ü	Ü	
UO ₂ +2 + 2F ⁻ <=> UO ₂ F ₂ (aq)	8.62	Grenthe et al. (1992)	Ü	Ü	
UO ₂ +2 + 3F ⁻ <=> UO ₂ F ₃ ⁻	10.9	Grenthe et al. (1992)	Ü	Ü	
UO ₂ +2 + 4F ⁻ <=> UO ₂ F ₄ -2	11.7	Grenthe et al. (1992)	Ü	Ü	
UO ₂ +2 + Cl ⁻ <=> UO ₂ Cl ⁺	0.17	Grenthe et al. (1992)	Ü	Ü	
UO ₂ +2 + 2Cl ⁻ <=> UO ₂ Cl ₂ (aq)	-1.1	Grenthe et al. (1992)	Ü	Ü	
UO ₂ +2 + ClO ₃ ⁻ <=> UO ₂ ClO ₃ ⁺	0.5	Grenthe et al. (1992)	Ü	Ü	
UO ₂ +2 + Br ⁻ <=> UO ₂ Br ⁺	0.22	Grenthe et al. (1992)	-	-	
UO ₂ +2 + BrO ₃ ⁻ <=> UO ₂ BrO ₃ ⁺	0.63	Grenthe et al. (1992)	Ü	Ü	
UO ₂ +2 + IO ₃ ⁻ <=> UO ₂ IO ₃ ⁺	2	Grenthe et al. (1992)	Ü	Ü	
UO ₂ +2 + 2IO ₃ ⁻ <=> UO ₂ (IO ₃) ₂ (aq)	3.59	Grenthe et al. (1992)	-	-	
UO ₂ +2 + SO ₃ -2 <=> UO ₂ SO ₃ (aq)	6.6	Grenthe et al. (1992)	-	-	
UO ₂ +2 + S ₂ O ₃ -2 <=> UO ₂ S ₂ O ₃ (aq)	2.8	Grenthe et al. (1992)	-	-	
UO ₂ +2 + SO ₄ -2 <=> UO ₂ SO ₄ (aq)	3.15	Grenthe et al. (1992)	Ü	Ü	
UO ₂ +2 + 2SO ₄ -2 <=> UO ₂ (SO ₄) ₂ -2	4.14	Grenthe et al. (1992)	Ü	Ü	
UO ₂ +2 + N ₃ ⁻ <=> UO ₂ N ₃ ⁺	2.58	Grenthe et al. (1992)	-	-	
UO ₂ +2 + 2N ₃ ⁻ <=> UO ₂ (N ₃) ₂ (aq)	4.33	Grenthe et al. (1992)	-	-	
UO ₂ +2 + 3N ₃ ⁻ <=> UO ₂ (N ₃) ₃ ⁻	5.74	Grenthe et al. (1992)	-	-	
UO ₂ +2 + 4N ₃ ⁻ <=> UO ₂ (N ₃) ₄ -2	4.92	Grenthe et al. (1992)	-	-	
UO ₂ +2 + NO ₃ ⁻ <=> UO ₂ NO ₃ ⁺	0.3	Grenthe et al. (1992)	-	-	
UO ₂ +2 + PO ₄ -3 <=> UO ₂ PO ₄ ⁻	13.23	Grenthe et al. (1992)	-	-	
UO ₂ +2 + HPO ₄ -2 <=> UO ₂ HPO ₄ (aq)	7.24	Grenthe et al. (1992)	-	-	
UO ₂ +2 + H ₃ PO ₄ (aq) <=> UO ₂ H ₂ PO ₄ ⁺ +H ⁺	1.12	Grenthe et al. (1992)	-	-	
UO ₂ +2 + H ₃ PO ₄ (aq) <=> UO ₂ H ₃ PO ₄ +2	0.76	Grenthe et al. (1992)	-	-	
UO ₂ +2 + 2H ₃ PO ₄ (aq) <=> UO ₂ (H ₂ PO ₄) ₂ (aq) +2H ⁺	0.64	Grenthe et al. (1992)	-	-	
UO ₂ +2 + 2H ₃ PO ₄ (aq) <=> UO ₂ (H ₂ PO ₄) (H ₃ PO ₄) + +H ⁺	1.65	Grenthe et al. (1992)	-	-	
UO ₂ +2 + CO ₃ -2 <=> UO ₂ CO ₃ (aq)	9.67	Silva et al. (1995)	Ü	Ü	
UO ₂ +2 + 2CO ₃ -2 <=> UO ₂ (CO ₃) ₂ -2	16.94	Grenthe et al. (1992)	Ü	Ü	
UO ₂ +2 + 3CO ₃ -2 <=> UO ₂ (CO ₃) ₃ -4	21.6	Grenthe et al. (1992)	Ü	Ü	
3UO ₂ +2 + 6CO ₃ -2 <=> (UO ₂) ₃ (CO ₃) ₆ -6	54	Grenthe et al. (1992)	Ü	Ü	
2UO ₂ (CO ₃) ₃ + PuO ₂ (CO ₃) ₄ <=> (UO ₂) ₂ (PuO ₂)(CO ₃) ₆ -6 + 3CC	-8.2	Silva et al. (1995)	-	-	
2UO ₂ (CO ₃) ₃ + NpO ₂ (CO ₃) ₄ <=> (UO ₂) ₂ (NpO ₂)(CO ₃) ₆ -6 + 3CC	-9.4	Silva et al. (1995)	-	-	
UO ₂ +2 + SCN ⁻ <=> UO ₂ SCN ⁺	1.4	Grenthe et al. (1992)	Ü	Ü	
UO ₂ +2 + 2SCN ⁻ <=> UO ₂ (SCN) ₂ (aq)	1.24	Grenthe et al. (1992)	Ü	Ü	
UO ₂ +2 + 3SCN ⁻ <=> UO ₂ (SCN) ₃ ⁻	2.1	Grenthe et al. (1992)	Ü	Ü	

Appendix III: Availability of enthalpy data in relevant databases(cont.)

Reactions	JNC-TDB (Yui et al., 1999)		NEA		remark
	log K	Reference	$\Delta_f H^\circ$	$\Delta_f H^\circ$	
3UO ₂ +2 +3H ₂ O+CO ₃ -2 => (UO ₂) ₃ O(OH) ₂ (HCO ₃) ₂ +3H+	0.652*	Grenthe et al. (1992)	-	-	
11UO ₂ +2 +12H ₂ O+6CO ₃ -2 => (UO ₂) ₁₁ (CO ₃) ₆ (OH) ₁₂ -2 +12H+	-63.006*	Grenthe et al. (1992)	-	-	
Np					
Redox Reaction					
NpO ₂ +2 + 2e- +4H+ => Np+4 +2H ₂ O	10.89	Fuger and Oetting (1976)	-	ü	
NpO ₂ +2 +e- => NpO ₂ +2	20.89	Fuger and Oetting (1976)	-	ü	
Np(IV)					
Reaction involving Solid Compounds Np(IV)					
NpO ₂ (am) +2H ₂ O => Np+4 +4OH-	-54.5	Rai et al. (1987)	-	(ü)	the solid in the NEA-TDB is NpO ₂ (cr)
NpO ₂ (am) +2H ₂ O => Np(OH) ₄ (aq)	< -8.5*	Rai and Ryan (1985)	-	-	
*this value is the detection limit of literature					
Reaction involving Solution Species					
Np+4 + H ₂ O => NpOH+3 + H+	-0.5	Rai et al. (1999b)	-	-	
Np+4 +SO ₄ -2 => NpSO ₄ +2	9	Xia et al. (1999)	(ü)	ü	the reaction in the NEA-TDB is written with HSO ₄ -
Np+4 +2SO ₄ -2 => Np(SO ₄) ₂ (aq)	11.7	Xia et al. (1999)	(ü)	ü	the reaction in the NEA-TDB is written with HSO ₄ -
Np+4 + 5CO ₃ -2 => Np(CO ₃) ₅ -6	33.37	Rai et al. (1998b)	-	-	
Np+4 + 2CO ₃ -2 +2OH- => Np(OH) ₂ (CO ₃) ₂ -2	42.75	Rai et al. (1998b)	-	-	
Np(V)					
Reaction Involving Solid Compounds					
NpO ₂ OH(am) => NpO ₂ + +OH-	-8.79	Roberts et al. (1996)	-	(ü)	the solid in the NEA-TDB is NpO ₂ OH(cr)
NaNpO ₂ CO ₃ (cr) => Na+ +NpO ₂ + +CO ₃ -2	-11	Neck et al. (1995)	-	-	
Na ₃ NpO ₂ (CO ₃) ₂ (cr) => 3Na+ +NpO ₂ + +2CO ₃ -2	-14.3	Neck et al. (1995)	-	-	
Reaction Involving Solution Species					
NpO ₂ + + OH- => NpO ₂ OH(aq)	5	Neck et al. (1992)	-	ü	
NpO ₂ + + 2 OH- => NpO ₂ OH ₂ -1	4.35	Neck et al. (1992)	-	ü	
NpO ₂ + + CO ₃ -2 => NpO ₂ CO ₃ -	5.1	Fuger et al. (1992)	-	-	
NpO ₂ + + Cl- => NpO ₂ Cl(aq)	-0.07	Choppin et al. (1999)	-	-	
NpO ₂ + + NO ₃ - => NpO ₂ NO ₃	1.1	Allard et al. (1978)	-	-	
NpO ₂ + + F- => NpO ₂ F(aq)	1.9	Fuger et al. (1992)	-	-	
NpO ₂ + +HPO ₄ -2 => NpO ₂ HPO ₄ -	3.4	Fuger et al. (1992)	-	-	
NpO ₂ + +H ₂ PO ₄ - => NpO ₂ H ₂ PO ₄ (aq)	1.5	Choppin et al. (1999)	-	-	
NpO ₂ + +SO ₄ -2 => NpO ₂ SO ₄ -	2	Wanner (1986)	ü	ü	
Pu					
Redox Reaction					
Pu+4 +e- => Pu ₃ +2	16.99	Fuger and Oetting (1976)	-	ü	
PuO ₂ +2 + 2e- +4H+ => Pu+4+2H ₂ O	18.6	Rai (1984)	-	ü	
PuO ₂ +2 +e- => PuO ₂ +2	16.16	Rai (1984)	(ü)	ü	the reaction in the NEA-TDB is formulated with H ₂ (g) instead of the electron
Pu(IV)					
Reaction Involving Solid compounds Pu(IV)					
PuO ₂ (am) +2H ₂ O => PuO ₂ +2 + 4OH-	-56.85	Rai (1984)	-	(ü)	the solid in the NEA-TDB is PuO ₂ (cr)
PuO ₂ (am) +2H ₂ O => Pu(OH) ₄ (aq)	< -10 *	Yamaguchi et al. (1994)	-	-	
Reaction Involving Solution Species					
Pu+4+ H ₂ O => PuOH ₃ + + H+	-0.5	Rai et al. (1999b)	ü	ü	
Pu+4+SO ₄ -2 => PuSO ₄ +2	9	Rai et al. (1999b)	-	-	
Pu+4+2SO ₄ -2 => Pu(SO ₄) ₂ (aq)	11.7	Rai et al. (1999b)	-	-	
Pu+4+ 5CO ₃ -2 => Pu(CO ₃) ₅ -6	34.18	Rai et al. (1999c)	-	-	
Pu+4+ 2CO ₃ -2 +2OH- => Pu(OH) ₂ (CO ₃) ₂ -2	44.76	Rai et al. (1999c)	-	-	
Pu(V)					
Reaction Involving Solid compounds					
PuO ₂ OH(am) => PuO ₂ + +OH-	-8.79	Roberts et al. (1996)	-	-	see also Np(V) as analog
NaPuO ₂ CO ₃ (cr) => Na+ +PuO ₂ + +CO ₃ -2	-11	Neck et al. (1995)	-	-	see also Np(V) as analog
Na ₃ PuO ₂ (CO ₃) ₂ (cr) => 3Na+ +PuO ₂ + +2CO ₃ -2	-14.32	Neck et al. (1995)	-	-	see also Np(V) as analog
Reaction Involving Solution Species					
PuO ₂ + + OH- => PuO ₂ OH(aq)	2.7	Neck et al. (1992)	-	-	see also Np(V) as analog
PuO ₂ + + 2OH- => PuO ₂ (OH) ₂ -	4.35	Neck et al. (1992)	-	-	see also Np(V) as analog
PuO ₂ + + CO ₃ -2 => PuO ₂ CO ₃ -	4.9	Fuger et al. (1992)	-	-	see also Np(V) as analog
PuO ₂ + + Cl- => PuO ₂ Cl(aq)	0.7	Choppin et al. (1999)	-	-	see also Np(V) as analog
PuO ₂ + + NO ₃ - => PuO ₂ NO ₃	1.1	Allard et al. (1978)	-	-	see also Np(V) as analog

Appendix III: Availability of enthalpy data in relevant databases(cont.)

Reactions	JNC-TDB (Yui et al., 1999)		NEA		remark
	log K	Reference	$\Delta_f H^\circ$	$\Delta_f H^\circ$	
PuO ₂ + F ⁻ <=> PuO ₂ F(aq)	1.9	Fuger et al. (1992)	-	-	see also Np(V) as analog
PuO ₂ + HPO ₄ ²⁻ <=> PuO ₂ HPO ₄ ⁻	3.4	Fuger et al. (1992)	-	-	see also Np(V) as analog
PuO ₂ + H ₂ PO ₄ ⁻ <=> PuO ₂ H ₂ PO ₄ (aq)	1.5	Choppin et al. (1999)	-	-	see also Np(V) as analog
PuO ₂ + SO ₄ ²⁻ <=> PuO ₂ SO ₄ ⁻	2	Wanner (1986)	-	-	see also Np(V) as analog
Pu(VI)					
Reaction Involving Solution Species					
PuO ₂ +2 + Cl ⁻ <=> PuO ₂ Cl ⁺	0.1	Fuger et al. (1992)	-	-	
PuO ₂ +2 + F ⁻ <=> PuO ₂ F ⁺	4.57	Fuger et al. (1992)	-	-	
PuO ₂ +2 + 2F ⁻ <=> PuO ₂ F ₂ (aq)	8.24	Fuger et al. (1992)	-	-	
PuO ₂ +2 + 3F ⁻ <=> PuO ₂ F ₃ ⁻	9.8	Fuger et al. (1992)	-	-	
PuO ₂ +2 + H ₂ O <=> PuO ₂ (OH) ⁺ + H ⁺	-5.27	Shibutani and Shibutani (1998b)	Ü	Ü	
PuO ₂ +2 + 2H ₂ O <=> PuO ₂ (OH) ₂ (aq) + 2H ⁺	-12.46	Shibutani and Shibutani (1998b)	-	-	
PuO ₂ +2 + 3H ₂ O <=> PuO ₂ (OH) ₃ ⁻ + 3H ⁺	-24.76	Shibutani and Shibutani (1998b)	-	-	
PuO ₂ +2 + NO ₃ ⁻ <=> PuO ₂ NO ₃ ⁺	0.3	Choppin et al. (1999)/Shibutani&Shibutani (1998b)	-	-	
PuO ₂ +2 + CO ₃ ²⁻ <=> PuO ₂ CO ₃ (aq)	9.56	Pashaliddis et al. (1997)	-	-	
PuO ₂ +2 + 2CO ₃ ²⁻ <=> PuO ₂ (CO ₃) ₂ ⁻²	15	Pashaliddis et al. (1997)	Ü	Ü	
PuO ₂ +2 + 3CO ₃ ²⁻ <=> PuO ₂ (CO ₃) ₃ ⁻⁴	17.53	Pashaliddis et al. (1997)	Ü	Ü	
PuO ₂ +2 + HPO ₄ ²⁻ <=> PuO ₂ HPO ₄ (aq)	7.24 *1	Shibutani and Shibutani (1998b)	-	-	
PuO ₂ +2 + H ₃ PO ₄ (aq) <=> PuO ₂ H ₂ PO ₄ ⁺ + H ⁺	1.12 *1	Shibutani and Shibutani (1998b)	-	-	
PuO ₂ +2 + SO ₄ ²⁻ <=> PuO ₂ SO ₄ (aq)	3.15 *1	Shibutani and Shibutani (1998b)	Ü	Ü	
PuO ₂ +2 + 2SO ₄ ²⁻ <=> PuO ₂ (SO ₄) ₂ ⁻²	4.14 *1	Shibutani and Shibutani (1998b)	Ü	Ü	
Nb					
Reaction Involving Solution Species					
Nb(OH) ₅ (aq) + H ₂ O <=> Nb(OH) ₆ ⁺ + H ⁺	-6.6	Lothenbach et al. (1999)	na	na	
Nb ₂ O ₅ (s) + 5H ₂ O <=> 2Nb(OH) ₅	-16	Lothenbach et al. (1999)	na	na	
Tc					
Reaction Involving Solid Compounds					
Tc(OH) ₃ (s) + H ⁺ <=> TcO ²⁺ + 2H ₂ O + e ⁻	-14.63	OECD/NEA (1989)	-	-	
Tc ₂ O ₇ (cr) + H ₂ O <=> 2TcO ₄ ⁻ + 2H ⁺	13.11	OECD/NEA (1989)	-	Ü	
Tc ₃ O ₄ (s) + 2H ⁺ <=> 3TcO ²⁺ + H ₂ O + 4e ⁻	-56.89	OECD/NEA (1989)	-	-	
Tc ₄ O ₇ (s) + 6H ⁺ <=> 4TcO ²⁺ + 3H ₂ O + 2e ⁻	-36.79	OECD/NEA (1989)	-	-	
TcO ₂ ·2H ₂ O(am) + 2H ⁺ <=> TcO ²⁺ + 3H ₂ O	-4.23	OECD/NEA (1989)	-	-	
TcO ₃ (cr) + 4H ⁺ + 2e ⁻ <=> TcO ²⁺ + 2H ₂ O	19.96	OECD/NEA (1989)	-	-	
NaTcO ₄ (cr) + 6H ⁺ + 3e ⁻ <=> Na ⁺ + TcO ²⁺ + 3H ₂ O	35.54	OECD/NEA (1989)	-	-	
HTcO ₄ (per techn) + 5H ⁺ + 3e ⁻ <=> TcO ²⁺ + 3H ₂ O	38.97	OECD/NEA (1989)	-	-	
TcO ₂ (cr) + 2H ⁺ <=> TcO ²⁺ + H ₂ O	-19.76	Phillips et al. (1988)	-	-	
Tc(OH) ₂ (s) <=> TcO ²⁺ + H ₂ O + 2e ⁻	-21.63	Phillips et al. (1988)	-	-	
Tc(cr) + H ₂ O <=> TcO ²⁺ + 2H ⁺ + 4e ⁻	-23.94	Phillips et al. (1988)	-	-	
Reaction Involving Solution Species					
2TcO ²⁺ + 4H ₂ O <=> (TcO(OH) ₂) ₂ (aq) + 4H ⁺	-0.133	OECD/NEA (1989)	-	-	
TcO ²⁺ + 3H ₂ O <=> H ₂ TcO ₄ (aq) + 4H ⁺ + 2e ⁻	-34.31	OECD/NEA (1989)	-	-	
TcO ²⁺ + 3H ₂ O <=> HTcO ₄ ⁻ + 5H ⁺ + 2e ⁻	-34.608	OECD/NEA (1989)	-	-	
TcO ²⁺ + 2H ₂ O + e ⁻ <=> Tc ₃ ⁴⁺ + 4H ⁺	5.391	OECD/NEA (1989)	-	-	
TcO ²⁺ + 2H ₂ O <=> TcO(OH) ₂ (aq) + 2H ⁺	-3.325	OECD/NEA (1989)	-	-	
TcO ²⁺ + 3H ₂ O <=> TcO ₄ ⁻ + 6H ⁺ + 3e ⁻	-32.993	OECD/NEA (1989)	-	-	
TcO ²⁺ + 3H ₂ O <=> TcO ₄ ⁻ ·2·6H ⁺ + 2e ⁻	-43.315	OECD/NEA (1989)	-	-	
TcO ²⁺ + 3H ₂ O <=> TcO ₄ ⁻ ·3·6H ⁺ + e ⁻	-53.287	OECD/NEA (1989)	-	-	
TcO ²⁺ + H ₂ O <=> TcOOH ⁺ + H ⁺	-1.137	OECD/NEA (1989)	-	-	
Pd					
Reaction Involving Solution Species					
Pd(cr) <=> Pd ²⁺ + 2e ⁻	-32.9	Lothenbach et al. (1999)	na	na	
Pd ²⁺ + Cl ⁻ <=> PdCl ⁺	5.1	Lothenbach et al. (1999)	na	na	
Pd ²⁺ + 2Cl ⁻ <=> Pd(Cl) ₂ (aq)	8.3	Lothenbach et al. (1999)	na	na	
Pd ²⁺ + 3 Cl ⁻ <=> Pd(Cl) ₃ ⁻	10.9	Lothenbach et al. (1999)	na	na	
Pd ²⁺ + 4 Cl ⁻ <=> Pd(Cl) ₄ ²⁻	11.7	Lothenbach et al. (1999)	na	na	
Pd ²⁺ + 3Cl ⁻ + H ⁺ + H ₂ O <=> PdCl ₃ OH ⁻²	2.5	Lothenbach et al. (1999)	na	na	
Pd ²⁺ + 2Cl ⁻ + 2H ⁺ + 2H ₂ O <=> PdCl ₂ (OH) ₂ ⁻²	-7	Lothenbach et al. (1999)	na	na	
Pd ²⁺ + NH ₃ (aq) <=> Pd NH ₃ ⁺	9.6	Lothenbach et al. (1999)	na	na	
Pd ²⁺ + 2NH ₃ (aq) <=> Pd(NH ₃) ₂ ²⁺	18.5	Lothenbach et al. (1999)	na	na	
Pd ²⁺ + 3NH ₃ (aq) <=> Pd(NH ₃) ₃ ²⁺	26	Lothenbach et al. (1999)	na	na	
Pd ²⁺ + 4NH ₃ (aq) <=> Pd(NH ₃) ₄ ²⁺	32.8	Lothenbach et al. (1999)	na	na	
Sn					
Redox Reaction					
Sn(cr) <=> Sn ²⁺ + 2e ⁻	4.63	Lothenbach et al. (1999)	na	na	
Sn ²⁺ <=> Sn ⁴⁺ + 2e ⁻	-5	Lothenbach et al. (1999)	na	na	
Sn ²⁺ + 4H ₂ O <=> Sn(OH) ₄ (aq) + 4H ⁺ + 2e ⁻	-5.4	Lothenbach et al. (1999)	na	na	

Appendix III: Availability of enthalpy data in relevant databases(cont.)

Reactions	JNC-TDB (Yui et al., 1999)		NEA		remark
	log K	Reference	$\Delta_f H^\circ$	$\Delta_f H^\circ$	
Reaction Involving Solid Compounds					
Sn(OH)2(am) + 2H+ <=> Sn+2 + 2H2O	2.82	Lothenbach et al. (1999)	na	na	
SnO(cr) + 2H+ <=> Sn+2 + H2O	2.41	Lothenbach et al. (1999)	na	na	
SnOHCl(s) + H+ <=> Sn+2 + Cl- + H2O	-2.42	Lothenbach et al. (1999)	na	na	
Sn+2 + H2O <=> SnOH+ + H+	-3.75	Lothenbach et al. (1999)	na	na	
Sn+2 + 2H2O <=> Sn(OH)2(aq) + 2H+	-7.71	Lothenbach et al. (1999)	na	na	
Sn+2 + 3H2O <=> Sn(OH)3- + 2H+	-17.54	Lothenbach et al. (1999)	na	na	
3Sn+2 + 4H2O <=> Sn3(OH)4+2 + 4H+	-6.51	Lothenbach et al. (1999)	na	na	
Sn+2 + Cl- <=> SnCl+	1.65	Lothenbach et al. (1999)	na	na	
Sn+2 + 2Cl- <=> SnCl2(aq)	2.31	Lothenbach et al. (1999)	na	na	
Sn+2 + 3Cl- <=> SnCl3-	2.09	Lothenbach et al. (1999)	na	na	
Sn+2 + Cl- + H2O <=> SnOHCl(aq) + H+	-2.27	Lothenbach et al. (1999)	na	na	
Sn+2 + F- <=> SnF+	4.46 *1	Lothenbach et al. (1999)	na	na	
Sn+2 + 2F- <=> SnF2(aq)	7.74 *1	Lothenbach et al. (1999)	na	na	
Sn+2 + 3F- <=> SnF3-	9.61 *1	Lothenbach et al. (1999)	na	na	
Sn+2 + NO3- <=> SnNO3+	1.25	Lothenbach et al. (1999)	na	na	
Sn+2 + 2NO3- <=> Sn(NO3)2(aq)	1.74	Lothenbach et al. (1999)	na	na	
Sn+2 + 3NO3- <=> Sn(NO3)3-	1.37	Lothenbach et al. (1999)	na	na	
Sn+2 + 4NO3- <=> Sn(NO3)4-2	0.30 *1	Lothenbach et al. (1999)	na	na	
Sn+2 + SO4-2 <=> SnSO4(aq)	2.91 *1	Lothenbach et al. (1999)	na	na	
Sn+2 + 2SO4-2 <=> Sn(SO4)2-2	2.83 *1	Lothenbach et al. (1999)	na	na	
SnO2(am) <=> Sn(OH)4(aq) + 2H2O	-7.46	Lothenbach et al. (1999)	na	na	
SnO2(cassiterite) <=> Sn(OH)4(aq) + 2H2O	-8	Lothenbach et al. (1999)	na	na	
Sn(OH)4(aq) + 4H+ <=> Sn+4 + 4H2O	0.4 *1	Lothenbach et al. (1999)	na	na	
Sn(OH)4(aq) + H2O <=> Sn(OH)5- + H+	-7.97	Lothenbach et al. (1999)	na	na	
Sn(OH)4(aq) + 2H2O <=> Sn(OH)6-2 + 2H+	-18.4	Lothenbach et al. (1999)	na	na	
Sb					
Redox Reaction					
Sb(cr) + 3H2O <=> Sb(OH)3(aq) + 3H+ + 3e-	-11.99	Lothenbach et al. (1999)	na	na	
Sb(OH)3(aq) + 2H2O <=> Sb(OH)5(aq) + 2H+ + 2e-	-21.84	Lothenbach et al. (1999)	na	na	
Reaction Involving Solid and Solution Species					
Sb2O3(valentinite) + 3H2O <=> 2Sb(OH)3(aq)	-8.72	Lothenbach et al. (1999)	na	na	
Sb2S3(stibnite) + 6H2O <=> 2Sb(OH)3(aq) + 3H+ + 3HS-	-55.14	Lothenbach et al. (1999)	na	na	
Sb(OH)3(aq) + 3H+ <=> Sb+3 + 3H2O	-0.73	Lothenbach et al. (1999)	na	na	
Sb(OH)3(aq) + 2H+ <=> SbOH+2 + 2H2O	0.83	Lothenbach et al. (1999)	na	na	
Sb(OH)3(aq) + H+ <=> Sb(OH)2+ + H2O	1.3	Lothenbach et al. (1999)	na	na	
Sb(OH)3(aq) + H2O <=> Sb(OH)4- + H+	-11.93	Lothenbach et al. (1999)	na	na	
2Sb(OH)3(aq) <=> Sb2(OH)6(aq)	0.08	Lothenbach et al. (1999)	na	na	
Sb(OH)3(aq) + 3H+ + Cl- <=> SbCl+2 + 3H2O	2.78	Lothenbach et al. (1999)	na	na	
Sb(OH)3(aq) + 3H+ + 2Cl- <=> Sb(Cl)2+ + 3H2O	3.27	Lothenbach et al. (1999)	na	na	
Sb(OH)3(aq) + 3H+ + F- <=> SbF+2 + 3H2O	6.48	Lothenbach et al. (1999)	na	na	
Sb(OH)3(aq) + 3H+ + 2F- <=> SbF2+ + 3H2O	12.65	Lothenbach et al. (1999)	na	na	
Sb(OH)3(aq) + 3H+ + 3F- <=> SbF3(aq) + 3H2O	18.36	Lothenbach et al. (1999)	na	na	
2Sb(OH)3(aq) + 2H+ + 4HS- <=> Sb2S4-2 + 6H2O	42.53	Lothenbach et al. (1999)	na	na	
2Sb(OH)3(aq) + 3H+ + 4HS- <=> HSb2S4- + 6H2O	52.18	Lothenbach et al. (1999)	na	na	
2Sb(OH)3(aq) + 4H+ + 4HS- <=> H2Sb2S4(aq) + 6H2O	57	Lothenbach et al. (1999)	na	na	
Sb2O5(am) + 5H2O <=> 2Sb(OH)5(aq)	-7.4	Lothenbach et al. (1999)	na	na	
Sb(OH)5(aq) + H2O <=> Sb(OH)6- + H+	-2.72	Lothenbach et al. (1999)	na	na	
12Sb(OH)5(aq) + 4H+ + 4H2O <=> Sb12(OH)64-4	20.34	Lothenbach et al. (1999)	na	na	
12Sb(OH)5(aq) + 5H+ + 5H2O <=> Sb12(OH)65-5	16.72	Lothenbach et al. (1999)	na	na	
12Sb(OH)5(aq) + 6H+ + 6H2O <=> Sb12(OH)66-6	11.89	Lothenbach et al. (1999)	na	na	
12Sb(OH)5(aq) + 7H+ + 7H2O <=> Sb12(OH)67-7	6.07	Lothenbach et al. (1999)	na	na	
Pb					
Redox Reaction					
Pb(cr) <=> Pb+2 + 2e-	4.25	Lothenbach et al. (1999)	na	na	
PbO2(s) <=> Pb+2 + 2H2O - 4H+ - 2e-	48.98 *1	Lothenbach et al. (1999)	na	na	
Pb3O4(s) <=> Pb+2 + 4H2O - 8H+ - 2e-	70.98 *1	Lothenbach et al. (1999)	na	na	
Reaction Involving Solid Compounds					
PbO(red, litharge) <=> Pb+2 + H2O - 2H+	12.68	Lothenbach et al. (1999)	na	na	
PbO(yellow, massicot) <=> Pb+2 + H2O - 2H+	12.96	Lothenbach et al. (1999)	na	na	
Pb(OH)2(am) <=> Pb+2 + 2H2O - 2H+	13.05	Lothenbach et al. (1999)	na	na	
PbCl2(s) <=> Pb+2 + 2Cl-	-4.81	Lothenbach et al. (1999)	na	na	
PbOHCl(cr) <=> Pb+2 + Cl- + H2O - H+	0.62	Lothenbach et al. (1999)	na	na	
PbF2(s) <=> Pb+2 + 2F-	-7.52	Lothenbach et al. (1999)	na	na	
PbFCl(matlockite) <=> Pb+2 + F- + Cl-	-8.82	Lothenbach et al. (1999)	na	na	
PbCO3(cerussite) <=> Pb+2 + CO3-2	-13.23	Lothenbach et al. (1999)	na	na	
Pb3(CO3)2(OH)2(hydrocerussite) <=> 3Pb+2 + 2CO3-2 + 2H2O - 2H+	-17.64	Lothenbach et al. (1999)	na	na	
Pb10(CO3)6(OH)6O(plumbonacrite)					

Appendix III: Availability of enthalpy data in relevant databases(cont.)

Reactions	JNC-TDB (Yui et al., 1999)		NEA		remark
	log K	Reference	$\Delta_f H^\circ$	$\Delta_f H^\circ$	
PbOHNO3(cr) <=> Pb+2 +NO3- +H2O -H+	2.94	Lothenbach et al. (1999)	na	na	
PbHPO4(s) <=> Pb+2 +H+ +PO4-3	-23.78	Lothenbach et al. (1999)	na	na	
Pb3(PO4)2(s) <=> 3Pb+2 +2PO4-3	-44.4	Lothenbach et al. (1999)	na	na	
Pb4(PO4)2O(s) <=> 4Pb+2 +2PO4-3 +H2O -2H+	-37.09	Lothenbach et al. (1999)	na	na	
Pb(H2PO4)2(s) <=> Pb+2 +2PO4-3 +2H+	-48.94	Lothenbach et al. (1999)	na	na	
Pb5(PO4)3OH (hydroxy pyromorphite) <=> 5Pb+2 +3PO4-3 +H2O -H+	-62.8	Lothenbach et al. (1999)	na	na	
Pb5(PO4)3Cl(chloro pyromorphite) <=> 5Pb+2 +3PO4-3 +Cl-	-84.4	Lothenbach et al. (1999)	na	na	
Pb5(PO4)3F(fluoro pyromorphite) <=> 5Pb+2 +3PO4-3 +F-	-71.6	Lothenbach et al. (1999)			
PbSO4(anglesite) <=> Pb+2 +SO4-2	-7.81	Lothenbach et al. (1999)	na	na	
PbS(galena) +H+ <=> Pb+2 + HS-	-12.17	Lothenbach et al. (1999)	na	na	
Reaction Involving Solution Species					
Pb+2 +H2O -H+ <=> PbOH+	-7.51	Lothenbach et al. (1999)	na	na	
Pb+2 + 2H2O - 2H+ <=> Pb(OH)2(aq)	-16.95	Lothenbach et al. (1999)	na	na	
Pb+2 + 3H2O - 3H+ <=> Pb(OH)3-	-28.02	Lothenbach et al. (1999)	na	na	
2Pb+2 + H2O -H+ <=> Pb2OH+3	-7.18	Lothenbach et al. (1999)	na	na	
4Pb+2 + 4H2O -4H+ <=> Pb4(OH)4+4	-20.63	Lothenbach et al. (1999)	na	na	
3Pb+2 + 4H2O -4H+ <=> Pb4(OH)4+2	-22.48	Lothenbach et al. (1999)	na	na	
3Pb+2 + 5H2O -5H+ <=> Pb4(OH)5+	-30.72	Lothenbach et al. (1999)	na	na	
6Pb+2 + 8H2O -8H+ <=> Pb6(OH)8+4	-42.68	Lothenbach et al. (1999)	na	na	
Pb+2 +Cl- <=> PbCl+	1.55	Lothenbach et al. (1999)	na	na	
Pb+2 +2Cl- <=> PbCl2(aq)	2	Lothenbach et al. (1999)	na	na	
Pb+2 +3Cl- <=> PbCl3-	2.01	Lothenbach et al. (1999)	na	na	
Pb+2 +4Cl- <=> PbCl4-2	1.35	Lothenbach et al. (1999)	na	na	
Pb+2 +F- <=> PbF+	2.27	Lothenbach et al. (1999)	na	na	
Pb+2 +2F- <=> PbF2(aq)	3.01	Lothenbach et al. (1999)	na	na	
Pb+2 +F- +Cl- <=> PbFCl(aq)	3.55	Lothenbach et al. (1999)	na	na	
Pb+2 +CO3-2 <=> PbCO3(aq)	7.3	Lothenbach et al. (1999)	na	na	
Pb+2 +2CO3-2 <=> Pb(CO3)2-2	10.13	Lothenbach et al. (1999)	na	na	
Pb+2 +NO3- <=> PbNO3+	1.06	Lothenbach et al. (1999)	na	na	
Pb+2 +2NO3- <=> Pb(NO3)2(aq)	1.48	Lothenbach et al. (1999)	na	na	
Pb+2 +3NO3- <=> Pb(NO3)3-	0.76 *1	Lothenbach et al. (1999)	na	na	
Pb+2 +H+ +PO4-3 <=> PbHPO4(aq)	15.45 *1	Lothenbach et al. (1999)	na	na	
Pb+2 +2H+ +PO4-3 <=> PbH2PO4+	21.05 *1	Lothenbach et al. (1999)	na	na	
Pb+2 +SO4-2 <=> PbSO4(aq)	2.82	Lothenbach et al. (1999)	na	na	
Pb+2 +2SO4-2 <=> Pb(SO4)2-2	2.37 *1	Lothenbach et al. (1999)	na	na	
Pb+2 +2HS- <=> Pb(HS)2(aq)	12.34 *1	Lothenbach et al. (1999)	na	na	
Pb+2 +3HS- <=> Pb(HS)3-	13.59 *1	Lothenbach et al. (1999)	na	na	
Bi					
Reaction Involving Solid Compounds					
a-Bi2O3(cr) +6H+ <=> Bi+3 +3H2O	0.76	Lothenbach et al. (1999)	na	na	
BiOCl(s) +2H+ <=> Bi+3 +H2O +Cl-	-8.47	Lothenbach et al. (1999)	na	na	
(BiO)2CO3(cr) +4H+ <=> 2Bi+3 +2H2O +CO3-2	-14.27	Lothenbach et al. (1999)	na	na	
(BiO)4(OH)2CO3(cr) +10H+ <=> 4Bi+3 +6H2O + CO3-2	-8.68	Lothenbach et al. (1999)	na	na	
BiONO3(s) +2H+ <=> Bi+3 +H2O +NO3-	-2.75	Lothenbach et al. (1999)	na	na	
Bi(cr) <=> Bi+3 + 3e-	-16.74	Lothenbach et al. (1999)	na	na	
Reaction Involving Solution Species					
Bi+3 +H2O <=> BiOH2+ +H+	-0.92	Lothenbach et al. (1999)	na	na	
Bi+3 +2H2O <=> Bi(OH)2+ +2H+	-2.56	Lothenbach et al. (1999)	na	na	
Bi+3 +3H2O <=> Bi(OH)3(aq) +3H+	-5.31	Lothenbach et al. (1999)	na	na	
Bi+3 +4H2O <=> Bi(OH)4- +4H+	-18.71	Lothenbach et al. (1999)	na	na	
6Bi+3 +12H2O <=> Bi6(OH)12+6 +12H+	1.34	Lothenbach et al. (1999)	na	na	
9Bi+3 +20H2O <=> Bi9(OH)20+7 +20H+	-1.36	Lothenbach et al. (1999)	na	na	
9Bi+3 +21H2O <=> Bi9(OH)21+6 +21H+	-3.25	Lothenbach et al. (1999)	na	na	
9Bi+3 +22H2O <=> Bi9(OH)22+5 +22H+	-4.86	Lothenbach et al. (1999)	na	na	
3Bi+3 +4H2O <=> Bi3(OH)4+5 +4H+	-0.8	Lothenbach et al. (1999)	na	na	
Bi+3 +Cl- <=> BiCl+2	3.65	Lothenbach et al. (1999)	na	na	
Bi+3 +2Cl- <=> BiCl2+	5.85	Lothenbach et al. (1999)	na	na	
Bi+3 +3Cl- <=> BiCl3(aq)	7.62	Lothenbach et al. (1999)	na	na	
Bi+3 +4Cl- <=> BiCl4-	9.06	Lothenbach et al. (1999)	na	na	
Bi+3 +5Cl- <=> BiCl5-2	8.33 *1	Lothenbach et al. (1999)	na	na	
Bi+3 +6Cl- <=> BiCl6-3	7.64 *1	Lothenbach et al. (1999)	na	na	
Bi+3 +NO3- <=> BiNO3+2	1.97	Lothenbach et al. (1999)	na	na	
Bi+3 +2NO3- <=> Bi(NO3)2+	2.95	Lothenbach et al. (1999)	na	na	
Bi+3 +3NO3- <=> Bi(NO3)3(aq)	3.62	Lothenbach et al. (1999)	na	na	
Bi+3 +4NO3- <=> Bi(NO3)4-	3.09	Lothenbach et al. (1999)	na	na	
Bi+3 +Cl- +NO3- <=> BiClNO3+	5.16	Lothenbach et al. (1999)	na	na	
Bi+3 +Cl- +2NO3- <=> BiCl(NO3)2(aq)	5.28	Lothenbach et al. (1999)	na	na	

Appendix III: Availability of enthalpy data in relevant databases(cont.)

Reactions	JNC-TDB (Yui et al., 1999)		NEA		remark
	log K	Reference	$\Delta_f H^\circ$	$\Delta_f H^\circ$	
Bi+3 +2Cl ⁻ +2NO ₃ ⁻ <=> BiCl ₂ (NO ₃) ₂ -	5.75	Lothenbach et al. (1999)	na	na	
Bi+3 +3Cl ⁻ +NO ₃ ⁻ <=> BiCl ₃ NO ₃ -	8.09	Lothenbach et al. (1999)	na	na	
Po					
Reaction Involving Solid Compounds					
Po(OH) ₄ (s) +4H ⁺ <=> Po ⁴⁺ + 4H ₂ O	19.52	Wagman et al. (1982)	na	na	
Ra					
Reaction Involving Solid Compounds					
RaSO ₄ (s) <=> Ra ²⁺ + SO ₄ ²⁻	-10.4	Cross et al. (1987)	na	na	
RaCO ₃ (s) <=> Ra ²⁺ + CO ₃ ²⁻	-7	Cross et al. (1987)	na	na	
Reaction Involving Solution Species					
Ra ²⁺ + H ₂ O <=> RaOH ⁺ +H ⁺	-13.6	Cross et al. (1987)	na	na	
Ra ²⁺ + SO ₄ ²⁻ <=> RaSO ₄ (aq)	0.022	Cross et al. (1987)	na	na	
Ni					
Reaction Involving Solid Compounds					
Ni(OH) ₂ (s) <=> Ni ²⁺ +2H ₂ O -2H ⁺	12.73	Baeyens and McKinley (1989)	na	na	
NiO(cr) <=> Ni ²⁺ +H ₂ O -2H ⁺	12.44	Baeyens and McKinley (1989)	na	na	
NiS(millerite) <=> Ni ²⁺ +SO ₄ ²⁻ -4H ₂ O +8H ⁺ +8e ⁻	-42.83	Baeyens and McKinley (1989)	na	na	
Ni ₃ S ₂ (heazlewoodite) <=> 3Ni ²⁺ + 2SO ₄ ²⁻ -8H ₂ O +16H ⁺ +18e ⁻	-82	Baeyens and McKinley (1989)	na	na	
NiCO ₃ (s) <=> Ni ²⁺ + CO ₃ ²⁻	-6.97	Baeyens and McKinley (1989)	na	na	
Ni ₃ (PO ₄) ₂ (cr) <=> 3Ni ²⁺ +2PO ₄ ³⁻	-29.59	Baeyens and McKinley (1989)	na	na	
Ni ₂ P ₂ O ₇ (cr) <=> 2Ni ²⁺ +2PO ₄ ³⁻ -H ₂ O +2H ⁺	-33.57	Baeyens and McKinley (1989)	na	na	
Ni ₂ SiO ₄ (olivine) <=> 2Ni ²⁺ +H ₄ SiO ₄ (aq) -4H ⁺	18.84	Baeyens and McKinley (1989)	na	na	
Ni ₂ SiO ₄ (spinel) <=> 2Ni ²⁺ +H ₄ SiO ₄ (aq) -4H ⁺	20.24	Baeyens and McKinley (1989)	na	na	
Ni ₂ SiO ₃ (cr) <=> Ni ²⁺ +H ₄ SiO ₄ (aq) -H ₂ O -3H ⁺	-2.28	Baeyens and McKinley (1989)	na	na	
Reaction Involving Solution Species					
Ni ²⁺ +H ₂ O -H ⁺ <=> NiOH ⁺	-9.9	Cross et al. (1987)	na	na	
Ni ²⁺ +2H ₂ O -2H ⁺ <=> Ni(OH) ₂ (aq)	-19	Cross et al. (1987)	na	na	
Ni ²⁺ +3H ₂ O -3H ⁺ <=> Ni(OH) ₃ ⁺	-30	Cross et al. (1987)	na	na	
2Ni ²⁺ +H ₂ O -H ⁺ <=> Ni ₂ OH ⁺	-10.7	Cross et al. (1987)	na	na	
4Ni ²⁺ +4H ₂ O -4H ⁺ <=> Ni ₄ (OH) ₄ ⁴⁺	-27.7	Cross et al. (1987)	na	na	
Ni ²⁺ + CO ₃ ²⁻ <=> NiCO ₃ (aq)	4	Berner, U. (1998)	na	na	
Ni ²⁺ + SO ₄ ²⁻ <=> NiSO ₄ (aq)	2.32	Cross et al. (1987)	na	na	
Se					
Reaction Involving Solid Compounds					
Se(cr) <=> SeO ₄ ²⁻ -4H ₂ O +8H ⁺ +6e ⁻	-88.92	Cross et al. (1987)	na	na	
SeO ₂ (cr) <=> SeO ₄ ²⁻ -2H ₂ O +4H ⁺ +2e ⁻	-35.82	Cross et al. (1987)	na	na	
SeO ₃ (cr) <=> SeO ₄ ²⁻ -H ₂ O +2H ⁺	19.2	Cross et al. (1987)	na	na	
Se ₂ O ₅ (cr) <=> 2SeO ₄ ²⁻ -3H ₂ O +6H ⁺ +2e ⁻	-19.6	Cross et al. (1987)	na	na	
FeSe ₂ (cr) <=> 2SeO ₄ ²⁻ +Fe ₂ ⁺ -8H ₂ O +16H ⁺ +14e ⁻	-181.1	Cross et al. (1987)	na	na	
FeSe(cr) <=> SeO ₄ ²⁻ +Fe ₂ ⁺ -4H ₂ O +8H ⁺ +8e ⁻	-84.78	Mills (1974), Silva et al. (1995), Wagman et al. (1982), Robie&Hemingway (1995)	na	na	
Reaction Involving Solution Species					
SeO ₄ ²⁻ -H ₂ O +2H ⁺ +2e ⁻ <=> SeO ₃ ²⁻	27.578*2	Silva et al. (1985) and Wagman et al (1982)	na	na	
SeO ₄ ²⁻ -H ₂ O +3H ⁺ +2e ⁻ <=> HSeO ₃ ⁻	35.978*2	Silva et al. (1985) and Wagman et al (1982)	na	na	
SeO ₄ ²⁻ -H ₂ O +4H ⁺ +2e ⁻ <=> H ₂ SeO ₃ (aq)	38.783*2	Silva et al. (1985) and Wagman et al (1982)	na	na	
SeO ₄ ²⁻ -4H ₂ O +8H ⁺ +8e ⁻ <=> Se ²⁻	66.3	Cross et al. (1987)	na	na	
SeO ₄ ²⁻ -4H ₂ O +9H ⁺ +8e ⁻ <=> HSe ⁻	81.2	Cross et al. (1987)	na	na	
SeO ₄ ²⁻ -4H ₂ O +10H ⁺ +8e ⁻ <=> H ₂ Se(aq)	85.1	Cross et al. (1987)	na	na	
SeO ₄ ²⁻ +H ⁺ <=> HSeO ₄ ⁻	1.9	Cross et al. (1987)	na	na	
Zr					
Reaction Involving Solid Compounds					
ZrO ₂ (am) <=> Zr(OH) ₄ (aq) -2H ₂ O	-8	not reported	na	na	
Zr(OH) ₄ (aq) +H ₂ O -H ⁺ <=> Zr(OH) ₅ ⁻	-10	not reported	na	na	

I) Check marks for reactions; PHREEQE.JNC from Arthur et al. (1999)

II) Check marks for reactions; NEA-TDB from Grenthe et al. (1992)

III) Check marks for product species; Nagra-TDB from Pearson and Berner (1991)

IV) Check marks for reactions where DH of all involved species are found; SPRONS.JNC from Arthur et al. (1999)

V) Check marks for reactions; HATCHES 3.0 from Pearson et al. (1992)

*log K value and reaction formalism are equal to Appendix A2

付録 2

COLFRAC-MRL ユーザーズガイド
(オハイオ州立大学による成果報告)

COLFRAC-MRL User's Guide

A Numerical Model for
Two-Dimensional, Saturated
Groundwater Flow and Colloid-Facilitated Solute
Transport in Porous or
Discretely-Fractured Porous Media

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Disclaimer

Although great care has been taken in preparing the COLFRAC-MRL routines and documentation, the authors cannot be held responsible for any errors or omissions. As such, this code is offered 'as is'. The user is expected to be familiar with the finite-element and finite-difference methods, preconditioned iterative solver techniques, and FORTRAN programming. The authors make no warranty of any kind, expressed or implied. The authors shall not be liable for any damages arising from a failure of these subroutines to operate in the manner desired by the user. The authors shall not be liable for any damage to data or property, which may be caused directly or indirectly by use of the subroutines. In no event will the authors be liable for any damages, including, but not limited to, lost profits, lost savings or other incidental or consequential damages arising out of the use, or inability to use, these subroutines. Use, attempted use, and/or installation of this program shall constitute implied acceptance of the above conditions.

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1 Introduction

COLFRAC-MRL is a highly efficient numerical model, which simulates combined steady-state groundwater flow and transient colloid-facilitated contaminant transport in porous or discretely-fractured porous media. Although it is normally applied to cross-sectional problems, COLFRAC-MRL can also be applied to plan-view problems, bearing in mind that the fractures are fully penetrating.

Computational efficiency for large-grid problems is achieved by employing a preconditioned, ORTHOMIN-accelerated iterative solver. Groundwater flow and contaminant transport (including matrix diffusion and advection in the porous matrix) are rigorously treated in both fractures and porous matrix blocks. Chemical reactions in the form of first-order decay and linear equilibrium and kinetic sorption are also accommodated.

The application of the program to complex real-world problems, which often require a fine spatial discretization, is facilitated by a pre-processor, PRECLD, which reads a data file containing relevant high-level descriptive information, and translates this information into a set of COLFRAC-MRL compatible input data files. Post-processing routines can then be used to produce plotted or printed output.

This guide is organized as follows. Chapters 2 to 4 discuss the function and operation of the various programs required to solve a given problem. Chapter 5 presents an example problem “sfbase”. The step-by-step procedure to perform a COLFRAC-MRL simulation is outlined below:

1. Create or modify a pre-processor (.PRE) file and run PRECLD to create the COLFRAC-MRL input files (Chapter 2).
2. Run COLFRAC-MRL to create the hydraulic head and concentration file (Chapter 3)
3. Run the post-processing program OUT2TECPLOT to produce output files that are in a format that can be read by the Tecplot (www.tecplot.com) visualization software developed by Amtec Engineering (Chapter 4).

2 PRECLD

PRECLD is a preprocessor, which reads a high-level user-defined data file (which contains problem specific information) and constructs all necessary input files for the COLFRAC-MRL program.

2.1 Starting PRECLD

Issue the appropriate command to run the executable program PRECLD. You should see the following:

' Give prefix of problem filename...'

This prompt is asking for the prefix of the .PRE file containing the problem-specific information necessary to construct the COLFRAC-MRL data files. Type in the prefix (up to 7 characters) and press return. The program automatically searches for the appropriate file by appending the suffix .PRE. The programs are designed to be run interactively unless you start them through some system dependent batch file and supply what would normally be keyboard input in the batch file.

PRECLD will now read the input .PRE data file and use the prefix to construct a set of output files with different extensions.

2.2 Setting up the PRECLD input file

The input data file for PRECLD is a special file with a three-letter extension .PRE. It can be divided into the following groups of data:

- Problem title and simulation control switches
- Overall problem size and grid constraints
- Grid refinement zones
- Porous media zones
- Fracture zones (if geologic medium is fractured)
- Head boundary conditions
- Decay constants applied to transport boundary conditions
- Transport boundary conditions
- Slice data (for calculating nodal groundwater and solute fluxes crossing specified slice Internal to domain)

- Non-varying physical parameters such as fluid density and viscosity
- Matrix equation solver parameters

A detailed description of the input data contained in each of these subsections is described below, but first, there are a few general points regarding data input, which should be mentioned.

The data items are listed and described in the order that they appear in the input data file. With the exception of the simulation control parameters (true/false switches), the following conventions or nomenclature are used throughout:

dataitem1 The FORTRAN variable name for the item is presented in bold font, in this case dataitem1. If it is lowercase, then this line must be present in the data file. For example, fluid density is a required data item for all problems although its value is only used when fractures are present.

dataitem2 Items set in italics are optional. Whether or not they appear in the data file is problem dependent. For example, vertical fracture zone data may or may not apply to a specific problem.

Free format is used for all reads except titles, which are A80 and file names, which are A32. In other words, real numbers can be input in E or F format (1.0e+3 or 1000.0 are both acceptable), with a blank or comma separating each required variable. Integer values are also separated by a blank or comma.

You must use consistent units for length and time throughout the data file. These can be any units (e.g. meters or feet for length, seconds, days or years for time). Be sure to check constants such as diffusion coefficients, acceleration due to gravity, fluid density etc. for proper units. For example, suppose your problem was 200 meters in length and you wanted to see a plume after 500 years. The easiest way to set up this problem is to specify everything in consistent units of m.year.kilograms. Hydraulic conductivity would be expressed as meters/year, acceleration due to gravity as metres/year², etc. Dimensionality is indicated where appropriate (eg. L/T is length/time, M is mass).

Currently, some input checking is done to ensure that problem dimensions input by the user are correct. They ensure that all sub regions of the problem fall within the overall problem domain, and that the values are listed in the proper order (e.g. that minimums are less than maximums), and that the arrays in the compiled code are of adequate size for the problem at hand.

Most of the titles that the user can give for the various porous media, fracture and boundary condition zones serve a dual purpose. This is because the title is used to indicate the end of input for a given type of data. In this case, specifying the first three characters of the title as 'don' signals the end of input. For example, suppose we want two different porous media zones for our problem. We would set up the data file like so:

Porous media zone 1 title
(zone 1 data would go here)
Porous media zone 2 title
(zone 2 data would go here)
Done porous media zones

PRECLD recognizes the character sequence `done' as a signal to end the current mode of input, in this case, reading porous media zone data. The program PRECLD would loop twice to read two porous media zones because the first three letters of the title are not `done'. The third time though, they are `done', and the porous media zone read loop is exited. Note that any mixture of upper and lowercase letters will satisfy the condition (i.e. Done = DONE = don etc.).

Titles which are given for boundary condition input data may also have an additional set of four three-letter character sequences. This sequence is used to indicate which of the four possible boundaries the data should be applied to. The four sequences are any uppercase/lowercase form of `top, bot, lef, rig '. We will explicitly identify such titles in the text associated with the variable.

2.2.0 Simulation control parameters

In reviewing this section, the user is urged to examine one of the .PRE files contained on the disk.

title A descriptive problem title up to 80 characters.

ldiff (Diffusion only)

- .true.** Do not perform a groundwater flow solution, set the Darcy fluxes to zero and treat the transport problem as transient diffusion only.
- .false.** No action.

lflow (Flow solution)

- .true.** Determine hydraulic heads at each node and Darcy fluxes at each element and use the Darcy fluxes for the transport solution if transport is desired.
- .false.** Read the results of a previous flow solution stored on disk. If the properties of the physical system have been modified since the files were constructed, you must be sure that the changes will not affect the flow solution, or inappropriate results may arise. If in doubt, solve for flow again to update the Darcy fluxes on disk.

ltrans (Transport solution)

- .true.** Solve the transport problem and write the concentrations to a binary file.
- .false.** Do not solve for transport.

lfrac (Fractured/Porous media)

- .true.** Treat the system as a discretely-fractured medium.
- .false.** Treat the system as a porous medium, ignoring any discrete fracture data given; however, one can still treat the medium in a dual-porosity manner for transport.

This means you do not have to remove the discrete-fracture data from the file if all you want to do is observe how the system behaves if no fractures are present.

lkdfm (Finite element/finite difference)

- .true.** Use a finite-element formulation (linear rectangular elements) to discretize the flow and transport equations for the porous matrix.
- .false.** Use a 5-point finite-difference formulation for the porous matrix. In order to take advantage of this memory-conserving feature, be sure to change the appropriate

dimensioning parameters in the include file COLFRAC.PRM and re-compile the source codes.

lpms (Print mesh data)

.true. Print mesh data including nodal coordinates, rectangular and (optional) fracture line element incidences in the ascii (.lst) file.

.false. Do not print the mesh data produced by COLFRAC.

lpvel (Print Darcy flux data)

.true. Print Darcy flux data in the ascii (.lst) file.

.false. Do not print Darcy flux data produced by COLFRAC.

lphed (Print head data)

.true. Print hydraulic head data in the ascii (.lst) file.

.false. Do not print hydraulic head data produced by COLFRAC.

ldvel (Write Darcy flux data)

.true. Write Darcy flux data to the binary (.vel) file. If you intend to turn off the flow solution (switch lflow) you must write the Darcy fluxes to disk at least once before performing an advective-dispersive transport solution.

.false. Do not write Darcy flux data.

ldhed (Write head data)

.true. Write hydraulic head data to the binary (.h01) file. This file is needed only for plotting or other post processing.

.false. No action.

lperm (Element/zoned hydraulic conductivity)

.true. Treat porous media hydraulic conductivities as a property of rectangular elements, which are defined element by element. Causes COLFRAC to read the values from the file REFIX.REK, which will override any zonally defined values. The file containing the hydraulic conductivities should be created by the following FORTRAN statements:

```
open(iunit, file=ifile, status='unknown', form='unformatted')  
write(iunit) ne  
write(iunit) (ckxx(i), ckzz(i), i=1, ne)
```

Where *iunit* is the FORTRAN output unit number, *ifile* is the file name, *ne* is the number of rectangular (ie. porous media) elements and *ckxx(i)* and *ckzz(i)* are the hydraulic conductivities (REAL*8) in the x and z direction respectively of the I'th element. Note the following:

1. The open statement accesses an UNFORMATTED or binary file.
2. Internal storage of integers is not declared explicitly as INTEGER*4 or INTEGER*2. This is set by a compiler default option. This allows you to save significant amounts of memory

when running smaller problems by using INTEGER*2 formats. You may have to declare integer formats explicitly in any program which writes a file to be read by COLFRAC in order to match the format set at compile time.

3. You may have to increase the array size in the file COLFRAC.PRM and re-compile the source code (the .lst file will tell you if re-compilation is necessary).
- .false.** Treat porous media hydraulic conductivities as a zoned property. Values for groups of elements are assigned according to the zones defined below in Section 2.2.2. This is the normal mode of operation and is used to conserve memory.

lap (Element/zoned fracture aperture)

- .true.** Treat fracture apertures as a property of line elements, which are defined element by element. Causes COLFRAC to read the values from the file PREFIX.FAP, which will override any zonally defined values. The file containing the hydraulic conductivities should be created by the following FORTRAN statements:

```
open(iunit,file=ifile,status='unknown',form='unformatted')
write(iunit) nfeh, nfev
write(iunit) (aph(i),i=1,nfeh)
write(iunit) (apv(i),i=1,nfev)
```

Where *iunit* is the FORTRAN output unit number, *ifile* is the file name, *nfeh* and *nfev* are the number of line (i.e. fracture) vertical and horizontal elements, respectively, and *aph(i)* and *apv(i)* are the fracture aperture for the horizontal and vertical fractures, respectively of the *I*'th element. Note the following:

1. The open statement accesses an UNFORMATTED or binary file.
 2. Internal storage of integers is not declared explicitly as INTEGER*4 or INTEGER*2. This is set by a compiler default option. This allows you to save significant amounts of memory when running smaller problems by using INTEGER*2 formats. You may have to declare integer formats explicitly in any program which writes a file to be read by COLFRAC in order to match the format set at compile time.
 3. You may have to increase the array size in the file COLFRAC.PRM and re-compile the source code (the .lst file will tell you if re-compilation is necessary).
- .false.** Treat fracture aperture as a zoned property. Values for groups of elements are assigned according to the zones defined below in Section 2.2.3. This is the normal mode of operation and is used to conserve memory.

lslice (Flux crossing a plane)

- .true.** Compute the fluid and mass flux crossing an arbitrary vertical or horizontal slice internal to the problem domain. This is useful for computing the groundwater flow rate and the contaminant mass crossing an internal boundary such as an aquifer/aquitard interface. In order to assign positive (inflow) and negative (outflow) attributes to fluxes normal to an internal slice, we adopt the following conventions. The region interior to a vertical slice is located to the left of the slice. The region interior to a horizontal slice is located above the slice. If the normal component of the nodal fluid or mass flux is positive, the quantity

is moving into the region interior to the slice. For example, if the flow is from left to right and a vertical slice is specified, then the normal components of the fluid and mass fluxes will be negative (i.e. leaving the region interior to the slice). The nodal groundwater flow results are contained in the .lst file. The time-domain mass transport results are output on a node-by-node basis along the slice in PREFIX.FAC file. Only one slice per run is allowed. As in the case of the fluid and mass balance calculations, some restrictions apply as to when this switch can be set. Warnings are issued to the COLFRAC output listing (.lst) file if the flow solution needs to be recalculated.

.false. Do not compute flux crossing a slice.

lrstrt (Restart)

.true. Causes COLFRAC to read the initial concentrations for all nodes from the file PREFIX.RST. A file called PREFIXO.RST is created automatically by COLFRAC. This file can be renamed (i.e. drop the o appended to the prefix) with the appropriate prefix to be read by COLFRAC as a restart file. The feature is useful if the transport problem is to be restarted with a new steady-state groundwater flow solution.

.false. Use the initial condition data as set up in Section 2.2.6.

kinec (kinetic reaction between solute and colloid)

.true. Treat reaction between solute and colloids as a kinetic reaction.

.false. Treat reaction between solute and colloids as an equilibrium reaction.

klangc (Langmuir reaction between solute and colloid)

.true. Perform Langmuir type reaction for solute/colloids.

.false. Perform Freundlich type reaction for solute/colloids.

ksrbst (Sorption start time at source)

.true. Sorption at source starts BEFORE colloids migrate in fracture.

.false. Sorption at source starts AFTER colloids migrate in fracture.

ksrbaf (Sorption type at source)

.true. Sorption at source is always equilibrium reaction.

.false. Sorption at source follows solute-colloid reaction in fracture

kinef (kinetic reaction between solute and fracture surface)

.true. Treat reaction between solute and fracture surface as a kinetic reaction.

.false. Treat reaction between solute and fracture surface as an equilibrium reaction.

klangf (Langmuir reaction between solute and fracture surface)

.true. Perform Langmuir type reaction for solute-fracture surface.

.false. Perform Freundlich type reaction for solute-fracture surface.

klist (Print concentration values)

.true. Print concentration values in the ascii (.lst) file.

.false. Do not print concentration values produced by COLFRAC.

kmslmp (mass lumping formulation for matrix assembly)

.true. Mass lumping formulation required for non-linear (Langmuir) sorption reaction.

.false. Consistence formulation for matrix assembly. Use this option if Freundlich reaction is used.

2.2.1 Overall problem size and grid constraints

xmin, xmax

The minimum and maximum x-values (L) of the rectangle, which completely bounds the problem. Currently, xmin should always be specified as zero, xmax can be any positive real number in machine range. By convention, the origin of the grid (0,0) is located at the lower left corner. If any subsequent user-specified x-coordinate is not within the range of xmin to xmax inclusive, a warning will be echoed to the screen and printed in the .eco file produced by PRECLD and program execution will be halted.

zmin, zmax

The minimum and maximum z-values (L) of the rectangle, which completely bounds the problem. Currently, zmin should always be specified as zero, zmax can be any positive real number in machine range. If any subsequent user-specified z-coordinate is not within the range of zmin to zmax inclusive, a warning will be echoed to the screen and printed in the .eco file and program execution will be halted.

dxmax, dzmax

These parameters impose a maximum allowable element length in the x and z directions respectively. For example, if any two adjacent columns of nodes were greater than dxmax units apart, a number of intervening columns would be generated such that the new average nodal spacing between columns would be less than dxmax. If any subsequent user-specified z-coordinate is not within the range of zmin to zmax inclusive, a warning will be echoed to the screen and printed in the .eco file and program execution will be halted.

nseed

Seed for random number generation in order to perform random fracture network generation.

2.2.2 Porous media zones

You must read in at least one zone, preferably the first, whose size matches that of the overall domain and through which default porous media properties are assigned.

btitle(mxzone)

The title of the porous media zone whose data follows. It can be any alphanumeric string up to 80 characters. `Done' ends input.

xbmin(),xbmax()

The minimum and maximum x-values (L) of the rectangle whose elements are assigned the properties that follow below.

zbmin(),zbmax()

As above except for the z-direction (L).

ckxx(),ckzz()

Hydraulic conductivity (L/T) in the x- and z-direction.

al(),at()

Longitudinal and transverse dispersivity for the solute (aqueous-phase contaminant) (L).

alcld(),atcld(),dstarcld()

Longitudinal and transverse dispersivity for the colloids(L), effective molecular diffusion coefficient for the colloid (L^2/T).

filMtx()

Colloid filtration coefficient (L^{-1}).

Kmob(),Kfld()

Equilibrium solute-colloid partition coefficient for the mobile and filtered colloids (L^3/M).

dstar(),por(),retard()

Effective molecular diffusion coefficient for the aqueous-phase solute (L^2/T), porosity (dimensionless), retardation factor (dimensionless) for the aqueous-phase solute.

2.2.3 Fracture zones

The domain is composed of rectangular elements, which represent the porous medium and one-dimensional line elements, which represent the fractures. PRECLD only generates fractures, which are coincident with the sides of the rectangular element so the fractures are limited to horizontal or vertical orientations. It is possible that diagonal fractures could be generated but this option has not been tested to date. The rectangular elements can also be distorted slightly without much loss of accuracy. Future versions may be extended to handle triangular or isoperimetric elements.

Fracture zones are subdivided into vertical and horizontal fracture types for the purposes of input. These two types are further subdivided into regular (i.e. user defined locations and lengths) and randomly spaced vertical and/or horizontal fractures, making a total of four sections of input for defining fractures. The following two seeds are always read in but are only used when generating sets of randomly spaced fractures.

2.2.3.1 Regular vertical fracture zones

vftitle(mxzonev)

The title of the vertical fracture zone whose data follows. It can be any alphanumeric string up to 80 characters. `Done' ends input.

xvfmin(),xvfmax()

The minimum and maximum x-values (L) of the rectangle within which the fracture line elements are assigned the fracture properties that follow below.

zvfmin(),zvfmax()

As above except for the z-direction (L).

vspace()

The fracture spacing (L). Starting at and including xvfmin(), fractures will be generated every vspace() length units until xvfmax() is exceeded. The fractures will extend vertically from

zvfmin() to zvfmax(). If vspace() is greater than the zone width xvfmax()-xvfmin() then a single vertical fracture will be generated at xvfmin().

alfracv()

Longitudinal dispersivity (L) along the fractures in the zone.

alphafv()

Forward kinetic reaction rate constant for solute-fracture surface ($L^3/M/T$). Note: the ratio of **alphafv/betafv** has the same units as the equilibrium partition coefficient, K_d (i.e., L^3/M).

betafv()

Backward kinetic reaction rate constant ($1/T$) for solute-fracture surface.

smaxfv()

Maximum sorbed concentration for solute-fracture surface (Langmuir reaction).

apv ()

The aperture of the fractures in the zone.

alfracmv()

Longitudinal dispersivity (L) for colloid along the fractures in the zone.

ftfracv()

Filtration coefficient ($1/L$) for colloid particles.

alphacfv()

Forward kinetic reaction rate constant for solute-colloid ($L^3/M/T$). Note: the ratio of **alphacfv/betacfv** has the same units as the equilibrium partition coefficient, K_d (i.e., L^3/M).

betacfv()

Backward kinetic reaction rate constant ($1/T$) for solute-colloid.

smaxcfv()

Maximum sorbed concentration for solute-colloid (Langmuir reaction).

2.2.3.2 Random vertical fracture zones

fxmin

This parameter imposes a minimum requirement on the spacing of randomly located vertical fractures. fxmin is the minimum allowable distance between any two randomly located fractures. Increasing fxmin reduces the number of fractures generated, at the expense of the degree of detail which can be represented.

nnxm

This parameter imposes a minimum requirement on the discretization between randomly located vertical fractures. nnxm is the minimum number of nodes which must be generated in the horizontal direction, between any two vertical fractures. In practice, there must be some nodes between two fractures in order to accurately account for the groundwater flow and matrix diffusion in the matrix blocks. Increasing nnxm causes the total number of nodes to increase, and in the case of dense arrays of fractures may quickly exhaust available memory. Our experience to date would suggest that nnxm equal to 3 is adequate, but experimentation is encouraged.

rvftitle(mxzonev)

The title of the vertical fracture zone whose data follows. It can be any alphanumeric string up to 80 characters. `Done' ends input.

xrvfmin(),xrvfmax()

The minimum and maximum x-values (L) of the rectangle within which the fracture line elements are assigned the fracture properties that follow below.

zrvfmin(),zrvfmax()

As above except for the z-direction (L).

rvidens()

This parameter is used to determine the number of fractures that need to be generated according to the formula:

$$\text{Number of fractures} = \text{AREA}_{\text{zone}} * \text{rvidens}()$$

You can think of rvidens() as an average vertical fracture density for the zone, with the generated spacings being drawn from a uniform probability density function. A random number generator is used to generate an x- and z-coordinate for each fracture midpoint, which falls within the zone limits defined above. NOTE: if the area of the zone is zero no fractures will be generated.

rvlmin(),rvlmax()

A random vertical fracture minimum and maximum target length (L).

The random number generator is used to generate a length which falls in the range defined by these two values, again according to a uniform probability density function.

rvunder(),rvover()

These are logical variables which are used to control whether a random fracture can extend beyond the upper and lower zone boundaries, in this case zrvfmin() and zrvfmax(). If rvunder() is true, then the fracture endpoint can be less than zrvfmin(). If it is false, it will be truncated at zrvfmin(). Rvover() works in the same manner, but applies to the upper zone boundary.

alfracv()

Longitudinal dispersivity (L) along the fractures in the zone.

alphafv()

Forward kinetic reaction rate constant for solute-fracture surface ($L^3/M/T$). Note: the ratio of **alphafv/betafv** has the same units as the equilibrium partition coefficient, K_d (i.e., L^3/M).

betafv()

Backward kinetic reaction rate constant ($1/T$) for solute-fracture surface.

smaxfv()

Maximum sorbed concentration for solute-fracture surface (Langmuir reaction).

apv ()

The aperture of the fractures in the zone.

alfracmv()

Longitudinal dispersivity (L) for colloid along the fractures in the zone.

ftfracv()

Filtration coefficient ($1/L$) for colloid particles.

alphacf()

Forward kinetic reaction rate constant for solute-colloid ($L^3/M/T$). Note: the ratio of ***alphacf/betacf*** has the same units as the equilibrium partition coefficient, K_d (i.e., L^3/M).

betacf()

Backward kinetic reaction rate constant ($1/T$) for solute-colloid.

smaxcf()

Maximum sorbed concentration for solute-colloid (Langmuir reaction).

2.2.3.3 Horizontal fracture zones

hftitle(mxzoneh)

The title of the horizontal fracture zone whose data follows. It can be any alphanumeric string up to 80 characters. `Done' ends input.

xhfmin(),xhfmax()

The minimum and maximum x-values (L) of the rectangle within which the fracture line elements are assigned the fracture properties that follow below.

zhfmin(),zhfmax()

As above except for the z-direction (L).

hspace()

The fracture spacing (L). Starting at an including *zhfmin()*, fractures will be generated every *hspace()* length units until *zhfmax()* is exceeded. The fractures will extend horizontally from *xhfmin()* to *xhfmax()*. If *hspace()* is greater than the zone height *zhfmax()-zhfmin()* then a single horizontal fracture will be generated at *zhfmin()*.

alfrach()

Longitudinal dispersivity (L) along the fractures in the zone.

alphafh()

Forward kinetic reaction rate constant for solute-fracture surface ($L^3/M/T$). Note: the ratio of ***alphafh/betafh*** has the same units as the equilibrium partition coefficient, K_d (i.e., L^3/M).

betafh()

Backward kinetic reaction rate constant ($1/T$) for solute-fracture surface.

smaxfh()

Maximum sorbed concentration for solute-fracture surface (Langmuir reaction).

aph ()

The aperture of the fractures in the zone.

alfracmh()

Longitudinal dispersivity (L) for colloid along the fractures in the zone.

ftfrach()

Filtration coefficient ($1/L$) for colloid particles.

alphacfh()

Forward kinetic reaction rate constant for solute-colloid ($L^3/M/T$). Note: the ratio of ***alphacfh/betacfh*** has the same units as the equilibrium partition coefficient, K_d (i.e., L^3/M).

betacfh()

Backward kinetic reaction rate constant (1/T) for solute-colloid.

smaxcfh()

Maximum sorbed concentration for solute-colloid (Langmuir reaction).

2.2.3.4 Random horizontal fracture zones

fzmin

This parameter imposes a minimum requirement on the spacing of randomly located horizontal fractures. *fzmin* is the minimum allowable distance between any two randomly located fractures. Increasing *fzmin* reduces the number of fractures generated, at the expense of the degree of detail that can be represented.

nnzm

This parameter imposes a minimum requirement on the discretization between randomly located horizontal fractures. *nnzm* is the minimum number of nodes which must be generated in the vertical direction, between any two horizontal fractures.

In practice, there must be some nodes between two fractures in order to accurately account for the groundwater flow and matrix diffusion in the matrix blocks. Increasing *nnzm* causes the total number of nodes to increase, and in the case of dense arrays of fractures may quickly exhaust available memory. Our experience to date would suggest that *nnzm* equal to 3 is adequate, but experimentation is encouraged.

rhftitle(mxzoneh)

The title of the random horizontal fracture zone whose data follows. It can be any alphanumeric string up to 80 characters. `Done` ends input.

xrhfmin(),xrhfmax()

The minimum and maximum x-values (L) of the rectangle within which the fracture line elements are assigned the fracture properties that follow below.

zrhfmin(),zrhfmax()

As above except for the z-direction (L). *rhdens()* This parameter is used to determine the number of fractures which need to be generated according to the formula:

$$\text{Number of fractures} = \text{AREA}_{\text{zone}} * \text{rhdens}()$$

You can think of *rhdens()* as an average horizontal fracture density for the zone, with the generated spacings being drawn from a uniform probability density function. A random number generator is used to generate an x- and z-coordinate for each fracture midpoint, which falls within the zone limits defined above. NOTE: if the area of the zone is zero no fractures will be generated.

rhlmin(),rhlmax()

A random horizontal fracture minimum and maximum target length (L). The random number generator is used to generate a length that falls in the range defined by these two values, again according to a uniform probability density function.

rhunder(),rhoover()

These are logical variables which are used to control whether a random fracture can extend beyond the left and right zone boundaries, in this case *xrhfmin()* and *xrhfmax()*. If *rhunder()* is

true, then the fracture endpoint can be less than `xrhfmin()`. If it is false, it will be truncated at `xrhfmin()`. `Rhover()` works in the same manner, but applies to the upper zone boundary.

alfrach()

Longitudinal dispersivity (L) along the fractures in the zone.

alphafh()

Forward kinetic reaction rate constant for solute-fracture surface ($L^3/M/T$). Note: the ratio of ***alphafh/betafh*** has the same units as the equilibrium partition coefficient, K_d (i.e., L^3/M).

betafh()

Backward kinetic reaction rate constant ($1/T$) for solute-fracture surface.

smaxfh()

Maximum sorbed concentration for solute-fracture surface (Langmuir reaction).

aph ()

The aperture of the fractures in the zone (L).

alfracmh()

Longitudinal dispersivity (L) for colloid along the fractures in the zone.

ftfrach()

Filtration coefficient ($1/L$) for colloid particles.

alphacfh()

Forward kinetic reaction rate constant for solute-colloid ($L^3/M/T$). Note: the ratio of ***alphacfh/betacfh*** has the same units as the equilibrium partition coefficient, K_d (i.e., L^3/M).

betacfh()

Backward kinetic reaction rate constant ($1/T$) for solute-colloid.

smaxcfh()

Maximum sorbed concentration for solute-colloid (Langmuir reaction).

2.2.4 Flow boundary conditions

Flow boundary conditions are subdivided into two types:

1. Specified head (also known as Dirichlet or first-type) where the fluid hydraulic head is fixed at a known value.
2. Specified fluid flux (also known as Neumann or second-type) where the fluid flux is fixed at a known value. By convention, positive fluid fluxes add mass to the system.

These are further subdivided into three modes of input, which are referred to as point values, fill segments and regions. This makes a total of six input areas, each of which are ended with a title whose first three characters are `Done`.

2.2.4.1 Specified head fill segments

A fill segment is a continuous piece of the outer boundary for which you want to specify a boundary condition, in this case the hydraulic head.

hsside(maxbc)

The title of the specified head fill segment whose data follows. It can be any alphanumeric string up to 80 characters. `Rig`, `Lef`, `Top` or `Bot` must be used as the first three letters of the title in order to identify which side the segment lies on. `Done` ends input.

hsmin(),hsmax()

hsmin() and hsmax() define the start and end coordinate points of the specified head fill segment on the selected boundary. On the top or bottom boundary these would represent x-coordinates, while on the right or left boundary they would be z-coordinates.

hsstrt(),hsend()

hsstrt() and hsend() represent start and end head values for this fill segment. Linear interpolation is used to fill in head values for any nodes falling on the segment between hsmin() and hsmax(). To specify a uniform head value along the entire segment, simply make hsstrt()=hsend()=desired value.

2.2.4.2 Specified head points

A point value is an x-, z-coordinate pair, which can be in the interior or on the boundary of the system, for which you want to specify a certain condition, in this case, the head. This could represent for example, a pumping well where the head is maintained at a known value.

hplabel(maxbc)

The title of the specified head point value whose data follows. It can be any alphanumeric string up to 80 characters. `Done` ends input.

hpx(),hpz()

hpx() and hpz() define the x-, z-coordinate of the point where the head is to be specified.

hpval()

hpval() is the desired head value.

2.2.4.3 Specified fluid flux fill segments

We use the same data structure outlined above for specified head fill segments, except we specify fluid flux values instead. These flux values are equivalent to groundwater Darcy fluxes.

fsside(maxbc)

The title of the specified fluid flux fill segment whose data follows. It can be any alphanumeric string up to 80 characters. `Rig`, `Lef`, `Top` or `Bot` must be used as the first three letters of the title in order to identify which side the segment lies on. `Done` ends input.

fsmin(),fsmax()

fsmin() and fsmax() define the start and end points of the fluid flux fill segment on the selected boundary. On the top or bottom boundary these would represent x-coordinates, while on the right or left boundary they would be z-coordinates.

fsstrt(),fsend()

fsstrt() and fsend() represent start and end fluid flux values (L/T) for this segment. Linear interpolation is used to fill in flux values for any nodes falling on the segment between fsmin() and fsmax(). To specify a uniform flux value along the entire segment, simply make

fsstrt(=fsend(=desired value. It is critical to remember that it is the Darcy flux (i.e. $q = -K dh/dx$) which is read; PRECLD handles all conversion to nodal fluxes.

2.2.4.4 Specified fluid flux points

A point value is an x-, z-coordinate pair, which can be in the interior of the system, for which you want to specify a certain condition, in this case, the fluid flux. This could represent for example, a pumping well where the rate is maintained at a known value.

fplabel(maxbc)

The title of the specified fluid flux point value whose data follows. It can be any alphanumeric string up to 80 characters. `Done' ends input.

fpz(),fpz()

fpz() and fpz() define the x-, z-coordinate of the point where the fluid flux is to be specified.

fpval() Fpval()

(L²/T) is the desired fluid flux value.

2.2.5 Transport boundary conditions

Transport boundary conditions are subdivided into three types:

1. Specified concentration (also known as Dirichlet, first-type) where the solute concentration is fixed at a known value.
2. Specified solute flux (also known as Neumann, second-type or source/sink) where the dispersive solute flux is fixed at a known value. By convention, positive solute fluxes add mass to the system.
3. Third-type concentration (also known as Cauchy or mixed) where the fluid flux and solute concentration entering the system are specified. Fluid fluxes are taken from the flow solution while solute concentrations are specified by the user.

Both specified concentration and third-type concentration boundary types can be set up as time-varying sources. In each case, the function describing the source concentration is subdivided into a number of panels, each panel having an associated start time and concentration value. Solute flux boundary conditions, on the other hand, are limited to a simpler time on/off form of input, which can only be specified once per simulation. There are two assumptions made regarding the time-varying source function. If the first panel in the source function starts at some time greater than zero, then a concentration of zero will be assigned up until that time. The concentration given for the last panel will be assigned until the end of the simulation.

2.2.5.1 Decay constants

First-order decay constants (1/T) describing how quickly the value of the boundary condition declines with time can be specified for five separate types of contaminant input. If you do not want any decay of contaminant to take place, specify a value of zero for the appropriate parameter.

decay_s

First-order decay constant for specified solute flux nodes.

decay_1

First-order decay constant for specified aqueous concentration nodes.

decay_3

First-order decay constant for third-type aqueous concentrations at rectangular elements.

decayv3

First-order decay constant for third-type aqueous concentrations at vertical fracture elements.

decayh3

First-order decay constant for third-type aqueous concentrations at horizontal fracture elements.

2.2.5.2 Specified concentration regions

Concentrations have to be input as regions in order to represent areal sources located in the interior of the grid; however, either the x- or z-range can be collapsed to zero to represent boundary conditions or internal line segments.

dctitle(maxsrc)

The title of the specified concentration region whose data follows. It can be any alphanumeric string up to 80 characters. `Done' ends input.

xcrmin(),xcrmax()

The minimum and maximum x-direction extent (L) of the rectangle whose nodes should be assigned the concentration data that follows. In order to specify a boundary condition on the left side ($X = 0.0$) both these values should be read as zero. For the right-hand side, read them both as xmax, the overall length of the system.

zcrmin(),zcrmax()

As above except in the z-direction. For a boundary condition on top, read these both as zmax, the overall thickness of the system.

crval()

The desired aqueous phase concentration value (M/L^3) for the panel, which will be assigned to the nodes falling within the rectangle defined above.

crmval()

The desired colloid concentration value (M/L^3) for the panel, which will be assigned to the node at the point defined above.

cron(), croff()

The start and end times (T) for the panel (aqueous phase solute concentration). $croff() = -1$ represents continuous source input.

cronM(), croffM()

The start and end times (T) for the panel (colloid concentration). $croffM() = -1$ represents continuous source input.

2.2.5.3 Specified concentration points

cplabel(maxsrc)

The title of the specified concentration point whose data follows. It can be any alphanumeric string up to 80 characters. `Done' ends input.

cpx(), cpz()

The x- and z-coordinate of the point at which the concentration is to be set. *cppanel()* The number of panels in the time-varying concentration function. To simulate a constant source condition for the duration of the simulation, set the number of panels to 1, and enter the desired concentration and a start time of zero below. For each panel, enter the following:

cpval()

The desired aqueous phase concentration value (M/L^3) for the panel, which will be assigned to the node at the point defined above.

cpmval()

The desired colloid concentration value (M/L^3) for the panel, which will be assigned to the node at the point defined above.

cpon(), cpoff()

The start and end times (T) for the panel (aqueous phase solute concentration). *cpoff()* = -1 represents continuous source input.

cponM(), cpoffM()

The start and end times (T) for the panel (colloid concentration). *cpoffM()* = -1 represents continuous source input.

2.2.5.4 Third-type concentration fill segments – Aqueous phase solute

c3sside(maxsrc)

The title of the third-type concentration fill segment whose data follows. It can be any alphanumeric string up to 80 characters. 'Rig', 'Lef', 'Top' or 'Bot' must be used as the first three letters of the title in order to identify which side the segment lies on. 'Done' ends input.

c3smin(),c3smax()

c3smin() and *c3smax()* define the start and end points of the third type concentration segment on the selected boundary. On the top or bottom boundary these would represent x-coordinates, while on the right or left boundary they would be z-coordinates.

c3sstrt(),c3send()

The desired concentration values (M/L^3) for the segment, which will be assigned to the elements falling within the segment defined above. *c3sstrt()* and *c3send()* represent start and end concentration values for this segment (M/L^3). Linear interpolation is used to fill in concentration values for any elements falling on the segment between *c3smin()* and *c3smax()*. Third-type concentration values are generated for rectangular (porous media) and line (fracture) elements falling within the segment. In the case of rectangles, the value generated is interpolated using the coordinate at the midpoint of the element boundary edge. To specify a uniform concentration value along the entire segment, simply make *c3sstrt()*=*c3send()*=desired value.

c3son(),c3soff()

The start and end times (T) and the desired concentration values (M/L^3) for the segment. *c3soff()* = -1 represents continuous source input.

2.2.5.5 Third-type concentration fill segments - Colloid

c3ssidec(maxsrc)

The title of the third-type concentration fill segment whose data follows. It can be any alphanumeric string up to 80 characters. `Rig`, `Lef`, `Top` or `Bot` must be used as the first three letters of the title in order to identify which side the segment lies on. `Done` ends input.

c3sminc(),c3smaxc()

c3sminc() and *c3smaxc()* define the start and end points of the third type concentration segment on the selected boundary. On the top or bottom boundary these would represent x-coordinates, while on the right or left boundary they would be z-coordinates.

c3sstrtc(),c3sendc()

The desired concentration values (M/L^3) for the segment, which will be assigned to the elements falling within the segment defined above. *c3sstrtc()* and *c3sendc()* represent start and end concentration values for this segment (M/L^3). Linear interpolation is used to fill in concentration values for any elements falling on the segment between *c3sminc()* and *c3smaxc()*. Third-type concentration values are generated for rectangular (porous media) and line (fracture) elements falling within the segment. In the case of rectangles, the value generated is interpolated using the coordinate at the midpoint of the element boundary edge. To specify a uniform concentration value along the entire segment, simply make *c3sstrtc()*=*c3sendc()*=desired value.

c3sonc(),c3soffc()

The start and end times (T) and the desired concentration values (M/L^3) for the segment. *c3soffc()* = -1 represents continuous source input.

2.2.5.6 Specified solute flux fill segments

We use the same data structure outlined above for specified head fill segments, except we specify solute flux (i.e. dispersive flux) values instead.

cssside(maxbc)

The title of the specified solute flux fill segment whose data follows. It can be any alphanumeric string up to 80 characters. `Rig`, `Lef`, `Top` or `Bot` must be used as the first three letters of the title in order to identify which side the segment lies on. `Done` ends input.

cssmin(),cssmax()

Cssmin() and *cssmax()* define the start and end coordinate points of the solute flux segment on the selected boundary. On the top or bottom boundary these would represent x-coordinates, while on the right or left boundary they would be z-coordinates.

cssstrtc(),csssend()

cssstrtc() and *csssend()* represent start and end flux values for this segment. Linear interpolation is used to fill in solute flux values for any nodes falling on the segment between *cssmin()* and *cssmax()*. To specify a uniform solute flux value along the entire segment, simply make *cssstrtc()*=*csssend()*=desired value.

csscst(),csscend()

csscst() and *csscend()* represent start and end concentration values for this segment. Linear interpolation is used to fill in solute flux values for any nodes falling on the segment between *cssmin()* and *cssmax()*. To specify a uniform solute flux value along the entire segment, simply make *csscst()*=*csscend()*=desired value.

csson(),cssoff()

The time at which this solute flux source will be turned on and off (T). In order to simulate a source for the duration of the simulation, read *csson()* as 0.0 and *cssoff()* as -1.0.

2.2.5.7 Specified solute flux points

sstlabel(maxsrc)

The title of the specified solute flux point whose data follows. `Done' ends input.

sstx(),sstz()

The x- and z-coordinate of the point at which the solute flux rate is to be set.

sstval()

The flux rate (M/T) which will be assigned to the node at the point defined above.

sstcval()

The concentration (M/L³) which will be assigned to the node at the point defined above.

sson(),ssoff()

The time at which the solute flux source will be turned on and off (T). In order to simulate a source for the duration of the simulation, read *sson()* as 0.0 and *ssoff()* as -1.0.

2.2.6 Initial conditions for transport

The following parameters define the initial conditions (concentrations) for the transport solution unless the switch *lrstrt* is true, in which case the values are read by COLFRAC from the file PREFIX.RST, which overrides the values defined here.

cinit

The default initial concentration to be assigned to every node in the system.

ictitle(maxsrc)

The title of the initial concentration region having a value different from that of *cinit*. `Done' ends input.

xicmin(),xicmax()

The minimum and maximum x-direction extent (L) of the rectangle whose nodes should be assigned the initial concentration data that follows.

zicmin(),zicmax()

As above except in the z-direction.

diffic()

The concentration (M/L³) to be assigned to each node in the rectangle defined above.

cmnit

The default initial mobile colloid concentration to be assigned to every node in the system.

icmtitle(maxsrc)

The title of the initial mobile colloid concentration region having a value different from that of *cinit*. `Done' ends input.

xicmmin(),xicmmax()

The minimum and maximum x-direction extent (L) of the rectangle whose nodes should be assigned the initial concentration data that follows.

zicmmin(),zicmmax()

As above except in the z-direction.

difficm()

The mobile colloid concentration (M/L^3) to be assigned to each node in the rectangle defined above.

csinit

The default initial filtered colloid concentration to be assigned to every node in the system.

icstitle(maxsrc)

The title of the initial filtered colloid concentration region having a value different from that of *cinit*. `Done' ends input.

xicsmin(),xicsmax()

The minimum and maximum x-direction extent (L) of the rectangle whose nodes should be assigned the initial concentration data that follows.

zicsmin(),zicsmax()

As above except in the z-direction.

diffics()

The filtered colloid concentration (M/L^3) to be assigned to each node in the rectangle defined above.

2.2.7 Slice data for flux calculation

slice_type

The title of the slice across which nodal groundwater flow and solute mass fluxes are to be calculated. `Row' must be used as the first three letters of the title in order to identify a horizontal slice, and `Col' for a vertical slice. Otherwise, it can be any alphanumeric string up to 80 characters.

xslice

The x (for a column) or z (for a row) coordinate of the slice, which must not be on the boundary, as boundary values are reported if fluid and solute mass balance calculations are requested.

2.2.8 Non-varying physical parameters

NOTE: If the medium is unfractured, the non-varying physical parameters (with the exception of *clamda*) are read but not used.

diffus

Free-solution diffusion coefficient (L^2/T)

diffusm

Free-solution diffusion coefficient for colloid (L^2/T)

velfac

The ratio between colloid and ground water velocities (-)

rho

Fluid density (M/L³)

visc

Fluid viscosity (M/LT)

clamda

Solute first-order decay constant (1/T). This constant can be calculated from the contaminant half-life according to the formula:

$$\text{clamda} = \ln(2) / t^{1/2}$$

Set clamda equal to zero for no decay.

grav

Acceleration due to gravity (L/T²)

2.2.9 Solver parameters

north

Number of orthogonalization for ORTHOMIN acceleration (used only if iacl = 1).

maxitf

Maximum allowable number of ORTHOMIN iterations for flow solution.

norderf

Ordering scheme used in preconditioning for matrix solution to obtain flow solution. norderf = 0 (natural ordering); norderf = 1 (RCM ordering); norderf = 2 (minimum degree ordering).

levelf

Level for incomplete L/U factorization used in preconditioning process in matrix solution to obtain flow solution.

dptolf

Perform drop-tolerance pre-processing for matrix solution to obtain flow solution.

epsrnf

Drop-tolerance value for matrix solution to obtain flow solution.

ctolf

Absolute convergence criteria for ORTHOMIN iterative solution of matrix equations for the flow problem. Convergence occurs when absolute error in the maximum value of the nodal residual is less than ctolf.

rrctolf

Relative convergence criteria for ORTHOMIN iterative solution of matrix equations for the flow problem. Convergence occurs when relative error in the maximum value of the nodal residual is less than rrctolf.

maxit

Maximum allowable number of matrix iterations for transport solution.

norder

Ordering scheme used in preconditioning for matrix solution to obtain transport solution. norder =0 (natural ordering); norder = 1 (RCM ordering); norder = 2 (minimum degree ordering).

level

Level for incomplete L/U factorization used in preconditioning process in matrix solution to obtain transport solution.

dptol

Perform drop-tolerance pre-processing for matrix solution to obtain transport solution.

epsrn

Drop-tolerance value for matrix solution to obtain transport solution.

ctol

Absolute convergence criteria for iterative solution of matrix equations for the transport problem. Convergence occurs when absolute error in the maximum value of the nodal residual is less than ctol.

rrctol

Relative convergence criteria for iterative solution of matrix equations for the transport problem. Convergence occurs when relative error in the maximum value of the nodal residual is less than rrctol.

ismstp

Perform symbolic factorization in preconditioning every ismstpth step. Symbolic factorization in preconditioning is an expensive process and performing this process every ismstpth step can reduce overall execution time. ismstp =5 is recommended.

iacl

Choice for matrix acceleration scheme. iacl = 0 (conjugate gradient); iacl = 1 (ORTHMIN) ; iacl = 2 (CGSTAB). iacl = 1 is recommended.

dt

Initial timestep size (T).

dtmax

Maximum allowable timestep size (T).

cstar

Maximum allowable concentration change over a timestep to calculate next timestep size. COLFRAC uses variable timestep size in order to accelerate overall execution time. COLFRAC start with dt and increase timestep size by:

$$dt_next = \max (dtmax, cstar * dt_current / dcmx)$$

where:

dt_current: current timestep size

dt_netx: next timesetp size

dcmx: maximum change in previous and current concentrations in the domain

tw

Time weighting factor for transport solutions. $tw = 0$ (explicit); $tw = 0.5$ (Crank-Nicholson); $tw = 1.0$ (implicit). $tw = 1$ is recommended.

TITLE

Text description of concentration vs. time points (not read in by program)

nct

Number of concentration vs. time observation points.

xct(),zct()

x- and z-coordinates of concentration vs. time point. Use a separate line for each point.

nts

Number of printing times.

Times()

Times (“nts” total values) at which to create concentration files. NOTE: Times(nts) (i.e., the last of the “nts” time values) is used as the total simulation time for the model.

2.3 PRECLD Output Files

PRECLD output files are constructed by appending the letter O to the prefix. If the prefix is eight characters, the eighth character will be replaced. This file naming convention makes it easy to keep track of groups of input and output files in the same directory, and delete output files as a group with a wildcard. The complete list of files generated by PRECLD is:

- PREFIXO.ECO PRECLD input file echo (ascii). While PRECLD is running, it creates this listing which contains information read from the preprocessor input data file. This file can be useful for debugging and should be checked first should problems arise. In any case, it should be checked before running COLFRAC to be sure the data is correct and that the codes were compiled with appropriate array dimensions (in most cases, insufficient array dimensions are reported in the listing file and echoed to the screen should PRECLD terminate prematurely).
- PREFIXO.GEN COLFRAC general input file (ascii)
- PREFIXO.XYC X, Z nodal coordinate pairs (binary). This file is written using the following FORTRAN statements:

```
open(11,file=dat_id(:flen)//'o.xyc',status='unknown', form='unformatted')
write(11) nn
write(11) (x(i),z(i),i=1,nn)
close(11)
```

Where DAT.ID(:FLEN) is the FORTRAN variable used to store the problem prefix, to which PRECLD adds the mandatory suffix, in this case, O.XYC.

- PREFIXO.INC Rectangular element incidences (binary). This file is written using the following FORTRAN statements:

```
open(12,file=dat.id(:flen)//'o.inc',status='unknown', form='unformatted')
write(12) ne
write(12) (in(1,i),in(2,i),in(3,i),in(4,i),i=1,ne)
close(12)
```

Where the appropriate file name for this and the following files is formed by combining the prefix and the appropriate suffix as was described above.

- PREFIXO.REZ Rectangular element property zone numbers (binary). This file is written using the following FORTRAN statements:

```
open(13,file=dat.id(:flen)//'o.rez',status='unknown', form='unformatted')
write(13) ne
write(13) (izone(i),i=1,ne)
close(13)
```

- PREFIXO.HFZ Horizontal fracture line element incidences, property zone numbers and fracture apertures (binary). This file is written using the following FORTRAN statements:

```
open(15,file=dat.id(:flen)//'o.hfz',status='unknown', form='unformatted')
write(15) nfeh
write(15) (ihzone(i),i=1,nfeh)
write(15) ((inhf(j,i),j=1,2),i=1,nfeh)
write(15) (aph(i),i=1,nfeh)
close(15)
```

- PREFIXO.VFZ Vertical fracture line element incidences, property zone numbers and fracture apertures (binary). This file is written using the following FORTRAN statements:

```
open(15,file=dat.id(:flen)//'o.vfz',status='unknown', form='unformatted')
write(15) nfev
write(15) (ivzone(i),i=1,nfev)
write(15) ((infv(j,i),j=1,2),i=1,nfev)
write(15) (apv(i),i=1,nfev)
close(15)
```

- PREFIXO.ICD Initial condition if different from default (binary). This file is written using the following FORTRAN statements:

```
open(15,file=dat.id(:flen)//'o.icd',status='unknown', form='unformatted')
write(15) nci
write(15) (nodi(i),conci(i),i=1,nci)
```

3 COLFRAC-MRL

COLFRAC-MRL reads the output files generated by PRECLD and, depending on the program control switches, performs various computations, which may include solving for the nodal hydraulic heads and elemental Darcy fluxes and the nodal mobile and immobile colloid, aqueous and total solute concentrations.

Issue the appropriate command to run the executable program COLFRAC-MRL. You should see the following:

' Give prefix of problem filename...'

This prompt is asking for the prefix of the .GEN file, which was created by PRECLD and is identical to the prefix of the .PRE file read by PRECLD. Type in the prefix (up to 7 characters) and press return. The program automatically searches for the appropriate file by appending the suffix O.GEN.

It uses the prefix to construct it's own set of output files with different extensions. The complete list of files generated by COLFRAC-MRL is:

- PREFIXO.CON, PREFIXO.COT are aqueous phase and total solute concentrations, respectively.
- PREFIXO.COC, PREFIXO.COF are mobile and filtered colloid concentration, respectively.
- PREFIXO.LST COLFRAC-MRL listing file (ascii). This file is created while COLFRAC-MRL is running and can be useful for debugging and should be checked in case of problems to ensure that the input data is correct. Fluid balance and nodal groundwater fluxes on the domain boundaries and along the prescribed slice will also be reported in the .LST file if requested in the .PRE file.
- PREFIXO.VEL Rectangular and line element Darcy fluxes (binary) and information necessary for calculating mass fluxes crossing an internal slice. The file is opened should any of the switches **ldvel** or **lslice** be set to true. The first part of the file contains the Darcy fluxes and is created by the following FORTRAN statements if the switch **ldvel** is set to true:

```
open(9,file=ofile,status='unknown',form='unformatted') write(9)
(vx(i),vz(i),i=1,ne)
if(nfev.gt.0) then
  write(9) (vfv(i),i=1,nfev)
endif
if(nfeh.gt.0) then
  write(9) (vfh(i),i=1,nfeh)
endif
write(9) kmbal
```

The next part of the file contains the information necessary for computing the mass fluxes crossing an internal slice and is created by the following FORTRAN statements if the switch **lslice** is set to true:

```
      write(9) kslice, islice, icut  
write(9) (qslice(i), i=1, ip)
```

The following line is always written:

```
      write(33) kslice
```

This part of the file is created by the following FORTRAN statements if the switch **kslice** is set to true:

```
      if(islice.eq.1) then  
        write(33) nx  
        write(33) (nodeslice(i), i=1, nx)  
        elseif(islice.eq.0) then  
          write(33) nz  
          write(33) (nodeslice(i), i=1, nz)  
        endif
```


4 Postprocessing

4.1 Plotted output

Output from COLFRAC-MRL can be imported to third-party visualization packages such as TECPLOT.

OUT2TECPLOT converts COLFRAC-MRL binary output files into ascii formatted files which are compatible with the third-party program TECPLOT. You may want to process these files with the TECPLOT program PREPLOT.EXE, which is a part of TECPLOT package and converts TECPLOT formatted ascii files into binary format, before reading them in TECPLOT. Due to the wide range of platforms and packages available, we leave it to the end user to implement plotting routines for their particular system.

5 Example Problem

This example problem is a simple one-dimensional test problem involving flow and transport in a single fracture surrounded by a uniform porous medium. Figure 1 shows the porous medium, the fracture, and the permeability of the porous matrix. A constant source of solute and colloids is introduced at a point located at the top of the fracture. The ASCII input data file *sfbase.pre* is the input file for this example.

Figure 2 is a plot of the simulated steady-state hydraulic head distribution. Constant-head boundaries were specified at the top and bottom of the domain. Figure 3 shows the computed Darcy velocity vectors based on the simulated head variation. The red arrows are the high-velocity fracture velocities and the small porous media velocity vectors are depicted in blue.

Figures 4 and 5 are snapshots of the total contaminant (aqueous-phase + sorbed to colloids) and mobile colloid concentrations, respectively, at 0.6, 4, 8, and 16 days. In this example the porous medium exerts a large influence on the extent of contaminant migration in the fracture due to the diffusion of mass and colloids (with mass adsorbed to them) into the matrix. This effect is illustrated by the concentration vs. time graphs where, for example, the rate of change of the contaminant concentration decreases significantly downgradient (e.g., $z=4$ m) from the source.

Figure 1

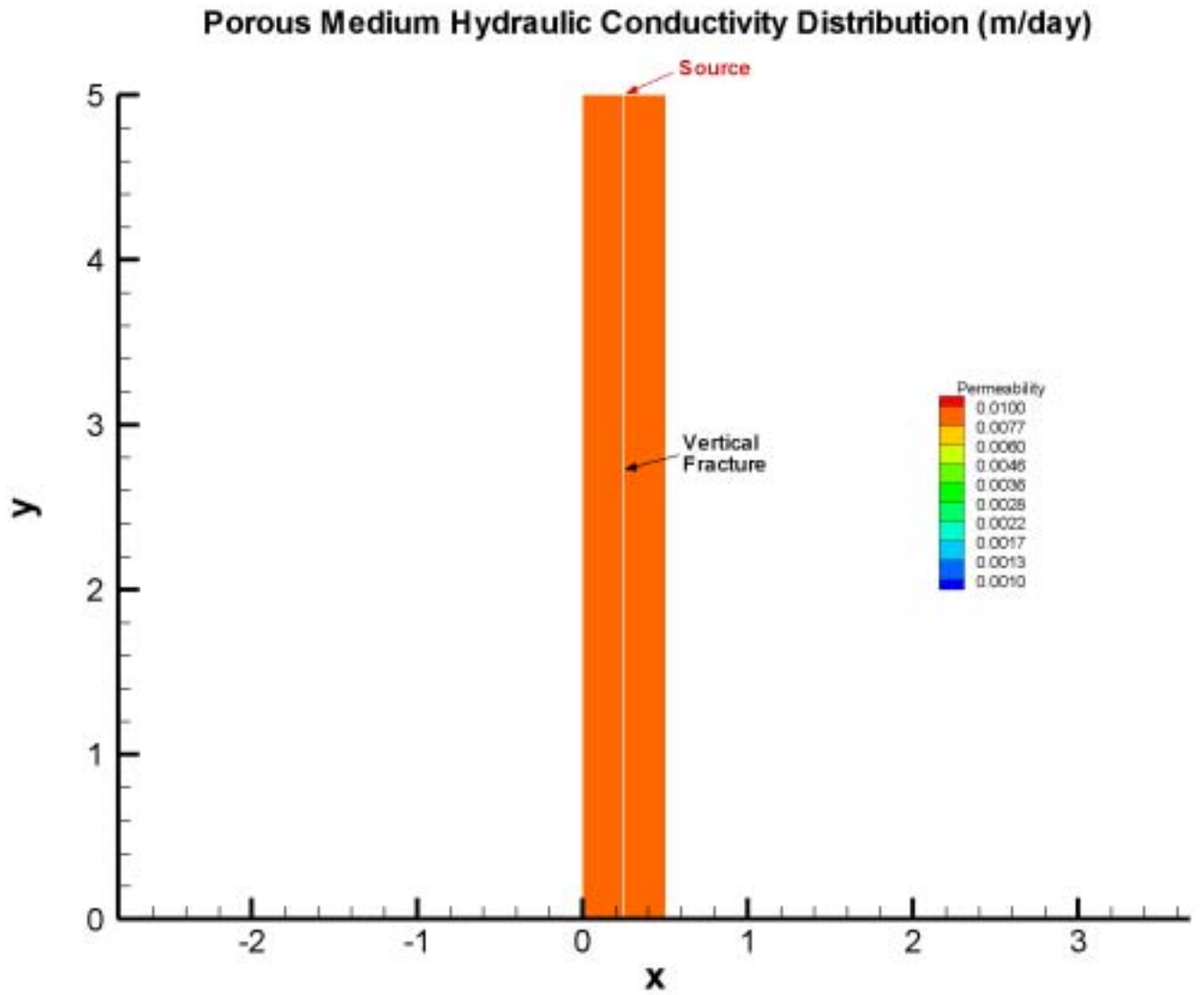


Figure 2

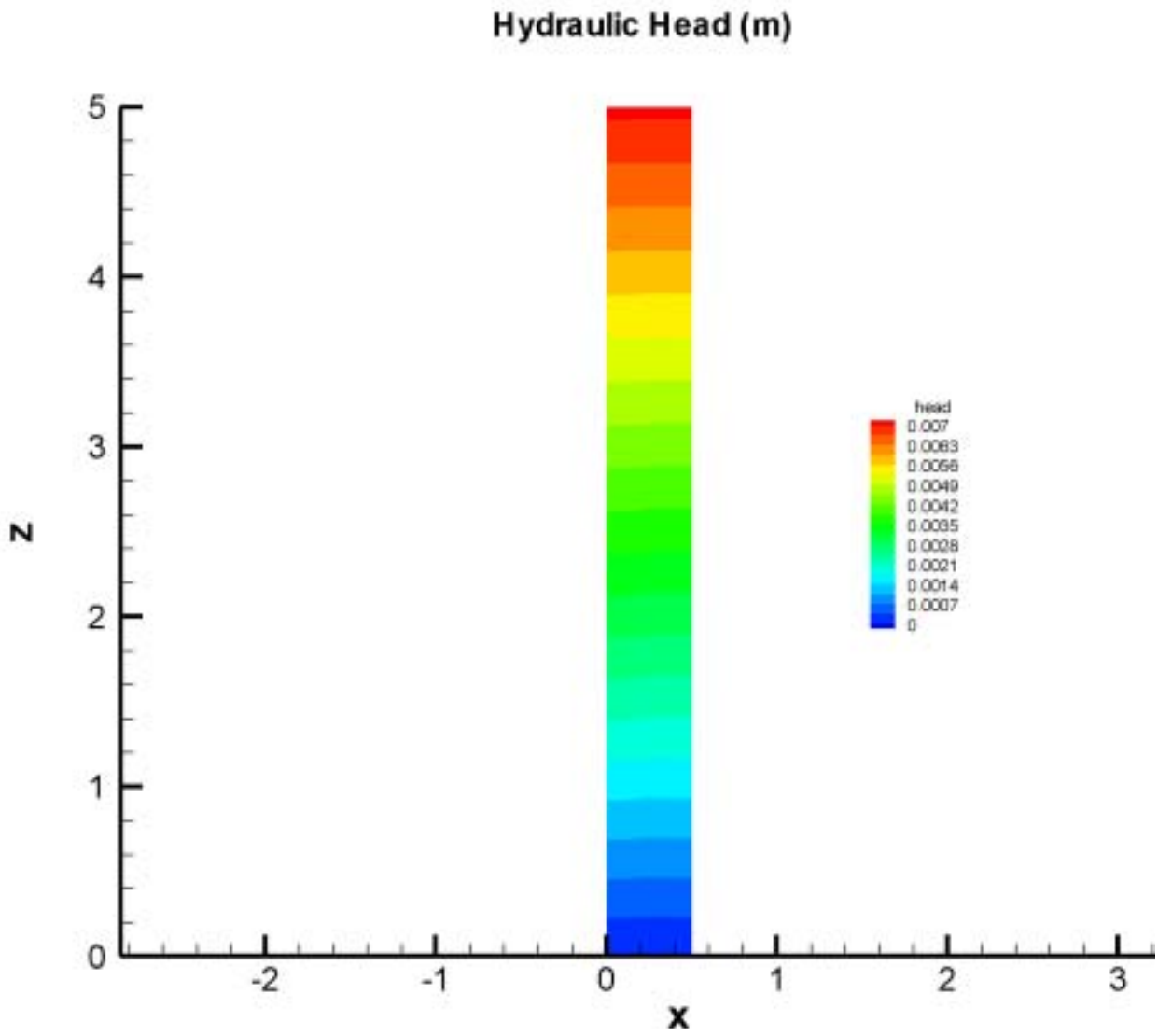


Figure 3

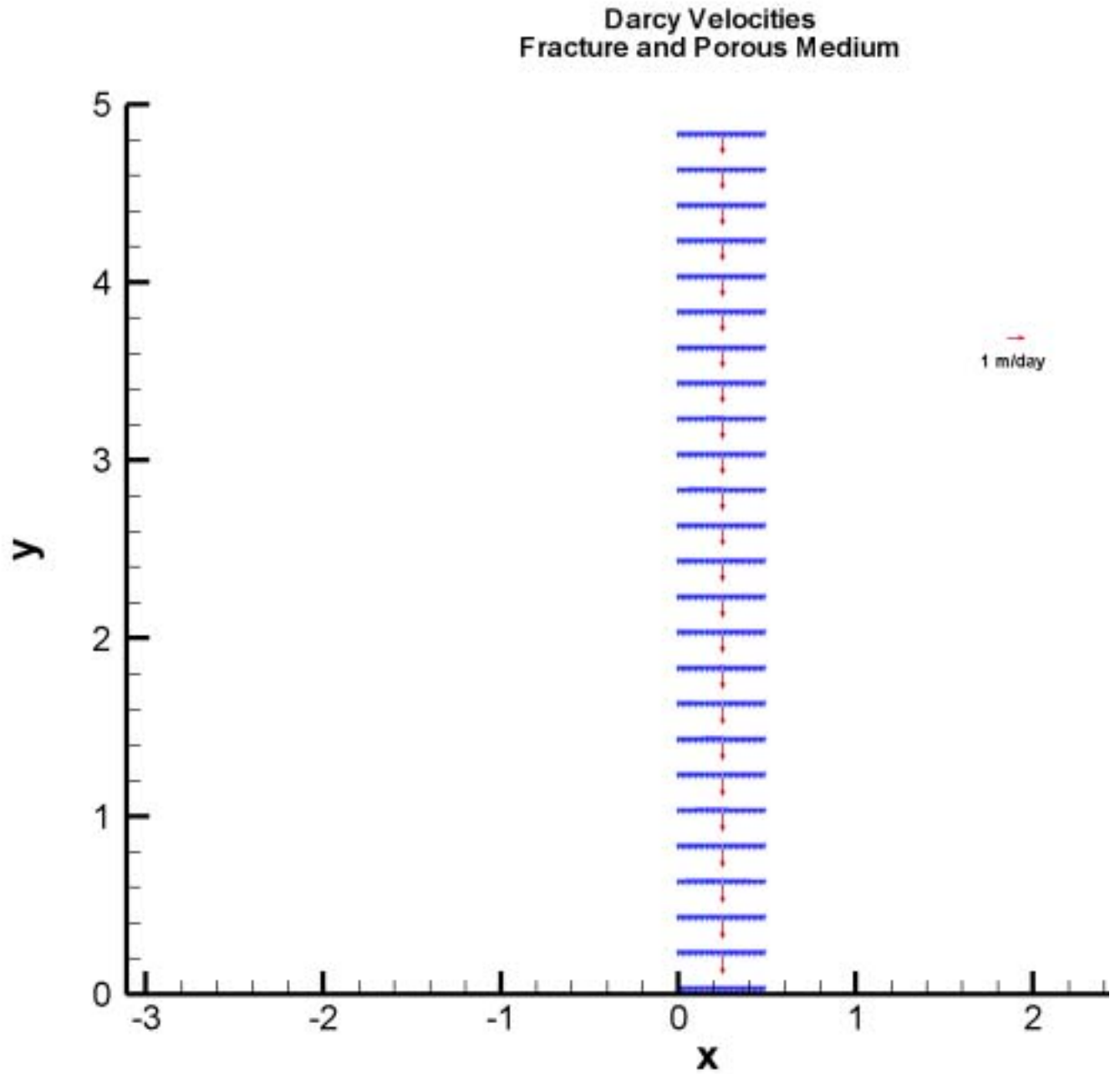


Figure 4

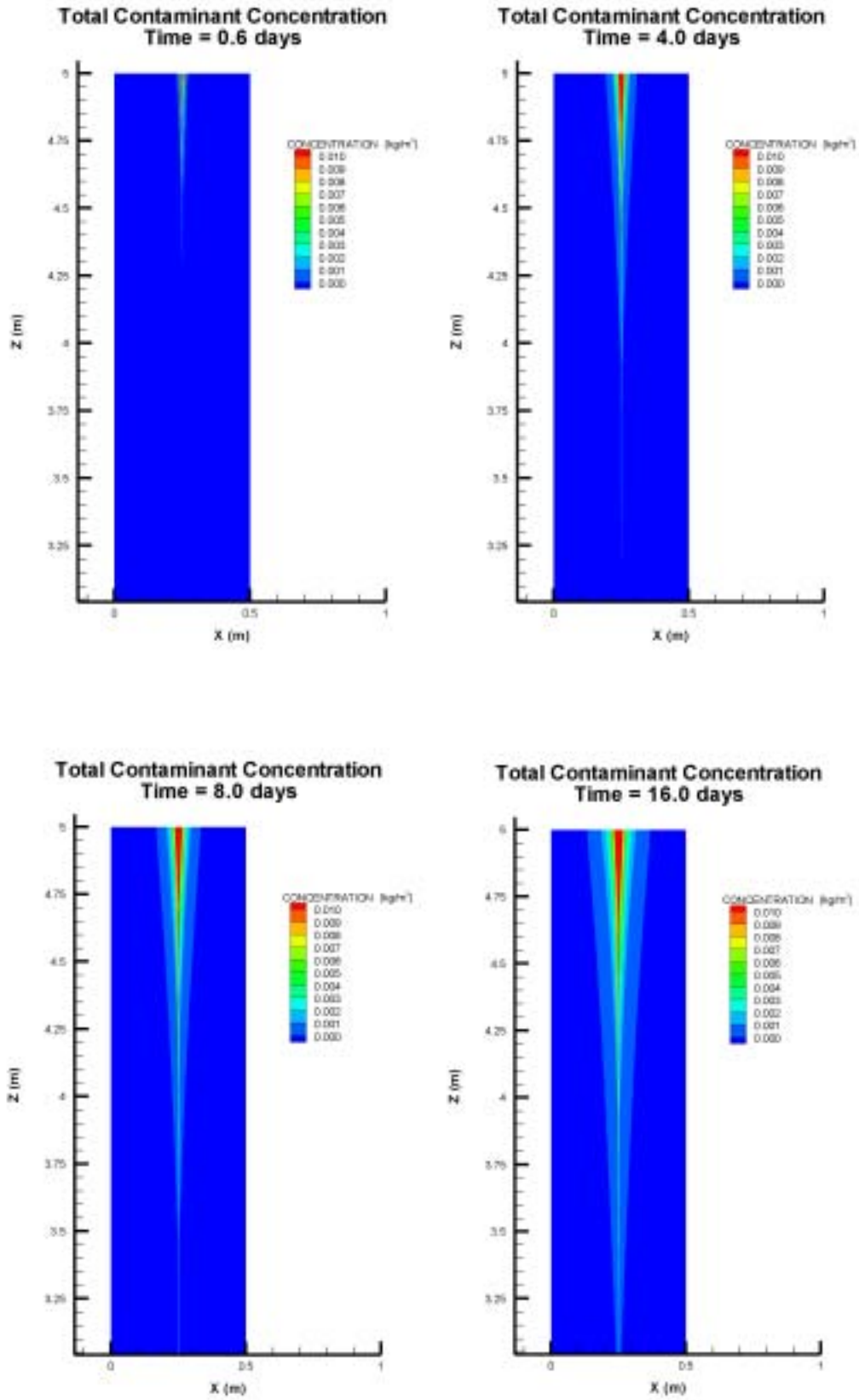


Figure 5

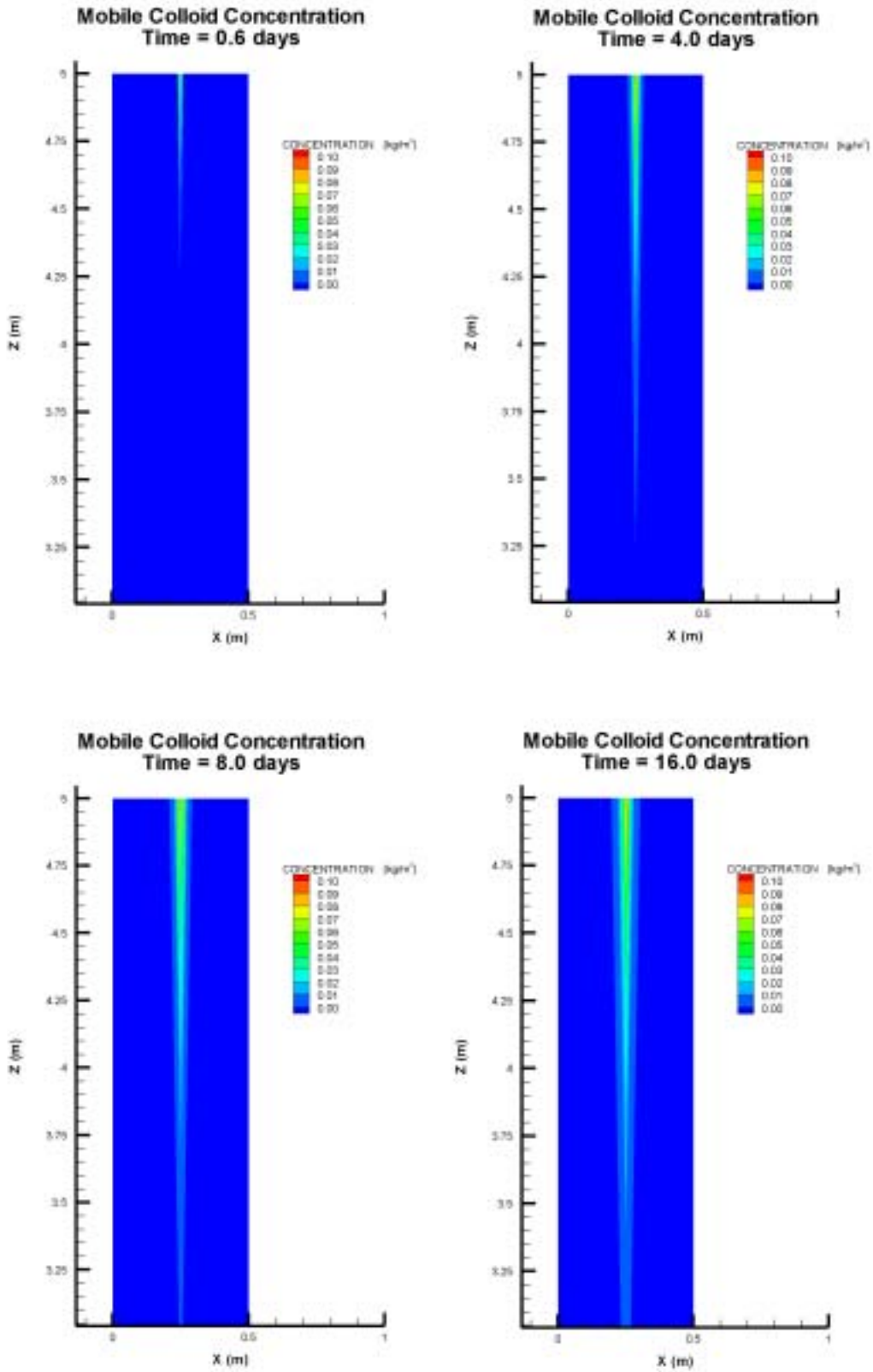
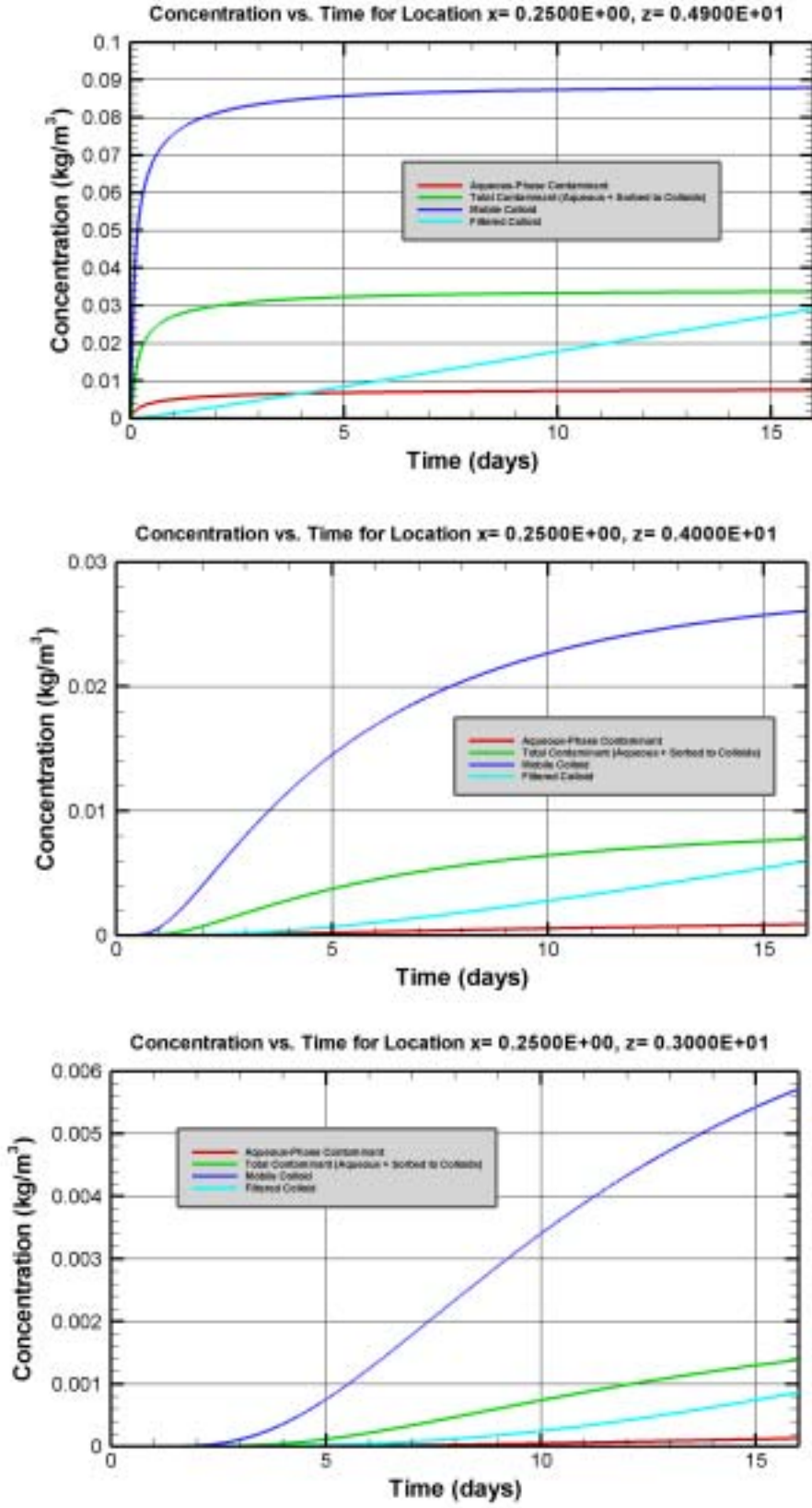


Figure 6



Attachment: Input file modification in 2004

2.2.5.3 Specified concentration points

cplabel(maxsrc)

The title of the specified concentration point whose data follows. It can be any alphanumeric string up to 80 characters. `Done' ends input.

cp_x()*, *cp_z()

The x- and z-coordinate of the point at which the concentration is to be set. *cppanel()* The number of panels in the time-varying concentration function. To simulate a constant source condition for the duration of the simulation, set the number of panels to 1, and enter the desired concentration and a start time of zero below. For each panel, enter the following:

NcpvalChange

The desired total numbers of time-series concentration data.

CpTimes()

The start times (T) for the time-series aqueous phase concentration data.

cpval()

The desired aqueous phase concentration value (M/L^3) for the panel, which will be assigned to the node at the point defined above.

CpmTimes()

The start times (T) for the time-series colloid concentration data.

cpmval()

The desired colloid concentration value (M/L^3) for the panel, which will be assigned to the node at the point defined above.