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変更する。

2001. 6. 20　　　[技術情報室]

OECD/NEA Sorption Workshop 出張報告書

1997年6月

動力炉・核燃料開発事業団
東　海　事　業　所

OECD/NEA Sorption Workshop出張報告

報告者　　　澁谷　朝紀

実施責任者　石川　博久

要　旨

　本会議は，放射性廃棄物処分の観点から，現象論的収着モデル（イオン交換モデル，表面錯体モデル等）の有効性について検討を行うために開催された会議で，13か国38機関から合計53名が参加して行われた。本会議は，大きく6つのセッションから構成され，性能評価のための収着データ(Kd)の予測および設定したKdの信頼性を補完するために用いる現象論的収着モデルの現状，最新の収着現象の研究及び現象論的収着モデルに関する知見を中心に，核種の収着挙動における現象論的モデルの性能評価への適用性について各国の研究開発に関するアプローチ，現象論的収着モデルの現状，Kdの予測，Kdの信頼性，Kdの原位置条件への適用性の問題点について議論し，今後の研究の方向性の検討を行った。

　動燃事業団では，本会議で現象論的収着モデルの性能評価への適用性に関する発表を行い，現象論的収着モデルを用いることによって，バッチ法による収着実験で得られたKdを説明することが可能であるが，拡散実験から得られたKdについては，本モデルだけで説明することが困難であることを示した。発表では，この原因として，核種の移行経路，空隙構造に起因する遅延効果の評価が現段階では困難であることを指摘した。これらの結果から，現象論的収着モデルは，性能評価で用いるKdを直接算出するために用いるのではなく，設定したKdの信頼性の補完，環境の変化に伴うKdの変動幅の推定に用いるべきとの動燃事業団としての見解を示した。本発表で示した圧縮ベントナイト中でのUのKdおよびモデル化については多くの議論が得られ，その手法，結果については妥当であるとの意見が出された。Uについては，近年現象論的収着モデルを用いた多くの研究がなされており，本結果が確証研究のケーススタディーになりうるとのコメントも出された。

　現象論的収着モデルについては従来から電気二重層モデルを中心とした研究が行われて来たが，スイスのPSIからは，スメクタイトへの核種の収着挙動を正確に研究した例が紹介され，スメクタイトについては電気二重層を考慮しないモデルがむしろ妥当であるという結論を導き注目を集めた。この結果については専門家から電荷の高い核種についても検討を行った上で結論を出すべきとのコメントが出された。

　現象論的収着モデルの性能評価への適用性に関する議論では，本モデルを用いて推定したKdは直接性能評価へ適用することはできないとの意見が大勢を占めた。これは，モデル化の中で用いる幾つかのパラメーター（岩盤中の核種の移行経路，核種と接触する鉱物，空隙水の化学的特性等）の推定に多くの仮定を含むことが予想されるためである。しかし，本モデルを用いることによって，環境条件の変化に伴うKdを推定できることから，性能評価で設定したKdの信頼性を補完することは可能であるとの意見も多く出された。本会議では，今後の方針として本モデルの研究については奨励されたが，性能評価への適用の可否に対しては明確なコンセンサスは得られなかった。OECD/NEAでは，本会議の内容を基に，１０月までに報告書を完成させる予定である。

東海事業所　環境技術開発部　地層処分開発室

OECD/NEA Sorption Workshop 出張報告書

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澁谷　朝紀

１．概要

本ワークショップは、放射性廃棄物処分の観点から、現象論的収着モデル（表面錯体モデル、イオン交換モデル等の収着モデル）の有効性につて検討を行うために開催された会議で、１３カ国３８機関から合計５８名が参加して行われた。本会議では、核種の収着挙動における現象論的収着モデルの性能評価への適用性について、各国の研究開発に関するアプローチ、現象論的収着モデルの現状、Kd 値の予測、Kd 値の信頼性、Kd 値の原位置条件への適用性の問題点について議論し、今後の研究の方向性の検討を行った。

議論は主に、性能評価のための信頼性の高い収着データセットの整備及びその妥当性の評価をどのように行うか、現象論的モデルはどういう意味で有効か、性能評価への現象論的モデル使用の必要性を裏付けるためには、どのような試験が必要かといった点に焦点が当てられた。会議の目的およびプログラムを別添１に示す。

２．会議開催期間および場所

平成９年５月６日～８日 Linton Lodge Hotel, Oxford, UK.

３．参加機関および人数

本会議には、

ベルギー　２名（ONDRF, CEN-SCK 各１名）

チェコ共和国　２名（チェコ工科大学）

フィンランド　３名（ヘルシンキ大学、VTT, Posiva　各１名）

フランス　５名（ANDRA ２名, CEA, GRECI, IPSN　各１名）

日本　１名（PNC）

韓国　１名（KAERI）

スウェーデン　２名（Chalmers 工科大学, SKI 各１名）

スイス　５名（PSI ２名, HSK, BMG, Nagra　各１名）

イギリス　１３名（BNFL, AEA 各４名, Galson Science ２名, Nirex, BGS, QuantiSci　各１名）

アメリカ　７名（Sandia 国立研究所２名、USGS, Los Alamos, NRC, SWRI,
スタンフォード大学　各１名）

ドイツ　２名（Rossendorf 研究所）

オーストラリア　２名（ANSTO, New South Wales 大学）

そのほかに、コンサルタント２名（SGN, QuantiSci）および事務局１名（OECD/NEA）の合

計５３名が参加した。詳細は別添２に示す。

４．会議内容

本会議は、６つのセッションから構成され、セッション１のテーマは「Kd と性能評価について」で、性能評価の観点、レビューアーの観点からの Kd について議論された。セッション２のテーマは「性能評価のための化学的モデルと Kd」でキーとなるパラメータおよびそれらの取得方法について、実験者とモデラーからそれぞれ発表があった。セッション３のテーマは「収着モデルの天然系への適用性」で、収着モデルを天然系へいかに適用するか、トップダウンおよびボトムアップのアプローチについて発表があった。放射性廃棄物以外の分野も含むいくつかのプロジェクトでの例についても報告があった。セッション４は「天然における収着挙動の理解及び評価に対する現象論的モデルの適用性」について、最先端の研究についての紹介があった。セッション５は本会議の議論として、技術的な議論および性能評価へのリンクに関するパネルディスカッションがおこなわれた。セッション６では、本会議のまとめが行われた。セッションの概要を以下に、要旨を別添３に示す。

4.1 セッション１「Kd と性能評価について」

本セッションでは最初に Nirex の Dr.A.Hooper より Nirex'95 で行った Kd 設定方法についての紹介があった。Nirex では、性能評価に Kd を用いているが、Kd は実験条件によって大きく変動するため、実験によって得られた Kd 値を統計学的に処理し、確率密度関数（PDF；Probability Density Functions）を与えることによってその信頼性を評価している。Kd の設定に際しては、１つの核種についてその信頼性に応じて７種類の Kd 値を設定している。さらに、intact rock 中の Kd については補正ファクター β を、バッチ法で得られた Kd に掛け合わせることによって計算し、最終的に性能評価へ与える分配係数を決定している。本発表では、例として Nirex'95 で行った BVG(Borrowdale Volcanic Group)への 20 元素の分配係数について評価した結果を示した。

また、Dr.H.Wanner は、レビューワーの立場から、Kd の設定について講演し、Dr.A.Hooper と同様に intact rock 中の Kd をバッチ法で得られた値から評価する際には、不確実性をどのように取り扱うかを明確にすべきであるとの意見を述べた。処分環境での核種移行挙動を評価する場合、Kd 以外にも地下水の変化、移流、分散、表面拡散等の評価を行う必要があり、個々に複雑なモデルを適用し、組み合わせることによって不確実性は大きなものになる。この現状を踏まえると、性能評価で用いる現象論的収着モデルは、できる限り単純なものがよいとの意見を述べた。重要なのは、収着挙動の詳細なモデル化ではなく、性能評価で設定した Kd が信頼できる値であることをどのように評価するかということである。一方、保守的な Kd の設定について、多くの性能評価研究者は、保守的→ワーストケース→実験値の最も低い値→できる限り小さい値→現実的な値より 1/10 の値という考え方で設定を行っているが、現実的には実験結果およびモデル予測結果等から、

各元素に合った設定を行うことが重要であるとの見解を示した。さらに、レビューのポイントとして以下の5項を挙げた。

- 得られた Kd 値の妥当性；一般的な経験を元にした知見、評価から、得られた Kd 値が妥当かどうか判断
- データ選定手順の明確さ；どうやって行ったか、なぜ選んだか、固相や液相、還元条件か？、安全解析上有益か？
- 最先端の考え方との整合性；関連した文献の収集状況、新しい知見が導入されているか？
- Transport model で用いる値との整合性；得られた Kd 値と拡散試験で得られた値(Da, De 等)に整合があるか？
- 不確実性の処理；どうやって不確実性を処理するか、どうやって不確実性を安全評価へ取り込むか？

不確実性をどのように性能評価へ取り込むかについては、今後、我が国の性能評価においても十分議論を行うことが重要であると考えられる。

4.2　セッション2「性能評価のための化学的モデルと Kd」

本セッションでは、コンサルタントの Dr.S.Altmann より、key questions, key parameter、Kd の研究のための戦略について発表があった。

性能評価に対する key questions として、

- Kd の空間的変化；どんなおおよその Kd を用いるか？それは異なった拡散場では異なった値を用いるか？
- Kd の時間的変化；設定された Kd は性能評価のタイムスケールの中で一定の値を用いるのか？

を上げた。

key となる物理的パラメーターについては
- 全空隙体積；通常の岩石中の空隙および核種の移行空隙
- 空隙内表面積；核種移行に寄与する空隙の表面積および収着サイト濃度

が上げられ、特に亀裂性媒体については、マトリックス部分の体積および表面積と亀裂中の体積および表面積とを区別する必要があることを示した。

key となる化学的パラメーターについては
- 収着化学種、溶存量

・空隙中の化学組成
・仮定する平衡反応と平衡定数

性能評価へ収着モデルを適用する手順として、以下のように示した。
・Bottom up アプローチ
　代表的な天然試料の採取→測定（表面固相の同定、地下水化学の特定）→支配的反応の抽出→単純な chemical thermodynamic modelling→より複雑な chemical thermodynamic modelling
・Top down アプローチ
　代表的な天然試料の採取→より複雑な chemical thermodynamic modelling⇔確証→必要であれば単純な chemical thermodynamic modelling

そして、性能評価へ適用するためには、キーとなる物理的パラメーターの特定、Kd のパラメーター依存性（地下水や鉱物の変化に対応できるもの）を把握した上で、他の化学的に異なった実験条件における Kd の推定を行い確証を行う。さらに、原位置試験で得られた Kd を許容範囲で（どの程度かは明確な基準がないが）予測しうることを確認することが重要であることを示した。

4.3　セッション3「収着モデルの天然系への適用性」

本セッションでは、「収着モデルの天然系への適用性」というタイトルで、性能評価に携わっている研究者の立場から発表があった。本議論では、ベントナイトおよび堆積岩のような多孔質媒体中の核種移行挙動については、比較的化学種が単純である Cs, Se, Zn についてある程度現象論的収着モデルを用いることによって説明が可能であるものの、アクチニドのような複雑な化学形態を示す元素の移行挙動や、花崗岩や変成岩のような亀裂性媒体中の移行挙動については、現象論的収着モデルだけで評価を行うことは困難であることが示された。
発表内容の概要を以下に、要旨を別添にそれぞれ示す。

AEA の Dr. C.Tweed は、性能評価へ適用する収着実験データの基本的な考え方として、
(1)Kd の信頼性評価は、さまざまな実験から得られる Kd から求めた確率密度関数 (PDF)を用いて行う。また、バッチ法の収着試験で得られた Kd 値は、未粉砕岩石へ単純には適用できないため、岩体中の幾何形状を考慮したスケールファクターを用いておおよその岩体中の Kd を推定する。
(2)線形吸着、可逆吸着の仮定、共沈および鉱物化は考慮しない。
(3)高い酸化状態の Kd （U(VI), Se(VI)等）を用いる。これは、経験的に、還元条件下で得られた Kd の方が高いことが知られており、酸化状態で得られた Kd を設定す

ることは Kd の保守性を担保できると考えられる。

(4)室温のデータを用いる。これは、経験的に Kd の温度依存性が小さいことが知られ
　ているためである。

(5)飽和の効果は考えない（定常拡散は考慮しない）。

　ことを上げた。また、これらの値の信頼性を担保するために、現象論的収着モデル、
原位置での実験結果も参照することを示した。発表では、実際に Sellafield サイトでの
U の Kd を評価した例を示し、U の移行経路に鉄鉱物があり、炭酸濃度の低いケースで
100000ml/g、石英、方解石が支配的で炭酸濃度が高いケースで 0.01 ml/g であった。

　SKI の Dr.S.Wingefors は、スウェーデンにおける SITE-94 での Kd 設定手法に関して
発表を行った。 SITE-94 では、 ベントナイトおよびÄspö仮想処分場の岩石を想定した
核種の分配係数を設定しており、設定に用いたデータは

　・1989 年以降の文献値
　・1989 年以前については OECD/NEA の Sorption Data Base の値
　・以前の性能評価報告書（スウェーデンのみならず、スイス、フィンランドを含む）
　　の値

である。また、設定では蒸留水系の地下水を考慮し、酸化状態は、酸化条件、還元条
件の２種類を考慮した。岩石に対する Kd については、亀裂充填鉱物を考慮せず（保守
的に）、遅延係数は母岩中へのマトリックス拡散と母岩への核種の収着のみから評価を
行っていた。選定された値は、実験値の低い値を元に保守的に決定されている。

　SITE-94 では、試験的に Np(V)について現象論的収着モデルを用いて、バッチ法で得
られた Kd 値を評価している。本解析では拡散層モデル(Dzombak and Morel, 1991)を用
いており、収着サイトは鉄酸化水酸化物のコーティングを考慮して決定している。これ
らの結果では、バッチ法で得られた Kd とモデル化によって予測した Kd はほぼ同様の
値を示した。しかし、核種移行挙動の評価に現象論的収着モデルを適用するためには、
いくつかの仮定（可逆反応、カイネティクスは考慮せず、Kd は移行経路・化学条件に
よらず一定、均一な収着固相等）に不備があると考察し、現象論的収着モデルを性能評
価へ適用するためにはこれらの仮定をいかに評価するかが重要であるとの見解を示し
た。ただし、収着モデルに用いられた実験値については、さまざまな Kd のパラメータ
ー依存性が調べられており、熱力学的意味があると位置づけている。

　PSI の Dr.B.Bayens は、Ni, Zn, Ca, Mn, Mg のスメクタイトへの収着メカニズムを実験
的に詳細に記述し、バッチ法によるこれらの元素の収着実験から、これらの支配的な収
着メカニズムが pH によって異なり、低 pH 側ではイオン交換反応、高 pH 側では表面
錯体生成反応がそれぞれ支配的に生じていることを示した。また、スメクタイトの表面
水和基への H+の収着量を酸塩基滴定法を用いて測定した結果、表面水和基には少なく
とも２種類の収着サイトが存在することが推定された。また、これらの収着挙動につい
て表面錯体モデルによるモデル化を行った結果、スメクタイトと収着する化学種との電

気的な相互作用を考慮しないモデルがもっとも実験値をよく説明できることが示された。本結果については、金属酸化物等への収着挙動を研究している Dr.J.Davis, Prof.J.O.Leckie らから、電気的な相互作用の存在は否定できないこと、電気的な相互作用を否定する場合、III 価、IV 価のような高い電荷を持つ元素の収着挙動を把握する必要があるとのコメントが出された。しかし、処分環境を想定した場合、 (1)+III, +IV 価を持つ陽イオンの存在は考えられないこと、(2)-III, -IV 価ではほとんど収着しないこと、(3)地下水には多くのイオンが含まれ、収着サイトは何らかの元素ですでに占有されている可能性があり、放射性核種はこれらの元素とイオン交換的に収着する（この場合、静電的な効果は無視される）ことが考えられること、(4)吸着する核種に対して吸着サイトがはるかに多い場合、一般に吸着等温線が成り立つことが知られており、仮に電位勾配によって核種の活量が変化しても分配係数にはほとんど影響しないことが考えられること等を考慮すると、性能評価に用いる収着モデルに、電気二重層モデルのような電気的相互作用を考慮したモデルは必ずしも必要がないのではないかとの意見も多く出された。

　動燃事業団からは、Cs, Se, U のベントナイトへの収着挙動に関する研究として、Cs については Cs 濃度および液固比、Se については pH、U については共存イオン濃度、液固比、酸化状態をそれぞれパラメーターとした Kd 値の算出およびイオン交換モデルまたは表面錯体モデルを用いた解析結果について紹介を行った。また、圧縮ベントナイト中の Cs, Se, U の拡散実験から評価された Kd についても、同様にモデル解析を行った結果の紹介を行った。この中で、イオン交換モデルおよび表面錯体モデルによって計算された Kd 値は、バッチ法で得られた Kd をよく説明できるが、拡散実験から得られた Kd 値は説明できないことを示した。これは、圧縮ベントナイト中の空隙水組成、核種移行経路上の収着サイト濃度の評価が現段階では困難であるためである。発表では、これらのことから現象論的収着モデルは、性能評価で用いる Kd を直接算出するために用いるのではなく、設定した Kd の信頼性の補完、環境の変化に伴う Kd の変動幅の推定に用いるべきとの動燃事業団としての見解を示した。本発表で示した圧縮ベントナイト中の U の収着挙動については多くの議論が得られ、Through-Diffusion 法で得られた De については、その評価手法について若干議論が残るものの、De と In-Diffusion 法で得られた Da から Kd を算出する手法についてはおおむね妥当であるとの意見が出された。本データについては、圧縮ベントナイト中の U の Kd に関するデータは少ない点、U の収着挙動に関する研究及びモデル化研究については多くの研究者によって行われている点、U の熱力学データが比較的信頼できると考えられる点等から、現象論的収着モデルの確証研究に用いることが可能であるというコメントも得られた。

　KAERI の Dr.Y-H.Cho は、韓国での研究例を示し、現象論的収着モデルについては FeOOH への表面錯体モデルを中心とした研究を行っているものの、性能評価へは、既存の実験データを元にした収着データベースが有効であり、モデル化は、ラングミュア

一、フリンドリッヒの吸着等温線を元にした経験的なモデルを適用することが望ましいとの見解を示した。また、天然の岩石では、風化に際し、 FeOOH だけでなく、 MnO_2 の寄与も大きくなることを示した。 MnO_2 は、等電点が高く(pH=12)、処分環境下で陰イオンの収着に大きな効果があることが期待されている。

ANSTO の Dr.T.Payne は、U(VI)のフェリハイドライト（$Fe_{10}O_{15}*9H_2O$→鉄の風化生成物）およびカオリナイトへの収着挙動に関する研究を行い、フェリハイドライトの表面水和基に2種類の収着サイトが存在すること、U の収着挙動が炭酸濃度の上昇によって変化し、フェリハイドライト、カオリナイトともに炭酸濃度の上昇とともに Kd が減少することを示した。また、Kd の pH 依存性も確認され、フェリハイドライト、カオリナイトともに中性付近で Kd の最大値を示し、酸性側、アルカリ性側で Kd が減少する傾向が確認された。これらの傾向は表面錯体モデルを用いた解析によっても同様の傾向が支持された。また、オーストラリアのクンガラウラン鉱床における U(VI)の移行挙動から評価した分配値（P 値として表現；Partitioning value）は、原位置条件と同様の条件で行った室内実験から得られた Kd 値とある程度傾向性が一致することも示された。しかし、原位置での P 値にはコロイドや沈殿の影響も存在しているため、実際に原位置での収着挙動を収着モデルから説明することは困難であり、さらに現象論的収着モデルを処分環境における核種移行挙動評価へ適用するためには、時間スケール、空間的な広がり、環境条件の複雑さといった unknown なパラメーターを設定しなければならず、現段階ではこれを評価することは困難であるとの見解を示した。

ONDRAF の Dr.R.Gens はベルギーで行っている核種移行実験の紹介を行い、Boom Clay を用いた移流拡散実験から、弱い Kd を示す元素については動水勾配の大きさによって移流支配または拡散支配で移行するが、高い Kd を示す元素については、高い動水勾配がかかっても拡散支配で移行することを示した。また、同様の実験を原位置で行った結果、すべての元素で拡散支配で移行することが確認された。現象論的収着モデルに関しては、拡散実験から得られる遅延係数の評価に用いることを検討しているものの現段階では具体的な適用例や考え方は出されなかった。

セッションの最後は USGS の Dr.J.Davis が下水廃棄物に汚染された砂岩および砂れき層中の Zn の移行挙動について、表面錯体モデルを用いて行った評価結果について紹介した。用いた表面錯体モデルは電気二重層モデルであり、収着サイトは AlOH 基および FeOH 基についてそれぞれ weak site, strong site を考慮した。これらの収着サイトと Zn との反応定数は文献で得られた値を用いている。モデル化の結果、バッチ法による収着実験結果については本モデルで説明できることが示された。また、これらのパラメーターと、別途原位置での広域トレーサー実験から得られた堆積岩中の空隙特性値を用いて原位置での Zn の移行挙動を評価した結果、原位置での Zn の移行挙動は本モデルを用いることによって説明できることが示された。本解析においては核種移行コード HYDROGEOCHEM が用いられている。

4.4 セッション4「天然における収着挙動の理解及び評価に対する現象論的モデルの適用性」

本セッションでは、「天然における収着挙動の理解及び評価に対する現象論的モデルの適用性」というタイトルで、収着モデルを用いた研究が紹介された。最近の収着モデルでは、収着サイトを2種類以上仮定するモデルが多く、これらのサイトは電気二重層モデルでは strong site（高い収着能力を持つものの、収着サイト濃度は低い）および weak site（収着能力自体は低いが、収着サイト濃度は高い）、電気三重層モデルでは inner sphere（電気三重層の内側）、outer sphere（電気三重層の外側）として記述されている。また、複雑な化学組成を持つ鉱物に対する収着メカニズムについては、それらに含有される単純な化学組成を持つ金属酸化物への収着を考慮することでおおむね説明できることが示されている。天然の系では SiOH 基、AlOH 基、FeOH 基の3種類の官能基および粘土の層間がほぼ支配的な収着サイトであり、これらについてはほぼ参加者の間で一致した見解であった。セッション3で議論されたように、従来の電気化学的反応から、いわゆる"静電項"（固相と溶液の反応を評価するためには、固相表面と固相表面近傍の核種の活量との相互作用を議論する必要がある。ここで用いる静電項は、固相表面近傍の核種の活量とバルクの溶液の核種の濃度との差を補正するために必要な項、一般的にポアソンーボルツマンの補正項が用いられる）を考慮しないモデルについても提案された。また、拡張 Wanner モデル、配位子交換モデルといった従来現象論的収着モデルに用いられていない新しいモデルについても議論がなされた。最後に、蛇足ではあるが圧縮ベントナイト中の核種移行評価に収着モデルを応用する例も2件あり（その他にセッション2で1件）、いずれも動燃事業団で得られた拡散実験をベースに議論されていた。

発表内容の概要を以下に、要旨を別添にそれぞれ示す。

Dr.L.Duro；Cd の am-Fe(OH)$_3$, TiO$_2$ への収着挙動についてバッチ法による収着実験および表面錯体モデルによる解析を行っている（ここで、am はアモルファスを示す）。個々の実験データは、am-Fe(OH)$_3$, TiO$_2$ の表面特性値および固相と Cd の反応定数をそれぞれ与えることによって評価可能であることを示した。また、これらのモデルは am-Fe(OH)$_3$, TiO$_2$ の混在する系でも適用可能であることを示した。

Dr.D.Waite；U(VI)の am-FeOOH への収着挙動についてバッチ法の収着実験結果およびクンガラウラン鉱床の風化帯の岩石（主な鉱物はカオリナイト）を用いた逐次抽出法による収着箇所の同定を行った結果を紹介した。U(VI)は主に鉱物表面の鉄に被覆された部分に濃集しており、濃集部にはほかにも Al,Si,P 等が存在している。また、この鉄コーティング部を詳細に測定した結果、ほとんどがアモルファスであるが、一部 goethite のような結晶パターンを示す構造も確認されている。また、逐次抽出法による H$^+$ の脱離挙動から、am-FeOOH についてはフェリハイドライトのような2つの収着サ

イトを持つことが推定された。表面錯体モデルでは、逐次抽出法によって得られた U(VI)の脱離挙動から、表面錯体として収着している U(VI)についてモデル化を行い、表面錯体モデルが天然の岩石の収着挙動を説明できることを示すとともに、天然の岩石への核種の収着挙動を表面錯体モデルを用いて説明するためには、鉱物化および沈殿物として取り込まれた核種と収着している核種とを明確に分ける必要があることを示した。

Dr.D.Turner；U(VI)の収着挙動に関する研究を行い、収着挙動の固液比依存性から、Kd ではなく、Ka で規格化すると、ほぼ同様の値を示すことが確認された。本結果については Np(V)についても同様の傾向が観察されている。また、いずれの核種も水酸化化学種を形成すると考えられる領域では Kd が高いものの、炭酸錯体を形成すると考えられる領域では Kd が低下することが確認された。

Dr.C.Linklater；Sellafield サイトに算出する堆積岩への U(VI)の収着挙動に関する研究を行い、表面錯体モデル（電気三重層モデル）による解析を行っている。本研究では収着サイトは、堆積岩表面を被覆している hematite を仮定しており、U(VI)の化学種は電気三重層の内側に UO_2OH^+, UO_2CO_3 が収着し、外側に $UO_2(OH)_2$, $UO_2(OH)^-$, $UO_2(CO_3)_2^{2-}$, $UO_2CO_3OH^-$ がそれぞれ収着する。本研究については、凝灰岩に対する U(VI)の収着挙動とモデル化による解析結果が一致していない点が指摘されていた。

Dr.M.Olin；本研究では Ni の天然の SiO_2, goethite, カオリナイトへの収着挙動の研究が行われた。この結果、Ni の goethite への収着挙動については表面錯体モデルを用いてある程度説明できるものの、SiO_2、カオリナイトへの収着挙動については説明が困難であることを示した。

また、狭い空隙中の電位分布について考察を行っており、イオン排斥バラメーターkを、イオン強度と間隙幅から計算し、圧縮ベントナイトのような狭い間隙中での Kd や溶解度算出のためには、固相表面の電気的な相互作用による陽イオン、陰イオンの濃度の変化を考慮すべきとの意見を示した。また、本モデルでは、陽イオン化学種については固相表面近傍で濃度が上昇するため、表面拡散の driving force になる可能性もあることを示唆した。

Dr.K.Bond；U(VI)と Pu(VI)の白雲母、緑泥石への収着挙動に関する研究を行い、電気三重層モデルによるモデル化を行っている。白雲母については SiOH 基、AlOH 基への収着を考慮し、サイト濃度はそれぞれ 1:1 を仮定している。一方緑泥石については、SiOH 基、AlOH 基、FeOH 基への収着を考慮し、サイト濃度はそれぞれ 5:5:6 を仮定している。この結果、天然に産出する複雑な化学組成を持つ鉱物の Kd 算出に際しても支配的な反応を考慮した表面錯体モデルの適用が可能であることが示された。

Dr.M.Crawford；本発表では CHEMVAL2 収着プロジェクトで得られた結果についての発表があった。CHEMVAL2 収着プロジェクトでは、MinUSil5（シリカ鉱物）への H^+ 滴定実験および Ni の収着挙動の pH 依存性結果について表面錯体モデルを用いてモデ

ル化を行っている。本結果では、多くのモデラーが異なった収着モデルを用いて解析を行っていたが、得られた結果はどれも実験値をよく説明できるものであった。また、intact な Clasach Sandstone 中の U(VI)の移行挙動を評価するために実験室でのカラム実験を行った。本実験では、U 単体での移行、U に Cd, EDTA, アルダル酸(saccaric acid)をそれぞれ別々に混合した場合の移行挙動について評価を行った。この結果、Cd,EDTA については U の移行挙動に変化はみられないものの、アルダル酸を用いた実験では U の拡散係数は高くなった。これらの実験結果についても、U の熱力学データ、実効拡散係数、Kd を用いた核種移行計算によって説明することができることがわかった。本解析で用いた Kd は、U の拡散に寄与する有効表面積を与えることによって、収着モデルから算出している。

これらの結果から、収着モデルを天然の岩石の収着挙動の説明に用いることは可能であり、実験室レベルでの拡散実験結果の評価に用いることも可能であるが、原位置での Kd の予測を行うためには不明確なパラメーターが多いため、困難であるとの意見を述べた。性能評価へ収着モデルを用いる場合は、単純なパラメーターのみを用いたおおまかなモデルが重要であり、サイトスペシフィックなデータベースが必要であるとの見解を示した。

<u>Dr.J.Davis</u>；U(VI)の石英への収着挙動に関する研究および表面錯体モデルによるモデル化を行っている。表面錯体モデルでは、1 つの収着サイトおよび 1 種類の収着反応を考慮したモデル、2 つの収着サイトおよび 2 種類の収着反応を考慮したモデル、2 つの収着サイトおよび 3 種類の収着反応を考慮したモデルの合計 3 種類のモデルを用いて解析を行った。この結果、後者のモデルがもっともよく実験結果を説明できるものであった。また、カラム実験を行い、石英粉末を充填したカラム中の U(VI)の移行挙動から算出される Kd は、表面錯体モデルによって評価した値とほぼ一致することが示された。

<u>Dr.Y.Albinsson</u>；Th(IV)の TiO_2 への収着挙動についてバッチ法による研究を行い、収着率のイオン強度、pH 依存性のデータ取得を行った。さらに、電気三重層モデルによる解析を行っている。本モデルでは、$Th(OH)_4$、$Th(OH)_3^+$が電気三重層の内側に収着すると仮定している。本モデルを用いて計算された Th(IV)の TiO_2 への収着率は、実験結果とほぼ一致する結果となった。 Th は IV 価が安定であることが知られており、収着実験でも還元剤等を用いずに容易に IV 価を得ることができる。このため、本実験データおよびモデル化による知見は、還元条件下で IV 価となる他のアクチニド(Pa,Np,U,Pu)のアナログデータになりうるものと考えられる。

<u>Dr.T.Arnold</u>；U(VI)のフィライト（千枚岩）への収着挙動に関する研究を行っている。また、フィライト構成鉱物についても U(VI)の収着挙動を調べ、収着を支配している鉱物の特定および収着モデルによるモデル化を行っている。この結果、フィライトへの収着挙動は風化によってフィライト中に生成した二次鉱物であるフェリハイドライト

への収着が支配的であることが推定された。

Dr.M.Siegel；Dr.Olin の研究と同様に、Ni の天然の SiO_2, 合成された goethite, カオリナイトへの収着挙動に関する研究について紹介があった。本研究では、電気三重層モデルを用いた Ni の goethite への収着挙動についての報告があり、Ni^{2+}の収着サイトが Na^+、Li^+と異なり、Ni^{2+}は電気三重層の内側へ収着するモデルを用いることによって実験結果をよく説明できることを示した。

Dr.T.Heath；本研究では、NRVB(Nirex Reference Vault Backfill；セメント質の埋め戻し材)に対する Cs, I の収着挙動について Rd の Ca/Si 依存性を取得し、電気二重層モデルによる解析を行っている。本解析では、収着する化学種はその電荷と反対の電荷を持つサイトへのみ収着することを仮定しており（中性の化学種については中性のサイト）、本モデルを用いることによって、NRVB に対する Cs, I の Rd を説明できることを示した。

Dr.M.Ochs；現在動燃事業団と共同研究を行っている収着データベースの現状およびモデル化について紹介を行った。文献収集の結果、イオン交換性の高い元素については、Kd が一般的に高い傾向が確認されたが、石英に対する Kd はどの元素についても小さい傾向が確認された。Cs, Ra, Sr の収着挙動については拡張 Wanner モデル(Dr.H.Wannerが提唱したイオン交換モデルと表面錯体モデルを組み合わせたモデルを基本としたモデル）を用いることによってほとんどの他の研究者の行った実験結果を説明することができることを示した。さらに Cs については拡散モデル（動燃事業団の佐藤氏が提唱したモデル）を組み合わせることによって、圧縮ベントナイト中の移行挙動を評価することが可能であることを示した。

Dr.L.Wang；Eu(III)のイライトおよび Boom Clay への収着挙動についての研究発表があった。 イライトへの Eu(III)は pH<6 でイオン交換性を示し、pH>6 でイオン交換性を示さなくなる結果が得られた。また、pH>6 ではイライトの陽イオン交換容量以上のEu(III)が収着しており、本領域ではイライト結晶端面への収着が生じていることを示した。

Prof.K.Stamberg；ベントナイトに対する U(VI)の収着挙動に関する研究発表があった。本研究では、U(VI)の Kd は HCO_3^-, CO_3^{2-}を含む溶液中で pH= 3-9.5 の領域で行われた。実験結果については、表面錯体モデルを用いた解析が行われ、CCM(constant capacitance model), DLM(diffuse layer model)の2種類の電気化学的モデルと電気化学的効果を考慮しないモデル CEM(chemical equilibrium model)の合計3種類のモデルが用いられた。モデル化では、3つのモデルに共通するパラメーター（収着サイト濃度、イオン濃度、様々な反応定数等）は固定してある。表面錯体モデルを用いた解析の結果、計算結果は DLM>CCM>CEM の順に実験結果をよく説明できるが、これらのモデルによる差はほとんどなく、必ずしも複雑なモデルが現象をよく説明しうるとは限らないことが示された。

Dr.J.O.Leckie；U(VI)の粘土への収着挙動の炭酸濃度依存性についての研究が紹介された。バッチ法による収着実験の結果、U(VI)は pH4-11 の領域で強く収着すること、Ca^{2+}/Mg^{2+}, Na^+は U(VI)の収着サイトと競合しないこと、クエン酸は 1:1 では U(VI)の収着には影響しないが、100:1 では収着挙動に影響を与えること、炭酸分圧は、U の炭酸錯体を生成させ、Kd を低下させること等が示された。

Dr.J.Ly；Cs, Co, Np, Am, U の粘土への収着挙動に関する研究を行った。本研究では FoCa7、Mx-80 の2種類の粘土が用いられた。本研究では、元素の吸着量の pH 依存性から、粘土鉱物へのこれらの元素の収着メカニズムは単純なイオン交換反応だけでなく、配位子交換(ligand exchange)反応も存在していることを示した。また、圧縮ベントナイトへの収着モデルへの適用例についてもふれ、動燃事業団で取得した圧縮ベントナイト中の Cs,Np の拡散実験から得られた Kd との整合性について議論を行った。この結果、モデル化で得られた Kd は実験値より若干高い結果となり、実験値は表面拡散の影響を受けているのではないかという推定を行った。

Dr.N.Marmier；Yb^{3+}のカオリナイト、モンモリロナイトへの収着挙動について研究を行った。この結果、カオリナイトへの Yb^{3+}の収着挙動は、カオリナイト中の主要な収着サイトと考えられるアルミナおよび hematite への収着を仮定することで説明できることがわかった。しかし、silica とアルミナへの収着を仮定すると実験結果を評価できないことがわかった。また、モンモリロナイトについては H^+/Na^+の交換、H_4SiO_4 の表面水和基への配位、 Na^+/Yb^{3+}の交換を仮定することで実験値を説明できることがわかった。

Dr.P.Brady；核種のカオリナイトへの収着挙動に関する研究を行い、Kd の温度依存性を確認した。また、本結果について収着サイト数、反応定数をパラメーターとして表面錯体モデル（constant capacitance model）を用いた解析を行った結果、SiOH 基および AlOH 基の酸解離定数(pK)が温度の上昇に伴い、低下する事が推定された。

4.5 セッション5「議論」

本セッションでは、コンサルタントの Dr.J.Bruno が座長をつとめ、Prof.O.Leckie, Drs. H.Wanner, S.Altmann, B.Ruegger, C.Tweed らをパネラーとしたパネルディスカッションが行われた。本セッションでは、現象論的収着モデルの限界、適用範囲、不確実性の処理、Transport model とどのようにリンクさせるか等に議論が集まった。以下に議論の概要を示す。

本セッションでは、最初に Dr.J.Bruno より、現象論的収着モデルが未だに実験室レベルのバッチ法による収着データのみの確証に用いられており、今後は多くの研究例を用いて現象論的収着モデルの性能評価への有用性を示すことが重要であるとの見解が述べられた。Dr.J.Bruno はさらに、現在の性能評価に用いられている Kd が、バッチ法の収着実験、インタクト岩石を用いた拡散実験、原位置試験から総合的に決定している値であ

り、保守的な値に際しては、あるファクターをかけて（通常 1/10）設定を行っているという現状を踏まえ、

- 現象論的収着モデルを用いることによって、現段階で評価している以上の情報が得られるのか？、
- 現象論的収着モデルは現段階では極めて貧弱な道具であり、本モデルを性能評価へ反映させるためには、伝統的な手法で得られた Kd のバックアップとして用いることが望ましいのではないか？

との疑問を投げかけた。また、性能評価において Kd を設定する上で、重要な点として、Kd が地球化学的条件の関数である点を指摘し、

- 性能評価で与えた Kd がなぜその値なのか？
- 性能評価で与えた Kd を支持する理屈は何か？

の２点が信頼性の構築（build up confidence; 本セッションでこの表現について盛んに議論がなされた）の点で重要であるとの見解を示した。

この点について、ANDRA の Dr. G.Ouzounian は、「処分環境へモデルを適用する場合、多くの現象を考慮するために、たくさんの情報、多くの仮定を行わなければならない、このように多くの不確実性の中でなぜ収着モデルを用いるのか？なぜ地球化学条件の関数として考えるのか？」との疑問を投げかけた。

これに対し、Dr.S.Altmann は、「サイトスペシフィックな条件で、地下水が特定でき、周辺の岩盤等の環境条件も特定できれば Kd はある程度の幅で決定されるが、処分シナリオではある程度の環境変化も予測しなければならない。Cs,Ni 等のベントナイトへの収着については収着モデルの適用も可能であると考えられるが、花崗岩のような岩石を対象とした場合、亀裂充填鉱物の特定が困難であるため、サイトスペシフィックでもモデルの適用は困難であると考えられる」との見解を示した。以下、議論の概要を示す。

Dr. G.Ouzounian「限定付きのモデルであれば、むしろ適用しない方がよいのではないか？」

Dr.H.Wanner「Nagra がヴェレンベルグサイト調査において地下水を調べた結果、地下水組成は広い変動幅を持つことがわかった。仮にサイトが決定していても必ずしも地球化学的条件は一定でない可能性がある。こうなると、それぞれの条件ですべて Kd を取得することの方が困難である」

Dr. G.Ouzounian「収着モデルでは、表面錯体モデルにおける gotehite コーティング、スメクタイト層間のイオン交換等、均一なモデルを用いるが、これで十分なのか、環境条

件の変化においては、これらのパラメーターも変化するのではないか？」

Dr.M.Bradbury「モデルが適用できるのはシンプルな系に限られる。グリムゼルの結果では、Cs^+の移行挙動でさえもNa^+,K^+,Ca^{2+}等の競合イオンの影響で評価が困難であった。」

Dr.S.Altmann「移行が伴う場合、地球化学条件の以外に、その場所、時間のファクターも必要」

Dr.J.Davis「pH 変化や不確実性があるのであれば、Dr.H.Wanner のファクターを用いて補正すればよい」（Dr.H.Wanner は、圧縮ベントナイトや intact rock 中での核種移行挙動について、不確実性が多いため、Kd を一律で下げた値を設定してはどうかと提案した、これが、本会議では、Wanner factor として慣用的に、たたき台的に用いられている）

Dr.M.Siegel「移行モデルと表面錯体モデルを組み合わせて、さらに処分環境の不確実性を取り込むことによって、Kd の設定はより困難となり、仮に設定したとしても、非常に広範囲な値となるだろう、しかし、化学条件の変化も入れた、ダイナミックコンディションでの確証研究は必要である」

Dr.P.Brady「Transport モデルと現象論的収着モデルを組み合わせた場合、移流・分散による Kd の影響をどのように評価するかが不明である」

Dr. G.Ouzounian「純粋な系の実験よりも、複雑な系によって Kd のみから単純なモデリングを行うことの方が重要ではないか？」

Dr.M.Bradbury「収着を支配する配位子(key legand)、競合イオンを探すためには、純粋な系で実験することが望ましい」

Dr. G.Ouzounian「純粋な系で得られた結果を、どのように天然へ適用するのか？特に intact rock 中の収着サイト濃度はどのように評価するのか」

Dr.P.Brady「収着モデルを intact rock 中の移行評価に用いる場合、移行経路のおおよその表面積を評価する必要がある。ただし、詳細なモデルでは、確証できない。例えモデルによる予測と実際の Kd が合っていたとしても、これだけ不確実性があると、どれが合っていてどれが間違っているかという評価は困難である。本会議では、まず、収着モデルの問題点の現状をまとめた上で、性能評価へ反映するならばその手順を決定すべきである」

Dr.Y.Albinsson「室内実験では、Transport モデルに収着モデルを組み合わせることによって評価できている例がある。しかし、in-situ では、不確実性が多すぎる。ただし、chemical transport モデルと収着モデルのカップリングは必要」

Dr.M.Siegel「性能評価側から早く chemical transport モデルと収着モデルの単純なカップリングモデルを開発すべきである」

Dr.Y.Albinsson「熱力学的な計算を行う場合、均一な沈殿だけでなく、共沈の影響はどのように考慮されるのか？熱力学データでは共沈の影響を考慮することは困難ではないか？」

Dr.J.Bruno「現段階では共沈の影響は考慮できない」

Dr.Y.Albinsson「共沈を収着モデルに入れずに chemical transport モデルを解くことは、それ自体間違っている」

Dr.M.Ochs「収着モデルは、Kd の感度(sensitivitiy)を評価することに用いるべきである。もし、熱力学的な計算を行わない場合、我々は Kd に関する多くのデータを取得しなければならない。処分場の極端な地球化学的特性を把握し、その変動幅を把握することが重要である」

ここで、コンサルタントの Dr.S.Altmann から、「性能評価で現象論的収着モデルを用いるためには、不確実性をどのように考慮すればよいか」との質問が投げられた。

Dr.S.Altmann「最初は酸化条件であっても、地下水が人工バリア中に達し、核種を溶出させる際に還元条件であれば、還元条件での評価を考慮すればよい。支配的な収着サイトは、金属酸化物よりも金属水酸化物またはそのアモルファスといったものを考慮すればよいのではないか？移流、分散に伴う不確実性は、実際の処分場で実験を行わない限り、収着モデルを用いようがバッチ法によって得られた Kd を用いようが同じようについてまわるのではないか？」

Dr.M.Ochs「α-FeOOH, HFO(ferric oxyhydroxite)にフォーカスするのは危険ではないか？鉄以外の官能基（SiOH 基、AlOH 基）も重要である」

Dr.S.Altmann「地球化学計算を行う場合は、単純化することが重要である。天然の岩石への収着挙動を把握する場合は、FeOH 基以外にも SiOH 基、AlOH 基も組み合わせることによってより現実的な結果が得られることはわかっている」

ここで、パネラーから参加者へ、いくつかの質問がなされた。まず、パネラーの Prof.O.Leckie より、「原位置試験か室内実験か何か１つ細かい仕事をやることによって、どのように Kd モデルを適用するかケーススタディーとして行ってはどうか？」との提案が出された。今回の会議でもオーストラリア、H.Wanner,PNC がこれらのアプローチを実際に行っている。しかし、本セッションでは明確にどのデータをもちいて行うかは決定しなかった。

また、Dr.S.Altmann より、「いかなる地球化学的なエンドメンバーを用いれば、モデルによって計算された Kd の信頼性を増すことができるか？」との質問も出されたが、参加者から明確な回答は得られなかった。

さらに、パネラーの Dr.C.Tweed から、「性能評価における Kd を設定する場合、メカニスティックモデルは用いず、実験から得られた値のみから設定することが望ましいか、メカニスティックモデルによって評価される Kd と実験から得られる Kd の両方を考慮して設定することが望ましいか？」との質問が出された。本質問に対しては、以下のような議論がなされた。

Dr.M.Siegel「性能評価では、メカニスティックモデルによって評価される Kd と実験から得られる Kd の両方を考慮して設定することが望ましい」

Dr.M.Bradbury「Kd は常に一定の値を与えられるものではない。違った条件において、違った値が存在する。したがって、性能評価ではむしろ、Kd ではなく、溶解度で移行系路上の核種の濃度を規制してはどうか？」

Dr.P.Brady「現象論的収着モデルを天然の系での Kd 評価へ用いるにはこのモデルはあまりにも単純すぎる。intact rock 中の Kd を評価することには用いるべきではない。ただし、Kd の信頼性構築のためにある程度の変動幅を規定するのに用いるのであればよい」

PNC「現象論的収着モデルは Kd の信頼性を構築する上で重要である、例えば、Cs^+ のベントナイトへの収着挙動については、ある程度イオン交換で説明ができ、pH, Eh よりも地下水中のイオン濃度によって Kd が支配される。このような挙動については、仮にデータが存在しなかったとしても、Sr^{2+}, Ra^{2+} についても予測が可能である。また、U は炭酸共存下では分配係数が下がる傾向が確認されており、このような挙動は他のアクチニドやランタニドについても予測することはできる。このような予測を行う上でも現象論的収着モデルの性能評価への適用は重要である」

Dr. G.Ouzounian「現象論的収着モデルでは、むしろ、収着メカニズムを考慮せずに単純化することが望ましい。すべての系ですべてのメカニズムを評価することはできない。複雑な系へ適用すればするほど、不確実性が出るので、モデルはよりシンプルなものがよい」

Dr.H.Wanner「すべての元素について複雑なモデル化は不要である。また、すべてのシステムで複雑なモデルを適用することも不要である。どれが安全で、どれが毒性に寄与する因子かを見極めた上で、モデル化を用いることが望ましい。例えば、移流支配の場では収着は考えないとか、ベントナイト中の拡散支配の場では詳細にモデル化を行うとか、溶解度で与えれば収着を考慮しなくてもいい元素もあるだろう、そうやって考えれば、必要な元素や、必要なモデルは限られてくる」

Dr.D.Waite「多孔質媒体や亀裂充填鉱物のようなある程度粉砕されているものに関しては、収着モデルは適用可能であると考えられる」

Dr.M.Ochs「現象論的収着モデルは Kd の信頼性を構築する上で重要である。ベントナイトの様に比較的均一な媒体であれば、Dr.H.Wanner のイオン交換モデルが有益であるし、実際評価を行うことは可能である。また、ダイナミックな場でも Dr.Sato（PNC）の拡散モデルによって、表面拡散の効果等を把握することができる」

ダイナミックな場への適用に関しては、表面拡散、移流分散、移行経路の不確実性について指摘されたものの、現象論的収着モデルとこれらの現象は明確に分けるべきとの意見が出された。

本議論については、最後に Dr.J.Bruno から、現段階で現象論的収着モデルの性能評価

への適用の可否は論じないが、もしあなたが性能評価で用いる Kd を設定せよといわれた場合、その defensible な Kd をどのように設定するかを常に念頭に置いて研究を進めるようにとのまとめがあった。

　　コーヒーブレークの後、再び座長の Dr.J.Bruno から収着モデルのアプローチに関する議論として、「性能評価に用いる Kd については、多くプロセスが存在するため、モデル化する上ではできるだけ単純なモデルでかつメカニズムに忠実なモデルにフォーカスする必要がある。いったいどんなモデルであれば性能評価へ適用可能であるか?」との質問が出された。それに対し、以下のような議論が展開された。

　　Dr.S.Altmann「環境の変化を想定した系においても、収着サイトについては Fe コーティングモデルが妥当であると考える。FeOH 基への核種の収着挙動や熱力学平衡定数についても Dzombak and Morel (1991)等でデータが豊富である。また、goehite についても、より安定なフェリハイドライトへ変化することが想定されるため、支配的な収着サイトとしては妥当である」

　　Dr.J.Davis「緩衝材については、モンモリロナイトリッチであれば、モンモリロナイトでモデル化することが妥当である」

　　Dr. G.Ouzounian「天然バリアについては、マイナー鉱物や不純物の影響で Kd を支配する固相が多様化することが考えられる。そのため、実際の処分サイトの性能評価を行う際にサイトに適した収着固相を考えることが妥当である。」

　　Dr.D.Waite「性能評価に際しては FeOH 基よりも AlOH 基、SiOH 基を考慮した方がより保守的ではないか?」

　　Prof.M.Hakanen「岩石中の核種の収着挙動を扱う場合、岩石中の核種の移行経路が重要である。地下水中の核種は、地下水と接している固相の表面と反応するわけであるから、固相の表面積を特定することが重要となる。現象論的収着モデルは、このようなスケーリングの効果を評価することに用いることが重要となる」

　　Dr.C.Tweed「いずれにしろ、一様な鉄コーティングモデルが妥当であり、スケーリング効果のためにも表面積を把握することが重要」

　　Dr.J.Davis「鉄コーティングモデルはトップダウンのアプローチ、単純化するにしてもあまりにもメカニズムを軽視していないか?」

　　Dr.C.Tweed「天然では、場所によって mineralogy が多少変化しても、だいたいケイ酸塩鉱物が主体であり、とくにアルミノケイ酸塩は普遍的に存在する。」

　　Dr.M.Bradbury「天然ではほぼ FeOH 基、AlOH 基、SiOH 基の３種類のコーティングを考えれば妥当であろう、あとは、どれが支配的であるかを考慮してモデル化すべきである」

　　Dr.Y.Albinsson「flow wetted surface 上での表面拡散および表面吸着はメインプロセスである。収着モデルは表面積補正に用いるべきである」

Dr.M.Bradbury「移行に寄与する表面積をどのように見積もるのか？我々が従来やってきた滴定法では見積もることは困難である」

Dr.C.Tweed「拡散実験または原位置試験からフィッティングによって決定することが妥当である」

Dr. G.Ouzounian「確かに、性能評価では、核種の移行経路上の液固比を把握することは重要である。しかし、原位置でどのようにこれらの値を取得するのか？また、今回の会議でも多くの研究者がU(VI)を用いて研究を行っていたが、U(IV)のデータがない場合、U(VI)で評価するつもりなのか？それはあまりにも悲観的なモデルではないか？」

Dr.M.Ochs「現象論的収着モデルの概念は正しい、また、移行経路の特定は、原位置試験等で把握するパラメーターであると考えられる。このため、移行経路に関する議論は、収着モデルの議論と分けて議論してはどうか」

Prof.O.Leckie「収着モデルだけでいえば、地球化学条件が推定でき、収着サイトを固定できれば、Kdの範囲を特定することは可能であると考えられる」

以上の議論から、性能評価には、Kdの感度を評価する上で、単純化した収着モデルによる評価を取り入れることに関しては、一定の理解が得られていた。また、性能評価へ適用するKdについて、実験値と現象論的収着モデルから計算された値に共通する不確実性（たとえば、空隙中の核種移行を支配する有効表面積、動水勾配、沈殿、イオン排斥、分子ふるい効果等）については、現象論的収着モデルの有効性の議論からは切り離して議論を行うべきであるとの見解で一致した。

4.6　セッション6「まとめ」

会議のまとめでは，単純なモデルの適用についてはOECD/NEAとしては今後奨励していくこととなった。また、性能評価への現象論的収着モデルの適用の可否に対しては、各研究者間でモデル化の手法等に明確なコンセンサスが得られなかったことから、OECD/NEAとして現象論的収着モデルの適用に関する勧告は現段階では行わない結果となった。OECD/NEAでは，本会議で議論された内容を基に，１０月までに現象論的収着モデルの現状および対応方針、将来の研究への勧告をまとめた報告書を完成させ、性能評価諮問グループ（PAAG）へ今後の研究課題に関する勧告を行う予定である。また、１０月の会議では、標準化した試験方法による国際協力下での確証研究およびデータベースの整備案をOECD/NEAから提案し、各国間でそれらの研究の可否を検討する予定である。本会議では、１０月に提出される予定の報告書の一部が提出された（別添４）。

5．第二次とりまとめに向けての事業団の方針（報告者意見）

事業団では、第二次とりまとめにおいて地層処分の技術的信頼性を示すために、ニアフィールドを中心とした処分システムの性能を充分な信頼性をもって評価することを目標として研究をすすめており、ニアフィールド性能の評価データの信頼性構築と品質保証がき

わめて重要となる。このため事業団としては、性能評価に用いる Kd については、従来通り既存の Kd データから得られる知見に加え、現象論的収着モデルによる計算結果を考慮して評価を行っていくことが望ましいと考えられる。しかし、前述したように現象論的収着モデルは、性能評価で用いる Kd を直接算出するために用いるのではなく、設定した Kd の信頼性の補完、環境の変化に伴う Kd の変動幅の推定に用いることが望ましい。

　今後は、本会議を通じて性能評価のための信頼性の高い収着データセットの整備およびその妥当性の評価の方法論を検討していくことが重要である。

別添1「会議の目的およびプログラム」

NEA INTERNATIONAL MEETING
ON
CHEMICAL MODELLING OF SORPTION
in the Field of Radioactive Waste Management

6-8 May 1997
Linton Lodge Hotel, Oxford, UK

OBJECTIVES AND PROGRAMME

NEA INTERNATIONAL MEETING ON CHEMICAL MODELLING OF SORPTION

6-8 May 1997, Linton Lodge Hotel, Oxford, UK

An international meeting on chemical modelling of sorption in the field of radioactive waste management will be held on 6-8 May 1997, at the Linton Lodge Hotel, located in central Oxford, UK. The objectives of the meeting are:

- to investigate the potential of mechanistic models for improving confidence in predictions of sorption values for performance assessment;
- to gather new information and promote discussions within the scientific and waste management communities
- to provide an input to a Status Report on mechanistic sorption modelling that will be published by the NEA and be given the widest possible dissemination.

BACKGROUND

This international meeting is organised by the Forum on Sorption Modelling for Performance Assessment, set-up within the NEA with the participation of fourteen radioactive waste management agencies and licensing authorities from Member countries. The decision to launch this project arose out of a growing awareness in the radioactive waste management performance assessment community that there would be a greater level of confidence in the use of sorption distribution coefficients (Kd's) if these were supported by an understanding of the underlying processes.

This activity is a follow up of two previous NEA meetings on related topics:

- Radionuclide sorption from the safety evaluation perspective, Interlaken, Switzerland, 16-18 October 1991; and
- Informal expert meeting on the use of Surface Complexation Models for representing sorption phenomena in natural systems, Stanford University, Stanford, California, USA, April 5-7, 1993

TOPICS COVERED BY THE MEETING

The meeting will concentrate on three topics:

- the demonstration of the usefulness of sorption chemical models to performance assessment with numerous examples where they have been used successfully;
- a review of the practical approach to sorption chemical modelling, identifying key questions facing experimentalists and modellers;
- an overview of what has been done to date with mechanistic models for understanding and estimating Kd's in natural systems.

Session 1 : Kd and Performance Assessment

- Performance assessment context and geochemical context of Kd
  - Performance assessor's point of view
  - Reviewer's point of view (safety authorities)
  (Invited papers and discussions)

Session 2 : Chemical models and Kd for Performance Assessment

- Review of chemical models for sorption
  - key parameters and how to get them

- emphasis on key questions facing experimentalists and modellers
(Invited papers and discussions)

Session 3 : Approach to sorption modelling of natural systems

- Strategic approaches to sorption modelling of natural systems
  - how it is done : top down and bottom up approaches
  - examples from several projects, including non radioactive waste examples
(Invited papers and discussions)

Session 4 : Application of mechanistic models to understanding/ estimating Kd's in natural systems

- State-of-the-art (mass action, mass balance sorption models and natural systems)
  - Short oral presentations (15-20 min., plus discussion).
  - In order to avoid repetitions with Session 3, contributions will be structured around a questionnaire called Data Sheet (see below).
  - The objective is to learn about practical experiences, not to scrutinise results.

Session 5 : Discussion of key questions

- Technical / chemical aspects
  - emphasis on model parameters
  - success / failures
  - problems /solutions
- Link to PA, better support of Kd's
(Panel discussions)

Session 6 : Consensus, Wrap-up

- Conclusions of the meeting

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List of Key Questions

The purpose of this list is to focus discussions on issues that have been identified as critical to successful use of chemical modelling of sorption in natural systems for the benefit of radioactive waste management. Authors have also been invited to consider these questions when preparing their abstract.

Key issues to be considered by the meeting are:

- Kd
- How to identify critical mechanism governing sorption of radionuclides (RN)
  - solid
  - RN
  - solution composition (majors)

- Thermodynamic Data Base (TDB) for aqueous chemistry of RN, etc.
  - activity coefficients

- How do you measure/quantify the real composition of the solid surface
  - phase identification
  - site type

- How much of each site type
  - site specific concentrations

- What are the key reactions between solutes/surface sites
  - stoichiometry, K, H+, major cations, RN

- Electrostatics necessary?
  - what conditions
  - which RN
  - what range of system composition

- Are Kd values measured in laboratory the same as those in-situ?
  - scale, s/s ratio
  - modification of surface composition

- How well compare batch sorption data (Kd's) with Kd's derived from diffusion measurements?
- How does approach used (data/model) support/aid use of Kd's
  - end user
  - why was approach chosen

Programme

Time	N°	Sessions, Objectives, Papers	Authors / Speakers

DAY 1, Tuesday, May 6

0830		(Meeting of Chairpersons and Speakers of the day)	
09.00		**Opening of the meeting**	*Cherry Tweed AEA T*
		Session 0 : Introduction	
09.05		*General objectives of the meeting*	*Cherry Tweed AEA T*
		Recent Developments in the UK	*Alan Hooper, NIREX*
		Session 1 : Kd and Performance Assessment	
			Chairperson Cherry Tweed
09.15	1.1	*Treatment of Sorption in Performance Assessment - the Nirex Perspective.*	*Alan Hooper, NIREX*
09.45		*Discussion*	
0950	1.2	K_d *and Performance Assessment : A reviewer's point of view.*	*Hans Wanner, HSK*
10.20		*Discussion*	
10.25		**COFFEE**	
		Session 2 : Chemical models and Kd for Performance Assessment	
			Chairperson **Michael Ochs**
10.45	2.1 2.2	*Key questions, Key parameters* *Strategies for Kd Studies*	*Scott Altmann, BRGM*
		Session 3 : Approach to sorption modelling of natural systems	
113.0 0	3.1	*Acquisition of Data to support Nirex Performance Assessment Studies*	*Cherry Tweed, AEA T*
12.00		**LUNCH**	

			Chairperson **David Waite**
	3.2	*On the application of the Kd concept and mechanistic models in performance assessments*	*Stig Wingefors & Randy Arthur, SKI*
13.30	3.3	*A Mechanistic Description of Ni Sorption on Na-montmorillonite*	*M. Bradbury & B.Baeyens, PSI*
14.00	3.4	*PNC Approach to Increase Confidence in Sorption Coefficients for Near-field*	*Mr. Shibutani,PNC*
14.20	3.5	*An approach to Provide a Sorption Database for Performance Assessment*	*YH Cho, KAERI*
14.50		**TEA**	
			Chairperson **Gerald Ouzounian**
15.10	3.6	*Uranium Sorption Studies within the Koongarra Natural Analogue Project*	*Tim Payne, ASARR*
15.50	3.7	*Determination of Radionuclides Migration Parameters in a Clay Formation : The Belgian Approach*	*Robert Gens, ONDRAF*
16.15	3.8	*Application of a Laboratory-derived Surface Complexation Model for Zinc Adsorption to Field Observations of Zinc Transport in Ground Water*	*James Davis, USGS*
17.00		**End of Session**	

Time	N°	Sessions, Objectives, Papers	Authors / Speakers

DAY 2, Wednesday, May 7

0830   (Meeting of Chairperson and Speakers of the day)

Session 4 : Application of Mechanistic Models to understanding/estimating Kd's in natural systems

Chairperson

Patrick Brady

09.00	4.1	*Proposal for the Development of Predictive Surface Complexation Models to be Used as a Supporting Tool to Kd Parameters in PA*	*Lara Duro*
09.20	4.2	*Characterisation of Natural Substrates with Regard to Application of Surface Complexation Models".*	*David Waite, UNSW*
09.40	4.3	*Sorption Modeling for Performance Assessment at the Center for Nuclear Waste Regulatory Analyses*	*David Turner, SWRI*
	4.4	*Development of a Mechanistic Model of Sorption of U(VI) onto Sellafield rocks.*	*Claire Linklater, AEA T Keeley, Bond*
10.20	4.5	*Modelling Sorption of Nickel on Silica, Goethite, and Kaolinite*	*Markus Olin, VTT*

10.40   **COFFEE**

Chairperson
Pedro Hernan

11.00	4.6	*Pore Water Composition and Bulk Solution in Crystalline Rock and in Bentonite Clay*	*Markus Olin, VTT*
11.20	4.7	*Mechanistic Modelling of Sorption of Uranium (VI), Plutonium and Thorium onto Aluminum Oxide, Muscovite and Chlorite.*	*Keeley. Bond, AEA T*
11.40	4.8	*A Summary of Sorption Investigations Performed on Behalf the UK Regulator of Radioactive Waste Disposal*	*Mark Crawford, David Bennet, Galson*
12.00	4.9	*Dolomite Surface Chemistry and Actinide Retention*	*Patrick Brady, Sandia (see also 4.23)*
12.20	4.10	*Uranium (VI) Transport Modeling under Variable Chemical Conditions Using Surface Complexation Concept*	*James Davis, USGS*

12.40   **LUNCH**

Chairperson
Malcolm Siegel

13.30	4.11	*Sorption of Th onto Titaniumdioxide*	*Yngve Albinsson, Chalmers*
13.50	4.12	*Uranium Sorption on Phyllite*	*T. Arnold, Rossendorf*
14.10	4.13	*Ni sorption by a natural sand*	*Malcom Siegel,*
14.30	4.14	*Mechanistic Modelling of Sorption onto Cementitious Materials*	*Tim. Heath, AEA T*
14.50	4.15	*Sorption of Sr/Ra, Cs and Pb on Bentonite:Ion exchange and Surface Complexation Modelling*	*Michael Ochs, BMG*
15.10	4.16	*Sorption of Europium onto Illite: Mechanistic Interpretations*	*Lian Wang, SCK·CEN*
15.30	4.17	*Modelling of sorption of U{VI}-species, HCO3{1-} and CO3{2-} on bentonite using SCM*	*K.Stamberg, P.Benes, Czech Technical University*

| 15.50 | | **TEA** | |

			Chairperson Bernhard Schwyn
16.10	4.18	*Comments on the Use of Kd Coefficient for the Modelling of Radionuclide Migration in Porous Media*	*K. Stamberg*
16.30	4.19	*U sorption by WIPP clay or other work*	*Jim Leckie*
16.50	4.20	*Ion exchange case*	*Jacques Ly, CEA*
17.10	4.21	*Modelling of radionuclide sorption on mixed solids using single oxides surface complexation models*	*Nicolas Marmier, Reims*
17.30	4.22	*Adsorption of metals and organic acids to kaolinite surfaces*	*Patrick Brady, Sandia (see also 4.10)*

| 17.50 | | **End of Session** | |

Time	N°	Sessions, Objectives, Papers	Authors / Speakers

DAY 3, Thursday, May 8 (1/2 day)

0830   (Meeting of Chairperson and Speakers of the day)

Session 5 : How are we doing vis à vis Key Questions (Panel discussion)

Objective : Start drawing conclusions. Consider:
- technical / chemical aspects
- put emphasis on model parameters
- consider success / failures
- review problems /solutions
- consider link to PA, better support of Kd's?

09.00   *1st subject : Technical, chemical aspects, emphasis on model parameters*

10.00   **COFFEE**

10.20   *2nd subject: Link to PA, better support of Kd's?*

Session 6 : Consensus, Wrap-up

11.20   Objective : Conclusions of the meeting.
Answers to Key Questions.
Recommendations?

12.30   **LUNCH**

End of Meeting

別添2「参加者リスト」

2 May, 1997

Sorption Modelling Project

Oxford Meeting

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別添 3 「講演要旨」

NEA INTERNATIONAL MEETING
ON
CHEMICAL MODELLING OF SORPTION
in the Field of Radioactive Waste Management

6-8 May 1997
Linton Lodge Hotel, Oxford, UK

ABSTRACTS AND DATA SHEETS
(April 1997)

LIST OF KEY QUESTIONS

The purpose of this list is to focus discussions on issues that have been identified as critical to successful use of chemical modelling of sorption in natural systems for the benefit of radioactive waste management. Authors are also invited to consider these questions when preparing their abstract.

Key issues to be considered by the meeting are:

- Kd
- How to identify critical mechanism governing sorption of radionuclides (RN)
  - solid
  - RN
  - solution composition (majors)

- Thermodynamic Data Base (TDB) for aqueous chemistry of RN, etc.
  - activity coefficients

- How do you measure/quantify the real composition of the solid surface
  - phase identification
  - site type

- How much of each site type
  - site specific concentrations

- What are the key reactions between solutes/surface sites
  - stoichiometry, K, H+, major cations, RN

- Electrostatics necessary?
  - what conditions
  - which RN
  - what range of system composition

- Are Kd values measured in laboratory the same as those in-situ?
  - scale, s/s ratio
  - modification of surface composition

- How well compare batch sorption data (Kd's) with Kd's derived from diffusion measurements?
- How does approach used (data/model) support/aid use of Kd's
  - end user
  - why was approach chosen

DATA SHEET QUESTIONNAIRE AND ABSTRACT
FOR CONTRIBUTIONS TO SESSION 4

Template

- Author
  - Name
  - Address
  - Telephone
  - Fax number
  - e-mail address

- Solid phase
  - Identify (name of solid)
  - Source (origin of solid)
  - Mineralogy : major & minor components, %, distribution.

- Aqueous phase
  - Solution composition: conditions (e.g. time, temperature, batch/flow, oxic/anoxic)
  - Radionuclides

- Brief description of model
  - Surface components, surface species
  - Parameters (measured, calculated, estimated)
  - Thermodynamic data used
  - Codes

- Publications
- Lessons learned

Draft for distribution at the NEA Sorption Workshop, Oxford, 6th May 1997

Session 1 : Kd and Performance Assessment

Contribution Number 1.1

Sorption in Performance Assessment - the Nirex Perspective

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Introduction

Nirex is responsible for the development of a deep geological repository for the disposal of solid intermediate-level and certain low-level radioactive wastes. The disposal concept in the UK is similar to those being considered in several other countries. Caverns will be excavated at depth in a stable geologic setting and the wastes, set in steel or concrete containers will be placed in the caverns. These will then be backfilled with a cement-based material.

The disposal concept makes use of multiple barriers, both engineered and natural, working in conjuncton to provide adequate isolation and containment of the waste. The role of the natural barriers includes to control the rate of access of groundwater to the waste, to delay and spread the migration of radionuclides to the biosphere and to limit the probability of disruption by human-initiated or natural events. An important part of the repository development process is the demonstration of adequate safety for future generations.

Long-Term Safety Requirements for the Nirex Repository

The long-term safety requirements are defined by the Authorising Departments (ref 1) of which the Environment Agency takes the lead in England and Wales. Technical requirements include :

- a demonstration of the understanding of the system
- that quantitative modelling be performed
- evaluation of individual risk against a target
- analysis of the performance of individual barriers
- comparison with radioactivity naturally occurring in the vicinity of the facility.

The main quantitative safety requirement is a target for individual risk to an individual from releases of radioactivity from the repository of 10^{-6} per year - i.e. the risk per year to an individual of a fatal cancer or hereditary defect must be less than 1 in a million. There is no time cut-off for this risk target. The timescale covered by assessment results is a matter for the developer to justify.

The concept of risk implies an acknowledgement that uncertainty will always exist and must be addressed in order to make a safety case. Uncertainty enters into evaluation of the long-term safety performance of a waste disposal facility for several reasons. These include:

- uncertainty as the characterisation of any potential repository site and disposal concept cannot lead to a complete understanding of the present-day situation;
- uncertainty about future environmental conditions such as climate or sea level and of the natural system and how this will influence the system performance;
- uncertainty in future human behaviour, as it affects not only personal exposures to radioactivity but the perturbations to the behaviour of the system;
- the existence of alternative defensible choices of conceptual and mathematical models;
- the effects of simplifications made in the modelling system such that it captures the aspects of interest in the system without unnecessary detail.

Probabilistic Safety Assessment

The regulatory concept of risk has led to the requirement to use Probabilistic Safety Assessment (PSA). PSA involves using mathematical models whose input parameters, such as radioelement solubilities and sorption, or groundwater flow rates, are uncertain quantities, to which a Probability Density Function (PDF) can be assigned, characterising the uncertainty. Practically, PSA is performed by the 'Monte Carlo' method and Nirex uses the MASCOT program for this purpose. The MASCOT model input parameters are set by a process of random sampling and then the whole system is run. This process is repeated a large number of times so as to yield distributions for the output parameters. These outputs can then be analysed to give an analysis of risk. Typical evaluations of risk from the MASCOT calculations are shown in Figures 1 and 2.

Obtaining Probability Density Functions for Input to the Mascot Model

The characterisation of uncertainty for a parameter such as sorption is a vital aspect of a performance assessment. The approach adopted is to use a structured elicitation process, guided by experts, to assess the uncertainty in a given parameter and so define a PDF for that parameter. The Nirex approach is to derive the functions primarily from experimental data, measured in the laboratory or the field as appropriate. For sorption, a single distribution coefficient Kd for each element is elicited, using the assumption of linear sorption. The PDF's are based mainly on laboratory measurements onto system-specific materials; the Nirex Reference Vault Backfill for the repository near field, and onto site-specific materials for the geosphere. This requirement has led to an extensive laboratory programme to measure sorption under the expected range of chemical conditions in the repository and surrounding geologies. A wide range of experimental techniques have been deployed, including methods for both crushed and intact rocks.
It is important to realise the range of uncertainties incorporated in the PDF is not the same as the uncertainty or error in the laboratory measurement. For example, experiments may measure a sorption distribution coefficient for a given radioelement onto a rock sample. However, the PDF required for a transport calculation is not simply identical to the distribution of experimental values obtained. The PDF must encompass uncertainties about the choice of conceptual and mathematical model as well as corresponding features of the experimental situation such as spatial variability of the measured property, biases in the experiment and differences between the experimental situation and that of the rock mass in which the transport will take place. This process is described in more detail in Reference 3 and will be illustrated for the case of the Nirex '95 treatment of uranium sorption in a companion paper at this meeting. For some parameters, there may be sufficient appropriate data to construct PDF's covering the full range of potential uncertainty. For others, only limited data will be available or the data will be only partly applicable and so an element of expert judgement is applied. In these cases, chemical models are used to support the elicitation.

Role of Modelling in the Elicitation of PDFs for Sorption

The role of chemical modelling in the elicitation process is to supplement the experimental data and assist the process of expert judgement. For example, speciation models can provide information of the likely chemical form of the radioelement in solution and how this may be expected to vary as a function of aspects such as groundwater chemistry, ionic strength, or presence of organic complexants. Knowledge of the important sorbing minerals and their surface chemistries provides the complementary information about the sorbing solid. Mechanistic models, fitted to laboratory data can be used by limited extrapolation to indicate the sorption behaviour as chemistry or mineralogy changes. This information is used to guide the PDF and provides confidence in the elicited distribution but does not necessarily constrain it. Mechanistic sorption models do not provide input directly for Nirex performance assessments.

Other sources of information used to provide confidence in the elicited PDF include::

- NSARP sorption data for sorption onto single minerals;
- Information from the Sellafield Site Characterisation Programme on the distribution of natural radioelements and their association with specific mineral phases within the Sellafield assemblages;

- Information from the literature of sorption onto single minerals and rocks of similar mineralogies to those found at Sellafield.

The role of chemical modelling is seen to be one aspect of a multi-strand approach to increasing confidence in the range of sorption behaviour expected in the Sellafield system.

Sorption in the Nirex '95 Assessment

The results of a Probabilistic Safety Assessment for the Sellafield site can be illustrated with the Nirex '95 assessment [ref. 2]. The Probability Density Functions for Sorption onto BVG rocks as used in the Nirex '95 assessment are given in Table 1. For this assessment, sorption PDF's were derived from consideration of sorption onto crushed rock. A correction factor was then elicited to provide data appropriate for an intact rock. Distributions have been elicited for the full suite of radioelements that contribute to risk. For some elements, such as zirconium, direct measurements for sorption have not been made as part of the NSARP and literature data are scarce. The sorption of zirconium was judged to be similar to that of thorium and the same PDF was adopted for both elements. This procedure of grouping elements by chemical analogy is adopted internationally.

A correction factor beta was applied to the values in Table 1 to account for the change in accessible surface area in an intact rock compared with a crushed one. The beta values were also obtained by formal elicitation. Beta values are given in Table 2.

Although the Nirex concept is a multi-barrier concept, the relative importance of the individual barriers differs for different radionuclides, depending on their chemistry, transport properties and half-lives. Sensitivity studies can be performed to assess the relative importance of the various barriers and the information can be used to focus the research programme to meet the requirements of PSA most effectively.

The Nirex '95 assessment showed that the calculated risk was dominated by a very small number of radionuclides:

Cl-36, I-129 and U-238 and its daughters.

Therefore establishing confidence in the behaviour of these nuclides is important in demonstrating the safety of a proposed repository.

In addition, geosphere containment was shown to be important for a further series of radionuclides:

Ni-59, Se-79, Zr-93, Nb-93m, Cs-135, Pu-242.

Future Developments

The treatment of sorption in Performance assessments is developing as additional information becomes available. The Nirex '97 assessment, currently nearing completion, contains several refinements on the Nirex '95 treatment. These include :

- Revision of the PDF's to reflect the knowledge acquired from recent experimental data for sorption onto Sellafield materials
- Elicitation of PDF's for lower oxidation states, where these would be expected
- Refinement of correction factors to convert data to a form appropriate for intact rocks.

The weight attached to the predictions of mechanistic models in the elicitation process will increase as they become more extensively validated for a real system However, it is envisaged that the role of mechanistic models will remain as support for the experiment data, and not as a replacement for data..

REFERENCES

1   *Disposal Facilities on Land for Low and Intermediate Level Radioactive Wastes : Guidance on Requirements for Authorisation,* Environment Agency, SEPA and Department of the Environment for Northern Ireland, 1997.

2   *Nirex '95: A preliminary Analysis of the groundwater pathway for a Deep repository at Sellafield, Volume 3 - Calculations of Risk,* United Kingdom Nirex Limited Report S/95/012, 1995

3   *Information Management,* United Kingdom Nirex Limited Report S/94/002, 1994.

Table 1   Far-field Sorption Distribution Coefficients used in Nirex '95 Assessment (BVG unless stated) (m^3 kg^{-1})

Element	Probability of sorption being less than stated in the Table						
	0.00	0.10	0.33	0.50	0.67	0.90	1.0
H	$1.0\ 10^{-6}$	$1.0\ 10^{-6}$	$1.0\ 10^{-6}$	$1.0\ 10^{-6}$	$1.0\ 10^{-6}$	$1.0\ 10^{-6}$	$1.0\ 10^{-6}$
C	$1.0\ 10^{-6}$	$8.1\ 10^{-6}$	$1.0\ 10^{-3}$	$7.1\ 10^{-3}$	$5.0\ 10^{-2}$	$4.0\ 10^{-1}$	$1.0\ 10^{0}$
Cl	$1.0\ 10^{-6}$	$1.0\ 10^{-6}$	$1.0\ 10^{-6}$	$1.0\ 10^{-6}$	$1.0\ 10^{-6}$	$1.0\ 10^{-6}$	$1.0\ 10^{-6}$
Ni	$1.0\ 10^{-2}$	$1.4\ 10^{-2}$	$3.0\ 10^{-2}$	$1.7\ 10^{-1}$	$1.0\ 10^{0}$	$2.5\ 10^{1}$	$1.0\ 10^{2}$
Se	$1.0\ 10^{-2}$	$5.0\ 10^{-2}$	$1.8\ 10^{-1}$	$3.0\ 10^{-1}$	$6.3\ 10^{-1}$	$2.0\ 10^{0}$	$1.0\ 10^{1}$
Sr	$1.0\ 10^{-6}$	$2.0\ 10^{-5}$	$2.0\ 10^{-2}$	$6.3\ 10^{-2}$	$2.0\ 10^{-1}$	$6.1\ 10^{-1}$	$1.0\ 10^{0}$
Zr	$1.0\ 10^{-2}$	$3.2\ 10^{-2}$	$4.5\ 10^{-1}$	$3.2\ 10^{0}$	$2.2\ 10^{1}$	$3.2\ 10^{2}$	$1.0\ 10^{3}$
Nb	$1.0\ 10^{-2}$	$3.2\ 10^{-2}$	$4.5\ 10^{-1}$	$3.2\ 10^{0}$	$2.2\ 10^{1}$	$3.2\ 10^{2}$	$1.0\ 10^{3}$
Tc	$1.0\ 10^{-6}$	$3.0\ 10^{-4}$	$1.8\ 10^{-3}$	$4.0\ 10^{-3}$	$1.0\ 10^{-2}$	$4.5\ 10^{-2}$	$1.0\ 10^{0}$
Sn	$1.0\ 10^{-2}$	$3.2\ 10^{-2}$	$4.5\ 10^{-1}$	$3.2\ 10^{0}$	$2.2\ 10^{1}$	$3.2\ 10^{2}$	$1.0\ 10^{3}$
I	$1.0\ 10^{-6}$	$1.0\ 10^{-6}$	$1.0\ 10^{-6}$	$1.0\ 10^{-6}$	$1.0\ 10^{-6}$	$1.0\ 10^{-6}$	$1.0\ 10^{-6}$
Cs [1]	$1.0\ 10^{-4}$	$1.0\ 10^{-2}$	$8.0\ 10^{-2}$	$1.6\ 10^{-1}$	$2.8\ 10^{-1}$	$8.0\ 10^{-1}$	$1.0\ 10^{1}$
Pb	$1.0\ 10^{-2}$	$3.2\ 10^{-2}$	$4.5\ 10^{-1}$	$3.2\ 10^{0}$	$2.2\ 10^{1}$	$3.2\ 10^{2}$	$1.0\ 10^{3}$
Ra	$1.0\ 10^{-6}$	$3.0\ 10^{-4}$	$8.0\ 10^{-3}$	$2.7\ 10^{-2}$	$6.0\ 10^{-2}$	$2.2\ 10^{-1}$	$1.0\ 10^{0}$
Ac	$1.0\ 10^{-2}$	$4.0\ 10^{-2}$	$1.0\ 10^{0}$	$3.2\ 10^{0}$	$1.0\ 10^{1}$	$2.5\ 10^{2}$	$1.0\ 10^{3}$
Th	$1.0\ 10^{-2}$	$1.0\ 10^{-1}$	$2.7\ 10^{-1}$	$3.5\ 10^{-1}$	$5.5\ 10^{-1}$	$4.0\ 10^{1}$	$1.0\ 10^{2}$
Pa	$1.0\ 10^{-1}$	$2.5\ 10^{-1}$	$2.0\ 10^{0}$	$4.5\ 10^{0}$	$1.0\ 10^{1}$	$2.5\ 10^{2}$	$1.0\ 10^{3}$
U	$1.0\ 10^{-5}$	$1.0\ 10^{-3}$	$1.0\ 10^{-2}$	$3.0\ 10^{-2}$	$1.0\ 10^{-1}$	$1.2\ 10^{0}$	$1.0\ 10^{2}$
Np	$1.0\ 10^{-3}$	$3.3\ 10^{-3}$	$5.0\ 10^{-2}$	$1.0\ 10^{-1}$	$2.0\ 10^{-1}$	$1.5\ 10^{1}$	$1.0\ 10^{2}$
Pu(P-T)	$1.0\ 10^{-1}$	$3.5\ 10^{0}$	$1.0\ 10^{1}$	$1.8\ 10^{1}$	$3.5\ 10^{1}$	$1.6\ 10^{2}$	$1.0\ 10^{3}$
Pu(BVG)	$1.0\ 10^{-1}$	$4.5\ 10^{-1}$	$3.0\ 10^{0}$	$1.0\ 10^{1}$	$4.0\ 10^{1}$	$3.5\ 10^{2}$	$1.0\ 10^{4}$
Am	$1.0\ 10^{-2}$	$4.0\ 10^{-2}$	$1.0\ 10^{0}$	$3.2\ 10^{0}$	$1.0\ 10^{1}$	$2.5\ 10^{2}$	$1.0\ 10^{3}$

Notes:

(1)   These data are for intact BVG, and were preferred by the expert group. The factor β should not be applied to these.

P-T   Permo-Triassic
BVG   Borrowdale Volcanic Group

Table 2   **Nirex '95 Values of the factor β for the BVG and for the Permo-Triassic Units**

Percentile	$\log_{10}\beta$ (BVG)	$\log_{10}\beta$ (P-T)
0	−4.1	−4.0
10	−3.0	−3.5
33	−2.25	−2.25
50	−1.9	−1.45
67	−1.55	−0.7
90	−1.0	−0.1
100	0.0	0.0

Figure 1   Results of Nirex '95 Asessment: Base-case probabilistic calculation: risk plotted against time for the heterogeneous resource area biosphere model for each of. the climate states with terrestrial discharge, and for the Temperate climate state with marine discharge.

Note that the results shown for the Periglacial state include contributions from ^{36}Cl, ^{129}I, ^{226}Ra, ^{230}Th, ^{234}U and ^{238}U only.
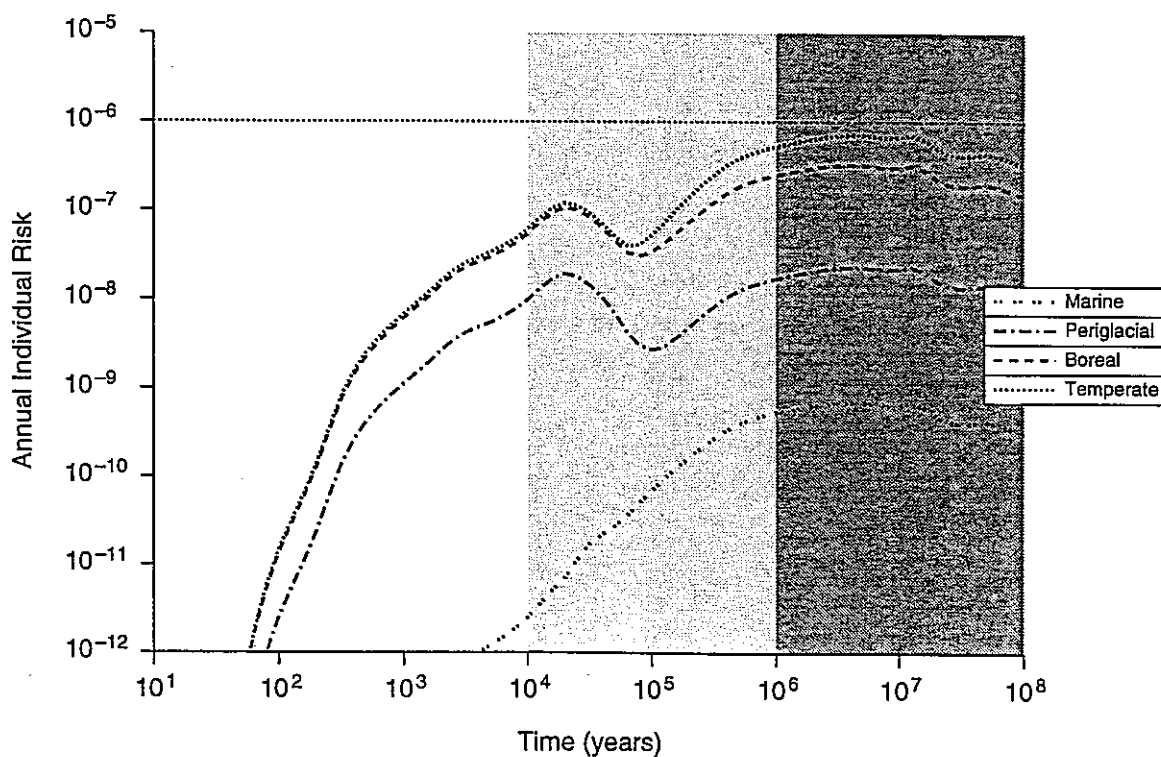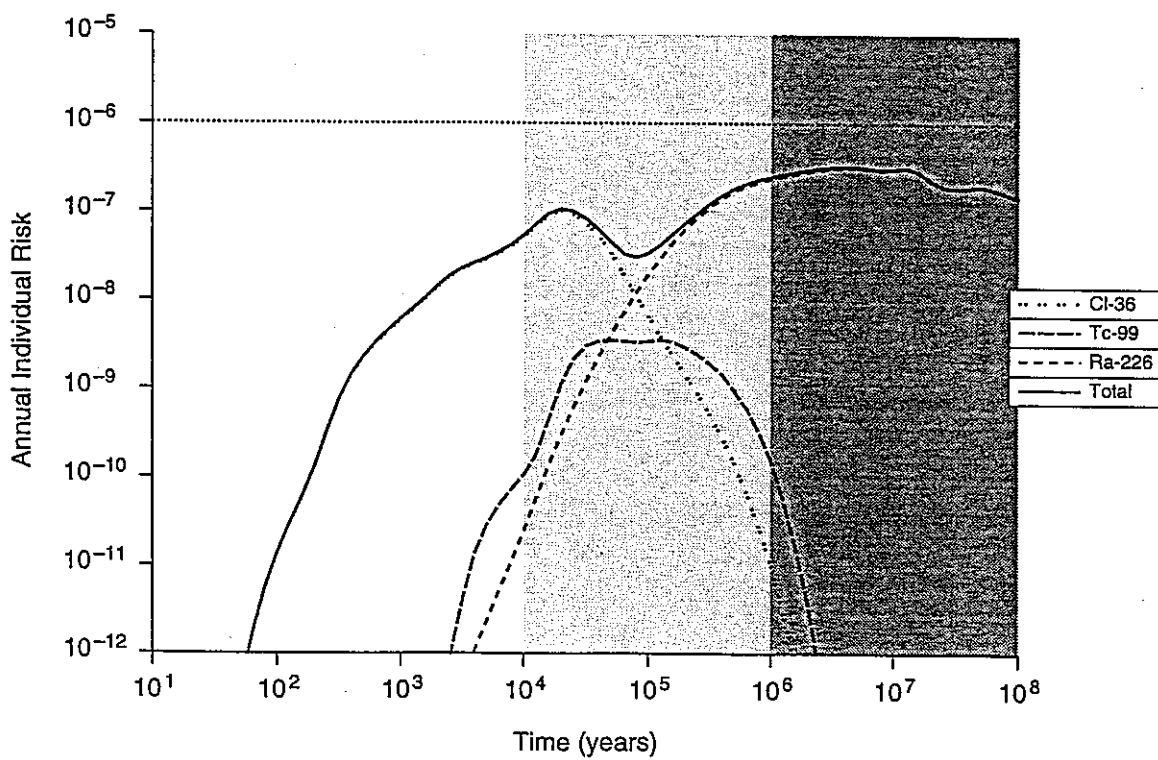
Figure 2   Results of Nirex '95 Assessment: Base-case probabilistic calculation: Boreal terrestrial risk against time with significant radionuclide contributions.

• Extended Abstract

K_d and Performance Assessment: A Reviewer's Point of View

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The construction of a final disposal facility for radioactive waste usually requires a series of licences which, in the case of Switzerland, are granted by the Federal Council (*i.e.*, the Government) based on advice given by the Nuclear Safety Inspectorate (HSK). HSK's task is to review the licence applications. This requires studying the underlying documentation and checking the conclusions of the applicant concerning nuclear and radiation safety, especially long term safety. The review of the long term safety assessment is therefore a major objective. In the conclusions of HSK's review of Project Gewähr 1985, it was noted that the determination of relevant sorption parameters was problematic because of their manyfold dependencies and of the difficulty to reproduce a specific water-rock system in the laboratory. They also noted the importance of sorption with respect to the safety of a final waste repository, and they concluded that it will be necessary in future to investigate more closely the many open questions in the context of sorption, especially the essential parameters of the specific solid phases. This was an unmistakable call for investigating the mechanisms that govern the sorption processes.

This was 10 years ago. What has happened in the meantime? Increasing awareness is noted in the performance assessment community of the fact that even the most sophisticated separation techniques and the greatest care to eliminate side effects cannot help in answering the inevitable question of the applicability of batch laboratory K_d data to intact rock-water systems. Yet I am not questioning the importance of batch data, on the contrary. The batch technique remains the most practical and the most widely used method for the investigation of interaction mechanisms between solutes and rock surfaces. Increasing awareness is also noted of the disadvantages of independent treatment of chemical (sorption) and physical (migration) processes. Projects to develop coupled models for chemical and physical processes have been undertaken by several organisations. The minimum requirement in this matter is the consistency of the model parameters in both the sorption and the transport (*e.g.*, diffusion) model. However, I have the impression that there are two rather general topics on which consensus has not been reached yet. These are the question about the level of detail required for the analysis of sorption mechanisms on one hand, and the way of dealing with uncertainties on the other hand. Let me give these two subjects some thoughts.

How to deal with uncertainties? This question has lead to innumerable discussions, disagreements and misunderstandings in the past. The term „uncertainty" is commonly connected with „error" in a statistical sense, but a statistical basis rarely exists for K_d values because they depend on too many unknown parameters. Hence, the assignment of an uncertainty to a K_d value is usually *a priori* unscientific and unjustifiable. A common practice to deal with this problem has been to define „realistic" and „conservative" K_d values. In some cases the selected K_d values were described as „realistic-conservative". It is these definitions, especially the term „conservative", that caused many misunderstandings. Examples of interpretations of the term „conservative" range from „worst case" over „lowest experimental value" and „as low as reasonably to be expected" to „about 10 times lower than realistic". In existing sorption databases the conservative K_d values are in general about an order of magnitude lower than the realistic ones, largely independent of their experimental basis. For an independent observer this looks like the result of a several years international opinion exchange exercise which had gradually deviated from experimental evidence and scientific experience, and whose only strong point, as it seems, is international consensus. Uncertainties are important enough to be handled in a case-specific manner, rather than in a simplified, categorical way. I would prefer to use

specific parameter variations rather than conservative values to analyse the effect of uncertainties. Of course, a mechanistic understanding of the sorption processes greatly facilitates the estimation of uncertainties in the K_d values.

How detailed does our understanding of the sorption mechanisms need to be? This is a legitimate question in view of the time-consuming and costly investigations that are necessary to acquire sufficient knowledge of the solute-solid interactions. The customary K_d values used in the safety analysis need not be replaced by complex surface interaction models. However, our knowledge of the sorption mechanisms needs to be sufficient to understand and support the K_d values. This does not mean that we have to understand each and every detail of the sorption processes, but we need sufficient knowledge to be able to credibly defend the selected K_d values. Information on the sorption mechanisms is essential if experimental data are rare or lacking, because this calls for approximations and estimations concerning the behaviour of the elements or rock surfaces in question. The assumption of analogous behaviour of two elements or two solid phases is only credible (and hence defendable) if there is convincing evidence that the reaction mechanisms are analogous under relevant conditions. It should also be emphasized that the required depth of mechanistic analysis is element-dependent. The safety analysis will reveal which radionuclides have a critical effect on the safety of the repository, and the priority list for mechanistic analysis should be determined by these findings.

The following list summarises the steps of the review procedure of sorption data as I have been using it. At the Oxford meeting I will present specific examples from my experience as a reviewer.

- *Plausibility of selected values:* A quick assessment based on general experience (by rule of thumb) may be useful as a first step.

- *Transparency and correctness of data selection procedure:* What has been done and why? Are solid and aqueous phases, redox conditions, *etc.*, representative for the safety analysis case?

- *Consistency with the state-of-the-art:* Has the relevant literature been considered? Has new evidence been reported from recent experiments and models?

- *Consistency with transport parameters:* Are the selected K_d values and transport parameters (*e.g.*, diffusion coefficients) compatible with *in situ* data and migration experiments?

- *Treatment of uncertainties:* How have uncertainties been assessed, and how have they been considered in the safety analysis?

SESSION 3 : APPROACH TO SORPTION MODELLING OF NATURAL SYSTEMS

Contribution Number 3.1

- ## Extended Abstract

Acquisition of Sorption Data for the Nirex Performance Assessment

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Introduction

Nirex is responsible for the development of a deep geological repository for the disposal of solid intermediate-level and certain low-level radioactive waste. Investigations have been carried out at a site near Sellafield in Cumbria to see if it is suitable as a repository site. The aim of this paper is to outline the Nirex strategy for obtaining sorption data for a Performance Assessment of the Sellafield site, as illustrated by the Nirex '95 assessment.

The overall Nirex approach to Performance Assessment has been outlined in a companion paper for this meeting. It described the use of a probabilistic safety assessment in the UK and the derivation of Probability Density Functions (PDFs) using a structured elicitation process. The PDFs for sorption used in the assessment are primarily based on the results of experimental determinations of sorption onto the various materials characteristic of the repository system. In the near field, this material is the Nirex Reference Vault Backfill - a cementitious material designed to provide the alkaline conditions and sorption capacity that are the principal basis of a chemical barrier to radionuclide migration. Far-field experiments have concentrated on rock samples from the Sellafield site as these provide the most relevant data for the performance assessment of the geosphere at Sellafield.

Assessment Basis for Treatment of Sorption

The following assumptions were made in deriving sorption PDFs for the Nirex '95 assessment

- The PDFs were derived on the basis of batch sorption Rd values. The correction to Rd values appropriate to intact rock was treated separately by the use of a scaling factor based largely on geometric considerations.
- The assessment model assumes linear reversible sorption. Therefore credit is only taken for short-timescale processes. Coprecipitation and mineralization processes are not included as, on current knowledge, it is difficult to quantify the additional credit that these would offer.
- The sorption values were elicited for elements in their highest expected oxidation states. e.g. uranium as U(VI), selenium as Se(VI). Experiments have shown that elements tend to sorb more strongly in lower oxidation states. Therefore the assessment treatment is expected to underestimate the extent of sorption in the geosphere.
- Sorption data measured at room temperature will be applicable to the repository situation at all times in the future. Sorption behaviour is not strongly temperature-dependent within the expected temperature range.
- The concentration of radionuclides in the geosphere is so small that saturation effects can be ignored.

Research on Radionuclide Sorption to Support the Assessment

The radionuclide sorption research on rocks at the Sellafield site comprises three main components:
- laboratory experimental studies;
- geochemical modelling, to build understanding of the sorption process and to enable extrapolation of sorption data to other geochemical environments;

- observation of the behaviour of natural radionuclides in groundwater systems and of the key minerals that control retardation on geological timescales to build confidence in the assessment treatment of radionuclide retardation.

  The contribution from these three aspects to supporting the assessment treatment of sorption is outlined below.

Laboratory Studies of Sorption in the Sellafield system

The standard experimental technique for measuring sorption data is the batch sorption technique. Experimental are generally performed in triplicate using a water:rock ratio of 50:1. The batch technique is chosen as it is quick and reproducible.

Experiments have been performed on a wide variety of Sellafield rocks:

- Permo-Triassic Sediments
  - ◊ Calder Sandstone Formation;
  - ◊ St Bees Sandstone Formation;
  - ◊ Brockram and St Bees Shale.
- Carboniferous Limestone.
- Lower Paleozoic Volcaniclastic Rocks
  - ◊ Borrowdale Volcanic Group (BVG) Tuff matrix;
  - ◊ BVG fracture infills.

The experiments have been carried out in site-specific groundwaters in a nitrogen/carbon dioxide atmosphere that reproduced the expected 'in-situ' partial pressure of carbon dioxide.

The main drawback of the 'batch sorption' technique is that it uses crushed rock and therefore may both alter the accessible surface area from the 'in-situ' value, and also expose fresh surfaces that may show different sorptive properties. Therefore the batch sorption experiments are complemented by a much smaller number of 'intact' experiments. The choice of experimental technique depends on the sorptive properties of the radionuclide and the transport properties of the rock sample. For weakly sorbing nuclides, the through-diffusion/sorption technique is used. For strongly-sorbing nuclides, the through-diffusion/sorption experiments did not achieve a steady state over a timescale of a few years and so the programme now uses transient techniques such as the 'rock beaker' technique.

Surface analytical techniques have been used to examine the distribution of the radionuclide between different minerals in the rock to give an indication of the important sorbing minerals in the system. These studies have identified iron oxides as important sorbing minerals in rocks from the Sellafield site.

The Sellafield-specific experiments have been complemented by a series of single mineral experiments, designed to investigate specific aspects of the sorption process and so build up an understanding of the behaviour of the site-specific samples. Sorption isotherms have also been measured, to increase confidence that a linear sorption mechanism is appropriate at the range of conditions expected in the geosphere around a repository.

Geochemical Modelling of Sorption

Geochemical models are used in the interpretation of sorption experiments to provide confidence in the experimental data. The detailed modelling approach will be described later in this conference.. Models for sorption onto hematite are parameterised from the literature where possible and fitted against the experimental data. They can be used by extrapolation to give an indication of sorption on rock samples in a range of hydrochemical environments.

Information from Naturally-occurring Radioelements at Sellafield

Confidence in the applicability of laboratory measurements to the repository situation is increased by the observations of the occurrence of natural uranium in rocks from Sellafield. Detailed mineralogical and chemical characterisation of samples of BVG has shown that most of the natural uranium is fixed within primary mineral phases but a small amount has been mobilised during water-rock interactions and is

associated with secondary hematite. Measurements using sequential extraction techniques have suggested that uranium is not only sorbed onto the iron oxide surface but is incorporated more deeply into the lattice. The absence of this additional mechanism in the laboratory could be due to the much shorter timescales involved , or the fact that the experimental conditions are carefully controlled to minimise mineral dissolution and precipitation.

Example of Data Elicitation for Uranium Sorption in the Geosphere

A demonstration of the elicitation process for uranium in the Nirex '95 assessment,, outlining the role of the various aspects of the programme onto rocks from Sellafield is described below.

The first stage in the elicitation process was to list the main variables to be considered in deriving sorption. values. These were identified as:

- groundwater chemistry and ionic strength;
- mineralogy, including both quantities and distributions of important sorbing minerals;
- competing metals, both radioelements and other trace elements.

Extreme outcomes were then considered, together with possible causes.

High values were expected for scenarios when the carbonate concentration in the groundwater was low, so that the speciation was dominated by hydroxy complexes. A high surface area of iron minerals would also tend to increase sorption.

Low Rd values were expected in a high-carbonate system or one with a quartz/calcite dominated mineralogy.

The exact shape of the distribution was then decided by consensus of the expert group.

The resultant PDF for uranium(VI) in the Nirex '95 assessment is shown in Figure 1.

From this example it can be seen that the elicitation process is heavily weighted towards measured sorption values. The role of mechanistic modelling in the elicitation process is to give confidence that the range of sorption values selected is an accurate representation of the uncertainty. It is thus one component of a multi-strand approach to understanding sorption behaviour. It is envisaged that, as the development of mechanistic models continues, the additional benefit that they bring will increase confidence in the assessment treatment of sorption behaviour in the geosphere.

Figure 1. Cumulative Density Function for Uranium(VI) Sorption in the Far Field
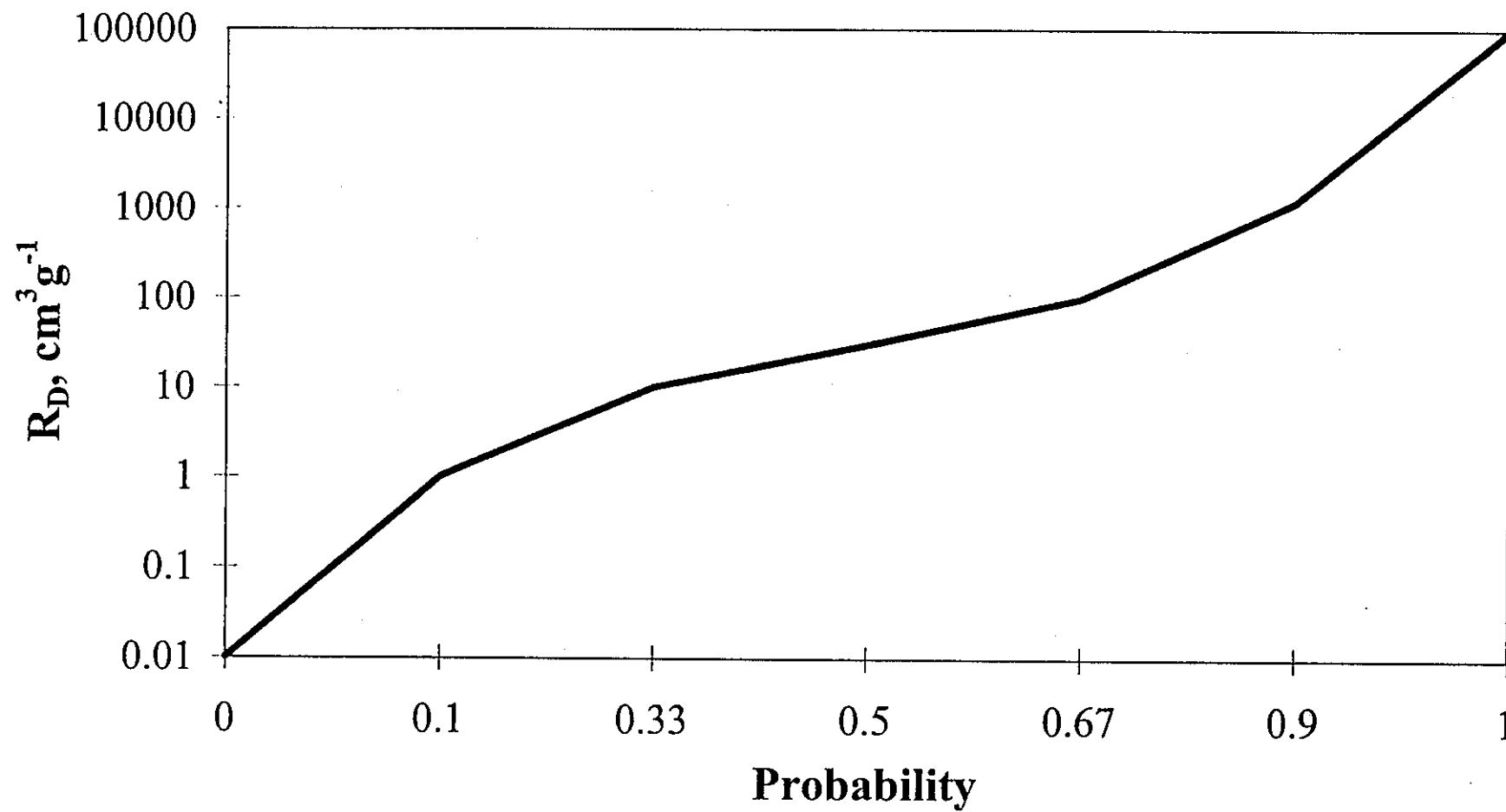
- ## Extended Abstract

A mechanistic description of Ni sorption on Na-montmorillonite

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Thermodynamic sorption models, based on cation exchange and surface complexation mechanisms have been available for some time. The former mechanism has been used predominantly to describe sorption processes on clay minerals whereas the latter has been mainly applied to relatively simple, pure, single oxide systems. Though the potential for using such models to interpret and predict sorption data in natural systems has been recognised, it is currently unclear whether, and to what extent, they can be used for complex mineral assemblages and water chemistries.

Clay minerals generally form one of the most important mineral components in crystalline and sedimentary rock formations as far as sorption is concerned. For this reason we decided to study a clay mineral and use it as a test material to develop experimental and modelling procedures for describing the uptake of various sorbates. Because of the importance of bentonite as a backfill material in the Swiss concept for a high level radioactive waste repository, Na-montmorillonite was selected.

A purification and conditioning procedure was applied to the SWy-1 Na-montmorillonite (Crook County, Wyoming) in order to remove background metal impurities, soluble salts and sparingly soluble minerals which could influence titration and sorption measurements. The purified clay, in the homo-ionic Na-form, was thoroughly physico-chemically characterised before carrying out batch titration measurements.

The sorption of Ni on conditioned Na-montmorillonite was studied at trace concentrations as a function of pH over a range from ~3 to ~10, at different total $NaClO_4$ concentrations, to produce so-called "sorption edges". In addition, sorption isotherms were determined at several fixed pH values in 0.1 M $NaClO_4$. From trends in the sorption edge and isotherm data it was deduced that two main uptake processes were responsible for the sorption behaviour of Ni. The first tended to be dominant at low pH and/or high sorbate concentrations and was strongly dependent on ionic strength. This mechanism was identified as cation exchange and is described in terms of selectivity coefficients. The dependency of sorption on pH and the non-linearity of the sorption isotherms was ascribed to a surface complexation mechanism involving two types of surface hydroxyl groups ($\equiv S^SOH$ and $\equiv S^WOH$ sites) at the clay mineral platelet edges having different sorption affinities and site capacities.

Titration and sorption edge/isotherm data were modelled in terms of these two mechanisms with the aid of a computer code called MINSORB. This code allowed the uptake of radionuclides by both mechanisms to be calculated simultaneously, also taking into account competitive reactions from other cations present. From the modelling of the titration results, values for site capacities and protonation/deprotonation constants were deduced. These values were then fixed and used in all further surface complexation modelling of the sorption measurements. The main study was carried out with Ni, but impurity cations present in the system, particularly Zn, had to be examined in addition due to their competitive effects on Ni sorption. The model, with the derived parameters, allowed all the experimental data from titration measurements through sorption edges to sorption isotherms to be quantitatively described. For the case of Na-montmorillonite it is demonstrated that an electrostatic term in the surface complexation model is not required.

As part of a continuing programme to check the applicability of the model and associated parameters for describing sorption in "natural systems", Ni sorption isotherms were determined on unconditioned SWy-1 material in more complex water chemistries at pH=7 and 8.2.

The two isotherms were modelled with the parameter set derived for the conditioned Na-montmorillonite and the $\equiv$ SOH site capacities for the unconditioned clay were obtained by scaling over the respective cation exchange capacities. At pH=7, where the formation of carbonate species was negligible, the fit to the experimental data was good. At pH=8.2, where the thermodynamic data predicted significant concentrations of Ni carbonate species, the model consistently underpredicted the measured R_d values by ~0.5 log units.

A literature search revealed that the thermodynamic constants for the Ni carbonate complexes had never in fact been directly measured (Hummel, pers. comm.). Since poor quality thermodynamic data could have be one of the reasons for the inconsistency between model prediction and the experimental sorption results, the Ni carbonate system was investigated and yielded a stability constant for the $NiCO_3^0$ complex of ~ 2 orders of magnitude lower than the value used in the initial calculations. The Ni isotherm modelled at pH 8.2 using the newly determined stability constant reproduced the sorption isotherm almost exactly.

The ability to model the sorption of radionuclides in natural systems in complex water chemistries depends not only on the development of a good sorption model but also on the thermodynamic data describing the aqueous chemistry of the radionuclide. The quality of this thermodynamic data may well be one of the limiting factors to the future developments of mechanistic sorption models for real systems.

- **Extended Abstract**

A PNC Approach to Increase Confidence in Sorption Coefficients for Near-Field Performance

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1. Focal Points to Develop Sorption Database

PNC has published a comprehensive performance assessment report focused on near field performance in 1992. On the sorption coefficients used for the performance analysis, refinements are required to increase their reliability.
- reliable sorption database development
- mechanistic understanding of sorption and support for sorption database
- consistencies of Kd values between batch and intact system
- increase in Kd data under reducing conditions
- the linkage between laboratory and in-situ measurements of sorption

2. Procedure for Sorption Database Development

For Second Progress Report in Japan, we have adopted the procedure shown in Fig. 1 to develop sorption database. Firstly we have conducted batch measurements in pure system and surface characterization of pure solid phases and developed intrinsic sorption database including surface complexation and ion exchange constants, surface electrochemical characteristics. Secondly we have checked the reliability of the intrinsic sorption database by comparison of Kd values between batch measurements in complex system such as crushed rock and model predictions. For model prediction we have used the thermochemical database (TDB) of radioelements and a geochemical code. If the reliability is confirmed, we have conducted diffusion measurements to check the reliability in complex intact system. In this way, if we confirm the reliability of the intrinsic sorption database and specify the type of bentonite, rock and groundwater chemistry for the repository, we can predict Kd values for performance analysis.

A critical point for the development of intrinsic sorption database is the reliability of the TDB. The poor quality of the TDB causes the poor intrinsic sorption database. In PNC, we have adopted this procedure in the near-field, especially in the engineered barrier system (EBS) ; compacted bentonite and also tried to apply it to the near-field host rock. However, since the site and geologic formation for the repository have not been fixed, it's very difficult to adopt the procedure in the near-field host rock.

3. Application of Mechanistic Sorption Model

The status of intrinsic sorption database according to the procedure mentioned above is shown in Table 1. PNC has carried out the batch sorption measurements of Cs and Se, representative of a typical cation and anion respectively, to understand sorption mechanism onto bentonite. Experimental Kd values have been interpreted by cation exchange for Cs and surface complexation for Se. The cation exchange site is assumed to be the interlayer in the smectite and the surface complexation site is the goethite group at the surface of pyrite, which is an accessory mineral in the bentonite. The validity has been confirmed by the comparison between diffusion measurements and sorption model prediction in the compacted bentonite. The results of comparison is shown in Fig. 2.

PNC has also carried out the batch measurements of actinides; Pu and Am, and Ni onto bentonite under oxidizing conditions. The sorption of actinides has been interpreted by cation exchanges, because the speciation of Pu and Am indicated cations existence even though the dominant species are anions. The sorption of Ni has been interpreted by ion exchange in the lower pH range and surface complexation at

the edge site of smectite in the higher pH range. The Ni combined sorption model has been validated preliminary through diffusion measurements.

Data acquisition under reducing conditions have been progressed under the collaboration with the AEA plc. for actinides; U, Np, Cm and Tc onto bentonite, granodiorite and tuff and these data except for Cm have been interpreted by using surface complexation model assuming that the dominant adsorbent was goethite coated on the bentonite particle and rock material. These mechanistic constants have not yet been validated through the diffusion experiments due to the strong retardation under the reducing condition. The differences of assumptions for mechanistic sorption models mentioned above are the dominant adsorbent; smectite or goethite and the amount of goethite site. These inconsistencies have to be solved through further investigations.

4. Linkage between Laboratory and In-situ Measurements

To develop the sorption database for near-field host rock, firstly we have to look into the dominant transport passway in deep underground and to develop the conceptual transport model. Based on the conceptual model, data acquisition should be planned. PNC has conducted the geoscientific research on granitic rock in Kamaishi Mine, north of Japan and accumulated the information related to transport process in deep underground. The fracture system by the observation of the drift wall is composed of three rock zone; fracture fillings, altered and unaltered rock. The conceptual model was proposed to be composed of these three rock zones in the fracture system. The sorption and diffusion data have been obtained on the three rock zones. Sorption data have been obtained for Cs, Se, Pu and U by batch measurements under oxidizing condition. The differences of these elements among three rock zones are not significant. It indicated that the complex conceptual model composed of three rock zones is not needed from the view points of performance assessment.

5. Status in PNC

- Mechanistic model has been developed focusing on the bentonite.
- Sorption data acquisition has been progressed under reducing conditions.
- Differences in sorption data in the fracture system have been identified and reflected to the conceptual model.

Table 1 Development of Intrinsic Constants for Sorption (Surface Complexation, Ion-Exchange)

radioelements	solid	atmosphere	dominant adsorbent	summary of results
Pu(IV)		air	Na-smectite	ion exchange
Am(III)				
Se(IV)	Kunigel V-1	reducing	FeOOH	surface complexation
			Al(OH)₃	
Cs		air	Na-smectite	ion exchange
Ni				ion exchange / surface complexation
U(IV)	Kunigel V-1			Kd; 1-4 orders of magnitude
Tc(IV)	Granodiorite	reducing	FeOOH	higher than those under
Np(IV)	Tuff			oxidizing conditions, Surface complexation

[Fig 1 and 2 to be provided later]

- ## Extended Abstract

An approach to Provide a Sorption Database for Performance Assessment.

Young-Hwan Cho

Experiences and lessons from the past sorption study to provide sorption database for P.A will be presented, and an improved approach will be discussed.

- **Extended Abstract**

Uranium Sorption Studies Within The Koongarra Natural Analogue Project

ASARR contribution to NEA workshop on sorption modelling.
Tim Payne, ANSTO

Introduction

Predictions of the long-term migration of radionuclides in the environment typically involve models based (at least in part) on laboratory sorption experiments. This raises several key questions:

- Can we carry out realistic and appropriate laboratory experiments?
- Can we devise a quantitative model of the results?
- How can results from simple minerals be applied to complex materials?
- Is it valid to simplify complex phenomena (*eg* using K^d values)?
- Is it possible to apply a mechanistic model developed for simple laboratory systems to the field environment?

The ASARR project aims to model U migration over long timescales in the geologic environment. In this project, the Koongarra uranium deposit (Northern Territory, Australia) is being studied as a natural analogue of a nuclear waste repository. The project has provided field and laboratory data that can be used to help answer the above questions.

This paper is in three main sections, each of which focuses on a key part of the sorption work within the ASARR project :

a) Laboratory U sorption experiments with model minerals (such as ferrihydrite and kaolinite) and development of a surface complexation model (SCM) for the experimental data.
b) Modeling experimental U sorption results on complex natural materials.
c) Comparing laboratory sorption results and field partitioning of uranium.

Surface complexation modeling of U(VI) adsorption on ferrihydrite and kaolinite

Uranium (VI) sorption on ferrihydrite and kaolinite is influenced by a large number of factors including: pH, ionic strength, partial pressure of CO_2, adsorbent loading, total amount of U present, and the presence of ligands such as phosphate and humic acid. The effect of complexing ligands may be to enhance or reduce U uptake. The adsorption model being used for ferrihydrite is a surface complexation model with a diffuse double layer, and both strong and weak sites for U sorption. Uranium uptake on a standard kaolinite (KGa-1) is much weaker than U uptake on ferrihydrite under similar experimental conditions. Titanium-rich impurity phases play a major role in U sorption on KGa-1.

Modeling of laboratory experimental results for U sorption on natural materials

As a step towards modeling U sorption in the environment, we are attempting to model laboratory sorption data for experiments involving complex natural substrates from Koongarra. Several approaches to modeling sorption on natural samples have been used. One simplification that has been tried is to assume that one phase (such as ferrihydrite) dominates the system. However, our modeling results have shown that ferrihydrite does not comprise a sufficient proportion of the Koongarra samples to dominate their sorption behaviour.

The most successful approach has been to use the measured surface areas (BET) of natural geologic materials as a normalising parameter, and to model U-sorption using the same site density as ferrihydrite. In simple terms, this may be thought of as approximating the surface with ferrihydrite of equivalent surface area. This approach may seem unrealistic in that natural surfaces are composed of a number of site types with different acid-base chemistry and affinity for the U(VI) species. However, it has the advantage that the U-sorption model for ferrihydrite may be simply transferred to any other mineral assemblage, provided the surface area is known.

Comparison of laboratory U sorption data with in-field measurements

There are usually substantial differences between laboratory and field conditions, and the timescales, spatial extent, and complexity of environmental phenomena cannot be duplicated in the laboratory. Thus, the applicability of laboratory sorption data has been questioned, and it has been claimed that field measurements ('in-situ distribution coefficients') provide a more accurate indication of 'true' partitioning coefficients.

Before discussing field and laboratory data, it is important to make some comments on sorption terminology. In transport modeling, distribution coefficients ('Kd values') have often been used to describe the equilibrium partitioning of radionuclides between adsorbed and liquid phases. Kd values may be estimated from the results of laboratory sorption experiments, preferably in which field conditions are closely simulated. However, as laboratory experiments cannot be assumed to be at equilibrium, we use the term 'R_d' to express the results of laboratory experiments. Measured R_d values typically vary over a wide range, and are influenced by parameters such as pH, ionic strength, and partial pressure of CO_2.

In the ASARR project, we have studied in-field U partitioning by comparing the U contents of groundwater and solid phases. The resulting parameter is often referred to as an 'in-situ K_d value'. However, processes other than sorption (*eg* precipitation) may influence U partitioning and the system may not be at equilibrium. Consequently, we refer to this parameter as a P (partitioning) value.

In the studies of the Koongarra uranium deposit an extensive suite of laboratory sorption measurements (Rd values) and field partitioning data (P values) has been obtained for U. A valid comparison between field and laboratory data can only be made when the influence of colloids is eliminated and attention is restricted to sorbed or 'accessible' uranium species (*ie* excluding precipitates or occluded phases). The correspondence between field measurements and laboratory data improves when the pH values and partial pressures of CO_2 in laboratory experiments are similar to those found in the field. However, factors such as non-equilibrium conditions (attributed to slow kinetic effects) and non-linear adsorption isotherms may result in discrepancies. The results obtained from the Koongarra study indicate that with appropriate control of laboratory conditions and careful field measurements a fair correspondence can be established between laboratory and in-field radionuclide partitioning data.

- ## Extended Abstract

Determination Of Radionuclides Migration Parameters In A Clay Formation: The Belgian Approach

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Summary

This presentation is a summary of papers recently published [1,2,3]. A overview of the major results of the migration programmes is reported in [4].

Host Rock

The Boom Clay Formation at the Mol site has been selected 20 years ago as candidate host rock for the deep geological disposal of high level and alpha bearing wastes. This formation is situated between -160 and -270 meters, and is the uppermost Clay Formation of an alternating sequence of clays and sands. The Boom Clay layer was deposited about 30 millions years ago. The main advantages of this tertiary sedimentary formation as long term natural barrier against radionuclides dissemination are:

- self healing properties due to its plasticity
- low hydraulic conductivity ($K \approx 2 \times 10^{-12}$ m.s^{-1})
- high sorption capacity for cations
- slightly alkaline and strongly reducing conditions limiting the solubility and the mobility of many radionuclides

Performance assessments of the geological disposal of HLW in the Boom Clay have shown that the most effective and reliable barrier of the multi-barrier system is the host Clay layer.

Selected Elements

The studied radionuclides (RN) and/or compounds are divided into three categories:

- the critical elements inferred from the performance assessments: ^{14}C, ^{99}Tc, ^{135}Cs, ^{129}I and ^{237}Np. The organic matter (OM) occurring naturally in Boom clay is also classified in this group because of its special contribution in controlling the mobility of some radionuclides, especially the actinides.

- the possibly critical elements: Se, Zr, Pd, isotopes U-Pu-Am-Cm, Pa, Ra and Be.

- the non critical elements: tritiated water (HTO), Sr^{2+}, Eu^{3+}, the haloid anions (I$^-$, Br$^-$, Cl$^-$), HCO_3^-, organic compounds radio-labelled with ^{14}C such as sucrose, lactose. The study of this last group of elements has for purpose a better understanding of the migration mechanisms and allows to simulate the behaviour of some compounds such as the mobile humic acid substances or the trivalent actinides.

Experiments Designed To Study Radionuclides Migration

Tests are performed in the laboratory and in the underground research facility. The tests performed in the laboratory are carried out under strictly anaerobic conditions. Depending on the application, real claywater or synthetic claywater is used. The real claywater and the clay core samples are taken from the underground facility. Different types of experiments with different configurations are carried out to determine the migration parameters required for the performance assessments:

- diffusion experiments: in this case, diffusion is the only mechanism underlying the migration.

- percolation experiments: solutions are hydraulically forced through the pores of the clay. The radionuclide is measured in the percolate. However, for the strongly sorbed elements, the amount of activity in the percolate is negligible compared to the activity in the solid phase. The activity profile in the clay core is determined after the experiment by slicing the clay plug and measuring the activity in each clay slice. Even under a high hydraulic gradient, diffusion is still the main transport mechanism for the strongly sorbed RN. The migration of the non-or-poorly sorbed tracers is a combination of advective and diffusive transport. Under in situ conditions, diffusion remains always the main transport mechanism whatever the chemical species.

- Percolation tests with radio-labelled organic matter: experiments are performed with OM labelled with ^{14}C. Tests with OM double-labelled with ^{14}C and ^{241}Am are also foreseen.

Boom Clay contains about 1-3% OM of which about 0.01% is estimated as mobile. The complexation of radionuclides by OM has a two-fold effect on the safety of the Boom Clay Formation. If immobile organic matter complexes the RN, the presence of OM will retard the migration. On the contrary, if the radionuclides are complexed by the mobile OM, the solubility of the RN will increase and the radionuclides transport would be enhanced. Preliminary results seem to indicate that the OM has a beneficial effect w.r.t. the retention of the actinides, at least for the trivalent ones. They appear to be strongly sorbed on the immobile OM intimately associated with the clay minerals. Furthermore the mobile concentration of the radionuclides seems to be lower when OM is present. An important fraction of the RN is by complexation associated with organic colloids which are partly filtered as well by the backfill (smectite) as by the Boom Clay with as consequence a decreasing of the mobile concentration [6].

The experimental results are interpreted by means of models developed by the CEN-SCK where the tests are performed. The diffusion experiments allow to determine only the apparent diffusion coefficient D_a while the percolation tests give access to the parameters ηR and D_a (η: diffusion accessible porosity, R: retardation factor). The interpretation of R in terms of a mechanistic model accounting for the sorption processes has so far not yet been undertaken.

The goals of the tests performed in the underground laboratory (which is operational since 1984) are:

- validation of the migration parameters acquired in the laboratory under in situ conditions

- validation of the transport models on a large scale (up-scaling factor of the considered volume of 100000, tests on a scale of a few meters). Till now only the non-sorbed species have been considered. The theoretical activities in the piezometers are calculated with the code MICOF also developed by the CEN-SCK [5].

Future Works

Besides the completion of the running experiments, new research topics have been identified and in most cases are already under way:

- influence of the concrete backfill for MLW on the migration properties of the Boom Clay (diffusion of an alkaline plume)

- influence of the diffusion of sodium nitrate from bituminized waste (MLW) on the migration properties of the Boom Clay

- homogeneity of the Clay layer (samples will be taken through the whole layer and migration tests performed with some selected radionuclides)

- study of the osmosis properties of Boom clay (if any)

- temperature effects on the migration properties of Boom Clay

- determination of the migration parameter in the biosphere (glauconite sands)

- determination of the speciation, solubility and mobile concentration of the redox sensitive elements (Tc, Se, U, Pu, Np).

A major challenge in the near future will be the development of a geochemical code for the Boom Clay which implies the knowledge of the main sorption processes involved. Such a step will help to build the required confidence in the values selected for the PA. Some preliminary works have already been performed.

References

[1] A. Dierckx, H. Moors, P. De Cannière, N. Maes and M. Put; Migration of Radionuclides; in Feasibility and Acceptability of Nuclear Waste Disposal in the Boom Clay Formation; CEN-SCK Report BLG-726, 1997 (Editor: A. Dierckx and V. Labiouse, Waste and Disposal Unit, CEN-SCK, Boeretang 200, B-2400 Mol).

[2] M. Put, J. Marivoet, G. Volckaert and B. Neerdael; How Performance Assessment of a Geological Waste Disposal in Clay Has Contributed to Focus the Radionuclide Migration Research; presented at WM 97, Tucson, Arizona, March 2-6, 1997.

[3] B. Neerdael; Geological Radwaste Disposal in Belgium-Reseach Programme, Review and Objectives; in Geological Problems in Radioactive Waste Isolation, Second Worldwide Review, Edited by P.A. Witherspoon, LBNL-38915/UC-814 (1996).

[4] P. De Cannière, H. Moors, P. Lolivier, P. De Preter and M. Put; Laboratory and In Situ Migration Experiments in the Boom Clay; Report EUR 16927 (1996).

[5] M. Put; A Unidirectional Analytical Model for the Calculation of the Migration of Radionuclides in a Porous Geological Medium; Radioactive Waste Management and the Nuclear Fuel Cycle 6, 361-390 (1985).

[6] J. Wei and P. Van Iseghem; Colloid Formation During Interaction of HLW Glass with Interstitial Clay Water; presented at Scientific Basis for Nuclear Waste Management XX, Boston, 02-06.12.96.

- **Extended Abstract**

Application Of A Laboratory-Derived Surface Complexation Model For Zinc Adsorption To Field Observations Of Zinc Transport In Ground Water

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The surface complexation concept is well accepted in the environmental chemistry research community but it has not yet been applied extensively in modeling natural or contaminated surface and ground waters. Significant obstacles remain in applying the concept to the heterogeneous mixtures of mineral phases and organic material found in soils and sediments. In particular, the physical and chemical characteristics of the surfaces of natural materials are often not well understood in comparison to those of pure reference mineral phases. Approaches for determining the types and quantities of surface functional groups are not yet developed as routine characterization methods. Electrical double layer (EDL) models that are appropriate for pure monomineralic precipitates may not be appropriate for soils and sediments, which contain mixtures of phases and coatings of variable chemical composition. Although many studies of metal ion and radionuclide sorption by soils and sediments have been reported in the literature, few have approached the problem with a goal of modeling sorption with the surface complexation concept. As a result, there have been very few applications of the surface complexation concept within performance assessment models for radioactive waste repositories or solute transport models that simulate contaminant mobility at polluted ground water sites.

In this paper we report on an application of the surface complexation concept as a tool for prediction of zinc (Zn) transport in a shallow sand and gravel aquifer contaminated with secondary sewage effluent at Cape Cod, Massachusetts (USA). Treated sewage effluent has been disposed onto infiltration beds at the site for about 60 years and has created a plume of contaminated ground water that had extended 5.4 km downgradient (in 1994) and was about 900 meters wide. Accretion of recharge water from precipitation on top of the plume, limited vertical mixing, and biological processes have created steep geochemical gradients within the plume. Within a 3 meter thick transition zone, from the accreted recharge water to the top of a suboxic zone of the sewage plume, dissolved O_2 concentrations decrease from several hundred micromoles per liter to nearly zero and the pH increases from about 5.5 to 6.5. The suboxic zone of the plume is mildly reducing and contains high concentrations of dissolved manganese and nitrate, but negligible ferrous iron. The core of the plume is anoxic, has a pH of about 6.5, and contains high concentrations of dissolved ammonium and ferrous iron.

In the vicinity of the disposal beds, Zn contamination extends relatively deep into the aquifer. Up to 50 meters downgradient of the source, the zone of Zn contamination averages approximately 15 meters in vertical thickness. This is somewhat less than the vertical thickness of the sewage plume, which averages about 25 meters. Zn concentrations in the groundwater range from 0.3 to 3 uM. Partitioning of Zn between the groundwater and the sediments is controlled by sorption; Zn-bearing mineral phases are highly undersaturated. Greater than 95 percent of the total Zn is associated with the aquifer sediments due to sorption.

At distances greater than 200 meters downgradient from the source, the Zn-contaminated region is restricted to the 3 meter thick transition zone at the top of the sewage plume. As mentioned above, there is a steep gradient in pH within this zone, and the lower boundary of the Zn-contaminated region correlates with the steep increase in pH. Maximum Zn concentrations in this region vary with distance downgradient from 4 to 12 uM. Sorbed Zn contamination on the sediments constitutes 90-95 percent

of the total Zn. The leading edge of the Zn-contaminated region is sharp and, in 1993-1994, was located 400 meters downgradient from the source. The occurrence of unreactive constituents of the sewage plume at 5 km downgradient, would indicate that the average retardation factors for Zn was of the order of 13 at the lowest pH values in the transition zone and is within the range 50-100 near the center of the plume.

A surface complexation model of Zn sorption was developed from a laboratory study of Zn adsorption by sediments collected from the field site. Quartz and feldspars constituted about 95% (by weight) of the mineral assemblage; accessory minerals included biotite, hornblende, and other ferroaluminosilicates and oxides. The results show that adsorption was dominated by surface coatings containing aluminum and iron; the coatings presumably formed on quartz grains as a result of chemical weathering of feldspars and iron-bearing minerals within the aquifer. Two modeling approaches without EDL correction were tested: 1) One and two-site models, where the chemical identity of the sites was unknown (dummy sites), and Zn sorption stability constants were determined by fitting the laboratory sorption data, and 2) An aluminol and ferrinol site model (each with weak and strong site populations) with the Zn sorption stability constants derived from independent published studies of Zn adsorption by poorly crytallline iron and aluminum hydroxides. For the latter approach, model simulations agreed reasonably well with the experimental Zn sorption data on the Cape Cod sand if it was assumed that the site density of the surface functional groups was greater than expected from the specific surface area of the sand. Analytical and spectroscopic characterization of the sand surface indicated that the surface coatings containing aluminum and iron were thick (>50 nm) and had a high surface area.

The distribution of Zn contamination in the aquifer was simulated with a coupled flow, transport, and equilbrium chemical reaction model (Yeh and Triphathi, 1991). The model incorporated the influence of variable chemistry (pH) on sorption and transport of Zn; parameters of the flow model were estimated from independent experimental data. Simulations were run for a 2-dimensional vertical cross section constructed along a flow line. The groundwater flow field was simulated with horizontal flow and uniform areal recharge. Transport parameters are known from the results of a large-scale tracer test conducted at the site (LeBlanc et al., 1991). The pH gradient was imposed in the model by setting the concentration of an arbitrary buffer entering the model domain at 1 mM and adjusting the ratio of the conjugate acid-base pair with depth to produce the desired pH as a function of depth. Zn was introduced into the model domain by assigning a Zn concentration to groundwater entering along the upgradient boundary. Zn sorption in the simulations was incorporated with the first surface complexation model described above, without any further fitting of data or manipulations.

Simulations carried out for a time period of 54 years agree with the important features of the distribution of Zn contamination in the aquifer. The Zn-contaminated zone deeper in the aquifer is limited to the near-source region by the extensive adsorption in the plume core due to higher pH values. Greater than 200 meters downgradient, the simulations show that the Zn-contaminated region is limited to a narrow zone at the upper boundary of the plume. The location of the leading edge is remarkably similar to that observed. The amount of retardation is similar with either a 1-site or 2-site surface complexation model, but the 2-site model produces a sharper leading edge. Near the leading edge, the range of retardation in the simulations due to pH variation was about 22 at the lower pH to about 63 in the core of the plume. The case study shows that the surface complexation concept may be valuable as a tool for estimating K_d values for performance assessment where there are spatially or temporally variable chemical conditions.

SESSION 4 : STATE-OF-THE-ART

Contribution Number 4.1

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- **Solid phase**

amorphous iron(III) oxy-hydroxide
synthetic

- **Aqueous phase**

Solution composition

T = 25 ± 0.1 °C; Batch experiments; oxic conditions.

Radionuclides

Cd; Background electrolyte: 0.1 M $NaNO_3$

- **Brief description of model**

Surface components, surface species

$>FeOH_2^+$; $>FeOH$; $>FeO^-$;
$>FeO-Cd^+$; $>FeO-Cd(OH)$; $>FeO-Cd(OH)_2-$

Parameters

Kd measured
Surface acidity constants from the literature
$>FeOH_2^+ \Leftrightarrow >FeOH + H^+$ $\log K_{a1} = -5.1$
$>FeOH \Leftrightarrow >FeO^- + H^+$ $\log K_{a2} = -10$
Surface complexation constants estimated
$>FeOH + Cd^{2+} + n H_2O \Leftrightarrow >FeO-Cd(OH)_n^{(1-n)} + (n+1) H^+$
$\log K_0^{Fe} = -4.5 \pm 0.5$
$\log K_1^{Fe} = -10.8 \pm 0.8$
$\log K_2^{Fe} = -19.4 \pm 1.0$
1 unique type of sorption sites
site density taken from the literature (Davis, 1977): $9.85 \cdot 10^{-3}$ moles of sites/g
Surface area (Davis, 1977): 182 m^2/g

Thermodynamic data used

Aqueous complexation for cadmium hydroxocomplexes: Baes and Mesmer (*)

Codes

PHREEQC
Home made worksheets

- **Solid phase**

  Titanium(IV) dioxide, (α-TiO$_2$)
   commercial solid. J.T. Baker Co. "Baker analyzed" reagent grade

- **Aqueous phase**

  Solution composition

  T = 25 $\pm$ 0.1 °C; Batch experiments; oxic conditions.

  Radionuclides

  Cd; Background electrolyte: 0.1 M NaNO$_3$

- **Brief description of model**

  Surface components, surface species

  >TiOH$_2^+$; >TiOH; >TiO$^-$;
  >TiO-Cd$^+$; >TiO-Cd(OH); >TiO-Cd(OH)$_2$-

  Parameters

  Kd measured
  Surface acidity constants from the literature
  >TiOH$_2^+$ $\Leftrightarrow$ >TiOH + H$^+$ log K$_{a1}$ = -2.5
  >TiOH $\Leftrightarrow$ >TiO$^-$ + H$^+$ log K$_{a2}$ = -8
  Surface complexation constants estimated
  >TiOH + Cd^{2+} + n H$_2$O $\Leftrightarrow$ >TiO-Cd(OH)$_n^{(1-n)}$ + (n-1) H$^+$
  log K$_0^{Ti}$ = -1.7$\pm$0.4
  log K$_1^{Ti}$ = -8.8$\pm$0.6
  log K$_2^{Ti}$ = -20.3$\pm$0.5
  1 unique type of sorption sites
  site density (assigned by Honeyman, 1984): 8.75$\cdot$10^{-5} moles of sites /g
  Surface area (BET, 100C) = 9.1 m^2/g

  Thermodynamic data used

  Aqueous complexation for cadmium hydroxocomplexes: Baes and Mesmer (*)

  Codes

  PHREEQC
  Home made worksheets

- ## Solid phase

  mixtures of Titanium(IV) dioxide (α-TiO$_2$) plus amorphous iron(III) oxy-hydroxide
  Titanium(IV) dioxide :commercial solid. J.T. Baker Co. "Baker analyzed" reagent grade
  amorphous iron(III) oxy-hydroxide: synthetic material.

- ## Aqueous phase

  ### Solution composition

  T = 25 ± 0.1 °C; Batch experiments; oxic conditions.

  ### Radionuclides

  Cd; Background electrolyte: 0.1 M NaNO$_3$

- ## Brief description of model

  ### Surface components, surface species

  $>TiOH_2^+$; $>TiOH$; $>TiO^-$; $>FeOH_2^+$; $>FeOH$; $>FeO^-$;
  $>TiO-Cd^+$; $>TiO-Cd(OH)$; $>TiO-Cd(OH)_2^-$; $>FeO-Cd^+$; $>FeO-Cd(OH)$; $>FeO-Cd(OH)_2^-$

  ### Parameters

  Kd measured
  Surface acidity constants from the literature (those specified in datasheets 2 and 3)
  Surface complexation constants estimated
  $>TiOH + Cd^{2+} + n\,H_2O \Leftrightarrow >TiO-Cd(OH)_n^{(1-n)} + (n-1)\,H^+$
  $>FeOH + Cd^{2+} + n\,H_2O \Leftrightarrow >FeO-Cd(OH)_n^{(1-n)} + (n-1)\,H^+$

$logK_0^{Ti}$	$logK_1^{Ti}$	$logK_2^{Ti}$	$logK_0^{Fe}$	$logK_1^{Fe}$	$logK_2^{Fe}$
-1.8±0.2	-9.7±0.3	-20.6±0.4	-4.4±0.3	-11.2±0.4	-18.8±1.1

  1 unique type of sorption sites for each solid
  site density taken from the literature

  ### Thermodynamic data used

  Aqueous complexation for cadmium hydroxocomplexes: Baes and Mesmer (*)

  ### Codes

  PHREEQC
  Home made worksheets

- ## Publications

  Honeyman, B. (1984) Cation nand anion adsorption at the oxide/solution interface in systems
  containing binary mixtures of adsorbents: An investigation of the concept of adsorptive additive. Ph.
  D. Thesis, Stanford University

- ## Lessons learned

- ## Abstract

Proposal for the development of predictive Surface Complexation Models (SCM) to be used as a supporting tool to Kd parameters in PA
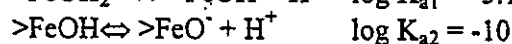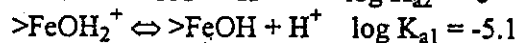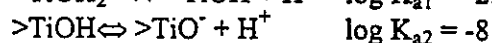
L. Duro, J. Bruno and B. Honeyman
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The objective of this work is to correlate the experimental values of Kd to surface complexation model parameters in order to extrapolate the results to natural systems. For this purpose, we have modelled the data obtained by Honeyman (1984) on sorption of Cd onto amorphous iron oxy-hydroxide, on rutile and on mixtures of both solids. Although these mixtures are not very complex and it is a very well controlled lab system, the approach may be used to describe sorption of trace metals on heterogeneous rocks by considering the percentage of each mineral in the rock.

We have not included any electrostatic contribution in the model in order to keep it as simple as possible. The surface equilibria considered are listed below:

Solid surface acidity equilibria:

$$>TiOH_2^+ \Leftrightarrow >TiOH + H^+ \quad \log K_{a1} = -2.5$$
$$>TiOH \Leftrightarrow >TiO^- + H^+ \quad \log K_{a2} = -8$$
$$>FeOH_2^+ \Leftrightarrow >FeOH + H^+ \quad \log K_{a1} = -5.1$$
$$>FeOH \Leftrightarrow >FeO^- + H^+ \quad \log K_{a2} = -10$$
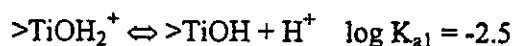
Surface complexation equilibria:

$$>FeOH + Cd^{2+} + n\,H_2O \Leftrightarrow >FeO\text{-}Cd(OH)_n^{(1-n)} + (n+1)\,H^+, \, n = 0 \text{ to } 2. \, (\log K_n^{Fe})$$
$$>TiOH + Cd^{2+} + n\,H_2O \Leftrightarrow >TiO\text{-}Cd(OH)_n^{(1-n)} + (n-1)\,H^+, \, n = 0 \text{ to } 2 \, (\log K_n^{Ti})$$
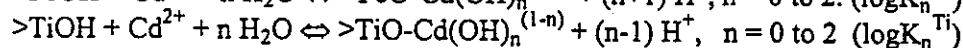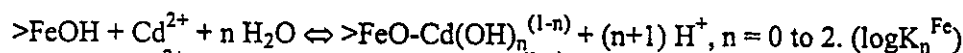
The best fits for the experiments where a unique solid is present (SSML system) have been obtained with the following set of surface complexation constants:

$\log K_0^{Ti}$	$\log K_1^{Ti}$	$\log K_2^{Ti}$	$\log K_0^{Fe}$	$\log K_1^{Fe}$	$\log K_2^{Fe}$
-1.7 ± 0.4	-8.8 ± 0.6	-20.3 ± 0.4	-4.5 ± 0.5	-10.8 ± 0.8	-19.4 ± 1.0

And these values compare fairly well with the ones obtained in experiments where a mixture of both solids is present (MSML systems):

$\log K_0^{Ti}$	$\log K_1^{Ti}$	$\log K_2^{Ti}$	$\log K_0^{Fe}$	$\log K_1^{Fe}$	$\log K_2^{Fe}$
-1.8 ± 0.2	-9.7 ± 0.3	-20.6 ± 0.4	-4.4 ± 0.3	-11.2 ± 0.4	-18.8 ± 1.1

From these sets of surface complexation constants we have used the following expression to obtain the Kd values for each system:

$$K_D = \frac{\sum_{S,q} K_{S,q} \left(\frac{A_S \, W_S}{1 + \frac{[H^+]}{K_{S,a}}} \right)^q}{1 + \sum_{L,p} K_{L,p} [L]^p}$$

where A_S stands for the density of sorption sites per kg of solid; W_S refers to the weight percentage of each mineral surface in the bulk of the solid; $K_{S,a}$ are the surface acidity constants for each solid

surface S; $K_{s,q}$ are the surface complexation constants for each complex q on each mineral surface S, and $K_{L,p}$ represents the aqueous complexation constants of each metal with each aqueous ligand L.

The Kd values obtained by using this expression have been compared with the experimentally determined Kd. This comparison is shown in the following figures:
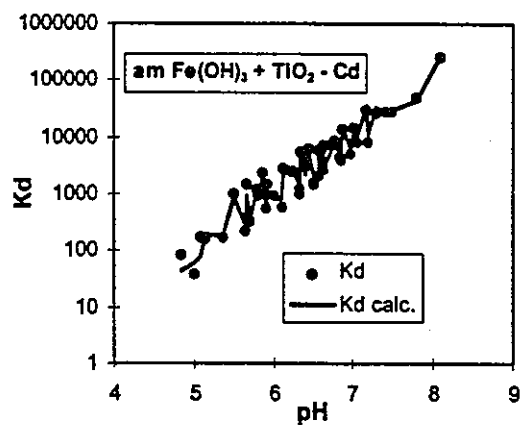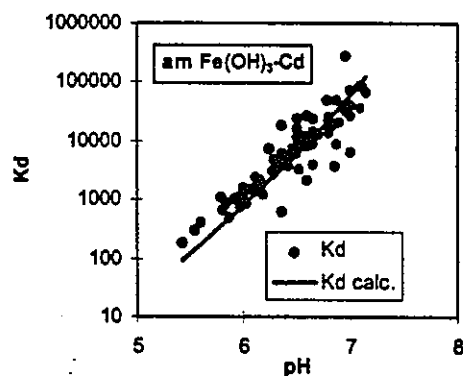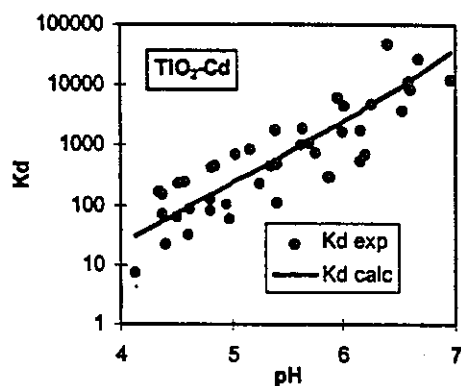
The results obtained are encourageous and the possibility of applying such approach to complex natural systems will be investigated in more detail with field data.

- **References**

Honeyman, B. D. (1984) Cation nand anion adsorption at the oxide/solution interface in systems containing binary mixtures of adsorbents: An investigation of the concept of adsorptive additive. Ph. D. Thesis, Stanford University

(D. Waite)

Data Sheet

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Affiliation: Brett Fenton (University of New South Wales)
               Gregory R. Lumpkin (Australian Nuclear Science and Technology Organisation)
               Molly McBeath (United States Geologic Survey)
               Timothy E. Payne (Australian Nuclear Science and Technology Organisation)

Solid Phase

Identity: W2 (14 metres)
Source: Koongarra weathered zone
Mineralogy: Major components: Kaolinite, altered chlorite, iron minerals, mica
               Size fractions: 56% > 1500 μm, 15μm < 36% < 1500μm, 7.7% < 15μm
               Surface area of < 15μm fraction: 52.3 m^2/g

Elemental distribution in fine fraction:

Extractant	mg element leached/g of solid							
	Fe	Al	Mn	Mg	Ca	Ti	K	U
Morgans	520	605	7.1	3,930	195	3	370	182
TAO	1,170	1,210	147	246	8	5.7	36	43
DCB	6,770	888	30	128	112	2.9	537	65
HCl	79,200	35,000	126	9,670	12	54	280	130
Fusion	20,800	90,300	35	3,480	31	841	7,840	6.4
Total (mg/g)	108.4	128.1	0.3	17.5	0.4	0.9	9.1	0.43

Aqueous phase

Solution composition: conditions
Batch studies undertaken where extent of uptake of radionuclide on solid phase (< 15 μm component) examined a a function of wide range of system conditions (pH, CO_2 partial pressure, ionic strength, radionuclide concentration, solid substrate concentration)

Radionuclide:
Uranium(VI) uptake on solid phase examined in all cases using either the intrinsic U(VI) content or added U(VI). Extent of U(VI) uptake determined after centrifugation by α-spectrometry.

Brief description of model

Surface components, surface species
A two-site (strong and weak affinity sites, SOH and WHO respectively) surface complexation model with inner sphere, mononuclear, bidentate complexes of the type SO_2UO_2 and WO_2UO_2 identical to that described for ferrihydrite by Waite et al. (GCA **58**, 5465-5478, (1994)) used throughout. Also assumed carbonate surface species of the type $SCO_3H°$ and $SOCO_3^-$ and ternary uranyl carbonate surface species of the type $SO_2UO_2CO_3^{2-}$ present at strong and weak sites.

Parameters
Variety of methods used for estimating weak surface site concentrations: i) from TAO-extractable Fe assuming 0.875 mol sites/mole Fe, ii) from sum of DCB-extractable Fe+Al+Mn assuming 0.875 mol sites/mol element, iii) from BET surface area assuming 3.84 μm sites/m2. In all cases a weak to strong site ratio of 580 used (as found previously for ferrihydrite).

Thermodynamic data used
MINTEQA2 data base used but modified for U(VI) species as detailed in Waite et al. (1994). The U(VI) constants used are similar (though not in all cases identical) to those prescribed in the NEA database.

Codes
MINTEQA2 has been used in most cases though earlier studies were undertaken using HYDRAQL. FITEQL was used in some instances to obtain estimates for constants.

Publications

The work on the natural substrates has not yet been published though raw data and preliminary modeling results are reported in Waite et al. (1992). Details of the modelling approach used here, which is essentially identical to that used for ferrihydrite, are reported in Waite et al. (1994).

Waite, T.D. Payne, T.E., Davis, J.A. and Sekine, K. (1992). Uranium sorption. Alligator Rivers Analogue Project Final Report, Volume 13. ISBN 0-642-59939-4, DOE/HMIP/RR/92/0823, SKI TR 92:20-13. 106 pp.

Waite, T.D., Davis, J.A., Payne, T.E., Waychunas, G.A. and Xu, N. (1994). Uranium(VI) adsorption to ferrihydrite: Application of a surface complexation model. Geochimica Cosmochimica Acta **58**, 5465-5478.

Lessons learned

An assumption that all U(VI) uptake on the natural substrate can be described by adsorption to Tamms acid oxalate (TAO) extractable iron leads to gross underestimation of uptake.

Use of a surface site concentration estimated from dithionite-citrate-bicarbonate (DCB) leached Fe, Al and Mn and assuming a site density identical to that found appropriate for ferrihydrite (0.875 mol sites/mol of element leached) yields close correspondence between model and batch laboratory sorption data in the pH range 5-8. The site concentration estimated in this way was (surprisingly/fortuitously!) very close to that estimated from surface area using a constant site density of 3.84 μmol sites/m².

For a low total U(VI) concentration of 3.8 μM, the model slightly underpredicted U(VI) sorption to the natural substrate at pH > 8 but seriously underpredicted uptake at low pH. Much better agreement between model and laboratory data was obtained at a higher U(VI) concentration (10^{-4} M) where the surface coverage was lower and the low pH edge at significantly higher pH.

Abstract

Characterisation of Natural Substrates with Regard to Application of Surface Complexation Models

T.D. Waite (UNSW), B. Fenton (UNSW), T.E. Payne (ANSTO), G.R. Lumpkin (ANSTO), J.A. Davis (USGS) and M. McBeath (USGS)

While good correspondence between laboratory sorption data and surface complexation modelling results has been obtained for single oxide phases, much poorer correspondence has been obtained for natural substrates. This result arises, atleast in part, from the difficulty in ascertaining the identity of sorbing surfaces and in assigning appropriate values for sorbing surface site concentrations.

In an attempt to clarify the nature of possible sorbing phases, we have used a variety of techniques to investigate the surfaces of natural solid substrates from the Koongarra weathered zone. Based on insights gained from the surface characterisation studies, we have then proceeded to assess the applicability of various surface complexation modelling approaches as applied to U(VI) uptake.

Major finding from surface characterisation studies using time-of-flight secondary ion mass spectrometry (TOF-SIMS), high resolution electron microscopy and microprobe analysis are that:

- most of the uranium either intrinsically present in the weathered zone Koongarra solid investigated (the W2 sample) or subsequently added to the sample was associated with iron-rich coatings;

- these coatings also showed significant concentrations of Al, Si, Mg and P

- the iron-rich coatings exhibited variable morphology and often possessed some crystallinity (generally exhibiting goethite-like electron diffraction patterns)

- leaching studies revealed that only a small portion of these coatings were removed using Tamms acid oxalate (TAO). A significantly greater fraction (particularly of the iron-rich phases) was rapidly removed using a dithionite-citrate-bicarbonate (DCB) leachant.

Surface complexation modelling using a two-site (strong and weak affinity sites, SOH and WHO respectively) surface complexation model with inner sphere, mononuclear, bidentate complexes of the type SO_2UO_2 and WO_2UO_2 identical to that described for ferrihydrite by Waite et al. (GCA 58, 5465-5478, (1994)) indicated that:

- An assumption that all U(VI) uptake on the natural substrate can be described by adsorption to Tamms acid oxalate (TAO) extractable iron leads to gross underestimation of uptake.

- Use of a surface site concentration estimated from dithionite-citrate-bicarbonate (DCB) leached Fe, Al and Mn and assuming a site density identical to that found appropriate for ferrihydrite (0.875 mol sites/mol of element leached) yields close correspondence between model and batch laboratory sorption data in the pH range 5-8. The site concentration estimated in this way was (surprisingly/fortuitously!) very close to that estimated from surface area using a constant site density of 3.84 μmol sites/m^2.

- For a low total U(VI) concentration of 3.8 μM, the model slightly underpredicted U(VI) sorption to the natural substrate at pH > 8 but seriously underpredicted uptake at low pH. Much better agreement between model and laboratory data was obtained at a higher U(VI) concentration (10^{-4} M) where the surface coverage was lower and the low pH edge at significantly higher pH.

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- **Solid phase**

  quartz, alpha alumina, clinoptilolite, Na-montmorillonite
  NIST (alumina), Wards Scientific
  Pure mineral separates

- **Aqueous phase**

  Solution composition

  Batch experiments,
  oxidizing environment,
  20 degrees C,
  1-3 weeks,
  controlled CO2 (atmospheric, CO2-free, 1E-2 atm)

  Radionuclides

  U(VI) and Np(V)

- **Brief description of model**

  Surface components, surface species

  DLM model, with monodentate, mononuclear U(VI) and Np(V) hydroxy species

  Parameters

  Estimated parameters using nonlinear parameter optimization (FITEQL, Version 2.0)

  Thermodynamic data used

  NEA thermodynamic data for U(VI), with exception of UO2(OH2) Log K=-13.0. EQ3/6 data (release data0.alt.r2) for Np(V)

  Codes

  FITEQL for parameter optimization, MINTEQA2, Version 3.11 for simulations

- **Publications**

  Turner, D.R., R.T. Pabalan, and F.P. Bertetti. 1997. Neptunium(V)-montmorillonite sorption: An experimental and surface complexation modeling study. Clays and Clay Minerals (in submission)

  Pabalan, R.T. and D.R. Turner. 1997. Uranium(6+) sorption on montmorillonite: experimental and surface complexation modeling study. Aqueous Geochemistry (in press).

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- **Lessons learned**

  These include, but are not limited to:

  1) In lab experiments, different minerals exhibited similar pH dependence for sorption which was linked to the onset of hydrolysis.

  2) In systems open to CO_2, sorption can be simulated without invoking formation of actinyl-carbonate surface complexes.

  3) Consistent application of a simplified model is perhaps adequate from the point of view of performance assessment.

• Abstract

Sorption Modeling For Performance Assessment At The Center For Nuclear Waste Regulatory Analyses

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A fundamental concern in safety assessments of nuclear waste repositories and in nuclear waste management is the potential release of radionuclides, particularly actinides such as U, Np, and Pu to the accessible environment as dissolved constituents in groundwater. An important mechanism for retarding radionuclide migration is sorption onto minerals present along groundwater flow paths, and a quantitative understanding of actinide sorption behavior is important in evaluating the suitability of proposed geologic repositories for nuclear wastes. However, this understanding is complicated by the dependence of sorption processes on various geochemical parameters. These system parameters include aqueous solution properties (e.g., pH, Eh, ionic strength, radionuclide concentration, complexing ligands) and sorptive phase characteristics (e.g., mineral composition, surface area, sorption site density, surface charge), as well as temperature which makes description and prediction of actinide sorption in geochemical systems of variable mineralogic composition and aqueous speciation difficult.

Sorption research at the Center for Nuclear Waste Regulatory Analyses (CNWRA) in San Antonio, Texas has combined experimental and modeling methods to develop a quantitative understanding of sorption processes in support of the U.S. Nuclear Regulatory Commission (USNRC) to help evaluate the suitability of the proposed HLW repository at Yucca Mountain, Nevada.

Batch sorption experiments have been conducted at the CNWRA to investigate the sorption of U(VI) and Np(V) on quartz, clinoptilolite, montmorillonite, and -alumina over wide ranges of experimental conditions. These minerals were selected in part because their mineralogic and surface characteristics, which could potentially influence actinide sorption behavior, are distinct from each other. For example, the points-of-zero-charge (pH_{ZPC}) for quartz, clinoptilolite, and -alumina are 2.9, 3.0, and 9.1, respectively, and pH_{ZPC} values reported for montmorillonite range from 6.5 to 8. Experiments were conducted over a wide range in solution pH (2-11 pH units), solid-mass/solution-volume ratio (M/V) (up to 50 g/L), $P(CO_2)$ (CO_2 free to $10^{2.0}$ atm), radionuclide concentration (10^5 to 10^8 M), and ionic strength (0.01 to 0.1 M). Results of these experiments as well as literature data were used in determining which of the various geochemical parameters are most important to understanding and predicting U(VI) and Np(V) sorption behavior.

To develop a quantitative understanding of sorption processes and to build a mechanistic modeling capability in support of performance assessment, the CNWRA has used a surface complexation (SCM) approach. Efforts have focused on developing a simplified approach that can be uniformly applied across different radionuclide-mineral-solution systems. While this approach is not intended to be an exact representation of the mineral-water interface, it does provide a useful common starting point for model development and a means for consistent comparison of model results for performance assessment. As a basis for model development, existing potentiometric titration data for a number of different simple oxides were examined and interpreted using the numerical nonlinear least-squares optimization code FITEQL to develop surface acidity constants for different SCM approaches. Sorption experiments at CNWRA and data from the literature were interpreted using FITEQL to develop a consistent set of binding constants for radionuclide sorption reactions. Relatively simple SCM models were generally sufficient to simulate radionuclide sorption over a wide range in conditions, particularly with respect to pH. Changes in other parameters such as M/V ratios and $P(CO_2)$ provided additional constraints on modeling parameters; the simplified modeling approach as

implemented was tested more severely over the wider range in these conditions, but still provided reasonable results.

Experiments at CNWRA have indicated, for U(VI) and Np(V), a common pattern for actinide sorption that is related to the formation of hydroxy complexes in solution. Geochemical conditions which inhibit the formation of actinide-hydroxy complexes (e.g., low pH, aqueous carbonate complexation) suppress actinide sorption. For different minerals, the similarity in pH-dependence of actinide sorption on quartz, -alumina, clinoptilolite, and montmorillonite and other simple minerals suggest that actinide sorption is not sensitive to the surface charge characteristics of the sorbent as compared to the effect of changing the total number of available sites. Sorption modeling generally provided good agreement between measured and predicted sorption results, indicating that SCMs will be useful in constraining the effects of geochemical parameters on sorption. Limitations to the modeling approach include uncertainties with regard to surface complex stoichiometry, a lack of a consensus on accepted thermodynamic data for many actinides (an uncertainty being addressed by the NEA), and uncertainties regarding realistic site concentrations in mineral-water systems.

• Abstract

Development of a mechanistic model of sorption of *(VI) onto rocks from the Sellafield site

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Radioelement sorption onto a range of Sellafield samples has been measured as part of the Nirex Safety Assessment Research Programme. Probability density functions (PDFs) for use in performance assessment calculations are elicited based on these measured sorption data. Geochemical models can be used to support the data elicitation process by allowing interpretation of experimental measurements supported by knowledge of the aqueous speciation of the sorbing element, and understanding of possible sorption reactions at mineral surfaces. Additionally, models can be used to extrapolate experimental data to conditions where measurements are unavailable, allowing assessment of sensitivity to key parameters and helping to guide further experimental investigation if necessary. This paper describes the methodology adopted in parameterisation of such a model (using the triple layer approach) and its application in the case of uranium(VI) sorption onto rocks from the Sellafield site.

When applying the triple layer model approach to sorption onto rock it is usual to select a phase which is considered to dominate the sorptive properties of the rock in question and parameterise the model according to that phase. Within the NSARP, mineralogical controls on sorption have been investigated. Following sorption experiments, surface analytical techniques have been employed to examine radioelement loadings on mineral surfaces. Also, extensive studies of the distribution of natural uranium series elements in rocks from the Sellafield site have been carried out. These studies have shown iron oxides (particularly hematite) to be important sorbing minerals. For this reason, the geochemical model used in this study was based on sorption onto hematite contained within the rock samples. The following steps were carried out during parameterisation and application of the model:

1. Compilation of available data describing the surface reactions of iron oxide minerals, particularly hematite. These data included:
   - measurements of the surface properties of hematite, e.g. surface area, site density and point of zero charge;
   - experimental studies of the sorption of relevant elements (uranium, groundwater ions) onto hematite and other iron oxides. Generally these were batch experiments involving pure phases and simple background electrolyte solutions, and typically were carried out as a function of key parameters such as pH, ionic strength, partial pressure of CO_2;
   - spectroscopic studies (e.g. infrared, X-ray absorption) designed to investigate speciation of the sorbed element.

2. Selection of sorption reactions that were consistent with the compiled data regarding the nature of the sorbed complex.

3. Modelling of the hematite batch sorption data. This stage was a fitting exercise. Equilibrium constants were assigned to the selected reactions so that good fits were obtained to the data. During this step, the philosophy adopted was to achieve the simplest possible reaction dataset that could reproduce all the experimental trends. It is often the case that more than one set of sorption reactions can achieve a good fit to experimental data. To examine the sensitivity of the model to choice of sorbing species, the uranium(VI) calculations were carried out using two different datasets: (i) involving outer-sphere sorption reactions and (ii) involving inner-sphere sorption reactions. It was found that both datasets gave an equally good fit to the experimental data. Both uranium sorption models were therefore investigated in Step 5.

4. Estimation of the proportion of the rock surface occupied by hematite in the Sellafield rock samples. Two bounding conditions were investigated:

   - the measured weight percent of hematite in the sample was equated to the percent of hematite surface present per gramme of rock. This method was expected to underestimate the amount of available hematite surface because in many samples hematite forms a surface film around other mineral grains. In this case it would follow that sorption would be underestimated;
   - the measured total surface area of the rock sample was used. Using this method it was expected that the amount of hematite surface (and consequently sorption) would be overestimated.

Calculations based on these bounding conditions should give a range of sorption values bounding the measured value.

5. Prediction of the amount of uranium(VI) sorption onto rock samples from the Sellafield site for which experimental data were available. All aspects of the experimental system were represented in the model, e.g. the groundwater chemistry and the partial pressure of carbon dioxide under which the experiments were carried out.

It was found that the two uranium sorption models (inner-sphere and outer-sphere) gave very different responses when applied to the Sellafield system. The ranges of R_D values calculated using the inner-sphere model were invariably significantly lower than those calculated using the outer-sphere model (by two orders of magnitude). This was unexpected as both models were parameterised using the same single mineral data (Step 3). The differing responses of the models has been related to the effect of competition for sorption sites between radioelements and groundwater ions (e.g. calcium, sulphate). The models were parameterised using experimental data for simple systems where these competitive effects were not addressed. There is therefore a residual uncertainty in applying these models to real rock/groundwater systems. They have not been validated against systems where groundwater ions were present in significant concentrations and possibly include an inadequate representation of competitive effects. Because of this uncertainty, the Step 5 calculations were repeated, having removed sorption reactions involving calcium, magnesium and sulphate. In the absence of these competing sorption reactions, the ranges of R_D values calculated by the inner-sphere and outer-sphere models were very similar.

Comparison of the calculated ranges of R_D values with the measured R_D values shows that in some cases there is good agreement (for the tuff and sandstone experiments), while in other cases the model tends to underestimate sorption (for the breccia). Underestimation of sorption may be because minerals other than hematite may make a significant contribution to the sorption properties of the rock samples. Surface analytical studies have shown that significant radioelement loadings can be associated with minerals such as ilmenite and chlorite, and single mineral studies have illustrated the potential of alternative minerals (e.g. muscovite, chlorite and clays) to sorb radioelements strongly.

This work has highlighted two key areas of uncertainty in the application of a hematite-based geochemical sorption model to the Sellafield system:

- the treatment of competitive effects in the model is currently untested;
- the role of other mineral phases in controlling sorption onto site-specific samples has not been quantified.

At the current level of understanding, we can 'fit' experimental data and use geochemical models as interpretative tools. Therefore they can be used by extrapolation to give an indication of sorption in a range of hydrochemical environments.

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- ## Solid phase

Quartz

Min-U-Sil 5 and Nilsiä quartz

SiO_2

Small amounts of

        iron (given as $Fe_2O_3 \cdot H_2O < 450$ µg/g SiO_2), and
        manganese (given as $MnO_2 < 3$ µg/g SiO_2).

- ## Aqueous phase

Solution composition

Radionuclides

a) $NaOH$-$NaNO_3$, pH = 3- 10
   0.001, 0.005, 0.01 and 0.1 mol/L

b) Simulated fresh groundwater

c) Simulated saline groundwater

mmol/L	b) fresh simulant	c) saline simulant
K^+	0.501	22.5
Na^+	11.1	171
Ca^{2+}	2.24	79.7
Mg^{2+}	0.889	2.0
Cl^-	6.79	356
SO_4^{2-}	0.5	-
HCO_3^-	*	*
Br^-	-	1.2
Ionic strength, I	22	.440
pH	≈8.1	≈7

* = open to atmosphere

conditions:

room temperature, batch, oxic

- ## Brief description of model

Surface components, surface species

Parameters

TLM-model for all surfaces. All manganese and iron parameters are estimated or calculated using data from literature and measured amounts of these elements. For silica the source of the parameter is given in the third column of the table.

Parameter or reaction, X =	SiO_2		MnO_2	HFO
Specific surface area, m^2/g	0.8 – 6.0	Meas.	300	600
N_s, sites, nm^{-2}	6	Liter.	55	3
N_s, moles, $\mu mol/m^2$	10	Liter.	90	5
Sites per mass, $\mu mol/g$	8	Liter.	27 200	3 000
Capacitance of inner layer, F/m^2	1.25	Liter.	1.25	1.40
Capacitance of outer layer, F/m^2	0.2	Liter.	0.2	0.2
$XOH = XO^- + H^+$	-7.8	Liter.	-4.2	-10.7
$XOH + H^+ = XOH_2^+$	-		-	5.1
$XOH + Na^+ = XO^- - Na^+ + H^+$	-5.7	Fitted	-3.3	-9.0
$XOH + K^+ = SO^- - K^+ + H^+$	-5.7	Estim.		-9.0
$XOH + Ca^{2+} = SO^- - Ca^{2+} + H^+$	-7.32	Liter.		-6.3
$XOH + Mg^{2+} = SO^- - Mg^{2+} + H^+$	-7.32	Liter.		-6.3
$XOH + H^+ + Cl^- = XOH_2^+ - Cl^-$	-	Liter.	-	6.9
$XOH + SO_4^{2-} + H^+ = SOH_2^+ - SO_4^{2-}$		Liter.		9.6
$XOH + SO_4^{2-} + 2H^+ = SOH_2^+ - HSO_4^-$		Liter.		14.5
$XOH + Ni^{2+} = XO^- - Ni^{2+} + H^+$	-5.5	Fitted	0.0	-2.0
$XOH + Ni^{2+} + H_2O = XO^- - Ni(OH)^+ + 2H^+$	-12.4	Fitted	-	-

Codes

HYDRAQL

Thermodynamic data used

Code	Notes	Aqueous species	log K
1000		$Ca^{2+} + CO_3^{2-} = CaCO_3(aq)$	3.33
1010		$Ca^{2+} + CO_3^{2-} + H^+ = CaHCO_3^+$	11.38
1020		$Ca^{2+} + SO_4^{2-} = CaSO_4(aq)$	2.11
1030		$Ca^{2+} + Cl^- = CaCl^+$	-0.7
1350		$Ca^{2+} + H_2O = CaOH^+ + H^+$	-12.85
1360		$Mg^{2+} + CO_3^{2-} = MgCO_3(aq)$	2.98
1370		$Mg^{2+} + CO_3^{2-} + H^+ = MgHCO_3^+$	11.37
1380		$Mg^{2+} + SO_4^{2-} = MgSO_4(aq)$	2.41
1385		$Mg^{2+} + Cl^- = MgCl^+$	-0.13
1740		$4Mg^{2+} + 4H_2O = Mg_4(OH)_4^{4+} + 4H^+$	-39.8

1960		$K^+ + SO_4^{2-} = KSO_4^-$	0.880
1962		$K^+ + Cl^- = KCl(aq)$	-1.49
2000		$Na^+ + CO_3^{2-} = NaCO_3^-$	0.516
2005		$Na^+ + CO_3^{2-} + H^+ = NaHCO_3$	10.48
2010		$Na^+ + SO_4^{2-} = NaSO_4^-$	0.820
12530		$H^+ + CO_3^{2-} = HCO_3^-$	10.33
12540		$2H^+ + CO_3^{2-} = H_2O + CO_2(aq)$	16.67
12550		$H^+ + SO_4^{2-} = HSO_4^-$	1.98
13595		$H_2O = H^+ + OH^-$	-13.99
		Minerals	
20000	Calcite	$Ca^{2+} + CO_3^{2-} = CaCO_3$	8.48
20002	Aragonite	$Ca^{2+} + CO_3^{2-} = CaCO_3$	8.34
20010	Gypsum	$Ca^{2+} + SO_4^{2-} + 2H_2O = CaSO_4 \cdot 2H_2O$	4.48
20012	Anhydrite	$Ca^{2+} + SO_4^{2-} = CaSO_4$	4.31
20130	Portlandite	$Ca^{2+} + 2H_2O = Ca(OH)_2 + 2H^+$	-22.6
20140	Nesquehonite	$Mg^{2+} + CO_3^{2-} + 3H_2O = MgCO_3 \cdot 3H_2O$	5.33
20142	Lansfordite	$Mg^{2+} + CO_3^{2-} + 5H_2O = MgCO_3 \cdot 5H_2O$	5.49
20144	Artinite	$2Mg^{2+} + CO_3^{2-} + 5H_2O =$ $Mg_2CO_3(OH)_2 \cdot 3H_2O + 2H^+$	-9.32
20145	Dolomite (dis)	$Ca^{2+} + Mg^{2+} + 2CO_3^{2-} = CaMg(CO_3)_2$	16.6
20146	Epsomite	$Mg^{2+} + SO_4^{2-} + 7H_2O = MgSO_4 \cdot 7H_2O$	1.96
20200	Brucite	$Mg^{2+} + 2H_2O = Mg(OH)_2 + 2H^+$	-16.3
		Gas	
25000		$2H^+ + CO_3^{2-} = H_2O + CO_2(gas)$	18.14

- **Publications**

Puukko, E. & Hakanen, M. 1995. Surface complexation modelling: experiments on the sorption of nickel on quartz. Helsinki, Nuclear Waste Commission of Finnish Power Companies, Report YJT-95-12. 20 p.

Olin, M. 1995. Surface complexation modelling applied to the sorption of nickel on silica. Report YJT-95-10. 47 p.

Puukko, E. & M. Hakanen. 1997. Surface complexation modelling: experiments on the sorption of nickel on quartz, goethite and kaolinite. To be published as a Posiva report.

Olin, M. & Lehikoinen, J. 1997. Surface complexation modelling applied to the sorption of nickel and thorium on silica, and nickel on kaolinite and goethite. To be published as a Posiva report.

- **Lessons learned**

- Planning and pre-modelling must be done more carefully
- Silica is not a "simple" system: especially the low ionic strength is problematic
- Surface complexation modelling had some predictive power in this case

- ## Abstract

Modelling Sorption Of Nickel On Silica, Goethite, And Kaolinite

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The work consists of several studies of nickel sorption on silica as well as some experiments of nickel sorption on goethite and kaolinite. These studies were performed during 1994 – 1997. The experimental part was carried out in the Laboratory of Radiochemistry (University of Helsinki) while the modelling was done at VTT Chemical Technology.

The objectives of the work were

- to develop the experimental and theoretical know-how to apply surface complexation modelling
- to test the predictive power of surface complexation modelling, and
- to find theoretical background for using the chosen values of K_d's in the performance analysis.

All the studies comprised the preliminary modelling phase, reporting and the subsequent delivery of the results to the experimentalists. The experimental work included the measurement of the specific surface area of the solid phase, the analysis of some important trace elements (Fe and Mn) present in the solid phase, and finally the sorption experiments. All the acidity constants and parameters were taken from the open literature. The silica and goethite systems were modelled by the triple layer model whereas kaolinite by the constant capacitance model.

In the silica experiments, three types of water were used: simple electrolyte, and fresh and saline groundwater simulants. Two different types of quartz – Min-U-Sil 5 and Nilsiä quartz – were used. Although the measured trace element concentrations were low, iron was included in the modelling due to its high influence at high pH-values. Preliminary modelling gave satisfactory results except at low ionic strength, where sorption onto the quartz surface was difficult to quantify with any kind of surface complexation model. This difficulty persisted even in the final modelling phase – at low ionic strength the observed sorption was much higher than modelled. The model predicted much lower sorption for the saline simulant compared to the fresh simulant, which was also experimentally verified.

The goethite system was described quite well even in the prelimary modelling phase (Figure 1), but for kaolinite the same kind of difficulties as for quartz occurred.

The conclusions were that

- the most difficult task in applying the surface complexation modelling is either the lack of data or in some cases the high amount of – controversial – data
- the surface complexation models do have some predictive power, which varies considerably depending on the system under consideration
- the surface complexation modelling and experiments are invaluable for the understanding the variations in measured K_d-values, giving also valuable hints as to how K_d-measurements should be done.

- ## References

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PNC PN8600 97-005

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Olin, M. & Lehikoinen, J. 1997. Surface complexation modelling applied to the sorption of nickel and thorium on silica, and nickel on kaolinite and goethite. To be published as a Posiva report.

The sorption of nickel on goethite
in 0.001 M, 0.01 M and 0.1 M NaNO₃

Figure 1. The sorption of nickel on goethite at three ionic strengths.

- **Abstract**

Pore Water Composition And Bulk Solution In Crystalline Rock And In Bentonite Clay

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In real systems, sorption processes often take place inside pores, the dimensions of which are small enough for the diffuse layers of the charged pore surfaces to extend over the entire pore. This extension will cause compositional differences between the bulk and pore waters. If surfaces are negatively charged, anions and cations are repelled from and attracted to the pore space, respectively, which in turn implies differences in solubilities and sorption inside the pores compared to the bulk solution.

We have studied the coupling of surface complexation and diffusion in the model system shown in Figure 1, with the largest and smallest dimension for diffusion simulations and for studying the effect of charged surfaces respectively. The surface charge is caused by a surface complexation reaction. The surface potential and concentrations are calculated by assuming the pore water in equilibrium with some external "bulk" solution, which, for the diffusion boundary condition, is the real bulk solution in contact with the porous sample. Deeper inside the pore, the "bulk" represents a "fictitious" solution composition. A numerical solution to the non-linear Poisson-Boltzmann equation subject to difficult boundary conditions was called for.
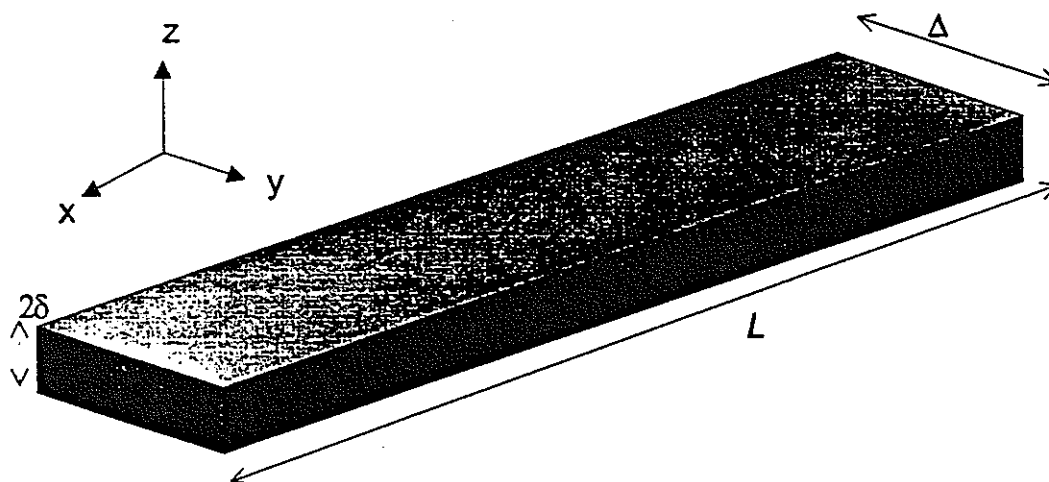
Figure 1. Sketch of a diffusion channel. Dimensions in different directions are of different magnitude: $\delta \approx 1 - 100$ nm, $\Delta \approx 50$ μm, $L \approx \tau L_0$, $L_0 \approx 10 - 100$ mm $\tau \approx 3 - 10$. L_0 is the physical length of the system and τ is the tortuosity correcting for the longer diffusion path through the system.

Figure 2 shows some results for anion exclusion in porous rock. The pores are assumed to be covered by silica. It is evident from this figure that both the low ionic strength and the small pore diameter decrease the anion concentration inside the pores thereby essentially changing the chemical conditions. Here, no specific sorption of cations was assumed. The (free) cation concentration is higher by about a factor inversely proportional to the anion exclusion parameter, κ. This may be an explanation for surface diffusion.

The future work includes the solubility and specific sorption studies inside the pores.
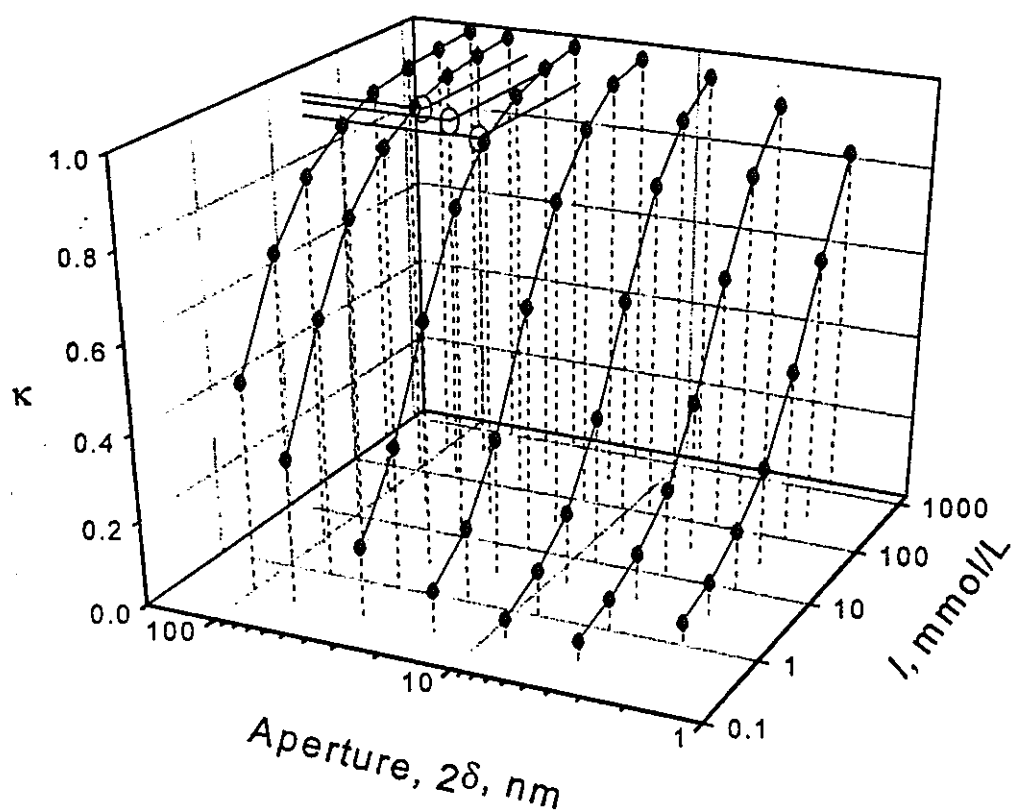
Figure 2. The ratio of concentrations inside the pore and in free water, κ, for a monovalent anion in silica pores at pH 6. Clear anion exclusion is noticed even at high ionic strength in very small pores or in large pores at very low ionic strength. The open symbols denote results from an experimental system.

- **Abstract**

Mechanistic Modelling of the Sorption of Uranium(VI), Plutonium and Thorium onto Aluminium Oxide, Muscovite and Chlorite

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Many of the experimental and modelling studies performed under the Nirex Safety Assessment Research Programme have involved site-specific geological materials, and their equilibrated groundwaters. However, these natural systems are complex, and detailed interpretation of the results can be difficult. One approach used to interpret these natural systems is to study component minerals individually and to use this information to build up a representation of the entire system. The current study has looked at radionuclide sorption onto sheet silicate minerals.

Experiments were performed to study the sorption of i) plutonium and uranium(VI) onto aluminium oxide, ii) plutonium and uranium(VI) onto chlorite and muscovite and iii) thorium onto muscovite. (In each case uranium(VI) and plutonium sorption were studied in the same experiment.) Muscovite consists of silica/aluminium oxide sheets with potassium ions in the interlayer sites whereas chlorite has alternate silica/aluminium oxide and iron/magnesium oxide layers. Since many data are available in the literature for sorption onto silica and iron oxides, aluminium oxide was included in the study to parameterise the sorption onto the aluminium-oxygen component of the sheet silicate surfaces.

Thermodynamic equilibrium modelling using the triple-layer sorption model (HARSORB) within the HARPHRQ program has been used to interpret the experimental results. (HATCHES version 6.0 was used throughout.) For the aluminium oxide modelling, the standard (single-site) triple-layer sorption model was used. However for muscovite a two-site triple-layer sorption model was employed, with one site (silica) representing the silicon-oxygen component of the sheet silicate surface and the other (aluminium oxide) the aluminium-oxygen component. In the chlorite modelling, a third site type (goethite) was added to the muscovite model to represent the iron-oxygen surface group of chlorite. Parameters to define the interactions between the three sorbing surface sites and the solution species were taken from the literature.

In order to parameterise uranium(VI) and plutonium sorption onto the aluminium-oxygen sites, initial modelling was performed to reproduce experimentally determined R_D values for uranium(VI) and plutonium sorption onto aluminium oxide. This resulted in a refined dataset which was then used, without further adjustment, to simulate the extent of uranium(VI) and plutonium sorption onto muscovite and chlorite.

For uranium(VI) sorption onto the sheet silicates, the model simulations are generally within an order of magnitude of the experimental data across the pH range 5 to 10. The model predicted that radioelement sorption was predominantly onto the silicon-oxygen sites and the background electrolyte components (sodium and nitrate) sorbed onto the aluminium and iron-oxygen sites. Therefore both types of site were required to simulate the experimental data. For plutonium, the model also predicted that radioelement sorption was predominantly onto the silicon-oxygen sites up to pH~10. At pH>10, the sheet silicate minerals are unstable and mineral dissolution/reprecipitation processes could determine the extent of actinide removal from solution.

The two-site model has also been used to simulate thorium sorption onto muscovite, using unrefined literature values to parameterise the interactions between the sheet silicate surface and thorium solution species. Again, the agreement with the experimental data is within an order of magnitude up to pH~10.

- ## Abstract

A Summary of Sorption Investigations Performed on Behalf of the UK Regulator of Radioactive Waste Disposal

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The Environment Agency of England and Wales (formerly HMIP) is responsible for the regulation of radioactive waste disposal. As part of this responsibility, the Agency is required to undertake a scientific review of the disposer's safety case. To this end, the Agency has funded a wide ranging research programme into scientific disposal issues to enable it to independently assess the adequacy of the disposer's safety case. Key aims of this research programme are to understand processes and performance assessment techniques to model these processes.

As part of its research into the migration of radionuclides thorough geological media, the Agency has conducted investigations into the modelling of retardation processes. Two investigations are described here: the CHEMVAL 2 sorption project, and the Winfrith column experiments. Both investigations had a number of objectives, including testing the ability of thermodynamic models to predict the retardation of radionuclides by natural geological media.

The CHEMVAL 2 exercise (part funded by the European Commission) provided modellers with experimental data for surface titrations on MinUSil 5 silica and for Ni sorption as a function of pH at two ionic strengths. Also provided were surface area measurements and petrographic descriptions for St. Bees Sandstone, and literature data for modelling Ni sorption onto Fe oxides. The modellers were asked to predict Ni sorption as a function of pH for silica at different ionic strengths and also onto the sandstone. Different modellers used different mechanistic models and assumed differed sorbing species, but there was little difference in the overall quality of modelling results. The position of the midpoint of the sorption edge was correctly predicted, but not the slope of the edge. The slope has subsequently been ratified by other experimental groups. In the case of the sandstone, a small quantity of Fe oxide was observed and modelled as the dominant sorbing phase.

The Winfrith experiments passed U-bearing solutions through intact columns of Clashach Sandstone. Modellers were provided with experimental batch data for surface tritations on silica and the sandstone, and for U sorption onto the sandstone. Hydraulic characteristics and surface area measurements for the columns were also provided. Modellers were asked to predict profiles of sorbed U through the columns and the concentration of U in the effluent solution as a function of time. Runs were conducted just injecting U, and injecting U with Cd, with EDTA, and with saccharic acid to investigate the effects of competition and complexation. The experimental results showed little influence of Cd on U migration but both EDTA and to a more significant degree, saccharic acid were effective in increasing U mobility. The modellers used a fully coupled chemical-transport code (CHEMTARD) which was calibrated using the boundary condition data provided. Dynamic modelling results were in good agreement with experimental observations, although the models tended to slightly overpredict the migration of U, the effect of Cd competition, and the desorption of U. Some of these overpredictions are clearly an artifact of not modelling kinetic effects.

The results of these two investigations indicate that thermodynamic models can be used to predict sorption by natural media, and that coupled models can be used to upscale laboratory data. However, the lack of confidence in extrapolating the models, especially to more complex natural systems, is such that at least limited experimental corroboration is required, and suggests that the models only be used for interpolation between experimental observations. To build confidence, a sensitivity analysis on

model parameters needs to be performed so that the simplest, most robust model can be developed. A similar analysis should be performed on the parameter data to determine if a generic or site-specific database is required. It then needs to be established that each key parameter can be properly determined experimentally or in the field. This will allow the uncertainty associated with the model and its application to be appraised and an assessment of adequacy made by both the safety case proponent and the regulator.

- **Abstract**

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- **Solid phase**

Dolomite from a skarn.

- **Aqueous Phase**

0.005 to 0.5M NaCl, 25C, flow-through, oxic, Ca, Mg, Sulfate, Np, U, Pu, Am, Th

- **Model**

Metal exchange on Ca and Mg sites was measured and the effect of sulfate on their magnitude was modeled.

- **Publications**

Brady P. V., J. L. Krumhansl and H. W. Papenguth. Surface Complexation Clues to Dolomite Growth. Geochimica et Cosmochimica Acta (60) 727-731.

Brady P. V. and W. A. House 1996. Surface-Controlled Dissolution and Growth of Minerals (Chapter 4 in Physics and Chemistry of Mineral Surfaces, CRC Press Ed. P.V. Brady) p. 221-302.

Brady P. V., H. W. Papenguth and J. Kelly J. Ca, Mg and Nd Sorption on Dolomite (In DOE Internal Review; to be subsequently submitted to Geochimica et Cosmochimica Acta).

Brady P. V. (Editor) 1996. Physics and Chemistry of Mineral Surfaces. CRC Press 352p.

- **Lessons learned**

see abstract

- ## Abstract

Dolomite Surface Chemistry and Actinide Retention

Dolomite surfaces are a common component of soils and sediments and are, in particular, a potentially important sorptive sink if human intrusion into the Waste Isolation Pilot Plant (WIPP) releases actinides into the Culebra Dolomite. Using a limited residence time reactor we have measured Ca, Mg, Nd adsorption/exchange as a function of ionic strength, PCO_2, and pH at 25oC. By the same approach, but using as input radioactive tracers, we measured adsorption/exchange of Am, Pu, U, Th, and Np on dolomite as a function of ionic strength, PCO_2, and pH at 25oC. Metal adsorption is favored at high pH. Ca and Mg adsorb in near-stoichiometric proportions except at high pH. Adsorption of Ca and Mg is diminished at high ionic strengths (e.g. 0.5M NaCl) pointing to counterion association with the dolomite surface, and the likelihood that Ca and Mg sorb as outer-sphere complexes. Sulfate amplifies sorption of Ca and Mg, and possibly Nd as well. Exchange of Nd for surface Ca is favored at high pH, and when Ca levels are low. Exchange for Ca appears to control attachment of actinides to dolomite as well, and high levels of $Ca2+$ in solution will decrease Kd s.

At the same time, to the extent that high PCO_2 s increase $Ca2+$ levels, Kd s will decrease with carbon dioxide levels as well, but only if actinide-carbonate complexes are not observed to form (Am-carbonate complexes appear to sorb; Pu-complexes might sorb as well. U-carbonate complexation leads to desorption). This indirect CO_2 effect is observed primarily at, and above, neutral pH. High NaCl levels do not appear affect actinide Kd s.

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• Solid phase

Min-U-Sil 30 (brand name)
Pennsylvania Sand and Glass Company, Pittsburgh, PA (USA)
>99% quartz, acid-refluxed to remove traces of iron and aluminum oxides.

• Aqueous phase

Solution composition

Typical electrolyte was 0.01M $NaNO_3$, sometimes with 10^{-4}M or $5 \cdot 10^{-4}$M fluoride, 10^{-4}M total acetate, atmospheric p_{CO2} ($NaHCO_3$),

U(VI) total concentration range of 10^{-9}M to 10^{-4}M.

Room temperature (22°C), oxic conditions, batch and column experiments

Typical equilibration times in batch experiments: 20 hours

Linear flow velocities: 8.7×10^{-4} and 3.5×10^{-3} cm/sec.

Radionuclides

^{238}U, ^{234}U, ^{233}U

• Brief description of model

Surface components, surface species:

Surface Complexation Model (SCM) without Electrical Double Layer Model (EDL) used. One, two and three site models studied with two different stoichiometries possible for uranium(VI) adsorption reactions (either one or two protons released per UO_2^{2+} adsorbed)

Surface components were the surface silanol groups, SiOH, but were represented as either one, two, or three types of silanol groups in one, two, and three site models, respectively.

Surface species were SiOH, $SiOUO_2OH$ and $SiOUO_2^+$ and the various uranium surface complexes (see Kohler et al., 1996)

Parameters (measured, calculated, estimated):

Specific surface area of the quartz measured by gas adsorption (Kr) and BET theory, determined to be 0.33m²/g. Non-porous material. Grain size approximately 8-30 m.

Total site density of the quartz estimated from U(VI) adsorption edges at 10^{-4}M total U(VI) and 100g quartz/L. ($3.5 \cdot 10^{-7}$ mol/g).

Formation constants for the surface complexes (binding constants) and distribution of sites (strong to weak site concentrations) estimated (see "Publications").

Thermodynamic data used:

"Chemical Thermodynamics of Uranium"; Grenthe et al., 1992.

"Critical Stability Constants"; Vol 6, 2nd suppl.;   Smith and Martell, 1989.

Codes:

FITEQL v 2.0 (John Westall, October 1982) for the estimation of binding constants from batch data.

FFSTM (G.P. Curtis and J. Rubin, 1997 in preparation) for solute transport modeling

- **Publications**

    M.Kohler; G.P.Curtis; D.B.Kent and J.A. Davis, 1996, Experimental investigation and modeling of uranium(VI) transport under variable chemical conditions, Water Resources Research, Vol. 32, No.12, Pages 3539-3551, December 1996.

- **Lessons learned**

    The uncertainty in parameters for surface complexation models is affected by the type of experiments conducted (batch vs. column) and the range of chemical conditions considered in the experiment. If the range of chemical conditions that must be considered in PA modeling or some other application is known, a surface complexation model can be simplified to eliminate unnecessary parameters, including components and species. That is, the required complexity of the surface complexation model depends on the range of conditions that must be considered in the model. The results of the study illustrate that reactive transport models that combine aqueous chemical speciation and surface complexation provide a powerful tool for predicting the complex transport behavior that may occur under variable chemical conditions.

- ## Abstract

Uranium(Vi) Transport Modeling Under Variable Chemical Conditions Using The Surface Complexation Concept

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The transport of adsorbing and complexing metal ions in porous media was investigated with a series of batch and column experiments and with reactive solute transport modeling. Pulses of solutions containing U(VI) were pumped through columns filled with quartz grains, and the breakthrough of U(VI) was studied as a function of variable solution composition (pH, total U(VI) concentration, total fluoride concentration, pH-buffering capacity). Decreasing pH and the formation of nonadsorbing aqueous complexes with fluoride increased U(VI) mobility. A transport simulation with surface complexation model (SCM) parameters estimated from batch experiments was able to predict U(VI) retardation in the column experiments within 30%. SCM parameters were also estimated directly from transport data, using the results of three column experiments collected at different pH and U(VI) pulse concentrations. SCM formulations of varying complexity (multiple surface types and reaction stoichiometries) were tested to examine the tradeoff between model simplicity and goodness-of-fit to breakthrough. A two site model (weak- and strong-binding sites) with three surface complexation reactions fit these transport data well. This reaction set was able to *predict* 1) the effects of fluoride complexation on U(VI) retardation at two different pH values and, 2) the effects of temporal variability of pH on U(VI) transport caused by low pH buffering. The results illustrate the utility of the SCM approach in modeling the transport of adsorbing inorganic solutes under variable chemical conditions.

- ## Author

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- ## Solid phase

Titaniumoxide
Degussa Corporation, Pigm. division, P.O. Box
2004, New Jersey 07608

- ## Aqueous phase

Solution composition

0.005 - 0.05 M NaClO4

2 days contact time, ambient temperature, batch experimens, anoxic

Radionuclides

234Th

- ## Brief description of model

This part is not finished at the moment.

Codes

FITEQL

- ## Lessons learned

Check the concentration. In our case was the concentration of 232Th the dominating.

- ## Abstract

Sorption of Th onto Titaniumdioxide

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The sorption of thorium onto titanium dioxide from aqueous solution was studied as a function of both pH (1-7) and ionic strength (0.005 - 0.05 M NaClO4) in a CO2 free environment at low thorium concentration (10-7-10-8 M). The concentrations were mesasured with ICP-MS. Titaniumdioxide has been choosen to represent minerals of a low/medium point of zero charge and because it is relatively insoluble and thorium to represent tetravalent actinides. The experimental method employed is batchwise where the pH of the individually prepared samples is measured after separation of the phases. The first and second acid dissociation constants, pKa1 and pKa2 of the titaniumdioxide surface were determined from potentiometric titrations. Preliminary results indicate the formation of innersphere complexes for Th as the sorption is independent of the ionic strength. The thorium sorption sharply increases between pH 2 and 3. All the data are to be modeled using a triple layer surface complexation model with the code FITEQL.

(Arnold)

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- ## Solid phases

A natural sand and its 3 component minerals were studied.

Natural sand: Wedron 510 Quartz Sand
Source :   St. Peter sandstone, sold by Wedron Silica Corp., Wedron, Illinois, 60557, USA

Mineralogy :
   major: quartz
   trace: kaolinite, mixture of iron oxyhydroxide phases

Chemical composition: 99.99% SiO_2

Trace elements in bulk rock (ppm):
   Li (1.5); Na (1.7); Mg (24.7); Al (2830); K (2.5); Ca (55); Ti (83); Fe (242); Ni (0.2); Br (1.7)

Trace elements in bulk fine (<74 micron) fraction (ppm):
   Li (2.5); Na (9.6); Mg (118); Al (11300); K (20); Ca (222); Ti (892); Fe (2280); Ni (2); Br (<0.8)

Trace elements in surface (hot 6 N HCl leach) of fine (<74 micron) fraction (ppm):
   Li (0.1); Na (0.9); Mg (84.6); Al (1200); K (1); Ca (198); Ti (13); Fe (1180); Ni (0.9); Br (nd)
   BET Specific surface area: 0.08 m2/g

Component Solid Phases:

1. synthetic goethite
   Synthesized by the method of Atkinson et al. (1967)
   BET specific surface area: = 33.8 - 45.4 m2/g

2. Min-U-Sil 5 quartz
   Fe content: 357 ppm extractable in boiling HCl
   source:U.S. Silica, Berkeley Springs, West Virginia
   BET specific surface area: = 4.05 - 5.81 m2/g

3. Kaolinite
   Fe content: 1270 ppm extractable in boiling HCl
   source: kaolin powder, U.S.P., J.T. Baker Co.
   BET specific surface area: = 24.6 m2/g

- ## Aqueous phase

Solution composition

0.001 or 0.1 M NaCl electrolyte; pH range: 4 - 10; competing cation: Li (100 ppm).

equilibration time: 8- 12 hr pre-equilibration; 8- 12 hr equilibration ("overnight")

temperature: room temp, about 22 C,

batch test: Wedron sand: 58 - 78 m^2/l (20 g sand /20 ml solution)
goethite: 4.8 - 55 m^2/l
Min-U-Sil5: 124 - 247 m^2/l
kaolinite: 124 m2/l

oxic atmosphere: atmospheric pCO_2 for pH <7.5;
(total carbonate = 10-3.74 M maintained by addition of NaHCO3 at higher pH)

radionuclides

Ni (100 - 230 ppb)

- ## Brief description of model

Surface complexation parameters were derived for the component minerals. The Ni sorption edge measured on the Wedron sand was compared to those calculated using the properties of the component minerals.

Surface components, surface species

Wedron 510 sand is more than 99% quartz in bulk mineralogy, yet its adsorption behavior is dominated by iron oxyhydroxide and kaolinite, two trace components. The presence of Fe-oxyhydroxide is inferred from the quantity of Fe leached during an acid wash. Fe-oxyhydroxides probably coat most (50 – 80%) of the available surface area in the raw sand. Kaolinite platelets were observed on sand grain surfaces by SEM. Qualitatively, the adsorption properties of the sand can be adequately modeled as a two-component system. Ni adsorption occurs primarily on the iron oxyhydroxide, on sites where Li does not compete; some of the Ni adsorbs to kaolinite, and competes with Li for adsorption sites on that mineral. Competition with Li leads to diminished Ni adsorption by both the raw sand and pure kaolinite. Ni adsorption by goethite is insensitive to the presence of Li, suggesting that in the sand, iron oxyhydroxide could not be the site of the Li-Ni competition. The presence of the carbonate cement is inferred from potentiometric titration of the raw sand and the amount of Ca and Mg that is leached by acid-stripping. Li adsorbs irreversibly, suggesting that kaolinite is the only important phase in the sand with respect to Li adsorption.

Two triple-layer surface-complexation models were developed for simulating Ni adsorption onto goethite. The models were fit to Ni adsorption data in batch systems with approximately 5 and 50 m^2/l geothite, under both CO_2-free and air-equilibrated conditions. The adsorption stoichiometry is modeled as a 1:1 $SONi^+$ inner-sphere complex. The simpler one-site model performs poorly at lower surface concentrations when optimized at the higher surface concentration. The two site model contains a small fraction of high energy sites and fits data for both goethite concentrations. A quantitative model of Ni adsorption onto kaolinite was also developed; attempts to develop a model for quartz were less successful. The Ni-adsorptive properties of the sand could be simulated using the 1-site goethite model assuming a iron oxyhydroxide surface area of 28 m^2/l in the sand/solution system. This corresponds to a specific surface area of the iron coatings of approximately 600 m^2/g.

Parameters (measured, calculated, estimated)

Goethite:

Surface area calculated from BET: 58 m^2/l.
Inner-layer capacitance (C_1): 1.20 F/m^2 - calculated from potentiometric data with FITEQL
Outer-layer capacitance (C_2): 0.20 F/m^2 - Davis *et al.* (1978)
Site density: 2.31 sites/nm^2 - as advocated by Davis and Kent (1990).
Fraction of high Ni affinity sites : 0.038 - This work (two-site model only).

Formation constants for surface species (pK values):

$SO^- = 9.9$, $SOH_2^+ = -7.9$ - van Geen et al. (1994)
$SO\text{-}Na = 8.9$, $SOH_2\text{-}Cl = -8.84$ - calculated from potentiometric data with FITEQL.
$SOCO_2^- = 4.23$ - van Geen et al. (1994)
$SO^-Ni^+ = -0.613$ - single site inner sphere complex calculated from sorption data with FITEQL.
$SO^{II}Ni^+ = 0.5$ - IS complex calculated from sorption data with FITEQL (2-site model).
$SO^{I}Ni^+ = -1.8$ - IS complex calculated from sorption data with FITEQL (2-site model).

Min-U-Sil-5 Quartz:

Surface area calculated from BET data: 265 m^2/l
Inner-layer capacitance (C_1): 2.0 F/m^2 - calculated from potentiometric data with FITEQL.
Outer-layer capacitance (C_2): 0.20 F/m^2 - Davis *et al.* (1978)
Site density: 6 sites/nm^2 - estimated from other studies in literature.

Formation constants for surface species (pK values):

$SO^- = 6$, $SO\text{-}Na = 7$ - calculated from potentiometric data with FITEQL.
$SOH_2^+ = 2$ $SOH_2\text{-}Cl = 3$ - calculated from formation constants for SO^-, $SO\text{-}Na$ assuming $pH_{zpc} = 2$.
$SO^-Ni^+ = 7.7$ - outer sphere complex visual fit from sorption data calculated with HYDRAQL.

Kaolinite:

AlOH and SiOH sites

Surface area calculated from 10x value of BET measurements: 1240 m^2/l
Site density: 6 sites/nm^2 - as advocated by Xie and Walther (1992).
Inner-layer capacitance (C_1): 2.4 F/m^2 - from Riese (1982).
Outer-layer capacitance (C_2): 0.20 F/m^2 - Davis et al. (1978)

AlOH sites

Fraction of total sites: 0.5 - as advocated by Riese (1982)

Formation constants for surface species (pK values):
$SO^- = 7.4$ - from Riese (1982).
$SO\text{-}Na = 7.4$ - from Riese (1982).
$AlO^-Ni^+ = 2.1$ - IS complex; visual fit from sorption data calculated with HYDRAQL.

SiOH sites

Fraction of total sites: 0.5 - as advocated by Riese (1982)

Formation constants for surface species (pK values):
$SO^- = 6.25$ - from Riese (1982).
$SO\text{-}Na = 3.5$ - from Riese (1982).
$SiO^-Ni^+ = 7.7$ - outer sphere complex; value from Min-U-Sil used.

Thermodynamic data

Thermodynamic calculations were carried out with using a critically evaluated set of formation constants for aqueous Ni species. Sources of data include compilations by Baes and Mesmer (1976), Mattigod and Sposito (1977), Wagman *et al.* (1982), van Geen et al. (1994). The formation constants for Ni carbonato-complexes are two orders of magnitude lower than the values commonly used in the literature. The lower values are consistent with the results of Ni solubility measurements in batch systems with low concentrations of CO_2 and Ni adsorption experiments at high pH.

Codes

HYDRAQL 94 (Ward, 1995), a revised version of HYDRAQL (Papelis *et al.*, 1988) and FITEQL 2.0 (Westall, 1982).

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- ## Lessons learned

  1. Acid-cleaning procedures strongly effect surface properties of sand and Min-U-Sil quartz reference.
  2. Sorption properties of sand were dominated by trace mineral coatings
  3. Dissolution of minerals (esp. SiO_2) and change in ionic strength during potentiometric titration introduces uncertainity in data interpretation and model fitting.
  4. Uncertainty in effective surface area of clays has strong effect in calculated SCM parameters.
  5. Large number of adjustable parameters in SCM and large number of reasonable interpretations of data produced from each experimental technique makes unique set of model parameters unattainable. A large degree of subjectivity is unavoidable.

• Abstract

A Model for Radionulcide Sorption onto Cementitious Surfaces

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In a Nirex repository for low and intermediate level wastes, a high-calcium cementitious backfill would be specified. Sorption onto this Nirex Reference Vault Backfill (NRVB) and onto cementitious encapsulation grouts would play an important role in retarding the release of radionuclides from the near field of a repository. In this work, a thermodynamic sorption model was developed that is consistent with the available experimental data and that allows prediction of radioelement sorption onto cementitious materials of varying calcium-silicon ratio (Ca/Si). The diffuse-layer model (DLM) has been applied, which includes the electrostatic interaction between a sorbing ionic species and a charged interface, but does not require the extra surface parameters associated with more detailed surface complexation models. It is assumed in the development of this modelling study that the surface is dominated by calcium and silicon sorption sites. The composition of the aqueous phase and the properties of the cementitious surface vary with the calcium-silicon ratio (Ca/Si) of the solid material.

For any given system, Ca/Si is fixed and the pH and the aqueous calcium and silicon concentrations are calculated using the Berner model [vii]. The surface properties of the cementitious solid are also dependent on the Ca/Si ratio. Two types of surface site are included: calcium sites (>CaOH) and silicon sites (>SiOH). Each type may take up or lose protons. In addition, sorption of calcium ion onto silicon sites may occur, creating further calcium surface sites. The proportion of calcium surface sites is therefore dependent on the calcium ion concentration and the pH, which in turn are dependent on Ca/Si. This mole fraction of calcium surface sites, $x_S(Ca)$, is a key parameter in the model.

It is fundamental to the model that the equilibrium constants for the surface equilibria (log K^{int}) do not keep the same values for solids of different Ca/Si. This is not unexpected since, for example, a calcium surface site is unlikely to behave identically when it is located on a calcium-rich surface and on a silicon-rich surface. The approach adopted was to select log K^{int} values for each surface equilibrium at $x_S(Ca) = 0$ (silica surface) and at $x_S(Ca) = 1$ (calcium hydroxide surface), based on literature values or the fitting of experimental data wherever possible. At $0 < x_S(Ca) < 1$, the log K^{int} values are assumed to vary linearly with $x_S(Ca)$, between the two sets of limiting values.

The surface model has been applied to predict the surface potential of cementitious solids after equilibration with pure water, at varying Ca/Si. Both the equilibrated pH and the surface potential are dependent on the Ca/Si. The surface potential is negative at low Ca/Si (weak calcium sorption) but positive at high Ca/Si (strong calcium sorption). This trend is also found in reported zeta potential measurements.

Radionuclide sorption is incorporated into the model by surface complexation of the major aqueous species with the surface sites. The model has been applied consistently to a range of batch sorption data including caesium and iodide sorption onto calcium silicate hydrate phases (see Figure 1), and to the sorption of several radionuclides onto a high calcium cement (NRVB). The model predictions under saline conditions are also consistent with the available data.
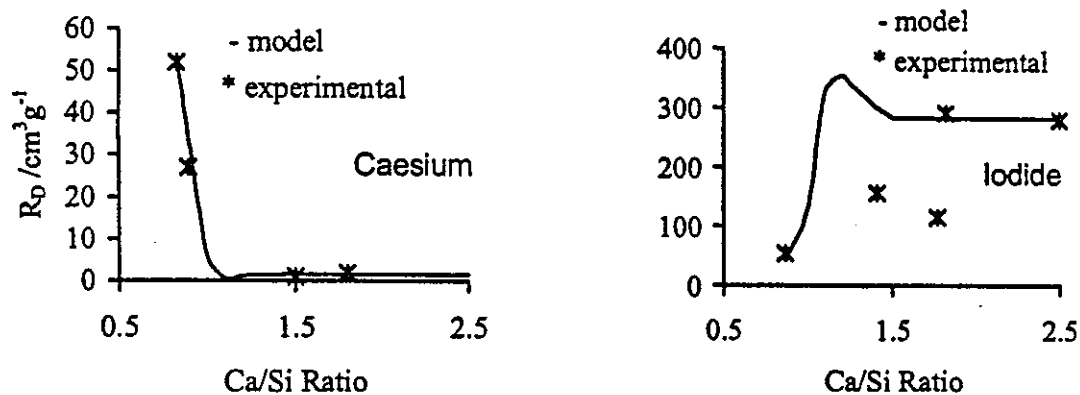
Figure 1   Sorption of caesium and iodide as a function of Ca/Si ratio

This work has been reported in more detail in reference [viii]. The model has been used to support the sorption data used in assessment calculations.

DATA SHEET QUESTIONNAIRE FOR CONTRIBUTIONS TO SESSION 4

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- **Solid phase**
  - Nirex Reference Vault Backfill (NRVB, a cementitious backfill), Calcium silicate hydrate phases (CSH)
  - Calcium hydroxide, CSH, calcite

- **Aqueous phase**
  - NRVB-equilibrated deionised water, NRVB-equilibrated saline water
  - radionuclides: Cs, I, Ni, Sn, Tc, Nb, Th, U, Np, Pu, Am

- **Brief description of model**
  - Diffuse double-layer model (DDLM): incorporating >SiOH and >CaOH sorption sites. The proportion of these sites is dependent on the Ca/Si ratio of the solid.
  - Parameters:
      obtained by fitting experimental data: site density, equilibrium constants for sorption equilibria
      estimated: specific area of solids
  - Thermodynamic data used: HATCHES database
  - HARPHRQ

- **Publications**

T.G. Heath, D.J. Ilett and C.J. Tweed, *Thermodynamic Modelling of the Sorption of Radioelements onto Cementitious Materials*, in Scientific Basis for Nuclear Waste Management XIX, ed. D.A. Knecht and W.M. Murphy, Mat. Res. Soc. Symp. Proc. **412**, pp443-449, 1996.

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• Solid phase

| Bentonite: | Kunipia-F, Japan | 99 % smectite, traces of quartz and calcite, 0.071 % NaCl, 0.005 % KCl, 0.694 % CaSO4. |

Bentonite: Kunipia-F, Japan   99 % smectite, traces of quartz and calcite,
                                        0.071 % NaCl, 0.005 % KCl, 0.694 % CaSO4.

                Kunigel-V1, Japan   46-49 % smectite, 29-38 % quartz, 2.1-6.6 % calcite,
                                        0.5-0.7 % pyrite, traces of other minerals (not considered),
                                        0.001 % NaCl, 0.004 % Kcl, 0.38 % CaSO4.

                MX-80, Wyoming (USA)   88.6 % smectite, 10 % quartz, 1.4 % calcite,
                                        0.007 % NaCl, 0.34 % CaSO4.

Pure montmorillonites

• Aqueous phase

Solution composition: conditions

1. The solution composition is always calculated as a function of the solid/water ratio, and the composition of the input solution, assuming equilibrium.
2. The amount of impurities in bentonite available for dissolution may be varied.
3. Calculations are performed in the present case for 25¡ C and batch systems (other temperatures can be handled, and flow-through systems can be simulated).
4. For the present presentation, only oxic systems are considered, but redox equilibria may be handled through the model used.

Radionuclides:

For the solid phase considered here (bentonite), data on Cs, Ra, Sr, Pb, as well as major electrolyte cations are available (for e. g. simple oxides, data on a number of other elements are available)

• Brief description of model

Surface components, surface species

Ion exchange sites (permanent charge sites) at the siloxane surface of clays.
Surface site: ZD, surface species: e. g. NaZ, CaZ2.
Surface complexation sites at the "edge surface" of clays.
Surface site: SOH, surface species: e. g. SOPb+, (SO)2Pb.

Parameters:

Most ion exchange and the SOH-site hydrolysis data are evaluated from measurements, other ion exchange and surface complexation data are taken from the open literature. Bentonite characteristics (composition, surface site density) are measured for some bentonites (e. g. MX-80), but need to be partly estimated in some cases.

Thermodynamic data used

For aqueous-phase thermodynamic data, the database used in connection with MIN_SURF (see below) is usually relied upon. This database includes the contents of the Nagra TDB (Pearson and Berner, 1991; Pearson, Berner and Hummel, 1992) but contains also additional species which were part of earlier versions of MINEQL. These additional species have been partly revised and listed by Pearson, Berner and Hummel (1992).

Codes

MIN_SURF (Berner, 1993) is a surface and solution chemical speciation code based on MINEQL/PSI and DSURF (Dzombak and Morel, 1990). MIN_SURF uses the diffuse double layer model to calculate surface complexation reactions in the solid surface/water interface, the formalisms used to calculate double layer characteristics are based on Hunter (1981) and de Levie (1990). The code MINEQL/PSI corresponds to the code MINEQL/EIR, made available for the NEA data bank in 1986 (OECD/NEA, 1986).

The BMG-version of MIN_SURF includes the possibility to model ion exchange reactions, using either the mole fraction or equivalent fraction approach to calculate the activity of the exchanger species.

- **Publications**

  The basic surface chemical model for bentonite is published by Wanner et al., 1994 (Radiochim. Acta 66/67, 157-162), the ion exchange model developed for Cs by Wanner et al., 1996 (Fresenius J. Anal. Chem. 354, 763-769). Publications regarding the application to Kd values of Ra, Sr and Pb are in preparation, as well as a publication on the integration of an ion exchange and mechanistic diffusion model for Cs.

- **Lessons learned**

  Kd values determined in batch and diffusion experiments can be explained and predicted by the above model. In particular for compacted bentonite, the most critical uncertainties are more related to the (lack of) characterisation of the solid phase (soluble impurities) and experimental conditions, rather than the actual model parameters.

- ## Abstract

Sorption of Sr/Ra, Cs and Pb on bentonite: ion exchange and surface complexation modelling

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The disposal strategies for high-level radioactive waste of many countries envisage the use of compacted bentonite as backfill material. The bentonite backfill is probably the most effective and predictable barrier on the entire migration path. High priority is therefore given to the thorough understanding of the processes, in particular sorption, affecting radionuclide transport in compacted bentonite. Sorption of radionuclides is quantified through distribution coefficients (Kd values) that may be used directly in performance assessment calculations. Thermodynamic ('mechanistic') sorption models are very effective tools for supporting and facilitating the selection of Kd values. Calculations carried out with such models can be used to (1) evaluate the quality of experimental sorption data, and (2) predict Kd values for situations where no experimental data are available.

Here, the application of thermodynamic models to calculate Kd values for radionuclides on bentonite is discussed, using elements with different behaviour for illustration: Ra, Sr and Cs do not form important complexes in aqueous solution and interact with bentonite through ion exchange, while Pb forms complexes and solid phases with e. g. hydroxide and carbonate ions, and sorbs through surface complexation as well as ion exchange. Thus, the sorption behaviour of these elements in bentonite is described by simultaneously addressing their solution/solid speciation and ion exchange/surface complexation reactions. At the same time, the model is used to calculate the solution composition and bentonite surface speciation as a function of the solid/water ratio, based on the bentonite model developed by [1]. Activities of dissolved species are calculated using the Davies-equation, activities of surface species are calculated through the mole-fraction approach for ion exchange and a diffuse double layer formalism for surface complexation reactions.

The model used is able to predict Kd's for the above elements reasonably well over a wide range of pH and ionic strength values and solid/water ratios. It becomes apparent that the major factor governing the distribution of Ra, Sr and Cs is the solution concentration of cations able to compete for the available ion exchange sites. This stresses the importance of the composition of the input solution and the amount of soluble impurities contained in the different bentonites. Solution pH is the dominating factor regarding sorption of Pb, which adsorbs onto bentonite both by ion exchange and surface complexation. Ion exchange takes place at the structural charge sites of smectite and dominates adsorption at pH values below 5, whereas at higher pH values surface complexation is more important. At high pH values, the precipitation of solid Pb-carbonate or -oxide has to be taken into account in order to explain the experimental data.

The model discussed here can be used to identify relevant sorption processes, as well as other factors that determine experimental Kd's, such as impurities contained in bentonite and artefacts (precipitation). Kd's can be modeled over a very wide range, indicating that such models may be used for predictive purposes.

- ## References:

[1] H. Wanner, Y. Albinsson, O. Karnland, E. Wieland, P. Wersin, and L. Charlet, Radiochim. Acta 66/67, 157-162, 1994

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• Solid phase

Identify: Silver Hill Montana illite
Source: Source Clay, USA.
Mineralogy: major components (Hower et al., 1966): SiO2 (55.1 %); Al2O3 (22 %);
             minor componenets: K2O (8 %), Fe2O3 (5.3 %), MgO (2.8 %).

This clay was further purified in our laboratory for removing carbonate and organic matter. Finally, the clay was transformed to sodium form before use.

• Aqueous phase

Solution composition:

sodium perchlorate (NaClO$_4$, 0.02~0.5 N);
3~7 days equilibrium; room temperature;
batch; oxic for sorption; anoxic for titration.

Radionuclide:

europium, Eu(NO$_3$)$_3$, 10^{-8} M.

• Brief description of model

Surface components, surface species

Illite surface is considered possessing two types of reactive sites which are responsible for sorption. They are (1) the permanently charged site arising from isomorphic substitution within the crystal lattice and (2) the variably charged surface functional groups due to the ionisation of the surface hydroxyl groups (S–OH) at the broken edges of the clay particles. The surface species considered in this study are: (1) Europium sorbed due to cation exchange (ill$_3$–Eu); (2) Europium surface species due to the surface complexation reaction (S–OEu^{2+}).

Parameters (measured, calculated, estimated)

1. BET surface area: measured;
2. total site density for the surface hydroxyl group: fitted (FITEQL) from the acid/base titration data;
3. Cation Exchange Capacity (CEC): measured by ^{22}Na$^+$ isotopic dilution and Cobaltihxmmine methods;
4. acidity constants of the surface hydroxyl group: fitted (FITEQL) from the acid/base titration data;
5. surface complexation constant: fitted (FITEQL) from the sorption data;
6. selectivity coefficient K_C for europium: measured;
7. selectivity coefficient K_C for proton: fitted from the sorption data.

Thermodynamic data used

EQ3/6 database (Lawrence Livermore National Laboratory, V8.R5, 1996).

Codes

1. FITEQL (Herbelin and Westall, 1996): for data optimisation;
2. CHESS (van der Lee, 1993): for sorption calculations.

- **Lessons learned**

1. Selectivity coefficients for cation exchange cannot be treated as thermodynamic constants. The value of selectivity coefficient is function of ionic strength. Due to the difficulty for defining the surface activity coefficient of cation exchange site, the selectivity coefficient has no intrinsic meaning. The selectivity coefficient for europium in this study is treated as a fitting parameter.
2. Difficulties for pH measurement is encountered concerning electrode calibration, back titration for compensating the effect of clay dissolution, influence of purification procedure on pH measurement, *etc.*

- **References**

Hower, J. and Mowatt, C. T. (1966): *The mineralogy of illites and mixed-layer illite/montmorillonites.* The American Mineralogist, Vol. 51, May–June, 825–854.

Herbelin, A. L., and Westall, J. C. (1996): *FITEQL – A Computer Program for Determination of Chemical Equilibrium Constants from Experimental Data.* Report 96–01. Department of Chemistry, Oregon State University.

Van der Lee, J. (1993): *CHESS – Another speciation & surface complexation computer code.* Technical report, HM/RD/93/39, Ecole des Mines de Paris, Centre d'Informatique Géologique, Laboratoire d'Hydrogéologie Mathématique, Fontainebleau, France.

• **Abstract**

Sorption of Europium onto illite: mechanistic interpretations

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Sorption of europium onto illite – one of the most abundant clay minerals present in Boom Clay (the candidate host rock for HLW disposal in Belgium) was studied. The batch sorption results are interpreted by a multi–site sorption model based on the surface complexation approach. Our sorption conceptual model is based on a fundamental hypothesis: clay mineral posses two types of reactive sites, *i.e.*, permanently charged cation exchange sites and pH dependent surface complexation sites. Further on, the mechanisms assumed are demonstrated by fitting the sorption data with the two mass action constants, *i.e.*, surface complexation constant $^{Eu}K_{int}$ and selectivity coefficient $^{Eu}K_C$. The surface site concentrations are quantified by cation exchange capacity (CEC) and titration measurements. The CEC of the illite is 71 µeq/g and the total site density of the surface hydroxyl group is 1.35 µeq/g. The key reactions between solutes/surface sites identified are: (1) europium exchange onto the illite surface; (2) proton exchange onto the illite surface; (3) proton association/dissociation of the surface hydroxyl groups; (4) surface complexation of europium with the surface hydroxyl groups. The titration and the sorption data are fitted with the FITEQL program using the diffuse layer model. The results indicate that the electrostatic term is necessary to obtain an acceptable fit. The *Kd* value measured on clay suspension in laboratory is always higher than that of measured under *in situ* condition on reconsolidated clay cores. The discrepancy may be due to the different accessible surface site densities encountered under the two conditions. The intrinsic and predictive features of the mechanistic approach can help to evaluate the uncertainty coming from empirical *Kd*'s for increasing the confidence in the performance assessment calculations. Moreover, the data obtained concerning the surface and solution speciation can be used by transport modeller to interpret the *in situ* migration experiments. The multi–site model used in this study was chosen mainly because of the success of the surface complexation modelling (SCM) on oxide/hydroxide system. Our objective is to extend the SCM to clay minerals and later to natural organic matter which are the main sinks for radionuclides in Boom Clay. It appears from this study that the multi–site model based on the surface complexation and ion exchange mechanisms can give a quantitative description of europium sorption onto illite.

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• Solid phase

bentonite SABENYL
KERAMO, Obrnice, Czech Republic

a) mineralogical composition: montmorillonite + nontronite 70%, quartz 7.9 %,
   muscovite +illite 6.9%, goethite 6.6%, feldspar 5% and anatase 4%,
b) chemical composition: SiO_2 41%, Fe_2O_3 12%, Al_2O_3 11%, CO_2 1.04%, TiO_2 3.5%,

• Aqueous phase

Solution composition and conditions

a) Synthetic granitic water (mol.l^{-1}): Na 2.3×10^{-3}, K 1.1×10^{-4}, Ca 3.6×10^{-4}, Mg 1.8×10^{-4}, Cl 2×10^{-3},
   SO_4 1.1×10^{-4}, CO_3 1.8×10^{-3}.
   pH = 8.2. Ionic strength = 0,1 ($NaNO_3$).
b) Equilibriation time ≥ 48 hours, room temperature, batch arrangement,
   oxic conditions.

Radionuclide

233U - starting concentration 6.67x10-7 mol.l^{-1} .

• Brief description of models

Three types of surface complexation models were used for the description of the equilibrium states of sorption of U(VI)-species and anions HCO_3^{1-} and CO_3^{2-}, namely Constant Capacitance Model (CCM), Diffuse (double) Layer Model (DLM) and the so-called Chemical Equilibrium Model (CEM, where Boltzman's factor equals one, i.e., the electrostatic surface charge is not considered). The behaviour of the system studied was described by the equations of protonation of surface group SO^{1-} (1) and (2), sorption of U(VI)-species (3) - (8) and sorption of carbonates (9) and (10) :

$$SO^{1-} + H^+ = SOH^0 \tag{1}$$
$$SOH^0 + H^+ = SOH_2^{1+} \tag{2}$$
$$SO^{1-} + UO_2^{2+} = SOUO_2^{1+} \tag{3}$$
$$SO^{1-} + UO_2OH^{1+} = SOUO_2OH^0 \tag{4}$$
$$SO^{1-} + UO_2CO_3 = SOUO_2CO_3^{1-} \tag{5}$$
$$SOH_2^{1+} + UO_2(CO_3)_2^{2-} = SOH_2UO_2(CO_3)_2^{1-} \tag{6}$$
$$SOH_2^{1+} + UO_2(CO_3)_3^{4-} = SOH_2UO_2(CO_3)_3^{3-} \tag{7}$$
$$SOH_2^{1+} + (UO_2)_2(OH)_3CO_3^{1-} = SOH_2(UO_2)_2(OH)_3CO_3^0 \tag{8}$$
$$SOH_2^{1+} + HCO_3^{1-} = SOH_2HCO_3^0 \tag{9}$$
$$SOH21+ + CO32- = SOH2CO31- \tag{10}$$
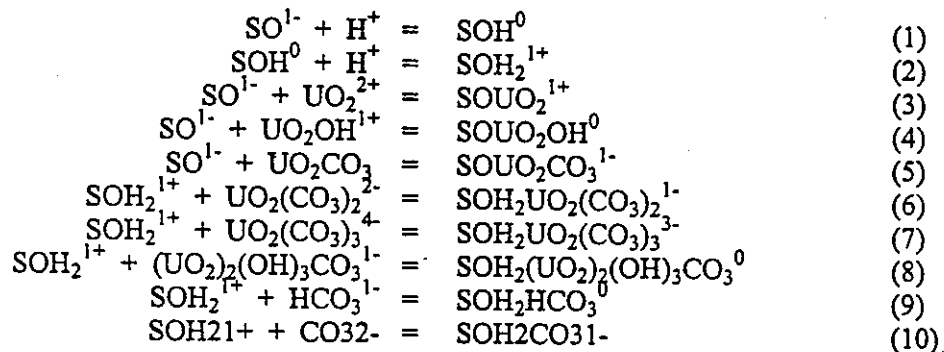
The experimental data, namely the titration curves of bentonite and the dependences of U(VI) and carbonates sorption on pH (approximately 3 - 9.5), were evaluated using our own computer codes (see

below), by means of which the following parameters were obtained: equilibrium constants of the reactions (1) - (10), site density ΣSOH and, in the case of CCM, Helmholtz capacitance G.

Bentonite powder was characterized by specific surface area (44.4 $m^2.g^{-1}$) using BET method, by total cation exchange capacity (0.88 $mval.g^{-1}$) and granulometric analyses (82.5% below 0.01 mm).

The stability constants taken from MINTEQ-A2 code were used to the calculation of the abundance of U(VI) species in the aqueous phase.

Four codes were constructed: P33 and P35 for the evaluation of titration curves of bentonite or similar materials, P34 for the evaluation of dependencies of carbonates sorption on pH and P38 for the evaluation of U(VI) sorption on pH. Code P38 makes it possible to choose suitable complexation reaction(s) and to calculate the corresponding equilibrium constant(s).

- **Publications**

- **Lessons learned**

  1. The calculated parameters corresponding to the individual models (CCM, DLM, CEM) depended to some extent on the type of model used and partly on the starting estimations of the values of parameters to be calculated, because non-linear regression method had to be used for the calculation.

  2. The time of calculation depended in some cases also on the starting estimations, especially if the experimental data for U(VI) = f(pH) were evaluated using the code P38.

  3. The sorption of $UO_2(CO_3)_2^{2-}$ has been found as the main reaction participating in the fixation of U(VI) on the bentonite surface in the pH interval studied. The following uranium species seem also to participate at the fixation: UO_2^{2+}, UO_2OH^+ and UO_2CO_3.

  4. The best fit of the experimental data was obtained when the reaction (8) was not considered, as seen from the lowest sum of square deviations of the experimental from calculated values. In this case, the ability of different models to describe the experimental pH dependence of sorption of uranium decreased in the order DLM $\geq$ CCM > CEM, but, the differences between the models in this respect were small.

- ## Abstract

Modelling of sorption of U(VI)-species, HCO31- and CO32- on bentonite using SCM

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We have been seeking parameters characterizing the interaction (sorption and desorption) of radionuclides with solid phase, suitable for description of migration of radionuclides in porous media. These parameters need not necessarily be the K_d factors, as K_d is not suitable parameter in the case of non-linear sorption isotherm (see attached text).

In this paper, modelling of uranium sorption on bentonite has been studied as the method of examining the mechanism of the sorption and obtaining the parameters sought.

The modelling has been based on the assumption that the sorption takes place on the „edge sites" of clay minerals in bentonite. These sites occur in three forms, SO^{1-}, SOH^0 and SOH_2^{1+}, whose proportion depends on the pH, ionic strength and two protonation reactions. The equilibrium constants of the reactions were determined from titration curves obtained with bentonite SABENYL and synthetic granitic water. In the same system, sorption of uranium(VI), HCO_3^{1-} and CO_3^{2-} was experimentally studied as a function of pH. The data set so obtained was examined using three types of surface complexation models, while the sorption was described by 6 tentative reactions for six U(VI) species and by two reactions for HCO_3^{1-} and CO_3^{2-} with the edge sites.

It has been found that the experimental data can be reasonably well described by all three models, differences among the models are rather small in this respect. $UO_2(CO_3)_2^{2-}$ seems to be the prevailing uranium form sorbed, sorption of UO_2^{2+}, UO_2OH^{1+} and UO_2CO_3 takes place to the less extent. The equilibrium constants for the sorption of these uranium forms were obtained, as well as those for the adsorption of HCO_3^{1-} and CO_3^{2-}.

See Data Sheet Questionnaire for more details.

• Note

Comments on the use of Kd coefficient for the modelling of radionuclide migration in porous media

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Most of the mathematical models of migration describe the interaction of radionuclides with solid phase by means of K_d. This approach is, however, strictly correct only if the sorption/desorption isotherm is linear ($q = K_d C$, where q is the equilibrium concentration of radionuclide in the solid phase and C is the equilibrium concentration in the liquid phase). Then K_d can be used for calculation of the retardation coefficient R using equation (1):

$$R = 1 + (\xi/\varepsilon)Kd \qquad (1)$$

where ξ denote bulk density and ε is porosity. (It holds: $(\xi/\varepsilon) = (\rho/\Theta)$, where ρ is the solid phase density of the host formation and Θ is the volume of circulating solution per volume of the host formation.)

The general equation for the retardation coefficient is derived by rearrangement of 1D equation of non-equilibrium dynamics of sorption/desorption (2) of radionuclides, under the assumption of equilibrium conditions, namely by means of the following procedure (equations (2) - (5)).

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2} - u\frac{\partial C}{\partial x} - \frac{\xi}{\varepsilon}\frac{\partial q}{\partial t} - \lambda\left(C + \frac{\xi}{\varepsilon}f(C)\right) \qquad (2)$$

Because the quantity q is the so-called composite function, which can be expressed as $q = f(C(t))$, its first derivative by t is given by the equation (3):

$$\frac{\partial q}{\partial t} = \frac{\partial q}{\partial C}\frac{\partial C}{\partial t} = f'(C)\frac{\partial C}{\partial t} \qquad (3)$$

If the migration takes place under the conditions of the equilibrium dynamics, then $f'(C)$ is the first derivative of the equilibrium isotherm function $q = f(C)$ and $\partial q/\partial t$ in the equation (2) can be substituted from the equation (3). After rearrangement, the equation (4) is obtained:

$$\frac{\partial C}{\partial t}\left(1 + \frac{\xi}{\varepsilon}f'(C)\right) = D\frac{\partial^2 C}{\partial x^2} - u\frac{\partial C}{\partial x} - \lambda\left(C + \frac{\xi}{\varepsilon}f(C)\right) \qquad (4)$$

The expression in parenthesis on the left-hand side of the equation (4) is usually designated as retardation coefficient (R) and it is evident, that it corresponds with the equation (1) on the assumption that $f'(C) = K_d$, i.e., if $q = K_d C$. By means of the last rearrangement, the well-known 1D-equation of equilibrium dynamics (5), including the equation (6), can be derived:

$$\frac{\partial C}{\partial t} = \frac{D}{R}\frac{\partial^2 C}{\partial x^2} - \frac{u}{R}\frac{\partial C}{\partial x} - \frac{\lambda}{R}\left(C + \frac{\xi}{\varepsilon}f(C)\right) \qquad (5)$$

$$R = 1 + (\xi/\varepsilon)f(C) \qquad (6)$$

The symbols used denote: D - dispersion coefficient (if u converges to zero, D converges approximately to the diffusion coefficient), u - flowrate of liquid phase through the pores, t - time, x - length parameter, λ - decay constant. Other symbols were explained above.

We see from it, that the retardation coefficient (see equation (6)) generally depends on the first derivative $f'(C)$ of the function of equilibrium isotherm $q=f(C)$. Therefore, the retardation coefficient is generally a function of concentration of radionuclide (or component studied) in liquid phase.

From the point of view of the application of K_d - model ($q=K_d C$, linear equilibrium isotherm) for the description of sorption/desorption in the migration process, it is necessary to look for systems, where the first derivative $f'(C)$ ($=dq/dC$) is constant, i.e., where $dq/dC = K_d$. Two such systems known from the theory of chromatography exist:

(i) the isotope exchange system, the equilibrium isotherm of which is in principle linear,
(ii) the system having the so-called favourable (concave) equilibrium isotherm, in the case of which - after certain time of migration, i.e., after the stabilization of the migrating sorption front - the retardation coefficient is the function of $(K_d)_o$ ($= q/C_o$, C_o is starting concentration in liquid phase) and R is constant.

However, if the system is characterized by the so-called unfavourable (convex) isotherm, the value of retardation coefficient is a function of concentration C and as a result, the migrating sorption front of the given component is washed away (i.e., extended in the axial direction). In such a case, strictly speaking, the first derivative of the function $q=f(C)$ must be used to the calculation of retardation coefficient (i.e., for each integration step in the course of solution of migration dynamic equation) and $f'(C)$ cannot be approximated by the value of K_d.

Contribution Number 4.19

(Leckie)

Contribution Number 4.20

(Ly)

- ## Abstract

Modelling of Radionuclides Sorption on Mixed Solids Using Single Oxides Surface Complexation Models

N. Marmier, Université de Reims Champagne Ardenne, France

In this work, surface complexation model was used to reproduce sorption behaviour of different solids surfaces, and to predict performance of their mixtures. Tested minerals were single oxides (alumina, silica, hematite), clays (kaolinite, montmorillonite), and zeolites. Using the methodology described as following, results of calculation were confirmed by experiments.

In a first step, modelling of alumina, silica and hematite was performed. Surface acidity and complexation constants, extracted from batches experiments, were used in a first prediction try of binary oxides mixtures behaviour. Then, the obtained calculated curves were compared to experimental one's for both acid-base titration and sorption experiments. The cations chosen for these sorption experiments were cesium (I), nickel (II) and ytterbium (III). If experimental and calculated curves were superimposed for alumina-hematite mixtures, results for alumina-silica one's have been overestimated. Then, a second modelling was performed, taken into account silica dissolution and binding of dissolved H_4SiO_4 on alumina surface. This new chemical description has been able to account or results of three different alumina-silica mixtures. Bindings of H_4SiO_4 on alumina was confirmed by independent experiments.

The second step of the study was based on the assumption that clay minerals surfaces may be described as "chemical" mixtures of alumina and silica, keeping the same surface constants. Using such simplification, modelling of clay surfaces is the same as the one used to describe alumina-silica mixtures. A first comparison of experiment and calculation was made with kaolinite. The results showed that the behaviour of this surface can be reproduced using the only two different types of surface sites present on alumina and silica. The second clay tested is montmorillonite. For the theoretic description of its surface, three different types of sites had to be used. if silanol and alumni sites are still present with the same constants fitted from oxides experiments, one ion-exchange site has to be added. The surface constants of this new type of site, not present on he previous tested surfaces, were fitted.

The methodology used, beginning with a very simple surface and going through more and more complicated ones, permits to have a minimum number of adjustable parameters. With the data set obtained in this way, and the above chemical description of the surface equilibria, behaviours of clays-oxides and clays-zeolite mixtures have been calculated without any adjustable parameters.

- **Abstrac2**

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- **Solid phase**

Kaolinite (KGa-1); Washington Co. Ga, USA

- **Aqueous Phase**

0.1M NaCl, 25-70C, batch, oxic, Cs, Sr, Cd, Ba, Zn, Oxalate, Acetate

- **Model**

FITEQL was used with both a constant capacitance and triple layer model to determine proton/hydroxyl adsorption stoichiometry and temperature dependent metal-binding (unidentate) constants.

- **Publications**

Brady, P. V., R. T. Cygan, and K. L. Nagy. 1996. Surface charge and metal sorption to kaolinite. in Metal Sorption to Earth Materials (ed. E. A. Jenne) Academic Press.

Brady P. V., R. T. Cygan and K. L. Nagy. 1996. Molecular Controls on Kaolinite Surface Charge. Journal of Colloid and Interface Science. (183) 356-364.

Brady P. V. (Editor) 1996. Physics and Chemistry of Mineral Surfaces. CRC Press 352p.

- **Lessons learned**

see abstract

- **Abstract**

Adsorption of metals and organic acids to kaolinite surfaces

Kaolinite surface charge can be described by proton donor and acceptor reactions occurring on edge Al sites, and by proton donor reactions occurring on edge Si sites. Edge Al sites are hypothesized to control pH-dependent sorption of metals, though there also appears to be minor pH-independent sorption of hard acids (Cs+ and Sr2+) on basal planes. Si site acidity at the kaolinite-solution interface differs minimally from that of pure SiO2, whereas Al sites became appreciably more acidic when a part of the kaolinite matrix. Increasing temperature decreases the pK values of Al and Si proton-exchange sites. Calculated site densities indicate either an elevated participation of edges (or substantial contribution from basal planes) in the development of surface charge. Independent evidence from scanning force microscopy points to a higher percentage of edge surface area due to thicker particles and basal surface steps than previously assumed.

Molecular modeling of the proton-relaxed kaolinite structure has been used to establish the elevated acidity of edge Al sites, to independently confirm the crystallochemical controls on surface acidity, and to establish likely bonding geometries for adsorbed organic acids, such as oxalate. Unidentate binding of metal ions on Al sites issuggested by constant capacitance model fits to measured metal sorption curves.

別添4 「Status Report Draft版」

STATUS REPORT

USING CHEMICAL THERMODYNAMIC MODELS FOR GUIDING RADIO ELEMENT K_d INVESTIGATIONS FOR PERFORMANCE ASSESSMENT

Dear Reader;

This document is obviously still very far from being completed - a result of a greatly delayed start date (mid-January) resulting from a combination of demands from my company to work urgently on other projects and lack of a contract from the OCDE to keep them at bay. Unfortunately, the relatively less complex period that I had intended to use to work full time on this document (first half of December, 1996) was lost; I have since been obliged to fit this in to very short, and highly interrupted, sessions while taking care of another full-time project. The result is what you see. The several pages at the end, as well as the missing figures and tables, will be finished this weekend, I hope. I am however not too pleased with its form and balance - lack of quiet time to go back over and focus it better.

This document is intended to be highly evolutionary; it will perhaps be quite unrecognizable after taking your comments, and the input gained during the meeting in Oxford, into account. There is most probably too much generality and I have purposefully left out specific examples since these are the realm of the 4 and 5 Chapters. Also, I am counting on Jordi BRUNO to blend in his comments and paragraphs, and eliminate many of mine.

As far as the use of the document for the Workshop is concerned, I think that we can have a clean and reviewed copy to present to participants at the meeting - the principal points should be those covered by the talks in Sessions 1 and 2. If you agree with the majority of what's presented, a "clean" version will be available for providing to prospective participants by the end of next week (14 March).

Scott Altman

[REPORT1.DOC = OCDE6.DOC]
[10/2/97]

1 ## FOREWARD

2 SEE PAGES 1 and 2 of Working Document prepared by Jordi BRUNO "The applicability of mechanistic (SCM)
3 models to radionuclide sorption in performance assessment"

4 ## INTRODUCTION

5 How to go about assuring the permanent, safe storage of radioactive wastes (radwaste) is a major preoccupation
6 for all countries exploiting the benefits of atomic energy. Many of these countries have undertaken extensive,
7 long-term research programs in order to obtain the massive amount of information and understanding needed to
8 select the most appropriate overall strategy for minimising, then "disposing", of an inevitable final quantity of
9 highly radioactive material. Disposal means confining radwaste elements in such a way as to insure that their flux
10 towards the biosphere always remains insignificant. For certain of the chemical elements (radioactive isotopes)
11 present in radwaste, thousands to millions of years will be required before they are rendered harmless through
12 decay to non-radioactive forms (stable isotopes). After considered rejection of various other potential solutions,
13 the present world-wide consensus is that radwaste should be stored in *specifically engineered facilities*
14 *(repositories) located deep underground in an appropriate geological formation.*

15 One of the principal types of information needed in judging the relative merits of different disposal facility
16 concepts is the estimated potential rate of migration of radio elements from the disposal structure, through the
17 surrounding geologic formations and into the biosphere. Rate of migration calculations, on the other hand, need to
18 know the degree to which radioisotope movement will be slowed due to chemical reactions with formation
19 minerals.

20 This report reviews the status of the use of chemical model-based approaches for measuring and predicting radio
21 element ground water / mineral distribution (i.e. K_d) in geological host formations for Performance Assessment
22 purposes.

23 ## 1 PERFORMANCE ASSESSMENT CONTEXT

24 ### Underground Storage and Performance Assessment

25 The underground storage concept is based on the use of two main confinement structures to isolate radwaste from
26 the biosphere after completion of waste disposal operations: the repository structure and the surrounding
27 geological host formation (figure 1). The repository includes (i) the radioactive waste itself, made up of known
28 quantities of specific radioactive elements (radioisotopes), and (ii) all of the specifically engineered structures
29 designed to isolate the waste from the biosphere: the waste matrix, canister, backfill materials, etc. The geological
30 host formation begins at the outer limit of repository structures and generally has a minimal thickness of several
31 hundred meters along any repository-biosphere axis. In many cases, other geological formations may also be
32 interposed between the host formation and the biosphere. The principal host formations under consideration at the
33 present time are: crystalline rock (United Kingdom, Canada, France, Switzerland, Sweden, ...), clay (France,
34 Japan, Belgium,...), tuff (USA), salt (Germany, USA,).

35 The principal way that waste radioisotopes might eventually be transported towards the biosphere is as dissolved
36 species present in water contained within the geological formation (arrow in Fig. 1). Research activities in the
37 fields of repository design and geological host formation selection are, to a large extent, driven by this main
38 preoccupation. Repository components are sought which will initially protect the radwaste from contact with
39 water for as long as possible (canister: steel, copper, titanium...), then insure that it has the lowest possible
40 solubility (waste form, vitrification matrix,...) and finally, retard the movement of any dissolved species away
41 from the canister and toward the surrounding geological formation (backfill materials: bentonite, concrete, etc.).
42 Promising host geological formations are those offering both long term geotechnical stability (seismic,

1   glaciation,...) and having properties ensuring the lowest possible water content and rate of water (and dissolved
2   RN) movement from the repository towards the biosphere.

FIGURE 1 : Schematic View of Underground Repository

(To be drawn, or left out)

3

4   The unbiased, scientific evaluation of the overall capacity of a particular disposal site concept (repository and
5   geological context) to safely and permanently confine radwaste is called Performance Assessment (PA). The
6   principal information sought during a PA study is the estimated probable radiation dose contributed by stored
7   wastes at suitably selected locations in the biosphere (e.g. Fig. 1), throughout the radwaste hazardous lifetime. The
8   dose, on the other hand, can be calculated only if it is possible to estimate the total amount of each radio element
9   present at these same locations as a function of time. Since, as noted above, radio element migration at most
10   disposal site locations is most likely to occur as dissolved species present in geological formation ground water,
11   PA must therefore be able to estimate the rate of movement of radio element mass (mass transfer) along potential
12   migration paths. Numerical models specifically designed for PA needs are used for carrying out these mass
13   transport calculations.

14   Mass transport involves movement through space of RN mass present in ground water, i.e. RN total dissolved
15   concentration. Mass movement can be caused by two main physical phenomena, convection-dispersion and
16   diffusion. Convection will generally predominate in host formations where ground water moves within fractures

1   (crystalline rock); diffusion will be the most important in fine-grained porous formations (clays). In addition,
2   calculation of mass transport through fractured rock will also need to take RN diffusion into the solid matrix of
3   fracture surface materials (i.e. matrix diffusion) into consideration.

4   **Distribution Constants and Retardation Factors**

5   For many radio elements, it is well known that various physical-chemical processes, e.g. sorption/desorption,
6   precipitation/dissolution, matrix diffusion, can lead to immobilisation of some fraction of the total amount of a
7   radio element present and consequent lowering of its dissolved concentration. Such processes will generally delay
8   the arrival of surface-reacting radio element mass at a given point in space relative to the arrival of non-reacting
9   element mass (conservative tracers). The delay for a given radio element is called its retardation factor, or R_f, and
10 nearly all PA models require this information in order to calculate radio element mass transfer. PA therefore needs
11 a means of correctly estimating the <u>distribution of the total amount of a radio element, present in a given migration
12 field volume, between immobile and dissolved forms</u>; this distribution has most frequently been expressed in the
13 form of the so-called Distribution Constant, or K_d.

14   *K_d and R_f defined*
15   In its most direct sense, a K_d value simply represents the results of an experimental measurement, in a closed
16   system containing a <u>known mass of a particular geological solid material</u> and a known volume of solution of a
17   given composition, of the partitioning of the total amount of a specific radio element between that associated
18   with the solid and that remaining in solution. Mathematically,

19
$$K_d = \frac{C_{solid}}{C_{soln}}\tag{1}$$

20   where C_{solid} is the total solid-associated RN concentration (e.g. in moles RN per kg solid) and C_{soln} is the total
21   solution phase RN concentration (e.g. moles RN / m^3 solution); K_d therefore has the units m^3/kg.

22   If an experimentally measured K_d value can be taken to represent the actual RN solid/solution partitioning which
23   would occur in a given region of the host geological formation, it can be used to estimate the corresponding
24   retardation factor, R_f, for RN mass transfer <u>relative to retarded solutes</u> (i.e. K_d = 0). For the simplest case of
25   convective flow through porous formations, R_f is generally estimated as:

26
$$R_f = 1 + K_d \frac{\rho}{\theta}\tag{2}$$

27   where ρ is the solid phase density of the host formation (in kg/m^3) and θ is the volume of circulating solution per
28   volume of formation (m^3/m^3); i.e. R_f is unitless.

29   Comparable proportional expressions exist for diffusion-dominated mass transport.

30 *Note: While we will continue to use the symbol, K_d, for representing the solid/solution distribution of a given*
31 *radio element, we prefer to switch immediately to use of the term Distribution <u>Coefficient</u> (instead of Constant).*
32 *This is because K_d for a given radio element and geological solid material can often vary significantly depending*
33 *on the chemical composition of the contacting ground water solution.*

34 Here we are specifically interested in the ways of measuring, representing and predicting the contribution of
35 <u>sorption</u> chemical reactions to a particular radio nuclide's K_d value, K_d(RN). We will use the term "sorption" to
36 encompass both <u>surface complexation</u> and <u>ion exchange</u> representations of reactions with solids (see Chapter
37 XX). We will not consider here other chemical processes (precipitation, co-precipitation, ion substitution, RN
38 oxidation-reduction on solids, etc.) which may contribute, or under certain circumstances even dominate, RN
39 immobilisation in migration field regions.

1 Existing K_d Data Bases

2 Historically, performance assessment has relied largely on databases of K_d values obtained either:

3 • directly, from measurements of radio nuclide solid/solution partitioning in "batch" reactors (i.e. closed,
4   completely mixed experimental systems containing: a known mass of a particular migration field solid
5   material, a known volume of solution of a more-or-less well-defined composition and a known total amount
6   of the radio nuclide).

7 • indirectly, from interpretation of changes in the rate of radio nuclide mass transfer, relative to a non-sorbing
8   tracer, in convection or diffusion experimental configurations.

9 While this extensive data gathering effort has provided us with much information regarding $K_d(RN)$ values in
10 solid-solution systems and has the merit of being based on a more-or-less direct procedure designed to provide the
11 single parameter required by many safety assessment models, it also has serious shortcomings which tend to
12 compromise its general applicability. The principal limitation of K_d determinations as generally practised is the
13 disparity between the often limited information reported (or measured) relative to a typical K_d measurement, and
14 the complexity of the physical-chemical processes governing the interaction of many dissolved species with
15 geological solid materials. This complexity is reflected in the fact that the solid/solution partitioning of many RN
16 is often observed to be highly dependent on the chemical composition of both the solid surface and the contacting
17 solution. It is also certainly at the root of the wide range in K_d values which can be found in K_d data bases (e.g.
18 NEA) for partitioning of certain RN onto apparently similar types of geologic materials.

19 For example, K_d values for radio element sorption onto geological materials can range over many orders of
20 magnitude depending on:

21 • the radio element itself (table 1, - K_d ranges for different RN in same solid + solution systems),

22 • the nature of the solid material (table 1 - K_d ranges for same RN on granite, clay,... at same ionic strength,
23   pH),

24 • the chemical composition of the solution phase (table 1 - $K_d(RN)$ for same solid = f(pH, ionic strength, ...)).

25 The principal difficulty in exploiting the information contained in K_d databases is, in fact, the lack of a unifying
26 conceptual framework for understanding, and exploiting to the maximum extent, existing and future K_d
27 information for a given radio element; simply compiling K_d values as a function of reported experimental
28 conditions seems to have reached its limit of utility for PA purposes.

29

30

TABLE 1		
Under construction (or possibly left out)		

1   Key PA Questions

2   The wide variability in $K_d(RN)$ values measured for similar types of geological materials (see ranges in table 1 for

3   granite, clay, etc.), coupled with K_d sensitivity to solution composition, implies that a <u>migration field specific</u>

4   approach for obtaining (or estimating) K_d values will generally be needed to provide answers to the two following

5   fundamental PA questions for each specific repository RN:

6   •   What is the most appropriate K_d (i.e. R_f) value to be used for the host formation migration field? Are different

7   K_d values needed for different migration field regions (K_d <u>spatial variability</u>) in order to account for known,

8   or predicted, variations in formation material characteristics or ground water composition?

9   •   Will the K_d value determined for a given migration field region remain valid over the entire radwaste hazard

10   time frame, or is it likely to change significantly over time (K_d <u>temporal variability</u>), most likely as a result of

11   changes in the composition of the circulating ground water?

12   The ability to supply PA with answers to these questions will depend on our ability to be able to:

13   •   identify the <u>key physical-chemical parameters</u> of a geological formation (key ground water and solid phase

14   constituents, surface to volume ratio,..) which are likely to influence the K_d values for RN from different

15   chemical families (alkaline, alkaline earth, transition and post-transition, rare earth,...).

16   •   properly <u>measure</u> the dependence of K_d values for selected RN on the various key parameters, over the range

17   of conditions known (or predicted) to exist in the migration field (ground water composition, changes in

18   surface mineralogy,...).

19   •   accurately <u>calculate</u> RN K_d values for unmeasured combinations of key parameters values (interpolation

20   within experimentally measured ranges), and provide reasonable <u>estimations</u> of K_d values for un-studied (or

21   un-study able) radio elements.

22   •   provide reasonable <u>predictions</u> of *in-situ* K_d values, i.e. appropriate for selecting the corresponding RN

23   retardation factors. This may require estimation of K_d values for key parameter values <u>outside</u> the

24   experimentally measured range (i.e. extrapolation) and an decisions as to how to properly "scale" K_d values

25   from laboratory to field parameter ranges.

26   An ability to estimate K_d values for potential, but unmeasured, migration field geochemical conditions, could be

27   quite important for PA for the following reasons:

28   •   Given the large dimensions of underground repository migration fields and the difficulties associated with

29   obtaining representative solid and ground water samples, only a relatively small number of samples

30   (compared to the migration field volume) are likely to be available for obtaining direct information on ground

31   water composition or solid phase sorption characteristics. It may be important to be able to predict K_d values

32   for geochemical compositions at migration field locations "intermediate" to those represented by sampling

33   points.

34   •   The long time frame which must be considered by PA, coupled with possible natural or repository-derived

35   perturbations, means that the present "natural" geochemical composition of migration field volumes may

36   change significantly at some time in the future. Here again, it may be important to be able to estimate K_d

37   values for the range of geochemical conditions predicted by various PA scenarios.

38   All of the foregoing will generally be very difficult to carry out unless we have:

1 • an understanding of the dominant processes governing RN sorption on migration field geologic materials, and

2 • an ability to predict the geochemical composition of migration field ground water and contacting surface
3   mineral phases.

1 ## 2 K_d IN MIGRATION FIELD GEOCHEMICAL SYSTEMS

2 ?????????? Opening sentences ??????????????????

3 ## 2.1 MIGRATION FIELD VOLUME ELEMENTS

4 The huge amount of space making up a repository's migration field must generally be divided into sub volumes
5 (see Figure 1) in order to allow PA models to take into consideration significant spatial variations in its physical
6 characteristics (e.g. formation transmissivity, permeability, fracturing) or chemical composition (ground water,
7 formation materials) which might affect RN mass transport. How this subdivision into what we will call
8 **Representative Volume Elements** (RVE) is carried out is of fundamental importance since all locations within
9 any given RVE are assumed to be described by <u>one set of physical and chemical properties</u>[1]. For PA purposes, this
10 means that only one K_d value is used for calculating a given radio element's R_f throughout the entire RVE volume.

11 *Near Field / Far Field*

12 A repository's migration field is typically described in terms of <u>near-field</u> and <u>far-field</u> regions. These two
13 regions will generally have significantly differing (i) physical-chemical properties, (ii) accessibility for
14 study (i.e. information availability) and (iii) in how strongly they will be affected physically and chemically
15 by the repository.

16 The *near-field* begins at the storage container and includes all artificial barriers and any portion of the surrounding
17 geologic formation significantly affected, either physically or chemically, by the repository. This region is likely to be
18 characterised by relatively dynamic, non-equilibrium geochemical processes driven by the temperature, concentration
19 and pressure gradients created by the repository. The initial chemical composition and physical structure (porosity,
20 fracture dimensions, solid surface area, etc.) of the near-field will generally be well understood as a result of high density
21 sampling and extensive experimental determinations. Potential changes in initial characteristics of near-field geologic
22 materials due to the presence of the repository are also likely to be predictable with reasonable confidence based on
23 experimental and numerical simulations. The near-field will also obviously be subject to the highest radio nuclide fluxes in
24 the event of container failure.

25 The *far-field*, on the other hand, includes all points in the surrounding geologic formation relatively unaffected,
26 geochemically and physically, by the repository. Relatively little data is likely to be available concerning the physical-
27 chemical characteristics of far-field regions. This limited information base is compensated somewhat by the probability
28 that the rate of change of solution and solid phase composition in the far-field will generally be much slower than in the
29 near-field due to the existence of near equilibrium conditions and much smaller physical and chemical gradients.

30 ### Physical Criteria

31 Physically speaking, and as far as soluble element migration is concerned, each RVE is an open system, i.e.
32 capable of exchanging matter with neighbouring RVEs (Figure XX), divided into two physical phases: *immobile*
33 *solid* and *continuous liquid*. The most important <u>physical characteristics</u> which should be taken into account when
34 determining RVE boundaries for K_d purposes are, on the other hand:

35 • the <u>total volume</u>, V_t (in m^3 ground water per m^3 RVE space), of the hydraulically continuous liquid phase,
36   i.e. all ground water potentially accessible to dissolved RN through convection (fractures) and/or diffusion
37   (porous matrices) processes, and

38 • the <u>total surface area</u>, A_t (in m^2 per m^3 RVE space), of the solid phase which is in contact with the liquid
39   phase volume, i.e. the wetted surface area, including both fracture and porous material surfaces.

---

[1] i.e. the RVE is physically and chemically isotropic.

1   In double porosity systems, i.e. fractures lined with porous solids, it is useful to distinguish <u>fracture</u> volume and

2   surface area (V_f, A_f) from <u>porous matrix</u> volume and surface area (V_m, A_m). V and A parameters can be

3   combined to describe an RVE in terms of corresponding surface to volume ratios: A_t/V_t, A_f/V_f, etc..(units: m^{-1}).

4   ## Chemical Composition Criteria

5   From a chemical point of view, the known influences of solid material and/or ground water composition on the K_d

6   values for many RNs means that known, or likely, significant differences in these migration field characteristics

7   should be taken into account when deciding on RVE boundaries. As far as sorption on RVE solids are concerned,

8   it is the mineral (and possible organic) phases in contact with the circulating ground water that are most important,

9   and it is well known that the chemical composition of the surfaces of geologic materials are generally quite

10   different from the underlying parent material due to weathering reactions and other diagenetic processes. The

11   result will be significant alteration of surface minerals and/or deposition of fine-grained, poorly crystalline, high

12   specific surface area solid phases, often in the form of inorganic and organic coatings on existing mineral grains.

13   This is illustrated by a description of Stripa fractures as having mineral coatings composed of chlorite > sericite >

14   calcite > epidote followed by lesser amounts of pyrite, chalcopyrite, fluorite, iron oxides, zinc sulphide and clay

15   minerals (Grimaud et al, 1990). The same observation holds for fractures in the Eye-Dashwa Lakes pluton

16   described by Kamineni et al (1983) as being "invariably filled, or coated, with mineral matter". The surface

17   chemical characteristics of many natural surfaces are therefore frequently dominated by secondary coatings which

18   may represent only a small fraction of <u>bulk</u> solid phase composition.

19   Consideration of ground water composition when defining RVEs is more difficult because of its potential

20   variability over time, particularly in the near field. Significant, and relatively stable, differences in composition in

21   the host formation far field, or other formations located along migration paths, should however be taken into

22   consideration. In any case, <u>an ability to predict significant changes in the composition of ground water entering</u>

23   <u>each RVE will be essential for predicting the corresponding potential effects on RN retardation factors.</u>

24   ## 2.2   SORPTION REACTIONS: KEY CONCEPTS, KEY PARAMETERS

25   ??????????? Opening sentences ????????????????????

26   ## Key Concepts

27   As mentioned previously, RN solid - solution partitioning sorption results from interactions with RVE solid phase

28   surfaces. Many of the features of these interactions, and the resulting RN K_d, can be understood and described in

29   terms of the same fundamental concepts governing reactions between dissolved species. The key concepts are:

30   •   Sorption involves physical-chemical interactions between a dissolved molecule (RN or other) and specific

31   molecular-scale structures, which we will call <u>sorption sites,</u> exposed at the solution-contacting surface of

32   an RVE solid material (mineral phase, organic macromolecule,...).

33   •   Sorption of a given RN can be described in terms of <u>chemical reactions</u> between specific RN molecular

34   forms (dissolved RN species) and a specific sorption site type to give particular sorbed species containing

35   both RN and the sorption site (see examples in table XX). Several sorption reactions may be responsible for

36   the overall sorption of a given RN onto a given site type (e.g. reactions for Ni^{2+} with FeO-, Sr^{2+} with X- in

37   table XX). A given sorption site can also react with other ground water dissolved molecules (H^+, Ca^{2+},

38   etc.) to give other sorbed species (e.g. table XX).

39   •   Sorption reactions are generally considered to be sufficiently rapid so as to reach <u>thermodynamic</u>

40   <u>equilibrium</u> within both experimental and migration field time frames (i.e. the local equilibrium assumption

41   holds for open systems). This means that sorption reactions can be described in terms of appropriate <u>Mass</u>

1   Action Laws (MAL) (i.e. relative reactant and product concentrations[2], stoichiometry, thermodynamic
2   formation constant - K). The value of K in a given MAL will be determined in part by the chemical
3   composition and structure of the sorption site's host solid phase. The sites present on an iron oxyhydroxide
4   are chemically distinct from those on a silica; the ion exchange sites located on the surface planes of clay
5   minerals are different from the oxyhydroxide-type sites exposed on the plate edges. In addition, different
6   crystalline forms of the same mineral family have different surface site characteristics (e.g. amorphous iron
7   oxyhydroxide, goethite, hematite).

8   Differences in K values for otherwise identical sorption reaction LAMs are the only means of
9   thermodynamically distinguishing one sorption site type from another.

10   •   There is a fixed total quantity of each sorption site type in a given RVE. The sum of the quantities of the
11   different possible chemical forms (sorbed species, free site) for a given site type is limited by the site total
12   quantity; this is the Mass Balance constraint. In general, we can expect that the site total quantity will
13   depend on the surface area of the solid phase accessible to dissolved molecules and on the surface density of
14   each site (number of sites per unit area).

15   While modifications must be made to certain of these basic concepts to take into account the fact that sorption
16   sites are not free to move about in space as are dissolved species (see Section XX), the fact that sorption reactions
17   can be understood and described in terms of Mass Action laws and Mass Balances is very important as far as the
18   determination and exploitation of K_d values for PA purposes is concerned. The principal advantage is that
19   information concerning the chemical characteristics of RN sorption onto RVE solid phases can be directly and
20   seamlessly incorporated into the same *Chemical Thermodynamics Model (CTM)* framework used for describing
21   and predicting RVE ground water and solid phase geochemistry and radio nuclide solution speciation and
22   precipitation-dissolution. This promises that a single CTM model may eventually be used to predict variations in
23   RN K_d values for differing RVE ground water and solid surface composition.

24

Reaction Type	Example Surface Reaction	Typical Minerals
Acid - Base	1) $S{\equiv}H \Leftrightarrow S{\equiv}^- + H^+$ 2) $S{\equiv}H + H^+ \Leftrightarrow S{\equiv}H_2^+$	Metal oxides, oxyhydroxides (e.g. Fe (ferrihydrite, goethite); Al (α,γ-alumina); Si (amorphous silica, quartz); Ti (rutile); Mn (δ-MnO$_2$) Clay (phyllosilicate) mineral "edge" sites
Complexation	3) $S{\equiv}^- + Ni^{++} \Leftrightarrow S{\equiv}Ni^+$ 4) $S{\equiv}^- + NiOH^+ \Leftrightarrow S{\equiv}NiOH$ 5) $S{\equiv}^- + UO_2^{++} \Leftrightarrow S{\equiv}UO_2^+$ 6) $S{\equiv}H_2^+ + SeO_4^- \Leftrightarrow S{\equiv}H_2SeO_4^-$	Organic substances (e.g. humic and fulvic compounds, polysaccharides, bacterial exopolymers)
Ion Exchange	7) $X{\equiv}^-{\cdot\cdot}Na^+ + Cs^+ \Leftrightarrow X{\equiv}^-{\cdot\cdot}Cs^+ + Na^+$ 8) $2X{\equiv}^-{\cdot\cdot}Na^+ + Sr^{++} \Leftrightarrow (X{\equiv})_2^{--}{\cdot\cdot}Sr^{++} + 2Na^+$ 9) $(X{\equiv}^-)_2{\cdot\cdot}Ca^{++} + Sr^{++} \Leftrightarrow (X{\equiv}^-)_2{\cdot\cdot}Sr^{++} + Ca^{++}$	Clay (phyllosilicate) minerals permanent charge sites (e.g. kaolinite, smectite, illite, bentonite)

---

[2] Actually, activity.

1   CTM Key Parameters

2   Many of the essential features of a CTM of K_d dependence on RVE physical and chemical characteristics can be

3   illustrated by the following simple demonstration based on an RVE with given A_t and V_t characteristics and

4   containing only the following three chemical "reactants":

5   •   a particular **radio nuclide** RN, (e.g. Cs, Sr, U, Pu). The total amount of RN in the RVE at a particular time,

6   expressed in mass or in moles (here we will use <u>moles</u>), can be divided by V_t to give the <u>total RN</u>

7   <u>concentration,</u> C_{RN}. We will also assume that RN has only <u>one dissolved species</u> (e.g. Cs^+, Sr^{2+}, UO_2^{2+},...);

8   the dissolved species concentration, in moles/m^3, will be denoted [RN].

9   •   a single type of "**sorption site**", S≡, located on the surface of a single RVE solid phase; i.e. there is only one

10   type of reacting group (e.g. ion exchange site, surface complexation site, etc.). We will also consider that

11   there is a constant amount of S≡ per unit of RVE surface area, i.e. a surface site density, $D_{S\equiv}$ (in moles/m^2).

12   The total amount of S≡ is therefore $A_t*D_{S\equiv}$, which we can express in terms of an equivalent total

13   concentration, $C_{S\equiv}$ (in moles S≡ / m^3 ground water), by dividing by V_t: i.e. $C_{\equiv S} = D_{\equiv S} \cdot (A_t/V_t)$. The solution

14   volume normalised concentrations of sorbed species (see below) will also be denoted by [ ].

15   •   a single **major ion**, M, (e.g. Ca^{2+}, H^+,...) which is naturally present in the ground water and is also able to

16   react with S≡, i.e. to "compete" with RN for sorption on surface sites. M will have its own total and dissolved

17   concentrations, C_M and [M] respectively.

18   We will further assume that the only reactions which can take place in the RVE are RN and M sorption onto S≡

19   with the following stoichiometries and corresponding <u>thermodynamic formation constants</u>:

20

21   ≡S + RN ⇔ ≡S-RN K_{RN} (3)

22   ≡S + M ⇔ ≡S-M K_M (4)

23   The respective K values are proportional to the strength, or intensity, of the chemical bond between ≡S and RN or

24   M. In addition, we will also assume for demonstration purposes that there are virtually no sites in the "free", ≡S,

25   state, i.e. all sites are either as ≡S-RN or ≡S-M. Under these conditions, RN sorption can be described by the

26   following exchange reaction, the only one we will consider to be possible in the RVE:

27

28             $$RN + \equiv S - M \Leftrightarrow \equiv S - RN + M \tag{5}$$

29   The <u>mass (mole) balance</u> for S≡ species will therefore be:

30

31             $$C_{S\equiv} = [S \equiv M] + [S \equiv RN] \tag{6}$$

32   Assuming that <u>thermodynamic equilibrium</u> is reached in the RVE, the concentrations[3] of all four species can be

33   described by the following <u>Mass Action Law</u>:

34

---

[3] Activity corrections are not considered for this example.

$$K_{ex} = \frac{K_{RN}}{K_M} = \frac{[S \equiv RN][M]}{[S \equiv M][RN]}$$

(7)

where K_{ex} is the thermodynamic <u>constant</u> describing RN exchange for M on the sorption site. If we further assume that the concentration of the major ion M in the RVE ground water remains constant and is unaffected by changes in [RN], [M] can be combined with K_{ex} in equation (5) to give a combined <u>conditional</u> constant, k = $K_{ex}[M]^{-1}$. Equation (5) can then be combined with equation (4) and rearranged into a form more useful for demonstrating the way various parameters can affect [S≡RN], and therefore K_d(RN):

$$[S \equiv RN] = \frac{k[RN]C_{S\equiv}}{1 + k[RN]}$$

(8)

The variation in RN sorption, log[S≡RN], and RN solid-solution ratio, [S≡RN]/[RN], predicted by equation (6) are shown in Figures XXa and b respectively, which can each be subdivided into three main regions (from left to right):

- one where log[S≡RN] increases linearly, and [S≡RN]/[RN] remains constant as a function of log[total RN]. This behaviour corresponds to conditions where the concentration of sorbed RN, [S≡RN], is small with regard to the total sorption site concentration, $C_{S\equiv}$. Under these conditions, equation (6) simplifies to the following linear equation:

$$[S \equiv RN] = k[RN]C_{S\equiv}$$

(9)

- an intermediate transition region where Δlog[S≡RN]/Δ(log[RN] and [S≡RN]/[RN] decrease rapidly due to progressive saturation of sorption sites by RN.

- one where log[S≡RN] remains constant at some maximum value and [S≡RN]/[RN] is effectively zero. This region is described by:

$$[S \equiv RN] = C_{S\equiv}$$

(10)

We will focus here largely on first region-type behaviour since it is the most likely for the trace RN amounts which will be present in virtually all migration field RVE. It is, however, worth noting that saturation-type behaviour might take place under conditions where $C_{S\equiv}$ for a particular site type is very small (case of highly specific sorption sites for Cs^+ on illitic clays).

Equation (9) shows that [S≡RN]/ [RN] will be determined by the values of the various parameters making up k and $C_{S\equiv}$, i.e. :

$$\frac{[S \equiv RN]}{[RN]} = K_{RN} \cdot \frac{1}{K_M \cdot [M]} \cdot D_{S\equiv} \cdot A_t$$

(11)
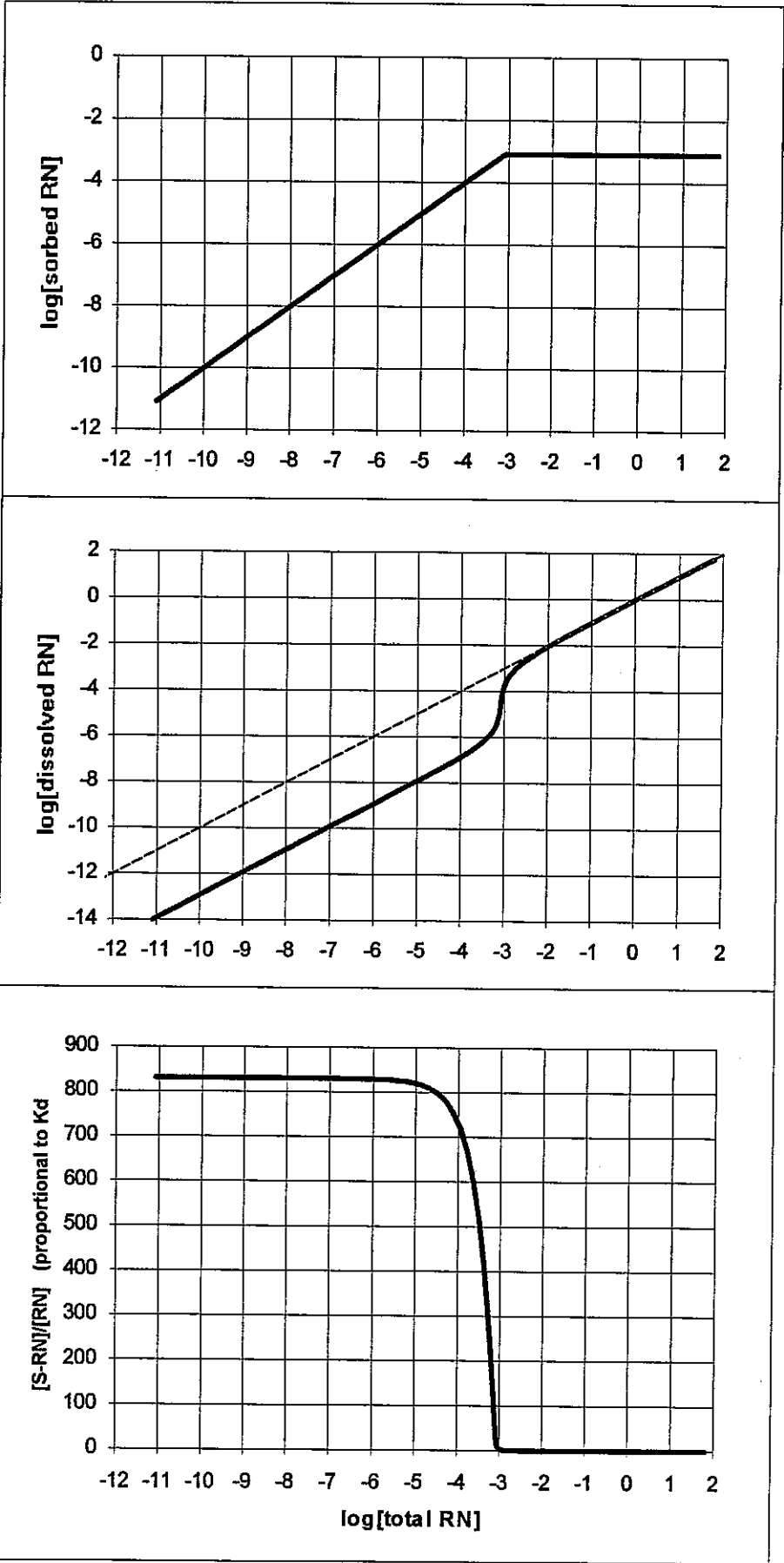
1   Equation (11) is useful in that it allows us to examine individually the different chemical and physical parameters
2   which can affect [S≡RN]/{RN}, i.e. K_d[4].

---

[4] Remember that $K_d(RN)$, on a surface area normalized basis, is simply:

$$K_d(RN)_A = \frac{[S \equiv RN]}{\{RN\}} * \frac{V_t}{A_t}$$

1   In particular, equation (11) shows that RN solid-solution partitioning will depend on:

2   • the intrinsic physical-chemical properties of the <u>solid phase sorption sites</u>, as represented by their
3   contribution to the value of K_{RN} (and to K_M); RVE solid phases having sites forming stronger bonds with
4   RN, i.e. higher K_{RN} (actually higher K_{RN}/K_M ratio) will have a higher $K_d(RN)$ value.

5   • the physical-chemical properties of the <u>RN molecule</u>, also as represented by their contribution to sorption
6   bond strength (i.e. K_{RN}).

7   • the physical-chemical properties and concentration of the <u>competing molecule</u>, M (K_M, [M]); RN K_d will
8   decrease with increasing S≡M bond strength (actually decreasing K_{RN}/K_M ratio) or M concentration.

9   • the <u>molecular structure</u> and <u>functional group composition</u> of the solid phase surface, as represented by the
10   sorption site density parameter, $D_{S\equiv}$.

11   • the <u>geometry</u> of the solid-solution interface, as represented by the wetted surface area, A_t.

12   One of the most important consequences of the foregoing is that the concentration of radio nuclide surface
13   species, i.e. $K_d(RN)$, will depend on <u>all reactions</u> in the system which can affect the concentration of (i) the
14   dissolved RN molecule (e.g. UO_2^{++}, Cs^+) and (ii) the sorption sites. The reactions which can take place will in
15   turn be determined by the <u>composition</u> of the system, i.e. total concentrations of all dissolved and sorption site
16   molecules. Since any given sorption site type has a fixed total concentration, any change in system composition
17   which increases the fraction of one sorption species must decrease the fraction available for all other sorption
18   species. For example, in the case of reactions 3-5 (table XX) any decrease in pH (i.e. increase in H^+
19   concentration) will increase the concentration of the S≡H, $S≡H_2^+$ species and reduce the concentration of the S
20   ≡⁻ species (reactions 1), resulting in a reduced concentration of RN surface species (e.g. $SO-UO_2^+$). The same
21   would be true for any of the ion exchange reactions (reactions 7-9, table XX), where any increase in the
22   concentration of the Na^+ or Ca^{2+} ions would reduce the amount of solid-associated Cs^+ or Sr^{2+}.

23

24   ## 2.3 ION EXCHANGE AND SURFACE COMPLEXATION: Variations on a CTM
25   ## Theme

26   While sorption reactions possess many features in common with reactions between dissolved species, there is one
27   major difference which must be taken into consideration when interpreting sorption data in terms of sorption
28   MAL: sorption sites are <u>physically immobilised</u> on the solid surface. This, coupled with the fact that sorption sites
29   are, or can become, <u>electrically charged</u> (re. Figure XX), means that solid surfaces can develop a <u>field of</u>
30   <u>electrostatic potential</u>. This field can influence the sorption of charged solution species, i.e. cations and anions, by
31   either promoting (negative surface - cation, positive surface - anion) or inhibiting (positive surface -cation,
32   negative surface - anion) sorption.

33   The effect of surface electrostatic potential on ion sorption can be understood by considering the overall free
34   energy of formation of a sorbed species, ΔG_{tot} (which is proportional to the formation constant K^5), as being the
35   sum of a constant <u>sorbed molecule-specific</u> free energy, ΔG^o_{mol}, determined by the site and dissolved species
36   molecular characteristics, and a free energy contribution due to the <u>electrostatic potential</u> field of the solid surface,
37   ΔG^o_{elec}.

---

5 $\Delta G^o = -RT \ln K$, where R and T are constants.

1

2
$$\Delta G^{o}{}_{tot} = \Delta G^{o}{}_{mol} + \Delta G^{o}{}_{elec} \tag{12}$$

3   The value, and above all, the variability, of $\Delta G^{o}{}_{elec}$ will depend only on the value, and variability, of the overall
4   net charge developed by all of the sites making up a surface, on the charge of a particular sorbing solution species
5   and on its distance from the surface once sorbed.

6   It is important to note that permanent charge surfaces will have a permanent but constant electrostatic field and,
7   therefore, a constant $\Delta G^{o}{}_{elec}$ term. This constant term can therefore be combined with $\Delta G^{o}{}_{mol}$ to give a $\Delta G^{o}{}_{tot}$
8   which will depend only on sorption site and sorbing molecule physical-chemical characteristics.

9   Natural mineral surfaces can be grouped into two broad classes based on the above considerations:

10   • Constant Charge (Potential) Surfaces: These are surfaces whose net electrostatic charge remains constant for
11   all solution phase compositions (i.e. constant electrostatic potential also). The most common examples are
12   layered clay minerals, whose sorption sites are represented by structurally-fixed negative charge
13   localisations[6]. The resulting permanent excess negative charge developed by these *ion exchange sites* is
14   compensated by sorption of solution cations.

15   • Variable Charge (Potential) Surfaces: The net electrostatic charge of these mineral surfaces, best exemplified
16   by the metallic oxyhydroxide minerals (Goethite, Alumina, Silica,...), can vary significantly depending on the
17   concentration (activity) of one or more dissolved ions (i.e. variable electrostatic potential); the dissolved
18   ion(s) are therefore called the Potential Determining Ion(s) (PDI). The proton, H^{+}, is the PDI for
19   oxyhydroxide surfaces. The sorption sites of oxyhydroxides are actually chemical functional groups which
20   are capable of undergoing *complexation reactions* with dissolved ions.

21   Two main variations of CTM are generally used for interpreting RN solid - solution partitioning onto these two
22   types of mineral phases:

23   • **Ion exchange (IE) models** for constant potential solids,

24   • **Surface complexation (SC) models** for variable potential solids.

25   But before over viewing the distinguishing features of the MAL used by each type of model for describing RN
26   sorption, it is useful to reiterate the many points these two CTM models have in common:

27   • Thermodynamic equilibrium is assumed.

28   • Sorption reactions are described in terms of mass action laws, written in terms of dissolved species bulk
29   solution activities and sorption site species concentrations[7] (i.e. no activity coefficient); different sorption
30   sites are distinguished by differences in their MAL formation constant.

31   • Sorption is constrained by a mass balance on each sorption site; the total quantity of each site is proportional
32   to total solid mass (or surface area).

33   • Competition of non-RN dissolved species for sorption sites can be taken into consideration.

---

[6] resulting either from substitution of divalent cations for trivalent cations in the octahedral layer or of trivalent
    ions for Si(IV) in the tetrahedral layer

[7] This is correct if sorption sites are considered to have identical activity coefficients, ie. cancelling; it avoids the
    question of how to define the thermodynamic activity of sorption sites.

1 • The effect of RN dissolved speciation on sorption can be accounted for using conventional thermodynamic
2 databases.

3 In fact, as shown in the following paragraphs, the only significant difference between IE and SC models is that the
4 latter incorporate an additional term for each sorbing ion to account for variations in sorption, e.g. $K_d(RN)$,
5 resulting from changes in the solid's net electrostatic charge.

6 **Ion Exchange CTM**

7 While other formalisms are possible, sorption of cationic RN molecules, RN^{m+}, on permanent charge surfaces
8 can generally be represented in terms of replacement of the charge number "m" of a major monovalent cation (e.g.
9 Na^+, K^+) located on "m" sorption sites, $X\equiv$:

10

11
$$RN^{m+} + mX \equiv Na \Leftrightarrow mNa^+ + X_m \equiv RN \tag{13}$$

12 Note that "free" sorption sites, i.e. $X\equiv^-$, are not allowed to exist as chemical species, and sorbed species are always
13 electrically neutral. The corresponding mass action law is:

14

$$K_{RN/Na} = \frac{[X_m \equiv RN]\{Na^+\}^m}{[X \equiv Na]^m \{RN^{m+}\}}$$

15 (14)

16 where sorbed species are expressed in molar concentrations and dissolved ions in terms of bulk solution activities;
17 i.e. classical activity coefficient expressions (Davies, Debuy-Hüeckel) can be used for converting to dissolved
18 concentrations.

19 The mass balance for cation exchange sorption sites is constrained by the Cation Exchange Capacity (CEC),
20 which is simply the total number of moles of $X\equiv$ per mass of solid (i.e. moles/kg). If the species in equation 13 are
21 the only ones in the system, the mass balance will therefore be:

22

$$C_{X\equiv} = CEC \cdot \left(\frac{mass_t}{V_t}\right) = [X \equiv Na] + m[X_m \equiv RN]$$

23 (15)

24 Similar exchange reactions for Na^+ (or another major cation) can be written for all other major (and minor)
25 cations in the system (see examples below) needed in order to account for competitive effects on RN sorption, i.e.
26 $K_d(RN)$.

$$K_{Ca/Na} = \frac{[X_2 \equiv Ca]\{Na^+\}^2}{[X \equiv Na]^2 \{Ca^{2+}\}}$$

27 (16)

$$K_{K/Na} = \frac{[X \equiv K]\{Na^+\}}{[X \equiv Na]\{K^+\}}$$, etc.

28 (17)

29 The mass balance constraint will of course need to be modified to include the additional sorbed species. In
30 addition, for certain radio nuclides, it may be necessary to consider the existence of more than one ion exchange

1   sorption site type in order to account for variations in $K_d(RN)$ as a function of the amount of sorbed RN. This is

2   the case, for example, of Cs^+ sorption onto illite clays (see figure XX). Such differences may generally be

3   attributed to the existence of exchange site populations having geometrical, stereochemical and charge density

4   characteristics more or less favourable to sorption of ions with particular ionic radii or charge densities. Multiple

5   ion exchange site types implies that there will need to be a mass balance for each site type; i.e. that a global CEC

6   value will need to be separated into its component total concentrations for each site, $X1\equiv$, $X2\equiv$,...:

7

$$CEC \cdot \left(\frac{mass_t}{V_t} \right) = C_{X1\equiv} + C_{X2\equiv} + ...$$

8   (18)

9   with each site type having its own set of MAL.

10 **Surface Complexation *CTM***

11 The distinguishing feature of surface complexation CTM is, as mentioned previously, the possibility of

12 calculating the effect of variations in the electrostatic potential of variable charge surfaces on RN sorption, i.e.

13 $K_d(RN)$. These charge variations result from changes in the dissolved concentration (activity) of solid-specific

14 Potential Determining Ions (PDI). While we will focus here on hydrous metal oxide minerals (Fe, Ti, Si, Al

15 oxides; "edge sites" on aluminosilicates;...) for which the proton, H^+, is the PDI, other minerals (e.g. carbonates,

16 sulphides) also possess variable charge surfaces.

17 For hydrous metal oxide minerals, the principal charge-determining reactions involve protonation or de-

18 protonation of surface hydroxyl groups to give positively charged, neutral and negatively charged surface species.

19 These reactions are typically represented by the following acid-base equilibria:

20 $$\equiv SO - H_2^+ \Leftrightarrow \ \equiv SO - H + H^+$$
                                                                                                (19)

21 $$\equiv SO - H \Leftrightarrow \ \equiv SO^- + H^+$$
                                                                                                (20)

22 with corresponding MAL:

$$K_{a1} = \frac{[\equiv SO - H]\{H^+\}}{[\equiv SO - H_2^+]}$$

23   (21)

24

$$K_{a2} = \frac{[\equiv SO^-]\{H^+\}}{[\equiv SO - H]}$$

25   (22)

26 where [] indicate surface species <u>concentrations</u> and {} the "<u>bulk</u>" <u>solution activity</u> of H^+, i.e. that measured

27 sufficiently far from the surface so as to not be influenced by its potential field. The K subscripts indicate the first

28 and second "acidity" constants. The relative proportions of the surface species will therefore be determined by the

29 values of K_{a1} and K_{a2}, and the proton activity $\{H^+\}$, i.e. pH.

30 Hydrous metal oxides can obviously also adsorb RN and other dissolved species, examples of some of the

31 principal types of reactions being given in Figure XX. The implication of H^+ in surface speciation means that all

32 sorption reactions onto such surfaces will be pH-dependent. One of the most common examples is the pH

33 dependence of cation and anion sorption onto Fe hydrous oxide surfaces as shown respectively in Figure XXa

34 (Kinniburgh and Jackson, 1981) and Figure XXb (fig. 13a in Davis and Kent, 1990). Each curve represents the

1   change in the percentage of total ion adsorbed, for constant C_M, $C_{\equiv S}$ systems, as a function of pH. Cations

2   typically show a sharp increase in sorption with increasing pH and anions a decrease with increasing pH.

3   The net electrostatic charge density on the surface, σ (in Coulombs/m^2), will vary in direct proportion to the

4   relative concentrations of all charged surface species. For the simple case where only equations 21 and 22 hold,

5   charge will depend on $\equiv SO^-$ and $\equiv SOH_2^+$ concentrations as given by:

$$\sigma = (F / A_t) \cdot \left([\equiv SOH_2^+] - [\equiv SO^-] \right)$$

6   (23)

7   where F is the Faraday constant (96,485 Coulombs/mole). Equation 23 shows that σ will be positive for [$\equiv$

8   SOH_2^+] > [$\equiv SO^-$], null for [$\equiv SOH_2^+$] = [$\equiv SO^-$], negative for [$\equiv SOH_2^+$] < [$\equiv SO^-$]. The electrostatic potential of

9   the surface, Ψ_o (in Volts), will, in turn, vary in intensity as a function of σ.

10   The overall free energy of formation, ΔG^o_{tot} (equation 12), of each sorbed species (for example $\equiv SOH_2^+$, $\equiv$

11     $SOUO_2^{2+}$) will depend on how strongly the sorbing ion (e.g. H^+, UO_2^{2+}) is 'attracted' or 'repelled' by the

12   electrostatic field created by Ψ_o. This influence, represented by the ΔG^o_{elec} term in equation 12, will depend on

13   the ion's charge (number and sign) and vary as a function of Ψ_o; ΔG^o_{elec} can either promote adsorption (negative

14   surface plus cation, positive surface plus anion), inhibit adsorption (positive surface plus cation, negative surface

15   plus anion) or have no influence when the surface has no net charge. In addition, sorbed ions will be located at

16   different distances from the solid surface "Ψ_o plane" depending on their physical-chemical characteristics; this in

17   turn means that they will be subjected to different electrostatic field intensities, decreasing with distance from the

18   surface.

19   Surface Complexation CTM (denoted hereafter as SCM) allow the ΔG^o_{elec} term to be calculated for each sorbed

20   species and, therefore, can take into account the effect of varying surface charge on sorbed species K_d. In order to

21   do this, SCMs need to make a number of "extra-thermodynamic" assumptions concerning the "geometry" and

22   certain electrostatic properties of the solid-solution interface, in particular, how different types of sorbing ions are

23   positioned in the electrostatic field. Here again, there are variations on a theme, with various hypotheses as to how

24   different types of ions are positioned in the electrostatic field leading to different mathematical formulations of the

25   so-called Electrostatic Double Layer models (EDLM) of ΔG^o_{elec} dependency on system composition: Constant

26   Capacitance model, Diffuse Layer model, Triple Layer model, etc.[8].

27   ************************** Paragraph under construction ******************************

28   •   Various EDL formulations are expressions of theoretical hypotheses concerning "extra-thermodynamic",

29   aspects of the molecular structure of sorbed species. Reflect an evolving understanding, and probably ever

30   more accurate theoretical model, BUT arguments for the use of one over another require "extra

31   thermodynamic" experimental information (spectroscopic...), generally on extremely simple solids. And

32   even when use of one EDL over another is based only on chemical speciation (macroscopic) information,

33   data quality must be extremely high quality and, above all, the chemical and structural nature of the solid

34   surface unambiguous (pure solids only).

35   •   For the same observed K_d data (i.e. observed $K = \Delta G^o_{tot}$), different EDL give different intrinsic sorption

36   reaction K (ΔG^o_{mol}) values (because of different ΔG^o_{elec} correction terms)

---

[8] For more detail, the reader is referred to one of the many excellent reviews in the literature (e.g. Davis and Kent, 1990; Hayes et al., 1990; Dzombak and Morel, 1990)

1 • This has led to much **confusion, and mistrust,** by PA community.

2 • K_d information for real solid materials are, and always will be, be only of macroscopic nature. The solid
3 phases will generally be heterogeneous (and their chemical and physical characteristics less certain, i.e. the
4 number of sorption site types and their respective concentrations), resulting in increased variability
5 (uncertainty) in K_d measurements on a/pparently identical solid samples.

6 • NEVERTHELESS - the general physical phenomena responsible for variations in radio nuclide K_d
7 resulting from variations in surface charge <u>are real</u> and <u>could be important</u> under certain circumstances.

8 • Under these conditions, it would appear that, whenever possible, <u>the simplest EDL model</u> should be used
9 (i.e. the one with the fewest independent "electrostatic" parameters).

10 • The <u>Diffuse Layer model,</u> as described (and elaborated) by Dzombak and Morel (1990), appears at present
11 to be the best choice for situations where RVE surface composition and radio nuclide type justify
12 electrostatic treatment.

13 • In addition, it would also seem advantageous to the entire PA K_d data gathering and interpretation effort if
14 the <u>same EDL was used by all researchers.</u> This would permit accumulation of a common sorption data base
15 for variable charge geological materials which could be used by all.

16

17 ෯෯෯෯෯෯෯෯෯෯ FROM HERE ON DOWN ෯෯෯෯෯෯෯෯෯෯෯෯෯෯෯෯෯෯෯෯෯෯෯෯෯

18 ************************* IDEAS FOR PARAGRAPHS IN PROGRESS **********************

19 <u>**Simultaneous Consideration of IE and SC Sorption Reactions in CTM**</u>

20 •

21 •

22 **2.4 CTM COMPUTER CODES: Essential Tools**

23 • Only means of computing equilibrium speciation for RVE containing more than several species

24 • mass balance, MAL, SCM (DDLM or no electrostatic correction term)

25 • Various equally good computer codes

26 • Data interpretation tools: FITEQL

27 • Foundation = Thermodynamic Data Base for non-sorption reactions

28 **2.5 THERMODYNAMIC DATA BASE**

29 • Absolutely essential due to interdependence of sorption reactions and solution speciation of RN and other
30 RVE components

31 • Non-sorption Reactions - RN, geochemical : Solution speciation, RedOx, Precipitation/dissolution

32 • Data Quality and Internal Consistancy

1 • Recent Review : see NEA/NSC/DOC Sept 1996

2   3 USING CTM FOR K_d DETERMINATIONS: KEY CHALLENGES

3   Natural Solid Material Complexity vs. Experimentally Available Information

4 In general there is a substantial disparity between experimentally observable information and the actual chemical
5 complexity of natural materials, i.e. number of different minerals present, number of different sorption site types.

6 • physical characteristics of solid phase (in-situ and laboratory samples)

7   - surface structure

8   - "specific surface area

9   - porosity

10 • chemical composition of natural solid material sorbing phases, i.e. true surface phases

11   One of the most difficult problems in interpreting reactions between dissolved species and complex natural
12   solid surfaces is how to quantify the sorption site composition of natural solid surfaces, i.e. the number of
13   distinct sorption site types (identified by their reaction MAL) and their respective total concentrations. This
14   problem can be subdivided into the following sub-questions for experimental determination and/or "value
15   decision" by expert judgement or convention:

16   - determination of the specific surface area (m^2/kg) for the RVE solid material used for experimental
17   investigation and under experimental conditions.

18   Note: One of the principal questions which will need to be addressed when transporting lab K_d data to in-
19   situ RVE conditions is - *How to scale from laboratory specific surface area to in-situ wetted surface area*.

20   - identification of key mineral phases present at the RVE solid-solution *interface*.

21   - determination, or assigning, of the relative amount of each key mineral phase; most appropriately
22   expressed in terms of a fraction of the specific surface area.

23   - determination, or assigning, of a sorption site density (moles/m^2) to each mineral phase.

24   - the total sorption site quantity (moles/kg) resulting from the above can be further distributed, if necessary,
25   among two or more mineral-specific sorption site types to give their respective total site type quantities.

26   Experimental Uncertainty and CTM Model Choice

27 • Sorption model complexity (number of sorption site types, number of MAL) should be kept in line with data
28   uncertainty

29

30 • To EDL or Not to EDL (see above)

31   natural system experimental K_d = f(system composition) data uncertainty vs. model K_d calculated sensitivity
32   to EDL correction factor for range of RVE conditions.

33

1

2

3 **4 GENERAL CTM-BASED APPROACH TO K_d DETERMINATION**

4 **4.1 STARTING POINT**

5 • Site-specific approach

6 • What PA modelers want: an estimate (with associated uncertainty) of the overall solid/solution partitioning
7 (Kd), as a function of time, of each repository radio element in each of the volume elements defining potential
8 migration trajectories.

9 • Geochemical information (the essential starting point) likely to be available for a given migration field zone:

10 limited number of samples of solid phases and contacting solution,

11 correlated mineralogy composition of solid (surface) phases and chemical composition of solution phase
12 (values, variability)

13 A geochemical model (classical plus transport coupled) will also be needed for: (i) interpreting observed
14 major ion/mineral composition chemistry (present local equilibrium or non-equilibrium vis-à-vis appropriate
15 complexation / dissolution-precipitation / redox reactions), (ii) predicting evolution of dissolved and surface
16 mineral species over PA lifetime due to natural processes or storage site induced perturbations (pH, Eh, major
17 and minor ion composition of circulating water).

18 • This information provides the chemical context (values and variability of mineral/solution combinations) for
19 which corresponding solid/solution partitioning values (uncertainty) for each radio element must be provided.
20 The above step is critical since RN chemistry will generally (except in near-field in certain cases) be
21 dependent on the concentration and speciation of non radio element dissolved components and solid phases,
22 and not the contrary.

23 • The problem of system composition variability can be addressed experimentally and conceptually by dividing
24 the possible system compositions into those where:

25 - The chemical composition of solid surface phases (i.e. surface complexation site identity and concentrations)
26 does not change as a function of solution composition. This would be the case for solid surfaces containing
27 non-dissolving/non-precipitating metal oxides and clays, non-desorbing organic matter, etc. subjected to
28 changes in solution pH, exchanging cation, complexing ligands, etc. A special case exists when the
29 concentration of one or more dissolved species important in determining RN partitioning (directly or
30 indirectly) is fixed by precipitation/dissolution of a solid (or gas) phase (e.g. Mg^{2+}, Ca^{2+} by dolomite,
31 HCO_3^- by gas phase CO_2). In short, RN partitioning in such system will be dominated by "reversible"
32 reactions between dissolved and surface species, the surface site composition remaining constant.

33 The chemical composition of the surface phase (surface site identity and concentration) is modified by the
34 concentration of one or more dissolved species predicted to vary significantly by the geochemical model
35 (influx of non-equilibrated solution). This would be the case for import of any solution under- or over-
36 saturated with respect to an adsorption-active solid phase (or coating of an active with an inert phase), e.g.
37 reductive dissolution of an amorphous Fe oxide phase, dissolution of a calcite phase, precipitation of a
38 gypsum coating, etc. The evolution of the solid phase (surface site) composition of such systems must be
39 determined either by geochemical modeling or experimental simulation. The quantification and modeling of
40 RN partitioning must also take into consideration the three principal states of such systems: i.e. initial solid

1   phase composition (with associated range of equilibrium solution compositions), transitional compositions,
2   and final solid phase composition (with associated range of equilibrium solution compositions).

3   4.2 GENERAL PROCEDURE

4   Assuming that we have an invariant (i.e. constant surface site composition) complex natural solid and that we have
5   identified the probable range of equilibrated solution compositions for non-radio element components[9], a CTM
6   based we can imagine progressing as follows:

7   • Use existing information concerning the chemistry of the radio element to identify principal dissolved phase
8   reactions (hydrolysis, complexation, redox, etc.) and, thereby, a subset of system components which might
9   need to be taken into account experimentally and computationally. This information is either contained in the
10 Thermodynamic Data Base which is to be used.

11 • Use information concerning principal surface phases (mineral, and eventually organic), plus knowledge
12 concerning their surface complexation / ion exchange reaction characteristics, to identify additional
13 components which might need to be taken into account experimentally and computationally (H^+, competing
14 cations, adsorbing anions, etc.).

15 The above information, along with that concerning site solid and solution composition and variability, would
16 the be used to define an initial experimental matrix of system compositions (variable components, range of
17 total concentrations) and to assign a priority based on those parameters most likely to govern partitioning of a
18 given RN (or class of RN species - alkaline earth cations, hydrolyzable transition metal cations, anionic
19 species, REE, etc.).

20 • In appropriately controlled batch experiments, determine the solid/solution partitioning of the RN (or a
21 suitable analog ion) as a function of system composition (for several points covering the range over the
22 experience), starting with the highest priority component (e.g. total RN, pH, competing ion, solid/solution
23 ratio, complexing ligands, ...).

24 • Carry out a preliminary assessment of the data using a general CTM framework including (i) ion exchange
25 reactions (ii) SCM reactions (EDL or no).

26 Identification of critical K_d determining reactions, mechanisms?

27 When should an DDLM correction be used, is necessary?

28 Attempts to fit one or the other of these models (or simple combinations of both) to critical data sets (e.g. Kd
29 = f(total RN, pH, competing cation)), along with surface complexation modeling "intuition", should indicate
30 whether or not the major features of the observed RN partitioning response are likely to be "model-able" with
31 acceptable precision using with refined versions of one or the other (or both) of these type reactions.

32 Given the relative simplicity of the allowed surface reactions, complex natural solids will almost certainly
33 give "imperfect fits" during the above exercise. Certain features may be more-or-less well represented, while
34 others may not be. This initial confrontation of a preliminary data set and a preliminary CTM model is critical
35 since it helps to crystallize what we appear to know, and what we don't know, about the system. At this point
36 we must refine our hypotheses concerning the set of essential reactions (components, stoichiometries)
37 governing RN partitioning. Have we taken into consideration all important dissolved phase reactions (e.g.
38 additional complexants), are there other processes occuring (e.g. unaccounted for modification of dissolved
39 phase components by dissolution of a solid phase), is the solid phase site composition too heterogeneous to be
40 represented by a small number of site types, etc.?

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[9] Created in reality by solution flux through an open system containing the solid; modeled in a batch reactor by
titration of the solid with the various components until the desired solution composition is achieved.

1   If the postulated new reactions do not require additional experimental data, they can be tested by introducing
2   them into the model (e.g. inclusion of additional oxide or ion exchange sites with different equilibrium
3   constants). In other cases, additional data will need to be acquired.

4   Figure XX shows the principal phases of a CTM guided approach to determination of $K_d(RN)$ for a specific
5   repository.

6   **Experimental data and Computer-aided Interpretation**

7   The experimental strategy and data needed for interpreting solid/solution partitioning in natural systems in terms
8   of sorption reactions follow directly from the points raised in the previous sections. In essence, the analytical
9   protocol must provide information concerning i) the composition of the solid and solution phases being studied
10   (components present, total molar amounts) and ii) the mass action laws describing those surface reactions
11   affecting radio nuclide solid/solution partitioning (species involved, stoichiometries, stability constants).

12

13   •   **Progressive, iterative procedure**

14   •

15   •   **Uncertainties, decisions**

16   **************************

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REPOSITORY MIGRATION FIELD

| RVE1 | RVE2 | RVE3 | RVE4 | RVE5 |

REPRESENTATIVE SAMPLING
RVE solids // mobile solution

MEASUREMENT
Identification of
solid surface phases

MEASUREMENT
Ground water
composition

INFORMATION
RVE composition
perturbation scenarios

INFORMATION
Disposal site
radionuclide
inventory

GEOCHEMICAL MODELING
Solution species, mineral phases
(major elements // RN)

DECISION
Probable surface phases

DECISION
Probable reactions
sorption sites - dissolved molecules
(major components, RN)

DECISION
Critical parameters,
Experimental system composition

MEASUREMENT
RVE solid phase
compositional stability

DECISION
Experimental protocol

MEASUREMENT
Experimental data
Kd(RN) = f(system composition)

DECISION
Thermodynamic
database

INTERPRETATION
-Sorption reaction model type
- Sorbed site type, number
(identity, total concentrations)
- Sorbed species
(stoichiometry, K)

ESTIMATION
RN Retardation
Factor
= f(solution composition)
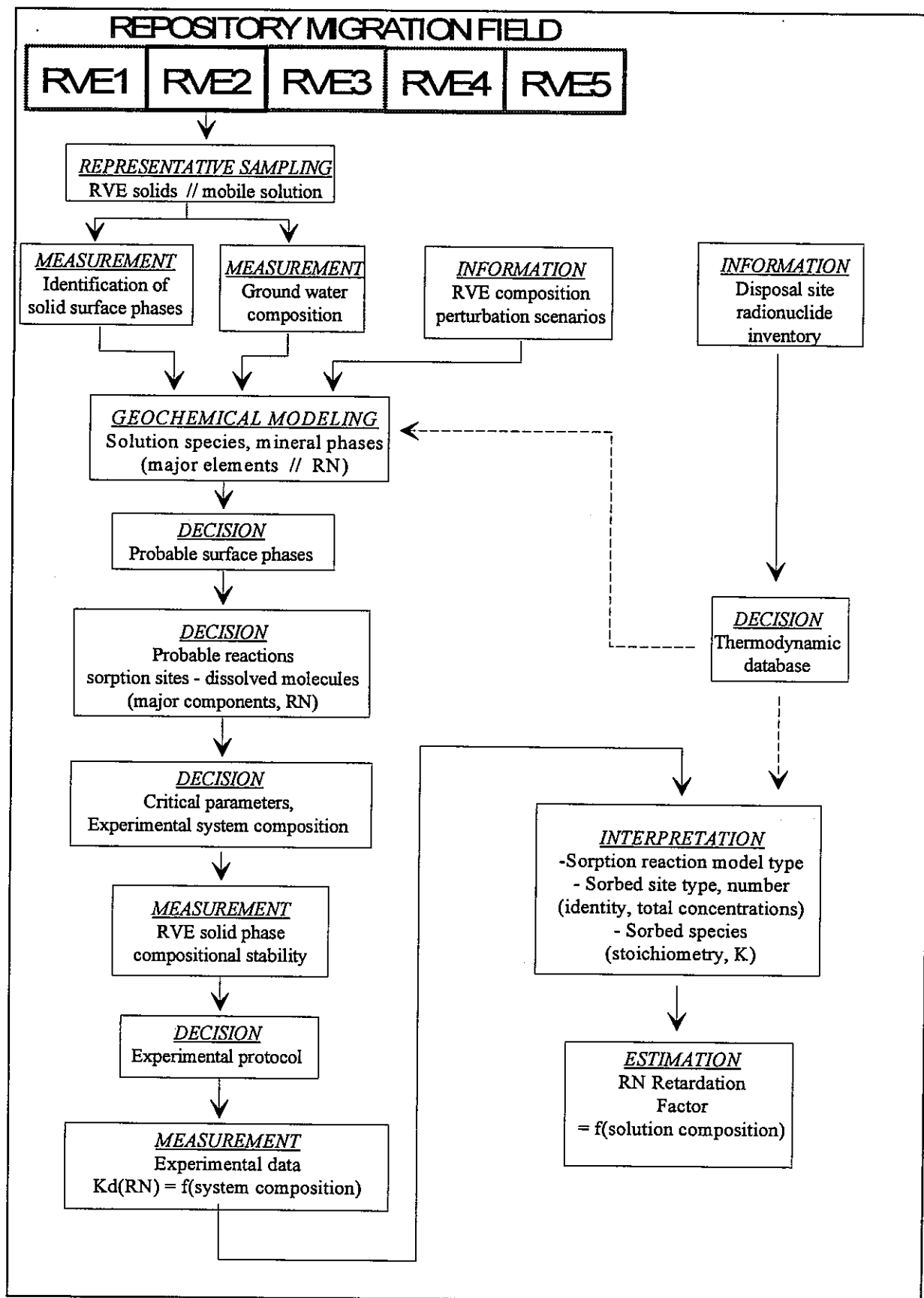
1   **5 STRATEGIC APPROACHES TO CTM MODELLING OF NATURAL SYSTEMS**

2   •   Bottom Up

3   •   Top Down

4   **6 STATE OF THE ART IN CTM - GUIDED K_d STUDIES**

5

6   **7 KEY P.A. QUESTIONS: HOW ARE WE DOING?**

7

8   **8 CONCLUSIONS AND RECOMMENDATIONS**

9   ********************* paragraph**************

10   The principal advantage of using a CTM for representing K_d(RN) information for PA purposes is the great
11   flexibility offered by such a computational framework. CTM model complexity, as represented in the number of
12   independent parameters it contains, can be "tailored" to fit virtually all levels of information concerning RVE
13   sorption site composition (identified site types, total concentrations) and sorption reaction characteristics
14   (stoichiometries, stabilities). For example:

15   •   Depending on the nature of the solid and on the range of solution compositions which must be modelled,
16   site type identification-quantification may be treated in a variety of ways: e.g. as a sum of discrete site types
17   or in terms of a single composite site type with average parameters.

18   •   The complexity of the chemical description of the system (i.e. number of sorption reactions) can be adapted
19   to different degrees of "conditionality".

20   •   Experimental data concerning solid-solution partitioning onto RVE solid surfaces can be represented using
21   the most appropriate sorption model(s): ion exchange (constant charge solid dominated systems) and/or
22   DDL-SCM (variable charge solid dominated systems).

23   •   A common Thermodynamic Data Base can be used for both sorption and non-sorption chemical reactions.

24   This means that a particular repository's CTM model of K_d(RN) data and site geochemistry can _evolve_ as more
25   and more information is obtained. Inconsistencies between the surface reaction representations present at a
26   particular stage of model development and experimental data, indicated by a poor "fit" between calculated and
27   observed partitioning, serve to indicate both how the model needs to be modified and additional experimental data
28   which needs to be obtained. This parallel evolution of model structure and information on the physical-chemistry
29   of the system stops when the model is capable of calculating (predicting) the total dissolved radio nuclide
30   concentration corresponding to each plausible chemical composition of the geochemical system in question.

31   The CTM approach offers significant advantages to the overall performance assessment effort for the following
32   reasons:

33   _Scientific Rationality_

1 The CTM approach is based on generally accepted and well-founded physical-chemical principles and
2 therefore can be readily defended on scientific grounds.

3 *Cost effectiveness*

4 The CTM approach should be the most cost effective approach over the long term. A great deal of effort has
5 been invested in experimentally determining K_d values for a relatively small number of radio nuclides on a
6 wide variety of geological solids. Unfortunately, it is beginning to be recognised that the K_d measured for a
7 given radio nuclide/solid phase combination under one set of conditions cannot generally be used to accurately
8 predict the K_d for another set of conditions. This is a direct consequence of the low information content and
9 high conditionality inherent in the K_d definition and, in practice, means that a new set of experiments must be
10 done for every new system. This non-general quality means, in effect, that the only defensible K_d for a site
11 specific performance assessment calculation is one measured on site-specific solid surfaces in contact with
12 site-specific ground water.

13 A comprehensive CTM based analytical approach should limit the overall effort needed to provide sufficiently
14 accurate predictions of radio nuclide partitioning over a wide range of systems. This is because the CTM
15 approach aims at identifying the processes and quantifying the fundamental parameters responsible for radio
16 nuclide partitioning. While the effort needed to gather this information may initially be substantial in many
17 cases, all properly measured and documented data is useful and contributes to our understanding both of a
18 particular radio nuclide/solid/solution system and of the overall validity and limits of the CTM approach.

19 This inherently cumulative characteristic of CTM information gathering means that its progress can be
20 evaluated and the data gathering process stopped for a given type of system, either when a sufficiently accurate
21 model has been developed and validated or when the CTM approach has reached its limits.

22 *Data reporting and organisation*

23 The logical and internally consistent structure of CTM-based mathematical representations is well adapted for
24 organising solid/solution partitioning data. Such a database could be organised around the component/total
25 concentration // species stoichiometry/stability constant matrix representation already employed in certain
26 numerical speciation programs. Such a representation, combined with a well-organised reference to critical
27 experimental parameters, is essential if the "cumulative" knowledge advantages of the CTM approach are to
28 be fully realised.

29

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