PNC ZJ1211 95-004

限定資料

緩衝材の化学的緩衝性に係わる固溶体モデル及び核種の吸着・拡散挙動に関する研究

（動力炉・核燃料開発事業団　研究委託内容報告書）

1995年2月

三菱マテリアル株式会社

本資料についての問合せは下記に願います。
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緩衝材の化学的緩衝性に係わる固溶体モデル及び核種の吸着・拡散挙動に関する研究

田中　皓*

要 旨

緩衝材の化学的緩衝作用をモデル化することは、性能評価上重要な課題である。平成6年度は、緩衝材の主要鉱物であるスメクタイトのイオン交換反応、表面電気化学的特性及びこれら特性データのデータベース化に関する検討を実施した。

1. 固溶体モデル開発のための試験研究及びモデル研究

(1) CaCl-Z及びMgCl-Zのイオン交換平衡定数の評価

感度解析により、CaCl-Z及びMgCl-Z（Z：スメクタイトの吸着相）の平衡定数は、それぞれLog 値で22.8、23.0と評価された。

(2) 固溶体モデルの適用性に関する検討

イオン交換平衡モデルを用いて3元系でのイオンの吸着分配を計算し、実験値と比較を行った。その結果、K$^+$については相違が見られたものの、Ca^{2+}及びH$^+$イオンについては実験値と計算値はほぼ一致することがわかった。

2．スメクタイトの表面電気化学的特性に関する研究

(1) ベンナイトと蒸留水及び人工地下水反応のモデリング

佐々木ら（1995）によるベントナイトのイオン交換反応試験の結果を用いて、拡張Wannerモデルの検証を行った。

(2) スメクタイト表面の酸／塩基特性の検討

小田（1994、1995）による酸／塩基滴定の実験結果について解析を行った。

3．核種の吸着及び拡散現象に関する固有データベースの開発研究

核種の吸着及び拡散現象に関する固有データベースについて検討を行った。その結果、吸着モデルと拡散モデルを総合するISD データベースシステムが提唱された。

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

契約番号：060D0247
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LIMITED DISTRIBUTION
PNC ZJ1211 95-004
February 1995

Development of Solid-solution Models on Bufffer Materials and Sorption/Diffusion Behavior of Nuclides

Hiroshi Tanaka*

Abstract

Development of chemical buffer model on bentonite is necessary in safty assessment of radioactive waste geological isolation. This report are described the study of interaction of bentnite with solution.

1. Study for development of solid-solution model.
 (1) Estimation of ionexchange equilibrium constant of CaCl-Z and MgCl-Z.
 Ionexchange equilibrium constant of CaCl-Z and MgCl-Z were estimated 22.8, 23.0, respectively.

 (2) Application of ionexchange model for sorption behavior.
 The concentrations of solution of ion in Na-smectite-water system are predicted by using the ionexchange model, and are comoared with measurements. The agreement is satisfactory excluding K^+ ion.

2. Acid/base Chemistry of Smectite
 (1) Modeling the interaction of bentonite with distilled water and artificial groundwater.
 The experimental data of Sasaki et al.(1995) on the interaction of different bentonites with artificial groundwater and distilled water are simulated by using the extended Wanner model. And the predictions are compared with the experimental data. The agreement is satisfactory in the case of Kunigel-V1 and Kunipia-F.

 (2) Acid/base chemistry of Smectite.
 The experimental data of Oda (1994、1995) on the Acid/base titration of suspensions of purified Na-snectite are simulated by using the extended Wanner model. A discrepancy in the proton balance is one experimention for the disagreements between model and measurements as observed in all the experiments with purified Na-smectite.

3. Recommendation for intergrated sorption/diffusion database system.
 It is proposed to intergrated sorption/diffusion (ISD) database system containing TDB, intrinsic database, and mechanistic models according to the PNC approach. The ISD database system includes a bypass option on the basis of systematic chemical analogy for radionuclides that are lacking data on either sorption or diffusion mechanism, or both.

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

Contract No. 060D0247
PNC Lieson : Yasuo Sasaki, Geological Isolation Development Section,
Tokai Works

*Naka Energy Research Center.

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第１章　固溶体モデル開発のための試験及びモデル研究

地下水中での緩衝材の化学的緩衝作用をモデル化し、長期的に評価することは性能評価上、重要な課題である。緩衝材の化学的緩衝作用は、主要構成成分である粘土鉱物（スメクタイト鉱物）のイオン交換反応により支配される。そこで、緩衝材の化学的緩衝作用についてイオン交換反応の観点からモデル化を行うため、平成４年度よりNa型スメクタイトを対象としたモデル研究に着手した。

平成５年度は、Na型スメクタイトのイオン交換平衡定数の取得を行った。また、Na型スメクタイトのイオン交換平衡について、実験による測定結果と取得されたイオン交換平衡定数による解析結果を比較した結果、２価の元素であるCa及びMgとの交換反応については、一致が見られなかった。この原因としては、$CaCl^+$ 及び$MgCl^+$ イオンによる交換反応が解析の中で考慮されていないことが挙げられた。

本年度は、平成５年度のイオン交換反応試験の結果を用いて、$CaCl^+$ 及び$MgCl^+$ イオンによる平衡定数（CaCl-Z及びMgCl-Z：Ｚはスメクタイトの吸着相）を評価取得する。また、平成５年度に実施したNa型スメクタイトの吸着試験について、$CaCl^+$ 及び$MgCl^+$ イオンによる交換反応を考慮して再解析を行い、イオン交換モデルの適用性について再度検討を行った。

1.1　CaCl-Z及びMgCl-Zのイオン交換平衡定数の評価

1.1.1　目的

Ca及びMgに対するイオン交換モデルの適用性を検討するため、Na型スメクタイトのCaCl-Z及びMgCl-Zのイオン交換平衡定数を取得する。

1.1.2　評価方法

平成５年度に測定されたCa－Na型スメクタイト系及びMg－Na型スメクタイト系での吸着試験の結果をもとに、感度解析によりCaCl-Z及びMgCl-Zの平衡定数を評価した。

(1)　解析方法

CaCl-Z及びMgCl-Z以外の平衡定数は、平成５年度に取得したイオン交換平衡定数を用いた。解析に使用したCaCl-Z及びMgCl-Z以外のNa型スメクタイトの平衡定数を表1.1.1に示す。

Table 1.1.1 Obtained ionexchange equilibrium constants in 1994

Ionexchange reaction	K	Log K
$Na^+ + Z^- \Rightarrow Na\text{-}Z$	1.00×10^{20}	20.00
$K^+ + Z^- \Rightarrow K\text{-}Z$	3.28×10^{20}	20.52
$H^+ + Z^- \Rightarrow H\text{-}Z$	3.21×10^{20}	20.51
$Ca^{2+} + 2Z^- \Rightarrow Ca\text{-}2Z$	0.78×10^{40}	39.89
$Mg^{2+} + 2Z^- \Rightarrow Mg\text{-}2Z$	1.90×10^{40}	40.28

解析には地球化学平衡計算コードであるPHREEQE 60を使用し、pH等の化学的環境条件は平成5年度の吸着試験において測定された値を入力した。

Na型スメクタイトに関するもの以外のデータベースは、PHREEQE オリジナルデータベースを使用した。なお、$CaCl^+$ 及び$MgCl^+$ イオンについてはPHREEQE オリジナルデータベースにないため、Chemval データベースより引用し、それぞれ以下の値を入力した。

$Ca^{2+} + Cl^- \Rightarrow CaCl^+ \qquad \mathrm{Log}\ K_{CaCl+} = -0.32$

$Mg^{2+} + Cl^- \Rightarrow MgCl^+ \qquad \mathrm{Log}\ K_{MgCl+} = -0.46$

以上の解析条件を表1.1.2にまとめて示す。感度解析は、CaCl-Z及びMgCl-Zの平衡定数（Log 値）の刻み幅を0.1 にして実施した。

Table 1.1.2 Conditions for estimation of ionexchange equilibrium about Na-smectite

Item	Contition
Calculation code	PHREEQE 60
pH	①Ca : pH 5.54 ②Mg : pH 7.0
pe	pe+5.9 (Eh+350mV)
Gas equilibrium	CO_2 gas $10^{-3.5}$atm
Solid solution ratio	①10g/ℓ (Ca : Z^- 1.40eq/ℓ) ② 〃 (Mg : Z^- 9.19eq/ℓ)
Data base	PHREEQE original database Chemval database ($CaCl^+$ Log K=-0.32) 〃 ($MgCl^+$ Log K=-0.46)
Ionexchange equilibrium	Table 1.1.1

(2) 測定データ

平成5年度に行ったNa型スメクタイト系でのCa及びMgの吸着試験の結果を表1.1.3及び表1.1.4に示す。なお、表1.1.3及び表1.1.4において、結果の解析に使用した式は以下の通りである。

(a) 液相中のイオンの活量補正式

Daviesの式により活量補正を行った。

$$\mathrm{Log}\ \gamma_{MCl} = -A\,|Z_+ Z_-|\,\frac{\sqrt{I}}{1+\sqrt{I}} - 0.3\ I \qquad (1.1.1)$$

A : 定数 0.5091 (25℃)

I : イオン強度〔$I = 1/2\Sigma\ (m_i \cdot Z_i^{\,2})$〕

(b) 固相に吸着したイオンの当量分率

理想固溶体と仮定し、固相中に吸着したイオンの活量係数は1とした。

(3) 評価方法

吸着試験の結果と解析結果は、イオン交換平衡後の液相中の濃度と固相中の全吸着サイトに対する吸着量の関係をそれぞれ当量分率を求めて整理し、比較することとした。

1.1.3 評価結果

Ca－Na型スメクタイト系及びMg－Na型スメクタイト系において、CaCl-Z及びMgCl-Zの平衡定数を感度解析した結果を図1.1.1～図1.1.2に示す。

また、それぞれ吸着試験によるデータとのフィッティング状態を調べるため、最小自乗法により相関係数（r^2）を求めた。その結果を表1.1.5に示す。

表1.1.5より、CaCl-Zについては、平衡定数（Log 値）22.8において相関係数が最も高く、試験結果とのフィッティング性も高いことから最適値であると判断した。なお、平衡定数は22.7から22.9までの間では、相関係数の差は極めて小さい。

また、MgCl-Zについては、平衡定数（Log 値）23.0において、相関係数が最も高く、試験結果とのフィッティング性も高いことから最適値であると判断した。なお、22.9から23.1までは間では、相関係数の差は極めて小さい。

以上のことから、CaCl-Z及びMgCl-Zの平衡定数（Log 値）は、それぞれ22.8、23.0ががであるものと判断した。

Table1.1.5 Result of sensetive analysis for ionexchange constants

CaCl-Z (LogK)	相関係数 (r^2)	MgCl-Z (LogK)	相関係数 (r^2)
22.4	0.976	22.6	0.952
22.6	0.987	22.8	0.982
22.7	0.992	22.9	0.986
22.8	0.993	23.0	0.988
22.9	0.991	23.1	0.987
23.0	0.982	23.2	0.982
23.2	0.907	23.4	0.967

Table 1.1.3 Measured data of ionexchange equilibrium in Ca^{2+} +Na-smectite system

設定値（mol/ℓ）		初期溶液			平衡後の溶液										平衡後の固相		
		測定濃度（mol/ℓ）			測定濃度（mol/ℓ）			活 量		活量係数（Log γ）		ｲｵﾝ 強度	当量濃度分率		固相中の分率		陽イオン交換容量 (meq/100g)
Ca^{2+}	Na^{+}	pH	Ca^{2+}	Na^{+}	pH	Ca^{2+}	Na^{+}	Ca^{2+}	Na^{+}	Ca^{2+}	Na^{+}		Ca^{2+}	Na^{+}	E_{Ca}	E_{Na}	
0.0005	0.099	5.42	2.87×10^{-4}	9.91×10^{-2}	4.74	2.18×10^{-4}	1.00×10^{-1}	1.13×10^{-4}	7.81×10^{-2}	−0.214	−0.107	0.101	0.004	0.996	0.010	0.990	140.3
		5.42	4.68×10^{-4}	9.66×10^{-2}	4.63	2.12×10^{-4}	1.01×10^{-1}	1.29×10^{-4}	7.89×10^{-2}	−0.215	−0.108	0.102	0.004	0.996	0.037	0.963	140.3
0.00125	0.0975	5.36	1.25×10^{-3}	9.43×10^{-2}	4.63	5.85×10^{-4}	9.92×10^{-2}	3.57×10^{-4}	7.75×10^{-2}	−0.215	−0.107	0.101	0.012	0.988	0.095	0.905	140.3
0.0025	0.095	5.30	2.46×10^{-3}	9.24×10^{-2}	4.61	1.25×10^{-3}	9.78×10^{-2}	7.62×10^{-4}	7.64×10^{-2}	−0.215	−0.108	0.102	0.025	0.975	0.173	0.827	140.3
		5.30	2.50×10^{-3}	9.70×10^{-2}	4.69	1.28×10^{-3}	9.87×10^{-2}	7.79×10^{-4}	7.70×10^{-2}	−0.216	−0.108	0.103	0.025	0.975	0.173	0.827	140.3
0.005	0.09	5.45	4.83×10^{-3}	8.87×10^{-2}	4.61	2.70×10^{-3}	9.40×10^{-2}	1.64×10^{-3}	7.34×10^{-2}	−0.215	−0.108	0.102	0.054	0.946	0.304	0.696	140.3
		5.45	4.97×10^{-3}	9.22×10^{-2}	4.71	2.75×10^{-3}	9.78×10^{-2}	1.66×10^{-3}	7.61×10^{-2}	−0.218	−0.109	0.106	0.053	0.947	0.317	0.683	140.3
0.0125	0.075	5.59	1.20×10^{-2}	7.39×10^{-2}	4.52	7.79×10^{-3}	8.14×10^{-2}	4.73×10^{-3}	6.34×10^{-2}	−0.217	−0.108	0.105	0.161	0.839	0.600	0.400	140.3
		5.59	1.29×10^{-2}	7.39×10^{-2}	4.65	8.56×10^{-3}	8.48×10^{-2}	5.15×10^{-3}	6.58×10^{-2}	−0.220	−0.110	0.110	0.168	0.832	0.615	0.385	140.3
0.025	0.05	5.72	2.50×10^{-2}	5.30×10^{-2}	4.53	2.00×10^{-2}	6.17×10^{-2}	1.19×10^{-2}	4.76×10^{-2}	−0.226	−0.113	0.122	0.393	0.607	0.711	0.289	140.3
		5.72	2.47×10^{-2}	5.10×10^{-2}	4.46	1.93×10^{-2}	5.92×10^{-2}	1.15×10^{-2}	4.58×10^{-2}	−0.224	−0.112	0.117	0.395	0.605	0.770	0.230	140.3
0.0375	0.025	5.81	3.70×10^{-2}	2.52×10^{-2}	4.44	3.09×10^{-2}	3.38×10^{-2}	1.83×10^{-2}	2.60×10^{-2}	−0.228	−0.114	0.127	0.646	0.354	0.870	0.130	140.3
0.05	0	5.89	4.92×10^{-2}	0.00	4.43	4.25×10^{-2}	1.00×10^{-2}	2.48×10^{-2}	7.64×10^{-3}	−0.233	−0.117	0.138	0.895	0.105	0.955	0.045	140.3

Table 1.1.4 Measured data of ionexchange equilibrium in Mg^{2+} +Na-smectite system

設定値（mol/ℓ）		初期溶液			平衡後の溶液										平衡後の固相		
		測定濃度（mol/ℓ）			測定濃度（mol/ℓ）			活量		活量係数（ Log γ ）		ｲｵﾝ 強度	当量濃度分率		固相中の分率		陽イオン交換容量 (meq/100g)
Ca^{2+}	Na^{+}	pH	Mg^{2+}	Na^{+}	pH	Mg^{2+}	Na^{+}	Mg^{2+}	Na^{+}	Mg^{2+}	Na^{+}		Mg^{2+}	Na^{+}	E_{Mg}	E_{Na}	
0.0005	0.099	5.44	3.72×10^{-4}	9.69×10^{-2}	4.72	1.80×10^{-4}	1.03×10^{-1}	1.09×10^{-4}	8.03×10^{-2}	−0.216	−0.108	0.104	0.003	0.997	0.042	0.958	91.9
		5.44	4.52×10^{-4}	1.00×10^{-1}	4.75	2.56×10^{-4}	1.00×10^{-1}	1.56×10^{-4}	7.81×10^{-2}	−0.215	−0.107	0.101	0.005	0.995	0.043	0.957	91.9
0.00125	0.0975	5.43	1.02×10^{-3}	9.48×10^{-2}	4.71	5.10×10^{-4}	1.01×10^{-1}	3.10×10^{-4}	7.88×10^{-2}	−0.216	−0.108	0.103	0.010	0.990	0.111	0.889	91.9
0.0025	0.095	5.41	2.16×10^{-3}	9.23×10^{-2}	4.70	1.19×10^{-3}	9.83×10^{-2}	7.25×10^{-4}	7.67×10^{-2}	−0.215	−0.108	0.102	0.024	0.976	0.211	0.789	91.9
		5.41	2.37×10^{-3}	9.48×10^{-2}	4.74	1.31×10^{-3}	9.70×10^{-2}	7.98×10^{-4}	7.57×10^{-2}	−0.215	−0.107	0.101	0.026	0.974	0.231	0.769	91.9
0.005	0.09	5.35	4.57×10^{-3}	8.91×10^{-2}	4.72	2.93×10^{-3}	9.78×10^{-2}	1.77×10^{-3}	7.61×10^{-2}	−0.218	−0.109	0.107	0.056	0.944	0.357	0.643	91.9
		5.35	4.39×10^{-3}	8.79×10^{-2}	4.68	2.55×10^{-3}	9.57×10^{-2}	1.55×10^{-3}	7.46×10^{-2}	−0.216	−0.108	0.103	0.051	0.949	0.400	0.600	91.9
0.0125	0.075	5.34	9.37×10^{-3}	7.34×10^{-2}	4.62	5.96×10^{-3}	8.35×10^{-2}	3.63×10^{-3}	6.52×10^{-2}	−0.215	−0.107	0.101	0.125	0.875	0.742	0.258	91.9
		5.34	1.19×10^{-2}	7.61×10^{-2}	4.15	8.19×10^{-3}	8.48×10^{-2}	4.94×10^{-3}	6.58×10^{-2}	−0.220	−0.110	0.109	0.162	0.838	0.814	0.186	91.9
0.025	0.05	5.34	2.03×10^{-2}	5.01×10^{-2}	4.53	1.61×10^{-2}	6.28×10^{-2}	9.69×10^{-3}	4.87×10^{-2}	−0.221	−0.110	0.111	0.339	0.661	0.914	0.086	91.9
0.0375	0.025	5.34	3.11×10^{-2}	2.52×10^{-2}	4.48	2.70×10^{-2}	3.49×10^{-2}	1.61×10^{-2}	2.70×10^{-2}	−0.223	−0.112	0.116	0.607	0.393	0.892	0.108	91.9
0.05	0	5.41	4.24×10^{-2}	0.00	4.46	3.79×10^{-2}	1.03×10^{-2}	2.25×10^{-2}	7.93×10^{-3}	−0.227	−0.114	0.124	0.880	0.120	0.979	0.021	91.9

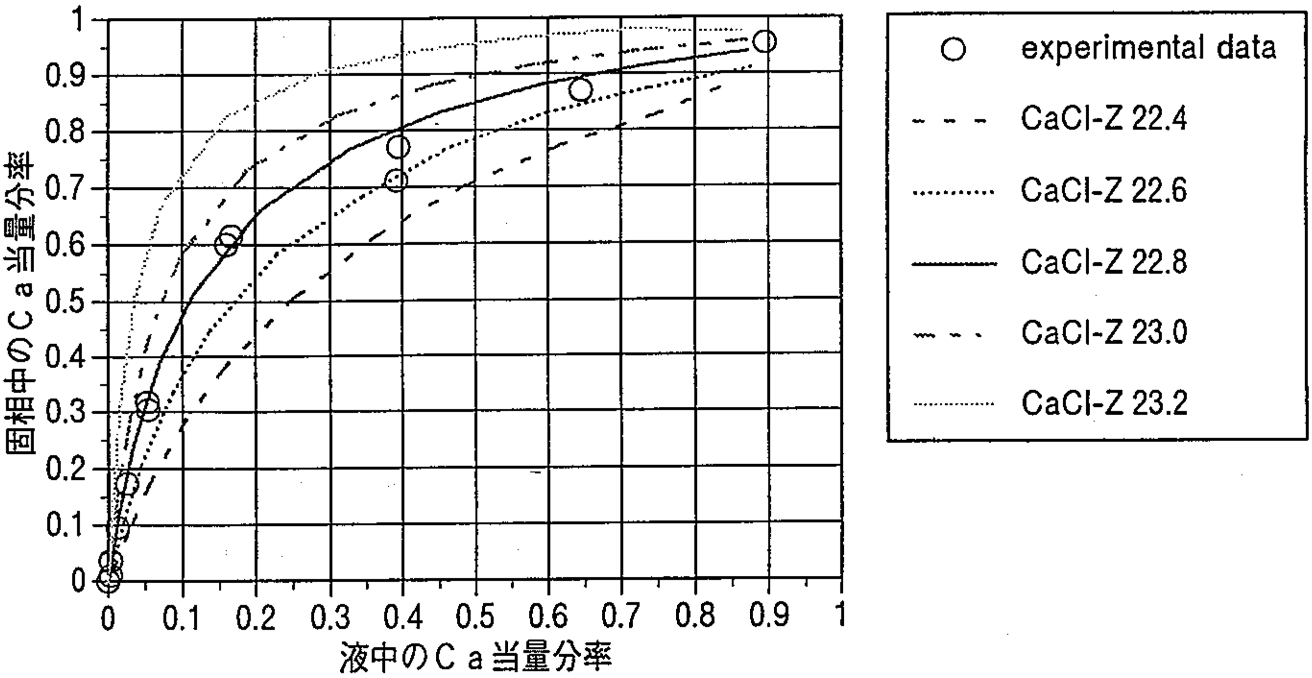

Figure 1.1.1 Sensetive analysis for ionexchange constant of CaCl-Z

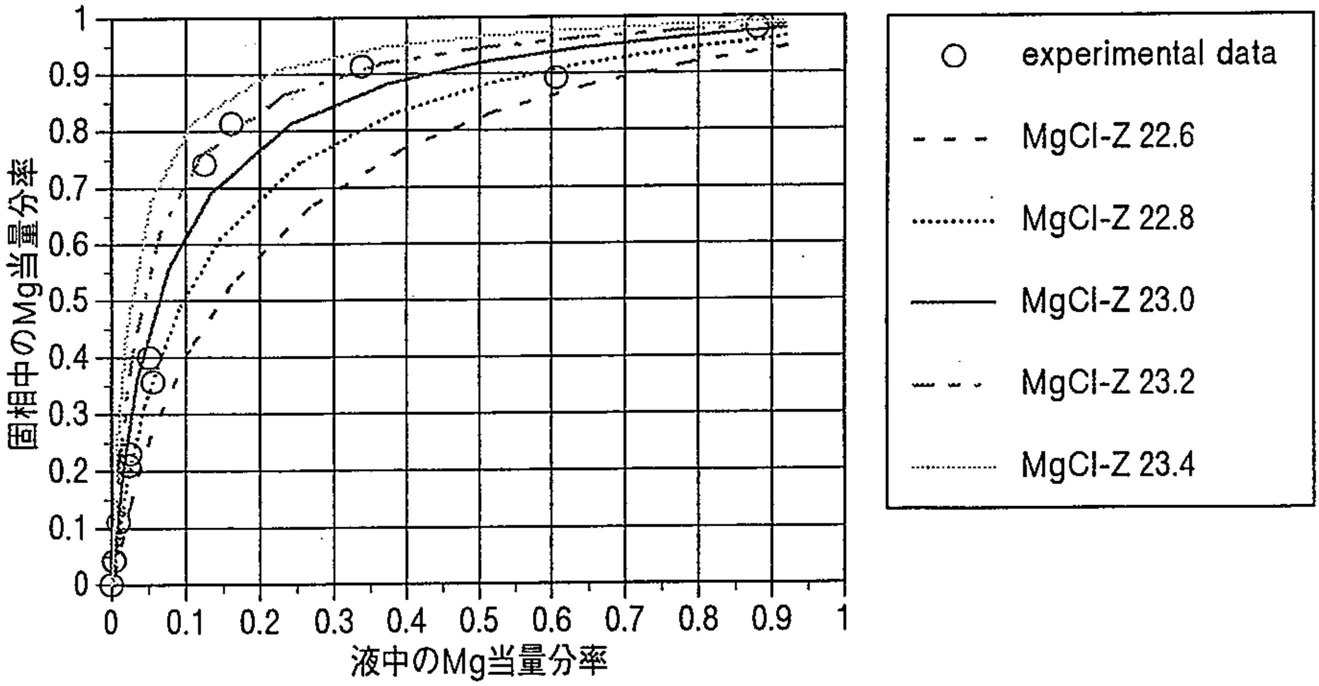

Figure 1.1.2 Sensetive analysis for ionexchange constant of MgCl-Z

1.2　固溶体モデルの適用性に関する検討

本節では、固溶体モデルの中心であるスメクタイトのイオン交換反応に着目し、多成分系において、イオンの分配平衡に対するイオン交換平衡モデルの適用性の検討を行った。

1.2.1　目的

イオン交換平衡モデルにより、多成分系でのスメクタイトのイオンの分配平衡を予測する際の妥当性を確認することを目的とした。

1.2.2　評価方法

以下の3成分系を対象に、イオン交換平衡モデルによる解析値と吸着試験による測定値の比較を行った。なお、測定値については、平成5年度に実施した吸着試験の結果を用いて評価した。

① K^+ ＋H^+ ＋Na型スメクタイト系

② K^+ ＋Ca^{2+}＋Na型スメクタイト系

(1)　解析方法

Na型スメクタイトのイオン交換平衡定数は、平成5年度に取得された値を引用した。また、CaCl-Z及びMgCl-Zの平衡定数については、1.1節において評価された値を使用した。解析に使用したNa型スメクタイトに関する平衡定数を表1.2.1に示す。

Table 1.2.1　Ionexchange equilibrium constants for estimation

Ionexchange reaction	Log K
$Na^+ + Z^- \Rightarrow Na\text{-}Z$	20.00
$K^+ + Z^- \Rightarrow K\text{-}Z$	20.52
$H^+ + Z^- \Rightarrow H\text{-}Z$	20.51
$Ca^{2+} + 2Z^- \Rightarrow Ca\text{-}2Z$	39.89
$CaCl^+ + Z^- \Rightarrow CaCl\text{-}Z$	22.8
$Mg^{2+} + 2Z^- \Rightarrow Mg\text{-}2Z$	40.28
$MgCl^+ + Z^- \Rightarrow MgCl\text{-}Z$	23.09

イオン交換平衡の計算にはPHREEQE 60を使用し、pH等の化学的環境条件は試験において取得された値に基づいて設定した。解析条件を表1.2.2にまとめて示す。

Table 1.2.2 Conditions for estimation of ionexchange equilibrium in K^++H^++Na-smectite and K^++Ca^{2+}+Na-smectite system

Item	Contition
Calculation code	PHREEQE 60
pH	①K^+ +H^+ +Na : pH 1.3~3.0 ②K^+ +Ca^{2+} +Na : pH 5.4
pe	pe+5.9 (Eh+350mV)
Gas equilibrium	CO_2 gas $10^{-3.5}$atm
Solid solution ratio	10g/ℓ (Ca : Z^- 1.08eq/ℓ)
Data base	PHREEQE original database
Ionexchange equilibrium	Table 1.2.1

(2) 測定データ

解析結果と比較検討するデータは、平成5年度のNa型スメクタイトの吸着試験で取得されたデータを使用した。K^+ +H^+ +Na型スメクタイト系及びK^+ +Ca^{2+}+Na型スメクタイト系において測定されたデータを表1.2.3及び表1.2.4に整理して示す。

なお、吸着試験の解析に使用した式は以下の通りである。

(a) 液相中のイオンの活量補正式

Daviesの式により活量補正を行った。

$$\mathrm{Log}\ \gamma_{MCl} = -A\,|Z_+ Z_-|\ \frac{\sqrt{I}}{1+\sqrt{I}} - 0.3\ I \qquad (1.2.1)$$

A：定数 0.5091 (25℃)

I：イオン強度〔$I = 1/2\ (\Sigma m_i \cdot z_i^2)$〕

(b) 固相に吸着したイオンの当量分率

理想固溶体と仮定し、固相中に吸着したイオンの活量係数は1とした。

(3) 評価方法

計算結果と測定結果の比較は、イオン交換平衡後における液相中の当量分率と固相中の吸着サイトに対する当量分率を求めて整理を行い、その関係について比較することとした。

1.2.3 評価結果

(1) $K^+ + H^+ +$Na型スメクタイト系

図1.2.1(1)～(4)はH^+濃度（pH）一定とした場合のK^+の液相－固相間の分配を、図1.2.1(5)～(8)は逆にK^+濃度を一定とした場合のH^+の分配を示した。

図1.2.1(1)～(4)より、K^+についてのイオン交換平衡定数による解析結果は、濃度が低い場合には液相と固相の分配は測定値とよく一致するが、K^+自身の濃度が高くなるにつれ、解析では固相中の分率が高く評価される傾向にあった。これは、K^+の分配を計算評価した場合、実際に吸着する量よりも高く評価される恐れがあることを示している。また、この結果は、H^+濃度に依存していない。

一方、図1.2.1(5)～(8)より、H^+についてはバラつきが大きいものの、イオン交換平衡定数による解析結果と測定結果は傾向性でほぼ一致することが予想された。H^+の分配についてはについては、K^+濃度に依らずイオン平衡定数による計算評価がほぼ可能であるものと考えられた。

(2) $K^+ + Ca^{2+} +$Na型スメクタイト系

図1.2.2(1)～(4)はCa濃度（pH）一定とした場合のK^+の液相－固相間の分配を、図1.2.2(5)～(8)は逆にK^+濃度を一定とした場合のCaの分配を示した。

図1.2.2(1)～(4)より、K^+についてのイオン交換平衡定数による解析結果は、濃度が低い場合には液相と固相の分配は測定値とよく一致するが、K^+自身の濃度が高くなるにつれ、解析では固相中の分率が高く評価される傾向にあった。これは、$K^+ + H^+ +$Na型スメクタイト系での結果とほぼ同様であることから、K^+特有の性質によるものと考えられる。

一方、図1.2.2(5)～(8)より、CaについてはCaCl-Zの平衡定数を加えて解析した場合、測定結果はよく一致することが確認された。Caの分配についてはイオン平衡定数による計算評価が可能であるものと判断された。

(3) まとめ

以上の結果により、K^+ については高濃度（0.01mol/ℓ以上）領域でイオン交換定数による解析値と測定値のズレが大きいものの、他のイオンについてはほぼ一致することが確認された。K^+ のみ問題はあるが、多元系についてもイオン交換平衡モデルによる吸着分配の予測評価は可能であるものと考えられる。

1.3 まとめ

第1章のまとめを以下に記述する。

(1) CaCl-Z及びMgCl-Zのイオン交換平衡定数の評価

$CaCl^+$ 及び $MgCl^+$ イオンに関するデータは知られていないため、平成5年度の測定結果に基づいて感度解析的に平衡定数を評価した。その結果、CaCl-Z及びMgCl-Zの平衡定数（Log 値）は、それぞれ22.8、23.0と評価することができた。

(2) イオン交換平衡モデルの適用性に関する検討

CaCl-Z及びMgCl-Zによるイオン交換反応を考慮して、$K^+ + H^+ +$Na型スメクタイト系及び$K^+ + Ca^{2+} +$Na型スメクタイト系でのイオンの吸着分配を解析し、実測値と比較した。その結果、K^+ については高濃度（0.01mol/ℓ以上）領域でイオン交換定数による解析値と測定値のズレが大きいものの、他のイオンについてはほぼ一致することを確認した。

Table 1.2.3 Measured data of ionexchange equilibrium in K$^+$ +H$^+$ +Na-smectite system

設定値 (mol/ℓ)			初期溶液				平衡後の液相																		平衡後の固相			
			測定濃度 (mol/ℓ)				測定濃度 (mol/ℓ)				活量			活量係数 (Logγ)			ｲｵﾝ強度	当量濃度分率			当量活量分率			固相中の当量分率			陽イオン交換容量 (meq/100g)
KCl	HCl	NaCl	pH	K	H	Na	pH	K	H	Na	K$^+$	H$^+$	Na$^+$	K$^+$	H$^+$	Na$^+$		K$^+$	H$^+$	Na$^+$	K$^+$	H$^+$	Na$^+$	E_K	E_H	E_{Na}	
0.001	0.001	0.098	3.04	1.24×10^{-3}	9.12×10^{-4}	9.87×10^{-2}	3.67	9.87×10^{-4}	2.14×10^{-4}	1.03×10^{-1}	7.69×10^{-4}	1.67×10^{-4}	8.03×10^{-2}	−0.108	−0.108	−0.108	0.104	0.009	0.002	0.988	0.009	0.002	0.988	0.023	0.129	0.847	108.1
	0.005	0.094	2.34	1.24×10^{-3}	4.57×10^{-3}	9.57×10^{-2}	2.57	1.07×10^{-3}	2.69×10^{-3}	9.92×10^{-2}	8.35×10^{-3}	2.10×10^{-3}	7.74×10^{-2}	−0.108	−0.108	−0.108	0.103	0.010	0.026	0.963	0.010	0.026	0.963	0.016	0.348	0.637	108.1
	0.01	0.089	2.04	1.23×10^{-3}	9.12×10^{-3}	9.24×10^{-2}	2.17	1.05×10^{-3}	6.76×10^{-3}	9.57×10^{-2}	8.19×10^{-3}	5.27×10^{-3}	7.46×10^{-2}	−0.108	−0.108	−0.108	0.104	0.010	0.065	0.925	0.010	0.065	0.925	0.017	0.437	0.547	108.1
	0.05	0.049	1.34	1.21×10^{-3}	4.57×10^{-2}	8.61×10^{-2}	1.38	1.06×10^{-3}	4.17×10^{-2}	5.74×10^{-2}	8.28×10^{-3}	3.26×10^{-2}	4.49×10^{-2}	−0.107	−0.107	−0.107	0.100	0.011	0.416	0.573	0.011	0.416	0.573	0.014	0.744	0.242	108.1
0.005	0.001	0.094	3.02	4.91×10^{-3}	9.55×10^{-4}	9.24×10^{-2}	3.59	4.58×10^{-3}	2.57×10^{-4}	9.67×10^{-2}	3.58×10^{-3}	2.01×10^{-4}	7.55×10^{-2}	−0.108	−0.108	−0.108	0.102	0.045	0.003	0.952	0.045	0.003	0.952	0.031	0.129	0.840	108.1
	0.005	0.090	2.34	5.22×10^{-3}	4.57×10^{-3}	9.17×10^{-2}	2.55	4.78×10^{-3}	2.82×10^{-3}	9.67×10^{-2}	3.72×10^{-3}	2.20×10^{-3}	7.53×10^{-2}	−0.108	−0.108	−0.108	0.104	0.046	0.027	0.927	0.046	0.027	0.927	0.041	0.324	0.635	108.1
	0.01	0.085	2.04	5.32×10^{-3}	9.12×10^{-3}	8.79×10^{-2}	2.17	4.83×10^{-3}	6.76×10^{-3}	9.24×10^{-2}	3.76×10^{-3}	5.27×10^{-3}	7.20×10^{-2}	−0.108	−0.108	−0.108	0.104	0.046	0.065	0.889	0.046	0.065	0.889	0.045	0.437	0.518	108.1
	0.05	0.045	1.35	5.22×10^{-3}	4.47×10^{-2}	4.63×10^{-2}	1.37	4.75×10^{-3}	4.27×10^{-2}	5.31×10^{-2}	3.71×10^{-3}	3.33×10^{-2}	4.15×10^{-2}	−0.107	−0.107	−0.107	0.101	0.047	0.424	0.528	0.047	0.424	0.528	0.044	0.372	0.585	108.1
0.01	0.001	0.089	3.03	1.14×10^{-2}	9.33×10^{-4}	8.96×10^{-2}	3.56	8.70×10^{-3}	2.75×10^{-4}	9.41×10^{-2}	6.78×10^{-3}	2.15×10^{-4}	7.34×10^{-2}	−0.108	−0.108	−0.108	0.103	0.084	0.003	0.913	0.084	0.003	0.913	0.250	0.122	0.629	108.1
	0.005	0.085	2.35	1.14×10^{-2}	4.47×10^{-3}	8.70×10^{-2}	2.54	9.21×10^{-3}	2.88×10^{-3}	9.24×10^{-2}	7.18×10^{-3}	2.25×10^{-3}	7.20×10^{-2}	−0.108	−0.108	−0.108	0.104	0.088	0.028	0.884	0.088	0.028	0.884	0.203	0.293	0.505	108.1
	0.01	0.080	2.04	1.09×10^{-2}	9.12×10^{-3}	8.26×10^{-2}	2.16	9.41×10^{-3}	6.92×10^{-3}	8.73×10^{-2}	7.34×10^{-3}	5.39×10^{-3}	6.81×10^{-2}	−0.108	−0.108	−0.108	0.104	0.091	0.067	0.842	0.091	0.067	0.842	0.138	0.407	0.454	108.1
	0.05	0.040	1.34	1.02×10^{-2}	4.57×10^{-2}	4.18×10^{-2}	1.37	9.41×10^{-3}	4.27×10^{-2}	4.82×10^{-2}	7.35×10^{-3}	3.33×10^{-2}	3.77×10^{-2}	−0.107	−0.107	−0.107	0.100	0.094	0.425	0.481	0.094	0.425	0.481	0.073	0.565	0.363	108.1
0.05	0.001	0.049	3.04	4.80×10^{-2}	9.12×10^{-4}	4.96×10^{-2}	3.44	4.49×10^{-2}	3.63×10^{-4}	5.65×10^{-2}	3.50×10^{-2}	2.83×10^{-4}	4.41×10^{-2}	−0.108	−0.108	−0.108	0.102	0.441	0.004	0.555	0.441	0.004	0.555	0.287	0.102	0.612	108.1
	0.005	0.045	2.35	4.91×10^{-2}	4.47×10^{-3}	4.63×10^{-2}	2.50	4.61×10^{-2}	3.16×10^{-3}	5.55×10^{-2}	3.59×10^{-2}	2.46×10^{-3}	4.32×10^{-2}	−0.108	−0.108	−0.108	0.105	0.440	0.030	0.530	0.440	0.030	0.530	0.278	0.241	0.481	108.1
	0.01	0.040	2.05	5.12×10^{-2}	8.91×10^{-3}	4.23×10^{-2}	2.14	4.76×10^{-2}	7.24×10^{-3}	5.05×10^{-2}	3.71×10^{-2}	5.64×10^{-3}	3.93×10^{-2}	−0.109	−0.109	−0.109	0.105	0.452	0.069	0.479	0.452	0.069	0.479	0.333	0.309	0.358	108.1
	0.05	0	1.34	5.12×10^{-2}	4.57×10^{-2}	0	1.38	4.76×10^{-2}	4.17×10^{-2}	1.02×10^{-2}	3.72×10^{-2}	3.26×10^{-2}	7.79×10^{-3}	−0.107	−0.107	−0.107	0.099	04789	0.419	0.103	04789	0.419	0.103	0.333	0.744	-0.077	108.1

Table 1.2.4 Measured data of ionexchange equilibrium in Ca^{2+}+H$^+$ +Na-smectite system

設定値 (eq/ℓ)			初期溶液				平衡後の液相																	平衡後の固相			
			測定濃度 (mol/ℓ)				測定濃度 (mol/ℓ)				活量			活量係数 (Log γ)			ｲｵﾝ 強度	当量濃度分率			当量活量分率			固相中の当量分率			陽イオン交換容量 (meq/100g)
KCl	CaCl$_2$	NaCl	pH	K	Ca	Na	pH	K	Ca	Na	K$^+$	Ca^{2+}	Na$^+$	K$^+$	Ca^{2+}	Na$^+$		K$^+$	Ca^{2+}	Na$^+$	K$^+$	Ca^{2+}	Na$^+$	E$_K$	E$_{Ca}$	E$_{Na}$	
0.001	0.0005	0.098	5.51	1.27×10^{-3}	4.52×10^{-4}	9.74×10^{-2}	4.74	9.72×10^{-4}	2.14×10^{-4}	9.78×10^{-2}	7.60×10^{-4}	1.31×10^{-4}	7.65×10^{-2}	−0.107	−0.214	−0.107	0.099	0.010	0.004	0.986	0.010	0.002	0.988	0.028	0.044	0.928	108.1
	0.0025	0.094	5.43	1.33×10^{-3}	2.39×10^{-3}	9.24×10^{-2}	4.73	9.87×10^{-3}	1.26×10^{-3}	9.48×10^{-2}	7.72×10^{-4}	7.70×10^{-4}	7.41×10^{-2}	−0.107	−0.214	−0.107	0.100	0.010	0.026	0.964	0.010	0.012	0.977	0.032	0.209	0.759	108.1
	0.005	0.089	5.53	1.27×10^{-3}	4.53×10^{-3}	8.96×10^{-2}	4.73	1.02×10^{-3}	2.66×10^{-3}	9.26×10^{-2}	7.96×10^{-4}	1.62×10^{-3}	7.23×10^{-2}	−0.108	−0.215	−0.108	0.102	0.010	0.054	0.936	0.011	0.026	0.963	0.023	0.346	0.631	108.1
	0.025	0.049	5.64	1.33×10^{-3}	2.33×10^{-2}	5.05×10^{-2}	4.57	1.13×10^{-3}	1.89×10^{-2}	5.71×10^{-2}	8.74×10^{-4}	1.13×10^{-2}	4.42×10^{-2}	−0.111	−0.223	−0.111	0.115	0.012	0.394	0.595	0.015	0.231	0.754	0.019	0.814	0.167	108.1
0.005	0.0005	0.094	5.50	5.12×10^{-3}	4.80×10^{-4}	9.38×10^{-2}	4.71	4.53×10^{-3}	2.47×10^{-4}	9.48×10^{-2}	3.54×10^{-3}	1.51×10^{-4}	7.41×10^{-2}	−0.107	−0.214	−0.107	0.100	0.045	0.005	0.950	0.045	0.002	0.952	0.055	0.043	0.902	108.1
	0.0025	0.090	5.51	5.12×10^{-3}	2.38×10^{-3}	8.96×10^{-2}	4.69	4.63×10^{-3}	1.35×10^{-3}	9.15×10^{-2}	3.62×10^{-3}	8.24×10^{-4}	7.15×10^{-2}	−0.107	−0.214	−0.107	0.100	0.047	0.027	0.926	0.048	0.013	0.939	0.045	0.191	0.764	108.1
	0.005	0.085	5.54	5.22×10^{-3}	4.68×10^{-3}	8.70×10^{-2}	4.69	4.91×10^{-3}	2.83×10^{-3}	8.96×10^{-2}	3.83×10^{-3}	1.72×10^{-3}	6.99×10^{-2}	−0.108	−0.216	−0.108	0.103	0.049	0.057	0.894	0.051	0.028	0.922	0.029	0.342	0.629	108.1
	0.025	0.045	5.66	5.22×10^{-3}	2.34×10^{-2}	4.62×10^{-2}	4.56	5.29×10^{-3}	1.91×10^{-2}	5.39×10^{-2}	4.09×10^{-3}	1.14×10^{-2}	4.17×10^{-2}	−0.112	−0.224	−0.112	0.116	0.054	0.392	0.553	0.069	0.230	0.701	-0.006	0.796	0.211	108.1
0.01	0.0005	0.089	5.43	1.22×10^{-2}	4.78×10^{-4}	8.87×10^{-2}	4.68	9.41×10^{-3}	2.67×10^{-4}	9.40×10^{-2}	7.33×10^{-3}	1.62×10^{-4}	7.32×10^{-2}	−0.108	−0.217	−0.108	0.104	0.091	0.005	0.904	0.091	0.002	0.907	0.258	0.039	0.703	108.1
	0.0025	0.085	5.50	1.14×10^{-2}	2.38×10^{-3}	8.46×10^{-2}	4.65	9.41×10^{-3}	1.47×10^{-3}	9.05×10^{-2}	7.33×10^{-3}	8.92×10^{-4}	7.05×10^{-2}	−0.108	−0.217	−0.108	0.104	0.091	0.029	0.880	0.093	0.014	0.893	0.184	0.168	0.648	108.1
	0.005	0.080	5.53	1.14×10^{-2}	4.57×10^{-3}	7.86×10^{-2}	4.66	9.41×10^{-3}	3.01×10^{-3}	8.70×10^{-2}	7.33×10^{-3}	1.89×10^{-3}	6.77×10^{-2}	−0.109	−0.217	−0.109	0.105	0.092	0.059	0.849	0.095	0.029	0.877	0.184	0.289	0.527	108.1
	0.025	0.040	5.64	1.14×10^{-2}	2.26×10^{-2}	4.18×10^{-2}	4.55	9.72×10^{-3}	1.94×10^{-2}	5.05×10^{-2}	7.51×10^{-3}	1.16×10^{-2}	3.90×10^{-2}	−0.112	−0.225	−0.112	0.118	0.098	0.392	0.510	0.124	0.229	0.647	0.155	0.592	0.253	108.1
0.05	0.0005	0.049	5.44	4.84×10^{-2}	4.70×10^{-4}	4.96×10^{-2}	4.56	4.60×10^{-2}	3.53×10^{-4}	5.92×10^{-2}	3.58×10^{-2}	2.14×10^{-4}	4.61×10^{-2}	−0.109	−0.218	−0.109	0.106	0.434	0.007	0.559	0.436	0.003	0.561	0.222	0.022	0.756	108.1
	0.0025	0.045	5.49	4.84×10^{-2}	2.31×10^{-3}	4.54×10^{-2}	4.51	4.55×10^{-2}	1.75×10^{-3}	5.48×10^{-2}	3.54×10^{-2}	1.06×10^{-3}	4.27×10^{-2}	−0.109	−0.217	−0.109	0.106	0.438	0.034	0.528	0.446	0.016	0.538	0.268	0.104	0.628	108.1
	0.005	0.040	5.56	4.80×10^{-2}	6.91×10^{-3}	4.04×10^{-2}	4.50	4.61×10^{-2}	3.58×10^{-3}	4.96×10^{-2}	3.59×10^{-2}	2.17×10^{-3}	3.86×10^{-2}	−0.109	−0.218	−0.109	0.106	0.438	0.070	0.482	0.465	0.034	0.501	0.176	0.616	0.208	108.1
	0.025	0	5.68	4.92×10^{-2}	2.26×10^{-2}	0	4.51	4.93×10^{-2}	2.01×10^{-2}	1.00×10^{-2}	3.80×10^{-2}	1.20×10^{-2}	7.72×10^{-3}	−0.113	−0.225	−0.113	0.120	0.495	0.404	0.101	0.634	0.238	0.129	-0.009	0.463	0.547	108.1

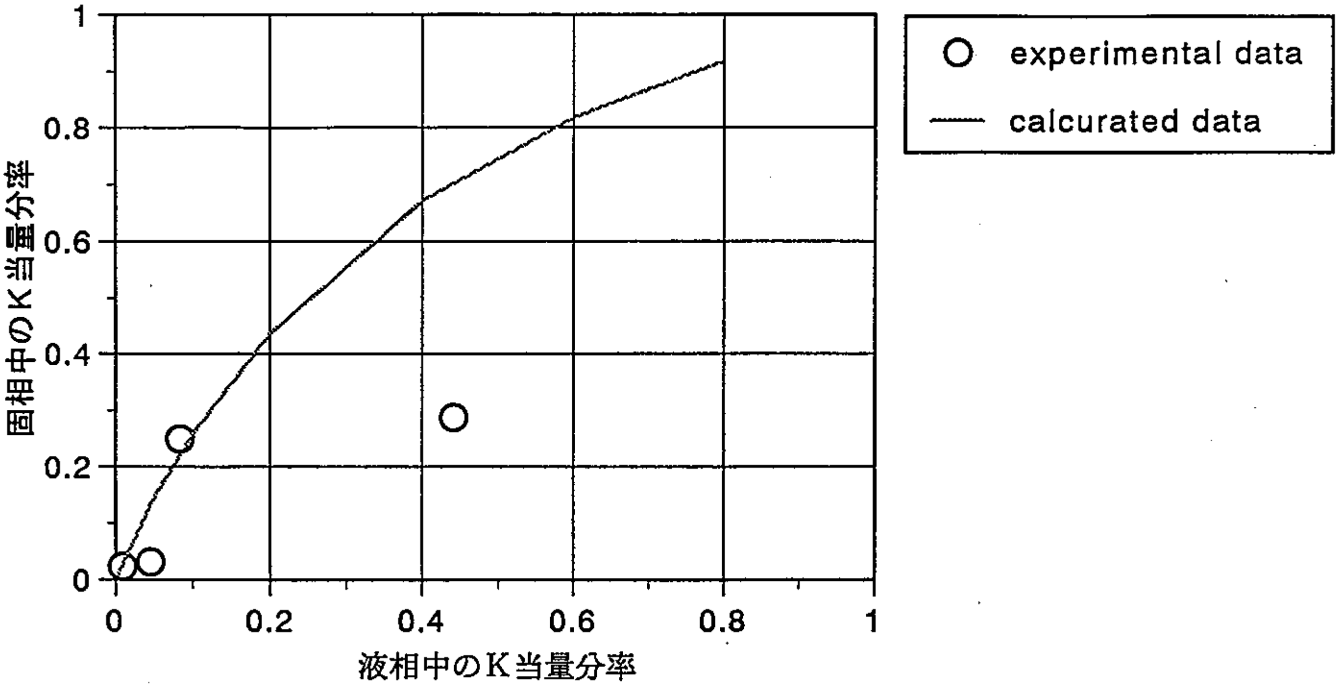

Figure 1.2.1(1) Comparison between estimated data and measured data

(K^+ +H^+ +Na-smectite system , H^+ : 0.001 mol/ℓ constant)

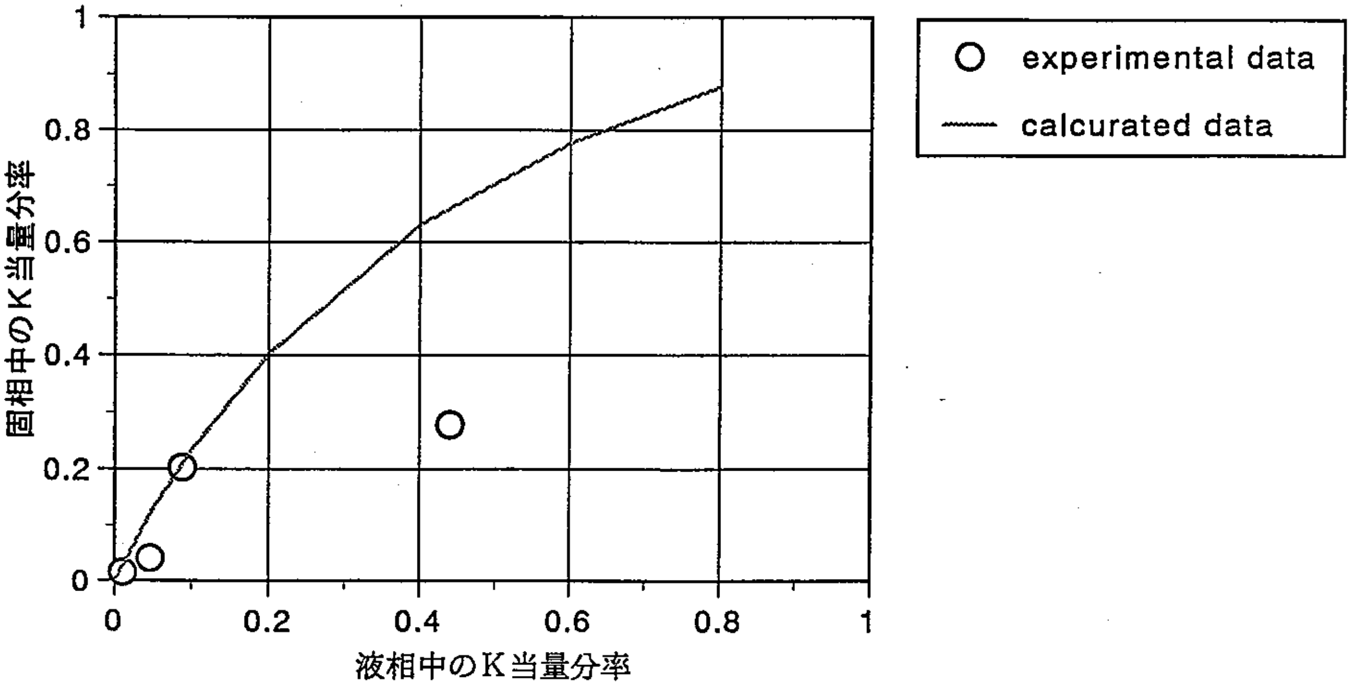

Figure 1.2.1(2) Comparison between estimated data and measured data

(K^+ +H^+ +Na-smectite system , H^+ : 0.005 mol/ℓ constant)

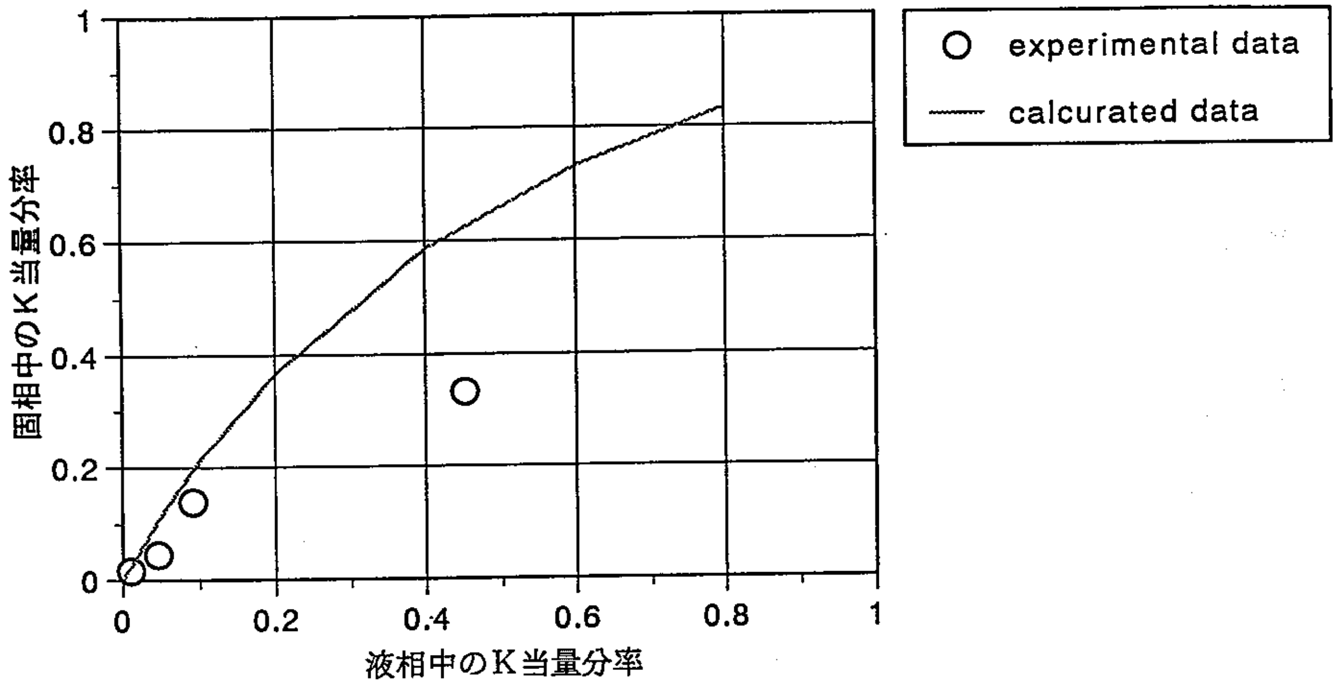

Figure 1.2.1(3) Comparison between estimated data and measured data

(K^{+} +H^{+} +Na-smectite system , H^{+} : 0.01mol/ℓ constant)

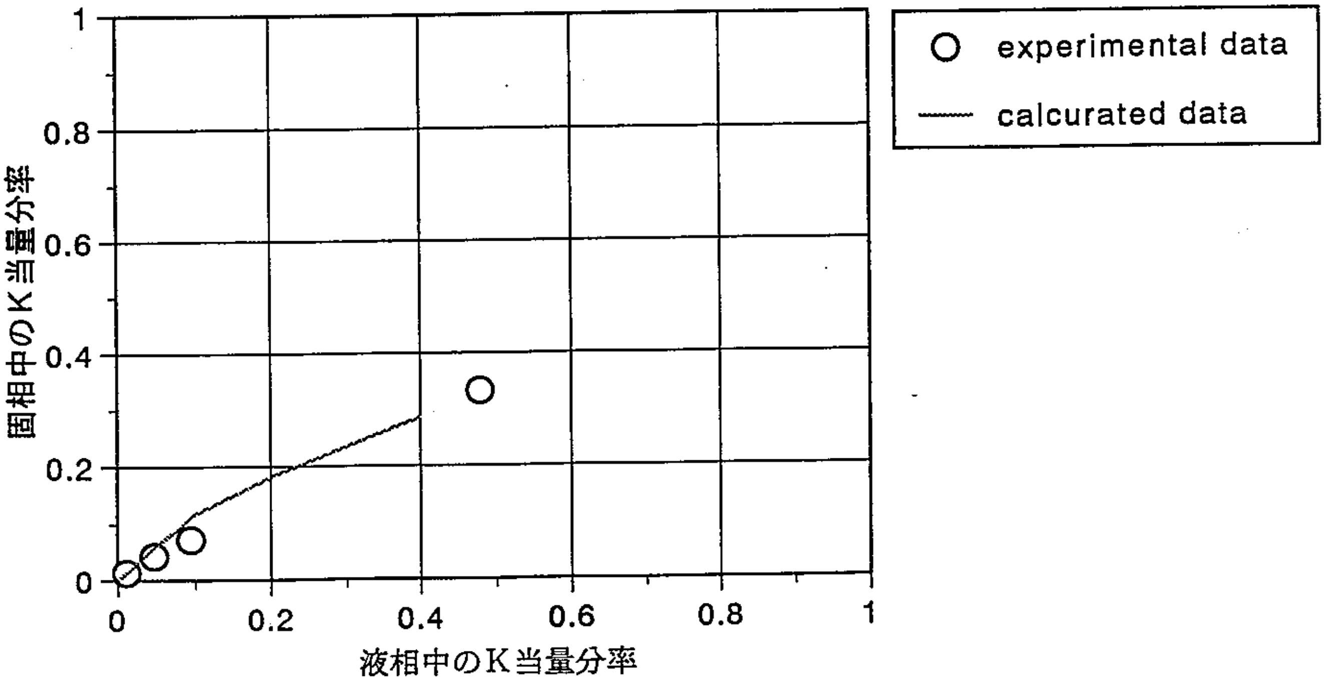

Figure 1.2.1(4) Comparison between estimated data and measured data

(K^{+} +H^{+} +Na-smectite system , H^{+} : 0.05mol/ℓ constant)

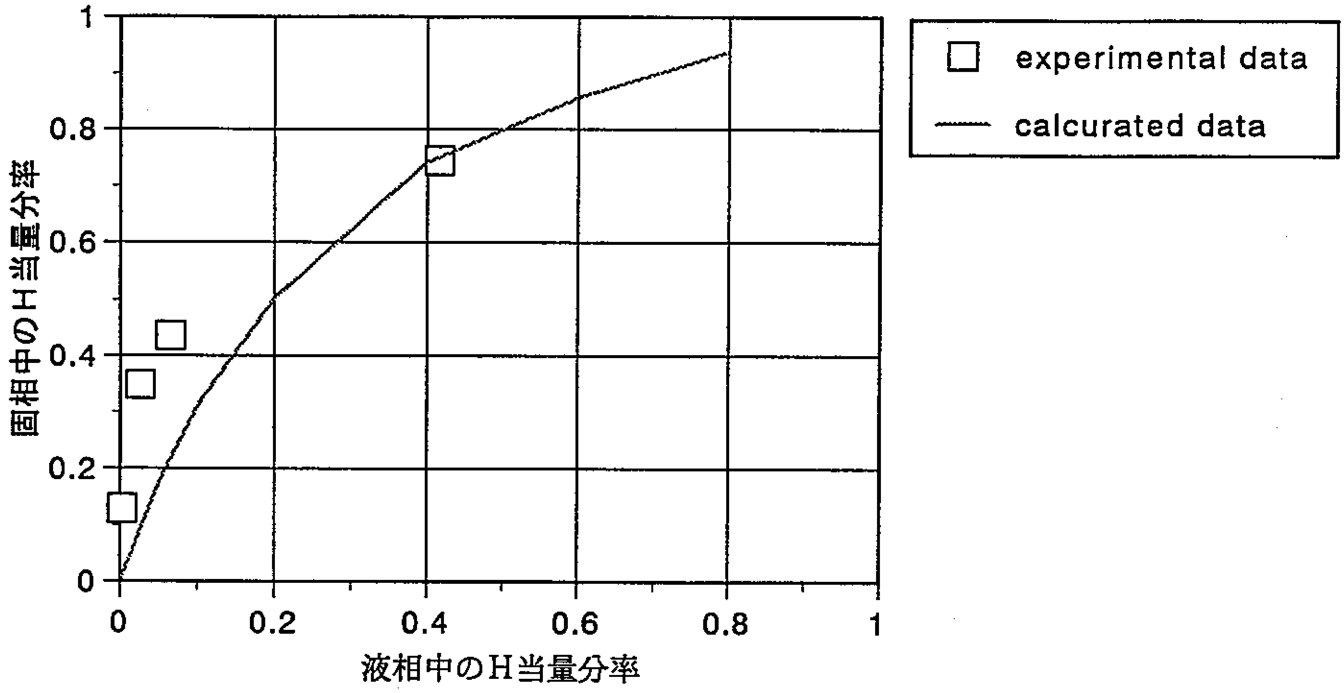

Figure 1.2.1(5) Comparison between estimated data and measured data

(K^+ +H^+ +Na-smectite system , K^+ : 0.001 mol/ℓ constant)

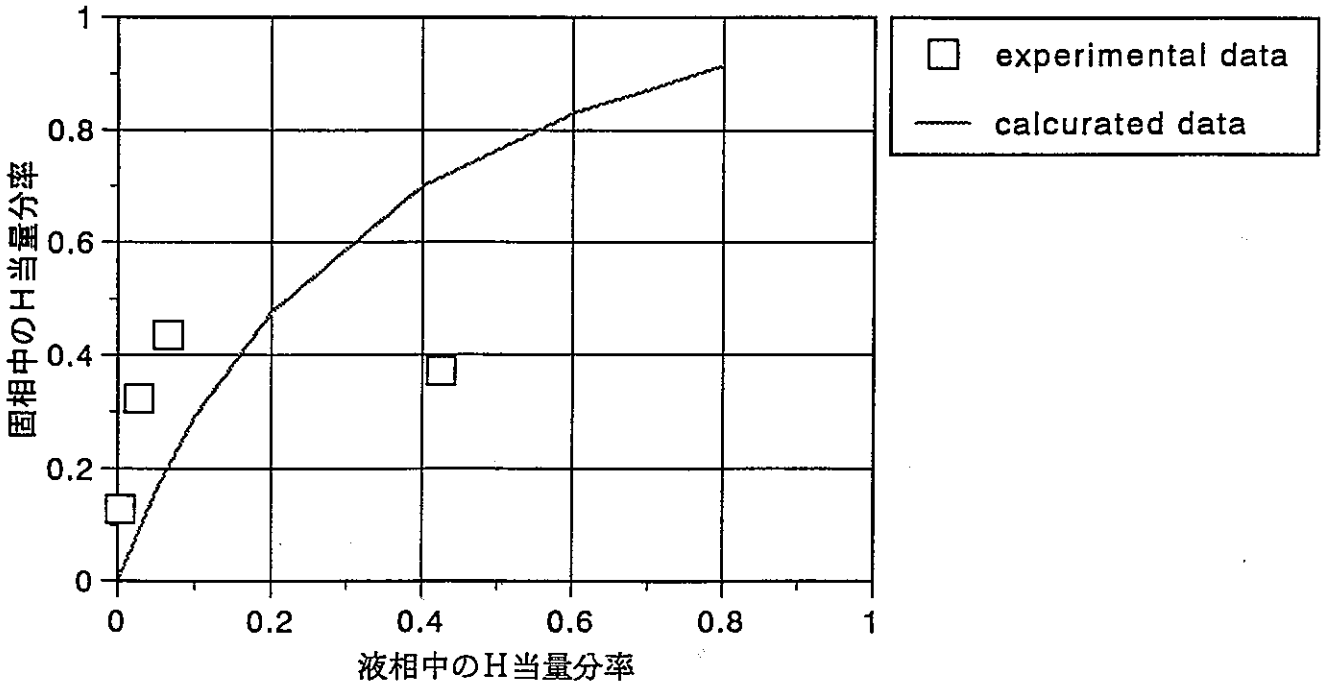

Figure 1.2.1(6) Comparison between estimated data and measured data

(K^+ +H^+ +Na-smectite system , K^+ : 0.005 mol/ℓ constant)

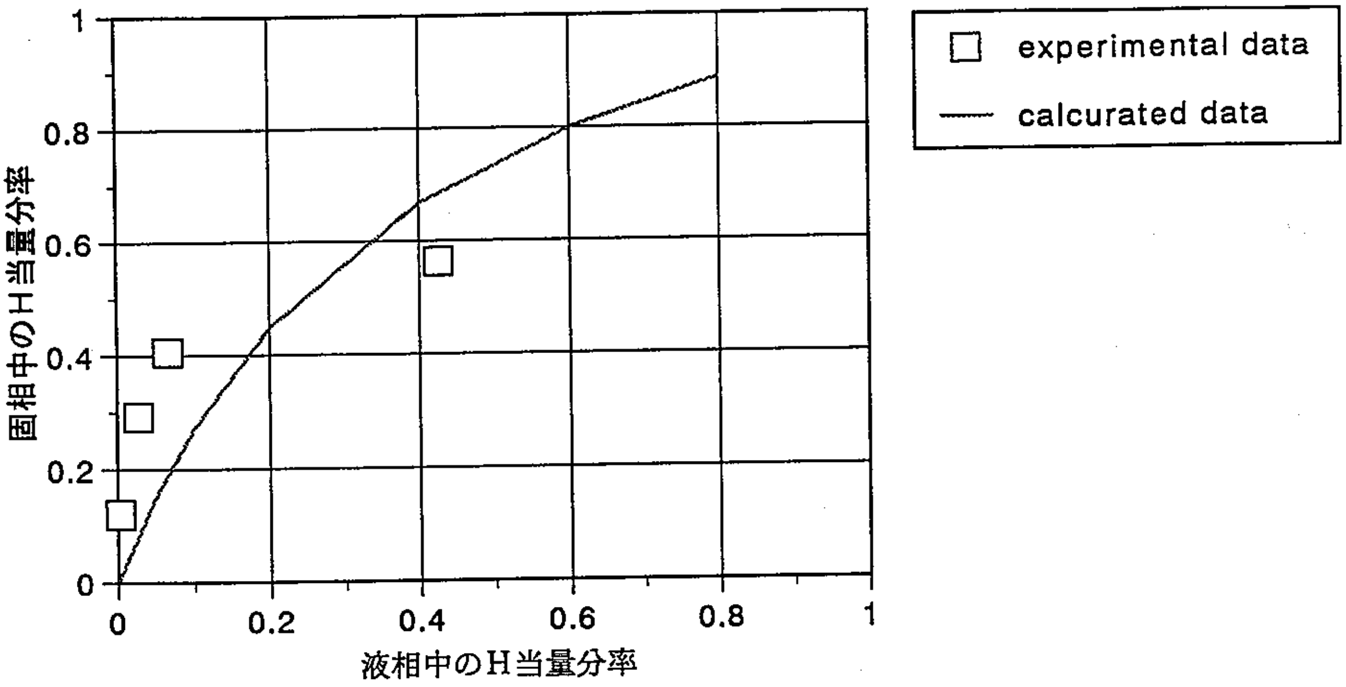

Figure 1.2.1(7) Comparison between estimated data and measured data

(K$^+$ +H$^+$ +Na-smectite system , K$^+$: 0.01mol/ℓ constant)

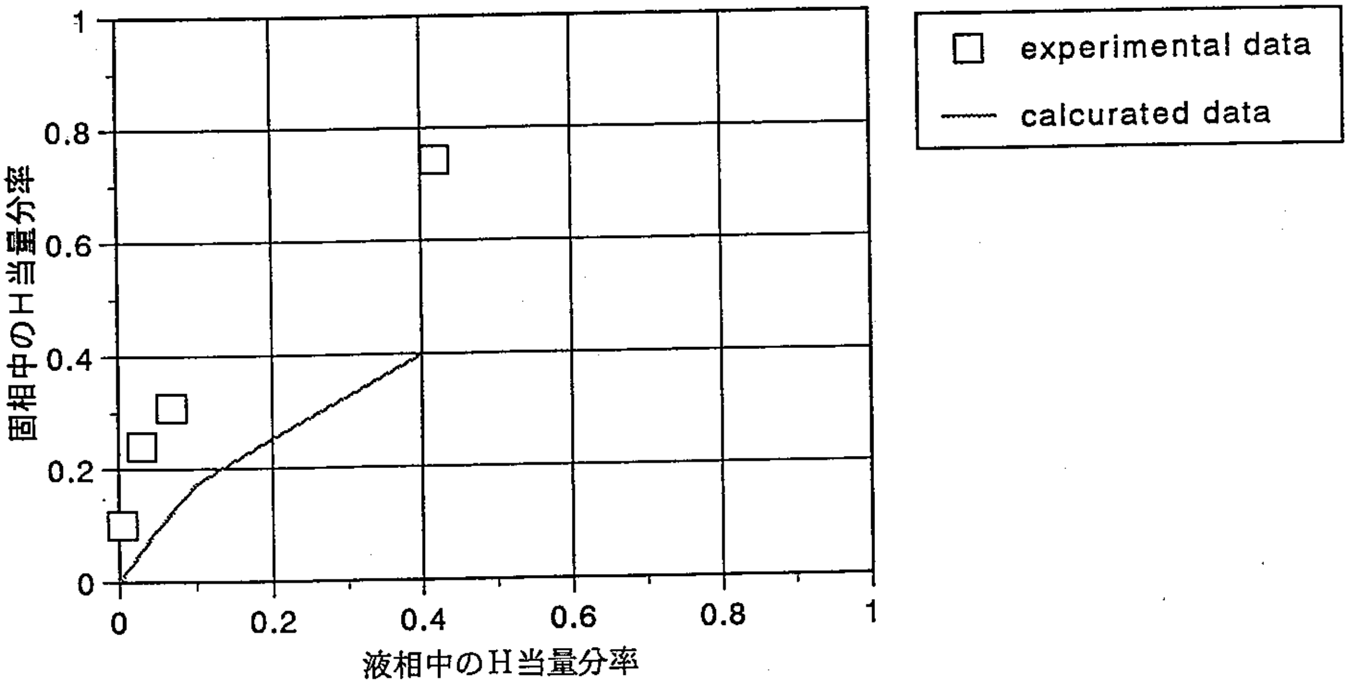

Figure 1.2.1(8) Comparison between estimated data and measured data

(K$^+$ +H$^+$ +Na-smectite system , K$^+$: 0.05mol/ℓ constant)

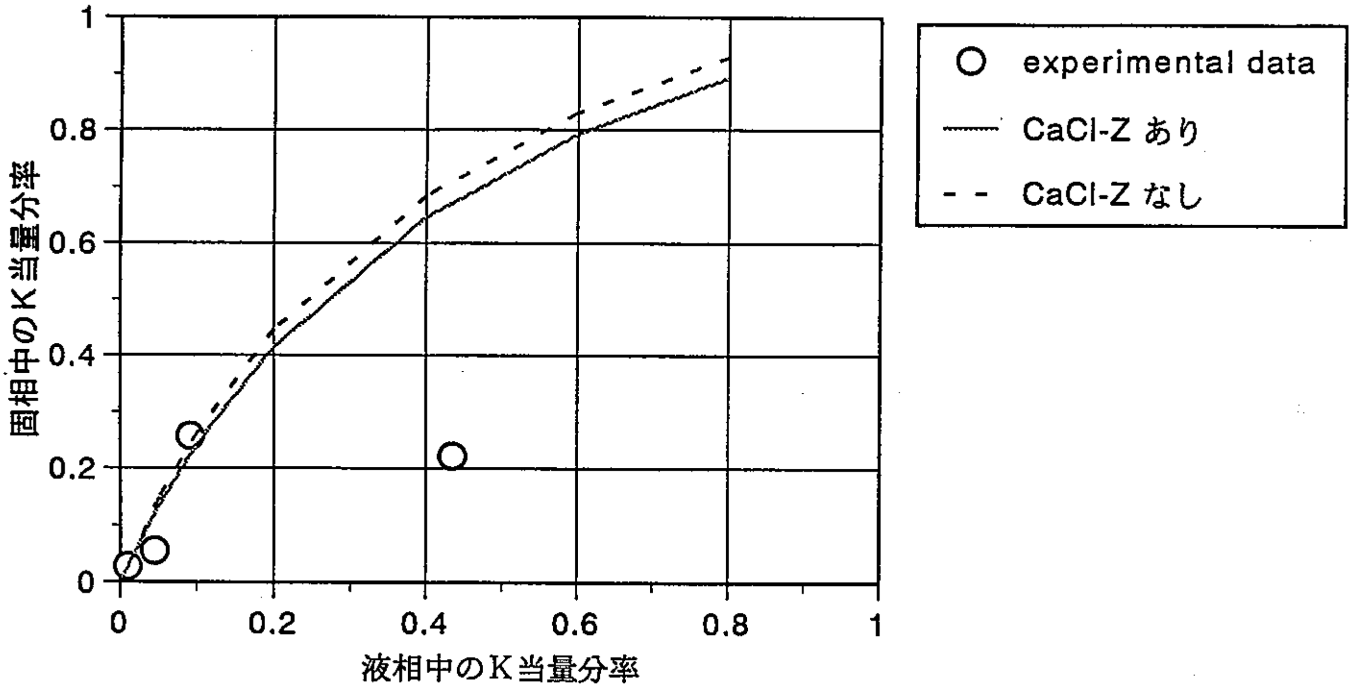

Figure 1.2.2(1) Comparison between estimated data and measured data

(K^+ $+Ca^{2+}$ +Na-smectite system , Ca^{2+} : 0.0005mol/ℓ constant)

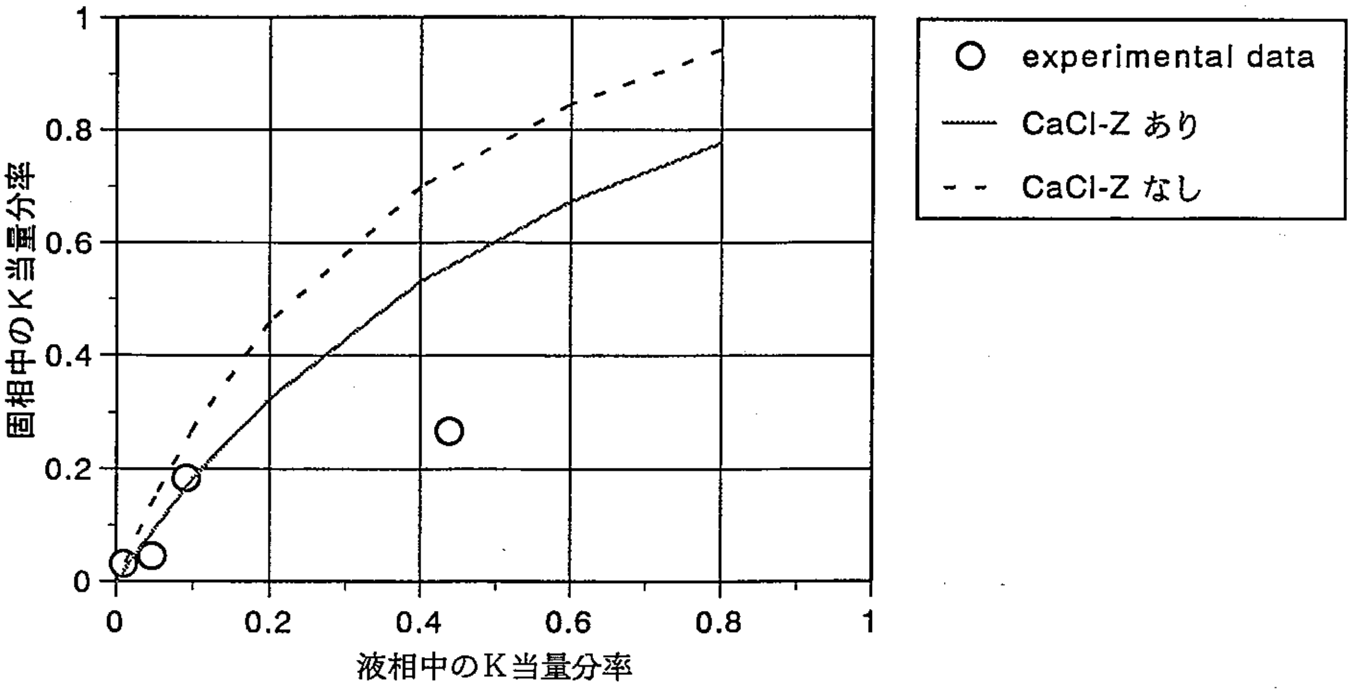

Figure 1.2.2(2) Comparison between estimated data and measured data

(K^+ $+Ca^{2+}$ +Na-smectite system , Ca^{2+} : 0.0025mol/ℓ constant)

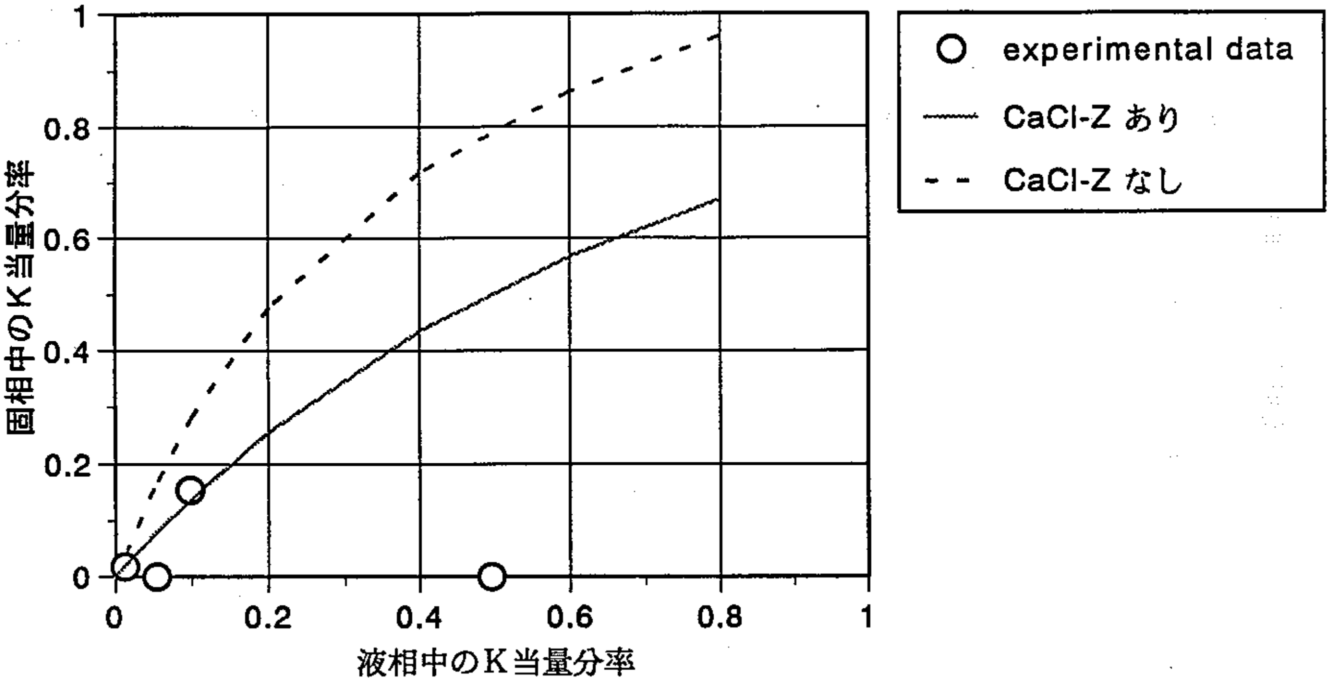

Figure　1.2.2(3)　Comparison between estimated data and measured data

(K^+ +Ca^{2+} +Na-smectite system , Ca^{2+} : 0.005 mol/ℓ constant)

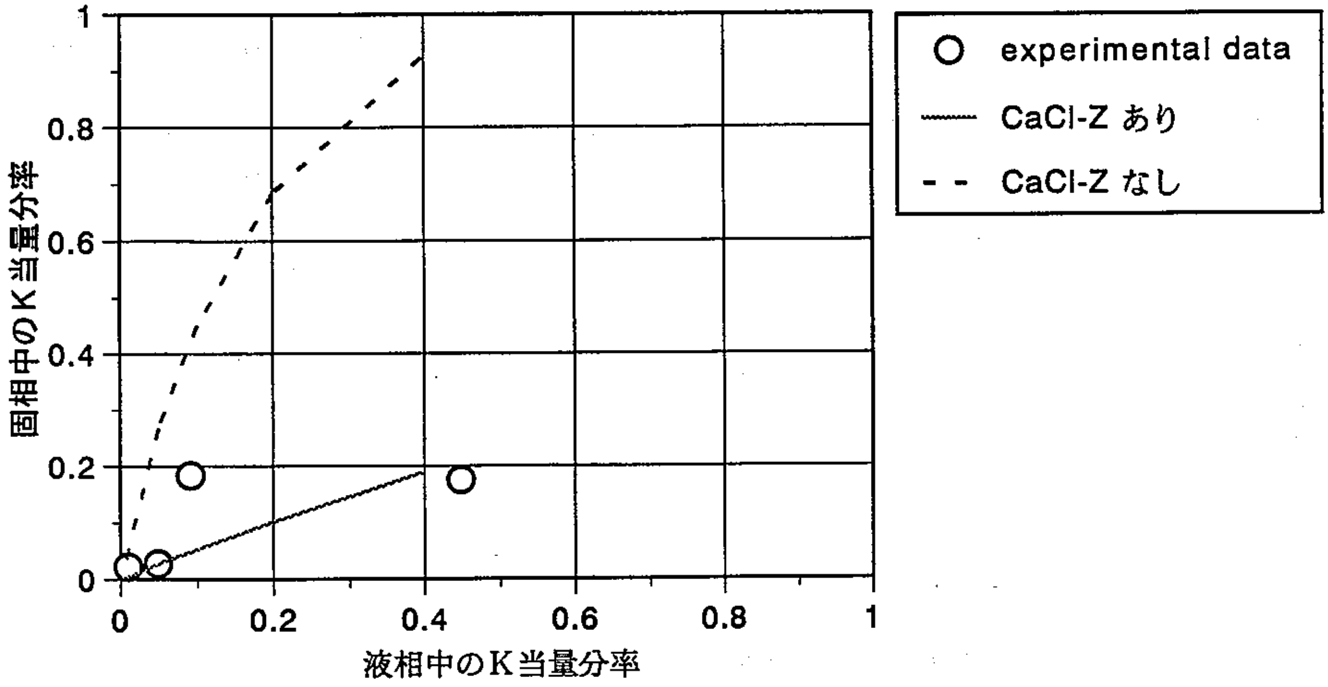

Figure　1.2.2(4)　Comparison between estimated data and measured data

(K^+ +Ca^{2+} +Na-smectite system , Ca^{2+} : 0.025 mol/ℓ constant)

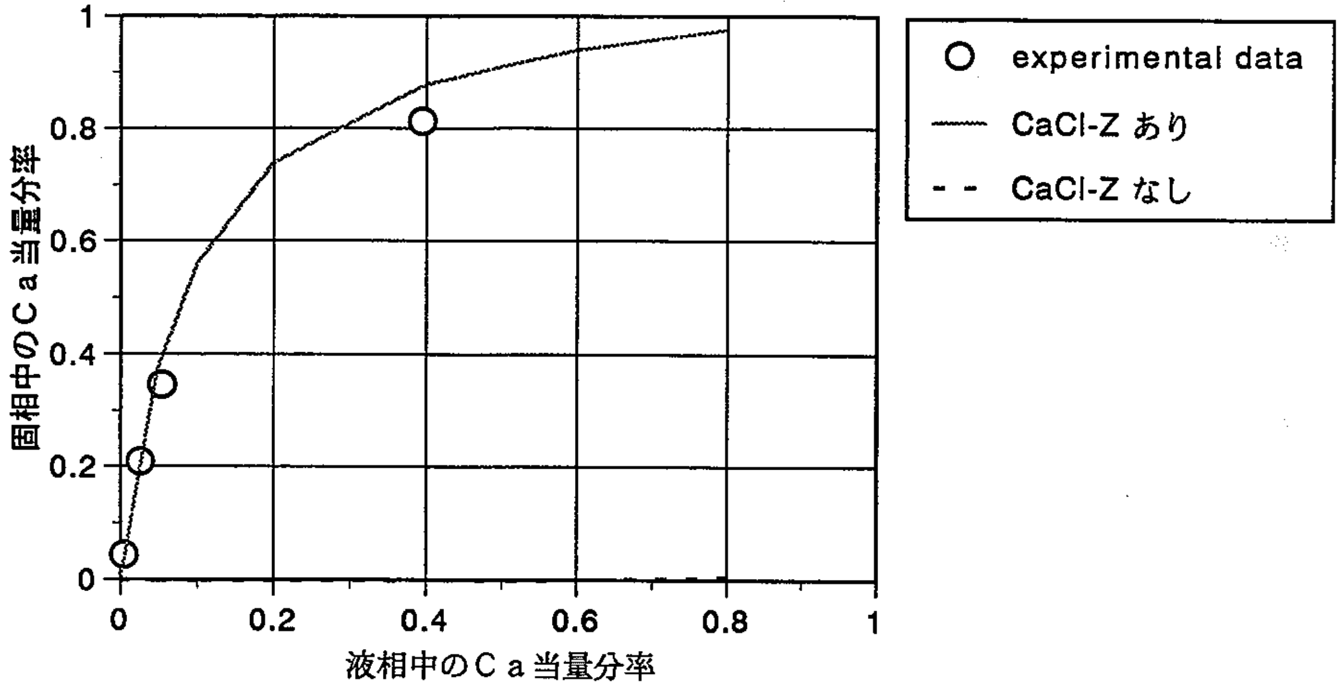

Figure 1.2.2(5) Comparison between estimated data and measured data

(K$^+$ +Ca^{2+} +Na-smectite system , K$^+$: 0.001 mol/ℓ constant)

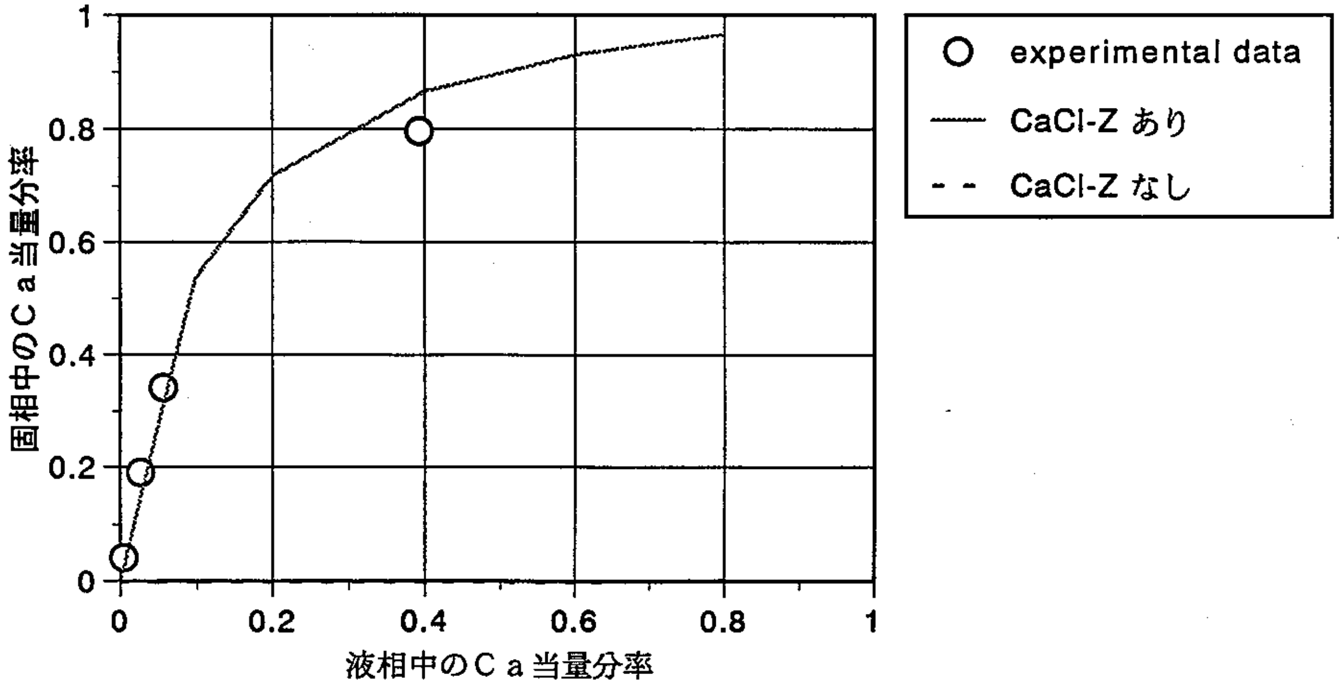

Figure 1.2.2(6) Comparison between estimated data and measured data

(K$^+$ +Ca^{2+} +Na-smectite system , K$^+$: 0.005 mol/ℓ constant)

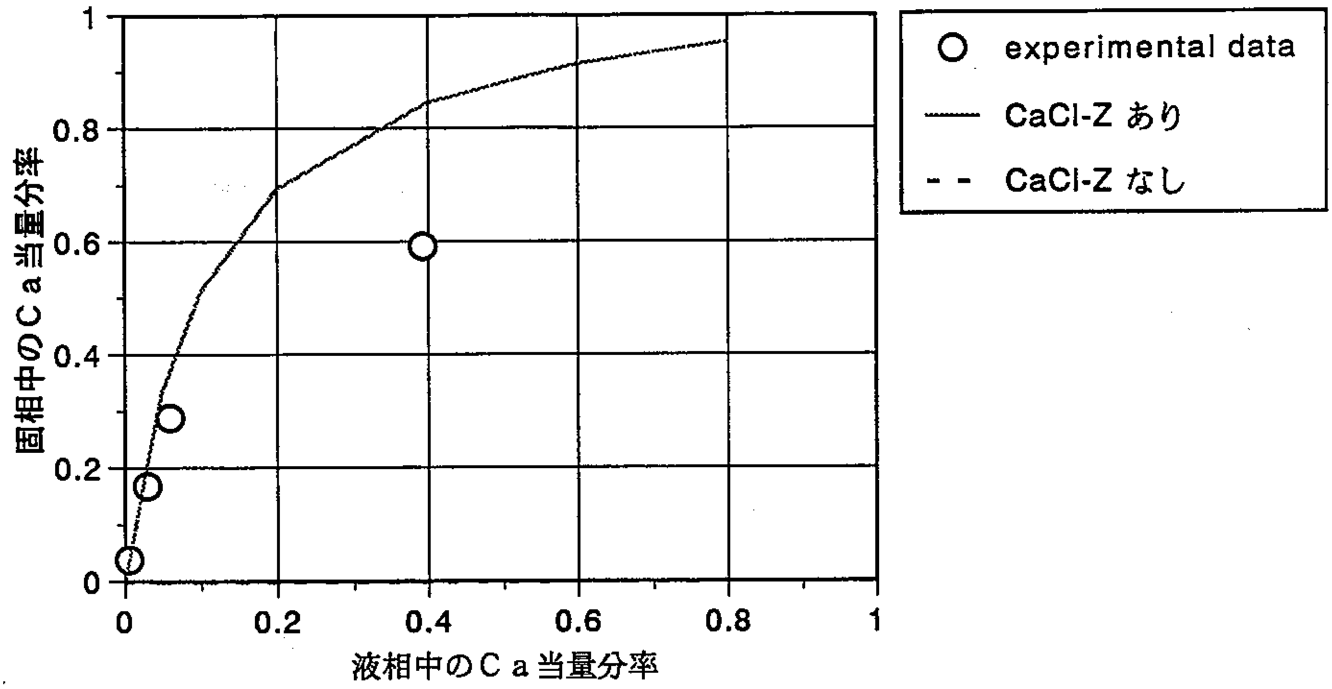

Figure 1.2.2(7) Comparison between estimated data and measured data

(K$^+$ +Ca^{2+} +Na-smectite system , K$^+$: 0.01mol/ℓ constant)

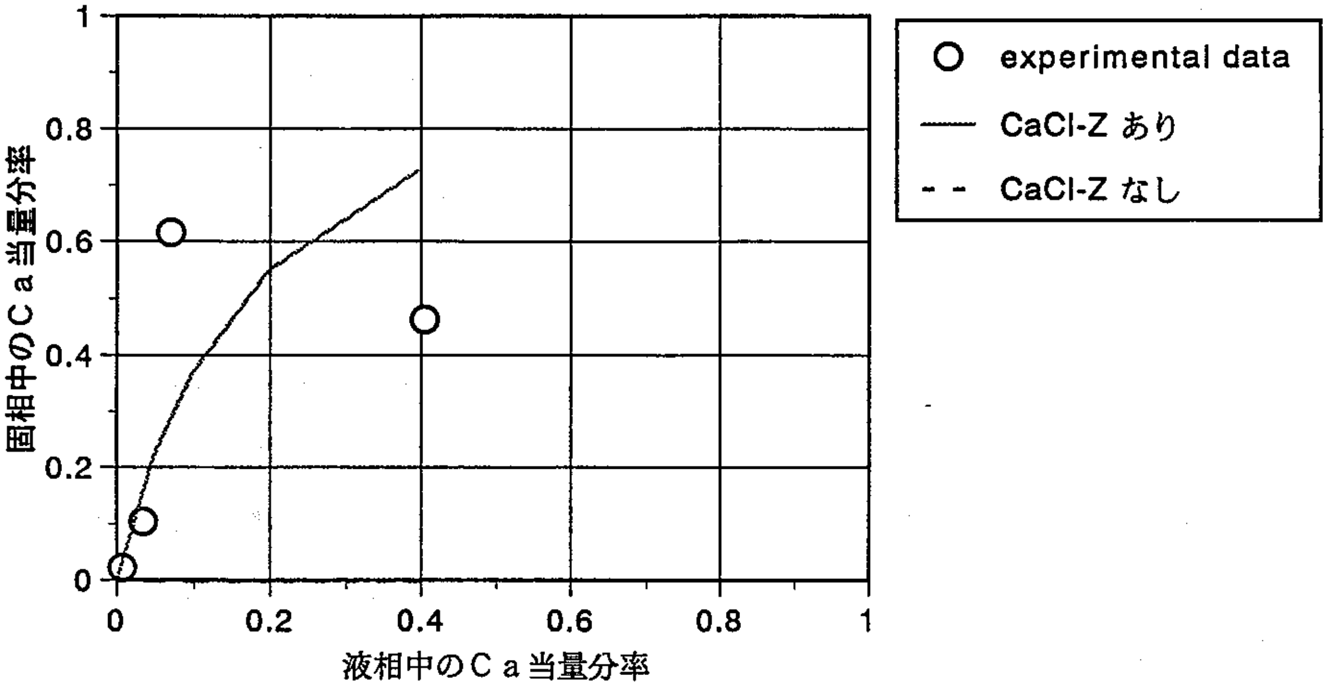

Figure 1.2.2(8) Comparison between estimated data and measured data

(K$^+$ +Ca^{2+} +Na-smectite system , K$^+$: 0.05mol/ℓ constant)

第2章　スメクタイトの表面電気化学的特性に関する研究

本章では、佐々木ら（1995）によるベントナイトと地下水及び蒸留水の反応実験及び小田（1994、1995）による精製Na型スメクタイトの酸／塩基滴定実験のデータの解析を、スイスのMBT 社と共同で行った。解析では拡張Wannerモデルによるシミュレートを行い、拡張Wannerモデルによる予測と実験値の比較を行った。MBT 社からの報告書を巻末資料1に示した。以下にその概要を記述する。

2.1　ベントナイトと蒸留水及び人工地下水の反応のモデリング

実験はすべて佐々木ら（1995）によって行われた。ベントナイトはKunigel-V1、Kunipai-F 及びKunipai-F から精製したNa型スメクタイトである。これらの鉱物組成は佐々木（1995）、Wanner and Wieland（1993）によって詳細に示されている。

ベントナイト—水系における表面の吸着濃度と溶液種の濃度は、イオン交換と表面錯体平衡による拡張Wannerモデルを使って予想できる。すべての特性データは、ワイオミング産ベントナイトのMX-80 により測定されたものである（Wanner, Wersin and Sierro 1992、Wanner et al. 1994、Wieland et al. 1994 ）。Table 1にこのようなパラメータを示す。コンピュータコードは、MINEQLを改良したMIN-SURFコード（Berner 1993 ）である。

2.1.1　クニゲルV1と蒸留水及び人工地下水の反応

Kunigel-V1の鉱物組成とCEC は、佐々木ら（1995）よって得られている。また、溶解性の不純鉱物量は、Wanner and Wieland（1993）、佐々木ら（1995）により得られている。Kunigel-V1の浸出性陽イオンについての報告はあるが、交換性陽イオンの濃度については、明確な報告はない。浸出したCa^{2+}及びMg^{2+}イオンは溶解性の不純物から発生するようなものであるため、イオン交換サイトに存在する初期の陽イオンの割合を次のように推定する。浸出したNa^{+} とK^{+} はイオン交換サイトから発生するものと仮定し、残りの交換サイトはCa^{2+}及びMg^{2+}イオンにより浸出液中の比率に従って占められている。

このようにKunigel-V1と水の反応モデルでは、以下のパラメータが選択された。

人工地下水は、花崗岩と風化が進んだ凝灰岩の2種類の岩石により、蒸留水から作成した。人工地下水の組成は佐々木ら（1995）によって示されている。

(1) Kunigel-V1と蒸留水との反応

(a) 溶液化学種の経時変化の研究

Kunigel-V1には多くの鉱物が含まれている（Table 2参照）。これらは周囲の溶液の化学組成を決定するのに重要である。表面の化学種の溶液との平衡到達時間は、以下仮定によりモデル化した。

① 長石、ゼオライトは無視する。これらの鉱物はTDB データベースに含まれていない。これらの鉱物の溶解速度は遅く、石英やスメクタイトと比較して量的にも少ない。

② すべての条件において、石英、カルサイト、ドロマイトの溶解平衡を仮定する。

③ 黄鉄鉱の溶解反応は時間依存性があり、pH及びSO_4^{2-}を決定する。Kunigel-V1中での黄鉄鉱の量は、0.5 ～0.7 %と報告されている。モデルでは0.6 %とする。

黄鉄鉱の平衡溶液のpHは、明らかに実験よりも低い（Figure 2参照）。黄鉄鉱の溶解反応では、Figure 1に示すような時間依存性を仮定する。

$$FeS_2(s) + 7/2\ O_2 + H_2O = Fe^{2+} + 2SO_4^{2-} + 2H^+ \quad (1a)$$

$$Fe^{2+} + 1/4\ O_2 + H^+ = Fe^{3+} + 1/2\ H_2O \quad (1b)$$

$$Fe^{3+} + 3/2\ H_2O = 1/2\ Fe_2O_3 + 3H^+ \quad (1c)$$

このような放物線的な溶解速度は、モデル計算によっても見ることができる。実験の初期段階では、粒径による影響が優先的に起こる。（Furrer and Stumm 1986）過飽和となり、固相（Fe-(hydr)oxide）が沈澱するかもしれない。沈澱は多分、アモルファスの、Fe-hydroxideか、Fe-oxyhydroxide であるだろう。沈澱に対する知識がない場合、沈澱は安定なものと仮定しなければならない。放出されるプロトン量は、実際にはモデルと一致しない。

④ CO_2 ガスの分圧は実験開始の段階で$10^{-3.5}$atm である。モデルでは、平衡時間中、この状態は保たれない。pCO_2は初期のプロトン濃度と炭酸化した化学種として扱い、一定には保たれない。

⑤ 実験温度に関する情報がないため、25℃一定と仮定する。

酸化される黄鉄鉱の時間変化をFigure 1に示す。Kunigel-V1の蒸留水による反応は、拡張Wannerモデルで表される。溶液の組成をTable 3に示す。

pH、Na^+、SO_4^{2-}、DIC（CO_3^{2-} +HCO_3^-）濃度の経時変化をFiguer 3からFiguer 6に示す。これらは黄鉄鉱の共存溶液である。

pHは、黄鉄鉱の酸化反応からインプットされるH^+濃度、及びカルサイト、ドロマイト、スメクタイトのイオン交換サイトと表面OH^-基との反応により決定される。

Na^+はKunigel-V1のNa^+から発生し、もともと存在するイオンはスメクタイト層のサイト上に存在する。Na^+の濃度はイオン交換反応により決定され、モデルでよく説明している。

硫酸塩は主に黄鉄鉱の溶解により供給され、$CaSO_4$となる。$CaSO_4$からの反応はない。

炭酸塩濃度については、満足な一致が得られていない。この原因は、CO_2ガス分圧の時間変化が無視されたためと考えられる。

DIC濃度の推定では、炭酸化学種の総量は一定に保持される。また、$10^{-3.5}$atmのCO_2ガスの分圧の一定により、初期のpHは低く推定されている。

Table 1: Parameters of the extended Wanner model used in the present evaluation of bentonite-water interaction (specific surface interaction database)

Surface species	$\log_{10} K^\circ$	Reference
Surface site master species: Z^-		(ion exchange database)
ZNa	20.0	Wanner (1986)
ZK	20.26	Fletcher and Sposito (1989)
Z_2Mg	40.13*	Wanner, Wersin and Sierro (1992)
Z_2Ca	40.21*	Wanner, Wersin and Sierro (1992)
ZH	23.0	Wieland et al. (1994)
Surface site master species: SOH		(intrinsic database)
SOH_2^+	5.4	Wanner et al. (1994)
SO^-	–6.7	Wanner et al. (1994)
Surface site density: 2.84×10^{-5} mol/g		

* after conversion to the mole fraction model

Table 2: Composition and other specific parameters of Kunigel-V1 used in the evaluation of Kunigel-V1-water interaction.

Parameters	Kunigel-V1	Reference
Minerals:		
smectite	46 - 49 %	Sasaki et al. (1995)
quartz	29 - 38 %	Sasaki et al. (1995)
calcite	2.1 - 2.6 %	Sasaki et al. (1995)
dolomite	2.0 - 3.8 %	Sasaki et al. (1995)
pyrite	0.5 - 0.7 %	Sasaki et al. (1995)
feldspar*	2.7 - 5.5 %	Sasaki et al. (1995)
zeolite*	3.0 - 3.5 %	Sasaki et al. (1995)
Soluble impurities:		
NaCl	0.001 %	Wanner and Wieland (1993)
KCl	0.004 %	Wanner and Wieland (1993)
$CaSO_4$	0.38 %	Wanner and Wieland (1993)
Cation exchange parameters:		
CEC	60.1 meq/100g	Sasaki et al. (1995)
exchangable Na^+	85.36 % **	estimation (this study)
exchangable K^+	1.48 % **	estimation (this study)
exchangable Mg^{2+}	2.28 % **	estimation (this study)
exchangable Ca^{2+}	10.88 % **	estimation (this study)

* Not considered in the model.

** These values are calculated from the amount of leachable cations reported by Sasaki et al. (1995).

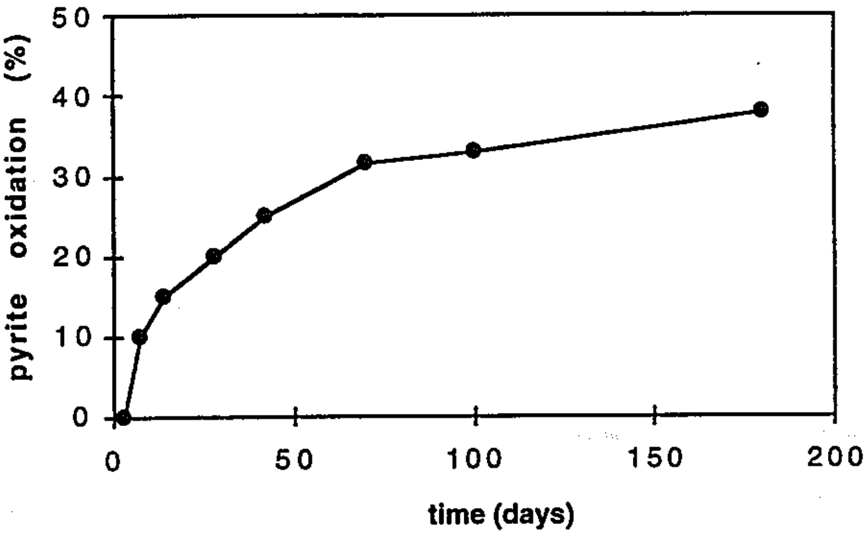

Figure 1 Modeled time-dependence of pyrite dissolution in the experiments with Kunigel-V1 (model developed according to experimental observations, cf. Figure 3).

Table 3: Chemical components and their input concentrations used to model the interaction of Kunigel-V1 with distilled water. Here, complete dissolution of pyrite is assumed; incomplete dissolution of pyrite is modeled according to Figure 1.

Component	contribution from solution (mol/L)	contribution from Kunigel-V1 (mol/L)	total conc. (mol/L)
Ca^{2+}	0	6.06×10^{-3}	6.06×10^{-3}
Mg^{2+}	0	6.85×10^{-4}	6.85×10^{-4}
Na^{+}	0	5.13×10^{-2}	5.13×10^{-2}
K^{+}	0	9.48×10^{-4}	9.48×10^{-4}
Fe^{3+}	5.00×10^{-3} *	0	5.00×10^{-3} *
H^{+}	5.03×10^{-3} **	0	5.03×10^{-3} **
SOH	0	2.84×10^{-3}	2.84×10^{-3}
CO_3^{2-}	1.27×10^{-4}	0	1.27×10^{-4}
Cl^{-}	0	7.78×10^{-5}	7.78×10^{-5}
SO_4^{2-}	1.00×10^{-2} *	2.79×10^{-3}	1.28×10^{-2}
$H_2SIO_4^{2-}$	0	0	0
Z^{-}	0	6.01×10^{-2}	6.01×10^{-2}

* from pyrite oxidation (see text)

** from pyrite oxidation and protonation of the carbonate ion (see text)

(b) 大気及び大気のない系における溶液のスペシエーション

Kunigel-V1に含まれる黄鉄鉱の影響を調べるため、佐々木ら（1995）は大気中と大気のない系において浸出試験を行った。Figure 2からFigure 6に示した大気中でのデータは、拡張Wannerモデルによる解析結果と比較するためものである。

大気のない系でのデータはFigure 7及びFigure 8に示し、拡張Wannerモデルによる解析結果と比較した。黄鉄鉱の酸化によるパラメータ以外、解析に使用したパラメータはTable 3に示した。以下の2つのシナリオを仮定した。

① 炭酸塩とプロトンの濃度は、それぞれ1.27×10^{-5}mol/ℓと2.53×10^{-5}mol/ℓである。蒸留水のpHは、CO_2 ガス平衡により5.67である。（model A）

② ①の場合と比較するため、酸素のない系とする。CO_2 ガスは存在する。（pCO_2は$10^{-3.5}$atm）（model B）

実験値とモデルによるpHの比較は、pCO_2のようなプロトンに影響するパラメータについても比較に含まれる。実験系でのpCO_2は、0から$10^{-3.5}$atm の間である。

佐々木ら（1995）によって測定されたSO_4^{2-} 濃度は、モデルによる値よりも低い。計算によるSO_4^{2-} 濃度（223.5ppm）は、Kunigel-V1に含まれる$CaSO_4$ の溶解によるものである。言い換えれば、黄鉄鉱の酸化による影響はない。Kunigel-V1の不純鉱物により、溶液中のSO_4^{2-} 濃度は最低223.5ppmとなる。佐々木ら（1995）データは、$CaSO_4$ の溶解を示しているのかもしれない。

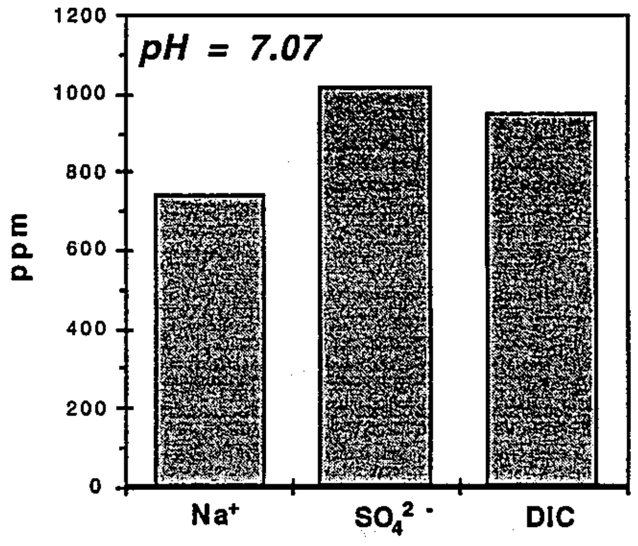

Figure 2 Calculated values of pH, and Na^+, SO_4^{2-}, and DIC concentration for the Kunigel-V1/water system, assuming complete oxidative dissolution of the pyrite present.

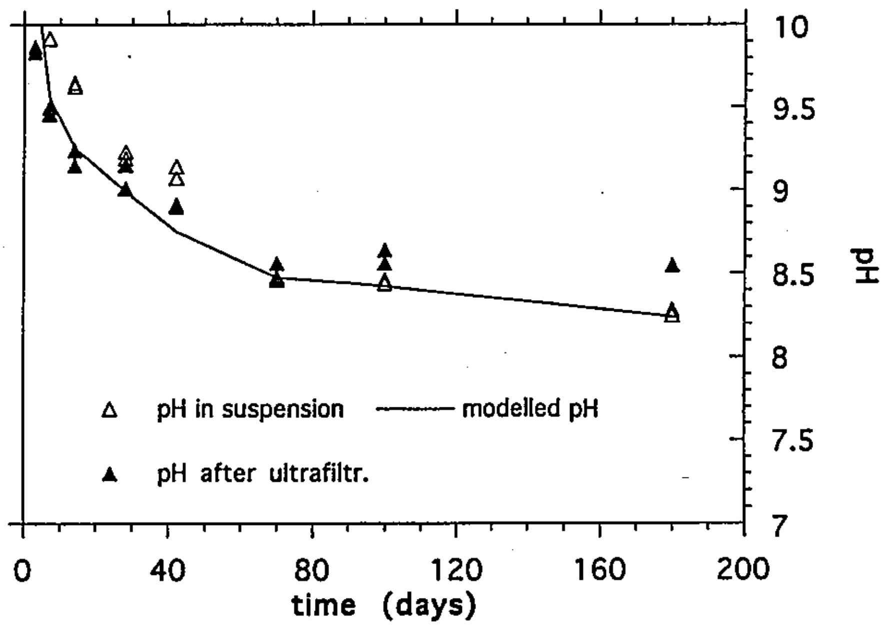

Figure 3 Development of pH during the interaction of Kunigel-V1 with water. Modeled pH values are compared with experimental data measured in suspension and after separation of solid and liquid phase by ultrafiltration (Sasaki, 1993; and Sasaki et al., 1995).

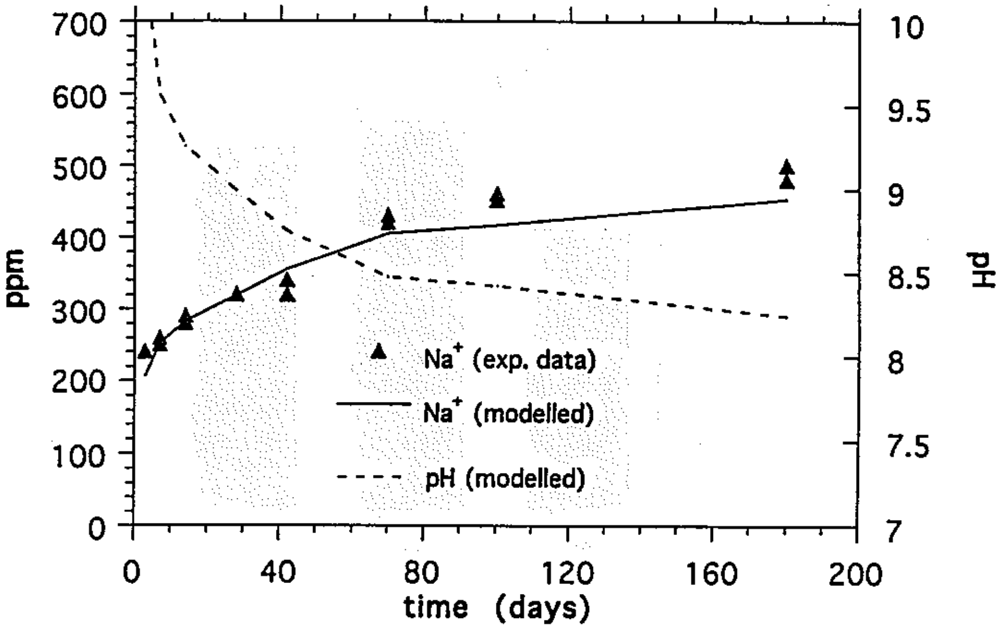

Figure 4 Development of Na^+ concentration during the interaction of Kunigel-V1 with water. Modeled pH values are shown for reference.

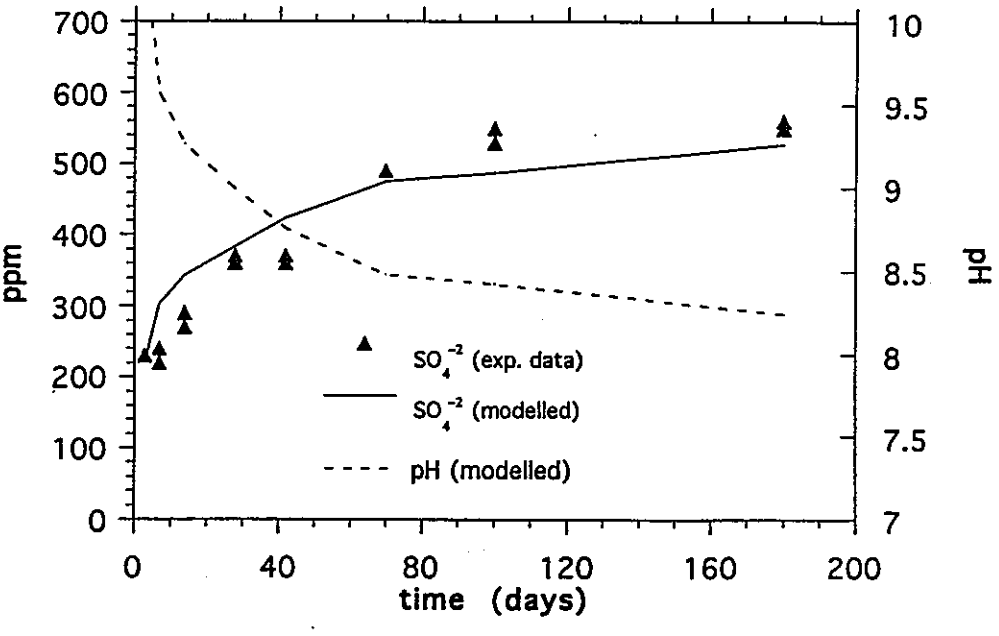

Figure 5 Development of SO_4^{2-} concentration during the interaction of Kunigel-V1 with water. Modeled pH values are shown for reference.

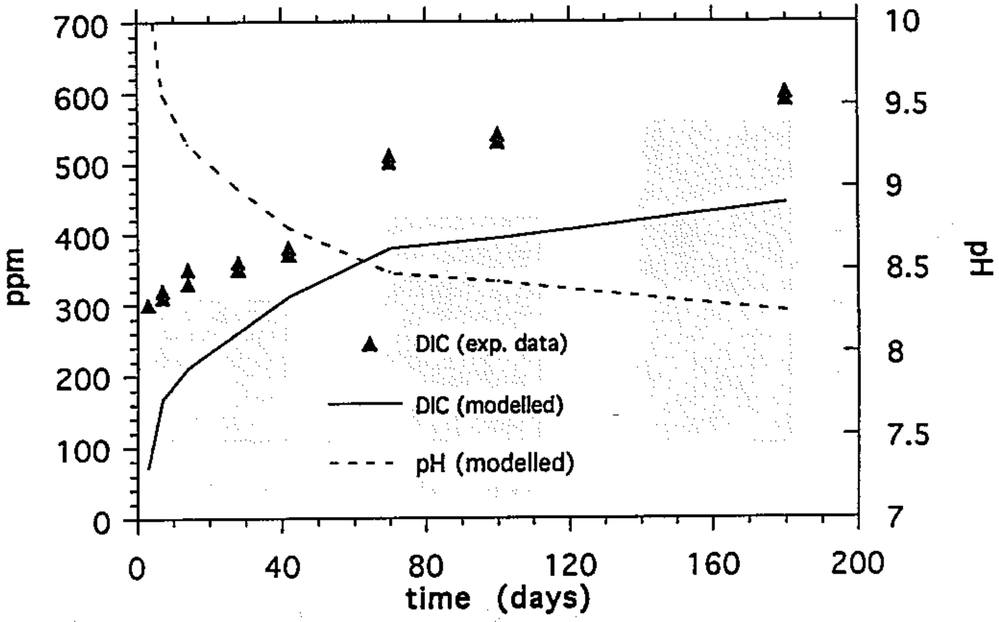

Figure 6 Development of (CO_3^{2-} + HCO_3^-) concentration, termed “dissolved inorganic carbon” (DIC), during the interaction of Kunigel-V1 with water. Modeled pH values are shown for reference.

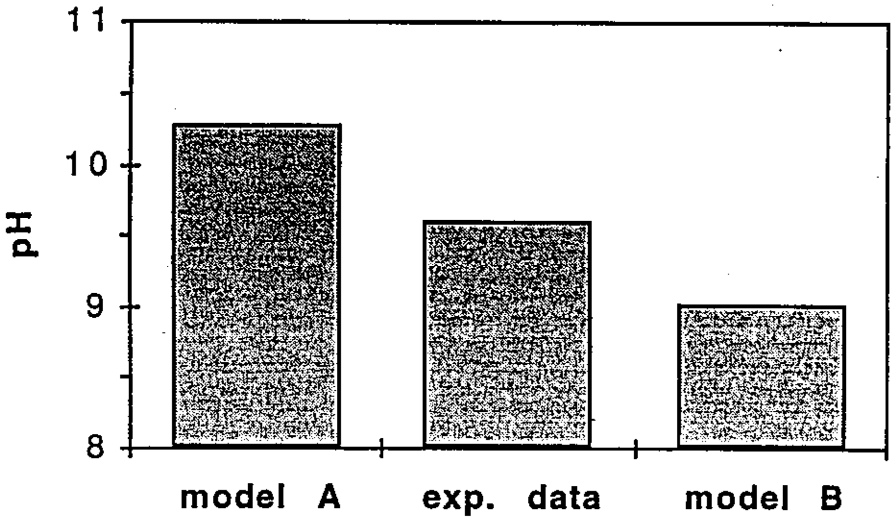

Figure 7 The pH measured in the anaerobic Kunigel-V1/water system in comparison with calculated pH values in anaerobic systems closed (model A) and open (model B) with respect to atmospheric CO_2.

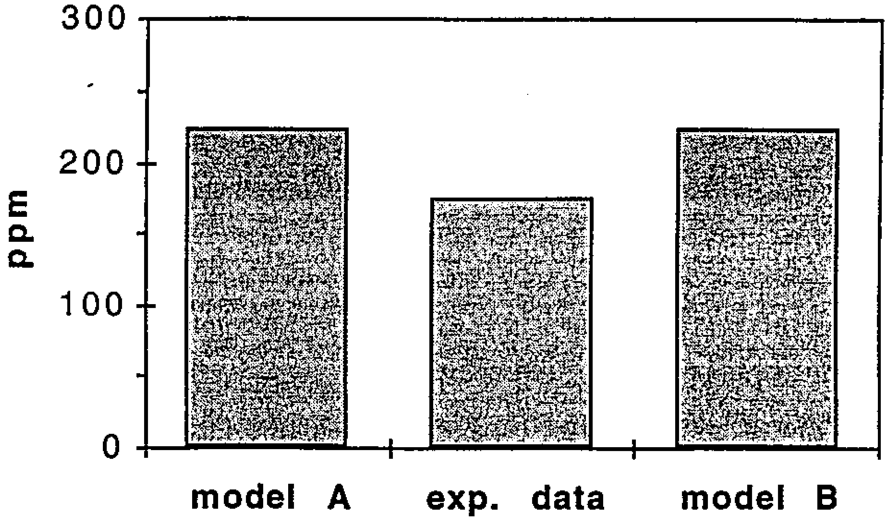

Figure 8 The SO_4^{2-} concentration measured in the anaerobic Kunigel-V1/water system in comparison with calculated SO_4^{2-} concentrations in anaerobic systems closed (model A) and open (model B) with respect to atmospheric CO_2.

(2) Kunigel-V1と人工地下水の反応

実験に使用された人工地下水は、２種類の岩石浸出液である。花崗岩と風化の進んだ凝灰岩である。それぞれ地下水Ａ（GWA ）と地下水Ｂ（GWB ）とする。

Kunigel-V1の溶解によるプロトンの量は、MIN-SURFによって計算される。スペシエーションのプログラムであるMINEQLのインプットデータとして、佐々木ら（1995）により示されているGWA とGWB のpH及び組成が使用されている。

(a) 花崗岩からの浸出液の反応（GWA ）

モデルは、蒸留水の場合と同じである。pHを正確に推定するため、CO_2 ガス分圧は$10^{-3.5}$atm に固定した。この値は、Kunigel-V1／蒸留水系において、黄鉄鉱の25％が酸化されたことを仮定したものである（$10^{-3.308}$ atm）。化学組成をTable 4に示す。

実験データは、GWA の組成とKunigel-V1の溶解性不純鉱物から拡張Wannerモデルを使って説明される（Figure 9）。モデルによって過剰に推定されたMg^{2+}濃度は、ドロマトの部分溶解によるものである。

(b) 凝灰岩からの浸出液の反応（GWB ）

Kunigel-V1とGWA の反応モデルと同じである。インプット濃度をTable 5に示す。実験データと拡張Wannerモデルによる計算値は、GWA と同様に一致した。（Figure10）実験において、ドロマイトは完全に溶解していないようである。

Table 4: Chemical components used to model the interaction of Kunigel-V1 with GWA. Dissolution of 25 % of the pyrite present is assumed.

Component	contribution from GWA (mol/L)	contribution from Kunigel-V1 (mol/L)	total (mol/L)
Ca^{2+}	1.95×10^{-4}	6.06×10^{-3}	6.26×10^{-3}
Mg^{2+}	8.20×10^{-6}	6.85×10^{-4}	6.93×10^{-4}
Na^{+}	1.70×10^{-4}	5.13×10^{-2}	5.15×10^{-2}
K^{+}	1.20×10^{-4}	9.49×10^{-4}	1.07×10^{-3}
Fe^{3+}	1.25×10^{-3} *	0	1.25×10^{-3} *
H^{+}	1.96×10^{-3} **	0	1.96×10^{-3} **
SOH	0	2.84×10^{-3}	2.84×10^{-3}
CO_3^{2-}	5.08×10^{-4}	0	5.08×10^{-4}
Cl^{-}	7.30×10^{-5}	7.78×10^{-5}	1.51×10^{-4}
SO_4^{2-}	2.51×10^{-3} *	2.79×10^{-3}	5.30×10^{-3}
$H_2SIO_4^{2-}$	9.60×10^{-5}	0	9.60×10^{-5}
Z^{-}	0	6.01×10^{-2}	6.01×10^{-2}

CO_2(g) partial pressure set equal to 3.16×10^{-5} atm

* from 25 % pyrite oxidation (see text)

** from 25 % pyrite oxidation and available protons in GWA (see text)

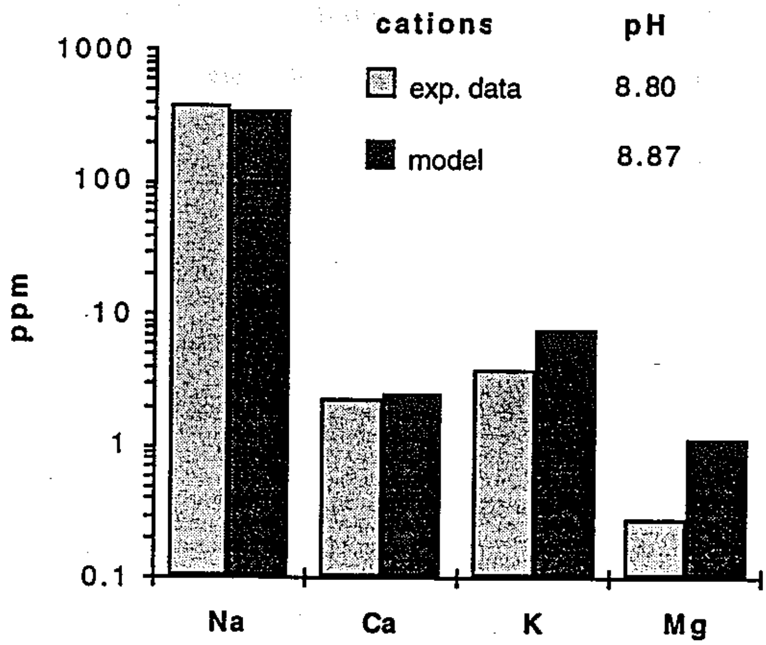

Figure 9 The interaction of Kunigel-V1 with GWA.

Table 5: Chemical components used to model the interaction of Kunigel-V1 with GWB. Dissolution of 25 % of the pyrite present is assumed.

Component	contribution from GWB (mol/L)	contribution from Kunigel-V1 (mol/L)	total (mol/L)
Ca^{2+}	6.00×10^{-3}	6.06×10^{-3}	1.21×10^{-2}
Mg^{2+}	6.20×10^{-4}	6.85×10^{-4}	1.31×10^{-3}
Na^{+}	1.48×10^{-3}	5.13×10^{-2}	5.28×10^{-2}
K^{+}	4.60×10^{-4}	9.49×10^{-4}	1.41×10^{-3}
Fe^{3+}	1.25×10^{-3} *	0	1.25×10^{-3} *
H^{+}	1.74×10^{-3} **	0	1.74×10^{-3} **
SOH	0	2.84×10^{-3}	2.84×10^{-3}
CO_3^{2-}	1.60×10^{-5}	0	1.60×10^{-5}
Cl^{-}	1.70×10^{-4}	7.78×10^{-5}	2.48×10^{-4}
SO_4^{2-}	1.08×10^{-2} *	2.79×10^{-3}	1.36×10^{-2}
$H_2SIO_4^{2-}$	1.05×10^{-4}	0	1.05×10^{-4}
Z^{-}	0	6.01×10^{-2}	6.01×10^{-2}

CO_2(g) partial pressure set equal to 3.16×10^{-4}atm

* from 25 % pyrite oxidation (see text)
** from 25 % pyrite oxidation and available protons in GWB (see text)

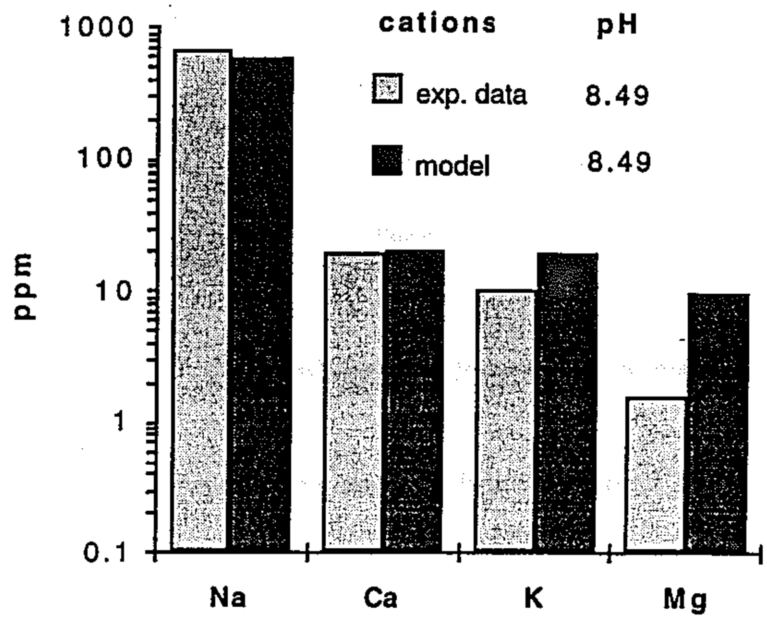

Figure 10 The interaction of Kunigel-V1 with GWB.

(3) 固液比による蒸留水とKunigel-V1の反応

2.1.1節に記述したモデルを使って、Kunigel-V1と蒸留水の固液比による影響を調べた。CO_2 ガス分圧は$10^{-3.5}$atm 一定とした。Figure 1 に示すように、180 日の平衡期間において、黄鉄鉱の38%が溶解するものと仮定した。黄鉄鉱の溶解に対する水／ベントナイト比による影響は無視した。

Figure11に示すように、Na^+ とDIC 濃度は水／ベントナイト比の広い範囲に渡って実験値とよく一致した。ベントナイトが多い領域では、モデルによるDIC 濃度は低かった。

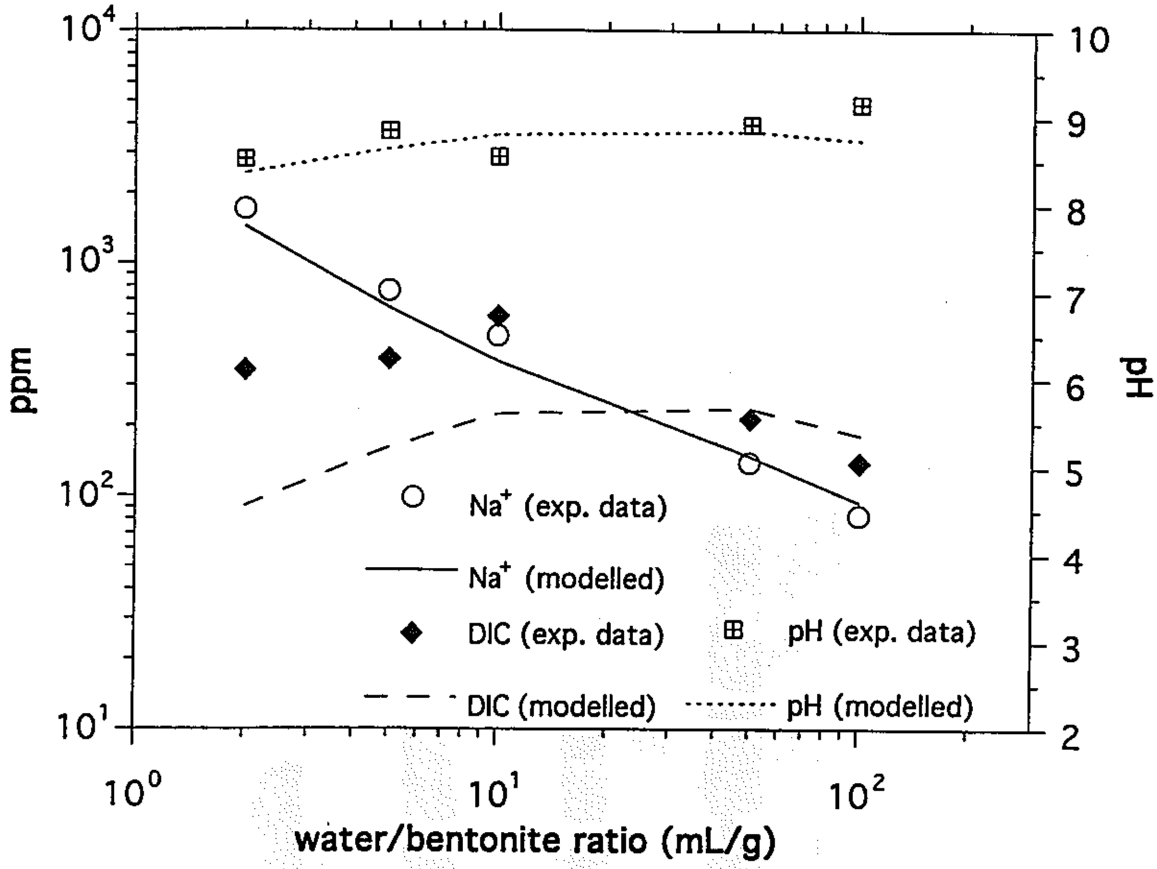

Figure 11 Interaction of Kunigel-V1 with distilled water as a function of the water/bentonite ratio.

2.1.2　Kunipia-F と蒸留水の反応

Kunipia-F の鉱物組成は、芦田ら（1994）及び佐々木ら（1995）により得られている。溶解性の不純鉱物は、Wanner and Wieland (1993) によるものである。CEC やLayer サイトにおける交換性陽イオンは、矢島（1993）により得られている。

モデル計算に使用したパラメータをTable 6に示す。

また、以下に一般的な仮定を示す。

① モデル系では、常に石英、カルサイトと平衡になる。

② モデル系の固相は、溶液と平衡にある。

③ 佐々木ら（1995）による実験値と同じ時間で比較する。平衡時間を14日間とする。

CO_2 ガス分圧に対する詳細な情報がないため、大気系と大気のない系でKunigel-V1と蒸留水の反応について解析した場合と同様に２つのシナリオを考えた。

① 炭酸とプロトン濃度は、それぞれ1.27×10^{-5}mol/ℓと2.53×10^{-5}mol/ℓである。
蒸留水のpHは、CO_2 ガス平衡により5.67である。（model A）

② ①の場合と比較するため、酸素のない系とする。CO_2 ガスは存在する。
（pCO_2は$10^{-3.5}$atm）（model B）

佐々木ら（1995）による実験データと計算値を比較した結果を、Figure12からFigure15に示した。SO_4^{2-} 及びDIC 濃度については、実験値と拡張Wannerモデルによる計算値は非常による一致した。大気系では、モデルのpHは低い。大気、スメクタイト及びカルサイトと平衡系では、カルサイト－CO_2 －水の反応によりpHが決定されるため、イオン交換反応の影響があることに注意しなければならない。CO_2 ガスとカルサイトが平衡状態にある場合、モデル計算によりDIC 及びNa^+ 濃度を正確に予想できることから、pHも正確に予想できるものと思われる。

Table 6: Composition and other specific parameters of Kunipia-F used in the evaluation of Kunipia-F/water interaction.

Parameters	Kunipia-F	Reference
Minerals:		
smectite	99 %	Ashida et al. (1994)
quartz	traces	Sasaki et al. (1995)
calcite	traces	Sasaki et al. (1995)
Soluble impurities:		
NaCl	0.071 %	Wanner and Wieland (1993)
KCl	0.005 %	Wanner and Wieland (1993)
$CaSO_4$	0.694 %	Wanner and Wieland (1993)
Cation exchange parameters:		
CEC	108 meq/100g	Yajima (1993)
exchangable Na^+	97.1 %	Yajima (1993)
exchangable K^+	0.9 %	Yajima (1993)
exchangable Mg^{2+}	1.3 %	Yajima (1993)
exchangable Ca^{2+}	0.7 %	Yajima (1993)

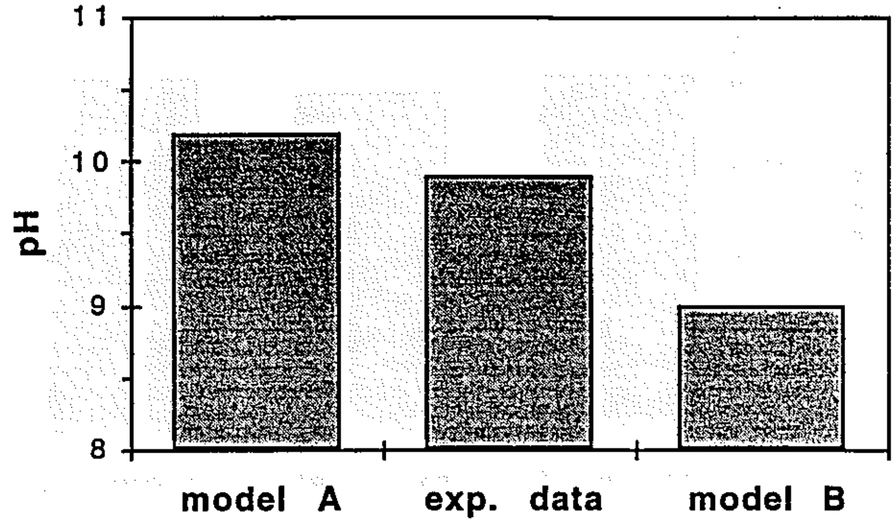

Figure 12 Interaction of Kunipia-F with distilled water. Predicted pH values assuming a system closed (model A) or open (model B) with respect to atmospheric CO_2 are compared with experimental data.

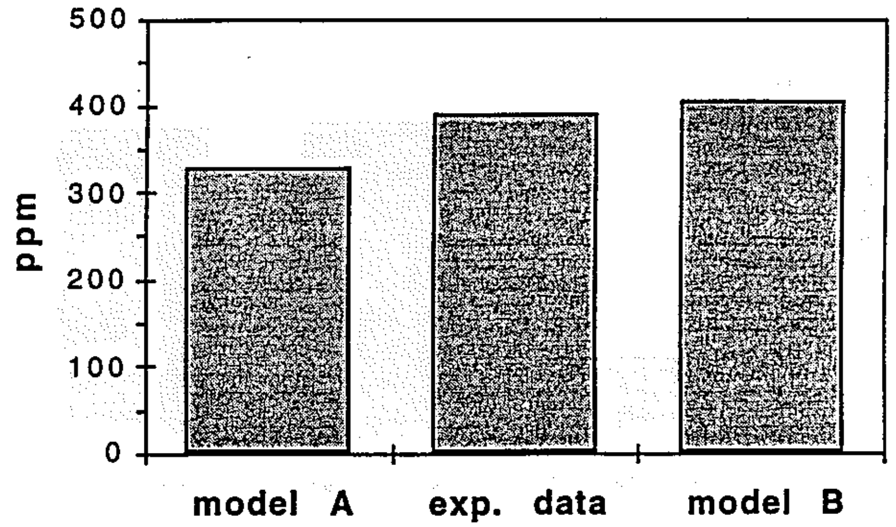

Figure 13 Interaction of Kunipia-F with distilled water. Na^+ concentrations predicted assuming a system closed (model A) or open (model B) with respect to atmospheric CO_2 are compared with experimental data.

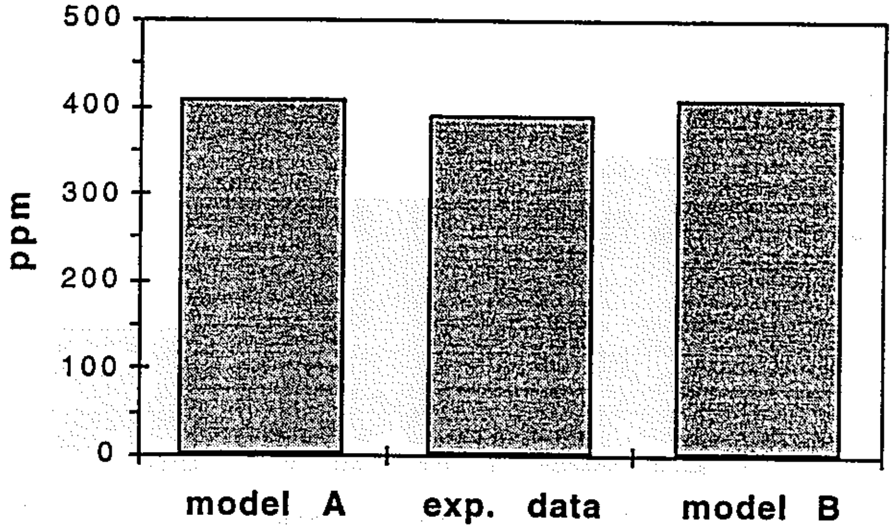

Figure 14 Interaction of Kunipia-F with distilled water. SO_4^{2-} concentrations predicted assuming a sytsem closed (model A) or open (model B) with respect to atmospheric CO_2 are compared with experimental data.

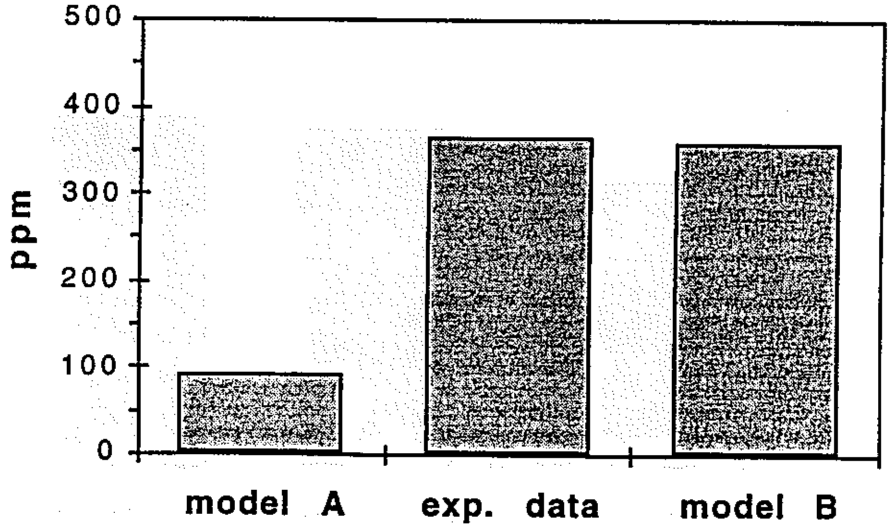

Figure 15 Interaction of Kunipia-F with distilled water. DIC concentrations predicted assuming a system closed (model A) or open (model B) with respect to atmospheric CO_2 are compared with experimental data.

2.1.3　精製Na型スメクタイトと蒸留水の反応

蒸留水中での精製Na型スメクタイトの反応を、Table 7に示すパラメータを使って解析した。

佐々木ら（1995）は、精製Na型スメクタイトに既知量のカルサイトを添加してpHを測定することにより、Kunigel-V1／水系でのpHの解析を試みた。実験結果と拡張Wannerモデルによる計算結果の比較をTable 8に示した。

佐々木ら（1995）によるカルサイト4％のpH測定値は、拡張Wannerモデルによる計算値と一致する。しかし、カルサイトがない場合、インプットにおけるプロント濃度は5.00×10^{-2}mol/ℓと仮定される。しかし、カルサイトがある場合、この濃度ではpHは過少評価となる。

拡張Wannerモデルでは、Kunigel-V1、Kunipia-F、精製Na型スメクタイト／カルサイト、ワイオミング産ベントナイトのMX-80のそれぞれの系において、pHとともに溶液化学種を推定することができる（Wanner et al. 1994、Wieland et al. 1994）。

カルサイトがない精製Na型ベントナイトのpHが実験値と計算値が相違するのは、実験において充分に緩衝されないことが考えられる。また、精製Na型ベントナイトの精製方法によっても実験誤差となる（小田 1994、1995、佐々木ら 1995）。

Table 7: Composition and other specific parameters of purified Na-smectite used in the evaluation of Na-smectite/water interaction.

Parameters	Na-smectite	Reference
Minerals:		
smectite *	100 %	assumption (this study)
Cation exchange parameters		
CEC	108.1 meq/100g	Wanner and Wieland (1993)
exchangable Na^+	100 %	Wanner and Wieland (1993)

* Since no detailed analysis of the mineralogy of this material is available as yet, we assume only smectite to be present.

Table 8: Interaction of purified Na-smectite (with and without added calcite) with distilled water. Both open and closed systems are considered in the model calculations.

calcite added	model assumption	pH	Reference
experimental data:			
-	-	6.00	Sasaki et al. (1995)
4 % $CaCO_3$	-	9.50	Sasaki et al. (1995)
model:			
-	A *	10.50	this study
-	B *	8.72	this study
-	C *	6.00	this study
-	D *	6.00	this study
4 % $CaCO_3$	B *	9.25	this study
4 % $CaCO_3$	C *	6.50	this study
4 % $CaCO_3$	D *	8.19	this study
calcite equilibrium	B *	9.25	this study

* The assumptions made regarding the input of H^+ and CO_2 are as follows:
A: initial input of 1.27×10^{-5} mol/L CO_3^{2-} and 2.53×10^{-5} mol/L H^+, closed system.
B: system open with respect to atmospheric CO_2, i.e., $pCO_2 = 10^{-3.5}$ atm, no further input of H^+ and CO_2.
C: 5.00×10^{-2} mol/L H^+ and 1.27×10^{-5} mol/L CO_3^{2-} added, closed system.
D: 5.00×10^{-2} mol/L H^+ added, $pCO_2 = 10^{-3.5}$ atm.

2.2　スメクタイト表面の酸／塩基特性の検討

佐々木ら（1995）及び小田（1994、1995）による精製Na型スメクタイトの化学的特性については、すでに2.1節で記述した。精製Na型スメクタイトとプロトンの反応を調べるため、小田（1994、1995）はバッチ式の滴定試験を行った。イオン強度条件は0.001 mol/ℓ（NaCl）である。

2.2.1　プロトンのバランス計算

小田（1994、1995）の滴定データは、プロトンのバランスを計算することによって説明される。モンモリロナイト表面のH^+及びOH^-の濃度（simple oxides のケースにおけるH^+とOH^-による表面電荷の部分）は、H^+及びOH^-濃度の平衡状態から、H^+もしくはOH^-を加えた場合のpH変化から計算できる。

$$\Delta〔\mathrm{H}^+〕 = \frac{C_A - C_B - 〔\mathrm{H}^+〕 + 〔\mathrm{OH}^-〕 - C}{a} \qquad 〔\mathrm{mol/g}〕 \qquad (2a)$$

もしくは

$$\Delta〔\mathrm{H}^+〕 = \frac{〔\mathrm{H}^+〕_t - 〔\mathrm{H}^+〕 + \dfrac{K_w}{〔\mathrm{H}^+〕} - C}{a} \qquad 〔\mathrm{mol/g}〕 \qquad (2b)$$

ここで　$〔\mathrm{H}^+〕_t$ ：（$=C_A - C_B$）総プロトン濃度〔mol/dm³〕
$〔\mathrm{H}^+〕$ ：溶液中のフリープロトン濃度
K_w ：水のイオン積
C ：プロトン消費サイド反応のための補正ファクター
a ：初期の溶液濃度　〔g/dm³〕
$C_A - C_B$ ：加えた塩基か酸の濃度〔mol/dm³〕

$\Delta〔\mathrm{H}^+〕$は表面におけるプロトン濃度、C_A及びC_Bは、加えられた酸もしくは塩基の濃度〔mol/dm³〕である。溶液の濃度C_s〔g/dm³〕は以下の式により算出される。

$$C_s = \frac{V_0\ a}{V_0 + V} \qquad 〔\mathrm{g/dm^3}〕 \qquad (3)$$

初期液量V_0に比べて酸及び塩基の量は非常に小さい（$V_0 >> V$）ため、希釈による影響は無視できる（$C_s \fallingdotseq a$）。

Cは、溶液中に存在するAlとSiによるプロトンの消費に対する補正係数である。

プロトンバランスの補正係数は(2a)及び(2b)式で与えられる。プロトンの消費は、Alの水酸化物とアルカリ領域での$Si(OH)_4$の生成によるものである。酸性領域では、Alの水酸化物（$=Al(OH)_m{}^{3-m}$）の寄与により以下の式となる。

$$C=\sum_{m=0}^{3}(3-m)\,\beta_{1,m}\,\alpha_H\,[Al]_t\,[H^+]^{-m}\quad[mol/\ell]\qquad(4a)$$

Alの総溶解量は、$\alpha_H=(1+\beta_{1,1}[H^+]^{-1}+\beta_{1,2}\,\alpha_H\,[H^+]^{-2}+\beta_{1,3}[H^+]^{-3}+\beta_{1,4}\,\alpha_H\,[H^+]^{-4})^{-1}$である。

アルカリ領域では、$Al(OH)_4{}^-$の生成及び$Si(OH)_4$によるプロントの消費により、以下の式となる。

$$C=\beta_{1,4}\,\alpha_H\,[Al]_t\,[H^+]^{-4}+K_1[Si]_t\,[H^+]^{-1}[mol/\ell]\quad(4b)$$

ここで、$[Si]_t$はSiの総溶解量である。Alの水和定数$\beta_{1,m}$は、Baes and Mesmer（1976）により得られている。ケイ素酸の定数K_1は、Grenthe et al.（1992）によって得られている。

$Si(OH)_4$による消費は、プロトンのバランスの補正に主に寄与する。酸性領域では、(4a)、(4b)式による補正係数Cは無視できる。滴定実験においてSiとAl濃度の情報は重要であり、平均濃度の10^{-4}Mは補正係数となる。また、Cの影響は$\Delta[H^+]$に対して非常に小さい。

2.2.2 モデリング

滴定実験のモデリングは、拡張Wannerモデルに$\Delta[H^+]$とpHのデータセットをインプットして行った。コンピュータコードには、GRFIT（Ludwig 1992）を用いた。

スメクタイトの酸／塩基特性を解析するため、2種類のLayer サイトを扱える拡張Wannerモデルにより、Wanner et al.（1994)及びWieland（1994)と同じアプローチを行った。これはLayer サイトがほとんど関係する酸性領域において、スメクタイトとプロトンの反応のフレキシビリティーを最大に保証するものである。中性及び元のpH領域における酸／塩基の平衡は、Layer サイトを選択に影響されない。適切なパラメータを

Table 9に示す。モデルは、pHに依存する表面と溶液のスペシエーションの計算に利用される。計算されたデータをFigure16に示す。

実験値と解析値が一致していないことは明らかである。滴定曲線における屈曲点か緩衝しているプラトーは、Δ〔H^+〕≒ 4×10^{-5}mol/g であることを示している。言い換えると、完全な滴定曲線から 4×10^{-5}mol/g 分シフトされている。しかし、カルサイトのないNa型スメクタイトを用いた佐々木ら（1995）による測定結果にプロトン（5×10^{-4}mol/g ）を加えて解析した結果と相違する。

プロトンの存在量を4.2×10^{-5}mol/g （Na型スメクタイトの精製において残っている）と仮定して解析した結果をFigure17に示した。

Table 9: Chemical components used to model the acid/base chemistry of purified Na-smectite. The water/smectite ratio is 200 mL/g.

Component	contribution from solution (mol/L)	contribution from smectite (mol/L)	total conc. (mol/L)
Na^+	1.00×10^{-3}	4.41×10^{-3}	5.41×10^{-3}
pH, Δ[H^+]	*	*	*
SOH	0	1.42×10^{-4}	1.42×10^{-4}
Cl^-	1.00×10^{-3}	0	1.00×10^{-3}
X^- **	0	1.10×10^{-4}	1.10×10^{-4}
Y^- **	0	4.30×10^{-3}	4.30×10^{-3}

* These parameters are varied and calculated according to the input given (see text).

** This terminology for the two layer sites is choosen to be consistent with Wieland et al. (1994) and Wanner et al. (1994) (see text).

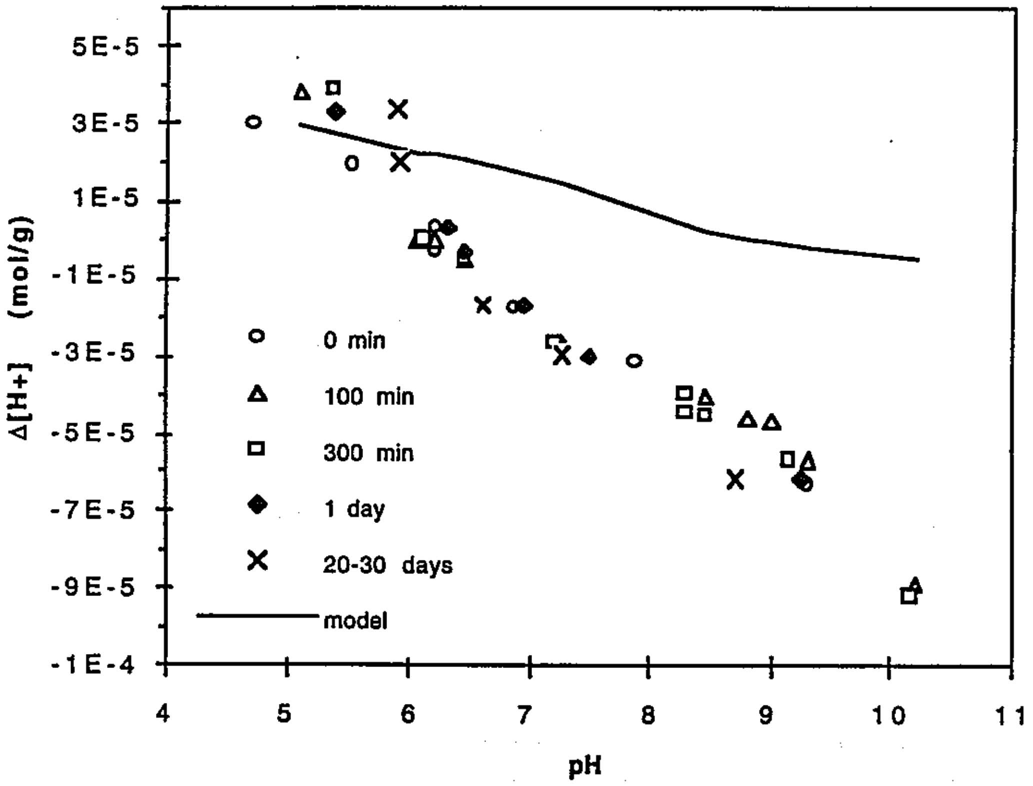

Figure 16 Experimental titration data (Oda, 1995) corresponding to a range of equilibration times in comparison with model predictions. Note that the equilibration times do not include the time needed to obtain a stable pH reading.

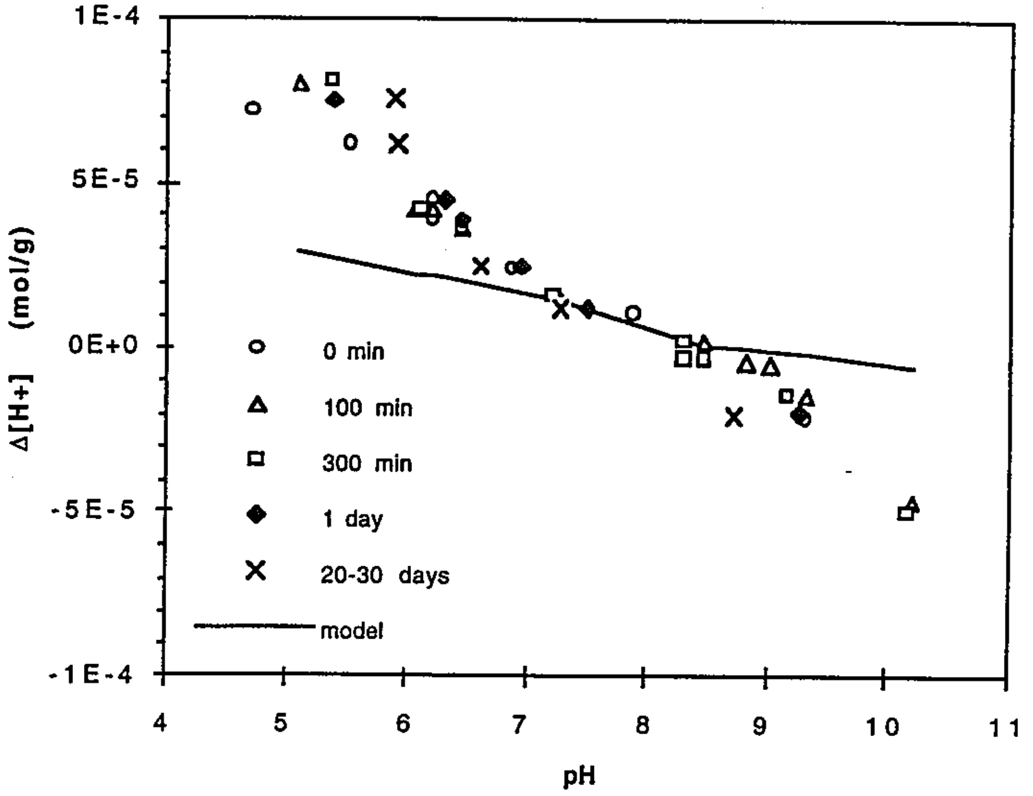

Figure 17 Experimental titration data (Oda, 1995) corresponding to a range of equilibration times in comparison with model predictions, assuming 4.2×10^{-5} mol resudial acid per g of purified Na-smectite. Note that the equilibration times do not include the time needed to obtain a stable pH reading.

2.3　結論

① Kunigel-V1及びKunipia-F と蒸留水及び人工地下水による実験結果は、拡張Wannerによって説明された。このモデルで使用されたパラメータは、ワイオミング産ベントナイトのMX-80 について評価されたものであり、2種類のベントナイトにより確証された。

② 佐々木ら（1995）及び小田（1995）による実験データは、pCO_2と温度が充分に制御されていなかったことが示された。今後はpCO_2と温度を一定に制御するか、既知条件として測定することを薦める。

③ 佐々木ら（1995）及び小田（1995）により測定された精製Na型スメクタイトの実験データについては、解析が困難であった。他のベントナイトについては拡張Wannerモデルにより評価できているため、スメクタイトの精製方法に問題がある可能性がある。精製Na型スメクタイトの特性を詳細に調べること、また文献による方法によって精製することを強く希望する（Wieland et al. 1994 、Wanner et al. 1994）。

④ 小田（1995）の実験データは、貴重な速度論的な速度である。残念ながら深い考察はできなかった。将来の研究において、拡張Wannerモデルのパラメータが精製Na型スメクタイトにおいて修正が必要になるなら、より完全で一貫したデータセットが要求される。

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第3章　核種の吸着及び拡散現象に関する固有データベースの開発研究

高レベル廃棄物の処分では圧密ベントナイトの使用を予定している。

核種は母岩に到達するまで間、圧密ベントナイト中を移行するため、圧密ベントナイト中での核種の移行プロセスをモデル化することは非常に重要である。圧密ベントナイト中での核種の移行は拡散によって生じる。圧密ベントナイト中の空隙は非常に小さく、空隙中では表面の電気的ポテンシャルの偏りにより、拡散イオンが分配していることが考えられる。分極化の度合いは主にイオンの電荷に依存し、見かけの拡散定数に影響する。見かけの拡散係数に影響する別のパラメータとしてKdがある。Kdは溶液中とベントナイト表面の分配であり、熱力学データベース（TDB ）、ベントナイトの特性、ベントナイト表面の相互作用による熱力学モデルに依存する。

本章では、核種の吸着及び拡散現象に関する固有データベースの開発するための研究をスイスのMBT 社と共同で行った。MBT 社からの報告書を巻末資料2に示す。以下にその概要を記述する。

3.1　吸着／拡散を総合したデータベース

吸着／拡散を総合したデータベースシステム（ISD ）の目的は、一貫したデータベースとすることである。それは、すべてのパラメータを含み、メカニスティックな吸着／拡散モデルにより、元素や化学種の分配係数、見かけの拡散係数（Da）を導くための変化にも対応できることが必要である。メカニスティックな拡散モデルは、吸着モデルによるアウトプットに強く影響されるため、吸着及び拡散モデルともベントナイトの特性に影響される。それは、KdとDaを導くために使用されるすべてのデータとモデルを含む情報システムとして理解できる。

地下水組成のようなイップットパラメータとTDB も、ISD データベースの一部である。これらのデータは吸着モデルや拡散モデルの結果に直接影響する。例えばTDB の変化は、溶液種を変化させ、Kdや拡散挙動を変化させる。

Figure 1は、ISD データベースシステムの構造の概要である。枠はデータベースやモデルを表す。矢印はインプットやアウトプットデータの移動を表す。データ及びモデルは、名前やバージョンナンバーでラベル化される。KdやDaは、ベントナイト（クニゲルV1等）、TDB 、地下水のタイプ、吸着モデル、拡散モデル、またこれらの融合により決定される。Figure 1について以下に説明する。重要な地球化学的パラメータである酸化還元電位（Eh）については、Figure 1中では、完全に説明できない。Ehはインプットパラメータでなく、地球化学的モデルの中で定義される。酸化還元電位の詳細は、3.1.11節に記述した。

3.1.1　地下水組成

地下水組成は、例えばAllard water、Sasaki-A 、Sasaki-Bのようにインプットデータとして記録する。インプットパラメータは、拡張Wannerモデルに必要である。各元素の定義ナンバー、親種の化学形、空隙水中での平衡濃度の推定、また地下水中での元素の合計濃度がリストされる。Table 1に地下水組成の記録例を示す。

レファレンス用の地下水として人工や天然の地下水がある。レファレンス用の地下水は特定のサイトや母岩の水和化学状態を表現する。レファレンス用の地下水は、モデリングの研究や化学分析の解釈の結果により定義される。もし、組成鉱物と地下水が平衡にあるならば、固有値である。

地下水の定義の総合的な部分である境界条件についても、記録に含まれる。例えば、カルサイト、石英、CO_2 ガス分圧、酸化還元電位である。また、地下水のpHは重要である。（pHは化学種計算のインプットパラメータではないが）プロトンのバランスを取るために必要なH^+濃度はpHよりも高い。pHはベントナイトとの接触により変化するためである。地下水のH^+濃度は、測定値や質量移動の計算値によって決定される。

3.1.2　熱力学データベース（TDB ）

熱力学データベース（TDB ）は、化学種の濃度の計算に必要である。
モデルに必要な特定の熱力学データ（イオン交換平衡定数、表面錯体定数）は変更されない。TDB に大きな変更が必要であれば、新しいTDB は新しい番号を付け、変更部分はTDB のユーザにわかるように記録する。

TDB はISD データベースシステムの基本である。高い信頼性と矛盾のないTDB はISDの前に必要である。TDB は、注意深く検証されなければならない。ほとんどの地下水化

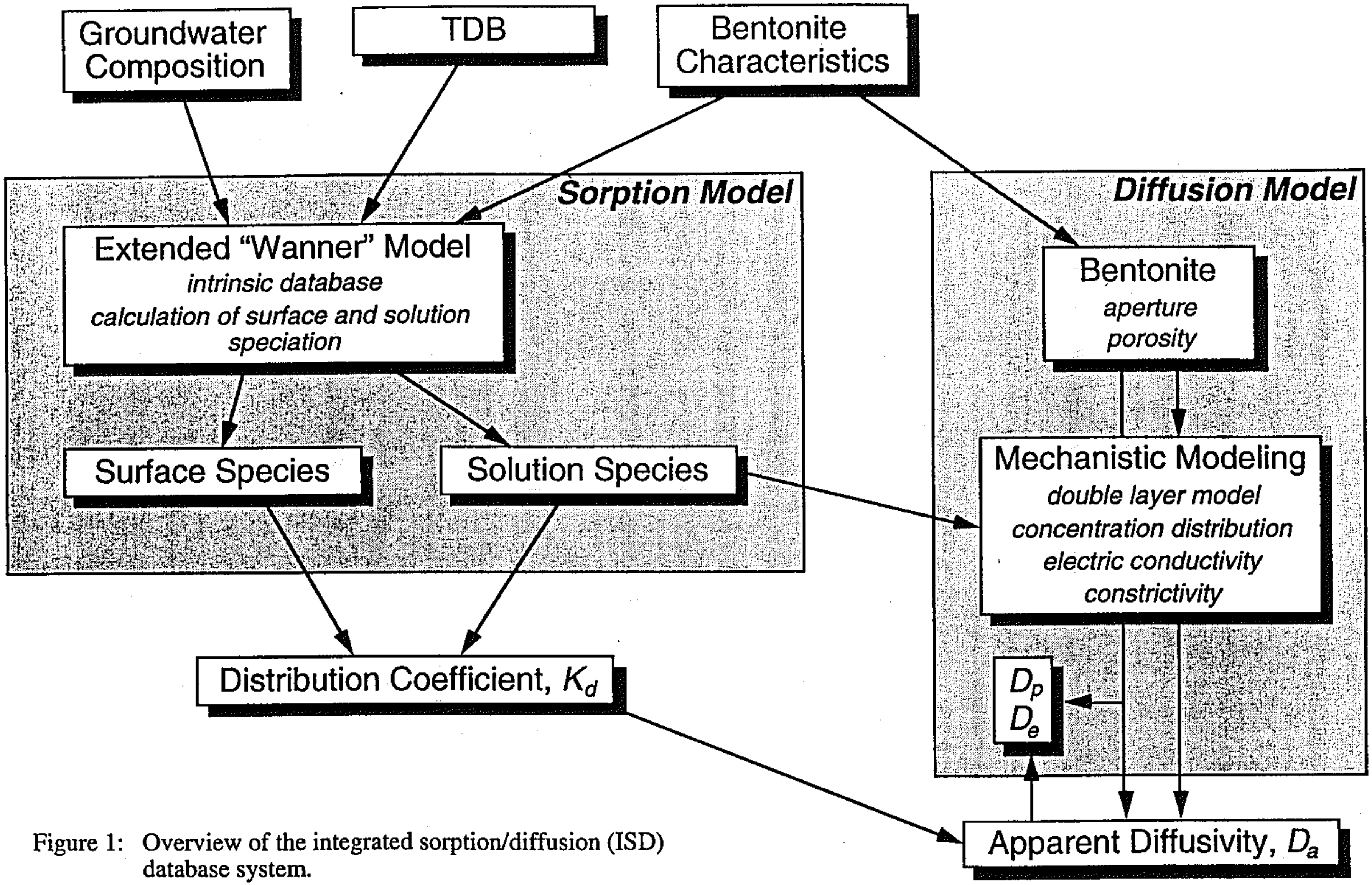

Figure 1: Overview of the integrated sorption/diffusion (ISD) database system.

Table 1: Example of a groundwater composition record. The ID numbers are code specific. The master species is taken as the representative species of the element. The total concentration (last column) refers to the master species. Here, the total H^+ concentration is calculated in view of the distribution of H^+ and OH^- at the relevant pH (8.2): carbonate will be protonated (HCO_3^-) and the silicon master species ($H_2SiO_4^{2-}$ or $SiO_2(OH)_2^{2-}$) will carry two protons (as $Si(OH)_4$). Hence, $[H^+]_{tot} = [CO_3^{2-}]_{tot} + 2[H_2SiO_4^{2-}]_{tot}$.

Allard synthetic granitic groundwater (Allard, 1982)			
ID (MIN_SURF)	master species	log c (estimated)	total conc. of element [mol/L]
1	Ca+2	-4.00	4.5 E-4
2	Mg+2	-4.00	1.8 E-4
4	K+	-4.00	1.0 E-4
5	Na+	-3.00	2.8 E-3
50	H+	-8.00	2.4 E-3
101	CO3-2	-5.00	2.0 E-3
102	SO4-2	-4.00	1.0 E-4
103	Cl-	-3.00	2.0 E-3
112	H2SiO4-2	-9.00	2.0 E-4
Boundary conditions:			
20000	calcite	saturated	
21440	quartz	saturated	
Usful information:			
pH	8.2		

学種のデータは、多くのデータベースにおいて一致している。しかし、トレーサ元素については、ほとんどのケースで検証が必要である。メカニスティックな拡散モデルでは、信頼性のの高いTDB を使用して化学種を得ることが重要である。これについては、3.1 節で記述する。TDB の信頼性は例えばPuについては重要であり、TDB が正確でなければ、推定されるKdの信頼性は低くなる。

TDB は、しばしば計算コードとともに提供される。PHREEQE 、EQ3/6 、MINEQLのようなコードでは、OECD/NEAを通じてデータベースも含めて提供されている。拡張Wannerモデルは、MIN-SURFコード（Berner 1993 ）で提供されたTDB を使って、MIN-SURFコード用に開発された。データベースの大半は2つのレポートからである。（Pearson and Berner 1991 、 Pearson, Berner and Hummel 1992）また、データベースは、NEA-TDB （Wanner 1988 、Grenthe et al. 1992 ）により更新されている。

3.1.3　ベントナイトの特性

インプットの記録には、物理、化学、ベントナイトの鉱物組成の独立する情報も含まれる。「地下水組成」の記録のように、「ベントナイト特性」の記録も、例えば「Kunipia-F 」「Kunigel-V1」「MX-80 」のように名前か番号でラベルされる。ベントナイトの特性では、以下の情報を記録する。

- 鉱物組成
- 溶解性不純物の量
- 陽イオン交換容量と交換性イオンの量
- 表面エッジサイトの密度
- 構造と物質パラメータ（密度、表面積、tortuosity等）

佐藤、油井、吉川（1995）による拡散モデルでは、空隙率ε、tortuosityτ^2 、表面積sは構造パラメータであり、拡散イオンの物理化学特性は独立している。佐藤、油井、吉川（1995）は、拡散イオンのベントナイト表面との相互作用を表すため、伝導度δを計算するモデルを提案した。

日本の一般的な２種類のベントナイト種、Kunigel-V1及びKunipia-F については、よく研究されている。溶解性不純物がよく調べられていることは、拡張Wannerモデルのために重要である。Table 2に２種類のベントナイトのパラメータリストを示す。

3.1.4　拡張Wannerモデルと基本的データベース

Wannerモデルは、ベントナイト中におけるメカニスティックな吸着モデルの基礎として提案された（Wanner 1986 ）。そして、このモデルの拡張バージョンが提案された（Wanner et al. 1994、Wieland et al. 1994 ）。それは、表面錯体の挙動とイオン交換サイトを比較する新しいタイプである。「edgeサイト」のようなサイトでは、弱アルカリ領域でプロトンが溶脱し、イオン交換よりも表面錯体のための主要な反応となる。拡張Wannerモデルではイオン交換反応を扱うため、モル分率が（Fletcher and Sposite 1989）、またedgeサイトにおける反応を扱うため、拡散二重層モデル（Dzombak and Morel 1990）を使うことが必要である。また、モデルの中で、共沈のメカニズムを含む可能性がある。拡張Wannerモデルは高いフレキシビリティーを持ち、主要核種のメカニスティックな吸着モデルに使用することができる。拡張Wannerモデルは、MIN-AURFコード（Berner 1993 ）によって計算することができる。拡張Wannerモデルに必要なパラメータは以下の通りである。

- Layer サイトにおけるイオン交換定数（Na^+ 、K^+ 、H^+ 、Ca^{2+}、Mg^{2+}）
  （モル分率モデルに適用できる形）
- Layer サイトにおける主要核種のイオン交換定数
- edgeサイトにおける拡散二重層モデルのためのintrinsic なacid／base定数
  （intrinsic データベース）
- edgeサイトにおける主要核種のintrinsic な表面錯体定数
- edgeサイトのサイト密度
- 鉱物平衡（カルサイト、石英飽和）

PNC はintrinsic なデータベースの開発を重点に行ってきた。intrinsic なデータベースには、ベントナイトの酸化型サイトにおける表面錯体反応を含んでいる。拡散二重層モデルは、拡張Wannerモデルの一部である。intrinsic なデータベースの整備には、特別なデータベースの構造は必要としない。拡張Wannerモデルの中で、intrinsic な定

Table 2: Kunigel-V1 and Kunipia-F: Composition and other specific parameters relevant to ISD modeling. Values readily available have been filled in as an example. The references are given in the footnote.

	Kunigel-V1	Kunipia-F
Minerals:		
smectite	46 - 49 % [1]	99 % [2]; >95% [1]
quartz	29 - 38 % [1]	traces [1]
feldspar	2.7 - 5.5 % [1]	
calcite	2.1 - 2.6 % [1]	traces [1]
dolomite	2.0 - 3.8 % [1]	
zeolite	3.0 - 3.5 % [1]	
pyrite	0.5 - 0.7 % [1]	
Soluble impurities:		
NaCl	0.001 % [3]	0.071 % [3]
$CaSO_4$	0.38 % [3]	0.694 % [3]
KCl	0.004 % [3]	0.005 % [3]
Surface sites and cation exchange parameters:		
SOH sites (edge sites)		2.84×10^{-5} mol/g [4]
Cation exchange capacity, CEC	60.1 meq/100g [1]	108 meq/100g [5]
exchangeable Na^+		97.1 % [5]
exchangeable K^+		0.9 % [5]
exchangeable Mg^{2+}		1.3 % [5]
exchangeable Ca^{2+}		0.7 % [5]
Structural and material parameters:		
specific density, ρ_s	2700 kg/m^3 [6]	
dry density, ρ_d	1500 kg/m^3	
porosity, ε	0.44 $(1 - \rho_d/\rho_s)$	
solid/water ratio	3375 kg/m^3 (ρ_d/ε)	
surface area of layer sites, *S(layer)*	810 m^2/g [6]	
surface area of edge sites, *S(edge)*	3 m^2/g [from 4]	
aperture distance, d	0.73 nm [6]	
tortuosity, τ^2	4.6 [6]	

References:

[1] Sasaki et al. (1995)

[2] Ashida, Kohara and Yui (1994)

[3] Wanner and Wieland (1993)

[4] Wieland et al. (1995), obtained for pretreated MX-80 which had a CEC of 108 meq/100g

[5] Yajima (1993)

[6] Sato, Yui and Yoshikawa (1995)

数は表面定数データセットに単に付加されるだけである。

モンモリロナイトとNa$^+$ 、K$^+$ 、H$^+$ 、Ca^{2+}、Mg^{2+}のイオン交換定数は知られている。Layer サイトのサイト密度はCEC と一致する。拡張Wannerモデルに必要なのデータベースをTable 3に示す。主要核種（Cs$^+$ ）のデータがこのデータベースに入れられている。

edgeのOHサイトのサイト密度は、ワイオミング産ベントナイトMX-80 によって知られている。（2.8 ×10^{-5} mol OH-site/g）この値とedgeのOHサイトのacid／base定数は、フィッティング（Wanner et al. 1994）により推定された。edgeサイトの密度はベントナイトの特性記録の一部である。

拡張Wannerモデルは、ベントナイトや地下水のタイプが特定されれば適用可能である。このモデルのバージョンは、簡単にトレースできるように及びQAのため、ISD データベースシステム中でラベルされなければならない。

3.1.5　表面化学種

固相の表面のスペシエーションは表面モデルの結果として得られる（イオン交換、表面錯体）。表面化学種の濃度の合計はmol/Kgで表現され、Kdの計算に使用される。

3.1.6　溶液化学種

ベントナイトの平衡溶液中における元素のスペシエーションは、２つの目的のために行われる。

- メカニスティックな拡散モデルへのインプット（2.8節参照）

  拡散モデルにおいて、支配的化学種の濃度（n_0）と電荷（z）、また、空隙水中の主イオンの濃度は重要である。

- Kd計算のインプット。

  このケースでは主要核種と反応する化学種濃度の合計は、mol/ℓからmol/m^{3}へ変換され、Kdの計算に直接使用される。

Table 3: Surface interaction database for the extended Wanner model, including an ion exchange database and an intrinsic database to be used with the diffuse double layer model (cf. Dzombak and Morel, 1990). Examples of data for key radionuclides are given for Cs^+ and Sr^{2+} (ion exchange database), and for SeO_3^{2-}, Co^{2+} and NpO_2^+ (intrinsic database).

Extended Wanner model: Specific surface interaction database			
1	*Ion exchange database:*		
	Surface site master species:		Z^-
	Total Z [mol/L]:		CECx(solid/water ratio)
	Surface species:	*log K:*	*Reference:*
	ZNa	20.0	Wanner (1986)
	ZK	20.26	Fletcher and Sposito (1989)
	Z_2Mg	40.13 *	Wanner, Wersin and Sierro (1992)
	Z_2Ca	40.21 *	Wanner, Wersin and Sierro (1992)
	ZH	23.0	Wieland et al. (1994)
	ZCs	21.6	Wanner, Albinsson and Wieland (1994)
	Z_2Sr	40.17	Fletcher and Sposito (1989)
2	*Intrinsic database (surface complexation):*		
	Surface site master species:		SOH
	Total SOH [mol/L]:		(SOH site density)x(solid/water ratio)
	Surface species:	*log K^{int}:*	*Reference:*
	SOH_2^+	5.4	Wanner et al. (1994)
	SO^-	-6.7	Wanner et al. (1994)
	$SSeO_3^-$	12.7 **	Dzombak and Morel (1990)
	$SOHSeO_3^{2-}$	5.2 **	Dzombak and Morel (1990)
	$SOCo^+$	-0.5 **	Dzombak and Morel (1990)
	$SONpO_2$	-1.0 **	Bradbury and Baeyens (1992)
*	After conversion to the mole fraction model		
**	Valid for hydrous ferric oxides (values rounded)		

3.1.7　分配係数Kd

分配係数Kdは、拡張Wannerモデルの２つのアウトプットパラメータ（表面濃度（mol/Kg）と溶液中濃度（mol/m³））から計算される。

$$\mathrm{Kd}\,〔\mathrm{m^3/Kg}〕 = \frac{\text{元素}\,x\,\text{の表面化学種の化学量論的合計}\,〔\mathrm{mol/Kg}〕}{\text{元素}\,x\,\text{の溶液化学種の化学量論的合計}\,〔\mathrm{mol/m^3}〕} \qquad (1)$$

Kdは、メカニスティクな拡散モデルのアウトプットパラメータ（D_0、d、ε、τ^2 またはε、D_p）とともに見かけの拡散係数D_aを計算するために使用される。

3.1.8　メカニスティックな拡散モデル

佐藤、油井、吉川（1995）は、種々のパラメータを使用してメカニスティックな拡散モデルを提案した。これらの関係についてFigure 2に示す。数学的な関係については、佐藤、油井、吉川（1995）の論文で示されている。

- 化学種：拡張Wannerモデルからのoutput（溶液種）

n	溶液m³当たりのイオンの数。（溶液中の電荷密度のために測定される）
Z	電荷（表面の電荷分布の計算のため。Zはz：z型の支配的な電解質の電荷数である。zは拡散化学種の電荷である。）

- モデル：佐藤、油井、吉川（1995）によって使用されたメカニスティックな拡散モデルの関数

$\phi\delta$	Stern 層の静電ポテンシャル（イオンの数nに依存）
Ψ	静電ポテンシャル
$\phi(X)$	ローカルな静電ポテンシャル
$n(X)$	ローカルなイオン濃度（伝導度の計算のため、平衡溶液濃度（n_0）に対するローカルな濃度n(X)は適当な値である。）
δ	伝導度（拡散イオンと電気二重層を基礎とした表面の間の相互作用を記述する）

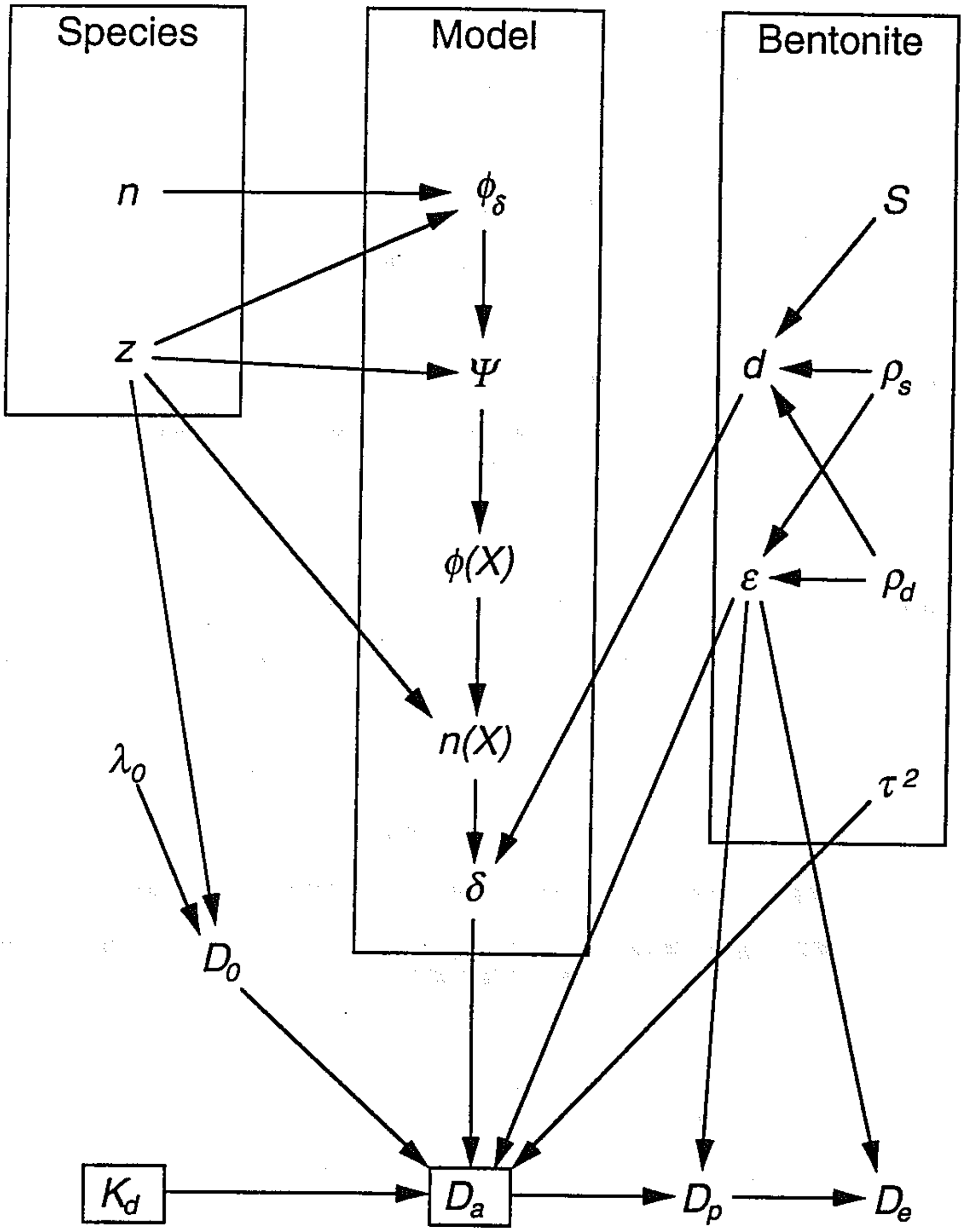

Figure 2: Variables required for the mechanistic diffusion model. The dependencies of the different variables are shown, e.g., an arrow from z to $n(X)$ means that z is one of the required input parameters to calculate $n(X)$. Variables in the "Species" box are a direct output of the extended Wanner model. Variables in the "Bentonite" box are constant for each bentonite specification. Variables in the "Model" box represent the different modeling steps as suggested by Sato, Yui and Yoshikawa (1995). The electric conductivity, λ_0, is species-specific, and K_d is the final output of the sorption model.

伝導度は、佐藤、油井、吉川（1995）により以下の式で計算される。

$$\delta = \frac{1}{n_0 d} \int_0^d n(X)\, dx \tag{2}$$

電気二重層理論により、定義された静電場でのイオンの分配は以下の式で計算される。

$$n(X) = n_0 \exp\left(\frac{-Ze\phi(X)}{kT}\right) \tag{3}$$

・ベントナイト：

ベントナイト特性の記録からのデータは、Figure 1及びTable 2（構造及び物質パラメータ）である。割れ目の距離（空隙径）d、空隙率εはベントナイト自身のパラメータではない。それらはベントナイト特性パラメータから導かれる。これはdやεがベントナイト特性の記録に含まれている理由である。

S	表面積
ρ_s	特性密度（通常2700 Kg/m^{3}程度）
ρ_d	乾燥密度
τ^2	tortuosity
d	割れ目の距離（空隙径の平均）
ε	空隙率（加藤ら（1995）は、HTO の拡散の有効空隙がバルクの空隙と等しいことを実験的に示した。）

・その他の値

Figure 2の中の残りの値は、メカニスティック拡散モデル（λ_0 D_0）へのインプットパラメータか、（D_p D_e）からのアウトプットパラメータである。最終的な結果として得られるパラメータD_aは、メカニスティックな吸着モデルによるKdにより計算される。

λ_0	無限希薄溶液における主要化学種の電気伝導度（このパラメータは化学種を特定し、主要化学種の電荷に依存する。）
D_0	自由水中における主要化学種の拡散係数
Kd	ベントナイト中における主要化学種の分配係数
D_a	ベントナイト中における主要化学種の見かけの拡散係数
D_p	ベントナイト空隙水中における主要化学種の拡散係数
D_e	ベントナイト中における主要化学種の実効拡散係数

D_pとD_eは、メカニスティックな拡散モデルを使わずにD_aを計算する。

$$D_a = \frac{\varepsilon}{\varepsilon + \rho_d Kd} \frac{\delta}{\tau^2} D_0 \tag{4}$$

D_pとD_eは、拡散データベースの矛盾をチェックするのに有効なパラメータである。なぜなら、物理化学的性質が近い化学種についても比較できるからである。これはまた、メカニスティックな拡散モデルを使用しなくても、アナログ的に推定できる理由にもなる。（３章のFigure３参照）

$$D_a = \frac{\varepsilon}{\varepsilon + \rho_d Kd} D_p \tag{5}$$

$$D_e = \varepsilon \quad D_p \tag{6}$$

3.1.9　空隙拡散D_pと実効拡散係数D_e

これらの拡散係数はクロスチェックに有用である。見かけの拡散係数D_aを計算する必要はない。(5)式及び(6)式により計算される。

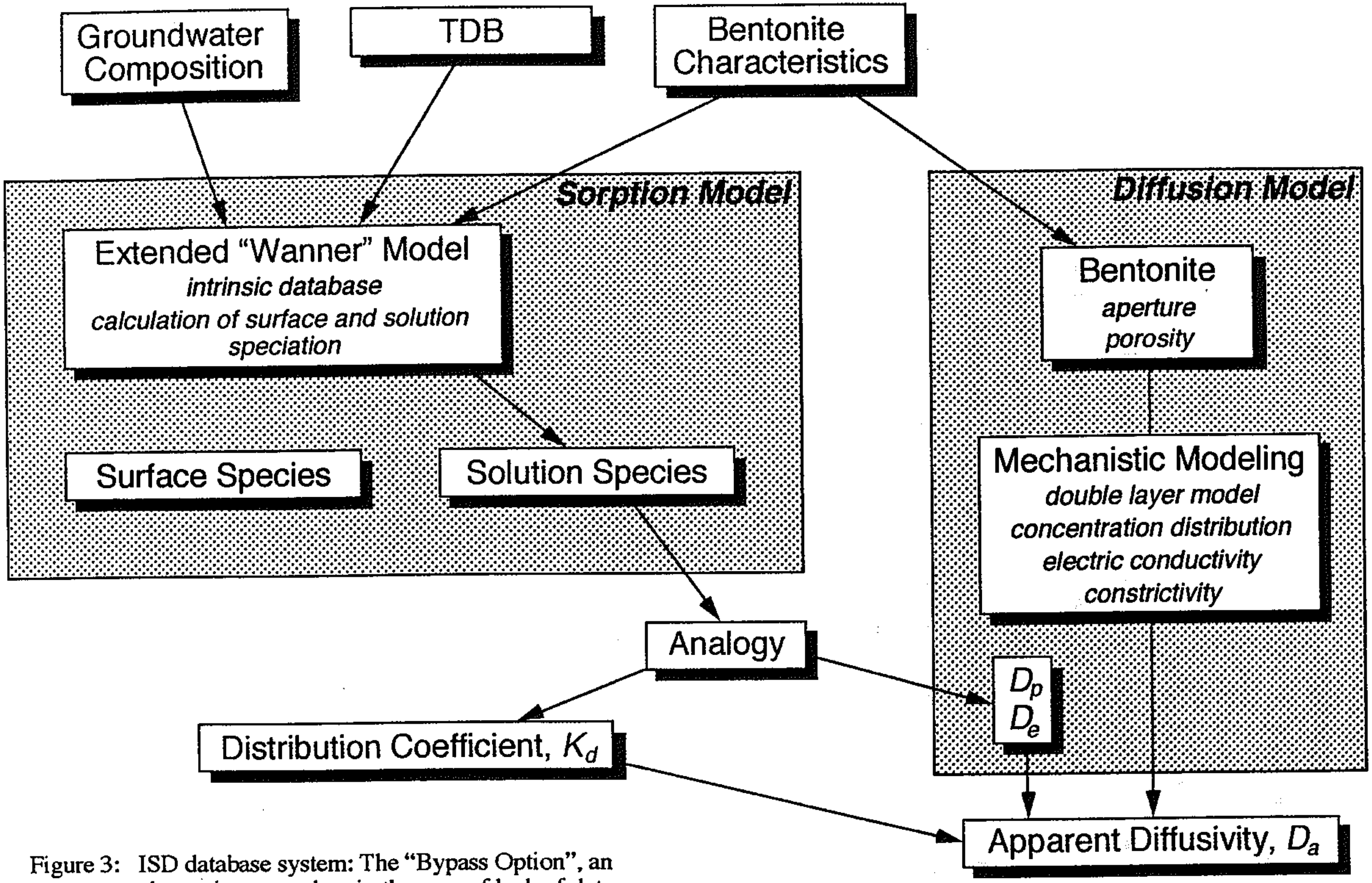

Figure 3: ISD database system: The "Bypass Option", an alternative procedure in the case of lack of data.

3.1.10　見かけの拡散係数D_a

見かけの拡散係数は、サイトスペシフィックな拡散モデルに使用される。(4)式及び(5)式で計算される。

3.1.11　酸化還元電位

酸化還元電位Ehは、酸化還元プロセスを支配する酸化還元物質が存在により決定される。私たちは、酸化還元条件に影響される元素について、還元条件や酸化条件におけるデータセットを用意する。たとえば、ウランについて還元状態ではU〔IV〕を、酸化状態ではU〔VI〕のデータセットを用意する。この方法は、フレキシビリティーがあり、性能評価における種々の酸化還元モデルに適用できる。

3.2　選択すべき性能評価手法（バイパスオプション）

ISD データベースシステムの目的は、放射性核種の移行モデルに一貫した化学的データベースを与えることである。圧密ベントナイトは、核種の移行経路を予想できるバリアである。ISD データベースシステムは、要求されるゴールに向けて適切で正しいツールを与えるものである。

しかし、要求されるデータベースは、Figure 1 に示すように完全なメカニスティックな吸着／拡散のデータベースである。1999年に予定されているPNC 性能評価レポートにおいて、すべての主要核種についてデータを取得することは間に合わない。特にintrinsic なデータベースについては、短期間で取得することは期待できない。

私たちは、KdやD_pのようなパラメータをメカニスティックな方法で推定することにより、抜けているデータを補完するようなISD データベースシステムをデザインしている。この方法を「バイパスオプション」とする。バイパスオプションは、優先度の高い核種に対するアプローチ方法である。

バイパスオプションの適用性をFigure 3 に示す。Figure 3 はFigure 1 をもとにした表である。Figure 3 とFigure 1 の重要な違いは、KdとD_p（D_e）の違いである。

3.2.1　Kdの推定

ベントナイト中における核種のKdの推定は、主な溶液種と表面サイトの反応が基礎となっている。私たちは、サイトスペシフィックな条件において、核種のスペシエーションを知ることが必要である。このスペシエーションは、拡張Wannerモデル及びインプットの記録（地下水組成、TDB 、ベントナイトの特性）から導かれる。以下の２つの例によって、このアプローチ方法を説明する。

・ラジウムのKd

ラジウムはアルカリ土類元素であり、イオン交換反応によってベントナイトに吸着することが予想される。Ra^{2+}のイオン交換定数は、実験により良く知られているSr^{2+}と近いことが推定される。Sr^{2+}はRa^{2+}のアナログとして使用される。Ra^{2+}のKdはSr^{2+}と同じとして使用される。

・プルトニウムのKd

プルトニウムは酸化還元電位により、Pu（Ⅲ）、Pu（Ⅳ）、Pu（Ⅴ）、Pu（Ⅵ）のように変化する。Kd値の予想において、Pu（Ⅲ）にはAm（Ⅲ）もしくはランタニド、Pu（Ⅳ）にはTh（Ⅳ）、Pu（Ⅴ）にはNp（Ⅴ）、Pu（Ⅵ）にはU（Ⅵ）のデータを使用することを推薦する。

この方法はプルトニウムのKd値のEhによる影響を考慮できるため、重要な進歩である。プルトニウムのスペシエーションは、Ehにより計算される。プルトニウムのためのTDB は必要ないことになる。

システマティックなアプローチによる場合やアナログ系において化学的特性の比較試験が行われている場合に、Kd値は正確に推定できる。

3.2.2　D_pとD_eの推定

空隙水中における拡散は、拡散メカニズムが不明な場合及びD_aの計算に必要な１つ以上のパラメータが抜けている場合に推定される。また、メカニスティックな拡散モデルが可能である場合、結果の確証するためのD_pの推定することが有用である。D_eは(6)式により推定される。

D_pの推定はKdの推定と非常に似ている。D_pの推定は化学的なアナログデータをベースにしていることをFigure３で示している。
アナログはスペシエーションの計算において使用される。その例は3.1節に記述した。しかしながら、D_pの推定に使用できるアナログ種は限られている。

ベントナイト表面の大部分は陰電荷であるため、拡散挙動において、化学種の電荷は非常に重要である。イオンの電荷による影響はサイズによる影響よりも大きい。(5)式により、非吸着性の核種であれば$D_a = D_p$である。メカニスティックな吸着モデルは、吸着性の化学種に対して信頼性の高いKd値を導く。D_pは実験的に測定されるD_aから計算される。

Wanner, Albisson and Wieland (1994) は、Cs^+のD_pを推定することによって、メカニスティックな吸着モデルを確証した。見かけの拡散係数から得られたKd値と予想されたKd値が誤差範囲で一致することを確認している。このような推定により、HTO とCs^+の場合のように、拡散用の空隙スペースはほぼ同じであるものと考えられる。

しかし、陰イオンについては全く相違する。HTO はD_pの予想のためのアナログにはならない。Cl^- やTcO_4^- のような非吸着性の陰イオンならば、アナログとして適当であるかもしれない。イオン種により分類された拡散データは、Muurinen（1994）及び佐藤ら（1993）により報告されている。

3.3　長期的なモデリング

長期的モデリングは、このレポートの課題ではないが、ISD データベースの長期的な適用性を評価するのに重要である。Figure 1 及びFigure 3 を見ると、ほとんどのパラメータが処分場により変化する。例外は地下水組成とTDB のみである。

一般的に変化は移動相によって起こる。例えば溶液相やガス相である。ガス相や溶液相は、核種を動かすことができる。また、核種と鉱物の双方が移動する経路となる。処分場を通過する水の流速は、ニアフィールドの予測における本質的なパラメータである。シンプルなミキシングタンクモデルは、すばやく安全評価を行うためのモデルである（Wanner 1986 ）。ミキシングタンクモデルには、鉱物相の浸出、溶解／沈澱平衡が含まれている。ミキシングタンクモデルを適用した後のモデルは、Wanner, Wersin and Sierro（1992)及びWersin et al.（1994） によって示されている。ミキシングタンクモデルはセメントの変質の予測にも適用されている（Berner 1990 、Nagra 1994）。

ミキシングタンクモデルは、ニアフィールドにおけるスペシエーションの変化やKdの変化の予想についても使用することができる。拡散パラメータの変化の予測はより難しいかもしれない。おおよその割れ目、空隙の変化については、浸出、溶解／沈澱の化学モデルによる質量移行モデルによって予測は可能かもしれない。

また、固溶体モデルにより、ニアフィールドの長期的変化の予測が可能かもしれない。固溶体モデルを拡張Wannerモデルに組み込むのは、次の段階である。

3.4　将来的な適用性（花崗岩、凝灰岩）

花崗岩のような地質学的システムにおいて、核種は岩石媒体よりも亀裂や割れ目によって移行することが推定されている。その場合、核種の移行メカニズムは、拡散よりも移流となる。Figure 1及びFigure 3において、右側部分（拡散モデル）は、移流モデルに入れ代えられる。

1．周囲の岩石と平衡にある地下水組成の定義
2．TDB データベースの定義
3．岩石の特性（CEC 、表面錯体サイト、鉱物）
4．適用するための拡張Wannerモデルのintrinsic データベースのチェック
5．表面及び溶液スペシエーションの計算
6．表面濃度や溶液種からの分配係数Kdの算出

もし、intrinsic なデータベースが完全でなければ、予備的にFigure 3による選択的な方法を使用することができる。

1．周囲の岩石と平衡にある地下水組成の定義
2．TDB データベースの定義
3．地下水中の主要元素のスペシエーションの計算
4．溶液化学種の分配。同一条件、同一スペシエーションとして知られているアナログ元素による核種のKdの推定。

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巻末資料　1

Modeling of bentonite-groundwater interactions

: Simulation of experiments of Y. Sasaki and C. Oda

Power Reactor and Nuclear Fuel Development Corporation (PNC)

Technical Report

Modeling of bentonite-groundwater interactions: Simulation of experiments of Y. Sasaki and C. Oda

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March 1995

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Environmental

Summary

This report presents an analysis of the experimental data of Sasaki et al. (1995) on the interaction of different bentonites with different groundwaters and distilled water, and of Oda (1994, 1995) on the acid/base titration of suspensions of purified Na-smectite. The experimental conditions are simulated by using the extended Wanner model, and the predictions of the extended Wanner model are compared with the measurements. The agreement is satisfactory in the case of Kunigel-V1 and Kunipia-F. A discrepancy in the proton balance is one explanation for the disagreements between model and measurements as observed in all the experiments with purified Na-smectite. The main results and recommendations are summarized as folows:

1. *Experiments by Sasaki et al. (1995):* Sasaki's bentonite/water contact experiments were carried out with Kunigel-V1, Kunipia-F, and a purified Na-smectite resulting from a chemical treatment of Kunipia-F. The aqueous solutions used were distilled water and two simulated groundwaters prepared by leaching granite (GWA) and a strongly weathered tuff (GWB), respectively. Pyrite oxidation kinetics can be extracted from the experiments with Kunigel-V1, and pH, Na^+ and SO_4^{2-} concentrations under aerobic conditions are predicted correctly by the model, while moderate deviations of 20-50% are observed between measured and predicted dissolved inorganic carbon (DIC), probably due to uncertainties in pCO_2. To simulate the experimental data measured under anaerobic conditions, some proton-releasing reaction must be assumed, such as a low pCO_2 or a slight oxidation of pyrite. The pH, Na^+ and Ca^{2+} concentrations from the interaction of Kunigel-V1 with the granite water, GWA, and with the tuff water, GWB, agree very well with the predictions of the extended Wanner model, while the model overestimates K^+ and Mg^{2+} for presently unknown reasons. The interactions of Kunigel-V1 (as a function of the water/bentonite ratio) and Kunipia-F, respectively, with distilled water are simulated well by the extended Wanner model, although we had to assume that the systems were not completely closed with respect to CO_2. Finally, the pH of the interaction of purified Na-smectite with distilled water can only be reproduced by assuming 5×10^{-4} mol/g of acid in the solid. On the other hand, the experiments with 4% $CaCO_3$ added are predicted well by the model.

2. *Experiments by Oda (1994, 1995):* Oda carried out batch acid/base titrations of purified Na-smectite at a very low electrolyte concentration of 0.001 M NaCl. These experiments cannot be simulated successfully by the extended Wanner model. The measured point of zero charge occurs at a pH lower than expected, indicating that excess acid is present in the system. However, there is a marked difference between the slope of the titration curve measured and the one predicted by the model. We believe that the accuracy and reliability of the titrations can be improved significantly by (1) using different electrolyte concentrations between 0.001 and 0.5 M NaCl or $NaNO_3$, (2) controlling the temperature, (3) carrying out continuous titrations in addition to the batch titrations, and (4) by carefully controlling the atmosphere (CO_2).

Table of Contents

1 Modeling the interaction of several Japanese bentonites with distilled water and artificial groundwaters ("Sasaki experiments")

All experimental data are taken from Sasaki et al. (1995). The bentonites used for their experiments are Kunigel-V1 (Kunimine Industries Co.), a crude Na-bentonite, Kunipia-F (Kunimine Industries Co.), a purified bentonite, and a purified Na-smectite prepared from Kunipia-F. These materials are described in more detail by Sasaki et al. (1995) and Wanner and Wieland (1993).

The concentrations of surface and solution species of an ion in the bentonite-water system are evaluated by using the extended Wanner model, a surface chemical speciation model that simultaneously addresses ion exchange and surface complexation equilibria. All model-specific parameters were calibrated with thoroughly characterized Wyoming bentonite MX-80 (Wanner, Wersin and Sierro, 1992; Wanner et al., 1994; Wieland et al., 1994). A summary of these parameters is provided in Table 1. Computations are performed with the aid of the computer code MIN_SURF (Berner, 1993) which is an extended version of the computer code MINEQL.

Table 1: Parameters of the extended Wanner model used in the present evaluation of bentonite-water interaction (specific surface interaction database)

Surface species	$\log_{10} K^\circ$	Reference
Surface site master species: Z^-		(ion exchange database)
ZNa	20.0	Wanner (1986)
ZK	20.26	Fletcher and Sposito (1989)
Z_2Mg	40.13*	Wanner, Wersin and Sierro (1992)
Z_2Ca	40.21*	Wanner, Wersin and Sierro (1992)
ZH	23.0	Wieland et al. (1994)
Surface site master species: SOH		(intrinsic database)
SOH_2^+	5.4	Wanner et al. (1994)
SO^-	–6.7	Wanner et al. (1994)
Surface site density: 2.84×10^{-5} mol/g		

* after conversion to the mole fraction model

1.1 Interaction of Kunigel -V1 bentonite with distilled water and different artificial groundwaters

The mineralogical analysis and CEC of Kunigel-V1 is given by Sasaki et al. (1995), and the amount of soluble impurities is taken from Wanner and Wieland (1993). Sasaki et al. (1995) report on the cations that can be leached from Kunigel-V1, but provide no clear information about the concentrations of exchangable cations. Since the leached Ca^{2+} and Mg^{2+} ions are likely to stem from soluble impurities, the proportion of cations initially present at the ion-exchange sites is estimated as follows. The contents of both Na^+ and K^+ in the leachate are assumed to stem from ion exchange sites, the rest of the exchange sites are filled up with Ca^{2+} and Mg^{2+} ions according to their proportions in the leachate. Thus, the following parameters are selected in order to model Kunigel-V1-water interaction (see Table 2).

Table 2: Composition and other specific parameters of Kunigel-V1 used in the evaluation of Kunigel-V1-water interaction.

Parameters	Kunigel-V1	Reference
Minerals:		
smectite	46 - 49 %	Sasaki et al. (1995)
quartz	29 - 38 %	Sasaki et al. (1995)
calcite	2.1 - 2.6 %	Sasaki et al. (1995)
dolomite	2.0 - 3.8 %	Sasaki et al. (1995)
pyrite	0.5 - 0.7 %	Sasaki et al. (1995)
feldspar*	2.7 - 5.5 %	Sasaki et al. (1995)
zeolite*	3.0 - 3.5 %	Sasaki et al. (1995)
Soluble impurities:		
NaCl	0.001 %	Wanner and Wieland (1993)
KCl	0.004 %	Wanner and Wieland (1993)
$CaSO_4$	0.38 %	Wanner and Wieland (1993)
Cation exchange parameters:		
CEC	60.1 meq/100g	Sasaki et al. (1995)
exchangable Na^+	85.36 % **	estimation (this study)
exchangable K^+	1.48 % **	estimation (this study)
exchangable Mg^{2+}	2.28 % **	estimation (this study)
exchangable Ca^{2+}	10.88 % **	estimation (this study)

* Not considered in the model.

** These values are calculated from the amount of leachable cations reported by Sasaki et al. (1995).

The artificial groundwaters were obtained by leaching two types of rock, a granite and a strongly weathered tuff, with distilled water. The compositions of the respective solutions are also given by Sasaki et al. (1995).

1.1.1 Interaction of Kunigel-V1 bentonite with distilled water

1.1.1.1 Development of solution speciation as a function of time

Kunigel-V1 contains a number of minerals other than clays in various proportions (Table 2), which are of importance in determining the composition of the surrounding solution. The development of solution and surface speciation with equilibration time is modeled by using the following set of assumptions throughout:

1) Feldspar and zeolite are neglected, since these minerals are not included in the TDB as yet. However, both minerals are likely to exhibit slow dissolution kinetics, and are present in small quantities compared to quartz and smectite.

2) The solution is under all conditions assumed to be in equilibrium with quartz, calcite, and dolomite.

3) The dissolution of pyrite is time-dependent (cf. Figure 1) and crucial in determining the solution pH and SO_4^{2-} concentration. The pyrite content of Kunigel-V1 is reported as 0.5-0.7 %; we take an average pyrite content of 0.6 % for all modeling purposes. Obviously, setting the solution in equilibrium with pyrite will result in a rather low pH throughout the whole experiment (see Figure 2). Thus, the dissolution of pyrite according to the reactions

   $$FeS_2(s) + 7/2\ O_2 + H_2O = Fe^{2+} + 2\ SO_4^{2-} + 2\ H^+ \tag{1a}$$
   $$Fe^{2+} + 1/4\ O_2 + H^+ = Fe^{3+} + 1/2\ H_2O \tag{1b}$$
   $$Fe^{3+} + 3/2\ H_2O = 1/2\ Fe_2O_3 + 3\ H^+ \tag{1c}$$

   is assumed to show the time dependence documented in Figure 1. Such parabolic dissolution kinetics are frequently observed in situations where small, reactive particles are preferentially dissolved at the beginning of an experiment (Furrer and Stumm, 1986). Upon supersaturation, the precipitation of a solid Fe-(hydr)oxide may occur. Presumably, the precipitate will be an amorphous Fe-hydroxide or -oxyhydroxide. In the absence of detailed knowledge about the precipitate, we choose the product most stable under the given conditions. Note that the amount of protons released is not dependent on the nature of the precipitate, however.

4) The partial pressure of CO_2 is assumed to be $10^{-3.5}$ atm at the beginning of an experiment. Preliminary modeling results indicate, however, that this condition cannot be kept up for longer equilibration times. Thus, the pCO_2 was treated like an initial input of protons and carbonate species and was not kept constant.

5) In lack of detailed information about the temperature the experiments were exposed to, a constant temperature of 25 °C is assumed.

Using the amount of pyrite oxidized as indicated in Figure 1, the interaction of Kunigel-V1 with distilled water is adequately described by the extended Wanner model. The development of pH, and the concentrations of Na^+, SO_4^{2-}, and (CO_3^{2-} + HCO_3^-), henceforth termed "dissolved inorganic carbon" (DIC), is shown in Figures 3 through 6 as a function of time and pyrite dissolution. The components used to describe all species in the system are listed in Table 3.

The pH is determined by an input of H^+ resulting from the oxidative dissolution of pyrite, and subsequent reactions of H^+ with calcite, dolomite, and ion-exchange sites plus surface OH-groups of smectite. As documented in Figure 3, the development of pH with reaction time can be modelled very satisfactorily using the extended Wanner model and the aforementioned assumptions. It has to be pointed out that the pH is considered as master variable in the Kunigel-V1/solution system. Consequently, once the pH is described adequately, the same approach is used to model the concentrations of Na^+, SO_4^{2-}, and DIC.

The input of Na^+ stems from the NaCl contained in Kunigel-V1 and the ions originally present on the smectite layer sites. The concentration of Na^+ is regulated by ion-exchange reactions and is described well by the present model.

Sulfate is supplied mainly through the dissolution of pyrite and, to a lesser extent, of $CaSO_4$. No further interaction with a solid phase is considered, and the experimental data are described in a satisfactory way.

In comparison, the development of the concentration of carbonate species is described somewhat less satisfactorily. This is attributable mainly to a lack of information with regard to the partial pressure of CO_2 as a function of time. Obviously, keeping the total amount of carbonate species in the system constant leads to an underestimation of DIC concentration. On the other hand, applying a constant partial pressure of CO_2 of $10^{-3.5}$ atm will seriously underestimate the pH at the beginning, and overestimate the pH towards the end of the experiment.

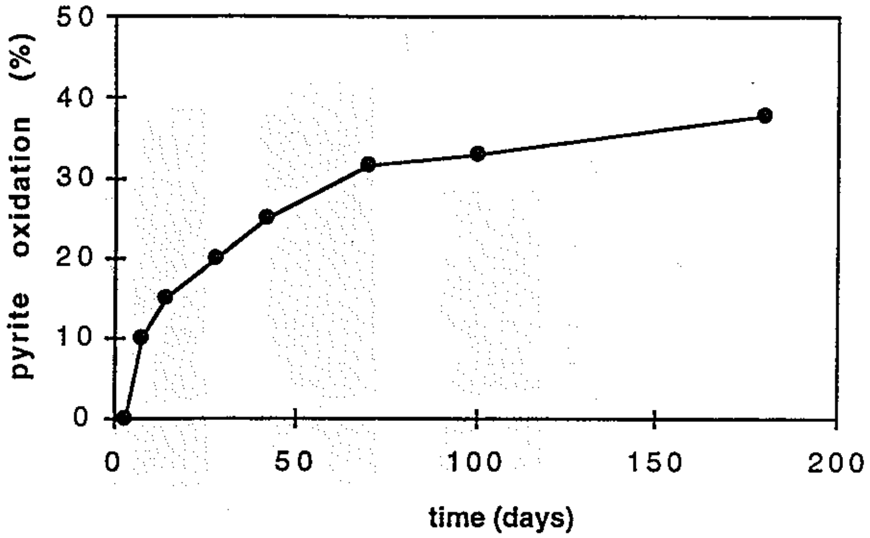

Figure 1 Modeled time-dependence of pyrite dissolution in the experiments with Kunigel-V1 (model developed according to experimental observations, cf. Figure 3).

Table 3: Chemical components and their input concentrations used to model the interaction of Kunigel-V1 with distilled water. Here, complete dissolution of pyrite is assumed; incomplete dissolution of pyrite is modeled according to Figure 1.

Component	contribution from solution (mol/L)	contribution from Kunigel-V1 (mol/L)	total conc. (mol/L)
Ca^{2+}	0	6.06×10^{-3}	6.06×10^{-3}
Mg^{2+}	0	6.85×10^{-4}	6.85×10^{-4}
Na^{+}	0	5.13×10^{-2}	5.13×10^{-2}
K^{+}	0	9.48×10^{-4}	9.48×10^{-4}
Fe^{3+}	5.00×10^{-3} *	0	5.00×10^{-3} *
H^{+}	5.03×10^{-3} **	0	5.03×10^{-3} **
$^{-}$SOH	0	2.84×10^{-3}	2.84×10^{-3}
CO_3^{2-}	1.27×10^{-4}	0	1.27×10^{-4}
Cl^{-}	0	7.78×10^{-5}	7.78×10^{-5}
SO_4^{2-}	1.00×10^{-2} *	2.79×10^{-3}	1.28×10^{-2}
$H_2SIO_4^{2-}$	0	0	0
Z^{-}	0	6.01×10^{-2}	6.01×10^{-2}

* from pyrite oxidation (see text)
** from pyrite oxidation and protonation of the carbonate ion (see text)

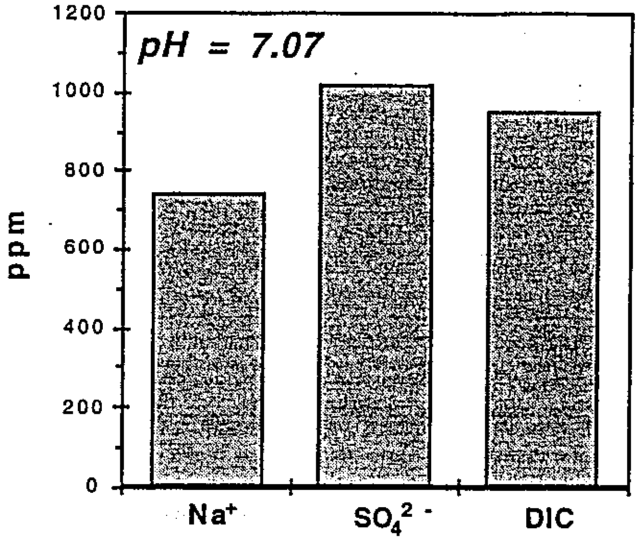

Figure 2 Calculated values of pH, and Na^+, SO_4^{2-}, and DIC concentration for the Kunigel-V1/water system, assuming complete oxidative dissolution of the pyrite present.

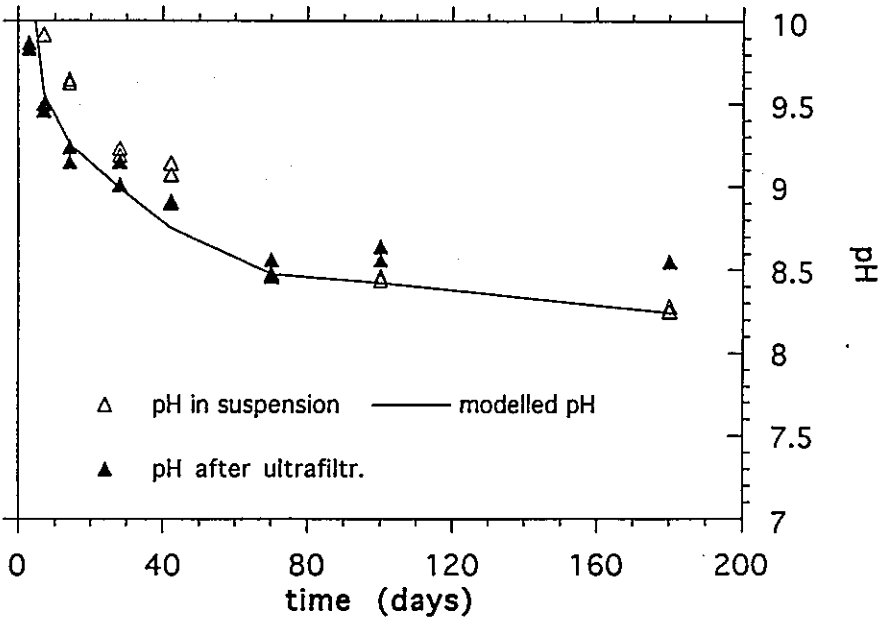

Figure 3 Development of pH during the interaction of Kunigel-V1 with water. Modeled pH values are compared with experimental data measured in suspension and after separation of solid and liquid phase by ultrafiltration (Sasaki, 1993; and Sasaki et al., 1995).

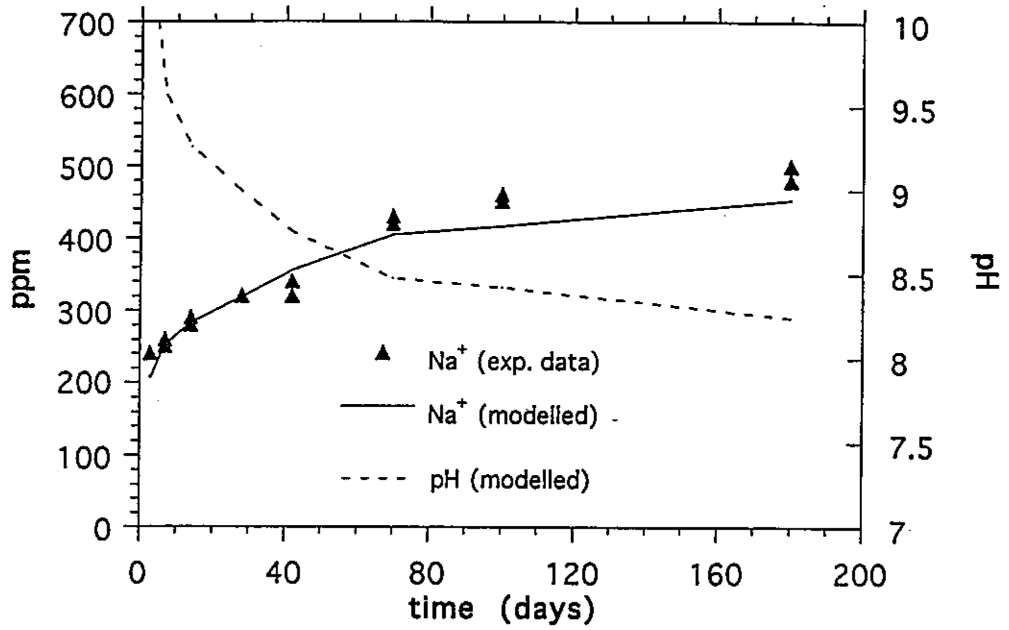

Figure 4 Development of Na+ concentration during the interaction of Kunigel-V1 with water. Modeled pH values are shown for reference.

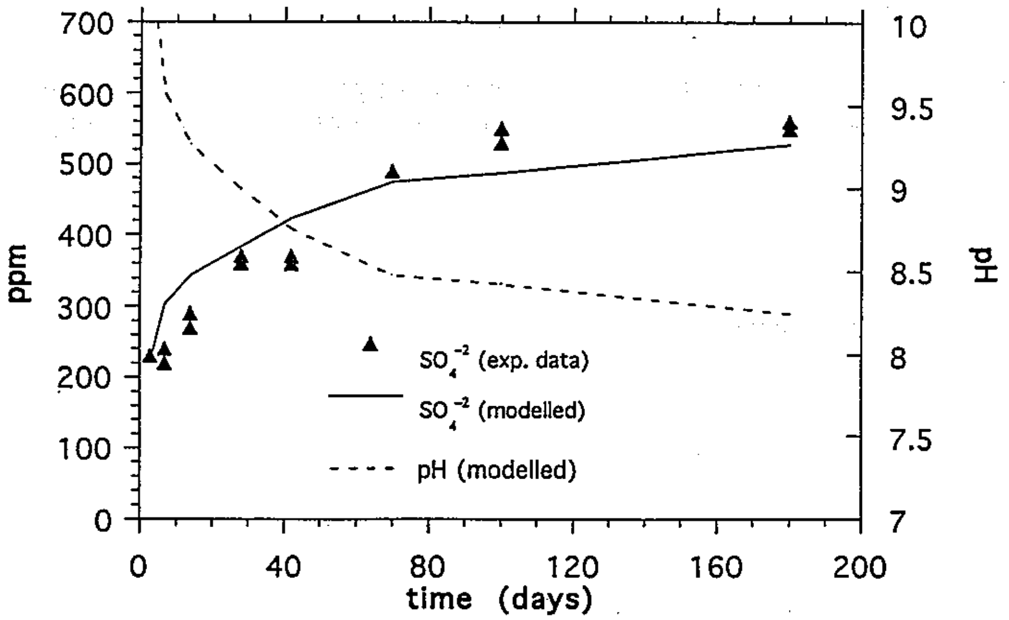

Figure 5 Development of SO_4^{2-} concentration during the interaction of Kunigel-V1 with water. Modeled pH values are shown for reference.

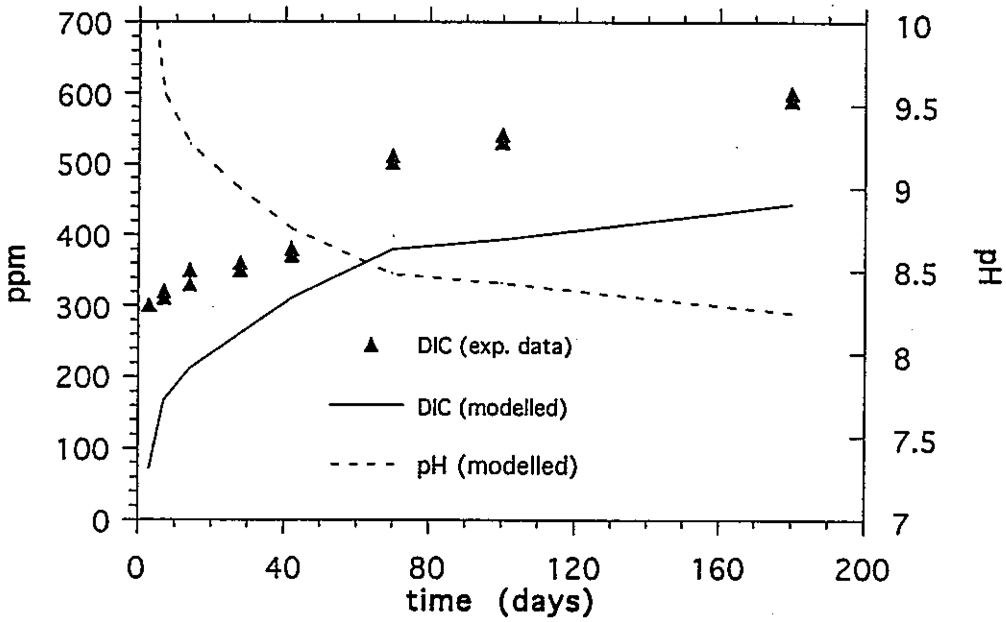

Figure 6 Development of (CO_3^{2-} + HCO_3^-) concentration, termed "dissolved inorganic carbon" (DIC), during the interaction of Kunigel-V1 with water. Modeled pH values are shown for reference.

1.1.1.2 Solution speciation under aerobic and anaerobic conditions

In order to gain information about the influence of pyrite contained in Kunigel-V1 on the composition of the surrounding solution, Sasaki et al. (1995) carried out leaching experiments under aerobic and anaerobic conditions. The data pertaining to aerobic conditions are documented in Figures 2 through 6 and compared to results obtained with the extended Wanner model.

The data pertaining to anaerobic conditions are documented in Figures 7 and 8 and compared to results obtained with the extended Wanner model. The model parameters used are identical to the ones listed in Table 3, except that no oxidation of pyrite is assumed. Further, the following two scenarios are considered:

1) The total carbonate and proton concentrations are set to 1.27×10^{-5} and 2.53×10^{-5} mol/L, respectively. This implies that distilled water with a pH of 5.67 and in equilibrium with atmospheric CO_2 is the only source of these species, and that the system is closed (model A).

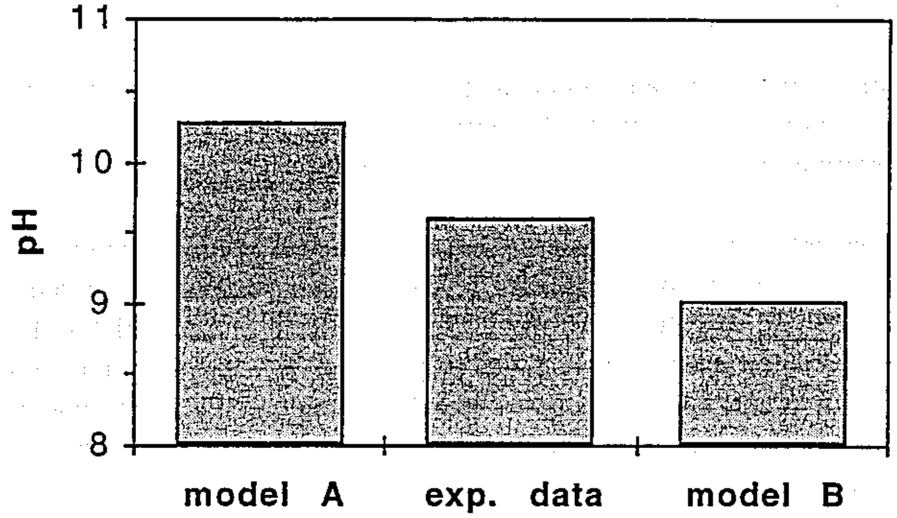

Figure 7 The pH measured in the anaerobic Kunigel-V1/water system in comparison with calculated pH values in anaerobic systems closed (model A) and open (model B) with respect to atmospheric CO_2.

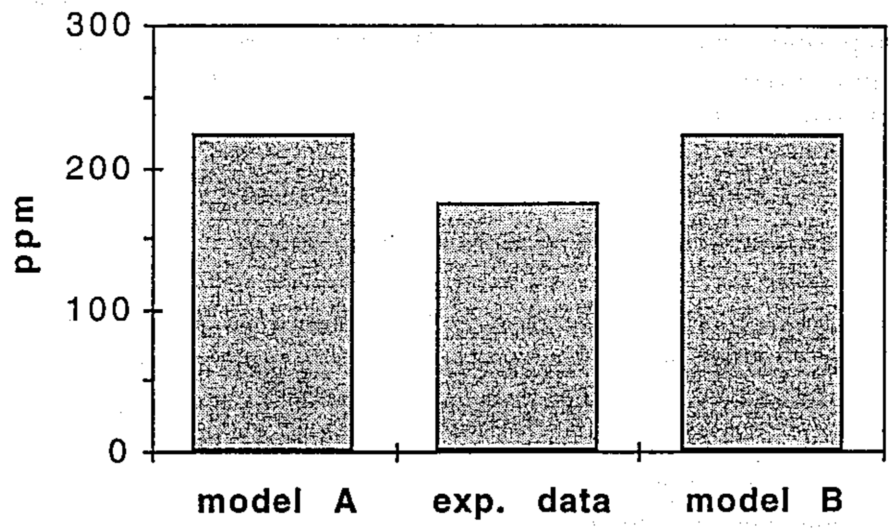

Figure 8 The SO_4^{2-} concentration measured in the anaerobic Kunigel-V1/water system in comparison with calculated SO_4^{2-} concentrations in anaerobic systems closed (model A) and open (model B) with respect to atmospheric CO_2.

2) For comparison, the system is assumed to be oxygen-free, but in equilibrium with atmospheric CO_2; accordingly, the pCO_2 is set equal to $10^{-3.5}$ atm (model B).

A comparison of measured and modeled pH values makes evident that proton-sensitive parameters such as pCO_2 are crucial. Apparently, the actual pCO_2 in the experimental system takes on an intermediate value of $0 < pCO_2 < 10^{-3.5}$ atm.

The SO_4^{2-} concentration determined by Sasaki et al. (1995) are somewhat lower than the results predicted by our model. However, the SO_4^{2-} concentration calculated (223.5 ppm) stems solely from the dissolution of the $CaSO_4$ contained in Kunigel-V1. In other words, there is no contribution due to the oxidation of pyrite. Given that the impurities contained in Kunigel-V1 are in equilibrium with the surrounding solution, 223.5 ppm may be regarded as a minimum SO_4^{2-} concentration. The data of Sasaki et al. (1995) may be explained by an incomplete dissolution of $CaSO_4$. Uncertainties in the measurements also may be considered.

1.1.2. Interaction of Kunigel-V1 with artificial groundwater

The artificial groundwaters used in the experiments with Kunigel-V1 comprise leachate solutions which were obtained by leaching two types of rock with water (Sasaki et al., 1995). The two types of rock were a granite and a strongly weathered tuff, the resulting solutions are henceforth refered to as "Groundwater A" (GWA) and "Groundwater B" (GWB), respectively. The total amounts of protons in these solutions available for interaction with Kunigel-V1 are estimated prior to running MIN_SURF. This is done by using the raw data regarding composition and pH of GWA and GWB reported by Sasaki et al. (1995) as input for the speciation program MINEQL. In turn, the results thus obtained are used as input for the extended Wanner model.

1.1.2.1 Interaction with leachate solution from granite (GWA)

The modeling approach taken is identical to the one used for modeling the interaction of Kunigel-V1 with distilled water, with one exception: in order to correctly predict the pH value, it is necessary to fix the partial pressure of CO_2. Here, a value of $10^{-3.5}$ atm is used. This value is close to the partial pressure of CO_2 calculated for the Kunigel-V1/distilled water-system if 25 % of the pyrite are oxidized ($10^{-3.308}$ atm). The chemical composition of the system is summarized in Table 4.

Taking into account the composition of GWA and the dissolution of impurities contained in Kunigel-V1, the experimental data are explained well by the extended Wanner model (Figure 9). The fact that Mg^{2+} concentrations are somewhat overestimated by the model may be explained by a merely partial dissolution of dolomite. We have demostrated the feasibility of this approach by predicting correctly the evolution of SO_4^{2-} with increasing partial dissolution of pyrite. Thus, no similar attempt is considered necessary for the case of dolomite.

Table 4: Chemical components used to model the interaction of Kunigel-V1 with GWA. Dissolution of 25 % of the pyrite present is assumed.

Component	contribution from GWA (mol/L)	contribution from Kunigel-V1 (mol/L)	total (mol/L)
Ca^{2+}	1.95×10^{-4}	6.06×10^{-3}	6.26×10^{-3}
Mg^{2+}	8.20×10^{-6}	6.85×10^{-4}	6.93×10^{-4}
Na^{+}	1.70×10^{-4}	5.13×10^{-2}	5.15×10^{-2}
K^{+}	1.20×10^{-4}	9.49×10^{-4}	1.07×10^{-3}
Fe^{3+}	1.25×10^{-3} *	0	1.25×10^{-3} *
H^{+}	1.96×10^{-3} **	0	1.96×10^{-3} **
SOH	0	2.84×10^{-3}	2.84×10^{-3}
CO_3^{2-}	5.08×10^{-4}	0	5.08×10^{-4}
Cl^{-}	7.30×10^{-5}	7.78×10^{-5}	1.51×10^{-4}
SO_4^{2-}	2.51×10^{-3} * -	2.79×10^{-3}	5.30×10^{-3}
$H_2SIO_4^{2-}$	9.60×10^{-5}	0	9.60×10^{-5}
Z^{-}	0	6.01×10^{-2}	6.01×10^{-2}

$CO_2(g)$ partial pressure set equal to 3.16×10^{-5} atm

* from 25 % pyrite oxidation (see text)

** from 25 % pyrite oxidation and available protons in GWA (see text)

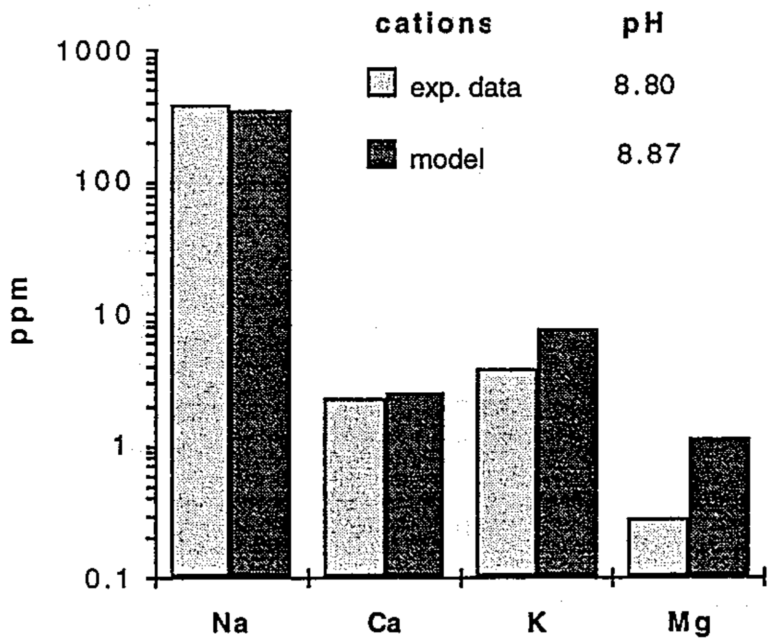

Figure 9 The interaction of Kunigel-V1 with GWA.

1.1.2.2 Interaction with leachate solution from tuff (GWB)

The modeling approach is identical to the one taken for the interaction of Kunigel-V1 and GWA. The input concentrations of the components are listed below (Table 5).

The agreement between experimental data and values predicted by the extended Wanner model for the interaction of Kunigel-V1 and GWB (Figure 10) is as good as in the case of GWA. Again, the dissolution of dolomite seems to be incomplete in the experiment.

1.1.3 Interaction of Kunigel-V1 with distilled water as a function of the liquid/solid ratio

The interaction of Kunigel-V1 with distilled water as a function of the water/bentonite ratio is modeled using the approach already outlined in Section 1.1.1, with the exception that the partial pressure of CO_2 had to be kept constant at $10^{-3.5}$ atm in order to explain the pH. As documented in Figure 1, an equilibration time of 180 days is assumed to result in a dissolution of 38% of the pyrite present in the system. Note that this assumption is made here for all water/bentonite ratios, although the rate of pyrite oxidation may depend on the water/bentonite ratio, too.

Table 5: Chemical components used to model the interaction of Kunigel-V1 with GWB. Dissolution of 25 % of the pyrite present is assumed.

Component	contribution from GWB (mol/L)	contribution from Kunigel-V1 (mol/L)	total (mol/L)
Ca^{2+}	6.00×10^{-3}	6.06×10^{-3}	1.21×10^{-2}
Mg^{2+}	6.20×10^{-4}	6.85×10^{-4}	1.31×10^{-3}
Na^{+}	1.48×10^{-3}	5.13×10^{-2}	5.28×10^{-2}
K^{+}	4.60×10^{-4}	9.49×10^{-4}	1.41×10^{-3}
Fe^{3+}	1.25×10^{-3} *	0	1.25×10^{-3} *
H^{+}	1.74×10^{-3} **	0	1.74×10^{-3} **
SOH	0	2.84×10^{-3}	2.84×10^{-3}
CO_3^{2-}	1.60×10^{-5}	0	1.60×10^{-5}
Cl^{-}	1.70×10^{-4}	7.78×10^{-5}	2.48×10^{-4}
SO_4^{2-}	1.08×10^{-2} *	2.79×10^{-3}	1.36×10^{-2}
$H_2SIO_4^{2-}$	1.05×10^{-4}	0	1.05×10^{-4}
Z^{-}	0	6.01×10^{-2}	6.01×10^{-2}

CO_2(g) partial pressure set equal to 3.16×10^{-4}atm

* from 25 % pyrite oxidation (see text)

** from 25 % pyrite oxidation and available protons in GWB (see text)

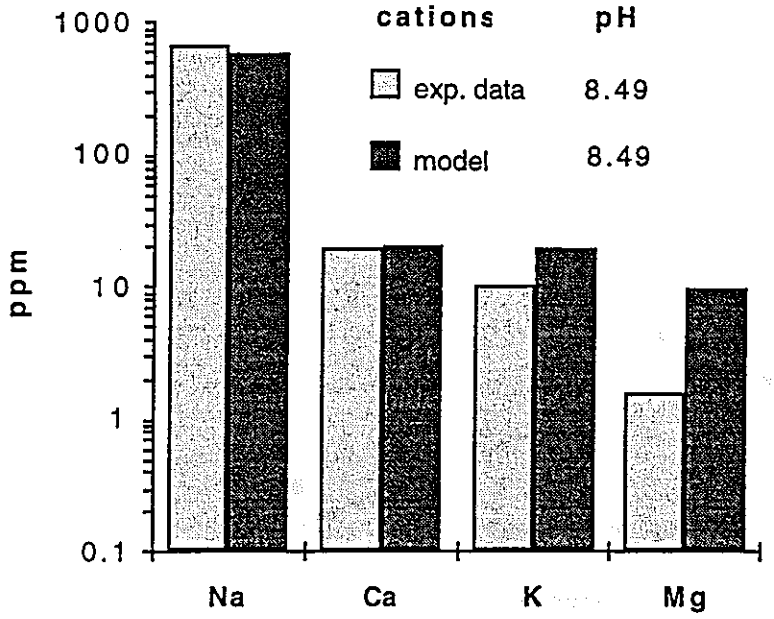

Figure 10 The interaction of Kunigel-V1 with GWB.

The Na^+ and DIC concentration, as well as the pH values measured by Sasaki et al. (1995) are compared with model predictions in Figure 11. The agreement between experimental and calculated pH values and Na^+ concentrations is excellent over a wide range of water/bentonite ratios. Carbonate species are underestimated by the model for higher bentonite concentrations. However, the predicted DIC concentrations correspond to a partial CO_2 pressure of $10^{-3.5}$ atm and the predicted pH values shown in Figure 11. Thus, the measured DIC concentrations obviously do not correspond to a CO_2 partial pressure in atmospheric equilibrium, but they correspond to a partial pressure of CO_2 of $>10^{-3.5}$ atm.

1.2 Interaction of Kunipia-F bentonite with distilled water

The mineralogical analysis of Kunipia-F is given by Ashida et al. (1994) and Sasaki et al. (1995), and the amount of soluble impurities is taken from Wanner and Wieland (1993). The CEC and the proportion of exchangable cations on the layer sites are given by Yajima (1993). The parameters used to model the interaction of Kunipia-F with distilled water are summarized in Table 6.

Additionally, the following general assumptions are made:

1) The system is always in equilibrium with quartz and calcite.
2) All solid phases in the system are assumed to be in equilibrium with the solution.

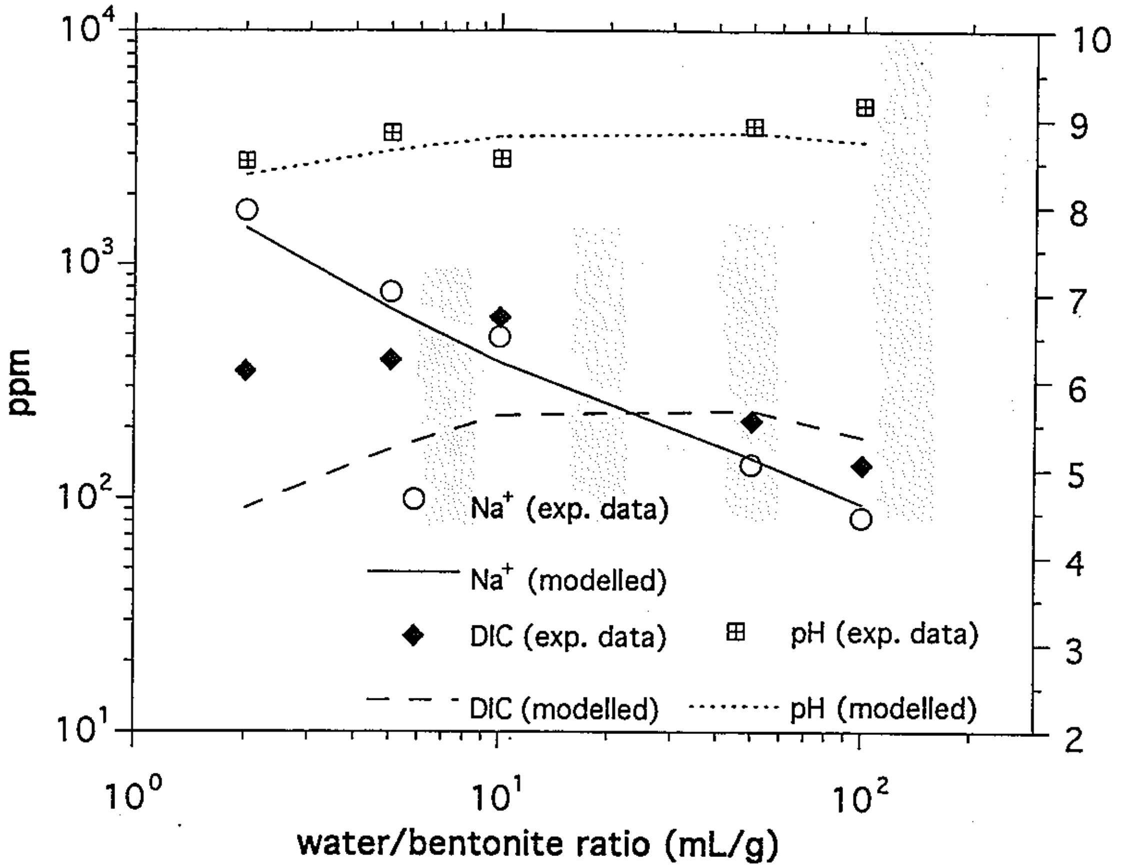

Figure 11 Interaction of Kunigel-V1 with distilled water as a function of the water/bentonite ratio.

3) All experimental data taken from Sasaki et al. (1995) have to correspond to the same equilibration time. For the present comparison of experimental and predicted data, an equilibration time of 14 days is assumed.

Since we have no detailed information regarding the partial pressure of CO_2, an approach considering two different scenarios is taken, similar to the one used to model the interaction of Kunigel-V1 with distilled water under aerobic and anaerobic conditions:

1) The total carbonate and proton concentrations are set to 1.27×10^{-5} and 2.53×10^{-5} mol/L, respectively. This implies that distilled water with a pH of 5.67 and in equilibrium with atmospheric CO_2 is the only source of these species, and that the system is closed (model A).

2) For comparison, the system is assumed to be in equilibrium with atmospheric CO_2; accordingly, the pCO_2 is set equal to $10^{-3.5}$ atm (model B).

Table 6: Composition and other specific parameters of Kunipia-F used in the evaluation of Kunipia-F/water interaction.

Parameters	Kunipia-F	Reference
Minerals:		
smectite	99 %	Ashida et al. (1994)
quartz	traces	Sasaki et al. (1995)
calcite	traces	Sasaki et al. (1995)
Soluble impurities:		
NaCl	0.071 %	Wanner and Wieland (1993)
KCl	0.005 %	Wanner and Wieland (1993)
$CaSO_4$	0.694 %	Wanner and Wieland (1993)
Cation exchange parameters:		
CEC	108 meq/100g	Yajima (1993)
exchangable Na^+	97.1 %	Yajima (1993)
exchangable K^+	0.9 %	Yajima (1993)
exchangable Mg^{2+}	1.3 %	Yajima (1993)
exchangable Ca^{2+}	0.7 %	Yajima (1993)

The experimentel data of Sasaki et al. (1995) are compared with predicted values based on the two approaches discussed above in Figures 12 through 15. While the agreement between the experiment and the extended Wanner model is excellent for SO_4^{2-}, and for DIC concentrations when equilibrium with the atmosphere is assumed, the pH is somewhat underestimated by this approach. One should note, however, that in a system that is in equilibrium with the atmosphere and that contains smectite and calcite, the pH is determined primarily through calcite-CO_2-H_2O interactions, and additionally influenced by ion exchange reactions. Since our model correctly predicts both DIC and Na^+ concentrations when equilibrium with atmospheric CO_2 and calcite is assumed, it seems not likely that the predicted pH value is not correct.

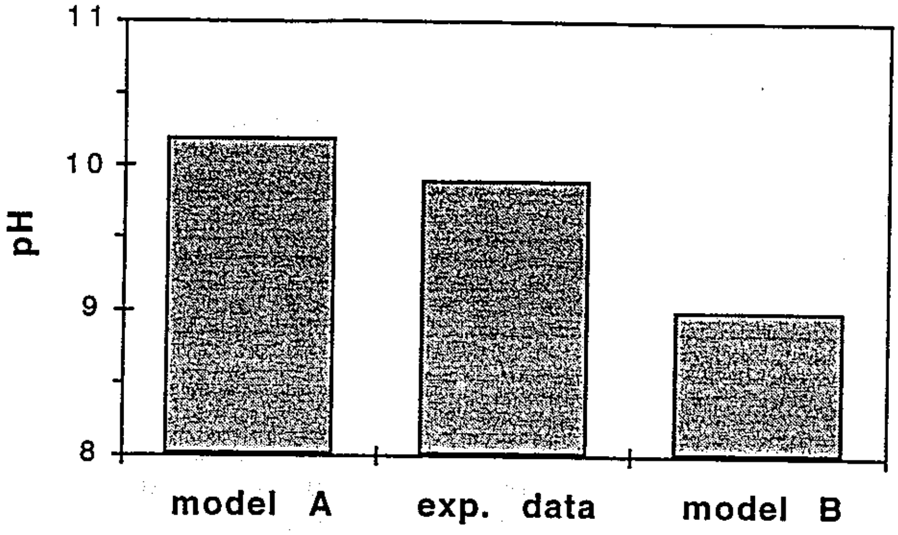

Figure 12 Interaction of Kunipia-F with distilled water. Predicted pH values assuming a system closed (model A) or open (model B) with respect to atmospheric CO_2 are compared with experimental data.

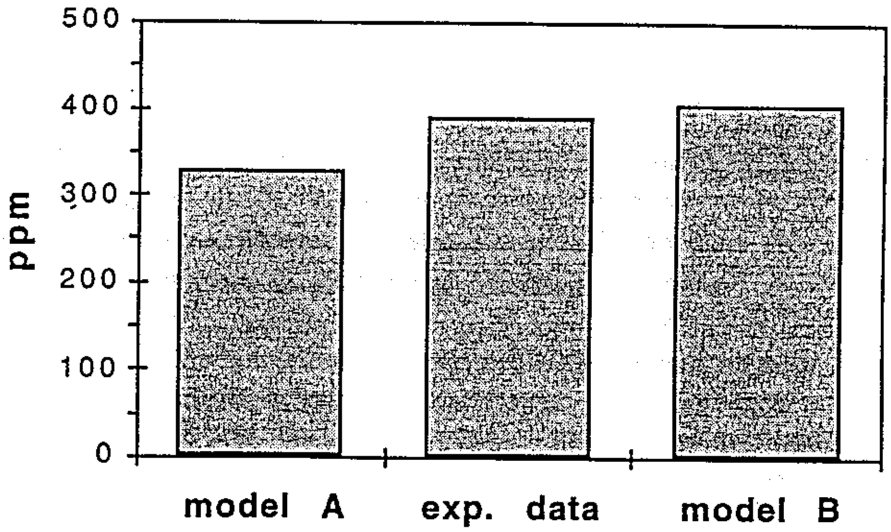

Figure 13 Interaction of Kunipia-F with distilled water. Na^+ concentrations predicted assuming a system closed (model A) or open (model B) with respect to atmospheric CO_2 are compared with experimental data.

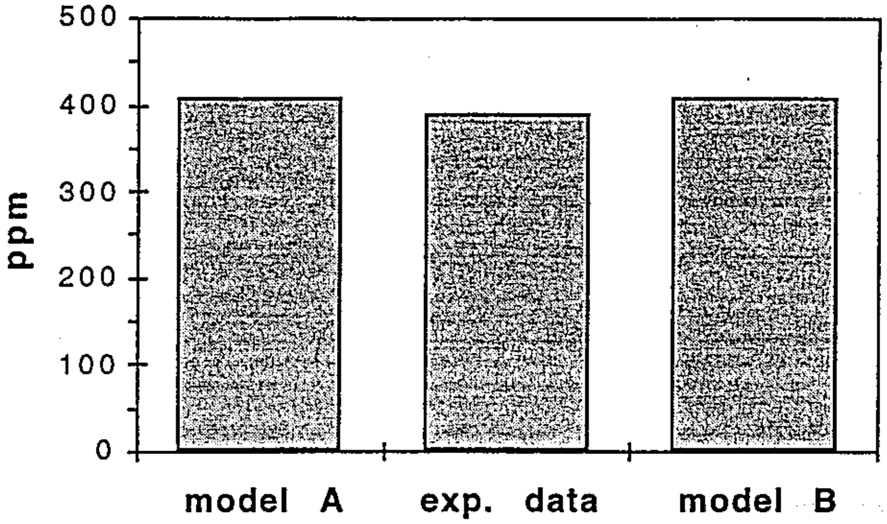

Figure 14 Interaction of Kunipia-F with distilled water. SO_4^{2-} concentrations predicted assuming a sytsem closed (model A) or open (model B) with respect to atmospheric CO_2 are compared with experimental data.

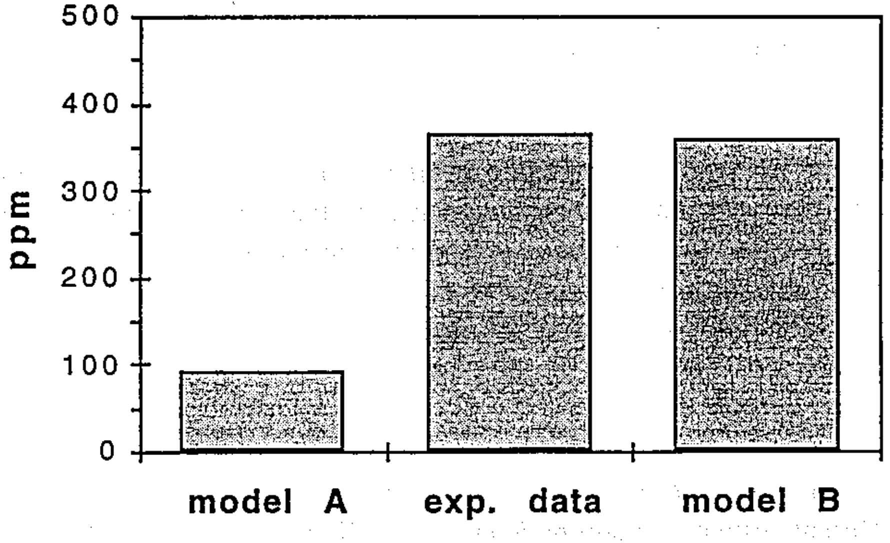

Figure 15 Interaction of Kunipia-F with distilled water. DIC concentrations predicted assuming a system closed (model A) or open (model B) with respect to atmospheric CO_2 are compared with experimental data.

1.3 Interaction of purified Na-smectite with distilled water

The interaction of purified Na-smectite with distilled water is modeled using the parameters given in Table 7.

Table 7: Composition and other specific parameters of purified Na-smectite used in the evaluation of Na-smectite/water interaction.

Parameters	Na-smectite	Reference
Minerals:		
smectite *	100 %	assumption (this study)
Cation exchange parameters		
CEC	108.1 meq/100g	Wanner and Wieland (1993)
exchangable Na^+	100 %	Wanner and Wieland (1993)

* Since no detailed analysis of the mineralogy of this material is available as yet, we assume only smectite to be present.

Sasaki et al. (1995) attempted to interpret the pH value observed for the Kunigel-V1/water system by adding either no or a known amount of calcite to the purified Na-smectite and measuring the resulting pH. Their experimental findings are compared with values predicted using the extended Wanner model in Table 8.

The pH measured by Sasaki et al. (1995) in the system containing 4 % calcite is decribed satisfactorily by the extended Wanner model. It is further demonstrated that an addition of calcite as an impurity (4 %) of smectite is equivalent to putting the solution into equilibrium with calcite as a separate phase. In order to explain the pH measured in the system without calcite, an input of 5.00×10^{-2} mol/L H^+ has to be assumed in the model calculations, however. Notably, such an input of protons causes the model to underestimate the pH in the system containing calcite.

The extended Wanner model is able to predict the solution speciation, including pH, in a number of different systems containing Kunigel-V1, Kunipia-F, purified Na-smectite/calcite, and Wyoming bentonite MX-80 (Wanner et al., 1994; Wieland et al., 1994). Thus, it seems likely that the discrepancy between experimental and modeled data in the system containing purified Na-smectite but no calcite are the result of uncertain pH measurements in solutions that are not buffered well enough. Furthermore, the procedure used to prepare the purified Na-smectite is rather uncommon (Oda, 1994; Oda 1995; Sasaki et al., 1995), and more information regarding the characteristics of this material would be helpful in order to exclude the possibilities of experimental errors.

Table 8: Interaction of purified Na-smectite (with and without added calcite) with distilled water. Both open and closed systems are considered in the model calculations.

calcite added	model assumption	pH	Reference
experimental data:			
-	-	6.00	Sasaki et al. (1995)
4 % $CaCO_3$	-	9.50	Sasaki et al. (1995)
model:			
-	A *	10.50	this study
-	B *	8.72	this study
-	C *	6.00	this study
-	D *	6.00	this study
4 % $CaCO_3$	B *	9.25	this study
4 % $CaCO_3$	C *	6.50	this study
4 % $CaCO_3$	D *	8.19	this study
calcite equilibrium	B *	9.25	this study

* The assumptions made regarding the input of H^+ and CO_2 are as follows:

A: initial input of 1.27×10^{-5} mol/L CO_3^{2-} and 2.53×10^{-5} mol/L H^+, closed system.

B: system open with respect to atmospheric CO_2, i.e., $pCO_2 = 10^{-3.5}$ atm, no further input of H^+ and CO_2.

C: 5.00×10^{-2} mol/L H^+ and 1.27×10^{-5} mol/L CO_3^{2-} added, closed system.

D: 5.00×10^{-2} mol/L H^+ added, $pCO_2 = 10^{-3.5}$ atm.

2 Acid/base chemistry of purified Na-smectite ("Oda experiments")

Information pertaining to the properties and chemistry of the purified Na-smectite used by Sasaki et al. (1995) and Oda (1994, 1995) is already given in the previous section of this report. In order to gain more information about the interaction of protons with purified Na-smectite, Oda (1994, 1995) carried out several batch titrations. This investigation employed a range of equilibration times, but only one ionic background medium (0.001 mol/L NaCl).

2.1 Proton balance calculations

The raw titration data of Oda (1994, 1995) are interpreted using proton balance calculations. The concentration of H^+ and OH^- bound onto the surface of montmorillonite (i.e., the portion of surface charge due to H^+ and OH^- surface interaction in the case of simple oxides) can be calculated from the difference between the total H^+ or OH^- added to the suspension and the equilibrium H^+ and OH^- concentration as a function of pH. The concentration of protons or hydroxide ions (further denoted $\Delta[H^+]$) bound onto the surface is given by:

$$\Delta[H^+] = \left(\frac{c_A - c_B - [H^+] + [OH^-] - C}{a}\right) \qquad [\text{mol/g}] \qquad (2a)$$

or

$$\Delta[H^+] = \left(\frac{[H^+]_t - [H^+] + \frac{K_W}{[H^+]} - C}{a}\right) \qquad [\text{mol/g}] \qquad (2b)$$

where:

$[H^+]_t$: ($=c_A - c_B$) total proton concentration [mol/dm^3]
$[H^+]$: free proton concentration in solution
K_W : ion product of water
C : correction factor for proton consuming side reactions
a : initial suspension concentration [g/dm^3]
$c_A - c_B$: concentrations of added base or acid [mol/dm^3]

$\Delta[H^+]$ is the surface proton (hydroxyl) concentration, c_A and c_B are the total concentrations of added acid and base [mol/dm^3], respectively. The suspension concentration, C_s [g/dm^3], is given by:

$$C_s = \frac{V_0\, a}{V_0 + v} \qquad [\text{g/dm}^3] \qquad (3)$$

Since the added volume of acid or base is small compared to the initial volume, V_0, of the suspension ($V_0 >> v$), dilution is negligible during the titration experiments and, hence, $C_s \approx a$.

C denotes a correction factor accounting for proton consumption due to dissolution processes and titration of soluble Al and Si species present in suspension. This correction factor in the proton balance as given in Eqs. (2a) and (2b) accounts for proton consumption due to hydrolysis of Al over the entire pH range and due to deprotonation of monomeric $Si(OH)_4$ in the alkaline pH range. In the acid pH range, contributions of soluble, monomeric hydrolysis products of Al ($= Al(OH)_m^{3-m}$) are considered according to

$$C = \sum_{m=0}^{3} (3-m)\, \beta_{1,m}\, \alpha_H\, [Al]_t\, [H^+]^{-m} \qquad [\text{mol/L}] \qquad (4a)$$

with $\alpha_H = (1 + \beta_{1,1} [H^+]^{-1} + \beta_{1,2} [H^+]^{-2} + \beta_{1,3} [H^+]^{-3} + \beta_{1,4}[H^+]^{-4})^{-1}$ and $[Al]_t$ as the total concentration of Al in solution. In the alkaline pH range, the formation of $Al(OH)_4^-$ and the deprotonation of silicic acid, $Si(OH)_4$, are considered as the interfering reactions:

$$C = \beta_{1,4}\, \alpha_H\, [Al]_t\, [H^+]^{-4} + K_1\, [Si]_t\, [H^+]^{-1} \qquad [\text{mol/L}] \qquad (4b)$$

with $[Si]_t$ as the total concentration of Si in solution. Equilibrium constants, $\beta_{1,m}$, for Al hydrolysis are taken from Baes and Mesmer (1976), and the acidity constant, K_1, for silicic acid is taken from Grenthe et al. (1992).

Deprotonation of $Si(OH)_4$ is the main contribution to corrections in the proton balance. Hence proton balance in the acidic pH range is adequately described by neglecting the correction factor, C, in Eqs. (3a) and (3b). Since no unambigous information concerning the Si and Al concentration in the titration experiments is available, an average concentration of 10^{-4} M for both Si and Al is assumed for calculating the correction factor. It is important to note, however, that the influence of C is very small with respect to $\Delta[H^+]$.

2.2 *Modeling*

Modeling of the titration experiments is performed by using data sets of $\Delta[H^+]$ vs. pH as input concentrations for the extended Wanner model implemented in the computer code GRFIT (Ludwig, 1992). For the interpretation of the acid/base chemistry of smectite, we use an approach identical to Wanner et al. (1994) and Wieland et al. (1994), i.e., the extended Wanner model with two different layer sites. This guarantees maximum flexibility in modeling the interaction of H^+ with smectite in the acid pH range, where layer sites are most relevant. The descripition of acid/base equilibria in the neutral and basic pH range is not influenced by choosing either one or two layer sites. The relevant parameters are given in Table 9. We would like to stress that no fitting procedures are used, i.e., the model is utilized exclusively to calculate the surface and solution speciation as a function of pH. The data thus calculated are presented in Figure 16.

It is obvious that there is no satisfactory agreement between the experimental and calculated data. An inspection of the plot suggests that the inflection point or buffering plateau of the experimental titration curve (which should correspond to $\Delta[H^+] \approx 0$ mol/g) corresponds to $\Delta[H^+] \approx 4\times10^{-5}$ mol/g. In other words, the system behaves as if the complete titration curve was shifted by a constant amount of about 4×10^{-5} mol/g into the basic region of the plot. It should be stressed at this point that the interpretation of the experiments that Sasaki et al. (1995) carried out with purified Na-smectite in the absence of calcite also can be explained only when the input of additional protons (5×10^{-4} mol/g) is assumed (cf. footnotes C and D of Table 8). Assuming the presence of 4.2×10^{-5} mol/g H^+ to be present in the system considered here (e.g. as residual acid from the preparation of Na-smectite) leads to the data presented in Figure 17.

Table 9: Chemical components used to model the acid/base chemistry of purified Na-smectite. The water/smectite ratio is 200 mL/g.

Component	contribution from solution (mol/L)	contribution from smectite (mol/L)	total conc. (mol/L)
Na^+	1.00×10^{-3}	4.41×10^{-3}	5.41×10^{-3}
pH, $\Delta[H^+]$	*	*	*
SOH	0	1.42×10^{-4}	1.42×10^{-4}
Cl^-	1.00×10^{-3}	0	1.00×10^{-3}
X^- **	0	1.10×10^{-4}	1.10×10^{-4}
Y^- **	0	4.30×10^{-3}	4.30×10^{-3}

* These parameters are varied and calculated according to the input given (see text).

** This terminology for the two layer sites is choosen to be consistent with Wieland et al. (1994) and Wanner et al. (1994) (see text).

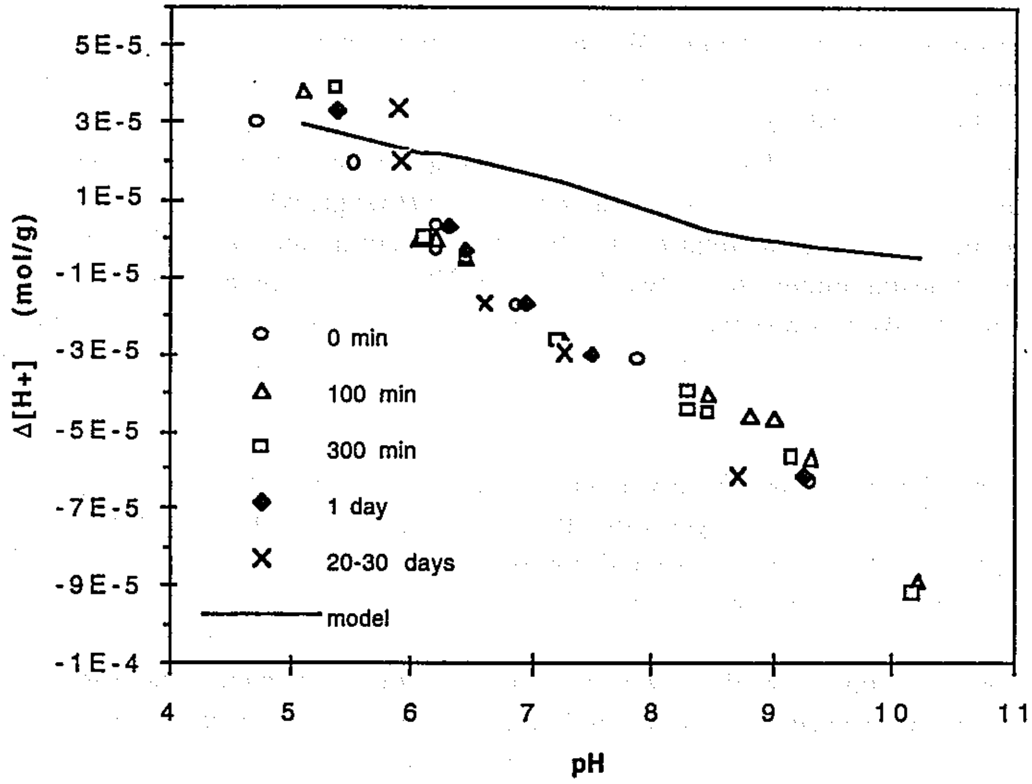

Figure 16 Experimental titration data (Oda, 1995) corresponding to a range of equilibration times in comparison with model predictions. Note that the equilibration times do not include the time needed to obtain a stable pH reading.

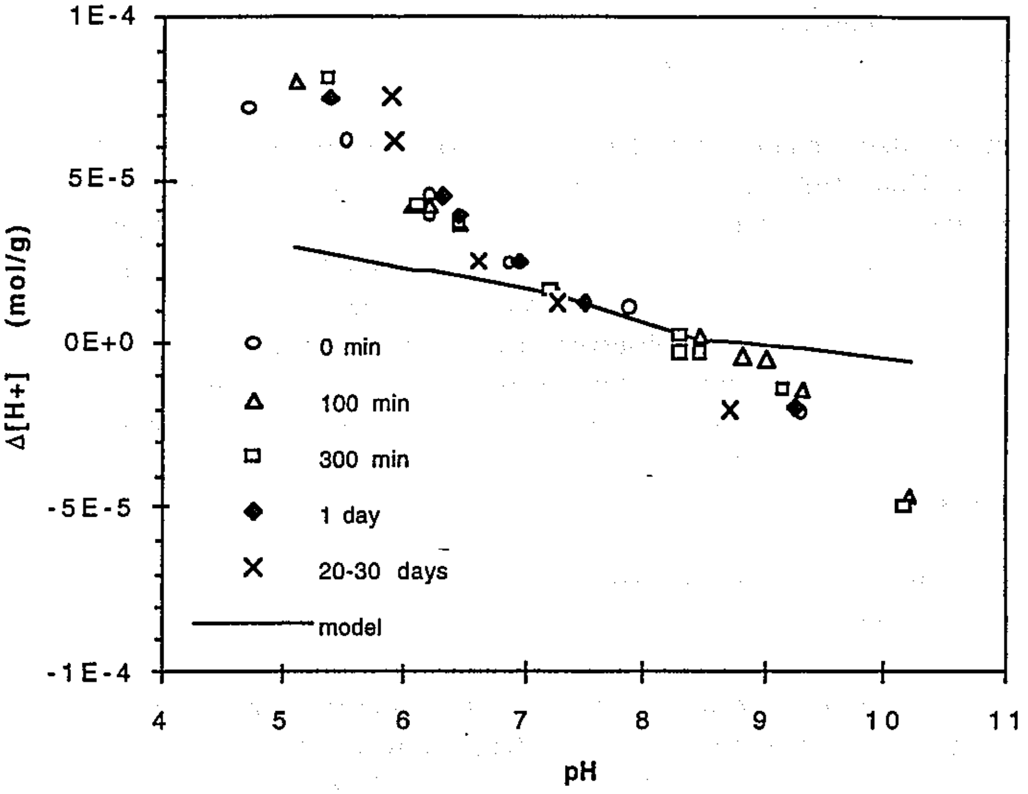

Figure 17 Experimental titration data (Oda, 1995) corresponding to a range of equilibration times in comparison with model predictions, assuming 4.2×10^{-5} mol resudial acid per g of purified Na-smectite. Note that the equilibration times do not include the time needed to obtain a stable pH reading.

The fact that similar amounts of protons have to be added to the system in order to explain the data of Sasaki et al. (1995) and Oda (1995) involving the purified Na-smectite, suggest that the discrepancies between experimental data and model may relate to this particular material. At this point, not enough information is available regarding the characteristics of the purified Na-smectite to make a serious attempt of improving this situation. Further, not enough titration data are available in order to justify any modifications of the extended Wanner model.

3 Concluding remarks and recommendations

- All experiments involving the interaction of Kunigel-V1 and Kunipia-F with either distilled water or artificial groundwater are explained well by the extended Wanner model. The model parameters established for Wyoming bentonite MX-80 are thus also valid for the two aforementioned bentonites.

- Interpretation of the data by Sasaki et al. (1995) and Oda (1995) was somewhat complicated by the fact that the control of pCO_2 and temperature was not rigorous enough. We recommend that great care is taken in the future to make sure that pCO_2 and temperature are always constant and known.

- Experimental data obtained with the purified Na-smectite used by both Sasaki et al. (1995) and Oda (1995) pose considerable problems regarding their interpretation. However, the good performance of the extended Wanner model with all other bentonites investigated so far, and the fact that very similar correction factors have to be assumed for the data of both Sasaki et al. (1995) and Oda (1995) suggests that the purified smectite itself may be the source of the observed discrepancies. We strongly recommend (1) a more detailed characterization of the purified Na-smectite prepared so far, and (2) preparation of purified Na-smectite by well established methods (cf. Wieland et al., 1994; and Wanner et al., 1994) in order to exclude the introduction of artefacts during the preparation step.

- The data of Oda (1995) contain potentially valuable kinetic information. Unfortunately, an in-depth interpretation is not possible due to the problems discussed in the previous paragraph. Further, if it should turn out in future investigations that the purified Na-smectite does require some modifications of the parameters of the extended Wanner model, a more complete and consistent data set would be required. Of particular importance in this regard is the utilization of a range of ionic background solutions. It is essential that at least one or two ionic media with an ionic strength of 0.05 to 0.1 mol/L or higher are included. In dilute ionic media, accurate potential (pH) measurements become also very difficult and require a very rigorous experimental protocol.

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巻末資料 2

Recommendation for Framework of Integrated Sorption/Diffusion (ISD) Database System

Power Reactor and Nuclear Fuel Development Corporation (PNC)

ISD Database System

Recommendation for Framework of Integrated Sorption/Diffusion (ISD) Database System

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Abstract

The understanding and the consistent treatment of sorption and diffusion mechanisms is of central importance in the assessment of the migration behavior of radionuclides in compacted bentonite. The present report proposes a concept for an integrated sorption/diffusion (ISD) database system containing TDB, intrinsic data bases, and mechanistic models according to the PNC approach. The model components are described, examples of data records are given, diffusion model approaches used in various performance assessment programs are compared with the PNC approach, and an action plan for the development of the ISD database system is proposed.

The ISD database system includes a bypass option on the basis of systematic chemical analogy for radionuclides that are lacking data on either sorption or diffusion mechanisms, or both. The bypass option is useful for radionuclides of lower priority or if time limitations do not allow lengthy experimental procedures. In particular, for the ISD database system to be developed in the framework of the next performance assessment report of PNC, the bypass option is likely to represent an essential tool for state-of-the-art estimations of missing parameters.

Executive Summary

A concept is proposed for the development of an integrated sorption/diffusion (ISD) database system as shown in Figure 1 which is reproduced below for convenience. An integrated approach is important to ensure consistency between the mechanistic sorption model and the mechanistic diffusion model, because a number of cross-links tie the two models together. These cross-links are the following:

1. Information on the bentonite characteristics (e.g., mineralogical composition, CEC, exchangeable ions, soluble impurities, dry density, specific density, surface area, tortuosity) is partly used in both models and must be consistent and fully traceable.

2. The physicochemical parameters of the diffusing species and of the major ions (charge, concentration) are needed as input data in the mechanistic diffusion model. A speciation calculation such as the one in the extended Wanner model provides information on the kind of solution species formed under the relevant bentonite/groundwater conditions.

3. The distribution coefficient, K_d, forms a link between the apparent diffusivity, D_a, and the mechanistic diffusion model. K_d is an output parameter of the mechanistic sorption model, and is needed together with the diffusion model to calculate D_a.

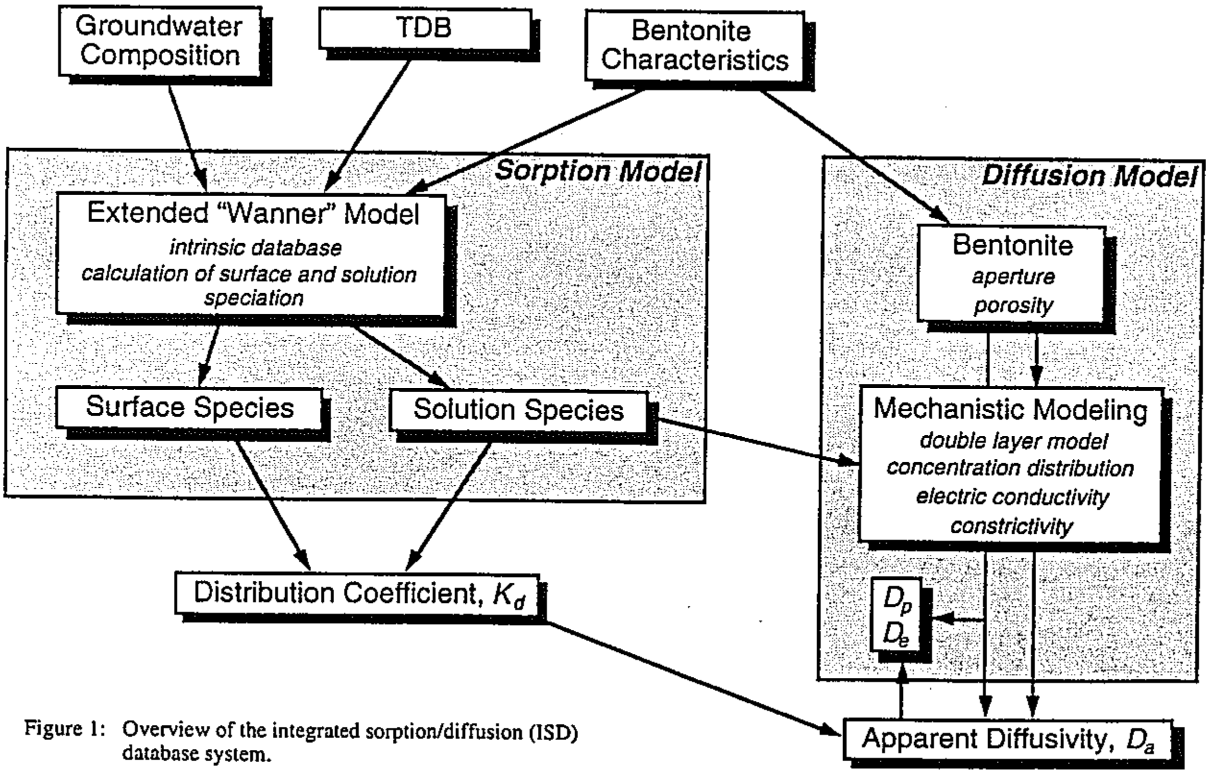

Figure 1: Overview of the integrated sorption/diffusion (ISD) database system.

The Figure shows that the ISD Database is a rather complex system. We therefore put much weight on a systematic approach in selecting input data and models. The input data records "Groundwater Composition", "TDB" and "Bentonite Characteristics" are described. They need to be defined carefully and labeled clearly for quality assurance. The TDB is used in all the applications of the ISD database. The availability of a reliable TDB is of crucial importance for mechanistic sorption and diffusion modeling. The mechanistic sorption model consists of the extended Wanner model which includes two different types of surface sites relevant in bentonite: ion exchange sites and surface complexation sites. The development of an intrinsic database (containing intrinsic constants for the surface complexation reactions) is required for mechanistic sorption modeling. The intrinsic database is a part of the extended Wanner model. The mechanistic diffusion model uses structural parameters and the electric double layer model to quantify the interactions of ions with the bentonite surface. The apparent diffusivity, D_a, is a direct result of this model plus the output parameter of the sorption model: the distribution coefficient, K_d. The pore and effective diffusivities, D_p and D_e, are not needed in the calculation if all the data required for the mechanistic model are available. However, since D_p and D_e are independent of K_d and of the chemical sorption model, they are very valuable to check the quality of the mechanistic diffusion model, and they are in any case derived from D_a (or directly from the mechanistic diffusion model).

It cannot be expected that a complete intrinsic database will be available on time for the next PNC Performance Assessment Report in 1999. In order to enable the performance of a safety assessment before 1999 (including transport analysis of radionuclides in compacted bentonite), we recommend a "bypass option", i.e., to use the same ISD database system but to estimate certain variables according to mechanistic considerations. A prerequisite for such estimations is a reliable TDB. Based on speciation calculations, the K_d value can be estimated by using valid analogs for the various oxidation states of the radionuclides. In the mechanistic diffusion model, lack of data can be compensated for by estimating D_p or D_e based on analogies. Here too, a reliable TDB is required to assess the quality of an analog.

Appendix A contains an action plan on how to develop and verify the ISD database with respect to the timeframe of the next PNC Performance Assessment Report in 1999 (meaning that the ISD database system will have to be frozen in 1997). Priorities and the best sequences of the activities can be seen from this chart.

The diffusion model developed at PNC is part of the ISD database system. Differences between the PNC model and the approaches used by other groups (TVO, SKB, AECL, Wanner) are presented and discussed in Appendix B.

The extended Wanner model and the differences to the earlier Wanner model are described in Appendix C. The preparation of data for the input records is outlined and examples of data records are presented in the corresponding sections in the report. In addition, an example of a full data set of the mechanistic sorption model and the mechanistic diffusion model according to the PNC approach is given in Appendix D for Cs^+ diffusion in Kunigel-V1. The TDB used in connection with the extended Wanner model is listed in full size in Appendix E.

Table of Contents

1 Introduction

Like in other countries, the Japanese disposal concept for high-level radioactive waste envisages the use of compacted bentonite as a backfill material (PNC, 1992). Performance assessment requires a safety analysis which consists in essence of a computer simulation of the migration of the radionuclides from the waste matrix to the biosphere including uptake by man. The resulting dose rates as a function of time allows to judge the safety of the repository. After the release from the waste matrix, the radionuclides will migrate through the backfill of compacted bentonite before reaching the host rock. The backfill is probably the most effective and predictable barrier on the entire migration path after release from the waste matrix. High importance is therefore attributed to the thourough understanding of the processes affecting radionuclide transport in compacted bentonite.

Migration of radionuclides in compacted bentonite takes place by diffusion. The pore sizes in compacted bentonite are very small, and the electric potential fields building up due to excess charges on the surfaces are expected to lead to an uneven distribution of the diffusing ions in the pores. The degree of polarization depends mainly on the charges of the ions and has an effect on the apparent diffusivities. Another parameter which has an effect on the apparent diffusivity is the distribution coefficient, K_d. The K_d value depends on the distribution of the species in solution and on the bentonite surface, and hence indirectly on the groundwater composition, the thermodynamic database (TDB), the bentonite characteristics, and the thermodynamic model for the interactions on the bentonite surface.

It is obvious that the datasets of dependent models should be developed in an integrated way to ensure consistency and traceability. Both the sorption model and the diffusion model require information on the bentonite characteristics. The mechanistic diffusion model requires information on the solution species provided by the sorption model. The apparent diffusivity can be derived only by means of the K_d value resulting from the sorption model. In the present report we present our recommendation for the development of an integrated sorption/diffusion database system.

2 Description of the proposed integrated sorption/diffusion database system

The purpose of the intrinsic sorption/diffusion (ISD) database system is to have a concise, complete and consistent database which includes all the parameters and variables required to derive a distribution coefficient, K_d, and an apparent diffusivity, D_a, for a given element or species, by using mechanistic sorption and diffusion models. Since the mechanistic diffusion model depends strongly on certain output parameters of the sorption model, and both the sorption and diffusion models depend on the characteristics of the bentonite, it makes sense to produce a combined information system containing all the data and models used in deriving K_d and D_a, values. Input parameters such as groundwater composition and TDB are also part of the ISD database, because these data have a direct impact on the results of the sorption model and indirectly on the results of the diffusion model. For example, a change in the TDB may lead to a change in the resulting solution species, leading to a different K_d value and a different diffusion behavior.

Figure 1 gives an overview of the structure of the proposed ISD database system. The figure consists of boxes and arrows. The boxes represent data records and models, respectively. The arrows represent input/output data transfers. Both the data records and the models carry labels in the form of names or version numbers. Hence, the resulting K_d and D_a values for a specific nuclide can be referred to a well-defined bentonite (e.g., Kunigel-V1), TDB, groundwater type, sorption model, and diffusion model, ensuring full internal consistency. In the following paragraphs each of the boxes of Figure 1 is described and explained. An important geochemical parameter, which is not explicitely mentioned in the structure presented in Figure 1, is the redox potential, Eh. The Eh value is not an input parameter but is defined by the geochemical model. Paragraph 2.11 presents a proposal on how to deal with uncertainties in the redox potential.

2.1 Groundwater composition

The groundwater composition is an input data record which is labeled with a name or a number. Examples would be "Allard water" or "Sasaki-A" and "Sasaki-B". The record contains essentially the input parameters required for the extended Wanner model: For each element the identification number, the chemical formula of the master species, an estimation of its free equilibrium concentrations in the porewater (used as a starting condition for the Newton-Raphson algorithm), and the total concentration of this element in the groundwater are listed. Table 1 shows an example of a groundwater composition record.

It is a matter of policy to define reference waters, either synthetic or natural. Reference waters represent the hydrochemical conditions at a specific site or in a certain type of host rock (preferably at the envisaged repository site). The definition of a reference groundwater is the result of modeling studies and of the interpretation of chemical analyses. This can only be done properly if the mineralogical composition of the rock in equilibrium with the groundwater is known, because the equilibria with mineral phases can then be more reliably defined.

Boundary conditions that are an integral part of the definition of the groundwater may also be included in this record, for example saturation with calcite or quartz, a partial pressure of CO_2 or a redox potential. In addition, it is useful to indicate the pH of the groundwater, although the pH is not an input parameter to the speciation calculation: The input parameter for the proton balance is the total H^+ concentration rather than the pH, because the pH value will change in contact with the bentonite. The total H^+ concentration of the groundwater can be determined, for example, by fixing the pH at the value measured and calculating the mass transfer of H^+.

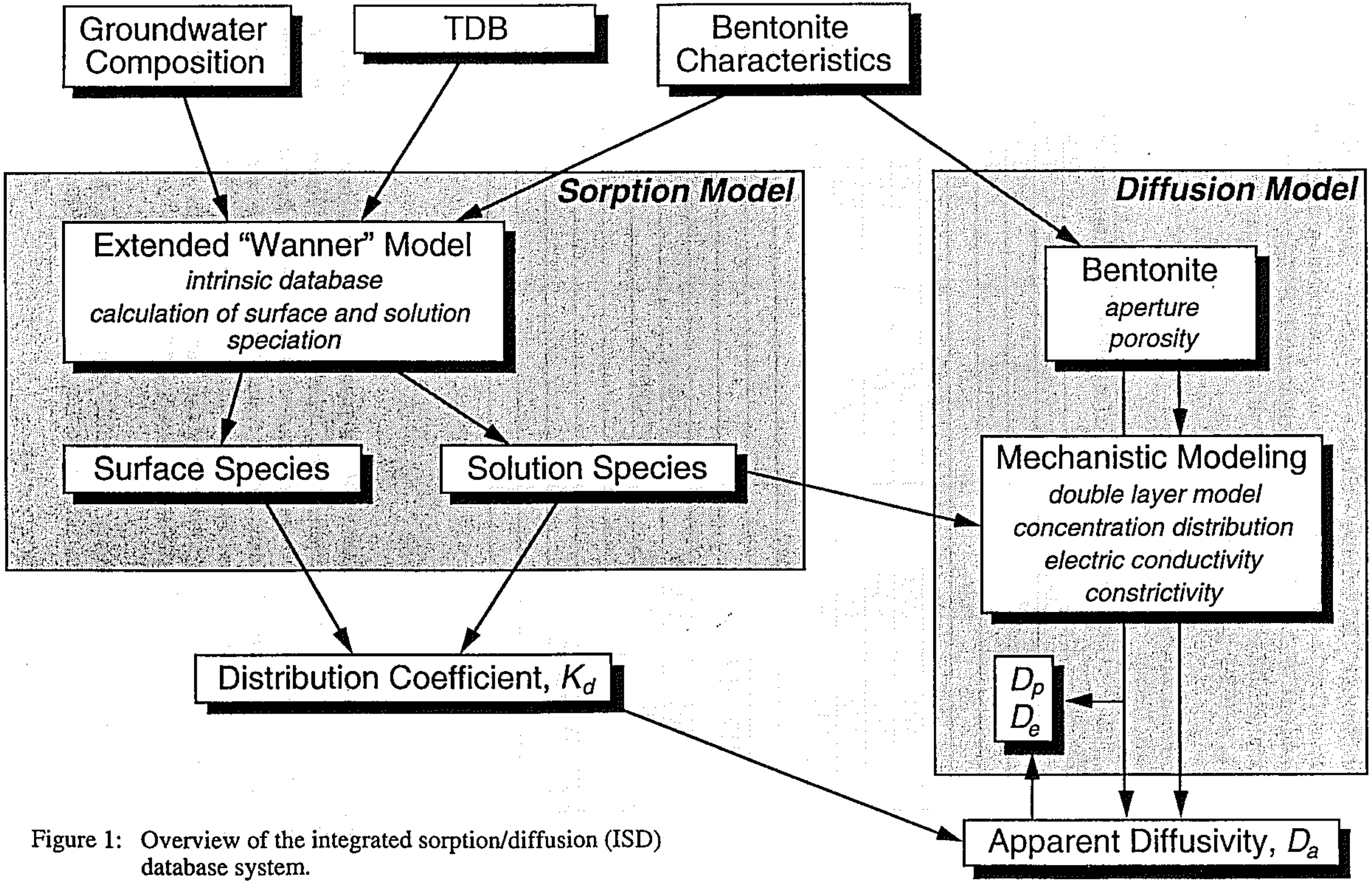

Figure 1: Overview of the integrated sorption/diffusion (ISD) database system.

Table 1: Example of a groundwater composition record. The ID numbers are code specific. The master species is taken as the representative species of the element. The total concentration (last column) refers to the master species. Here, the total H^+ concentration is calculated in view of the distribution of H^+ and OH^- at the relevant pH (8.2): carbonate will be protonated (HCO_3^-) and the silicon master species ($H_2SiO_4^{2-}$ or $SiO_2(OH)_2^{2-}$) will carry two protons (as $Si(OH)_4$). Hence, $[H^+]_{tot} = [CO_3^{2-}]_{tot} + 2[H_2SiO_4^{2-}]_{tot}$.

Allard synthetic granitic groundwater (Allard, 1982)			
ID (MIN_SURF)	master species	log c (estimated)	total conc. of element [mol/L]
1	Ca+2	-4.00	4.5 E-4
2	Mg+2	-4.00	1.8 E-4
4	K+	-4.00	1.0 E-4
5	Na+	-3.00	2.8 E-3
50	H+	-8.00	2.4 E-3
101	CO3-2	-5.00	2.0 E-3
102	SO4-2	-4.00	1.0 E-4
103	Cl-	-3.00	2.0 E-3
112	H2SiO4-2	-9.00	2.0 E-4
Boundary conditions:			
20000	calcite	saturated	
21440	quartz	saturated	
Usful information:			
pH	8.2		

2.2 *Thermodynamic Database (TDB)*

The chemical thermodynamic database (TDB) is used to calculate the concentrations of the species that may be formed under well-defined chemical conditions. Thermodynamic data which are model-specific (e.g., ion exchange constants and surface complexation constants) should be part of the extended Wanner model, rather than of TDB. It is essential that the contents of a certain TDB version are never modified. If important modification in TDB are necessary, the new TDB will have a new version number, and the changes made are documented in a report which is available to the users of TDB.

The TDB is the source of consistency in an ISD database system. A high-quality and consistent TDB is a prerequisite for ISD modeling. Hence, the TDB must be carefully verified. The data for most groundwater species are of good quality in many databases, but the data for trace elements such as radionuclides need to be verified in most cases. One of the key parameters for mechanistic diffusion modeling, namely the charge of the dominant species of a key element, is obtained from a speciation calculation using a high-quality TDB. In the case of an abbreviated procedure according to the description in Paragraph 3.1 (lack of intrinsic sorption data), the quality of the TDB, for example for plutonium, is critically important, and the estimated K_d value may be wrong if the TDB is incorrect.

Thermodynamic databases are often supplied together with a speciation code. Codes like PHREEQE, EQ3/6 and MINEQL are distributed through the OECD/NEA and include each their own databases. The extended Wanner model, which has been developed as a MIN_SURF program version, uses the TDB which was supplied with the MIN_SURF code (Berner, 1993). The largest part of this database has been documented in two reports (Pearson and Berner, 1991, and Pearson, Berner and Hummel, 1992), and the database is kept updated and consistent with the NEA-TDB (Wanner, 1988; Grenthe et al., 1992). The contents of this TDB, which we may for example label as MIN_SURF.1 (cf. Appendix D), are listed in Appendix E.

2.3 *Bentonite Characteristics*

This input record contains all the model-independent information on the physical, chemical and mineralogical composition of the bentonite. Like the record "Groundwater Composition", each of the records "Bentonite Characteristics" is labeled with a name or a number. Examples would be "Kunipia-F", "Kunigel-V1" or "MX-80", cf. Appendix D. The information required for this record contains the following parameters:

- mineralogical composition
- quantities of soluble impurities
- cation exchange capacity (CEC) and quantities of exchangeable ions
- surface edge site density
- structural and material parameters such as densities, surface areas, tortuosity

In the diffusion model used by Sato, Yui and Yoshikawa (1995) the porosity, ε, tortuosity, τ^2, and surface area, S, are structural parameters, and as such are independent of the physico-chemical characteristics of the diffusing ions. Sato, Yui and Yoshikawa (1995) present a model to calculate the constrictivity, δ, describing the interaction of a diffusing ion with the surface of bentonite.

The two most common bentonite types of Japan, Kunigel-V1 and Kuipia-F, have both been well characterized and examined. It is important for the extended Wanner model that the soluble impurities are known for these two bentonites. Table 2 lists the parameters for these two bentonite types.

Table 2: Kunigel-V1 and Kunipia-F: Composition and other specific parameters relevant to ISD modeling. Values readily available have been filled in as an example. The references are given in the footnote.

	Kunigel-V1	Kunipia-F
Minerals:		
smectite	46 - 49 % [1]	99 % [2]; >95% [1]
quartz	29 - 38 % [1]	traces [1]
feldspar	2.7 - 5.5 % [1]	
calcite	2.1 - 2.6 % [1]	traces [1]
dolomite	2.0 - 3.8 % [1]	
zeolite	3.0 - 3.5 % [1]	
pyrite	0.5 - 0.7 % [1]	
Soluble impurities:		
NaCl	0.001 % [3]	0.071 % [3]
$CaSO_4$	0.38 % [3]	0.694 % [3]
KCl	0.004 % [3]	0.005 % [3]
Surface sites and cation exchange parameters:		
SOH sites (edge sites)		2.84×10^{-5} mol/g [4]
Cation exchange capacity, CEC	60.1 meq/100g [1]	108 meq/100g [5]
exchangeable Na^+		97.1 % [5]
exchangeable K^+		0.9 % [5]
exchangeable Mg^{2+}		1.3 % [5]
exchangeable Ca^{2+}		0.7 % [5]
Structural and material parameters:		
specific density, ρ_s	2700 kg/m^3 [6]	
dry density, ρ_d	1500 kg/m^3	
porosity, ε	0.44 $(1 - \rho_d/\rho_s)$	
solid/water ratio	3375 kg/m^3 (ρ_d/ε)	
surface area of layer sites, *S(layer)*	810 m^2/g [6]	
surface area of edge sites, *S(edge)*	3 m^2/g [from 4]	
aperture distance, *d*	0.73 nm [6]	
tortuosity, τ^2	4.6 [6]	

References:

[1] Sasaki et al. (1995)
[2] Ashida, Kohara and Yui (1994)
[3] Wanner and Wieland (1993)
[4] Wieland et al. (1995), obtained for pretreated MX-80 which had a CEC of 108 meq/100g
[5] Yajima (1993)
[6] Sato, Yui and Yoshikawa (1995)

2.4 *Extended Wanner Model and Intrinsic Database*

The Wanner model presented several years ago (Wanner, 1986) is used as a basis for mechanistic sorption modeling in bentonite. An extended version of this model has been published recently (Wanner et al., 1994, and Wieland et al., 1994). It includes a new type of surface site exhibiting a distinctly different surface complexation behavior compared with the ion exchange sites. These sites, which have been refered to as "edge sites", are deprotonated in the mildly alkaline pH region and may be the major surface ligands for surface complexation mechanisms other than ion exchange. The extended Wanner model uses the mole fraction approach (cf. Fletcher and Sposito, 1989) for ion exchange reactions, and the diffuse double layer model (cf. Dzombak and Morel, 1990) for the interactions at the edge sites. It is also possible to include a coprecipitation mechanism in the model if desired. The extended Wanner model thus exhibits a high degree of flexibility and can be used for mechanistic sorption modeling of any type of key nuclide.

The extended Wanner model uses the MIN_SURF code (Berner, 1993) in order to ensure full flexibility with respect to extensions and long-term model development. The parameters specific to the extended Wanner model are as follows:

- ion exchange constants on layer sites for Na^+, K^+, H^+, Ca^{2+} and Mg^{2+}, in a form compatible with the mole fraction model
- ion exchange constants of key nuclides on layer sites
- intrinsic acid/base constants of edge sites for the diffuse double layer model (intrinsic database)
- intrinsic surface complexation constants of key nuclides on edge sites (intrinsic database)
- site density of the edge sites
- mineral equilibria (calcite and quartz saturation)

PNC puts a large weight on the development of an intrinsic database. The intrinsic database contains the so-called "intrinsic constants" describing surface complexation reactions on the oxide-type sites of bentonite. The diffuse double layer model is already part of the extended Wanner model, so we do not need an extra database structure to develop the intrinsic database. The intrinsic constants can simply be added to the surface constants dataset in the extended Wanner model.

The ion exchange constants for Na^+, K^+, H^+, Ca^{2+} and Mg^{2+} on montmorillonite are well established. Differences between single studies are usually insignificant for modeling purposes. The site density of the layer sites corresponds to the CEC (cf. record on Bentonite Characteristics). Table 3 presents an example of a specific database (ion exchange and intrinsic database) for the extended Wanner model. The data on key nuclides (e.g., Cs^+) are also included in this database.

The site density of the edge OH sites are only known for Wyoming bentonite MX-80 at the present time (2.8×10^{-5} mol OH sites per gram of Wyoming bentonite MX-80). Since this value and the acid/base constants of the edge OH sites have been evaluated simultaneously by fitting (Wanner et al., 1994), they are included in the extended Wanner model, although the edge site density is also part of the Bentonite Characteristics record.

The extended Wanner model can be adapted to specific bentonite and groundwater types. The model version should therefore be labeled for easy traceability and QA in the ISD database system.

Table 3: Surface interaction database for the extended Wanner model, including an ion exchange database and an intrinsic database to be used with the diffuse double layer model (cf. Dzombak and Morel, 1990). Examples of data for key radionuclides are given for Cs^+ and Sr^{2+} (ion exchange database), and for SeO_3^{2-}, Co^{2+} and NpO_2^+ (intrinsic database).

Extended Wanner model: Specific surface interaction database			
1	***Ion exchange database:***		
	Surface site master species:		Z^-
	Total Z [mol/L]:		CECx(solid/water ratio)
	Surface species:	*log K:*	*Reference:*
	ZNa	20.0	Wanner (1986)
	ZK	20.26	Fletcher and Sposito (1989)
	Z_2Mg	40.13 *	Wanner, Wersin and Sierro (1992)
	Z_2Ca	40.21 *	Wanner, Wersin and Sierro (1992)
	ZH	23.0	Wieland et al. (1994)
	ZCs	21.6	Wanner, Albinsson and Wieland (1994)
	Z_2Sr	40.17	Fletcher and Sposito (1989)
2	***Intrinsic database (surface complexation):***		
	Surface site master species:		SOH
	Total SOH [mol/L]:		(SOH site density)x(solid/water ratio)
	Surface species:	*log K^{int}:*	*Reference:*
	SOH_2^+	5.4	Wanner et al. (1994)
	SO^-	-6.7	Wanner et al. (1994)
	$SSeO_3^-$	12.7 **	Dzombak and Morel (1990)
	$SOHSeO_3^{2-}$	5.2 **	Dzombak and Morel (1990)
	$SOCo^+$	-0.5 **	Dzombak and Morel (1990)
	$SONpO_2$	-1.0 **	Bradbury and Baeyens (1992)
*	After conversion to the mole fraction model		
**	Valid for hydrous ferric oxides (values rounded)		

2.5 *Surface Species*

The speciation on the surface of the solid phase is a result of the surface model (ion exchange, surface complexation). The stoichiometric sum of the concentrations of the surface species of a key element at equilibrium is expressed in mol/kg and used for the calculation of K_d.

2.6 *Solution Species*

The speciation of an element in solution in equilibrium with bentonite is used for two purposes:

- as input to the mechanistic diffusion model (see Paragraph 2.8 below). For the diffusion model the concentrations (n_0) and charges (z) of the dominant species of the key element are of importance, but also the concentrations of the major ions in the porewater (expressed in the variable n in the diffusion model).
- as an input to the calculation of K_d. In this case the stoichiometric sum of the concentrations of the species containing the key nuclide is converted from mol/L to mol/m^3 and used directly to calculate K_d.

2.7 *Distribution Coefficient, K_d*

The K_d value, called distribution or sorption coefficient, of a key element is calculated from the two main output parameters of the extended Wanner model: the concentration of the key element on the surface (in mol/kg) and the concentration of the key element in solution (in mol/m^3):

$$K_d\,[\mathrm{m^3/kg}] = \frac{\text{stoichiometric sum of surface species of element X [mol/kg]}}{\text{stoichiometric sum of solution species of element X [mol/m}^3\text{]}} \quad (1)$$

The K_d value is used with the output parameters of the mechanistic diffusion model (either D_0, d, ε and τ^2, cf. Figure 2 below; or ε and D_p) to calculate the apparent diffusivity, D_a.

2.8 *Mechanistic Diffusion Model*

Sato, Yui and Yoshikawa (1995) have proposed a mechanistic diffusion model which makes use of all the auxiliary variables traditionally related to diffusion modeling. These variables and their dependencies are shown in Figure 2. The mathematical relationships are given in the paper of Sato, Yui and Yoshikawa (1995). For better understanding, the various variables are divided into classes according to their origin, cf. Figure 2:

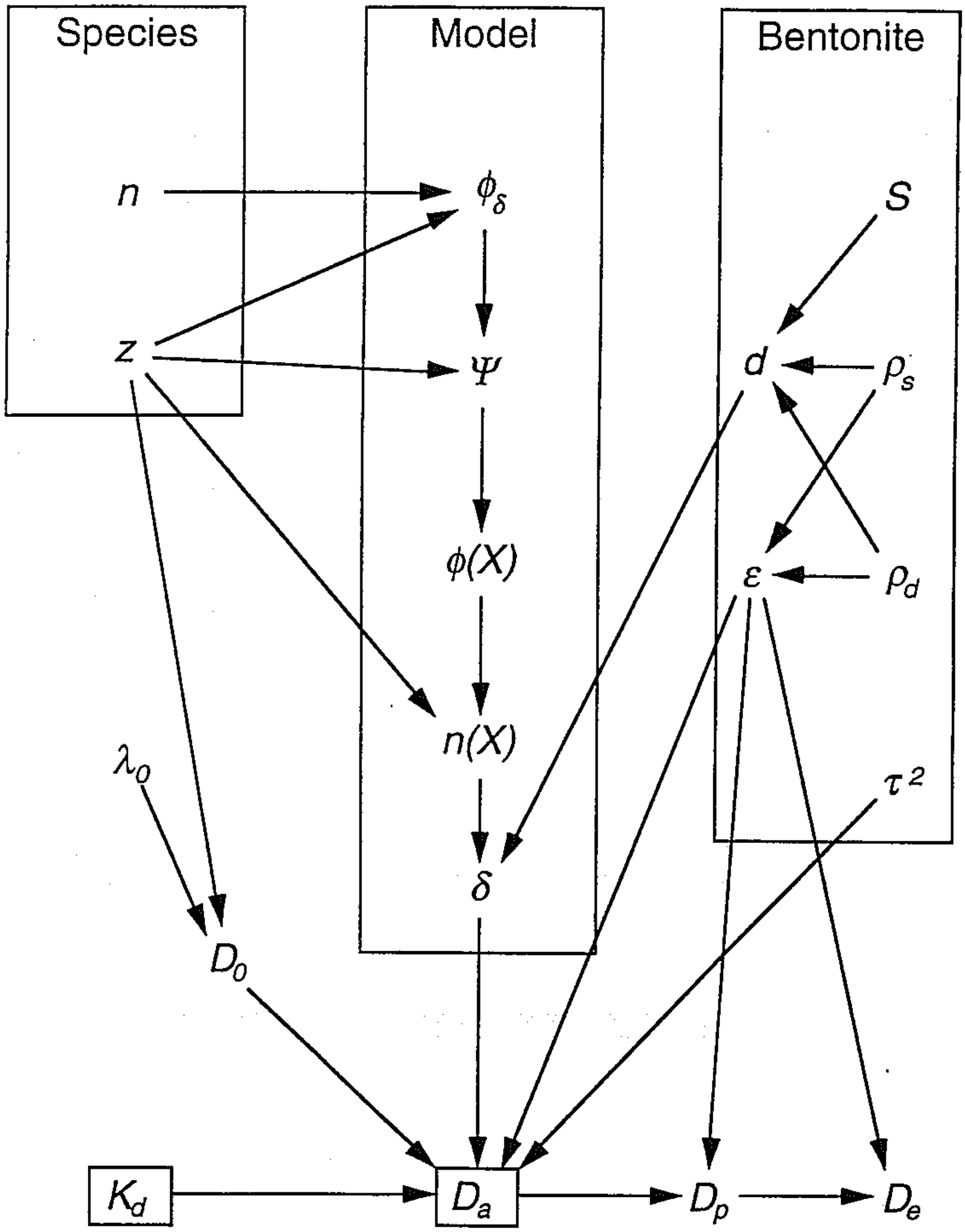

Figure 2: Variables required for the mechanistic diffusion model. The dependencies of the different variables are shown, e.g., an arrow from *z* to *n(X)* means that *z* is one of the required input parameters to calculate *n(X)*. Variables in the "Species" box are a direct output of the extended Wanner model. Variables in the "Bentonite" box are constant for each bentonite specification. Variables in the "Model" box represent the different modeling steps as suggested by Sato, Yui and Yoshikawa (1995). The electric conductivity, λ_0, is species-specific, and K_d is the final output of the sorption model.

- *Species:* Output data from the extended Wanner model (solution species):

n	number of ions per m^3 of solution (this is a measure for the charge density in solution)
z	charge (for the calculation of the potential distribution on the surface, z is the charge of the dominating electrolyte of $z{:}z$ type, i.e., $z_+ = z_-$; for the calculation of the constrictivity, see below, z is the charge of the diffusing species)

- *Model:* Contains the functions of the mechanistic diffusion model used by Sato, Yui and Yoshikawa (1995):

ϕ_δ	electric potential at Stern plane (dependent on the number of ions, n)
Ψ	electric potential
$\phi(X)$	local electric potential
$n(X)$	local ion concentration (for the calculation of the constrictivity value the ratio of the local concentration, $n(X)$, to the concentration in the equilibrium solution, n_0, is relevant)
δ	constrictivity (describing the interaction between the diffusing ion and the surface based on the electric double layer theory)

The constrictivity is calculated according to Sato, Yui and Yoshikawa (1995):

$$\delta = \frac{1}{n_0 d} \int_0^d n(X)\, dX \tag{2}$$

The distribution of ions in the electric field defined by the electric double layer model is as follows:

$$n(X) = n_0 \exp\left(\frac{-Z\, e\, \phi(X)}{k\, T}\right) \tag{3}$$

- *Bentonite:* Contains bentonite-specific data from the "Bentonite Characteristics" record, cf. Figure 1 and Table 2 (structural and material parameters). Although the aperture distance (pore diameter), d, and the porosity, ε, are not primary bentonite parameters, they are derived from bentonite-specific parameters and are therefore also bentonite-specific. This is the reason why d and ε are also included in the record "Bentonite Characteristics", cf. Table 2.

S	surface area
ρ_s	specific density (usually around 2700 kg/m^3 for bentonite)
ρ_d	dry density
τ^2	tortuosity
d	aperture distance (the average pore diameter, assuming that the total pore space is evenly distributed throughout the bentonite)
ε	porosity (Kato et al., 1995, have found that the porosity available for diffusion of HTO is equal to the bulk porosity within the experimental uncertainties)

- *Other variables:* The remaining variables in Figure 2 are either input parameters to the mechanistic diffusion model (λ_0, D_0) or output parameters from it (D_p, D_e). The final resulting parameter, D_a, can only be calculated with the help of the principal output parameter from the mechanistic sorption model: K_d.

λ_0	electric conductivity of the key species at infinite dilution (this parameter is species-specific and depends mainly on the charge of the key species and to a lesser extent on its size including the hydration shell)
D_0	diffusivity of the key species in free water
K_d	distribution coefficient of the key species in the specified bentonite
D_a	apparent diffusivity of the key species in the specified bentonite
D_p	pore diffusivity of the key species in the specified bentonite
D_e	effective diffusivity of the key species in the specified bentonite

It should be noted that D_p and D_e are not needed in the mechanistic diffusion model to calculate D_a:

$$D_a = \frac{\varepsilon}{\varepsilon + \rho_d K_d} \frac{\delta}{\tau^2} D_0 \tag{4}$$

However, D_p and D_e are useful parameters to check consistency within the diffusion database, because they may be expected to be comparable for species of similar physicochemical properties. This is also the reason why these diffusivities may be estimated by analogy in the absence of a reliable mechanistic diffusion model, cf. Figure 3 in Section 3 below, and be used to derive D_a:

$$D_a = \frac{\varepsilon}{\varepsilon + \rho_d K_d} D_p \tag{5}$$

$$D_e = \varepsilon D_p \tag{6}$$

2.9 *Pore Diffusivity, D_p, and Effective Diffusivity, D_e*

These diffusivities are useful for cross-checking but are not needed to calculate the apparent diffusivity, D_a, cf. Eqs. (5) and (6) above.

2.10 *Apparent Diffusivity, D_a*

The apparent diffusivity is used for the modeling of site-specific diffusion through bentonite and is calculated according to Eqs. (4) or (5) above.

2.11 Redox potential

The redox potential, Eh, is only well determined if an active redox couple is present which dominates all the redox processes in the system considered. Natural geochemical systems are usually heterogeneous, and assuming an overall redox potential is unlikely to be a realistic approach. We therefore propose to consider redox active elements under several redox conditions, i.e., to prepare a consistent data set under reducing and one under oxidizing conditions. For example, in the case of uranium we propose to compile a data set for uranium(IV), which will be valid for reducing conditions, and one for uranium(VI), which will be valid for oxidizing conditions. This procedure ensures full flexibility as it can be adapted to various redox models in the performance assessment analysis, see also the discussion on the estimation of K_d for plutonium, Paragraph 3.1 below.

3 Alternative Procedure For Performance Assessment (The "Bypass Option")

The purpose of the development of an ISD database system is to provide a reliable and consistent scientific basis for the modeling of radionuclide transport from a radioactive waste repository to the biosphere. The backfill of compacted bentonite is probably the most effective and predictable barrier on the entire migration path of the radionuclides. This explains the high degree of importance attributed to a thorough understanding of the processes affecting radionuclide transport in compacted bentonite. The ISD database system proposed in the present report will provide an adequate and justifiable tool to meet the required goal.

However, the data required to establish a complete and fully mechanistic sorption/diffusion database according to Figure 1 may not be available for all the key nuclides in time for the next PNC Performance Assessment Report planned for 1999. In particular, the intrinsic database is not expected to be completed within such a short period. We have therefore designed the ISD database system in such a way that it allows to bypass lacking data by estimating certain parameters, such as K_d and D_p, according to mechanistic considerations (speciation). We call this procedure the "bypass option". While estimations according to the bypass option may be considered as a preliminary approach for high-priority radionuclides, they may be found to provide a sufficient degree of quality for some of the low-priority nuclides. In any case, the bypass option will be consistent with the mechanistic model if the recommendations presented here are followed.

The procedure recommended in the case of lacking data is shown in Figure 3. It is obvious that we follow the same basic scheme as in Figure 1, which is important to maintain consistency and systematics. The principal difference is that the variables K_d and D_p (D_e) in Figure 3 have a different origin compared to Figure 1: These variables are now not the result of a quantitative modeling of sorption and diffusion mechanisms, respectively, but are rather the result of a systematic estimation by analogy with other radionuclides whose mechanistic behavior is known from experimental investigations.

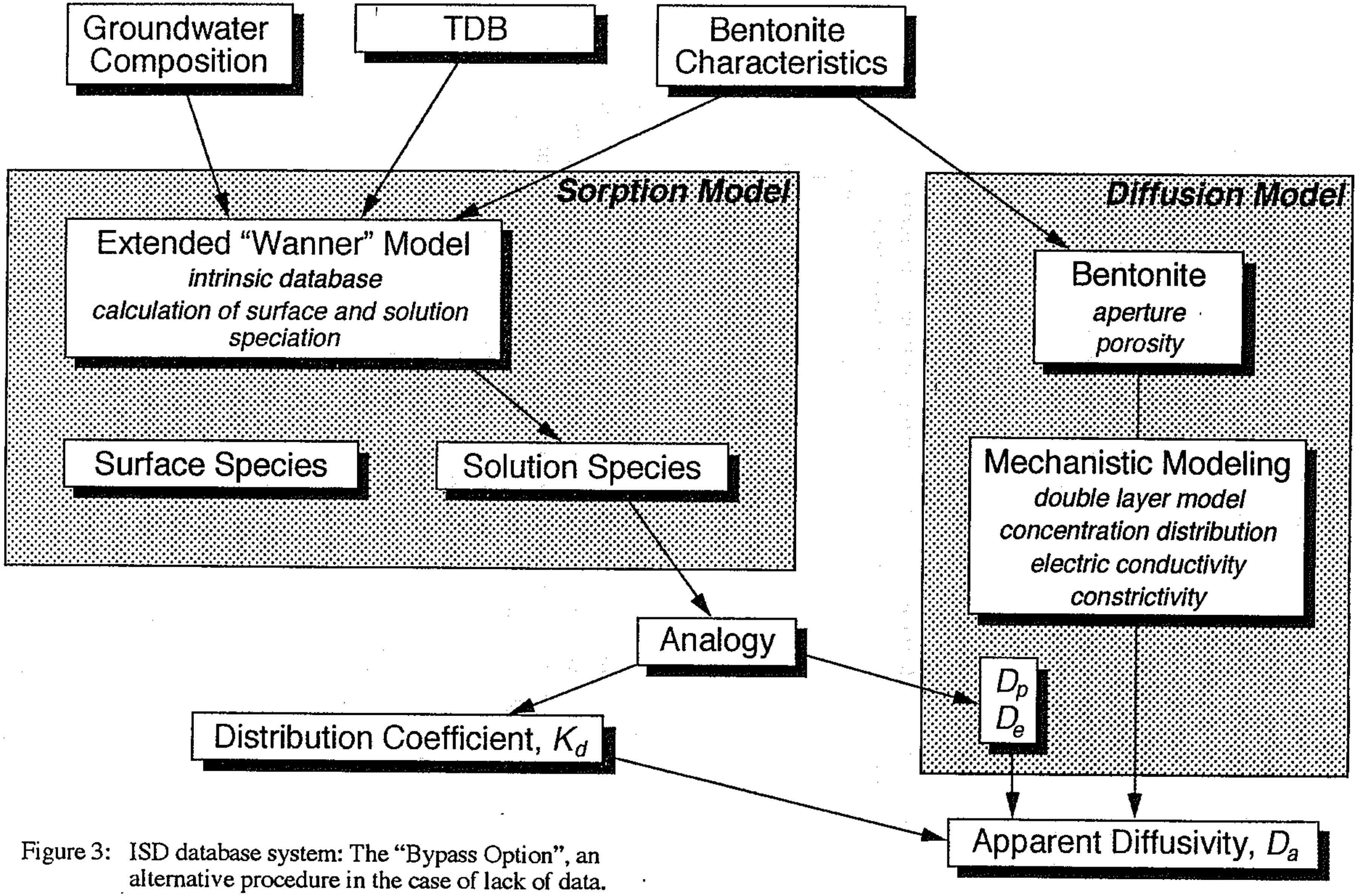

Figure 3: ISD database system: The "Bypass Option", an alternative procedure in the case of lack of data.

3.1 Estimation of K_d

The estimation of K_d for a radionuclide in bentonite is based on the expected interactions of its major solution species with the surface sites available under the relevant conditions. We therefore need to know the speciation of the radionuclide under the site-specific conditions. This information is obtained by using the extended Wanner model and the same input records as above: Groundwater composition, TDB, and bentonite characteristics. We would like to illustrate this approach by presenting two examples:

- K_d of radium:
  Radium is an alkaline earth element, occurs as Ra^{2+}, and can be expected to adsorb on bentonite via an ion exchange mechanism. As an approximation, the ion exchange constant of Ra^{2+} can be set equal to the ion exchange constant of the well-examined Sr^{2+}. Like Sr^{2+}, Ra^{2+} is expected to exhibit weak interactions with potential ligands present in the porewater. Hence, Sr^{2+} may be used as an analog for Ra^{2+} and the K_d value of Ra^{2+} set equal to the K_d of Sr^{2+}.

- K_d of plutonium:
  Depending on the redox potential, plutonium may be present as Pu(III), Pu(IV), Pu(V) or Pu(VI) complexes in solution. This is a very difficult starting point, in particular if the Eh value cannot (yet) be predicted with confidence. If no reliable surface complexation experiments are available, we recommend to estimate separate K_d values for each oxidation state of plutonium. As analogs we could for example use Am(III) or the lanthanides for Pu(III), Th(IV) for Pu(IV), Np(V) for Pu(V) and U(VI) for Pu(VI), after ensuring that the solution speciation of the analog element can be expected to be similar to that of the corresponding Pu oxidation state, by using a speciation code (e.g., the extended Wanner model). This procedure has an important advantage: It is allows to examine the Eh dependency of the K_d value of plutonium. For this purpose, the speciation of plutonium is calculated at different Eh values, and the distribution between the different oxidation states is recorded (note that the stability fields of different Pu oxidation states may overlap). The K_d value can then be estimated for each Eh value by weighting the single K_d values according to the abundance of the corresponding oxidation state. It is needless to say that this approach requires a reliable TDB for plutonium.

These examples show that the estimation of K_d values is justifiable and defendable when a systematic approach is used and when the analog systems are carefully examined as to the comparability of their chemical characteristics.

3.2 Estimation of D_p or D_e

The pore diffusivity may be estimated if the diffusion mechanism is unknown or uncertain, or if one or more parameters or functions required to calculate D_a are missing. In addition, in order to verify the results, it may be useful to estimate D_p even when mechanistic diffusion modeling is possible. As is obvious from Eq. (6), the discussion in this paragraph also applies for the estimation of D_e.

The estimation of D_p is very similar to the estimation of K_d. Figure 3 shows that the estimation is based on the selection of a chemical analog. Analogs are found via speciation calculations. Again, as with the estimation of K_d, it is preferable to choose analogs with simple and well predictable chemical behavior under the relevant conditions. The examples given in Paragraph 3.1 apply here as well.

However, the number of available chemical analogs for D_p estimations may be very limited, especially in the starting period of the ISD database development. For D_p approximations a similar unretarded diffusion behavior is more directly relevant than a similar chemical speciation.

Since the largest part of the bentonite surfaces carry a permanent negative charge, the charge of a species is of principal importance for its diffusion behavior. The ionic charge certainly outweighs the size in importance, as long as the size of a diffusing species is smaller than the pore width. As can be seen from Eq. (5), $D_a = D_p$ for non-sorbing species (i.e., $K_d = 0$). For sorbing species a mechanistic sorption model may allow to derive a reliable K_d value, and D_p can then be calculated from an experimentally determined D_a value.

Wanner, Albinsson and Wieland (1994) have verified their mechanistic sorption model for Cs^+ by estimating D_p of Cs^+ as being equal to D_a of tritium (HTO) and assuming the diffusion porosity to be equal to the bulk porosity. This approximation seems to work fairly well, and the K_d values thus obtained from measured apparent diffusivities agreed with the predicted K_d values within the expected error ranges. Such approximations are expected to work well if the pore space available for diffusion is roughly the same as this is probably the case with HTO and Cs^+. However, for anions the situation may be quite different and HTO may not be a good analog for estimating D_p. Here, expectedly non-sorbing anions such as Cl^- or TcO_4^- may be more appropriate as analogs. Diffusion data on these ions at different compaction degrees of bentonite have been reported by Muurinen (1994) and Sato et al. (1993).

4 Long-term modeling

Although long-term modeling is not a subject of the present report, it is essential to assess the impact of long-term effects on the applicability of the ISD database. Looking at Figures 1 and 3, the contents of almost all the boxes may change with the development of the repository. Exceptions are the groundwater composition (scenario dependent, but usually constant) and the TDB.

In general, changes occur via the mobile phases, i.e., the aqueous and gaseous phases, respectively. In contrast to the gaseous phase, the aqueous phase can carry virtually all the radionuclides and is therefore the relevant pathway, both for radionuclide transport and for mineral transformations. The water flow rate past the repository is the principal parameter for the prediction of the long-term behavior of the near-field. A simple mixing tank model has been proposed for quick assessments (Wanner, 1986). The model considers leaching of soluble phases and dissolution/precipitation equilibria of selected minerals. Later applications of this model have been presented by Wanner, Wersin and Sierro (1992) and Wieland et al. (1994). The mixing tank model has also been adopted to predict the long-term evolution of a cementious near field (Berner, 1990: Nagra, 1994).

The mixing tank model accounts for the chemical changes in the near field and can be used to predict the evolution of the speciation and the K_d values with time. Predicting the changes in the diffusion parameters may be more difficult, but rough estimations of the evolution of aperture and porosity may be possible from mass transfer data from the chemical model due to leaching and dissolution/precipitation.

Solid solution modeling may also be used to predict the long-term evolution of the near field of a nuclear waste repository. A combination of a solid solution model with the extended Wanner model may be used at a more advenced stage.

5 Further Applications (Granite, Tuff)

In geological systems such as granite, radionuclide transport is expected to take place in fractures and fissures, rather than in the rock matrix. The dominant transport mechanism will therefore be by advective flow, rather than by diffusion. In Figures 1 and 3, the right hand side (diffusion model) will therefore have to be replaced by an advective flow model. However, the rest of the figure can be used in an analogous way to obtain a reliable K_d database:

1. Define groundwater composition in equilibrium with corresponding rock.
2. Define TDB to be used.
3. Define rock characteristics (CEC, surface complexation sites, minerals).
4. Check intrinsic database in extended Wanner model for applicability.
5. Calculate surface and solution speciation.
6. Derive distribution coefficient, K_d, from concentrations of surface and solution species.

If the intrinsic database is incomplete with respect to the specific type of application, we can use the alternative procedure according to Figure 3 to obtain a preliminary but nevertheless useful K_d database:

1. Define groundwater composition in equilibrium with corresponding rock.
2. Define TDB to be used.
3. Calculate speciation of key element in the groundwater.
4. Based on the solution species distribution, estimate K_d by analogy with radionuclides that exhibit similar speciation under the same conditions.

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Appendix

This Appendix contains an action plan for the development of an ISD database system (Appendix A), a comparison of sorption and diffusion models for bentonite used by selected performance assessment programs (Appendix B), a description of the extended Wanner model which is a central part of the ISD database system (Appendix C), and Examples of ISD data sheets for Cs^+ sorption and diffusion in Kunigel-V1 at different compaction degrees (Appendix D). The TDB used with the code MIN_SURF is listed in Appendix E for completeness of the data examples (cf. Appendix D) and for traceability. The purpose of Appendix E is also to give an example of a complete TDB including aqueous species, minerals and gases. Due to its length (55 pages) and its mere documentation character, *Appendix E is presented as a separate enclosure.*

A Action plan for the development of an ISD database system

The action plan proposed in this Apendix is a suggestion based on the deadline for the submission of the next performance assessment report in 1999. This implies that the ISD database system has to be frozen in 1997 for the safety assessment and drafting of the report. It will not be possible to present complete ISD data sets based on experimental research for all key radionuclides by 1997. However, we consider it possible to present ISD data sets based on the "bypass option" (cf. Figure 3) for all key radionuclides by 1997. The experimental research on sorption and diffusion mechanisms of key radionuclides in bentonite should nevertheless continue.

The action plan presented on the following page is determined by the deadline of 1997. It is essential for effective ISD database development to define, as soon as possible, one or several reference groundwaters, a reference bentonite, and priority 1, 2 and 3 radionuclides.

Action Plan for ISD Database Development	1995									1996												1997		
	4	5	6	7	8	9	10	11	12	1	2	3	4	5	6	7	8	9	10	11	12	1	2	3
1. Key ISD activities for 1999 PA report:																								
Definition of reference groundwaters	■																							
Definition of bentonite characteristics	■																							
Identification of accessory minerals		■	■	■																				
Definition of key radionuclides (priorities 1, 2 and 3)	■																							
Definition of TDB (including key nuclides)		■																						
Review and update TDB according to priority list			■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■
Modeling of porewater composition in reference bentonite using the extended Wanner model			■																					
Collection of ISD data for key nuclides (all priorities) for bentonite and accessory minerals				■	■																			
Identification of gaps of ISD data (all priorities)						■																		
Development of ISD models for the priority 1 nuclides (sorption and diffusion measurements)							■	■	■	■	■	■	■	■	■	■	■	■	■	■	■			
Identification of chemical and physical analogs for the priority 2 and 3 nuclides: "bypass option"							■	■	■															
Grouping of the analogs, identification of "key analogs" for priority 2 and 3 nuclides and for accessory minerals										■														
Development of ISD models for the "key analogs" (sorption and diffusion measurements)											■	■	■	■	■	■	■	■	■	■	■			
Establishment of ISD data sheets (according to Appendix D) for all priority nuclides																						■	■	■
Freezing of ISD database for the 1999 Performance Assessment Report of PNC																								■
2. Parallel (ongoing) activities:																								
Identification and overview of contractors	▨																							
Redistribution of tasks among the contractors according to the ISD database system concept		▨	▨	▨	▨	▨	▨																	
Development of mechanistic sorption models	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨
Development of mechanistic diffusion models	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨
Further development of extended Wanner model													▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨

B Comparison of sorption and diffusion models used by specialized groups working for different performance assessment programs

In this Appendix, we present a selection of different approaches for modeling diffusion mechanisms. In general, agreement seems to prevail concerning anion diffusion modeling. Some minor differences concern the parameters of the diffusion equation affected by the electrostatic repulsion. While some groups (e.g., in Sweden, Finland and Canada) translate this repulsion into a reduction of the effective diffusion porosity, others (PNC) use different variables such as the constrictivity to express this effect. The results, however, are in good agreement. In contrast, various different mechanisms have been proposed for modeling cation diffusion through compacted bentonite. The suggestion of a surface diffusion mechanism to explain some unexpectedly high diffusivities of supposedly strongly sorbing cations (Cs^+, Na^+, Sr^{2+}) has had much response, both positive and negative. Some groups have adopted the surface diffusion approach (Finland, Sweden), while others have found different ways to explain these effects (Canada, Japan). An obvious advantage of the Japanese approach is the quantitative consideration of chemical speciation. This is a subject that has been largely neglected in the past. Mechanistic diffusion and mechanistic sorption models rely to a large extent on the same parameters, and the examination of the chemical mechanisms is a prerequisite for the interpretation of diffusion mechanisms.

B.1 Finland

The Finnish group of Dr. Arto Muurinen in VTT Chemical Technology at Espoo has been active in the field of diffusion measurements of radionuclides in bentonite for many years. Two comprehensive publications about the work performed in this group during the past 12 years have appeared recently (Muurinen, 1994; Olin, 1994). The experimental investigations include diffusion measurements of cesium, strontium, cobalt, chloride, uranium, sodium and copper in compacted sodium bentonite MX-80, usually with the in-diffusion method. Cesium and strontium were also investigated by the through-diffusion method.

In general, Muurinen's (1994) approach is similar to that of Sato, Yui and Yoshikawa (1995): It is recognized that the electrostatic interactions between the diffusing ions and the charged bentonite surfaces influence the diffusion behavior. Both approaches use the electric double-layer model to explain the repulsion between anions and the bentonite surface. However, while Sato, Yui and Yoshikawa (1995) express this repulsion effect in a modification of the constrictivity ($\delta < 1$ for anions), the Finnish approach uses the porosity as a variable which, for anions, is decreased to account for ion-exclusion due to electrostatic interaction with the negatively charged surfaces. Hence, the porosity is not taken as a structural parameter but depends on the charge value of the diffusing anion and the salinity of the solution. The resulting variable is then called "effective porosity", ε_{eff}. The factor δ/τ^2 is not explicitely considered by Muurinen (1994). The difference between the two approaches for diffusion of anions can be visualized by looking at the effective diffusivity, D_e:

$$D_e = \frac{\varepsilon\,\delta}{\tau^2} D_0 \qquad \text{(B.1)}$$

For the diffusion of chloride ion, Cl^-, Muurinen (1994) has obtained values for D_e and D_a as a function of the effective porosity:

$$D_e(Cl^-) = (\varepsilon_{\text{eff}})^{1.62} D_0(Cl^-) \qquad \text{(B.2)}$$

$$D_a(Cl^-) = (\varepsilon_{\text{eff}})^{0.61} D_0(Cl^-) \qquad \text{(B.3)}$$

Hence, in the model of Muurinen (1994) the factor $\varepsilon\delta/\tau^2$ (called "formation factor" by Brandberg and Skagius, 1991) depends on the diffusing ion. In the approach of Sato, Yui and Yoshikawa (1995), the factor ε/τ^2 is a structural parameter and therefore constant, and $\delta = \delta_{\text{Sato}}$ is determined from the electric double layer model as the ratio of the average ionic concentration in the porewater to the concentration in the equilibrium liquid. In practice, the following equations are used in the two approaches for D_a:

Muurinen (1994):
$$D_a = (\varepsilon_{\text{eff}})^y D_0 \qquad (y \text{ is a fitting parameter}) \qquad \text{(B.4)}$$

Sato, Yui and Yoshikawa (1995):
$$D_a = \frac{\delta_{\text{Sato}}}{\tau^2} D_0 \qquad \text{(B.5)}$$

Eqs. (B.4) and (B.5) lead to:

$$(\varepsilon_{\text{eff}})^y = \frac{\delta_{\text{Sato}}}{\tau^2} \qquad \text{(B.6)}$$

Eq. (B.6) is the actual conversion formula between the approaches of Muurinen (1994) and Sato, Yui and Yoshikawa (1995) for diffusion of anions in bentonite.

The diffusion mechanism of cations is interpreted in a different way by Muurinen (1994). From diffusion experiments it turned out that some cations diffused faster than had been expected. In batch experiments, cations are usually adsorbed more strongly on the bentonite than anions. Hence, their apparent diffusivities were expected to be considerably smaller. In practice this has not been observed to the extent expected, and the interpretation used by the Finnish group is that the cations keep their mobility although they are sorbed onto the bentonite surface. The proposed mechanism is called "surface diffusion" (Muurinen, 1994, and references cited therein). Surface diffusion is considered as an additional mechanism and is expressed in the form of an additional term in the diffusion equation:

Muurinen (1994):
$$D_{as} = \frac{\varepsilon D_p}{\varepsilon + K_d \rho_d} + \frac{K_d \rho_d D_s}{\varepsilon + K_d \rho_d} \qquad \text{(B.7)}$$

The surface diffusivity, D_s, is a new variable, and ε is the bulk porosity of bentonite. The first term corresponds to the normal diffusion equation and may also be written as:

Sato, Yui and Yoshikawa (1995): $$D_a = \frac{\varepsilon}{\varepsilon + K_d \rho_d} \frac{\delta}{\tau^2} D_0 \tag{B.8}$$

The main difference between the Finnish approach and the approach of Sato, Yui and Yoshikawa (1995) is that Muurinen (1994) adds an additional term to explain a phenomena that Sato, Yui and Yoshikawa (1995) explain by developing a model for the constrictivity, δ. In the Finnish case, the constrictivity is not used as an independent parameter but is considered as a structural parameter, just like the tortuosity. This factor can be derived from diffusion measurements of tritium, HTO, by assuming zero adsorption. Sato, Yui and Yoshikawa (1995) derived $1/\tau^2$ from diffusivity measurements of HTO by assuming that HTO does not interact with the bentonite surface (i.e., $\delta = 1$). In order to distinguish between Muurinen's approach and the one of Sato, Yui and Yoshikawa (1995), we use the labels "VTT" (for Muurinen, 1994) and "Sato" (for Sato, Yui and Yoshikawa, 1995).

From HTO: $$\left(\frac{\delta}{\tau^2}\right)_{\text{VTT}} = \left(\frac{1}{\tau^2}\right)_{\text{Sato}} \tag{B.9}$$

Both Eq. (B.7) and Eq. (B.8) represent equations for the apparent diffusivity. For the derivation of the conversion factor between the two models, we can use Eqs. (B.7) and (B.8) with $D_{as} = D_a$ and $D_p = (\delta/\tau^2)D_0$:

$$\frac{\varepsilon}{\varepsilon + K_d \rho_d}\left(\frac{\delta}{\tau^2}\right)_{\text{VTT}} D_0 + \frac{K_d \rho_d D_s}{\varepsilon + K_d \rho_d} = \frac{\varepsilon}{\varepsilon + K_d \rho_d}\left(\frac{1}{\tau^2}\right)_{\text{Sato}} \delta_{\text{Sato}} D_0 \tag{B.10}$$

The left hand side of Eq. (B.10) represents the Finnish approach, and the right hand side represents the approach of Sato, Yui and Yoshikawa (1995) for mechanistic diffusion modeling. By multiplication of Eq. (B.10) with $(\varepsilon + K_d\rho_d)$ we obtain:

$$\varepsilon\left(\frac{\delta}{\tau^2}\right)_{\text{VTT}} D_0 + K_d \rho_d D_s = \varepsilon\left(\frac{1}{\tau^2}\right)_{\text{Sato}} \delta_{\text{Sato}} D_0 \tag{B.11}$$

The diffusion of a tracer which is non-sorbing ($K_d = 0$) and uncharged ($\delta_{\text{Sato}} = 1$) can be used to derive the parameters in Eq. (B.9). Using Eq. (B.9) in Eq. (B.11) leads to:

$$K_d \rho_d D_s = \varepsilon D_0 \left(\frac{1}{\tau^2}\right)_{\text{Sato}} (\delta_{\text{Sato}} - 1) \tag{B.12}$$

Eq. (B.12) is the actual conversion formula between the approach of Muurinen (1994) and Sato, Yui and Yoshikawa (1995) for cation diffusion in bentonite. In the Finnish approach, the surface diffusivity, D_s, is determined experimentally, while Sato, Yui and Yoshikawa

(1995) determined their corresponding variable, δ_{Sato}, by calculation assuming evenly distributed pore space throughout the bentonite. As also mentioned by Sato, Yui and Yoshikawa (1995), it cannot be presumed that this assumption is realistic, and experimental verifications and validations are required for correct modeling and for confidence-building.

B.2 Sweden

The Swedish concept for diffusion modeling in compacted bentonite was outlined by Brandberg and Skagius (1991). It is analogous to the one used in Finland. Anion diffusion is modeled by assuming a diffusion porosity which is significantly lower than the bulk porosity, whereas for cation diffusion a surface diffusion mechanism is expected. However, no data are presented on the surface diffusivities. Brandberg and Skagius (1991) proposed values for D_e, D_p and the diffusion porosity (called "effective porosity" by Muurinen, 1994). These data are presented in Table B.1.

For radionuclide sorption, Brandberg and Skagius (1991) proposed K_d values which originate from batch sorption measurements. Speciation of radionuclides is considered in a qualitative or semi-quantitative way, but mechanistic sorption models have not been developed.

Table B.1: Diffusion parameters as proposed by Brandberg and Skagius (1991, Table 21).

Elements	effective diffusivity, D_e	pore diffusivity, D_p	diffusion porosity, ε_p
Se, Zr, Tc(red.) Sn, Ce, Sm, C, Ni, Nb, Am, Pu, Np, U, Th, Rn, Pb	1.0×10^{-10} m²/s	4.0×10^{-10} m²/s	25 %
Sr, Cs, Pa, Ra	2.5×10^{-8} m²/s	1.0×10^{-7} m²/s	25 %
Tc(ox.), I, Cl	2.5×10^{-12} m²/s	5.0×10^{-11} m²/s	5 %

The Swedish approach is still an approximative one. The radionuclides are divided into three classes (cf. Table B.1), and no account is taken of potential differences in the charges of dominant species within the classes. It is likely that the Swedish sorption/diffusion database will be updated and refined in the near future. However, no concept has been presented so far on the mechanistic approaches to be applied.

B.3 Canada

Several publications on diffusion of radionuclides in clays have appeared from Oscarson's group of AECL at Pinawa. Some recent ones include: Oscarson (1994); Oscarson (1994a);

Oscarson and Hume (1994); Oscarson et al. (1992); Cho, Oscarson and Hahn (1993); Cho et al. (1993). Here, too, anion diffusion is modeled by taking the diffusion porosity as a variable, rather than the constrictivity. However, Oscarson (1994) points out that an uncertainty may be associated with the precise meaning of the porosity values used in Eqs. (4) or (5) of the present report:

$$D_a = \frac{\varepsilon_1}{\varepsilon_2 + \rho_d K_d} D_p \qquad \text{(B.13)}$$

While the ε of the numerator (ε_1) represents the transport porosity (i.e., the diffusion porosity), the ε of the denominator (ε_2) represents the storage porosity. Transport porosity and storage porosity are not necessarily the same. We note here an advantage of the PNC approach (Sato, Yui and Yoshikawa, 1995), which does not distinguish between transport porosity and storage porosity. This helps to avoid confusion, because it seems more logical to have structural parameters which are independent of the diffusing species (such as porosity), and to define species-dependent values for the constrictivity which, hence, is not a fully structural parameter.

Oscarson and coworkers use different notations and symbols, and we shall not discuss their theories in great detail here. Their approach is not inconsistent with the one of Sato, Yui and Yoshikawa (1995). Oscarson and coworkers defined an "apparent tortuosity factor", τ_a (Oscarson and Hume, 1993), which seems to be equal to the factor δ/τ^2 of Sato, Yui and Yoshikawa (1995):

Tortuosity factor: $$(\tau_a)_{\text{AECL}} = \left(\frac{\delta}{\tau^2}\right)_{\text{Sato}} \qquad \text{(B.14)}$$

Oscarson et al. (1992) state that their tortuosity factor may include ion exclusion effects, but they have not quantified this effect yet. In addition, Oscarson (1994a) has defined a "diffusibility", Ψ, which corresponds to the formation factor, $\varepsilon\delta/\tau^2$, of Sato, Yui and Yoshikawa (1995):

Diffusibility: $$(\Psi)_{\text{AECL}} = \left(\frac{\varepsilon\,\delta}{\tau^2}\right)_{\text{Sato}} \qquad \text{(B.14)}$$

Oscarson (1994a) states that Ψ values for I^- are found to be significantly lower than for HTO. This observation is consistent with the model of Sato, Yui and Yoshikawa (1995) who consider ε/τ^2 as a structural factor, and who calculate δ from the electric double layer model: $\delta = 1$ for HTO (no interactions), $\delta < 1$ for I^- (ion exclusion).

Values of the diffusion porosity and of τ_a have been determined for I^- (Oscarson et al., 1992) and HCO_3^- (Oscarson and Hume, 1994). For iodide, the diffusion porosity was found from through-diffusion experiments to be roughly an order of magnitude lower than the bulk porosity (between 2% and 19% of the bulk porosity), while for bicarbonate the diffusion porosity was found to be even lower (between 0.6% and 9% of the bulk porosity). For HCO_3^- the effective porosity was calculated using the following equation:

Diffusion porosity: $$\varepsilon = \frac{D_e}{\tau_a D_0} \qquad \text{(B.15)}$$

Oscarson and Hume (1994) explained this observation by pointing at the larger ionic size of bicarbonate than of iodide. It should, however, also be mentioned that HCO_3^- may not be the only diffusing ^{14}C species.

Oscarson (1994a) finds no evidence for surface diffusion. He states that the apparently increased diffusivity of certain cations is based on using K_d values from batch experiments. Lowering the K_d value as a function of the compaction degree is claimed to have the same effect as adding a surface diffusion term. Oscarson (1994a) recommends to use a scaling factor to correct batch K_d values to be valid at different solid/water ratios. According to Oscarson (1994a) the reason for reduced sorption at high compaction of bentonite is the reduced availability of pores and surfaces. He thus expresses the K_d as a function of the effective porosity. If ε is the total porosity and ε_{eff} the accessible porosity, then Oscarson (1994a) suggests to estimate K_d in compacted bentonite as follows:

Scaling factor for K_d: $$K_d = \frac{\varepsilon_{\text{eff}}}{\varepsilon} K_d(\text{batch}) \qquad \text{(B.16)}$$

There is a contradiction between this approach and the approach of Muurinen (1994) and Sato, Yui and Yoshikawa (1995), who assume that virtually all the porosity in compacted bentonite is accessible for diffusion, except in the case of anion exclusion. Kato et al. (1995) have shown on the basis of the diffusion of HTO that dead-end pores and unaccessible pores are negligible at dry densities between 500 kg/m^3 and 2000 kg/m^3. Moreover, it seems that chemical effects, rather than physical effects, are the reason for the lowering of K_d values at increasing solid/water ratios (Wanner, Albinsson and Wieland, 1994).

B.4 Wanner

Although the extended Wanner model includes no diffusion model, a straightforward method for the interpretation of diffusion experiments has been developed for Cs^+ (Wanner, 1993; Wanner, Albinsson and Wieland, 1994). This was necessary to demonstrate the applicability of the extended Wanner model for dense bentonite systems, because the extended Wanner model was developed at low bentonite/water ratios. The method is based on mechanistic modeling of the sorption coefficient, K_d, and the estimation of the pore diffusivity, D_p, by analogy with HTO diffusion at different bentonite densities. Since Cs^+ has a very simple speciation in solution, and is known to adsorb via an ion exchange mechanism, the basic version of the Wanner model (Wanner, 1986; Wanner, Wersin and Sierro, 1992) could be used. While this approach uses a fully mechanistic sorption model according to Figure 1 of the present report, the diffusion model is not fully mechanistic but is based on analogy of D_p according to Figure 3.

Figure 7 of Wanner, Albinsson and Wieland (1994) shows that the thermodynamic surface model derived for Cs^+ is sufficiently accurate to predict K_d values of Cs^+ over a range of three orders of magnitude. An improvement of the diffusion model, however, appears necessary, and Sato, Yui and Yoshikawa's (1995) approach looks very promising to combine with the extended Wanner model to produce an ISD database system.

B.5 Switzerland

The Swiss program for high-level nuclear waste disposal has not yet presented any concept for modeling diffusion of radionuclides in compacted bentonite. In the performance assessment report of Project Gewähr (Nagra, 1985) the retention properties of the bentonite backfill were considered as zero (an extremely conservative approach) due to lacking quantitative information.

B.6 Overview of some mechanistic diffusion modeling approaches

Table B.2 gives an overview of the approaches used for diffusion modeling as described in the previous sections of this Appendix. The purpose of Table B.2 is to summarize the compatibility of the models used by PNC, TVO, SKB, AECL and Wanner, respectively, with data evaluated by other models in this list (PNC, TVO, SKB, AECL and Wanner, respectively). The features and assumptions of the various models considered important in connection with an integrated sorption/diffusion database, are listed in the (*x*,*x*) fields of Table B.2, e.g., the PNC model approach is outlined in the box "PNC/PNC", and so on. In some cases, the compatibility can be shown by a conversion formula, such as PNC/TVO or PNC/AECL. The approach used by SKB is not convertible to other models, because SKB uses a simplified approximation with the same values of D_e, D_p and ε for a very large number of radionuclides. Although SKB accepts the surface diffusion model, they have not quantified the surface diffusion effect in their diffusion database (Brandberg and Skagius, 1991) due to lack of data. The Wanner approach (Wanner, Albinsson and Wieland, 1994) strongly focuses on sorption mechanisms and uses diffusion models only to verify the chemical sorption model in compacted bentonite. The extended Wanner model is therefore compatible with any diffusion model that accepts site-specific variations of the distribution coefficients.

Table B.2: Overview of some mechanistic diffusion modeling approaches. If possible, conversion formulas are given. More detailed explanations can be found in the text.

Data→ Model[1] ↓	PNC	TVO	SKB	AECL	Wanner
PNC	• one model for both anions and cations • el. DL model to calculate δ • ε and τ^2 are structural par. • requires input from chemical sorption model	**Anions:** $\left(\frac{\delta}{\tau^2}\right)_{PNC} = ((\varepsilon_{eff})^Y)_{VTT}$ **Cations:** $\varepsilon D_0 \left(\frac{\delta - 1}{\tau^2}\right)_{PNC} = (K_d \rho_d D_s)_{VTT}$	SKB diffusion data should be directly re-evaluated by using the PNC model (references to Swedish diffusion studies are listed by Brandberg and Skagius, 1991)	1. $\left(\frac{\delta}{\tau^2}\right)_{PNC} = (\tau_a)_{AECL}$ 2. $\left(\frac{\varepsilon \delta}{\tau^2}\right)_{PNC} = (\Psi)_{AECL}$	Compatible
TVO	**Anions:** $((\varepsilon_{eff})^Y)_{VTT} = \left(\frac{\delta}{\tau^2}\right)_{PNC}$ **Cations:** $(K_d \rho_d D_s)_{VTT} = \varepsilon D_0 \left(\frac{\delta - 1}{\tau^2}\right)_{PNC}$	**Anions:** • ion exclusion expressed in a reduction of ε_{eff} • (δ/τ^2) considered as a structural parameter **Cations:** • surface diffusion • ε_{eff} taken as equal to bulk ε	Swedish diffusion measurements have been considered by Muurinen (1994).	$((\varepsilon_{eff})^Y)_{VTT} = (\tau_a)_{AECL}$ TVO considers surface diffusion for cations, AECL does not.	Compatible if K_d values are modeled thermodynamically. Surface diffusion term may be estimated by analogy.
SKB	No conversion is possible at this time, because the SKB model is not species-specific. Cooperation between SKB and TVO might lead to the adoption of the same diffusion model by the two organizations.	No conversion possible. Cooperation between SKB and TVO might lead to the adoption of the same diffusion model by the two organizations.	• database for D_e, D_p and ε_p • ε_{eff} for simple anions (TcO_4, I, Cl) 20% of total ε • identical values for Th, U, Np, Pu, Am, Rn, Pb, Zr, Se, Sn, Ce, Sm, C, Tc(red) • surface diffusion accepted • K_d values from batch exp.	No conversion possible because the SKB model is not species-specific.	No conversion possible because the SKB model is not species-specific. For Cs, the results are not compatible.
AECL	1. $(\tau_a)_{AECL} = \left(\frac{\delta}{\tau^2}\right)_{PNC}$ 2. $(\Psi)_{AECL} = \left(\frac{\varepsilon \delta}{\tau^2}\right)_{PNC}$	$(\tau_a)_{AECL} = ((\varepsilon_{eff})^Y)_{VTT}$ AECL considers no surface diffusion.	See comment under AECL/TVO.	• ε dependent on nuclide • no credit for surf. diffusion • Cs, Sr, I, CO_3 considered • K_d scaling from batch exp.	In principal compatible, but the scaling factor is replaced by mechanistic modeling of sorption.
Wanner	Use of analogs to cover missing exp. information. Equivalent to the "alternative procedure" presented in Section 3 of the present report.	In principle compatible. Effects of surface diffusion might in some cases be explained by mechanistic sorption modeling in the approach of Wanner.	Wanner: Specific modeling of sorption mechanisms. SKB: Using batch sorption data.	Using the extended Wanner model to predict K_d values in dense bentonite may improve the AECL approach. The focusing on chemical effects will thus be improved.	• focus on chemistry • ion exchange (Cs) • D_a of HTO used as analog for D_p of Cs • K_d values modeled for specific conditions

[1] The models listed here are not necessarily officially adopted by the respective performance assessment programs. The most recent reference publications for these models are: "PNC": Sato, Yui and Yoshikawa (1995); "TVO": Muurinen (1994); "SKB": Brandberg and Skagius (1991); "AECL": Oscarson (1994); "Wanner": Wanner, Albinsson and Wieland (1994).

C The extended Wanner model

The extended Wanner model consists of the earlier Wanner model plus the acid/base reactions of the oxide-type edge sites of montmorillonite. Although the abundance of the edge sites is small compared to the layer sites, their chemical behavior is important because they may have surface complexation properties similar to those of hydrous ferric oxides or aluminates.

C.1 Description of the earlier Wanner model

The Wanner model (Wanner, 1986) for the thermodynamic modeling of the interaction of groundwaters with bentonite includes the following model characteristics:

- Ion exchange between Na^+, K^+, Mg^{2+} and Ca^{2+} is modeled as simple complexation reactions (cf. for example Westall, 1994) with a surface site, Z^-, whose concentration is taken as equal to the cation exchange capacity (CEC). Note that other authors prefer to use the symbol X^- rather than Z^- to denote ion exchange sites (e.g., Fletcher and Sposito, 1989; Dzombak and Hudson, 1995). The exchange constants were derived from preliminary results of an experiment of Snellman, which was later published by Snellman, Uotila and Rantanen (1987):

$$\begin{array}{rcll} ZNa + K^+ & \rightleftarrows & ZK + Na^+ & \log K^\circ = 0.4 \\ 2\,ZNa + Mg^{2+} & \rightleftarrows & Z_2Mg + 2\,Na^+ & \log K^\circ = 1.7 \\ 2\,ZNa + Ca^{2+} & \rightleftarrows & Z_2Ca + 2\,Na^+ & \log K^\circ = 2.4 \end{array}$$

- Equilibrium with carbonate impurities in bentonite, modeled as calcite saturation equilibrium with the bentonite porewater.
- Equilibrium with silicates in bentonite, modeled as quartz saturation equilibrium with the bentonite porewater.

A few years later, new bentonite/water contact experiments had become available, and SKB asked us for a verification of the model. The model could be successfully verified (cf. Wanner, Wersin and Sierro, 1992), but two constants were slightly modified based on the new measurements:

$$\begin{array}{rcll} 2\,ZNa + Mg^{2+} & \rightleftarrows & Z_2Mg + 2\,Na^+ & \log K^\circ = 1.3 \\ 2\,ZNa + Ca^{2+} & \rightleftarrows & Z_2Ca + 2\,Na^+ & \log K^\circ = 1.6 \end{array}$$

In the meantime, Fletcher and Sposito (1989) had published an extensive work that included many data and evaluations for the interaction between montmorillonite and electrolyte solutions. The authors concluded that, in addition to the traditional layer sites (ion exchange sites) there must be less abundant sites with distinctly different affinities to the cations, and they called these sites "edge sites". Fletcher and Sposito assigned ion exchange properties and a proton exchange mechanism to the edge sites:

$$\mathrm{ZNa} + \mathrm{H}^+ \rightleftarrows \mathrm{ZH} + \mathrm{Na}^+ \qquad \log K^\circ = 4.0$$

The modeling study by Wanner, Wersin and Sierro (1992) showed that the influence of the edge sites was not significant except if the edge sites are loaded with protons before equilibration with groundwater, because the proton exchange equilibrium above is relevant in the acidic pH range only. A qualification of this model was not possible with the experimental information available, and new experiments were therefore planned to investigate the acid/base behavior of montmorillonite. This research study lead to significant additions to the Wanner model, and the new model is therefore called the "extended Wanner model".

C.2 Description of the extended Wanner model

As mentioned in the previous section of this Appendix, the principal improvement in the extended Wanner model, compared to the earlier Wanner model, is the inclusion of an additional surface site exhibiting amphoteric acid/base properties, cf. Wanner et al. (1994) and Wieland et al. (1994). The experimental titration curves of pretreated bentonite, measured in 0.005, 0.05 and 0.5 M $NaNO_3$, as well as 0.5 M NaCl, clearly show an oxide-type behavior of a type of site whose abundance was roughly 3% of the CEC. Protonation of the layer sites was not a relevant mechanism in the alkaline pH range. Use of the diffuse double layer model to evaluate the experimental curves yielded the following fitting results for the edge sites:

Reaction:	Mass law equation:	log K°:
$\mathrm{SOH_2^+} \rightleftarrows \mathrm{SOH} + \mathrm{H^+}$	$K_{a1}^{int} = \frac{(\mathrm{SOH})\{\mathrm{H^+}\}}{(\mathrm{SOH_2^+})} \exp\left(\frac{-F\Psi}{RT}\right)$	–5.4 ± 0.1
$\mathrm{SOH} \rightleftarrows \mathrm{SO^-} + \mathrm{H^+}$	$K_{a2}^{int} = \frac{(\mathrm{SO^-})\{\mathrm{H^+}\}}{(\mathrm{SOH})} \exp\left(\frac{-F\Psi}{RT}\right)$	–6.7 ± 0.1

Edge site density of montmorillonite: 2.8×10^{-5} mol/g

In the above list, K_{a1}^{int} and K_{a2}^{int} denote the intrinsic acidity constants, SOH the edge sites and Ψ the surface potential. The surface area of the edge sites was estimated to 3 m^2/g, which corresponds to about 10% of the BET surface area (Wieland et al., 1994).

For the cation exchange constants, the values published by Wanner, Wersin and Sierro (1992) are still valid, see Section C.1 above. However, these concentration constants have been converted to mole fraction constants commonly used in the soil science community (cf., e.g., Fletcher and Sposito, 1989). This allows to compare our ion exchange constants with literature values which in most cases are mole or equivalent fraction constants (see, e.g., Benson, 1982; Bruggenwert and Kamphorst, 1982; Fletcher and Sposito, 1989). The conversion is briefly illustrated here using the example of the Na^+/Ca^{2+} exchange, assuming Na^+ and Ca^{2+} to be the only exchangeable cations present:

$$2\,\mathrm{ZNa} + \mathrm{Ca}^{2+} \rightleftarrows \mathrm{Z_2Ca} + 2\,\mathrm{Na}^{+} \tag{C.1}$$

The Wanner model (Wanner, 1986; Wanner, Wersin and Sierro, 1992) treated the surface species, ZNa and Z_2Ca, as hypothetical aqueous species with the following equilibrium constant:

$$K(\mathrm{C.1}) = \frac{[\mathrm{Z_2Ca}]\,[\mathrm{Na^+}]^2}{[\mathrm{ZNa}]^2\,[\mathrm{Ca^{2+}}]} \tag{C.2}$$

In the mole fraction model, the equilibrium constant of Reaction (C.1) is expressed by the following equation:

$$K_x(\mathrm{C.1}) = \frac{x_{\mathrm{Ca}}\,[\mathrm{Na^+}]^2}{(x_{\mathrm{Na}})^2\,[\mathrm{Ca^{2+}}]} \tag{C.3}$$

where x is the mole fraction defined as follows:

$$x_{\mathrm{Ca}} = \frac{[\mathrm{Z_2Ca}]}{[\mathrm{Z_2Ca}]+[\mathrm{ZNa}]} \quad \text{and} \quad x_{\mathrm{Na}} = \frac{[\mathrm{ZNa}]}{[\mathrm{Z_2Ca}]+[\mathrm{ZNa}]}\text{, respectively.}$$

The conversion from concentration units to mole fraction units thus has the following form:

$$K_x(\mathrm{C.1}) = K(\mathrm{C.1})\,([\mathrm{Z_2Ca}]+[\mathrm{ZNa}]) \tag{C.4}$$

Note that the correction factor, $[Z_2Ca]+[ZNa]$, is not equal to the cation exchange capacity (CEC), since CEC = $2[Z_2Ca]+[ZNa]$.

In general terms, for a reaction of the form

$$z_A\,\mathrm{Z}_{z_B}\mathrm{B(surface)} + z_B\,\mathrm{A(aq)} \rightleftarrows z_B\,\mathrm{Z}_{z_A}\mathrm{A(surface)} + z_A\,\mathrm{B(aq)} \tag{C.5}$$

where A and B are ions, z_A and z_B their charges and Z denotes the ion exchange site. The corresponding conversion then has the following form:

$$K_x(\mathrm{C.5}) = K(\mathrm{C.5})\left([\mathrm{Z}_{z_A}\mathrm{A}]+[\mathrm{Z}_{z_B}\mathrm{B}]\right)^{(z_A - z_B)} \tag{C.6}$$

As can be seen, for homovalent reactions the correction term cancels out and $K_x = K$.

Hence, the ion exchange constants in mole fraction units are as follows in the extended Wanner model:

$$\mathrm{ZNa} + \mathrm{K}^+ \rightleftarrows \mathrm{ZK} + \mathrm{Na}^+ \qquad \log K^\circ = 0.26 \tag{C.7}$$

$$2\,\mathrm{ZNa} + \mathrm{Mg}^{2+} \rightleftarrows \mathrm{Z_2Mg} + 2\,\mathrm{Na}^+ \qquad \log K^\circ = 0.13 \tag{C.8}$$

$$2\,\mathrm{ZNa} + \mathrm{Ca}^{2+} \rightleftarrows \mathrm{Z_2Ca} + 2\,\mathrm{Na}^+ \qquad \log K^\circ = 0.21 \tag{C.9}$$

The proton exchange constants are only relevant in the acidic pH range. The exchange constant for the reaction

$$\mathrm{ZNa} + \mathrm{H}^+ \rightleftarrows \mathrm{ZH} + \mathrm{Na}^+ \tag{C.10}$$

is uncertain. The value given by Wanner et al. (1994) and Wieland et al. (1994), log K_x(C.10) = 4.6, only applies to a type of site whose concentration is about 2% of the CEC. Wieland et al.'s (1994) evaluation of data from Avena, Cabrol and de Pauli (1990) yielded log K_x(C.10) = 3.0 for all the ion exchange sites (= CEC). The proton exchange constant at some "edge site" given by Fletcher and Sposito (1989), log K_x(C.10) = 4.0, also falls in this range. Although these data agree that the value of log K_x(C.10) may lie in the range of about (4 ± 1), there is a need to determine the correct constant for the proton exchange reaction at the layer sites. In the present model we use log K_x(C.10) = 3.0.

In addition, the extended Wanner model offers input options for various impurities, such as NaCl, KCl, $CaSO_4$, $NaNO_3$, $CaCO_3$. The impurities are entered in % of total clay mass. The code is programed such that the total amount of given impurities dissolve readily in the equilibrium solution. Stepwise dissolution of the impurities can also be modeled by a reaction path calculation in the extended Wanner model.

C.3 Future development of the extended Wanner model

The ion exchange models described in Appendices C.1 and C.2 include activity corrections for the charged species according to some extended Debye-Hückel expression (the Davies' equation in this case), representing long-range electrostatic interactions. It is, however, most probable that the permanent negative surface charge on montmorillonite is not exactly neutralized by the adsorbed cations. The electric potential created at the surface by such a surface charge excess will lead to activity changes. It is difficult to estimate the significance of the error introduced by neglecting these activity changes. In the case of symmetrical ion exchange reactions ($z_A = z_B$ in Eq. C.5) as represented in Eqs. (C.7) and (C.10), the activity corrections of the adsorbed species can be expected to cancel out. Only a partial canceling effect is expected for unsymmetrical ion exchange reactions ($z_A \neq z_B$ in Eq. C.5) such as the Na/Ca exchange reaction (Eq. C.1). The sum of the errors introduced by neglecting surface potential effects is probably limited in most systems, as the fair agreement of the measured values with mole fraction and equivalent fraction modeling may indicate (cf. Bruggenwert and Kamphorst, 1982; Fletcher and Sposito, 1989; and Wanner, Albinsson and Wieland, 1994). The sorption measurements of Cs^+ by Wanner, Albinsson and Wieland (1994) nevertheless result in higher selectivities of Cs^+ in a solution dominated by Ca^{2+} and Mg^{2+}, respectively, than predicted by the mole fraction model. This deviation may be due to incomplete canceling out of activity correction errors in Cs/Ca and Cs/Mg exchange systems.

The problematics of ion exchange modeling and activity corrections have been described in detail very recently by Dzombak and Hudson (1995). They suggest to calculate the electric potential at the surface of the layer sites of montmorillonite, and to use this to calculate the activity coefficients of the reacting cations. This approach looks like a very promising tool in obtaining a more realistic thermodynamic description of the ion exchange reactions. We have plans to develop the extended Wanner model further to include activity coefficient changes based on electric field effects near the surface of montmorillonite.

D Examples of ISD data sheets

In this Appendix we present three examples of ISD data sheets for well-defined input/output systems. We use Cs^+ as a sample nuclide for demonstration purposes and Kunigel-V1 as a model bentonite. The data records shown on the following three pages (Figures D.1, D.2 and D.3) differ only in one input parameter: the compaction level of the bentonite. The compaction level is characterized by the dry density, for which values of 1500, 1140 and 400 kg/m^3 have been chosen. Note that the source records ("Groundwater Composition", "TDB", and "Bentonite Characteristics") carry labels, the models carry vewrsion numbers, and that the other records on each sheet are tied strictly to these three source records on each data sheet.

We would like to mention that the contents of the ISD data sheet examples shown in this Appendix have not been verified for correctness and consistency. They serve only for demonstration purposes, and they may serve as a starting point for the development of an ISD database. In particular, the input data and modeling results of the mechanistic diffusion model have to be selected in collaboration with the diffusion specialists at PNC (H. Sato and coworkers).

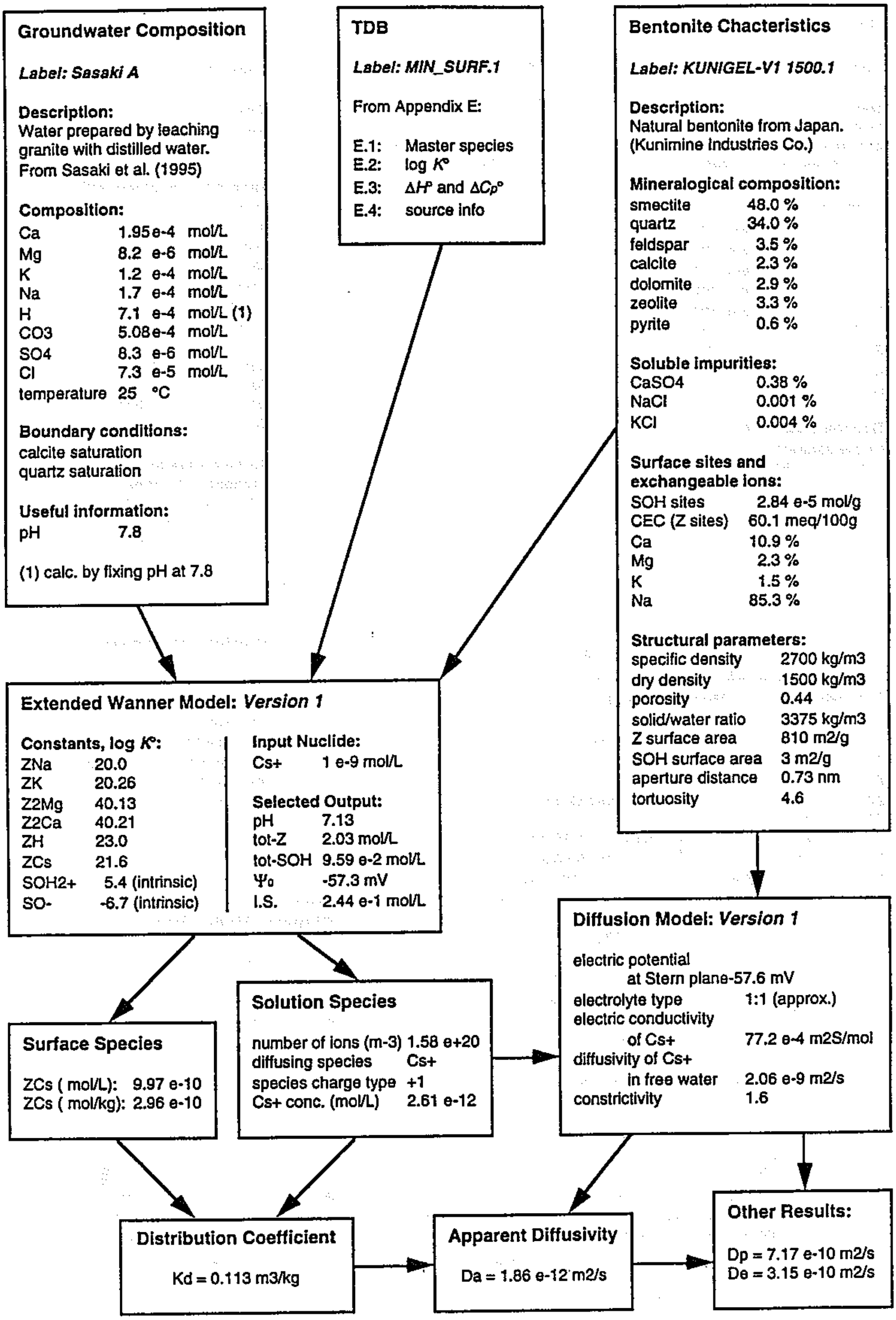
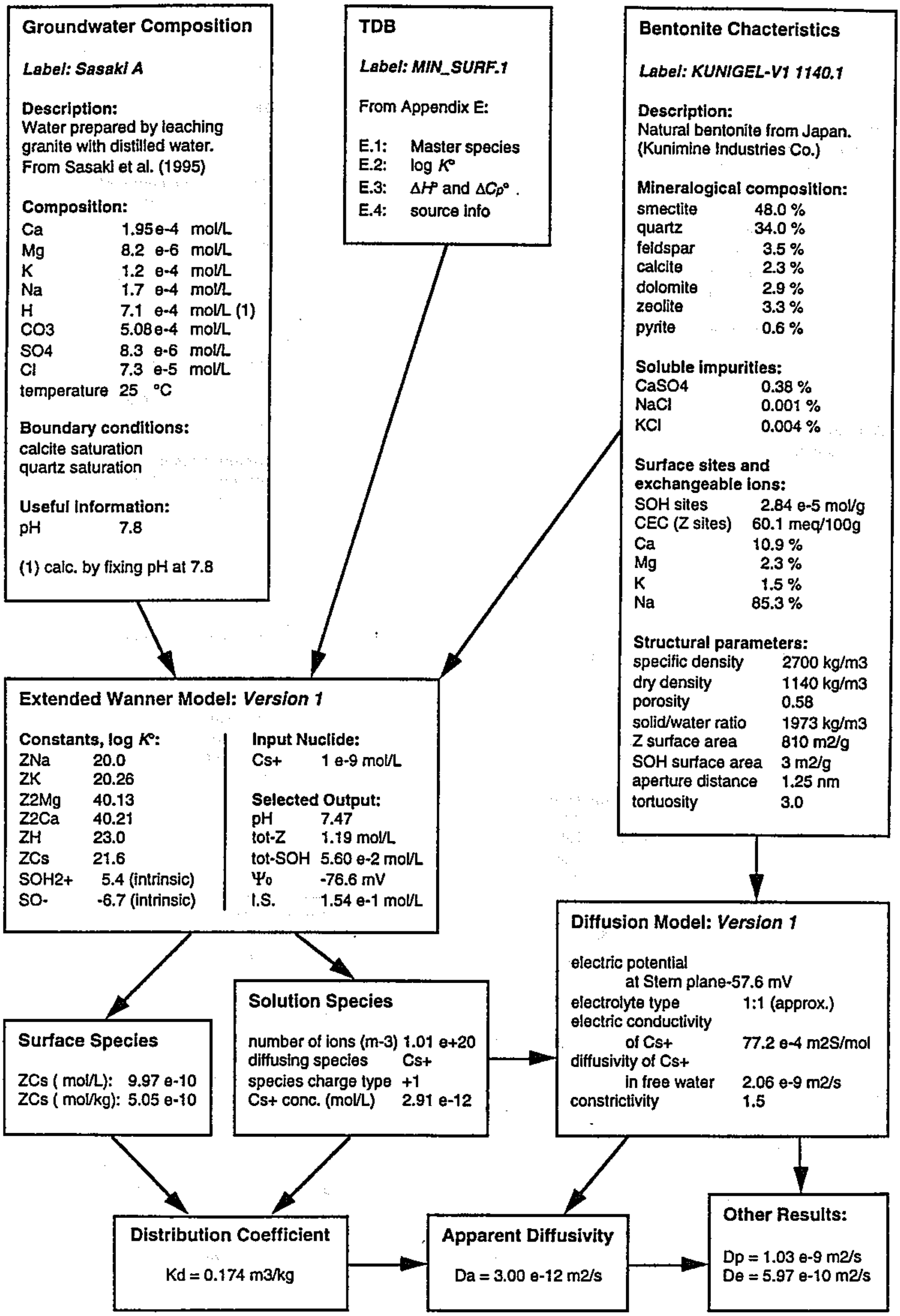


Figure D.1: Example of an ISD data record (not verified for diffusion data) for Kunigel-V1 at a dry density of 1500 kg/m^3. I.S. = ionic strength.



Groundwater Composition

Label: Sasaki A

Description:
Water prepared by leaching granite with distilled water.
From Sasaki et al. (1995)

Composition:

Ca	1.95e-4	mol/L
Mg	8.2 e-6	mol/L
K	1.2 e-4	mol/L
Na	1.7 e-4	mol/L
H	7.1 e-4	mol/L (1)
CO3	5.08e-4	mol/L
SO4	8.3 e-6	mol/L
Cl	7.3 e-5	mol/L
temperature	25	°C

Boundary conditions:
calcite saturation
quartz saturation

Useful information:
pH 7.8

(1) calc. by fixing pH at 7.8

TDB

Label: MIN_SURF.1

From Appendix E:

E.1: Master species
E.2: $\log K^\circ$
E.3: ΔH° and ΔC_p° .
E.4: source info

Bentonite Chacteristics

Label: KUNIGEL-V1 1140.1

Description:
Natural bentonite from Japan.
(Kunimine Industries Co.)

Mineralogical composition:

smectite	48.0 %
quartz	34.0 %
feldspar	3.5 %
calcite	2.3 %
dolomite	2.9 %
zeolite	3.3 %
pyrite	0.6 %

Soluble impurities:

CaSO4	0.38 %
NaCl	0.001 %
KCl	0.004 %

Surface sites and exchangeable ions:

SOH sites	2.84 e-5 mol/g
CEC (Z sites)	60.1 meq/100g
Ca	10.9 %
Mg	2.3 %
K	1.5 %
Na	85.3 %

Structural parameters:

specific density	2700 kg/m3
dry density	1140 kg/m3
porosity	0.58
solid/water ratio	1973 kg/m3
Z surface area	810 m2/g
SOH surface area	3 m2/g
aperture distance	1.25 nm
tortuosity	3.0

Extended Wanner Model: ***Version 1***

Constants, $\log K^\circ$:

ZNa	20.0
ZK	20.26
Z2Mg	40.13
Z2Ca	40.21
ZH	23.0
ZCs	21.6
SOH2+	5.4 (intrinsic)
SO-	-6.7 (intrinsic)

Input Nuclide:
Cs+ 1 e-9 mol/L

Selected Output:

pH	7.47
tot-Z	1.19 mol/L
tot-SOH	5.60 e-2 mol/L
Ψ_0	-76.6 mV
I.S.	1.54 e-1 mol/L

Surface Species

ZCs (mol/L): 9.97 e-10
ZCs (mol/kg): 5.05 e-10

Solution Species

number of ions (m-3)	1.01 e+20
diffusing species	Cs+
species charge type	+1
Cs+ conc. (mol/L)	2.91 e-12

Diffusion Model: ***Version 1***

electric potential at Stern plane	-57.6 mV
electrolyte type	1:1 (approx.)
electric conductivity of Cs+	77.2 e-4 m2S/mol
diffusivity of Cs+ in free water	2.06 e-9 m2/s
constrictivity	1.5

Distribution Coefficient

Kd = 0.174 m3/kg

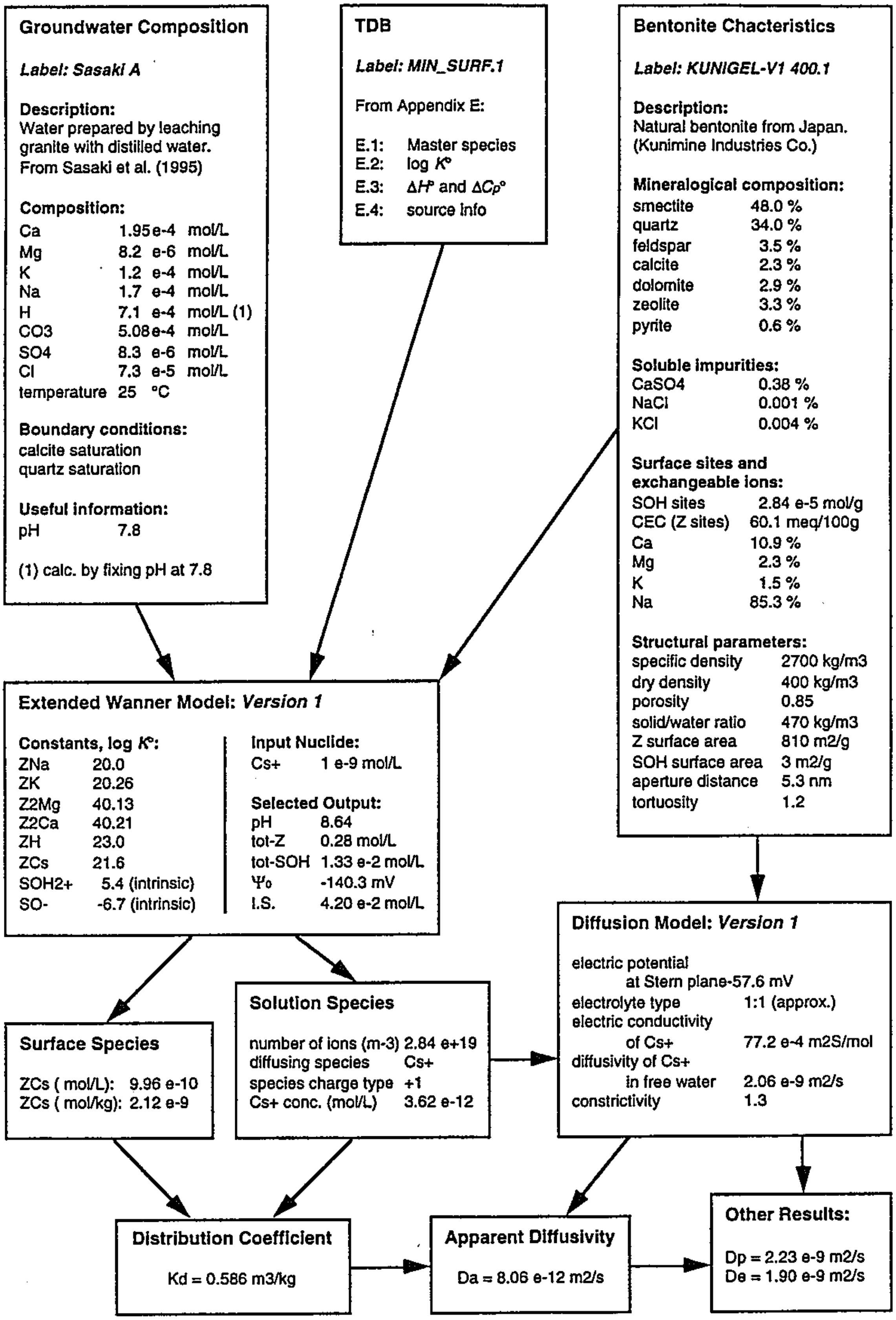
Apparent Diffusivity

Da = 3.00 e-12 m2/s

Other Results:

Dp = 1.03 e-9 m2/s
De = 5.97 e-10 m2/s

Figure D.2: Example of an ISD data record (not verified for diffusion data) for Kunigel-V1 at a dry density of 1140 kg/m^3. I.S. = ionic strength.



Groundwater Composition

Label: Sasaki A

Description:
Water prepared by leaching granite with distilled water.
From Sasaki et al. (1995)

Composition:

Ca	1.95e-4	mol/L
Mg	8.2 e-6	mol/L
K	1.2 e-4	mol/L
Na	1.7 e-4	mol/L
H	7.1 e-4	mol/L (1)
CO3	5.08e-4	mol/L
SO4	8.3 e-6	mol/L
Cl	7.3 e-5	mol/L
temperature	25	°C

Boundary conditions:
calcite saturation
quartz saturation

Useful information:

pH	7.8

(1) calc. by fixing pH at 7.8

TDB

Label: MIN_SURF.1

From Appendix E:

E.1:	Master species
E.2:	log $K°$
E.3:	$\Delta H°$ and $\Delta C_p°$
E.4:	source info

Bentonite Chacteristics

Label: KUNIGEL-V1 400.1

Description:
Natural bentonite from Japan.
(Kunimine Industries Co.)

Mineralogical composition:

smectite	48.0 %
quartz	34.0 %
feldspar	3.5 %
calcite	2.3 %
dolomite	2.9 %
zeolite	3.3 %
pyrite	0.6 %

Soluble impurities:

CaSO4	0.38 %
NaCl	0.001 %
KCl	0.004 %

Surface sites and exchangeable ions:

SOH sites	2.84 e-5 mol/g
CEC (Z sites)	60.1 meq/100g
Ca	10.9 %
Mg	2.3 %
K	1.5 %
Na	85.3 %

Structural parameters:

specific density	2700 kg/m3
dry density	400 kg/m3
porosity	0.85
solid/water ratio	470 kg/m3
Z surface area	810 m2/g
SOH surface area	3 m2/g
aperture distance	5.3 nm
tortuosity	1.2

Extended Wanner Model: *Version 1*

Constants, log $K°$:

ZNa	20.0
ZK	20.26
Z2Mg	40.13
Z2Ca	40.21
ZH	23.0
ZCs	21.6
SOH2+	5.4 (intrinsic)
SO-	-6.7 (intrinsic)

Input Nuclide:

Cs+	1 e-9 mol/L

Selected Output:

pH	8.64
tot-Z	0.28 mol/L
tot-SOH	1.33 e-2 mol/L
Ψ_0	-140.3 mV
I.S.	4.20 e-2 mol/L

Diffusion Model: *Version 1*

electric potential at Stern plane	-57.6 mV
electrolyte type	1:1 (approx.)
electric conductivity of Cs+	77.2 e-4 m2S/mol
diffusivity of Cs+ in free water	2.06 e-9 m2/s
constrictivity	1.3

Surface Species

ZCs (mol/L):	9.96 e-10
ZCs (mol/kg):	2.12 e-9

Solution Species

number of ions (m-3)	2.84 e+19
diffusing species	Cs+
species charge type	+1
Cs+ conc. (mol/L)	3.62 e-12

Distribution Coefficient

Kd = 0.586 m3/kg

Apparent Diffusivity

Da = 8.06 e-12 m2/s

Other Results:

Dp = 2.23 e-9 m2/s
De = 1.90 e-9 m2/s

Figure D.3: Example of an ISD data record (not verified for diffusion data) for Kunigel-V1 at a dry density of 400 kg/m^3. I.S. = ionic strength.

E TDB Used With the Extended Wanner Model (from MIN_SURF, May 1992)

The TDB version of May 1992 of the MIN_SURF code is listed here in full size. This chemical thermodynamic database has been used in the modeling studies in context with the extended Wanner model, and it is recommended as a starting database in view of improving and extending it for special applications. This database includes the contents of the Nagra TDB (Pearson and Berner, 1991; Pearson, Berner and Hummer, 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). Of course, this TDB contains the uranium data of the NEA-TDB (Grenthe et al., 1992). Table B.1 of Pearson, Berner and Hummel (1992) contains a comparison of the formation energies, $\Delta_f G^\circ$, of these species in various available TDB's (Nagra 05/92, Hatches 3.0, MINEQL-PSI 03/92, PHREEQE-PSI 04/91).

Note that thermodynamic databases are in a permanent process of improvement, extension and revision. The quality of the data is not uniform. Some data are updated and of high quality, such as the core data (Pearson and Berner, 1991) and the uranium data from the NEA-TDB (Grenthe et al., 1992), other data may not correspond to the state of the art, or may even be inconsistent with other contents of the database. We have not critically reviewed the contents of the database presented here, and it is recommended that the database be verified progressively during its application.

It should be mentioned that the code MIN_SURF (Berner, 1993) is an extended version of the code MINEQL/EIR (OECD/NEA, 1994). The extension essentially consists in the inclusion of the diffuse double layer model to calculate the reactions in the solid surface/water interface, cf. Dzombak and Morel (1990), de Levie (1990) and Hunter (1981). The code MINEQL/EIR (EIR was the former Swiss Federal Institute for Reactor Research, now named Paul Scherrer Institute) was an extension of the well-known speciation code MINEQL (Westall, Zachary and Morel, 1976) by including activity coefficients and temperature dependence routines.

The TDB consists of a master species table (E.1) in which the ID's are defined, a log K° table (E.2) in which the ID's and the compositions of the complexes are defined, a $\Delta_r H^\circ$ and $\Delta_r C_p^\circ$ table (E.3) in which the enthalpies and heat capacities are given if available, and a reference list (E.4) containing literature citations for certain TDB entries.

E.1 Table of Master Species

Each element has at least one master species whose ID and chemical composition ist shown in this table. Redox sensitive elements may have more than one master species, allowing to separate the modeling of the different oxidation states in case of kinetic inhibition. Example: 107 = NH_3, 198 = N_2(aq), 157 = NO_3^-. Equilibrium between these three oxidation states is modeled by defining the three master species in the input file (Table 1).

1	CA+2	2	MG+2	3	SR+2	4	K+	IDKO	10
5	NA+	6	FE+3	7	FE+2	8	MN+2	IDKO	20
9	CU+2	10	BA+2	11	CD+2	12	ZN+2	IDKO	30
13	NI+2	14	HG+2	15	PB+2	16	CO+2	IDKO	40
17	CO+3	18	AG+	19	CR+3	20	AL+3	IDKO	50
21	CS+	22	LI+	23	BE+2	24	SC+3	IDKO	60
25	TIO+2	26	SN+2	27	SN+4	28	LA+3	IDKO	70
29	CE+3	30	AU+	31	TH+4	32	UO2+2	IDKO	80
33	CU+	34	ND+3	35	PUO2+2	36	PUO2+	IDKO	90
37	PU+4	38	PU+3	39	U+3	40	U+4	IDKO	100
41	UO2+	42	NP+3	43	NP+4	44	NPO2+	IDKO	110
45	NPO2+2	46	TC+2	47	TCO+2	48	EU+3	IDKO	120
49	SM+3	50	H+	51	ZR+4	52	PD+2	IDKO	130
53	PA+4	54	PAO2+	55	AM+3	56	TCO+	IDKO	140
57	SB(OH)3	58	SB(OH)5	59	BI(OH)3	60		IDKO	150
61		62		63		64		IDKO	160
65		66		67		68	RB+	IDKO	170
69	RA+2	70		71		72		IDKO	180
73		74		75		76		IDKO	190
77		78		79		80	PSI-X	IDKO	200
81	=XSOH	82	=XWOH	83		84		IDKO	210
85	PSI-Y	86	=YSOH	87	=YWOH	88		IDKO	220
89		90	PSI-Z	91	=ZSOH	92	=ZWOH	IDKO	230
93		94		95		96		IDKO	240
97		98		99	E-	100		IDKO	250
101	CO3-2	102	SO4-2	103	CL-	104	F-	IDKO	260
105	BR-	106	I-	107	NH3	108	HS-	IDKO	270
109	PO4-3	110	P2O7-4	111	P3O10-5	112	H2SIO4-2	IDKO	280
113	S2O3-2	114	CN-	115	AC-	116	ACAC-	IDKO	290
117	CIT-3	118	OX-2	119	SAL-2	120	TART-2	IDKO	300
121	EN	122	DIP	123	SUSAL-3	124	GLY-	IDKO	310
125	GLU-2	126	PIC-	127	NTA-3	128	EDTA-4	IDKO	320
129	DCTA-4	130	CYST-2	131	NOC-3	132	PHTH-2	IDKO	330
133	ARG-	134	ORN-	135	LYS-	136	HIS-	IDKO	340
137	ASP-	138	SER-	139	ALA-	140	TYR-2	IDKO	350
141	MET-	142	VAL-	143	THR-	144	PHE-	IDKO	360
145	ISO-	146	LEU-	147	PRO-	148	B(OH)4-	IDKO	370
149	SO3-2	150	SCN-	151	NH2OH	152	MOO4-2	IDKO	380
153	WO4-2	154	ASO4-3	155	HVO4-2	156	SEO3-2	IDKO	390
157	NO3-	158	TRIS	159	TCO4-	160	ASO2-	IDKO	400
161	NBO3-	162		163	TCO4-2	164		IDKO	410
165	ZET-	166	EDG-	167	TCO4-3	168		IDKO	420
169		170	CLO-	171	CLO2-	172	CLO4-	IDKO	430
173	BRO-	174		175	IO3-	176		IDKO	440
177	HSE-	178	SEO4-2	179		180	N3-	IDKO	450
181	NO2-	182		183		184		IDKO	460
185		186		187		188		IDKO	470
189		190		191		192		IDKO	480
193		194		195		196		IDKO	490
197	CH4(AQ)	198	N2(AQ)	199	H2(AQ)	200	O2(AQ)		

E.2 Table of Formation Constants

This Table contains the formation constants of all the complexes and solids of the May 1992 version of the MIN_SURF database. A large part of it was published by Pearson and Berner (1991) and Pearson, Berner and Hummel (1992). The ID number is followed by the $\log_{10} K^\circ$ value and by the ID's and stoichiometric coefficients of the master species of which the corresponding complexes are composed of. The species type number is a MINEQL-specific code number: 1: master species; 2: aqueous complexes; 3: boundary conditions; 4: precipitated solids (calculation-specific); 5: potential solids; 6: species excluded from the mass balance. The information and references are given in Appendix E.4.

Example for reading the contents of the database:

```
 1000    3.224   1  1 101  1                      2 CORE  (7602)           1.6.90
32037   -0.88   32  2 101  1  50 -3           3.0 2 NEA           (NEW  ) 20.7.90
```

First check:

- Species 1000 is composed of the components 1 and 101 (one of each). From the list in Appendix D.1 we can see that component 1 is Ca^{2+}, and component 101 is CO_3^{2-}. Species 1000 thus represents $CaCO_3$ with a formation constant of $\log K^\circ = 3.224$.
- Species 32037 is composed of the following components: 2×32, 1×101 and –3×50. The list in Appendix E.1 tells us that component 32 is UO_2^{2+}, 101 is CO_3^{2-}, and 50 is H^+. Negative coefficients with H^+ stand for "$H_2O - H^+$" (H_2O is not explicitely considered by MINEQL) and indicate OH^-. Species 32037 thus represents $(UO_2)_2CO_3(OH)_3^-$. The correct formation reaction is

$$2\,UO_2^{2+} + CO_3^{2-} + 3\,H_2O(l) \quad = \quad (UO_2)_2CO_3(OH)_3^- + 3\,H^+$$

  with a formation constant of $\log K^\circ = -0.88$.

Second check:

- The species type is 2, meaning that $CaCO_3$ is an aqueous species (and not solid $CaCO_3$). The "Info" column tells us that this species is part of the Nagra core database (cf. Pearson and Berner, 1991), and its origin is from Ref. 7602, i.e. Smith and Martell (1976), cf. Appendix E.4. The last update was made on 1 June 1990.
- The number 3.0 just before the species type code (2 = aqueous complex) is not currently used by the MINEQL code. It represents the number of H_2O molecules involved in the formation reaction. "NEA" means that the value is from the NEA-TDB (Grenthe et al., 1992), and "new" indicates that this species was not included in earlier versions of the MINEQL database at PSI. The last update was on 20 July 1990.

This database presented here contains 1807 aqueous complexes (species type 2), 28 fixed boundary conditions (species type 3, e.g., redox reactions), 415 potential solids (species type 5) and 30 species which by default are excluded from the mass balance (species type 6, e.g., gaseous species and test species or uncertain species).

```
  ID     log K  ID1 c1  ID2 c2  ID3 c3   (etc.)  type Info + Ref.      last update

 1807                                LAST UPDATE MADE ON 27.4.92 BY U.BERNER
  1000     3.224    1    1 101   1                   2 CORE    (7602)           1.6.90
  1010    11.435    1    1 101   1   50   1          2 CORE                     1.6.90
  1020      2.30    1    1 102   1                   2 CORE    (7602)           1.6.90
  1030      0.94    1    1 104   1                   2 STAND   (7602)           1.6.90
  1040     -0.10    1    1 107   1                   2                         V4    5
  1050     -0.70    1    1 107   2                   2                         V4    6
  1060     -1.50    1    1 107   3                   2                         V4    7
  1070     -2.60    1    1 107   4                   2                         V4    8
  1080     15.10    1    1 109   1   50   1          2 7602                  14.2.84
  1081      6.46    1    1 109   1                   2 7602                  14.2.84
  1082     20.96    1    1 109   1   50   2          2 7602    DEP.             1.6.90
  1090      7.50    1    1 110   1                   2                         V4   10
  1100     13.80    1    1 110   1   50   1          2                         V4   11
  1110     14.80    1    1 111   1   50   1          2                         V4   12
  1120      8.40    1    1 111   1                   2                         V4   13
  1130      1.90    1    1 113   1                   2                         V4   14
  1140      1.10    1    1 115   1                   2                         V4   15
  1150      4.85    1    1 117   1                   2 HUMM    8903             Cacit-
  1160      9.33    1    1 117   1   50   1          2 HUMM    8903             CaHcit
  1170      12.6    1    1 117   1   50   2          2 HUMM    8903           CaH2cit+
  1180      3.19    1    1 118   1                   2 HUMM    8903               Caox
  1181       3.8    1    1 118   2                   2 HUMM    7705            Caox2-2
  1182      6.11    1    1 118   1   50   1          2 HUMM    7705            CaHox+
  1183      10.9    1    1 118   2   50   2          2 HUMM    7705           Ca(Hox)2
  1190     14.80    1    1 119   1   50   1          2                         V4   20
  1200      5.80    1    1 120   1   50   1          2                         V4   21
  1210      2.80    1    1 120   1                   2                         V4   22
  1220      1.80    1    1 124   1                   2                         V4   23
  1230      2.50    1    1 125   1                   2                         V4   24
  1240      2.30    1    1 126   1                   2                         V4   25
  1250      7.61    1    1 127   1                   2 HUMM    8903             Canta-
  1251      9.44    1    1 127   2                   2 HUMM    8903           Canta2-4
  1260      12.3    1    1 128   1                   2 HUMM    8903           Caedta-2
  1270      15.9    1    1 128   1   50   1          2 HUMM    8903           CaHedta-
  1280     15.00    1    1 129   1                   2                         V4   29
  1290     13.10    1    1 131   1                   2                         V4   30
  1300      2.70    1    1 132   1                   2                         V4   31
  1310      2.10    1    1 137   1                   2                         V4   32
  1320      1.90    1    1 138   1                   2                         V4   33
  1330      1.70    1    1 139   1                   2                         V4   34
  1340      2.70    1    1 140   1                   2                         V4   35
  1345       0.7    1    1 157   1                   2 7602              20.12.89 BU41
  1346       0.6    1    1 157   2                   2 7602              20.12.89 BU41
  1350    -12.78    1    1  50  -1               1.0 2 CORE                     1.6.90
  1360      2.98    2    1 101   1                   2 CORE    (7602)           1.6.90
  1370    11.397    2    1 101   1   50   1          2 CORE                     1.6.90
  1380      2.37    2    1 102   1                   2 CORE    (7602)           1.6.90
  1390      1.82    2    1 104   1                   2 STAND   (7602)           1.6.90
  1400      0.10    2    1 107   1                   2                         V4   41
  1410      0.00    2    1 107   2                   2                         V4   42
  1420     -0.30    2    1 107   3                   2                         V4   43
  1430     -1.00    2    1 107   4                   2                         V4   44
  1440     15.26    2    1 109   1   50   1          2 7602                  14.2.84
  1450      7.00    2    1 110   1                   2                         V4   46
  1460     15.50    2    1 111   1   50   1          2                         V4   47
  1470      8.70    2    1 111   1                   2                         V4   48
  1480      1.80    2    1 113   1                   2                         V4   49
  1490      1.10    2    1 115   1                   2                         V4   50
  1500      3.70    2    1 116   1                   2                         V4   51
  1510      6.40    2    1 116   2                   2                         V4   52
  1520      4.84    2    1 117   1                   2 HUMM    8903             Mgcit-
  1530       9.0    2    1 117   1   50   1          2 HUMM    8903             MgHcit
  1531      12.3    2    1 117   1   50   2          2 HUMM    8903           MgH2cit+
  1540      3.42    2    1 118   1                   2 HUMM    8903               Mgox
```

```
1541       5.08  2  1 118  2                     2 HUMM  7705        Mgox2-2
1550       2.30  2  1 120  1                     2                   V4   56
1560       5.60  2  1 120  1  50  1              2                   V4   57
1570       0.30  2  1 121  1                     2                   V4   58
1580       0.50  2  1 122  1                     2                   V4   59
1590       3.90  2  1 124  1                     2                   V4   60
1600       7.40  2  1 124  2                     2                   V4   61
1610       3.00  2  1 125  1                     2                   V4   62
1620       2.70  2  1 126  1                     2                   V4   63
1630       6.50  2  1 127  1                     2 HUMM  8903         Mgnta-
1640       10.5  2  1 128  1                     2 HUMM  8903       Mgedta-2
1650       14.8  2  1 128  1  50  1              2 HUMM  8903       MgHedta-
1660      12.70  2  1 129  1                     2                   V4   67
1670       4.20  2  1 130  1                     2                   V4   68
1680      15.90  2  1 131  1                     2                   V4   69
1690       1.80  2  1 133  1                     2                   V4   70
1700       4.90  2  1 137  2                     2                   V4   71
1710       2.60  2  1 139  1                     2                   V4   72
1720       3.20  2  1 140  1                     2                   V4   73
1730       4.90  2  1 147  2                     2                   V4   74
1740     -11.44  2  1  50 -1                 1.0 2 CORE  (7602)       1.6.90
1749     11.514  3  1 101  1  50  1              2 CORE  (8401)      21.3.91
1750      14.10  3  1 109  1  50  1              2                   V4   76
1760       6.00  3  1 109  1                     2                   V4   77
1770       5.70  3  1 110  1                     2                   V4   78
1780      15.60  3  1 111  1  50  1              2                   V4   79
1790       6.80  3  1 111  1                     2                   V4   80
1800       2.00  3  1 113  1                     2                   V4   81
1810       0.90  3  1 115  1                     2                   V4   82
1820        4.3  3  1 117  1                     2 HUMM  8903         Srcit-
1830       2.54  3  1 118  1                     2 HUMM  7705           Srox
1831        2.7  3  1 118  2                     2 HUMM  7705        Srox2-2
1832       5.80  3  1 118  1  50  1              2 HUMM  7705         SrHox+
1833       10.8  3  1 118  2  50  2              2 HUMM  7705       Sr(Hox)2
1840       1.40  3  1 124  1                     2                   V4   85
1850       1.80  3  1 125  1                     2                   V4   86
1860       2.20  3  1 126  1                     2                   V4   87
1870       6.25  3  1 127  1                     2 HUMM  8903         Srnta-
1880       10.4  3  1 128  1                     2 HUMM  8903       Sredta-2
1890       14.8  3  1 128  1  50  1              2 HUMM  8903       SrHedta-
1900      12.50  3  1 129  1                     2                   V4   91
1910      13.70  3  1 131  1                     2                   V4   92
1920       2.10  3  1 137  1                     2                   V4   93
1930       0.90  3  1 138  1                     2                   V4   94
1940       1.20  3  1 139  1                     2                   V4   95
1950     -13.29  3  1  50 -1                 1.0 2 CORE  (7602)       1.6.90
1951      2.805  3  1 101  1                     2 CORE  (8300*)      1.6.90
1952       2.29  3  1 102  1                     2 CORE  (7602)       1.6.90
1953       0.00  3  1 103  2                     2 8201             17/2/83
1954       0.80  3  1 157  1                     2 7602             17/2/83
1955       0.80  3  1 157  2                     2 7602             17/2/83
1959     -14.46  4  1  50 -1                 1.0 2 CORE               1.6.90
1960       0.85  4  1 102  1                     2 CORE  (7602)       1.6.90
1970       3.40  4  1 110  1                     2                   V4   98
1980       4.20  4  1 111  1                     2                   V4   99
1990       0.90  4  1 113  1                     2                   V4  100
1995       1.22  4  1 117  1                     2 HUMM  8903         Kcit-2
1996        0.9  4  1 118  1                     2 HUMM  8903           Kox-
1997        1.2  4  1 127  1                     2 HUMM  8903         Knta-2
1998        1.6  4  1 128  1                     2 HUMM  8903        Kedta-3
1999     -14.18  5  1  50 -1                 1.0 2 CORE               1.6.90
2000       1.27  5  1 101  1                     2 CORE               1.6.90
2001     10.079  5  1 101  1  50  1              2 CORE               1.6.90
2010       0.70  5  1 102  1                     2 CORE  (7602)       1.6.90
2014      -0.24  5  1 104  1                     2 CORE               1.6.90
2020       3.80  5  1 110  1                     2                   V4  103
2030       4.20  5  1 111  1                     2                   V4  104
```

2040	0.60	5	1	113	1				2			V4 105
2045	1.34	5	1	117	1				2	HUMM	8903	Nacit-2
2047	1.0	5	1	118	1				2	HUMM	8903	Naox-
2050	1.8	5	1	127	1				2	HUMM	8903	Nanta-2
2060	2.7	5	1	128	1				2	HUMM	8903	Naedta-3
2070	4.04	6	1	102	1				2	STAND		1.6.90
2075	4.468	6	1	102	1	50	1		2	STAND		1.6.90
2080	5.38	6	1	102	2				2	STAND		1.6.90
2090	1.48	6	1	103	1				2	STAND		1.6.90
2100	2.13	6	1	103	2				2	STAND		1.6.90
2110	1.13	6	1	103	3				2	STAND		1.6.90
2120	6.20	6	1	104	1				2	STAND		1.6.90
2130	10.80	6	1	104	2				2	STAND		1.6.90
2140	14.00	6	1	104	3				2	STAND		1.6.90
2150	0.70	6	1	105	1				2			V4 116
2160	2.10	6	1	106	1				2			V4 117
2170	20.70	6	1	109	1	50	1		2			V4 118
2180	26.00	6	1	110	1	50	2		2			V4 119
2190	23.73	6	1	112	1	50	1		2		DEP.	1.6.90
2200	3.90	6	1	113	1				2			V4 121
2210	43.60	6	1	114	6				2			V4 122
2220	4.20	6	1	115	1				2			V4 123
2230	7.50	6	1	115	2				2			V4 124
2240	10.50	6	1	115	3				2			V4 125
2250	10.10	6	1	116	1				2			V4 126
2260	19.30	6	1	116	2				2			V4 127
2270	26.90	6	1	116	3				2			V4 128
2280	9.04	6	2	117	2	50	-2	2.0	2	HUMM	9102	Fe2(OH)2cit2-2
2285	10.87	6	1	117	1	50	-1	1.0	2	HUMM	9102	FeOHcit-
2286	2.93	6	1	117	1	50	-2	2.0	2	HUMM	9102	Fe(OH)2cit-2
2287	3.00	6	1	117	2	50	-2	2.0	2	HUMM	9102	Fe(OH)2cit2-5
2290	12.64	6	1	117	1				2	HUMM	9102	Fecit
2291	18.11	6	1	117	2				2	HUMM	9102	Fecit2-3
2295	14.19	6	1	117	1	50	1		2	HUMM	9102	FeHcit+
2296	19.81	6	1	117	2	50	1		2	HUMM	9102	FeHcit2-2
2297	26.28	6	1	117	2	50	2		2	HUMM	9102	Fe(Hcit)2-
2310	9.1	6	1	118	1				2	HUMM	7705	Feox+
2320	15.8	6	1	118	2				2	HUMM	7705	Feox2-
2330	20.1	6	1	118	3				2	HUMM	7705	Feox3-3
2331	9.4	6	1	118	1	50	1		2	HUMM	7705	FeHox+2
2340	18.20	6	1	119	1				2			V4 135
2350	30.70	6	1	119	2				2			V4 136
2360	17.10	6	1	123	1				2			V4 137
2370	27.90	6	1	123	2				2			V4 138
2380	32.00	6	1	123	3				2			V4 139
2390	10.90	6	1	124	1				2			V4 140
2400	18.15	6	1	127	1				2	HUMM	6701	Fenta
2410	26.2	6	1	127	2				2	HUMM	7403	Fenta2-3
2420	13.9	6	1	127	1	50	-1	1.0	2	HUMM	7403	FeOHnta-
2430	5.7	6	1	127	1	50	-2	2.0	2	HUMM	7403	Fe(OH)2nta-2
2440	27.6	6	1	128	1				2	HUMM	8903	Feedta-
2450	29.1	6	1	128	1	50	1		2	HUMM	8903	FeHedta
2460	19.8	6	1	128	1	50	-1	1.0	2	HUMM	8903	FeOHedta-2
2480	33.00	6	1	129	1				2			V4 149
2490	23.40	6	1	129	1	50	-1	1.0	2			V4 150
2500	33.60	6	1	130	2				2			V4 151
2510	35.30	6	1	131	1				2			V4 152
2520	9.50	6	1	133	1				2			V4 153
2530	9.50	6	1	134	1				2			V4 154
2540	5.50	6	1	136	1				2			V4 155
2550	12.20	6	1	137	1				2			V4 156
2560	10.00	6	1	138	1				2			V4 157
2570	11.20	6	1	139	1				2			V4 158
2580	10.40	6	1	142	1				2			V4 159
2590	9.40	6	1	143	1				2			V4 160
2600	9.70	6	1	144	1				2			V4 161
2610	10.70	6	1	145	1				2			V4 162

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  2620     10.70    6  1 146   1                          2                     V4  163
  2630     10.90    6  1 147   1                          2                     V4  164
  2640      8.90    6  1 148   1                          2                     V4  165
  2650     15.80    6  1 148   2                          2                     V4  166
  2660      3.10    6  1 150   1                          2                     V4  167
  2670     -2.19    6  1  50  -1                      1.0 2 STAND                 1.6.90
  2680     -5.67    6  1  50  -2                      2.0 2 STAND                 1.6.90
  2690    -12.56    6  1  50  -3                      3.0 2 STAND                 1.6.90
  2700    -21.60    6  1  50  -4                      4.0 2 STAND                 1.6.90
  2710     -2.95    6  2  50  -2                      2.0 2 STAND                 1.6.90
  2711     -6.30    6  3  50  -4                      4.0 2 SUPPL            Fe3(OH)4+5
  2716    12.329    7  1 101   1   50   1                 2 STAND                 1.6.90
  2717      4.38    7  1 101   1                          2 STAND                 1.6.90
  2720      2.25    7  1 102   1                          2 STAND (7602)          1.6.90
  2725     3.068    7  1 102   1   50   1                 2 STAND                 1.6.90
  2730      0.14    7  1 103   1                          2 STAND                 1.6.90
  2731     15.95    7  1 109   1   50   1                 2 7602                14.2.84
  2732     22.56    7  1 109   1   50   2                 2 7602     DEP.         1.6.90
  2735      1.00    7  1 104   1                          2 STAND                 1.6.90
  2740      1.30    7  1 107   1                          2                     V4  175
  2750      2.10    7  1 107   2                          2                     V4  176
  2760      3.60    7  1 107   4                          2                     V4  177
  2770     35.40    7  1 114   6                          2                     V4  178
  2780      3.70    7  1 115   1                          2                     V4  179
  2790      5.20    7  1 116   1                          2                     V4  180
  2800      8.90    7  1 116   2                          2                     V4  181
  2820       6.1    7  1 117   1                          2 HUMM   8903          Fecit-
  2830      10.1    7  1 117   1   50   1                 2 HUMM   8903         FeHcit
  2835       4.1    7  1 118   1                          2 HUMM   7705           Feox
  2836       6.2    7  1 118   2                          2 HUMM   7705        Feox2-2
  2850     12.40    7  1 119   2                          2                     V4  186
  2860      4.20    7  1 121   1                          2                     V4  187
  2870      7.50    7  1 121   2                          2                     V4  188
  2880      9.50    7  1 121   3                          2                     V4  189
  2890      4.30    7  1 122   1                          2                     V4  190
  2900      8.00    7  1 122   2                          2                     V4  191
  2910     17.50    7  1 122   3                          2                     V4  192
  2920      7.70    7  1 123   1                          2                     V4  193
  2930     10.90    7  1 123   2                          2                     V4  194
  2940      4.30    7  1 124   1                          2                     V4  195
  2950      4.70    7  1 125   1                          2                     V4  196
  2960      5.40    7  1 126   1                          2                     V4  197
  2970      9.90    7  1 126   2                          2                     V4  198
  2980     13.10    7  1 126   3                          2                     V4  199
  2990     10.09    7  1 127   1                          2 HUMM   7403          Fenta-
  2991      13.5    7  1 127   2                          2 HUMM   7403        Fenta2-4
  2992      12.3    7  1 127   1   50   1                 2 HUMM   7403          FeHnta
  3000      -0.9    7  1 127   1   50  -1             1.0 2 HUMM   7403      FeOHnta-2
  3010      16.0    7  1 128   1                          2 HUMM   8903       Feedta-2
  3020      19.2    7  1 128   1   50   1                 2 HUMM   8903       FeHedta-
  3021       6.3    7  1 128   1   50  -1             1.0 2 HUMM   8903     FeOHedta-3
  3022      -4.4    7  1 128   1   50  -2             2.0 2 HUMM   8903  Fe(OH)2edta-4
  3030     20.60    7  1 129   1                          2                     V4  204
  3040     12.20    7  1 130   1                          2                     V4  205
  3050      3.80    7  1 133   1                          2                     V4  206
  3060      3.60    7  1 134   1                          2                     V4  207
  3070      5.10    7  1 135   1                          2                     V4  208
  3080      6.30    7  1 136   1                          2                     V4  209
  3090     10.90    7  1 136   2                          2                     V4  210
  3100      4.80    7  1 137   1                          2                     V4  211
  3110      9.40    7  1 137   2                          2                     V4  212
  3120      7.90    7  1 138   2                          2                     V4  213
  3130      3.90    7  1 138   1                          2                     V4  214
  3140      4.10    7  1 139   1                          2                     V4  215
  3150      8.10    7  1 139   2                          2                     V4  216
  3160      8.20    7  1 140   2                          2                     V4  217
  3170      3.70    7  1 141   1                          2                     V4  218
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 3180      7.50   7  1 141  2                          2                      V4  219
 3190      3.90   7  1 142  1                          2                      V4  220
 3200      7.60   7  1 142  2                          2                      V4  221
 3210      3.80   7  1 143  1                          2                      V4  222
 3220      3.80   7  1 144  1                          2                      V4  223
 3230      7.10   7  1 144  2                          2                      V4  224
 3240      3.90   7  1 145  1                          2                      V4  225
 3250      3.90   7  1 146  1                          2                      V4  226
 3260      4.60   7  1 147  1                          2                      V4  227
 3270      9.10   7  1 147  2                          2                      V4  228
 3280     -9.50   7  1  50 -1                      1.0 2 STAND (7602)           1.6.90
 3289      4.90   8  1 101  1                          2 STAND                  1.6.90
 3290    12.279   8  1 101  1  50  1                   2 STAND                  1.6.90
 3300      2.25   8  1 102  1                          2 STAND (7602)           1.6.90
 3310      0.61   8  1 103  1                          2 STAND                  1.6.90
 3320      0.25   8  1 103  2                          2 STAND                  1.6.90
 3330     -0.31   8  1 103  3                          2 STAND                  1.6.90
 3335      0.84   8  1 104  1                          2 STAND                  1.6.90
 3340      0.70   8  1 107  1                          2                      V4  235
 3350      1.20   8  1 107  2                          2                      V4  236
 3360     16.20   8  1 109  1  50  1                   2                      V4  237
 3370      6.00   8  1 110  1                          2                      V4  238
 3380      1.90   8  1 113  1                          2                      V4  239
 3390      1.10   8  1 115  1                          2                      V4  240
 3400      2.20   8  1 115  2                          2                      V4  241
 3410      4.30   8  1 116  1                          2                      V4  242
 3420      7.40   8  1 116  2                          2                      V4  243
 3430       5.1   8  1 117  1                          2 HUMM  8903             Mncit-
 3440       9.5   8  1 117  1  50  1                   2 HUMM  8903            MnHcit
 3450      3.95   8  1 118  1                          2 HUMM  7705               Mnox
 3460       5.2   8  1 118  2                          2 HUMM  7705           Mnox2-2
 3470      7.00   8  1 119  1                          2                      V4  248
 3480     10.90   8  1 119  2                          2                      V4  249
 3490      2.60   8  1 121  1                          2                      V4  250
 3500      4.70   8  1 121  2                          2                      V4  251
 3510      5.60   8  1 121  3                          2                      V4  252
 3520      2.50   8  1 122  1                          2                      V4  253
 3530      4.50   8  1 122  2                          2                      V4  254
 3540      6.20   8  1 122  3                          2                      V4  255
 3550      7.00   8  1 123  1                          2                      V4  256
 3560      9.00   8  1 123  2                          2                      V4  257
 3570      3.70   8  1 124  1                          2                      V4  258
 3580      6.40   8  1 124  2                          2                      V4  259
 3590      4.30   8  1 125  1                          2                      V4  260
 3600      4.10   8  1 126  1                          2                      V4  261
 3610      7.10   8  1 126  2                          2                      V4  262
 3620      8.90   8  1 126  3                          2                      V4  263
 3630      8.57   8  1 127  1                          2 HUMM  7403             Mnnta-
 3640      15.6   8  1 128  1                          2 HUMM  8903          Mnedta-2
 3650      19.1   8  1 128  1  50  1                   2 HUMM  8903          MnHedta-
 3660     19.20   8  1 129  1                          2                      V4  267
 3670     22.60   8  1 129  1  50  1                   2                      V4  268
 3680      4.70   8  1 130  1                          2                      V4  269
 3690     13.70   8  1 131  1                          2                      V4  270
 3700     20.30   8  1 131  1  50  1                   2                      V4  271
 3710      2.60   8  1 133  1                          2                      V4  272
 3720      4.70   8  1 133  2                          2                      V4  273
 3730      2.70   8  1 135  1                          2                      V4  274
 3740      4.10   8  1 136  1                          2                      V4  275
 3750      8.50   8  1 136  2                          2                      V4  276
 3760      4.60   8  1 137  1                          2                      V4  277
 3770      3.70   8  1 139  1                          2                      V4  278
 3780      6.90   8  1 139  2                          2                      V4  279
 3790      3.50   8  1 140  1                          2                      V4  280
 3800      3.30   8  1 142  1                          2                      V4  281
 3810      6.40   8  1 142  2                          2                      V4  282
 3820      3.30   8  1 145  1                          2                      V4  283
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3830       6.20  8  1 145  2                      2                       V4  284
3840       3.30  8  1 146  1                      2                       V4  285
3850       6.20  8  1 146  2                      2                       V4  286
3860       3.80  8  1 147  1                      2                       V4  287
3870       6.40  8  1 147  2                      2                       V4  288
3880       1.40  8  1 150  1                      2                       V4  289
3890       0.50  8  1 151  1                      2                       V4  290
3900     -10.59  8  1  50 -1                  1.0 2 STAND (7602)            1.6.90
3910     -34.20  8  1  50 -3                  3.0 2                       V4  292
3920       6.77  9  1 101  1                      2 7002                 18.3.83
3930      10.01  9  1 101  2                      2 7002                 18.3.83
3935     14.619  9  1 101  1   50  1              2 8201   DEP.            1.6.90
3940       2.36  9  1 102  1                      2 8201                 18.3.83
3950       0.40  9  1 103  1                      2 8201                 18.3.83
3960       0.16  9  1 103  2                      2 8201                 18.3.83
3961      -2.30  9  1 103  3                      2 8201                 18.3.83
3962      -4.60  9  1 103  4                      2 8201                 18.3.83
3970       1.30  9  1 104  1                      2                       V4  298
3980       1.10  9  1 105  1                      2                       V4  299
3990       5.80  9  1 107  1                      2                       V4  300
4000      10.70  9  1 107  2                      2                       V4  301
4010      16.60  9  1 109  1   50  1              2                       V4  302
4020       9.10  9  1 110  1                      2                       V4  303
4030       9.10  9  1 110  2                      2                       V4  304
4040      16.50  9  1 111  1   50  1              2                       V4  305
4050      10.30  9  1 111  1                      2                       V4  306
4060       2.20  9  1 115  1                      2                       V4  307
4070       3.50  9  1 115  2                      2                       V4  308
4080       3.90  9  1 115  3                      2                       V4  309
4090       3.40  9  1 115  4                      2                       V4  310
4100       8.30  9  1 116  1                      2                       V4  311
4110      15.10  9  1 116  2                      2                       V4  312
4120       2.42  9  1 117  1   50 -1              2 7602Z I-corrected      2.9.90
4121       6.3   9  2 117  2   50 -2              2 7602Z I-corrected      2.9.90
4130       7.13  9  1 117  1                      2 7602Z I-corrected      2.9.90
4131      10.67  9  1 117  1   50  1              2 7602Z I-corrected      2.9.90
4140      13.85  9  1 117  1   50  2              2 7602Z I-corrected      2.9.90
4141       9.82  9  2 117  1                      2 7602Z I-corrected      2.9.90
4142      16.2   9  2 117  2                      2 7602Z I-corrected      2.9.90
4150       6.40  9  1 118  1   50  1              2                       V4  316
4160       5.10  9  1 118  1                      2                       V4  317
4170       9.70  9  1 118  2                      2                       V4  318
4180      11.70  9  1 119  1                      2                       V4  319
4190      19.70  9  1 119  2                      2                       V4  320
4200       4.30  9  1 120  1                      2                       V4  321
4210       6.20  9  1 120  2                      2                       V4  322
4220       4.60  9  1 120  3                      2                       V4  323
4230       3.90  9  1 120  4                      2                       V4  324
4240      10.50  9  1 121  1                      2                       V4  325
4250      19.50  9  1 121  2                      2                       V4  326
4260       8.00  9  1 122  1                      2                       V4  327
4270      13.50  9  1 122  2                      2                       V4  328
4280      17.00  9  1 122  3                      2                       V4  329
4290      11.40  9  1 123  1                      2                       V4  330
4300      17.40  9  1 123  2                      2                       V4  331
4310       8.70  9  1 124  1                      2                       V4  332
4320      16.00  9  1 124  2                      2                       V4  333
4330       8.90  9  1 125  1                      2                       V4  334
4340      15.50  9  1 125  2                      2                       V4  335
4350       8.60  9  1 126  1                      2                       V4  336
4360      15.90  9  1 126  2                      2                       V4  337
4370      14.50  9  1 127  1                      2                       V4  338
4380      17.10  9  1 127  2                      2                       V4  339
4390       4.90  9  1 127  1   50 -1          1.0 2                       V4  340
4400      20.60  9  1 128  1                      2                       V4  341
4410      24.00  9  1 128  1   50  1              2                       V4  342
4420       8.70  9  1 128  1   50 -1          1.0 2                       V4  343
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4430    23.70   9  1 129  1                    2                  V4  344
4440    27.40   9  1 129  1  50   1            2                  V4  345
4450    15.50   9  1 131  1                    2                  V4  346
4460    24.60   9  1 131  1  50   1            2                  V4  347
4470     4.20   9  1 132  1                    2                  V4  348
4480     5.50   9  1 132  2                    2                  V4  349
4490     8.10   9  1 133  1                    2                  V4  350
4500    14.90   9  1 133  2                    2                  V4  351
4510     7.40   9  1 134  1                    2                  V4  352
4520    13.20   9  1 134  2                    2                  V4  353
4530    14.40   9  1 135  2                    2                  V4  354
4540    11.10   9  1 136  1                    2                  V4  355
4550    19.40   9  1 136  2                    2                  V4  356
4560     8.90   9  1 137  1                    2                  V4  357
4570    16.00   9  1 137  2                    2                  V4  358
4580    15.40   9  1 138  2                    2                  V4  359
4590     8.70   9  1 139  1                    2                  V4  360
4600    15.90   9  1 139  2                    2                  V4  361
4610    16.20   9  1 140  2                    2                  V4  362
4620    15.50   9  1 141  2                    2                  V4  363
4630     8.40   9  1 142  1                    2                  V4  364
4640    15.20   9  1 142  2                    2                  V4  365
4650    15.40   9  1 143  2                    2                  V4  366
4660     8.20   9  1 144  1                    2                  V4  367
4670    15.40   9  1 144  2                    2                  V4  368
4680     8.60   9  1 145  1                    2                  V4  369
4690    16.60   9  1 145  2                    2                  V4  370
4700     8.60   9  1 146  1                    2                  V4  371
4710    16.60   9  1 146  2                    2                  V4  372
4720    17.60   9  1 147  2                    2                  V4  373
4730     7.10   9  1 148  1                    2                  V4  374
4740    12.40   9  1 148  2                    2                  V4  375
4750     2.40   9  1 150  1                    2                  V4  376
4760     2.40   9  1 151  1                    2                  V4  377
4770     4.10   9  1 151  2                    2                  V4  378
4775     0.50   9  1 157  1                    2 7602            18.3.83
4776    -0.40   9  1 157  2                    2 7602            18.3.83
4780     4.00   9  1 158  1                    2                  V4  379
4790     7.60   9  1 158  2                    2                  V4  380
4800    11.10   9  1 158  3                    2                  V4  381
4810    14.10   9  1 158  4                    2                  V4  382
4820     1.30   9  1 158  2  50  -1        1.0 2                  V4  383
4830    -6.60   9  1 158  2  50   2            2                  V4  384
4840    -8.00   9  1  50 -1                1.0 2 7002            18.3.83
4841   -16.20   9  1  50 -2                2.0 2 8201            18.3.83
4842   -26.30   9  1  50 -3                3.0 2 7002            18.3.83
4843   -39.40   9  1  50 -4                4.0 2 7002            18.3.83
4845   -10.95   9  2  50 -2                2.0 2 7002            18.3.83
4851    2.713  10  1 101  1                    2 CORE   (7602)     1.6.90
4852   11.310  10  1 101  1  50   1            2 CORE              1.6.90
4853     2.70  10  1 102  1                    2 CORE   (7602)     1.6.90
4854     3.40  10  1 102  2                    2 8300*           17/2/83
4856    -0.13  10  1 103  1                    2 7602            17/2/83
4860     7.00  10  1 110  1                    2                 V4  387
4870     9.30  10  1 111  1                    2                 V4  388
4880     2.30  10  1 113  1                    2                 V4  389
4890     0.90  10  1 115  1                    2                 V4  390
4900     4.08  10  1 117  1                    2 7602Z I-corrected  2.9.90
4901     9.01  10  1 117  1  50   1            2 7602Z I-corrected  2.9.90
4902    12.38  10  1 117  1  50   2            2 7602Z I-corrected  2.9.90
4910     1.70  10  1 118  1                    2                 V4  392
4920     1.40  10  1 119  1                    2                 V4  393
4930     5.60  10  1 120  1  50   1            2                 V4  394
4940     2.70  10  1 120  1                    2                 V4  395
4950     1.30  10  1 124  1                    2                 V4  396
4960     2.40  10  1 125  1                    2                 V4  397
4970     2.20  10  1 126  1                    2                 V4  398
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4980      6.50  10  1 127   1                    2                           V4  399
4990     10.20  10  1 128   1                    2                           V4  400
5000     15.40  10  1 128   1  50  1             2                           V4  401
5010     10.50  10  1 129   1                    2                           V4  402
5020     17.70  10  1 129   1  50  1             2                           V4  403
5030      2.70  10  1 132   1                    2                           V4  404
5040      1.60  10  1 137   1                    2                           V4  405
5050      1.30  10  1 139   1                    2                           V4  406
5055      0.90  10  1 157   1                    2 7602                     17/2/83
5056      1.00  10  1 157   2                    2 7602                     17/2/83
5060    -13.47  10  1  50  -1                1.0 2 CORE  (7602)               1.6.90
5070      4.30  11  1 101   1                    2 8300*                    17/2/83
5080      2.46  11  1 102   1                    2 7602                     17/2/83
5081      3.25  11  1 102   2                    2 7602A                    17/2/83
5082      2.70  11  1 102   3                    2 7602A                    17/2/83
5090      1.98  11  1 103   1                    2 7602                     17/2/83
5100      2.60  11  1 103   2                    2 7602                     17/2/83
5110      2.40  11  1 103   3                    2 7602                     17/2/83
5111      1.70  11  1 103   4                    2 7602                     17/2/83
5120      1.10  11  1 104   1                    2                           V4  413
5130      2.10  11  1 105   1                    2                           V4  414
5140      2.90  11  1 105   2                    2                           V4  415
5150      3.00  11  1 105   3                    2                           V4  416
5160      3.10  11  1 105   4                    2                           V4  417
5170      2.90  11  1 106   1                    2                           V4  418
5180      4.20  11  1 106   2                    2                           V4  419
5190      5.90  11  1 106   3                    2                           V4  420
5200      6.60  11  1 106   4                    2                           V4  421
5210      2.50  11  1 107   1                    2                           V4  422
5220      4.50  11  1 107   2                    2                           V4  423
5230      6.00  11  1 107   3                    2                           V4  424
5240      6.80  11  1 107   4                    2                           V4  425
5250      6.50  11  1 107   5                    2                           V4  426
5260      4.80  11  1 107   6                    2                           V4  427
5270      3.90  11  1 109   1                    2                           V4  428
5280      9.60  11  1 110   1                    2                           V4  429
5290     11.20  11  1 111   1                    2                           V4  430
5300     -0.80  11  1 111   1  50 -1         1.0 2                           V4  431
5310      3.90  11  1 113   1                    2                           V4  432
5320      6.10  11  1 114   1                    2                           V4  433
5330     11.40  11  1 114   2                    2                           V4  434
5340     16.10  11  1 114   3                    2                           V4  435
5350     19.40  11  1 114   4                    2                           V4  436
5360      1.60  11  1 115   1                    2                           V4  437
5370      2.70  11  1 115   2                    2                           V4  438
5380      2.60  11  1 115   3                    2                           V4  439
5390      1.80  11  1 115   4                    2                           V4  440
5400      3.90  11  1 116   1                    2                           V4  441
5410      6.90  11  1 116   2                    2                           V4  442
5430      5.36  11  1 117   1                    2 7602                       2.9.90
5431       5.4  11  1 117   2                    2 7602Z I-corrected          2.9.90
5440      9.45  11  1 117   1  50  1             2 7602Z I-corrected          2.9.90
5441     12.56  11  1 117   1  50  2             2 7602Z I-corrected          2.9.90
5450      3.40  11  1 118   1                    2                           V4  446
5460      5.50  11  1 118   2                    2                           V4  447
5470      6.70  11  1 119   1                    2                           V4  448
5480      3.90  11  1 120   1                    2                           V4  449
5490      5.50  11  1 121   1                    2                           V4  450
5500     10.00  11  1 121   2                    2                           V4  451
5510     12.00  11  1 121   3                    2                           V4  452
5520      4.50  11  1 122   1                    2                           V4  453
5530      8.00  11  1 122   2                    2                           V4  454
5540     10.50  11  1 122   3                    2                           V4  455
5550      6.50  11  1 123   1                    2                           V4  456
5560      4.40  11  1 124   1                    2                           V4  457
5570      7.90  11  1 124   2                    2                           V4  458
5580      5.80  11  1 125   1                    2                           V4  459
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5590    8.50  11  1 125  2                              2           V4  460
5600    5.10  11  1 126  1                              2           V4  461
5610    9.00  11  1 126  2                              2           V4  462
5620   11.60  11  1 126  3                              2           V4  463
5630   11.90  11  1 127  1                              2           V4  464
5640   15.40  11  1 127  2                              2           V4  465
5650   19.00  11  1 128  1                              2           V4  466
5660   22.40  11  1 128  1  50   1                      2           V4  467
5670   21.60  11  1 129  1                              2           V4  468
5680   25.20  11  1 129  1  50   1                      2           V4  469
5690   10.60  11  1 131  1                              2           V4  470
5700   18.10  11  1 131  1  50   1                      2           V4  471
5710    3.70  11  1 132  1                              2           V4  472
5720    3.80  11  1 133  1                              2           V4  473
5730    7.40  11  1 133  2                              2           V4  474
5740    4.20  11  1 134  1                              2           V4  475
5750    7.20  11  1 134  2                              2           V4  476
5760    6.10  11  1 136  1                              2           V4  477
5770   10.60  11  1 136  2                              2           V4  478
5780    4.90  11  1 137  1                              2           V4  479
5790    8.40  11  1 137  2                              2           V4  480
5800    6.60  11  1 139  1                              2           V4  481
5810    8.60  11  1 139  2                              2           V4  482
5820   10.00  11  1 139  3                              2           V4  483
5830    4.40  11  1 141  1                              2           V4  484
5840    7.90  11  1 141  2                              2           V4  485
5850    5.20  11  1 142  1                              2           V4  486
5860    9.20  11  1 142  2                              2           V4  487
5870    4.60  11  1 145  1                              2           V4  488
5880    8.20  11  1 145  2                              2           V4  489
5890    4.60  11  1 146  1                              2           V4  490
5900    8.20  11  1 146  2                              2           V4  491
5910    9.50  11  1 147  2                              2           V4  492
5920    5.40  11  1 149  2                              2           V4  493
5930    0.50  11  1 157  1                              2 7602      17/2/83
5931    0.20  11  1 157  2                              2 7602      17/2/83
5940  -10.10  11  1  50 -1                          1.0 2 7602      17/2/83
5941  -20.30  11  1  50 -2                          2.0 2 7602      17/2/83
5942  -31.80  11  1  50 -3                          3.0 2 8300*     17/2/83
5943  -47.30  11  1  50 -4                          4.0 2 7602      17/2/83
5944   -9.40  11  2  50 -1                          1.0 2 7602      17/2/83
5945  -32.80  11  4  50 -4                          4.0 2 7602      17/2/83
5955    5.30  12  1 101  1                              2 8300*     17/2/83
5960    2.38  12  1 102  1                              2 7602      17/2/83
5961    4.20  12  1 102  2                              2 8201      17/2/83
5970    0.43  12  1 103  1                              2 7602      17/2/83
5980    0.61  12  1 103  2                              2 7602      17/2/83
5990    0.50  12  1 103  3                              2 7602      17/2/83
5991    0.20  12  1 103  4                              2 7602      17/2/83
6000    1.30  12  1 104  1                              2           V4  501
6010    0.10  12  1 105  1                              2           V4  502
6020    2.20  12  1 107  1                              2           V4  503
6030    4.50  12  1 107  2                              2           V4  504
6040    7.00  12  1 107  3                              2           V4  505
6050    9.00  12  1 107  4                              2           V4  506
6060   15.70  12  1 109  1  50   1                      2           V4  507
6070    8.7   12  1 110  1                              2 7602       2.9.90
6080   11.00  12  1 110  2                              2           V4  509
6090   -0.9   12  1 110  1  50  -1                  1.0 2 7602       2.9.90
6100   16.10  12  1 111  1  50   1                      2           V4  511
6110    9.90  12  1 111  1                              2           V4  512
6120    2.30  12  1 113  1                              2           V4  513
6130   17.20  12  1 114  4                              2           V4  514
6140    1.80  12  1 115  1                              2           V4  515
6150    2.90  12  1 115  2                              2           V4  516
6160    5.10  12  1 116  1                              2           V4  517
6170    9.10  12  1 116  2                              2           V4  518
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6180     6.21  12  1 117  1              2 7602Z I-corrected      2.9.90
6181     6.7   12  1 117  2              2 7602Z I-corrected      2.9.90
6182    10.33  12  1 117  1  50  1       2 7602Z I-corrected      2.9.90
6183    12.84  12  1 117  1  50  2       2 7602Z I-corrected      2.9.90
6190     4.20  12  1 118  1              2                      V4  520
6200     6.90  12  1 118  2              2                      V4  521
6210     5.70  12  1 118  1  50  1       2                      V4  522
6220    11.10  12  1 118  2  50  2       2                      V4  523
6230     8.00  12  1 119  1              2                      V4  524
6240     5.60  12  1 120  1  50  1       2                      V4  525
6250     3.50  12  1 120  1              2                      V4  526
6260     5.60  12  1 121  1              2                      V4  527
6270    10.30  12  1 121  2              2                      V4  528
6280    12.00  12  1 121  3              2                      V4  529
6290     5.30  12  1 122  1              2                      V4  530
6300     9.70  12  1 122  2              2                      V4  531
6310    13.50  12  1 122  3              2                      V4  532
6320     7.90  12  1 123  1              2                      V4  533
6330    11.40  12  1 123  2              2                      V4  534
6340     5.30  12  1 124  1              2                      V4  535
6350     9.70  12  1 124  2              2                      V4  536
6360     6.50  12  1 125  1              2                      V4  537
6370    10.70  12  1 125  2              2                      V4  538
6380     5.80  12  1 126  1              2                      V4  539
6390    10.40  12  1 126  2              2                      V4  540
6400    13.70  12  1 126  3              2                      V4  541
6410    12.40  12  1 127  1              2                      V4  542
6420    14.20  12  1 127  2              2                      V4  543
6430    18.30  12  1 128  1              2                      V4  544
6440    21.70  12  1 128  1  50  1       2                      V4  545
6450    21.10  12  1 129  1              2                      V4  546
6460    24.70  12  1 129  1  50  1       2                      V4  547
6470    11.00  12  1 130  1              2                      V4  548
6480    19.80  12  1 130  2              2                      V4  549
6490    14.00  12  1 131  1              2                      V4  550
6500    20.40  12  1 131  1  50  1       2                      V4  551
6510     3.30  12  1 132  1              2                      V4  552
6520     4.70  12  1 133  1              2                      V4  553
6530     9.00  12  1 133  2              2                      V4  554
6540     4.60  12  1 134  1              2                      V4  555
6550     8.10  12  1 134  2              2                      V4  556
6560     8.40  12  1 135  2              2                      V4  557
6570     7.30  12  1 136  1              2                      V4  558
6580    13.00  12  1 136  2              2                      V4  559
6590     6.30  12  1 137  1              2                      V4  560
6600    11.20  12  1 137  2              2                      V4  561
6610     5.70  12  1 139  1              2                      V4  562
6620    10.40  12  1 139  2              2                      V4  563
6630    10.20  12  1 140  2              2                      V4  564
6640     4.90  12  1 141  1              2                      V4  565
6650     9.40  12  1 141  2              2                      V4  566
6660     5.10  12  1 142  1              2                      V4  567
6670     9.90  12  1 142  2              2                      V4  568
6680     4.60  12  1 145  1              2                      V4  569
6690     8.20  12  1 145  2              2                      V4  570
6700     4.60  12  1 146  1              2                      V4  571
6710     8.20  12  1 146  2              2                      V4  572
6720    11.00  12  1 147  2              2                      V4  573
6730     0.50  12  1 151  1              2                      V4  574
6735     0.40  12  1 157  1              2 7602                17/2/83
6736    -0.30  12  1 157  2              2 7602                17/2/83
6740    -9.00  12  1  50 -1          1.0 2 7602                17/2/83
6745   -16.90  12  1  50 -2          2.0 2 7602                17/2/83
6750   -28.40  12  1  50 -3          3.0 2 7602                17/2/83
6760   -41.20  12  1  50 -4          4.0 2 7602                17/2/83
6761    -9.00  12  2  50 -1          1.0 2 7602                17/2/83
6765     5.78  13  1 101  1              2 7902                 21.3.91
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6766   10.11  13  1 101  2                   2 8105            21.3.91
6767   13.41  13  1 101  1  50  1            2 7902            21.3.91
6770    2.31  13  1 102  1                   2 8208            21.3.91
6771    3.2   13  1 102  2                   2 8102            21.3.91
6780    0.4   13  1 103  1                   2 8105            21.3.91
6781    0.96  13  1 103  2                   2 SUPPL 8105        NiCl2
6790    1.3   13  1 104  1                   2 8105            21.3.91
6800    0.6   13  1 105  1                   2                 V4  581
6820    5.11  13  1 107  2                   2 SUPPL 8208   Ni(NH3)2+2
6860    8.88  13  1 107  6                   2 SUPPL 8208   Ni(NH3)6+2
6861    8.37  13  1 109  1                   2 7902            21.3.91
6862   15.28  13  1 109  1  50  1            2 7902            21.3.91
6863   21.1   13  1 109  1  50  2            2 7902            21.3.91
6870    6.52  13  1 110  1                   2 8208            21.3.91
6871   12.69  13  1 110  1  50  1            2 8208            21.3.91
6880    7.10  13  1 110  2                   2                 V4  589
6890    2.20  13  1 113  1                   2                 V4  590
6900   30.12  13  1 114  4                   2 8208            21.3.91
6910    1.20  13  1 115  1                   2                 V4  592
6920    2.10  13  1 115  2                   2                 V4  593
6930    6.10  13  1 116  1                   2                 V4  594
6940   10.60  13  1 116  2                   2                 V4  595
6950   12.70  13  1 116  3                   2                 V4  596
6970    6.5   13  1 117  1                   2 HUMM  8903        Nicit-
6971    8.7   13  1 117  2                   2 HUMM  8903     Nicit2-4
6980   10.5   13  1 117  1  50  1            2 HUMM  8903        NiHcit
6981   13.4   13  1 117  1  50  2            2 HUMM  8903     NiH2cit+
6990    5.13  13  1 118  1                   2 HUMM  9006          Niox
7000    8.72  13  1 118  2                   2 HUMM  7101      Niox2-2
7020    8.20  13  1 119  1                   2                 V4  603
7030   12.90  13  1 119  2                   2                 V4  604
7040    7.60  13  1 121  1                   2                 V4  605
7050   14.00  13  1 121  2                   2                 V4  606
7060   18.50  13  1 121  3                   2                 V4  607
7070    7.00  13  1 122  1                   2                 V4  608
7080   13.80  13  1 122  2                   2                 V4  609
7090   20.00  13  1 122  3                   2                 V4  610
7100    8.20  13  1 123  1                   2                 V4  611
7110   11.00  13  1 123  2                   2                 V4  612
7120    6.30  13  1 124  1                   2                 V4  613
7130   11.40  13  1 124  2                   2                 V4  614
7140    7.00  13  1 125  1                   2                 V4  615
7150   11.40  13  1 125  2                   2                 V4  616
7160    7.30  13  1 126  1                   2                 V4  617
7170   13.40  13  1 126  2                   2                 V4  618
7180   18.00  13  1 126  3                   2                 V4  619
7190   12.76  13  1 127  1                   2 HUMM  7403        Ninta-
7191   16.95  13  1 127  2                   2 HUMM  7403      Ninta2-4
7192    1.48  13  1 127  1  50 -1        1.0 2 HUMM  7403    NiOHnta-2
7200   20.1   13  1 128  1                   2 HUMM  8903      Niedta-2
7210   23.6   13  1 128  1  50  1            2 HUMM  8903      NiHedta-
7211    7.6   13  1 128  1  50 -1        1.0 2 HUMM  8903   NiOHedta-3
7220   21.80  13  1 129  1                   2                 V4  623
7230   19.90  13  1 130  2                   2                 V4  624
7240   14.00  13  1 131  1                   2                 V4  625
7250   20.60  13  1 131  1  50  1            2                 V4  626
7260    3.20  13  1 132  1                   2                 V4  627
7270    5.60  13  1 133  1                   2                 V4  628
7280   10.10  13  1 133  2                   2                 V4  629
7290   13.40  13  1 133  3                   2                 V4  630
7300    5.30  13  1 134  1                   2                 V4  631
7310    9.50  13  1 134  2                   2                 V4  632
7320    9.60  13  1 135  2                   2                 V4  633
7330    9.30  13  1 136  1                   2                 V4  634
7340   16.60  13  1 136  2                   2                 V4  635
7350    7.60  13  1 137  1                   2                 V4  636
7360   13.50  13  1 137  2                   2                 V4  637
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7370	6.10	13	1	138	1				2			V4	638
7380	10.90	13	1	138	2				2			V4	639
7390	14.00	13	1	138	3				2			V4	640
7400	6.60	13	1	139	1				2			V4	641
7410	11.50	13	1	139	2				2			V4	642
7420	11.20	13	1	140	2				2			V4	643
7430	6.20	13	1	141	1				2			V4	644
7440	11.40	13	1	141	2				2			V4	645
7450	14.00	13	1	141	3				2			V4	646
7460	5.90	13	1	142	1				2			V4	647
7470	10.50	13	1	142	2				2			V4	648
7480	13.00	13	1	142	3				2			V4	649
7490	6.10	13	1	145	1				2			V4	650
7500	10.90	13	1	145	2				2			V4	651
7510	6.10	13	1	146	1				2			V4	652
7520	10.90	13	1	146	2				2			V4	653
7530	12.10	13	1	147	2				2			V4	654
7540	1.65	13	1	150	1				2	8208		21.3.91	
7550	1.50	13	1	151	1				2			V4	656
7560	9.70	13	1	151	2				2			V4	657
7565	0.4	13	1	157	1				2	7602		17/2/83	
7566	-0.6	13	1	157	2				2	7602		21.3.91	
7570	2.60	13	1	158	1				2			V4	658
7580	4.50	13	1	158	2				2			V4	659
7590	-9.71	13	1	50	-1			1.0	2	8208		21.3.91	
7591	-20.0	13	1	50	-2			2.0	2	7602		21.3.91	
7592	-30.0	13	1	50	-3			3.0	2	7601		21.3.91	
7593	-44.00	13	1	50	-4			4.0	2	7601		21.3.91	
7594	-10.70	13	2	50	-1			1.0	2	7601		21.3.91	
7595	-27.74	13	4	50	-4			4.0	2	7601		21.3.91	
7600	2.50	14	1	102	1				2	7602A		17/2/83	
7610	3.60	14	1	102	2				2	7602A		17/2/83	
7620	7.35	14	1	103	1				2	7602A		17/2/83	
7630	14.15	14	1	103	2				2	7602A		17/2/83	
7640	15.00	14	1	103	3				2	7602A		17/2/83	
7650	15.70	14	1	103	4				2	7602A		17/2/83	
7660	1.60	14	1	104	1				2			V4	667
7670	9.60	14	1	105	1				2			V4	668
7680	18.10	14	1	105	2				2			V4	669
7690	20.50	14	1	105	3				2			V4	670
7700	21.60	14	1	105	4				2			V4	671
7710	13.40	14	1	106	1				2			V4	672
7720	24.60	14	1	106	2				2			V4	673
7730	28.40	14	1	106	3				2			V4	674
7740	30.30	14	1	106	4				2			V4	675
7750	8.70	14	1	107	1				2			V4	676
7760	17.50	14	1	107	2				2			V4	677
7770	18.50	14	1	107	3				2			V4	678
7780	19.30	14	1	107	4				2			V4	679
7790	40.2	14	1	108	2				2		SULPH	21.3.91	
7800	26.4	14	1	108	2	50	-2		2		SULPH	21.3.91	
7810	5.20	14	1	110	1	50	-1	1.0	2			V4	682
7820	29.90	14	1	113	1				2			V4	683
7830	32.80	14	1	113	2				2			V4	684
7840	18.60	14	1	114	1				2			V4	685
7850	35.50	14	1	114	2				2			V4	686
7860	39.40	14	1	114	3				2			V4	687
7870	42.10	14	1	114	4				2			V4	688
7880	23.30	14	1	121	2				2			V4	689
7890	10.80	14	1	124	1				2			V4	690
7900	20.00	14	1	124	2				2			V4	691
7910	8.20	14	1	126	1				2			V4	692
7920	16.40	14	1	126	2				2			V4	693
7930	14.50	14	1	127	1				2			V4	694
7940	8.80	14	1	127	1	50	-1	1.0	2			V4	695
7950	24.20	14	1	128	1				2			V4	696
7960	27.90	14	1	128	1	50	1		2			V4	697

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7970   14.50  14  1 128  1  50 -1   1.0 2                         V4  698
7980   26.70  14  1 129  1              2                         V4  699
7990   30.40  14  1 129  1  50  1       2                         V4  700
8000   15.60  14  1 129  1  50 -1   1.0 2                         V4  701
8010   45.20  14  1 130  2              2                         V4  702
8020    7.80  14  1 136  1              2                         V4  703
8030   13.10  14  1 136  2              2                         V4  704
8035    0.80  14  1 157  1              2 8300*                17/2/83
8036    1.00  14  1 157  2              2 8300*                17/2/83
8040   -3.40  14  1  50 -1          1.0 2 7602                 17/2/83
8050   -6.20  14  1  50 -2          2.0 2 7602                 17/2/83
8051  -21.10  14  1  50 -3          3.0 2 7602                 17/2/83
8052   -3.30  14  2  50 -1          1.0 2 7602                 17/2/83
8053   -6.40  14  3  50 -3          3.0 2 7602                 17/2/83
8060    7.00  15  1 101  1              2 8201                 17/2/83
8070   10.35  15  1 101  2              2 8201                 17/2/83
8080    2.75  15  1 102  1              2 7602                 17/2/83
8081    4.00  15  1 102  2              2 8300*                17/2/83
8090    1.59  15  1 103  1              2 7602                 17/2/83
8100    1.80  15  1 103  2              2 7602                 17/2/83
8110    1.70  15  1 103  3              2 7602                 17/2/83
8111    1.40  15  1 103  4              2 7602                 17/2/83
8120    1.60  15  1 105  1              2                         V4  713
8130    2.20  15  1 105  2              2                         V4  714
8140    3.00  15  1 105  3              2                         V4  715
8150    1.80  15  1 106  1              2                         V4  716
8160    3.60  15  1 106  2              2                         V4  717
8170    4.20  15  1 106  3              2                         V4  718
8180    4.40  15  1 106  4              2                         V4  719
8190    5.20  15  1 110  2              2                         V4  720
8200    6.20  15  1 113  1              2                         V4  721
8210    7.50  15  1 113  2              2                         V4  722
8220   10.60  15  1 114  4              2                         V4  723
8230    2.40  15  1 115  1              2                         V4  724
8240    4.10  15  1 115  2              2                         V4  725
8250    4.70  15  1 116  1              2                         V4  726
8260    7.40  15  1 116  2              2                         V4  727
8270   10.46  15  1 117  1  50  1       2 7602Z I-corrected     2.9.90
8271   13.21  15  1 117  1  50  2       2 7602Z I-corrected     2.9.90
8272   17.7   15  1 117  2  50  2       2 7602Z I-corrected     2.9.90
8273   25.2   15  1 117  2  50  4       2 7602Z I-corrected     2.9.90
8280    5.68  15  1 117  1              2 7602Z I-corrected     2.9.90
8281    6.91  15  1 117  2              2 7602Z I-corrected     2.9.90
8282    4.5   15  1 117  3              2 7602Z I-corrected     2.9.90
8300    4.90  15  1 120  1              2                         V4  731
8310    3.00  15  1 122  1              2                         V4  732
8320    6.10  15  1 124  1              2                         V4  733
8330   10.60  15  1 124  2              2                         V4  734
8340    5.10  15  1 126  1              2                         V4  735
8350    8.70  15  1 126  2              2                         V4  736
8360   13.60  15  1 127  1              2                         V4  737
8370   20.50  15  1 128  1              2                         V4  738
8380   23.80  15  1 128  1  50  1       2                         V4  739
8390   22.10  15  1 129  1              2                         V4  740
8400   25.60  15  1 129  1  50  1       2                         V4  741
8410   13.40  15  1 130  1              2                         V4  742
8420    4.50  15  1 132  1              2                         V4  743
8430    4.50  15  1 132  2              2                         V4  744
8440    5.10  15  1 133  1              2                         V4  745
8450    9.50  15  1 133  2              2                         V4  746
8460    7.30  15  1 136  1              2                         V4  747
8470    5.60  15  1 139  1              2                         V4  748
8480    9.00  15  1 139  2              2                         V4  749
8490    4.90  15  1 141  1              2                         V4  750
8500    5.20  15  1 148  1              2                         V4  751
8510   11.10  15  1 148  2              2                         V4  752
8520    1.17  15  1 157  1              2 7602                 17/2/83
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8521      1.40  15  1 157  2                     2 7602                 17/2/83
8540     -7.70  15  1  50 -1                 1.0 2 7602                 17/2/83
8541    -17.10  15  1  50 -2                 2.0 2 7602                 17/2/83
8542    -28.10  15  1  50 -3                 3.0 2 7602                 17/2/83
8543     -6.40  15  2  50 -1                 1.0 2 7602                 17/2/83
8544    -23.90  15  3  50 -4                 4.0 2 8201                 21.11.90
8545    -20.90  15  4  50 -4                 4.0 2 7602                 17/2/83
8560      2.36  16  1 102  1                     2 7602                 18.3.83
8570     -0.05  16  1 103  1                     2 7602                 18.3.83
8580      0.60  16  1 105  1                     2                       V4   759
8590      2.00  16  1 107  1                     2                       V4   760
8600      3.50  16  1 107  2                     2                       V4   761
8610      4.50  16  1 107  3                     2                       V4   762
8620      5.20  16  1 107  4                     2                       V4   763
8630      5.30  16  1 107  5                     2                       V4   764
8640      6.50  16  1 107  6                     2                       V4   765
8650     16.00  16  1 111  1   50   1            2                       V4   766
8660      9.60  16  1 111  1                     2                       V4   767
8670      2.00  16  1 113  1                     2                       V4   768
8680      1.60  16  1 115  1                     2                       V4   769
8690      2.40  16  1 115  2                     2                       V4   770
8700      5.60  16  1 116  1                     2                       V4   771
8710      9.70  16  1 116  2                     2                       V4   772
8720      6.29  16  1 117  1                     2 7602Z I-corrected      2.9.90
8730     10.42  16  1 117  1   50   1            2 7602Z I-corrected      2.9.90
8731     12.84  16  1 117  1   50   2            2 7602Z I-corrected      2.9.90
8740      4.10  16  1 118  1                     2                       V4   775
8750      6.60  16  1 118  2                     2                       V4   776
8760      5.70  16  1 118  1   50   1            2                       V4   777
8770     10.90  16  1 118  2   50   2            2                       V4   778
8780      7.90  16  1 119  1                     2                       V4   779
8790     12.70  16  1 119  2                     2                       V4   780
8800      3.20  16  1 120  1                     2                       V4   781
8810      5.80  16  1 121  1                     2                       V4   782
8820     10.60  16  1 121  2                     2                       V4   783
8830     13.70  16  1 121  3                     2                       V4   784
8840      5.60  16  1 122  1                     2                       V4   785
8850     11.10  16  1 122  2                     2                       V4   786
8860     16.00  16  1 122  3                     2                       V4   787
8870      7.90  16  1 123  1                     2                       V4   788
8880     10.60  16  1 123  2                     2                       V4   789
8890      5.10  16  1 124  1                     2                       V4   790
8900      9.20  16  1 124  2                     2                       V4   791
8910     11.70  16  1 124  3                     2                       V4   792
8920      6.20  16  1 125  1                     2                       V4   793
8930      9.70  16  1 125  2                     2                       V4   794
8940      6.20  16  1 126  1                     2                       V4   795
8950     11.20  16  1 126  2                     2                       V4   796
8960     14.90  16  1 126  3                     2                       V4   797
8970     12.40  16  1 127  1                     2                       V4   798
8980     18.10  16  1 128  1                     2                       V4   799
8990     21.60  16  1 128  1   50   1            2                       V4   800
9000     21.30  16  1 129  1                     2                       V4   801
9010     24.80  16  1 129  1   50   1            2                       V4   802
9020     10.20  16  1 130  1                     2                       V4   803
9030     17.50  16  1 130  2                     2                       V4   804
9040     13.60  16  1 131  1                     2                       V4   805
9050     20.30  16  1 131  1   50   1            2                       V4   806
9060     26.00  16  1 131  1   50   2            2                       V4   807
9070      5.20  16  1 132  2                     2                       V4   808
9080      4.30  16  1 133  1                     2                       V4   809
9090      7.70  16  1 133  2                     2                       V4   810
9100      4.60  16  1 134  1                     2                       V4   811
9110      7.70  16  1 134  2                     2                       V4   812
9120      7.60  16  1 135  2                     2                       V4   813
9130      7.40  16  1 136  1                     2                       V4   814
9140     13.20  16  1 136  2                     2                       V4   815
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9150	6.40	16	1	137	1				2			V4 816
9160	11.00	16	1	137	2				2			V4 817
9170	8.90	16	1	138	2				2			V4 818
9180	4.80	16	1	139	1				2			V4 819
9190	8.50	16	1	139	2				2			V4 820
9200	10.40	16	1	139	3				2			V4 821
9210	9.20	16	1	140	2				2			V4 822
9220	8.70	16	1	141	2				2			V4 823
9230	8.70	16	1	144	2				2			V4 824
9240	5.10	16	1	145	1				2			V4 825
9250	8.90	16	1	145	2				2			V4 826
9260	5.10	16	1	146	1				2			V4 827
9270	8.90	16	1	146	2				2			V4 828
9280	10.10	16	1	147	2				2			V4 829
9290	1.60	16	1	150	1				2			V4 830
9295	0.20	16	1	157	1				2	7602		18.3.83
9300	-9.70	16	1	50	-1			1.0	2	7602		18.3.83
9310	-19.60	16	1	50	-2			2.0	2	7602		18.3.83
9320	-32.30	16	1	50	-3			3.0	2	7602		18.3.83
9321	-45.80	16	1	50	-4			4.0	2	7602		18.3.83
9323	-11.30	16	2	50	-1			1.0	2	7602*		18.3.83
9325	-30.40	16	4	50	-4			4.0	2	7602*		18.3.83
9330	5.20	17	1	104	1				2			V4 834
9340	9.10	17	1	104	2				2			V4 835
9350	12.00	17	1	104	3				2			V4 836
9360	7.10	17	1	107	1				2			V4 837
9370	13.90	17	1	107	2				2			V4 838
9380	19.90	17	1	107	3				2			V4 839
9390	25.50	17	1	107	4				2			V4 840
9400	30.60	17	1	107	5				2			V4 841
9410	35.00	17	1	107	6				2			V4 842
9420	46.70	17	1	121	3				2			V4 843
9430	39.80	17	1	128	1				2			V4 844
9440	41.20	17	1	128	1	50	1		2			V4 845
9450	1.10	18	1	102	1				2			V4 846
9460	3.10	18	1	103	1				2			V4 847
9470	4.90	18	1	103	2				2			V4 848
9480	4.90	18	1	103	3				2			V4 849
9490	5.10	18	1	103	4				2			V4 850
9500	4.30	18	1	105	1				2			V4 851
9510	7.30	18	1	105	2				2			V4 852
9520	7.70	18	1	105	3				2			V4 853
9530	8.10	18	1	105	4				2			V4 854
9540	6.58	18	1	106	1				2	7602E		V4 855
9550	11.70	18	1	106	2				2	7602E		V4 856
9551	13.10	18	1	106	3				2	7602E		240982
9552	14.20	18	1	106	4				2	7602C		240982
9560	3.20	18	1	107	1				2			V4 857
9570	7.20	18	1	107	2				2			V4 858
9580	0.1	18	1	108	1				2		SULPH	21.3.91
9590	-8.8	18	1	108	2				2		SULPH	21.3.91
9600	3.4	18	1	108	1	50	-1		2		SULPH	21.3.91
9610	8.80	18	1	113	1				2			V4 862
9620	13.60	18	1	113	2				2			V4 863
9630	22.00	18	1	114	3				2			V4 864
9640	21.30	18	1	114	2				2			V4 865
9650	0.60	18	1	115	1				2			V4 866
9670	2.60	18	1	118	1				2			V4 868
9680	4.50	18	1	121	1				2			V4 869
9690	7.50	18	1	121	2				2			V4 870
9700	6.60	18	1	122	2				2			V4 871
9710	3.90	18	1	124	1				2			V4 872
9720	7.30	18	1	124	2				2			V4 873
9730	3.60	18	1	126	1				2			V4 874
9740	6.10	18	1	126	2				2			V4 875
9750	8.40	18	1	128	1				2			V4 876
9760	15.30	18	1	128	1	50	1		2			V4 877

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  9770       3.60   18   1 133   1                                2                       V4  878
  9780       7.40   18   1 133   2                                2                       V4  879
  9790       7.60   18   1 136   1                                2                       V4  880
  9800      16.50   18   1 136   2                                2                       V4  881
  9810       2.30   18   1 137   1                                2                       V4  882
  9820       3.80   18   1 139   1                                2                       V4  883
  9830       7.40   18   1 139   2                                2                       V4  884
  9840       5.60   18   1 149   1                                2                       V4  885
  9850       7.90   18   1 149   2                                2                       V4  886
  9860       3.10   18   1 158   1                                2                       V4  887
  9870       6.60   18   1 158   2                                2                       V4  888
  9880     -11.70   18   1  50  -1                            1.0 2                       V4  889
  9890       4.90   19   1 102   1                                2                       V4  890
  9900       5.20   19   1 104   1                                2 7602                  V4  891
  9910       9.10   19   1 104   2                                2                       V4  892
  9920       6.40   19   1 118   1                                2                       V4  893
  9930      12.30   19   1 123   1                                2                       V4  894
  9940      26.80   19   1 128   1                                2                       V4  895
  9950      29.20   19   1 128   1   50   1                       2                       V4  896
  9960      19.00   19   1 128   1   50  -1                   1.0 2                       V4  897
  9970       4.40   19   1 137   1                                2                       V4  898
  9980       2.80   19   1 150   1                                2                       V4  899
  9990       4.50   19   1 150   2                                2                       V4  900
 10000      -3.81   19   1  50  -1                            1.0 2 7401               14.2.84
 10010     -10.00   19   1  50  -2                            2.0 2 7401               14.2.84
 10020     -27.00   19   1  50  -4                            4.0 2 7401               14.2.84
 10030       3.02   20   1 102   1                                2 9001                  1.6.90
 10035      2.448   20   1 102   1   50   1                       2 9001                  1.6.90
 10040       4.92   20   1 102   2                                2 9001                  1.6.90
 10050       7.00   20   1 104   1                                2 9001                  1.6.90
 10060      12.70   20   1 104   2                                2 9001                  1.6.90
 10070      16.80   20   1 104   3                                2 9001                  1.6.90
 10080      19.40   20   1 104   4                                2 9001                  1.6.90
 10090      20.60   20   1 104   5                                2 9001                  1.6.90
 10100      20.60   20   1 104   6                                2 9001                  1.6.90
 10110       8.90   20   1 116   1                                2                       V4  912
 10120      17.10   20   1 116   2                                2                       V4  913
 10130      23.00   20   1 116   3                                2                       V4  914
 10140        9.9   20   1 117   1                                2 HUMM  8903             Alcit
 10141       14.1   20   1 117   2                                2 HUMM  8903          Alcit2-3
 10145       12.9   20   1 117   1   50   1                       2 HUMM  8903           AlHcit+
 10146        6.4   20   1 117   1   50  -1                       2 HUMM  8903         AlH-1cit-
 10169        7.6   20   1 118   1                                2 HUMM  8903             Alox+
 10170       13.1   20   1 118   2                                2 HUMM  8903            Alox2-
 10180       17.2   20   1 118   3                                2 HUMM  8903           Alox3-3
 10190      15.90   20   1 119   1                                2                       V4  920
 10200      15.60   20   1 123   1                                2                       V4  921
 10210      25.60   20   1 123   2                                2                       V4  922
 10220      28.90   20   1 123   3                                2                       V4  923
 10230       13.6   20   1 127   1                                2 HUMM  8903             Alnta
 10240       15.5   20   1 127   1   50   1                       2 HUMM  8903           AlHnta+
 10250        8.3   20   1 127   1   50  -1                   1.0 2 HUMM  8903          AlOHnta-
 10260       19.0   20   1 128   1                                2 HUMM  7403           Aledta-
 10270       21.7   20   1 128   1   50   1                       2 HUMM  7403           AlHedta
 10280       12.8   20   1 128   1   50  -1                   1.0 2 HUMM  7403        AlOHedta-2
 10290      21.30   20   1 129   1                                2                       V4  930
 10300      23.50   20   1 129   1   50   1                       2                       V4  931
 10310      13.50   20   1 129   1   50  -1                   1.0 2                       V4  932
 10320       7.50   20   1 133   1                                2                       V4  933
 10330      14.50   20   1 133   2                                2                       V4  934
 10340     -5.003   20   1  50  -1                            1.0 2 9001                  1.6.90
 10341    -10.109   20   1  50  -2                            2.0 2 9001                  1.6.90
 10342     -16.94   20   1  50  -3                            3.0 2 9001                  1.6.90
 10350    -22.665   20   1  50  -4                            4.0 2 9001                  1.6.90
 10360      -0.10   21   1 103   1                                2                       V4  937
 10370       0.00   21   1 104   1                                2                       V4  938
 10380       2.30   21   1 110   1                                2                       V4  939
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10390     3.10  21  1 111  1                  2                         V4  940
10400     0.96  21  1 117  1                  2 7602Z I-corrected        2.9.90
10410     1.40  21  1 128  1                  2                         V4  942
10420     0.64  22  1 102  1                  2 CORE  (7602)             1.6.90
10430     3.10  22  1 110  1                  2                         V4  944
10440     4.20  22  1 111  1                  2                         V4  945
10450     0.20  22  1 115  1                  2                         V4  946
10455     1.47  22  1 117  1                  2 7602Z I-corrected        2.9.90
10460     4.00  22  1 128  1                  2                         V4  947
10470     5.30  22  1 129  1                  2                         V4  948
10480   -13.64  22  1  50 -1              1.0 2 CORE  (7602)             1.6.90
10490     1.90  23  1 102  1                  2                         V4  950
10500     3.00  23  1 102  2                  2                         V4  951
10510     2.00  23  1 102  3                  2                         V4  952
10520     1.60  23  1 103  1                  2                         V4  953
10530     5.60  23  1 104  1                  2                         V4  954
10540     9.70  23  1 104  2                  2                         V4  955
10550    12.70  23  1 104  3                  2                         V4  956
10560     8.00  23  1 116  1                  2                         V4  957
10570    14.80  23  1 116  2                  2                         V4  958
10580     5.90  23  1 117  1                  2 7602Z I-corrected        2.9.90
10590     9.50  23  1 117  1  50  1           2 7602Z I-corrected        2.9.90
10600    13.0   23  1 117  1  50  2           2 7602Z I-corrected        2.9.90
10610     4.20  23  1 118  1                  2                         V4  962
10620     6.30  23  1 118  2                  2                         V4  963
10630    13.70  23  1 119  1                  2                         V4  964
10640    23.50  23  1 119  2                  2                         V4  965
10650    18.90  23  1 119  1  50  1           2                         V4  966
10660     4.10  23  1 120  1                  2                         V4  967
10670    13.40  23  1 123  1                  2                         V4  968
10680    21.30  23  1 123  2                  2                         V4  969
10690    18.50  23  1 123  1  50  1           2                         V4  970
10700    13.20  23  1 124  2                  2                         V4  971
10710    14.00  23  1 125  2                  2                         V4  972
10720     9.00  23  1 127  1                  2                         V4  973
10730    12.70  23  1 128  1                  2                         V4  974
10740    13.30  23  1 129  1                  2                         V4  975
10750     5.20  23  1 132  1                  2                         V4  976
10760     6.90  23  1 132  2                  2                         V4  977
10770    -6.30  23  1  50 -1              1.0 2                         V4  978
10780     4.50  24  1 102  1                  2                         V4  979
10790     2.00  24  1 103  1                  2                         V4  980
10800     7.10  24  1 104  1                  2                         V4  981
10810    13.00  24  1 104  2                  2                         V4  982
10820    17.40  24  1 104  3                  2                         V4  983
10830     2.10  24  1 105  1                  2                         V4  984
10840     3.20  24  1 105  2                  2                         V4  985
10850     9.20  24  1 116  1                  2                         V4  986
10860    18.20  24  1 118  3                  2                         V4  987
10870    15.00  24  1 120  2                  2                         V4  988
10880     4.80  24  1 123  1                  2                         V4  989
10890    26.90  24  1 128  1                  2                         V4  990
10900    16.10  24  1 128  1  50 -1       1.0 2                         V4  991
10910    29.20  24  1 129  1                  2                         V4  992
10920    -3.80  24  1  50 -1              1.0 2                         V4  993
10930    -8.00  24  1  50 -2              2.0 2                         V4  994
10940   -11.10  24  1  50 -3              3.0 2                         V4  995
10950    10.30  25  1 118  1                  2                         V4  996
10960    15.70  25  1 118  2                  2                         V4  997
10970    10.90  25  1 120  1                  2                         V4  998
10980    14.20  25  1 127  1                  2                         V4  999
10990    20.00  25  1 128  1                  2                         V4 1000
11000    22.40  25  1 129  1                  2                         V4 1001
11001    -2.3   25  1  50 -1              2.0 2 7601                     2.9.90
11002    -4.8   25  1  50 -2              3.0 2 7601                     2.9.90
11005     0.62  26  1 103  1                  2 SUPPL 9102               SnCl+
11006     1.43  26  1 103  2                  2 SUPPL 9102               SnCl2
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11007     0.88  26  1 103   3                  2 SUPPL 9102              SnCl3-
11010     6.90  26  1 104   1                  2                      V4 1002
11020     9.70  26  1 104   2                  2                      V4 1003
11030    10.20  26  1 104   3                  2                      V4 1004
11040     1.10  26  1 105   1                  2                      V4 1005
11050     1.70  26  1 105   2                  2                      V4 1006
11060     1.40  26  1 105   3                  2                      V4 1007
11070    14.10  26  1 110   1                  2                      V4 1008
11075    12.9   26  1 118   2                  2 HUMM  7904           Snox2-2
11080     6.40  26  1 120   1                  2                      V4 1009
11090    11.10  26  1 120   2                  2                      V4 1010
11095    20.4   26  1 128   1                  2 HUMM  7403           Snedta-2
11096    23.4   26  1 128   1   50 1           2 HUMM  7403           SnHedta-
11101    -1.55  26  1   50 -1              1.0 2 SUPPL 9102              SnOH+
11102    -7.06  26  1   50 -2              2.0 2 SUPPL 9102             Sn(OH)2
11103   -16.61  26  1   50 -3              3.0 2 SUPPL 9102            Sn(OH)3-
11104    -4.77  26  2   50 -2              2.0 2 SUPPL 9102          Sn2(OH)2+2
11105    -6.88  26  3   50 -4              4.0 2 SUPPL 9102          Sn3(OH)4+2
11106   -16.05  26  1   50 -3              2.0 2 SUPPL 9102   ??         SnOOH-
11110    -9.25  27  1   50 -5              5.0 2 SUPPL 9102            Sn(OH)5-
11111   -21.26  27  1   50 -6              6.0 2 SUPPL 9102           Sn(OH)6-2
11112   -23.45  27  1   50 -6              3.0 2 SUPPL 9102   ??         SnO3-2
11115     8.2   28  1 101   1                  2 8207Y I-corrected   26.10.90
11116    13.6   28  1 101   2                  2 8207Y I-corrected   26.10.90
11120     3.64  28  1 102   1                  2 7602                17/2/83
11121     5.29  28  1 102   2                  2 7602                17/2/83
11130     0.80  28  1 103   1                  2 8300*               17/2/83
11131     1.00  28  1 103   2                  2 8300*               17/2/83
11140     3.60  28  1 104   1                  2                      V4 1015
11150    17.70  28  1 110   1                  2                      V4 1016
11160    19.10  28  1 110   2                  2                      V4 1017
11170    17.30  28  1 111   2                  2                      V4 1018
11180    17.80  28  1 111   1   50   1         2                      V4 1019
11190    29.60  28  1 111   2   50   2         2                      V4 1020
11200     3.50  28  1 113   1                  2                      V4 1021
11210     2.90  28  1 115   1                  2                      V4 1022
11220     4.80  28  1 115   2                  2                      V4 1023
11230     5.50  28  1 116   1                  2                      V4 1024
11240     9.50  28  1 116   2                  2                      V4 1025
11250    12.70  28  1 116   3                  2                      V4 1026
11260     9.18  28  1 117   1                  2 7602                  2.9.90
11270    12.10  28  1 117   2                  2 7602Z I-corrected     2.9.90
11271    17.70  28  1 117   2   50   1         2 7602Z I-corrected     2.9.90
11290     5.20  28  1 118   1                  2                      V4 1030
11300     9.40  28  1 118   2                  2                      V4 1031
11310    12.20  28  1 118   3                  2                      V4 1032
11320     4.60  28  1 119   1                  2                      V4 1033
11330    17.60  28  1 119   1   50   1         2                      V4 1034
11340     4.10  28  1 124   1                  2                      V4 1035
11350     7.70  28  1 124   2                  2                      V4 1036
11360     4.10  28  1 126   1                  2                      V4 1037
11370     7.50  28  1 126   2                  2                      V4 1038
11380     9.80  28  1 126   3                  2                      V4 1039
11390    13.20  28  1 127   1                  2                      V4 1040
11400    20.90  28  1 127   2                  2                      V4 1041
11410    19.20  28  1 128   1                  2                      V4 1042
11420    21.40  28  1 128   1   50   1         2                      V4 1043
11430    20.10  28  1 129   1                  2                      V4 1044
11440    22.90  28  1 129   1   50   1         2                      V4 1045
11450     6.00  28  1 132   1                  2                      V4 1046
11460     9.80  28  1 132   2                  2                      V4 1047
11465     1.20  28  1 157   1                  2 7602B               17/2/83
11467   -36.9   28  1   50 -4              4.0 2 7804                26.10.90
11468   -25.9   28  1   50 -3              3.0 2 7804                26.10.90
11469   -17.2   28  1   50 -2              2.0 2 7804                26.10.90
11470    -8.50  28  1   50 -1              1.0 2 7804                26.10.90
11471   -71.20  28  5   50 -9              9.0 2 7602 CHECK CONSIST. 17/2/83
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11478     8.2    29  1 101  1                      2 8207Y I-corrected   26.10.90
11479    13.6    29  1 101  2                      2 8207Y I-corrected   26.10.90
11480     3.59   29  1 102  1                      2 7602                26.10.90
11481     5.2    29  1 102  2                      2 7602                26.10.90
11490     0.80   29  1 103  1                      2                      V4 1050
11500     4.10   29  1 104  1                      2                      V4 1051
11510     7.50   29  1 104  2                      2                      V4 1052
11520     0.70   29  1 105  1                      2                      V4 1053
11530    19.30   29  1 109  1                      2                      V4 1054
11540    18.20   29  1 110  1                      2                      V4 1055
11550     3.00   29  1 115  1                      2                      V4 1056
11560     5.00   29  1 115  2                      2                      V4 1057
11570     5.70   29  1 116  1                      2                      V4 1058
11580     9.90   29  1 116  2                      2                      V4 1059
11590    13.40   29  1 116  3                      2                      V4 1060
11600     9.32   29  1 117  1                      2 7602Z I-corrected     2.9.90
11610    12.30   29  1 117  2                      2 7602Z I-corrected     2.9.90
11611    18.10   29  1 117  2  50  1               2 7602Z I-corrected     2.9.90
11630     6.80   29  1 118  1                      2                      V4 1064
11640    10.70   29  1 118  2                      2                      V4 1065
11650    11.60   29  1 118  3                      2                      V4 1066
11660     4.60   29  1 119  1                      2                      V4 1067
11670    17.70   29  1 119  1  50  1               2                      V4 1068
11680     9.60   29  1 123  1                      2                      V4 1069
11690    15.20   29  1 123  2                      2                      V4 1070
11700    16.20   29  1 123  1  50  1               2                      V4 1071
11710     4.30   29  1 124  1                      2                      V4 1072
11720     7.90   29  1 124  2                      2                      V4 1073
11730     4.60   29  1 126  1                      2                      V4 1074
11740     8.10   29  1 126  2                      2                      V4 1075
11750    11.40   29  1 126  3                      2                      V4 1076
11760    13.50   29  1 127  1                      2                      V4 1077
11770    21.40   29  1 127  2                      2                      V4 1078
11780    20.10   29  1 128  1                      2                      V4 1079
11790    20.60   29  1 129  1                      2                      V4 1080
11800     5.90   29  1 132  1                      2                      V4 1081
11810     9.60   29  1 132  2                      2                      V4 1082
11820     8.50   29  1 149  1                      2                      V4 1083
11830     1.50   29  1 150  1                      2                      V4 1084
11837   -38.0    29  1  50 -4                  4.0 2 7804                26.10.90
11838   -26.0    29  1  50 -3                  3.0 2 7804                26.10.90
11839   -16.3    29  1  50 -2                  2.0 2 7804                26.10.90
11840    -8.1    29  1  50 -1                  1.0 2 7804                26.10.90
11841   -32.8    29  3  50 -5                  5.0 2 7804                26.10.90
11850    26.90   30  1 107  2                      2                      V4 1086
11860    38.20   30  1 114  2                      2                      V4 1087
12500    24.20   33  1 114  2                      2                      V4 1088
12510    28.90   33  1 114  3                      2                      V4 1089
12520    30.10   33  1 114  4                      2                      V4 1090
12530    10.329  50  1 101  1                      2 CORE                  1.6.90
12540    16.681  50  2 101  1                      2 CORE                  1.6.90
12550     1.988  50  1 102  1                      2 CORE                  1.6.90
12560     3.176  50  1 104  1                      2 CORE  (9001)          1.6.90
12561     3.62   50  1 104  2                      2 CORE  (NEA)          21.3.91
12570     9.24   50  1 107  1                      2 CORE  (7602)          1.6.90
12580   -19.0    50 -1 108  1                      2 STAND  SULPH. (NEA)  21.3.91
12590     6.99   50  1 108  1                      2 CORE   SULPH. (NEA)  21.3.91
12600    12.35   50  1 109  1                      2 CORE  (NEA)           1.6.90
12610    19.56   50  2 109  1                      2 CORE  (NEA)           1.6.90
12620    21.70   50  3 109  1                      2 CORE  (NEA)           1.6.90
12630     9.40   50  1 110  1                      2 CORE  (NEA)           1.6.90
12640    16.10   50  2 110  1                      2 CORE  (NEA)           1.6.90
12650    18.35   50  3 110  1                      2 CORE  (NEA)           2.9.90
12660    19.35   50  4 110  1                      2 CORE  (NEA)           2.9.90
12670     9.25   50  1 111  1                      2 7602                 V4 1105
12680    18.80   50  2 111  1                      2 7602                 V4 1106
12690    21.30   50  3 111  1                      2 7602                 V4 1107
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12700     22.80  50  4 111  1                      2                               V4 1108
12710     13.33  50  1 112  1                      2 CORE   (NEA ) (7602)           1.6.90
12712     27.28  50  2 112  2                      2 STAND  (NEA )                  2.9.90
12713     38.18  50  3 112  2                      2 STAND  (NEA )                  2.9.90
12715     40.82  50  3 112  3                      2 STAND  (NEA ) CYCL.            2.9.90
12716     39.42  50  3 112  3                      2 STAND  (9005) LIN.             2.9.90
12718     54.56  50  4 112  4                      2 STAND  (9005)                  2.9.90
12719     67.06  50  5 112  4                      2 STAND  (NEA )                  2.9.90
12720     23.14  50  2 112  1                      2 CORE   (NEA)  (7602)           1.6.90
12725     53.32  50  6 112  1 104   6         -4.0 2 STAND                          1.6.90
12726     14.93  50  1 112  1   5   1              2 STAND  (9005)                  2.9.90
12730      1.59  50  1 113  1                      2 NEA                            2.9.90
12731      2.20  50  2 113  1                      2 7602                          V4 1114
12740      9.21  50  1 114  1                      2 7602                          V4 1115
12750      4.70  50  1 115  1                      2                               V4 1116
12760      8.90  50  1 116  1                      2                               V4 1117
12770     6.396  50  1 117  1                      2 HUMM   8903                   Hcit-2
12780    11.157  50  2 117  1                      2 HUMM   8903                   H2cit-
12790    14.285  50  3 117  1                      2 HUMM   8903                    H3cit
12810     4.266  50  1 118  1                      2 HUMM   8903                     Hox-
12820     5.518  50  2 118  1                      2 HUMM   8903                     H2ox
12830     14.00  50  1 119  1                      2                               V4 1124
12840     17.00  50  2 119  1                      2                               V4 1125
12850      4.50  50  1 120  1                      2                               V4 1126
12860      7.70  50  2 120  1                      2                               V4 1127
12870      9.70  50  1 121  1                      2                               V4 1128
12880     16.50  50  2 121  1                      2                               V4 1129
12890     12.30  50  1 123  1                      2                               V4 1130
12900     15.50  50  2 123  1                      2                               V4 1131
12910      9.90  50  1 124  1                      2                               V4 1132
12920     12.20  50  2 124  1                      2                               V4 1133
12930     10.00  50  1 125  1                      2                               V4 1134
12940     14.30  50  2 125  1                      2                               V4 1135
12950     16.70  50  3 125  1                      2                               V4 1136
12960      5.50  50  1 126  1                      2                               V4 1137
12970      7.10  50  2 126  1                      2                               V4 1138
12980    10.334  50  1 127  1                      2 HUMM   8903                   Hnta-2
12990    13.274  50  2 127  1                      2 HUMM   8903                   H2nta-
13000    14.924  50  3 127  1                      2 HUMM   8903                    H3nta
13001      15.9  50  4 127  1                      2 HUMM   8903                   H4nta+
13010    11.014  50  1 128  1                      2 HUMM   8903                  Hedta-3
13020    17.334  50  2 128  1                      2 HUMM   8903                 H2edta-2
13030     20.44  50  3 128  1                      2 HUMM   8903                  H3edta-
13040      22.6  50  4 128  1                      2 HUMM   8903                   H4edta
13041      24.1  50  5 128  1                      2 HUMM   8903                  H5edta+
13042      23.9  50  6 128  1                      2 HUMM   8903                 H6edta+2
13050     11.80  50  1 129  1                      2                               V4 1146
13060     18.80  50  2 129  1                      2                               V4 1147
13070     11.00  50  1 130  1                      2                               V4 1148
13080     19.50  50  2 130  1                      2                               V4 1149
13090     21.50  50  3 130  1                      2                               V4 1150
13100     10.60  50  1 131  1                      2                               V4 1151
13110     20.60  50  2 131  1                      2                               V4 1152
13120     29.40  50  3 131  1                      2                               V4 1153
13130      5.50  50  1 132  1                      2                               V4 1154
13140      8.50  50  2 132  1                      2                               V4 1155
13150      9.30  50  1 133  1                      2                               V4 1156
13160     11.40  50  2 133  1                      2                               V4 1157
13170     10.80  50  1 134  1                      2                               V4 1158
13180     19.60  50  2 134  1                      2                               V4 1159
13190     21.20  50  3 134  1                      2                               V4 1160
13200     10.80  50  1 135  1                      2                               V4 1161
13210     19.90  50  2 135  1                      2                               V4 1162
13220     21.70  50  3 135  1                      2                               V4 1163
13230      9.30  50  1 136  1                      2                               V4 1164
13240     15.30  50  2 136  1                      2                               V4 1165
13250     16.70  50  3 136  1                      2                               V4 1166
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13260      9.70   50   1 137  1                      2                    V4 1167
13270     13.60   50   2 137  1                      2                    V4 1168
13280     14.90   50   3 137  1                      2                    V4 1169
13290      9.20   50   1 138  1                      2                    V4 1170
13300     11.40   50   2 138  1                      2                    V4 1171
13310      9.90   50   1 139  1                      2                    V4 1172
13320     12.30   50   2 139  1                      2                    V4 1173
13330      9.60   50   1 140  1                      2                    V4 1174
13340      2.80   50   2 140  1                      2                    V4 1175
13350      9.20   50   1 141  1                      2                    V4 1176
13360     11.40   50   2 141  1                      2                    V4 1177
13370      9.70   50   1 142  1                      2                    V4 1178
13380     12.10   50   2 142  1                      2                    V4 1179
13390      9.00   50   1 143  1                      2                    V4 1180
13400     11.10   50   2 143  1                      2                    V4 1181
13410      9.30   50   1 144  1                      2                    V4 1182
13420     11.40   50   2 144  1                      2                    V4 1183
13430      9.70   50   1 145  1                      2                    V4 1184
13440     12.10   50   2 145  1                      2                    V4 1185
13450      9.70   50   1 146  1                      2                    V4 1186
13460     12.10   50   2 146  1                      2                    V4 1187
13470     10.80   50   1 147  1                      2                    V4 1188
13480     12.60   50   2 147  1                      2                    V4 1189
13490     9.235   50   1 148  1                 -1.0 2 CORE              21.3.91
13500      7.22   50   1 149  1                      2 NEA                2.9.90
13501      9.06   50   2 149  1                      2 NEA                2.9.90
13510      6.00   50   1 151  1                      2                    V4 1192
13520      4.30   50   1 152  1                      2                    V4 1193
13530      3.70   50   1 153  1                      2                    V4 1194
13540    11.596   50   1 154  1                      2 CORE    (7602)    21.3.91
13550     18.35   50   2 154  1                      2 CORE    (7602)    21.3.91
13555     20.60   50   3 154  1                      2 CORE    (7602)    21.3.91
13560      8.10   50   1 155  1                      2 7802               V4 1197
13561     11.90   50   2 155  1                      2 7802                   .84
13562     15.10   50   3 155  1                      2 7802                   .84
13570      8.40   50   1 156  1                      2 NEA                2.9.90
13571     11.20   50   2 156  1                      2 NEA                2.9.90
13575      8.10   50   1 158  1                      2                    V4 1200
13576      7.42   50   1 170  1                      2 NEA                2.9.90
13577      1.96   50   1 171  1                      2 NEA                2.9.90
13578      8.63   50   1 173  1                      2 NEA                2.9.90
13579      0.79   50   1 175  1                      2 NEA                2.9.90
13580      3.82   50   1 177  1                      2 SUPPL 8208           H2Se
13581      1.91   50   1 178  1                      2 SUPPL 8208         HSeO4-
13582      4.70   50   1 180  1                      2 NEA                2.9.90
13583      3.21   50   1 181  1                      2 NEA                2.9.90
13592     9.233   50   1 160  1                  1.0 2 CORE    (7602)    21.3.91
13594    -14.94  177   1  50 -1                      2 SUPPL 8208           Se-2
13595    -14.00   50  -1                         1.0 2 CORE                1.6.90
13600   -135.20   19   2  50-14  99 -6           7.0 2                    V4 1202
13610    -68.40   19   1  50 -7  99 -3           4.0 2                    V4 1203
13620    -74.90   19   1  50 -8  99 -3           4.0 2                    V4 1204
13630     30.70   14   2  99  2                      2                    V4 1205
13640    -20.95  106   2  99 -2                      2 SUPPL                  I2
13641    -18.08  106   3  99 -2                      2 SUPPL                  I3-
16101      6.9   161   1  50  2                  1.0 2 SUPPL  8208      Nb(OH)4+
16102      7.34  161   1  50  1                  2.0 2 SUPPL  8208      Nb(OH)5
16301      8.7   163   1  50  1                      2 SUPPL  9102     HTc(VI)O4-
16302      9.3   163   1  50  2                      2 SUPPL  9102     H2Tc(VI)O4
31001     -3.20   31   1  50 -1                  1.0 2 8002 7602 7801     V4 1206
31002     -6.95   31   1  50 -2                  2.0 2 8002 7602 7801     V4 1207
31003    -11.70   31   1  50 -3                  3.0 2 8002U7801*         V4 1208
31004    -15.90   31   1  50 -4                  4.0 2 8002 7801          V4 1209
31005     -6.10   31   2  50 -2                  2.0 2 8002*7602*         V4 1210
31006    -21.10   31   4  50 -8                  8.0 2 8002*7602*         V4 1211
31007    -36.70   31   6  50-15                 15.0 2 8002*7602*         V4 1212
31008      8.00   31   1 104  1                      2 8002               V4 1213
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31009    14.20  31  1 104  2                  2 8002                V4 1214
31010    18.90  31  1 104  3                  2 8002                V4 1215
31011    22.30  31  1 104  4                  2 8002                V4 1216
31012     1.10  31  1 103  1                  2 8002                V4 1217
31013     0.80  31  1 103  2                  2 8002                V4 1218
31014     1.65  31  1 103  3                  2 8002                V4 1219
31015     1.26  31  1 103  4                  2 8002                V4 1220
31016     5.45  31  1 102  1                  2 8002                V4 1221
31017     9.75  31  1 102  2                  2 8002                V4 1222
31018    10.50  31  1 102  3                  2 8002                V4 1223
31019     8.50  31  1 102  4                  2 8002                V4 1224
31020    25.55  31  1 109  1  50  1           2 8002A  DEP.           1.6.90
31021    51.10  31  1 109  2  50  2           2 8002A  DEP.           1.6.90
31022    72.00  31  1 109  3  50  3           2 8002A  DEP.           1.6.90
31023    24.10  31  1 109  1  50  2           2 8002   DEP.           1.6.90
31024    48.02  31  1 109  2  50  4           2 8002   DEP.           1.6.90
31025    23.60  31  1 109  1  50  3           2 8002   DEP.           1.6.90
31026     0.94  31  1 157  1                  2                     V4 1231
31027     1.97  31  1 157  2                  2                     V4 1232
31031     6.80  31  1 119  1                  2                     V4 1236
31032    11.41  31  1 119  2                  2                     V4 1237
31033    13.90  31  1 119  3                  2                     V4 1238
31034    14.10  31  1 119  4                  2                     V4 1239
31035     9.50  31  1 116  1                  2                     V4 1240
31036    17.50  31  1 116  2                  2                     V4 1241
31037    24.00  31  1 116  3                  2                     V4 1242
31038    28.20  31  1 116  4                  2                     V4 1243
31043    28.30  31  1 129  1                  2                     V4 1248
31047    11.00  31  1 101  1                  2 8201*               19.01.83
31400     28.7  31  1 128  1                  2 HUMM  6701            Thedta
31410     30.7  31  1 128  1  50  1           2 HUMM  8209          ThHedta+
31415     21.5  31  1 128  1  50 -1       1.0 2 HUMM  8209         ThOHedta-
31416     47.0  31  2 128  2  50 -2       2.0 2 HUMM  8209     (ThOHedta)2-2
31421     19.4  31  1 127  1                  2 HUMM  8903             Thnta+
31425     10.8  31  1 127  1  50 -1       1.0 2 HUMM  8903            ThOHnta
31431     15.0  31  1 117  1                  2 HUMM  7502             Thcit+
31432     24.4  31  1 117  2                  2 HUMM  7502          Thcit2-2
31441     10.6  31  1 118  1                  2 HUMM  7705            Thox+2
31442     20.2  31  1 118  2                  2 HUMM  7705             Thox2
31443     26.4  31  1 118  3                  2 HUMM  7705           Thox3-2
31445     12.3  31  1 118  1  50  1           2 HUMM  7705           ThHox+3
32001    -5.21  32  1  50 -1              1.0 2 NEA           (32001) 20.7.90
32002   -10.32  32  1  50 -2              2.0 2 NEA           (32006) 20.7.90
32003   -19.21  32  1  50 -3              3.0 2 NEA           (32007) 20.7.90
32004   -33.01  32  1  50 -4              4.0 2 NEA           (32008) 20.7.90
32007    -2.72  32  2  50 -1              1.0 2 NEA           (32002) 20.7.90
32008    -5.64  32  2  50 -2              2.0 2 NEA           (32003) 20.7.90
32014   -11.93  32  3  50 -4              4.0 2 NEA           (32004) 20.7.90
32015   -15.58  32  3  50 -5              5.0 2 NEA           (32005) 20.7.90
32017   -31.03  32  3  50 -7              7.0 2 NEA           (32056) 20.7.90
32023   -21.90  32  4  50 -7              7.0 2 NEA           (NEW  ) 20.7.90
32030     9.62  32  1 101  1                  2 NEA           (32036) 20.7.90
32031    16.99  32  1 101  2                  2 NEA           (32026) 20.7.90
32032    21.62  32  1 101  3                  2 NEA           (32027) 20.7.90
32037    -0.88  32  2 101  1  50 -3       3.0 2 NEA           (NEW  ) 20.7.90
32040     0.76  32  3 101  1  50 -3       4.0 2 NEA           (NEW  ) 20.7.90
32045    53.98  32  3 101  6                  2 NEA           (NEW  ) 20.7.90
32050    36.32  32 11 101  6  50-12      12.0 2 NEA           (NEW  ) 20.7.90
32060     3.14  32  1 102  1                  2 NEA           (32012) 20.7.90
32061     4.14  32  1 102  2                  2 NEA           (32013) 20.7.90
32090     0.07  32  1 103  1                  2 NEA           (32016) 20.7.90
32091    -1.10  32  1 103  2                  2 NEA           (NEW  ) 20.7.90
32120     5.09  32  1 104  1                  2 NEA           (32017) 20.7.90
32121     8.62  32  1 104  2                  2 NEA           (32018) 20.7.90
32122    10.90  32  1 104  3                  2 NEA           (32019) 20.7.90
32123    11.71  32  1 104  4                  2 NEA           (32020) 20.7.90
32130     0.20  32  1 105  1                  2 NEA           (32021) 20.7.90
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32180     13.69  32  1 109  1            2 NEA              (NEW  ) 20.7.90
32181     20.07  32  1 109  1  50  1     2 NEA              (32037) 20.7.90
32182     22.83  32  1 109  1  50  2     2 NEA              (32039) 20.7.90
32183     22.48  32  1 109  1  50  3     2 NEA              (NEW  ) 20.7.90
32192     44.30  32  1 109  2  50  4     2 NEA              (32040) 20.7.90
32193     45.12  32  1 109  2  50  5     2 NEA              (NEW  ) 20.7.90
32220      2.00  32  1 175  1            2 NEA              (NEW  )  2.9.90
32221      3.59  32  1 175  2            2 NEA              (NEW  )  2.9.90
32225      2.80  32  1 113  1            2 NEA              (NEW  )  2.9.90
32230      2.58  32  1 180  1            2 NEA              (NEW  )  2.9.90
32231      4.33  32  1 180  2            2 NEA              (NEW  )  2.9.90
32232      5.74  32  1 180  3            2 NEA              (NEW  )  2.9.90
32233      4.92  32  1 180  4            2 NEA              (NEW  )  2.9.90
32250      6.59  32  1 149  1            2 NEA              (NEW  ) 20.7.90
32260      0.29  32  1 157  1            2 NEA              (32025) 20.7.90
32270      1.39  32  1 150  1            2 NEA              (NEW  ) 20.7.90
32271      1.23  32  1 150  2            2 NEA              (NEW  ) 20.7.90
32272      2.09  32  1 150  3            2 NEA              (NEW  ) 20.7.90
32400     13.1   32  1 128  1            2 HUMM  8202        U(VI)O2edta-2
32405     19.2   32  1 128  1  50  1     2 HUMM  8202        U(VI)O2Hedta-
32410     20.3   32  2 128  1            2 HUMM  8202       (U(VI)O2)2edta
32416     13.9   32  2 128  1  50 -1 1.0 2 HUMM  8202    (U(VI)O2)2OHedta-
32417      8.7   32  2 128  1  50 -2 2.0 2 HUMM  8202  (U(VI)O2OH)2edta-2
32421     10.8   32  1 127  1            2 HUMM  7403           U(VI)O2nta-
32431      8.7   32  1 117  1            2 HUMM  7705           U(VI)O2cit-
32436     21.18  32  2 117  2            2 HUMM  7705       (U(VI)O2cit)2-2
32441      7.0   32  1 118  1            2 HUMM  9006              U(VI)O2ox
32442     11.2   32  1 118  2            2 HUMM  8903           U(VI)O2ox2-2
34001     -8.00  34  1  50 -1        1.0 2 7804                     26.10.90
34002    -16.3   34  1  50 -2        2.0 2 7804                     26.10.90
34003    -24.5   34  1  50 -3        3.0 2 7804                     26.10.90
34004    -36.0   34  1  50 -4        4.0 2 7804                     26.10.90
34005    -13.90  34  2  50 -2        2.0 2 7804 7601 7602           26.10.90
34007      3.64  34  1 102  1            2 7602                     26.10.90
34008      5.1   34  1 102  2            2 7602                     26.10.90
34009      4.00  34  1 104  1            2 7602B                     V4 1286
34010      1.20  34  1 157  1            2 7602B                     V4 1287
34015      8.2   34  1 101  1            2 8207Y I-corrected        26.10.90
34016     13.6   34  1 101  2            2 8207Y I-corrected        26.10.90
35001     -5.60  35  1  50 -1        1.0 2 8004 7602 7701 7801     2/11/83
35002    -11.00  35  1  50 -2        2.0 2 7801*8001                 V4 1289
35003    -20.70  35  1  50 -3        3.0 2 7801*8001                 V4 1290
35005     -4.30  35  2  50 -1        1.0 2 7701                      V4 1291
35006     -8.30  35  2  50 -2        2.0 2 8004 7602 7701 7801B      V4 1292
35007    -21.70  35  3  50 -5        5.0 2 8004 7602 7701 8001       V4 1293
35008     13.20  35  1 101  1            2 7801B                     V4 1294
35009     14.90  35  1 101  2            2 8004 7801                 V4 1295
35011     20.90  35  1 101  3            2 7801B                     V4 1296
35012      9.85  35  1 101  1  50 -1 1.0 2 7801*                     V4 1297
35013     -5.00  35  1 101  1  50 -2 2.0 2 7801*                     V4 1298
35014      0.20  35  1 103  1            2 8004 7602C7801C           V4 1299
35015     -0.25  35  1 103  2            2 7602C7801C                V4 1300
35016     23.51  35  1 109  1  50  2     2 8004  DEP.                 1.6.90
35017      5.70  35  1 104  1            2 8004 7301B                V4 1302
35018     11.00  35  1 104  2            2 8004 7301B                V4 1303
35019     15.80  35  1 104  3            2 8004 7301B                V4 1304
35020     18.70  35  1 104  4            2 8004 7301B                V4 1305
35023      3.00  35  1 102  1            2 8004                      V4 1307
35400     17.71  35  1 128  1            2 HUMM  9102       Pu(VI)O2edta-2
35421     11.    35  1 127  1            2 HUMM  estim.      Pu(VI)O2nta-
35431     10.6   35  1 117  1            2 HUMM  7502        Pu(VI)O2cit-
35432     15.5   35  1 117  2            2 HUMM  7502       Pu(VI)O2cit2-4
35441      7.    35  1 118  1            2 HUMM  estim.         Pu(VI)O2ox
35442     10.5   35  1 118  2            2 HUMM  7705        Pu(VI)O2ox2-2
36001     -9.70  36  1  50 -1        1.0 2 8004 7601 8001 7701       V4 1308
36003      0.17  36  1 103  1            2 7801 8001                 V4 1309
36400     10.9   36  1 128  1            2 HUMM  7101        Pu(V)O2edta-3
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36405    16.44  36  1 128  1  50  1            2 HUMM  7403        Pu(V)O2Hedta-2
36421     7.54  36  1 127  1                   2 HUMM  7004         Pu(V)O2nta-2
36431     5.5   36  1 117  1                   2 HUMM  estim.       Pu(V)O2cit-2
36441     4.30  36  1 118  1                   2 HUMM  7904           Pu(V)O2ox-
36442     6.70  36  1 118  2                   2 HUMM  7904         Pu(V)O2ox2-3
36445     6.80  36  1 118  1  50  1            2 HUMM  7904          Pu(V)O2Hox
37001    -0.70  37  1  50 -1               1.0 2 8004 7602B7701 7601A  V4 1310
37002    -2.30  37  1  50 -2               2.0 2 8004*7601             V4 1311
37003    -5.30  37  1  50 -3               3.0 2 8004*7601             V4 1312
37004    -9.50  37  1  50 -4               4.0 2 8004*7601             V4 1313
37007    -1.00  37  1 101  1  50 -3        3.0 2 8001*                 V4 1314
37009     5.80  37  1 102  1                   2 8004                  V4 1316
37010    10.20  37  1 102  2                   2 8004                  V4 1317
37011    11.50  37  1 102  3                   2 7801A                 V4 1318
37012     0.90  37  1 103  1                   2 8004                  V4 1319
37013     1.90  37  1 103  2                   2 7602B8004             V4 1320
37014     7.90  37  1 104  1                   2 8004 7801 7602B       V4 1321
37016     1.80  37  1 157  1                   2 7602 7801B            V4 1322
37019    25.90  37  1 109  1  50  1            2 8004 7801C            V4 1323
37020    49.00  37  1 109  2  50  2            2 8004                  V4 1324
37021    11.40  37  1 116  1                   2 7301A                 V4 1325
37022    21.20  37  1 116  2                   2 7301A                 V4 1326
37023    30.10  37  1 116  3                   2 7301A                 V4 1327
37024    36.20  37  1 116  4                   2 7301A                 V4 1328
37025   -15.00  37  1  50 -5               5.0 2 8004*                 V4 1329
37026    70.00  37  1 109  3  50  3            2 8004                  V4 1330
37027    92.40  37  1 109  4  50  4            2 8004                  V4 1331
37101    19.1   37  1 101  1                   2 9102  8601      Pu(IV)(CO3)+2
37102    33.1   37  1 101  2                   2 9102  8601       Pu(IV)(CO3)2
37103    42.3   37  1 101  3                   2 9102  8601     Pu(IV)(CO3)3-2
37400    30.1   37  1 128  1                   2 HUMM  9102         Pu(IV)edta
37421    21.    37  1 127  1                   2 HUMM  estim.       Pu(IV)nta+
37431    16.9   37  1 117  1                   2 HUMM  7502         Pu(IV)cit+
37432    28.5   37  1 117  2                   2 HUMM  7502       Pu(IV)cit2-2
37441    10.9   37  1 118  1                   2 HUMM  6401         Pu(IV)ox+2
37442    20.1   37  1 118  2                   2 HUMM  6401          Pu(IV)ox2
37443    26.6   37  1 118  3                   2 HUMM  6401        Pu(IV)ox3-2
38001    -7.00  38  1  50 -1               1.0 2 7602 7801 7701 8001   V4 1332
38002   -15.00  38  1  50 -2               2.0 2 7701*                 V4 1333
38003   -26.00  38  1  50 -3               3.0 2 7701*                 V4 1334
38004   -33.00  38  1  50 -4               4.0 2 7701*                 V4 1335
38007     9.60  38  1 101  1                   2 8001                  V4 1336
38008    12.90  38  1 101  2                   2 8001                  V4 1337
38009    16.20  38  1 101  3                   2 8001                  V4 1338
38010     3.10  38  1 102  1                   2 7602B7801B8001B8004   V4 1339
38011     6.90  38  1 102  2  50  2            2 7602B7801B            V4 1340
38012     0.80  38  1 103  1                   2 7602B                 V4 1341
38016    22.01  38  1 109  1  50  2            2 8004  DEP.             1.6.90
38400    20.64  38  1 128  1                   2 HUMM  9102        Pu(III)edta-
38405    22.6   38  1 128  1  50  1            2 HUMM  9102        Pu(III)Hedta
38421    13.1   38  1 127  1                   2 HUMM  7904          Pu(III)nta
38431     9.5   38  1 117  1                   2 HUMM  estim.        Pu(III)cit
38441     6.5   38  1 118  1                   2 HUMM  estim.        Pu(III)ox+
40001    -0.53  40  1  50 -1               1.0 2 NEA             (40001) 20.7.90
40004    -4.53  40  1  50 -4               4.0 2 NEA             (40004) 20.7.90
40005   -16.54  40  1  50 -5               5.0 2 NEA             (40005) 20.7.90
40033    35.12  40  1 101  4                   2 NEA             (NEW  ) 20.7.90
40034    34.00  40  1 101  5                   2 NEA             (NEW  ) 20.7.90
40060     6.58  40  1 102  1                   2 NEA             (40009) 20.7.90
40061    10.51  40  1 102  2                   2 NEA             (40010) 20.7.90
40090     1.72  40  1 103  1                   2 NEA             (40011) 20.7.90
40120     9.29  40  1 104  1                   2 NEA             (40013) 20.7.90
40121    16.23  40  1 104  2                   2 NEA             (40014) 20.7.90
40122    21.58  40  1 104  3                   2 NEA             (40015) 20.7.90
40123    25.52  40  1 104  4                   2 NEA             (40029) 20.7.90
40124    27.03  40  1 104  5                   2 NEA             (40030) 20.7.90
40125    29.11  40  1 104  6                   2 NEA             (40031) 20.7.90
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40130        1.45  40  1 105  1               2 NEA                    (40012) 20.7.90
40140        1.25  40  1 106  1               2 NEA                    (NEW  ) 20.7.90
40260        1.47  40  1 157  1               2 NEA                    (40018) 20.7.90
40261        2.30  40  1 157  2               2 NEA                    (40019) 20.7.90
40290        2.97  40  1 150  1               2 NEA                    (NEW  ) 20.7.90
40291        4.28  40  1 150  2               2 NEA                    (NEW  ) 20.7.90
40400        29.1  40  1 128  1               2 HUMM  7403                   U(IV)edta
40415        24.2  40  1 128  1   50 -1   1.0 2 HUMM  7403                U(IV)OHedta-
40417        51.1  40  2 128  2   50 -2   2.0 2 HUMM  7403            (U(IV)OHedta)2-2
40421         20.  40  1 127  1               2 HUMM  estim.                 U(IV)nta+
40431        15.8  40  1 117  1               2 HUMM  7502                   U(IV)cit+
40432        24.7  40  1 117  2               2 HUMM  7502                 U(IV)cit2-2
40441        11.1  40  1 118  1               2 HUMM  7904                   U(IV)ox+2
41032        7.43  41  1 101  3               2 NEA                    (NEW  ) 20.7.90
42001       -7.00  42  1  50 -1           1.0 2 7701                           V4 1383
42002      -15.00  42  1  50 -2           2.0 2 7701*                          V4 1384
42003      -25.00  42  1  50 -3           3.0 2 7701*                          V4 1385
42004      -35.00  42  1  50 -4           4.0 2 7701*                          V4 1386
42006      -14.00  42  2  50 -2           2.0 2 7701*                          V4 1387
42007      -32.00  42  3  50 -5           5.0 2 7701*                          V4 1388
42008        9.60  42  1 101  1               2 8001*                          V4 1389
42009       12.90  42  1 101  2               2 8001*                          V4 1390
42010       16.20  42  1 101  3               2 8001*                          V4 1391
43001       -1.50  43  1  50 -1           1.0 2 7701 7602 7601 7301B           V4 1392
43002       -4.00  43  1  50 -2           2.0 2 7701*                          V4 1393
43003       -8.00  43  1  50 -3           3.0 2 7701*                          V4 1394
43004      -13.00  43  1  50 -4           4.0 2 7701*                          V4 1395
43005      -20.00  43  1  50 -5           5.0 2 7701*                          V4 1396
43008       -1.00  43  1 101  1   50 -3   3.0 2 8001*                          V4 1397
43009        3.90  43  1 102  1               2 7801C7602Z                     V4 1398
43010        5.70  43  1 102  2               2 7801C7602Z                     V4 1399
43011        1.20  43  1 103  1               2 7801B7602G7301G                V4 1400
43012        1.90  43  1 103  2               2 7801B7602G                     V4 1401
43014        8.30  43  1 104  1               2 7602U8001*                     V4 1403
43015       14.50  43  1 104  2               2 7602U8001*                     V4 1404
43016       20.30  43  1 104  3               2 7602U8001*                     V4 1405
43017       25.10  43  1 104  4               2 7602U8001*                     V4 1406
43018        1.60  43  1 157  1               2 7801B                          V4 1407
43019        2.20  43  1 157  2               2 7801B                          V4 1408
43020       11.40  43  1 116  1               2 7301A                          V4 1409
43021       22.20  43  1 116  2               2 7301A                          V4 1410
43022       30.10  43  1 116  3               2 7301A                          V4 1411
43023       36.20  43  1 116  4               2 7301A                          V4 1412
43400        29.9  43  1 128  1               2 HUMM  6202                  Np(IV)edta
43421        20.5  43  1 127  1               2 HUMM  7103                  Np(IV)nta+
43422        36.0  43  1 127  2               2 HUMM  7103                Np(IV)nta2-2
43431         16.  43  1 117  1               2 HUMM  estim.                Np(IV)cit+
43441        11.8  43  1 118  1               2 HUMM  7101                 Np(IV)ox2+2
44001       -9.00  44  1  50 -1           1.0 2 7701 7601A                     V4 1414
44003       -0.10  44  1 103  1               2 7801                           V4 1415
44004      12.599  44  1 101  1   50  1       2 7801  DEP.                      1.6.90
44005       -0.05  44  1 157  1               2 7801C7602C                     V4 1417
44006       15.90  44  1 109  1   50  1       2 7801                           V4 1418
44007      24.598  44  1 101  2   50  2       2 8201  DEP.                      1.6.90
44400         8.2  44  1 128  1               2 HUMM  7004               Np(V)O2edta-3
44405        16.9  44  1 128  1   50  1       2 HUMM  7004              Np(V)O2Hedta-2
44407        -4.2  44  1 128  1   50 -1   1.0 2 HUMM  7004             Np(V)O2OHedta-4
44421         7.4  44  1 127  1               2 HUMM  7004                Np(V)O2nta-2
44425        12.5  44  1 127  1   50  1       2 HUMM  7004                Np(V)O2Hnta-
44427        -4.7  44  1 127  1   50 -1   1.0 2 HUMM  7004              Np(V)O2OHnta-3
44431         5.5  44  1 117  1               2 HUMM                      Np(V)O2cit-2
44435        9.51  44  1 117  1   50  1       2 HUMM  7101                Np(V)O2Hcit-
44441        4.38  44  1 118  1               2 HUMM  7705                  Np(V)O2ox-
44442        7.36  44  1 118  2               2 HUMM  7705                Np(V)O2ox2-3
44445        7.14  44  1 118  1   50  1       2 HUMM  7705                  Np(V)O2Hox
45001       -5.10  45  1  50 -1           1.0 2 7602 7601 7701 8001*           V4 1419
45002      -11.50  45  1  50 -2           2.0 2 7701*8001*                     V4 1420
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45003   -20.70  45  1   50  -3                3.0 2 8001*                      V4 1421
45005    -6.40  45  2   50  -2                2.0 2 7602 7601 7701             V4 1422
45006   -17.50  45  3   50  -5                5.0 2 7602 7601 7701             V4 1423
45007    -4.00  45  2   50  -1                1.0 2 7701*                      V4 1424
45008    10.00  45  1  101   1                    2 8001*                      V4 1425
45009    17.00  45  1  101   2                    2 8001*                      V4 1426
45010    21.00  45  1  101   3                    2 8001*                      V4 1427
45011     3.30  45  1  102   1                    2 7602 7801B                 V4 1428
45012     4.70  45  1  102   2                    2 7602A                      V4 1429
45013     0.25  45  1  103   1                    2 7801A7602B7301C            V4 1430
45014     4.50  45  1  104   1                    2 7801B7602A7301B            V4 1431
45015     7.80  45  1  104   2                    2 7801B7602A7301B            V4 1432
45016    -0.25  45  1  157   1                    2      7602A7801A            V4 1433
45400      15.  45  1  128   1                    2 HUMM  estim.    Np(VI)O2edta-2
45421      11.  45  1  127   1                    2 HUMM  estim.     Np(VI)O2nta-
45431      10.  45  1  117   1                    2 HUMM  estim.     Np(VI)O2cit-
45441      7.1  45  1  118   1                    2 HUMM  7904          Np(VI)O2ox
45442     11.2  45  1  118   2                    2 HUMM  7904       Np(VI)O2ox2-2
47001     -1.1  47  1   50  -1                1.0 2 SUPPL 9102         Tc(IV)OOH+
47002     -3.3  47  1   50  -2                2.0 2 SUPPL 9102        Tc(IV)O(OH)2
47003     -0.1  47  2   50  -4                4.0 2 SUPPL 9102     (Tc(IV)O(OH)2)2
47415     18.8  47  1  128   1  50 -1         1.0 2 HUMM  7904      TcO(OH)edta-3
47425     13.3  47  1  127   1  50 -1         1.0 2 HUMM  7904       TcO(OH)nta-2
48001    -7.80  48  1   50  -1                1.0 2 7804                     26.10.90
48002    -16.2  48  1   50  -2                2.0 2 7804                     26.10.90
48003    -25.0  48  1   50  -3                3.0 2 7804                     26.10.90
48004    -37.0  48  1   50  -4                4.0 2 7804                     26.10.90
48010      8.2  48  1  101   1                    2 8207Y I-corrected        26.10.90
48011     13.6  48  1  101   2                    2 8207Y I-corrected        26.10.90
48020     3.67  48  1  102   1                    2 7602                     17/2/83
48021     5.41  48  1  102   2                    2 7602                     17/2/83
48030     0.80  48  1  103   1                    2 8201                     17/2/83
48031     0.99  48  1  103   2                    2 8201                     17/2/83
48040     1.23  48  1  157   1                    2 7602                     17/2/83
49001     -7.9  49  1   50  -1                1.0 2 7804                     26.10.90
49002    -16.5  49  1   50  -2                2.0 2 7804                     26.10.90
49003    -25.0  49  1   50  -3                3.0 2 7804                     26.10.90
49004    -37.0  49  1   50  -4                4.0 2 7804                     26.10.90
49010    -13.7  49  2   50  -2                2.0 2 7804                     26.10.90
49020      8.2  49  1  101   1                    2 8207Y I-corrected        26.10.90
49021     13.6  49  1  101   2                    2 8207Y I-corrected        26.10.90
49030     3.67  49  1  102   1                    2 7602                     26.10.90
49031      5.2  49  1  102   2                    2 7602                     26.10.90
51001      0.3  51  1   50  -1                1.0 2 SUPPL 9102                ZrOH+3
51004     -9.7  51  1   50  -4                4.0 2 SUPPL 9102                Zr(OH)4
51005     -16.  51  1   50  -5                5.0 2 SUPPL 9102                Zr(OH)5-
51007     -0.6  51  3   50  -4                4.0 2 SUPPL 9102   !!        Zr3(OH)4+8
51008       6.  51  4   50  -8                8.0 2 SUPPL 9102   !!!       Zr4(OH)8+8
51020   3.05    51  1  102   1                    2 SUPPL 9102                ZrSO4+2
51030   0.2     51  1  103   1                    2 SUPPL 9102                  ZrCl+
51400     32.8  51  1  128   1                    2 HUMM  8209                  Zredta
51415     26.4  51  1  128   1  50 -1         1.0 2 HUMM  8209              ZrOHedta-
51421     24.1  51  1  127   1                    2 HUMM  8903                  Zrnta+
51431      17.  51  1  117   1                    2 HUMM  estim.                Zrcit+
51435     19.3  51  1  117   1  50  1             2 HUMM  7101               ZrHcit+2
51441     12.4  51  1  118   1                    2 HUMM  7101                 Zrox+2
52001    -1.87  52  1   50  -1                1.0 2 SUPPL 7003Z               Pd(OH)+
52002     -3.8  52  1   50  -2                2.0 2 SUPPL 7003Z               Pd(OH)2
52003   -15.94  52  1   50  -3                3.0 2 SUPPL 7003Z              Pd(OH)3-
52004   -29.36  52  1   50  -4                4.0 2 SUPPL 7003Z             Pd(OH)4-2
52050     9.59  52  1  107   1                    2 SUPPL 7804              Pd(NH3)+2
52051    18.48  52  1  107   2                    2 SUPPL 7804             Pd(NH3)2+2
52052    25.96  52  1  107   3                    2 SUPPL 7804             Pd(NH3)3+2
52053    32.75  52  1  107   4                    2 SUPPL 7804             Pd(NH3)4+2
52061     4.16  52  1  102   2                    2 SUPPL 8204Z            Pd(SO4)2-2
52080     10.5  52  1  114   1                    2 8208                      21.3.91
52083     41.7  52  1  114   4                    2 8208                      21.3.91
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52090     3.97   52  1 103  1                2 8208               21.3.91
52091     7.51   52  1 103  2                2 8208               21.3.91
52092    10.32   52  1 103  3                2 8208               21.3.91
52093    12.04   52  1 103  4                2 8208               21.3.91
52130     7.22   52  1 105  1                2 SUPPL 8204           PdBr+
52132    12.06   52  1 105  3                2 8208               21.3.91
52133    13.78   52  1 105  4                2 8208               21.3.91
52140    10.42   52  1 106  1                2 SUPPL 8204            PdI+
52143    22.64   52  1 106  4                2 8208               21.3.91
52263    20.9    52  1 181  4                2 7602Z              21.3.91
52271    16.9    52  1 150  2                2 8204               21.3.91
52273    25.6    52  1 150  4                2 8204               21.3.91
52400    27.6    52  1 128  1                2 HUMM  8903        Pdedta-2
52405    31.1    52  1 128  1  50  1         2 HUMM  8903        PdHedta-
52421    18.6    52  1 127  1                2 HUMM  8209          Pdnta-
52422    26.7    52  1 127  1  50  1         2 HUMM  8209          PdHnta
53001     0.8    53  1  50 -1            1.0 2 7601          Pa(IV)(OH)+3
53002    -0.01   53  1  50 -2            2.0 2 7601          Pa(IV)(OH)2+2
53003    -2.     53  1  50 -3            3.0 2 7601          Pa(IV)(OH)3+
54001     0.5    54  1  50  1                2 7601          Pa(V)O(OH)+2
54002    -4.5    54  1  50 -1            1.0 2 7601           Pa(V)O2(OH)
55001    -6.5    55  1  50 -1            1.0 2 8801Y I-corrected  26.10.90
55002   -13.8    55  1  50 -2            2.0 2 8801Y I-corrected  26.10.90
55003   -25.2    55  1  50 -3            3.0 2 8801Y I-corrected  26.10.90
55010     4.5    55  1 104  1                2 7602Y I-corrected  26.10.90
55011     8.0    55  1 104  2                2 7602Y I-corrected  26.10.90
55012    11.2    55  1 104  3                2 7602Y I-corrected  26.10.90
55020     1.10   55  1 103  1                2 8201               12/O/83
55022     0.7    55  1 101  1  50 -1     1.0 2 8801Y I-corrected  26.10.90
55023     4.8    55  1 101  2  50 -1     1.0 2 8801Y I-corrected  26.10.90
55024    -7.2    55  1 101  1  50 -2     2.0 2 8801Y I-corrected  26.10.90
55026     8.1    55  1 101  1                2 8207Y I-corrected  26.10.90
55027    12.6    55  1 101  2                2 8207Y I-corrected  26.10.90
55028    14.2    55  1 101  3                2 8801Y I-corrected  26.10.90
55030     4.0    55  1 102  1                2 7602Y I-corrected  26.10.90
55031     5.7    55  1 102  2                2 7602Y I-corrected  26.10.90
55040    22.21   55  1 109  1  50  2         2 8201  DEP.            1.6.90
55041    42.82   55  1 109  2  50  4         2 8201  DEP.            1.6.90
55400    20.3    55  1 128  1                2 HUMM  8903          Amedta-
55401    24.2    55  1 128  2                2 HUMM  9102        Amedta2-5
55405    22.3    55  1 128  1  50  1         2 HUMM  9102          AmHedta
55415     8.3    55  1 128  1  50 -1     1.0 2 HUMM  7904       AmOHedta-2
55421    13.     55  1 127  1                2 HUMM  7403             Amnta
55422    22.     55  1 127  2                2 HUMM  7403          Amnta2-3
55431     9.63   55  1 117  1                2 HUMM  7705             Amcit
55432    12.8    55  1 117  2                2 HUMM  7705          Amcit2-3
55435    12.5    55  1 117  1  50  1         2 HUMM  7705          AmHcit+
55437    18.5    55  1 117  2  50  1         2 HUMM  7705         AmHcit2-
55441     6.51   55  1 118  1                2 HUMM  7705             Amox+
55442    10.53   55  1 118  2                2 HUMM  7705            Amox2-
55443    12.8    55  1 118  3                2 HUMM  7705           Amox3-3
57001     1.42   57  1  50  1           -1.0 2 7601          Sb(III)(OH)2+
57002   -11.82   57  1  50 -1            1.0 2 7601          Sb(III)(OH)4-
58002    -2.72   58  1  50 -1            1.0 2 7601            Sb(V)(OH)6-
59001     9.0    59  1  50  3           -3.0 2 8903                  Bi+3
59002     7.9    59  1  50  2           -2.0 2 8903              Bi(OH)+2
59003     5.     59  1  50  1           -1.0 2 7601              Bi(OH)2+
59004   -12.2    59  1  50 -1            1.0 2 8903              Bi(OH)4-
59010    51.3    59  6  50  6           -6.0 2 8903           Bi6(OH)12+6
59011    72.85   59  9  50  7           -7.0 2 8903           Bi9(OH)20+7
59012    69.45   59  9  50  6           -6.0 2 8903           Bi9(OH)21+6
59013    66.55   59  9  50  5           -5.0 2 8903           Bi9(OH)22+5
68117     1.13   68  1 117  1                2 7602Z I-corrected    2.9.90
69001   -13.5    69  1  50 -1            1.0 2 8501                 RaOH+
69010     2.50   69  1 101  1                2 8501                 RaCO3
69015     2.75   69  1 102  1                2 8501                 RaSO4
69020    -0.1    69  1 103  1                2 8501                 RaCl+
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69117     3.82  69   1 117   1                        2 7602Z I-corrected      Racit-
   28
12661    21.26 110  -1 109   2  50   2           -1.0 3 CORE  (NEA)            1.6.90
15000    13.02   7  -1   6   1  99   1                3 CORE                  21.3.91
15010    31.60  16  -1  17   1  99   1                3                       V4    2
15020     5.10  26  -1  27   1  99   2                3 5201  corrected BU41  21.1.91
15030     2.70  33  -1   9   1  99   1                3                       V4    4
15040    33.69 108  -1 102   1  50   9  99   8   -4.0 3 CORE  SULPH           21.3.91
15041    -3.40 149  -1 102   1  50   2  99   2   -1.0 3 SUPPL 9101 8208   SO3-2/SO4-2
15042    44.81 113  -1 149   2  50   6  99   4   -3.0 3 SUPPL 9101 8208  S2O3-2/SO3-2
15050   30.805 160  -1 154   1  50   4  99   2   -2.0 3 CORE  (8104)          21.3.91
15060    49.94 170  -1 171   1  50   2  99   2   -1.0 3 NEA                    2.9.90
15156    29.02 156  -1 178   1  50   2  99   2   -1.0 3 8208                  21.3.91
15177    81.17 177  -1 178   1  50   9  99   8   -4.0 3 8208                  21.3.91
36000    16.28  36  -1  35   1  99   1                3 SUPPL 9101 7603  PuO2+/PuO2+2
37000    18.59  37  -1  36   1  50   4  99   1   -2.0 3 SUPPL 9101 7603    Pu+4/PuO2+
38000    16.99  38  -1  37   1  99   1                3 SUPPL 9101 7603     Pu+3/Pu+4
39000    -9.35  39  -1  40   1  99   1                3 SUPPL NEA1 7603       U+3/U+4
40000     7.56  40  -1  41   1  50   4  99   1   -2.0 3 SUPPL NEA              U+4/UO2+
41000     1.48  41  -1  32   1  99   1                3 SUPPL NEA            UO2+/UO2+2
42000     2.49  42  -1  43   1  99   1                3 SUPPL 9101 7603     Np+3/Np+4
43000    10.89  43  -1  44   1  50   4  99   1   -2.0 3 SUPPL 9101 7603    Np+4/NpO2+
44000    20.88  44  -1  45   1  99   1                3 SUPPL 9101 7603  NpO2+/NpO2+2
47000     6.25  56  -1  47   1  99   1                3 8302                  29/5/84
56000    -0.52  46  -1  56   1  50   2  99   1   -1.0 3 8302                  29/5/84
99159    36.50  47  -1 159   1  50   6  99   3   -3.0 3 8302                  29/5/84
99163    43.3   47  -1 163   1  50   6  99   2   -3.0 3 SUPPL 9102           Tc(VI)O4-2
99167    53.3   47  -1 167   1  50   6  99   1   -3.0 3 SUPPL 9102            Tc(V)O4-3
99199   -3.106 199  -1  50   2  99   2                3 CORE  (7401)           1.6.90
99200   85.988  50   4 200   1  99   4           -2.0 3 CORE  (7401)           1.6.90
    0
  415
20000     8.48   1   1 101   1                        5 CORE  CALCITE          1.6.90
20001    8.336   1   1 101   1                        5 CORE  ARAGONITE        1.6.90
20010    4.581   1   1 102   1                    2.0 5 CORE  GYPSUM           1.6.90
20011    4.357   1   1 102   1                        5 CORE  ANHYDRITE        1.6.90
20020    10.60   1   1 104   2                        5 STAND FLUORITE         1.6.90
20030    43.00   1   5 109   3  50  -1            1.0 5 8104U OH-APAT.        14.2.84
20031    59.00   1   5 109   3 104   1                5 8104U F-APAT.         14.2.84
20040    46.90   1   4 109   3  50   1                5 8104                  14.2.84
20050    18.93   1   1 109   1  50   1            2.0 5 7602  *2H2O           14.2.84
20060    15.50   1   2 110   1                        5                       V4    9
20070   -15.80   1   2 112   1  50  -2                5 8301  LARNITE         14.2.84
20080     8.78   1   1 118   1                    1.0 5 HUMM  8903          Caox.H2O
20081     8.32   1   1 118   1                    3.0 5 HUMM  8903         Caox.3H2O
20090     6.50   1   1 149   1                        5                       V4   12
20100     7.40   1   1 152   1                        5                       V4   13
20110    22.90   1   3 154   2                        5                       V4   14
20120     5.50   1   1 156   1                        5                       V4   15
20130   -22.81   1   1  50  -2                    2.0 5 CORE  (7601) PORTLAN.  1.6.90
20140     8.04   2   1 101   1                        5 8301  MAGNESITE       14.2.84
20145    17.09   1   1   2   1 101   2                5 CORE  DOLOMITE ord.   21.3.91
20149    16.54   1   1   2   1 101   2                5 CORE  DOLOMITE disord 21.3.91
20150     8.18   2   1 104   2                        5 7602                  V4   19
20160    28.40   2   3 109   2                        5                       V4   20
20170     3.70   2   1 118   1                        5                       V4   21
20180    24.40   2   3 154   2                        5                       V4   22
20190     4.90   2   1 156   1                        5                       V4   23
20200   -16.84   2   1  50  -2                    2.0 5 CORE  BRUCITE          1.6.90
20210    9.271   3   1 101   1                        5 CORE  STRONTIANITE     1.6.90
20220    6.632   3   1 102   1                        5 CORE  CELESTITE        1.6.90
20230     8.54   3   1 104   2                        5 7602                  V4   27
20240     2.40   3   1 112   1                        5                       V4   28
20250     6.70   3   1 118   1                        5                       V4   29
20260    22.80   3   3 154   2                        5                       V4   30
20270     6.10   3   1 156   1                        5                       V4   31
20280    25.80   6   1 109   1                        5                       V4   32
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20290     21.00   6  1 154  1                 5                          V4   33
20300     31.60   6  2 156  3                 5                          V4   34
20309      -5.0   6  1  50 -3           3.0 5 SUPPL 9001           Fe(OH)3-B
20310      -3.0   6  1  50 -3           3.0 5 SUPPL 9001           Fe(OH)3-A
20311     -0.80   6  1  50 -3           3.0 5 8104  Fe(OH)3-AGED    14.2.84
20312      -0.5   6  1  50 -3           2.0 5 SUPPL                GOETHITE-B
20313      3.80   6  2  50 -6           3.0 5 8104  HEMATITEa-FE2O326.10.90
20314        1.   6  1  50 -3           2.0 5 SUPPL 9001           GOETHITE-A
20320     10.89   7  1 101  1               5 STAND SIDERITE cryst.  1.6.90
20321     10.45   7  1 101  1               5 STAND SIDERITE precip. 1.6.90
20325     2.209   7  1 102  1           7.0 5 STAND MELANTERITE      1.6.90
20330       4.2   7  1 108  1  50 -1        5 7602  FeS SULPH       21.3.91
20340     36.00   7  3 109  2               5 8301  VIVIANITE      14.2.84
20350      5.74   7  2 112  1  50 -2        5 8301  FAYALITE       14.2.84
20360    -12.90   7  1  50 -2           2.0 5 7602                  V4   40
20370     11.13   8  1 101  1               5 STAND RHODOCHR. cry.   1.6.90
20371     10.39   8  1 101  1               5 STAND RHODOCHR. synth. 1.6.90
20380      -0.4   8  1 108  1  50 -1        5 7602  MnS   SULPH     21.3.91
20390     19.50   8  2 110  1               5                       V4   43
20400     10.70   8  1 112  1               5                       V4   44
20410     29.60   8  3 154  2               5                       V4   45
20420      7.30   8  1 156  1               5                       V4   46
20430    -15.20   8  1  50 -2           2.0 5 STAND PYROCHROITE      1.6.90
20440      4.00   9  2 101  1  50 -2    2.0 5 7002  MALACHITE      18.3.83
20441     15.00   9  3 101  2  50 -2    2.0 5 7002  AZURITE        18.3.83
20442      9.63   9  1 101  1               5 7602                 18.3.83
20445    -15.40   9  4 102  1  50 -6    6.0 5 7602                 18.3.83
20447     -7.40   9  2 103  1  50 -3    3.0 5 7602                 18.3.83
20450      22.2   9  1 108  1  50 -1        5 7602  CuS   SULPH     21.3.91
20460     37.70   9  3 109  2               5                       V4   50
20470     18.80   9  2 110  1               5                       V4   51
20480     39.80   9  3 154  2               5                       V4   52
20490      7.70   9  1 156  1               5                       V4   53
20495     -9.80   9  2 157  1  50 -3    3.0 5 7602                 18.3.83
20500     -7.65   9  1  50 -2           1.0 5 7002  CuO            18.3.83
20501     -8.68   9  1  50 -2           2.0 5 7602  Cu(OH)2        18.3.83
20509    -24.40  10  1  50 -2          10.0 5 7602  Ba(OH)2 .8H2O  17/2/83
20510     8.562  10  1 101  1               5 CORE  WITHERITE        1.6.90
20520      9.97  10  1 102  1               5 CORE  BARITE           1.6.90
20530      6.10  10  1 104  2               5                       V4   57
20540      6.20  10  1 118  1               5                       V4   58
20550     54.80  10  3 154  2               5                       V4   59
20560      6.60  10  1 156  1               5                       V4   60
20570     13.74  11  1 101  1               5 7602                 17/2/83
20580      13.1  11  1 108  1  50 -1        5 7602  CdS   SULPH     21.3.91
20590      7.20  11  1 118  1               5                       V4   63
20600     37.40  11  3 154  2               5                       V4   64
20610      8.30  11  1 156  1               5                       V4   65
20620    -13.65  11  1  50 -2           2.0 5 7602  Cd(OH)2        17/2/83
20630     10.00  12  1 101  1               5 7602                 17/2/83
20640      10.8  12  1 108  1  50 -1        5 7602  a-ZnS  SULPH    21.3.91
20641       8.6  12  1 108  1  50 -1        5 7602  b-ZnS  SULPH    21.3.91
20650     36.70  12  3 109  2               5                       V4   69
20660     18.50  12  1 112  1               5                       V4   70
20670      8.20  12  1 118  1               5                       V4   71
20680     27.90  12  3 154  2               5                       V4   72
20690      7.70  12  1 156  1               5                       V4   73
20700    -11.34  12  1  50 -2           1.0 5 7602  ZnO            17/2/83
20701    -11.80  12  1  50 -2           2.0 5 7602  Zn(OH)2        17/2/83
20702    -12.48  12  1  50 -2           2.0 5 7602  Zn(OH)2 am.    17/2/83
20710      6.97  13  1 101  1               5 7102  NiCO3           21.3.91
20711     -5.33  13  1 102  1               5 8208  NiSO4           21.3.91
20712      2.01  13  1 102  1           6.0 5 7805  NiSO4.6H2O      21.3.91
20713      2.02  13  1 102  1           7.0 5 7805  NiSO4.7H2O      21.3.91
20715     -8.36  13  1 103  2               5 7903  NiCl2           21.3.91
20716     -3.89  13  1 103  2           2.0 5 8208  NiCl2.2H2O      21.3.91
20717      -3.8  13  1 103  2           4.0 5 8208  NiCl2.4H2O      21.3.91
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20718    -3.09  13  1 103  2                  6.0 5 8208  NiCl2.6H2O      21.3.91
20720      5.5  13  1 108  1  50 -1               5 7602  a-NiS  SULPH    21.3.91
20721     11.0  13  1 108  1  50 -1               5 7602  b-NiS  SULPH    21.3.91
20722     12.7  13  1 108  1  50 -1               5 7602  g-NiS  SULPH    21.3.91
20723     4.03  13  1 108  1  50 -1               5 SUPPL 7805     NiS(millerite)
20724     7.75  13  1 108  2  50 -2  99 -2        5 SUPPL 7402               NiS2
20725     4.61  13  3 108  2  50 -2  99  2        5 SUPPL 8208   Ni3S2(haezlewo.)
20726    18.24  13  3 108  4  50 -4  99 -2        5 SUPPL 7402              Ni3S4
20730    30.20  13  3 154  2                      5                       V4   77
20731     0.35  13  1 104  2                      5 7903  NiF2            21.3.91
20732     5.13  13  1 104  2                  4.0 5 8208  NiF2.4H2O       21.3.91
20733    -9.42  13  1 105  2                      5 7903  NiBr2           21.3.91
20734   -11.79  13  1 106  2                      5 7903  NiI2            21.3.91
20735    29.6   13  3 109  2                      5 7703  Ni3(PO4)2       21.3.91
20736    12.32  13  2 110  1                      5 8208  Ni2P2O7         21.3.91
20737    25.2   13  1 112  1                 -1.0 5 7704  NiSiO3          21.3.91
20738     3.83  13  2 112  1  50 -2               5 8403  NiSiO4 olivine  21.3.91
20739     2.43  13  2 112  1  50 -2               5 8403  NiSiO4 spinel   21.3.91
20740     5.30  13  1 156  1                      5                       V4   78
20745    -5.32  13  1   6  2  50 -8           4.0 5 SUPPL 7805  NiFe2O4(trevori.)
20750   -12.73  13  1  50 -2                  2.0 5 8208  Ni(OH)2         21.3.91
20751   -12.45  13  1  50 -2                  1.0 5 8208  NiO bunsenite   21.3.91
20752   -19.2   13  2 103  1  50 -3           3.0 5 8204  Ni(OH)1.5Cl0.5  21.3.91
20753   -44.    13  4 103  1  50 -7           7.0 5 8204  Ni(OH)1.75Cl0.2521.3.91
20754    30.44  13  1 148  2                      5 8208  Ni(OH)2.2H3BO3  21.3.91
20755     8.7   13  1 148  2                 -4.0 5 8208  Ni(BO2)2        21.3.91
20760    38.8   14  1 108  1  50 -1               5 7602  HgS-bla  SULPH  21.3.91
20761    39.4   14  1 108  1  50 -1               5 7602  HgS-red  SULPH  21.3.91
20770    -2.56  14  1  50 -2                  1.0 5 7602  HgO-red        17/2/83
20780    13.13  15  1 101  1                      5 7602                 17/2/83
20790    18.80  15  3 101  2  50 -2           2.0 5 7002                 17/2/83
20800     7.79  15  1 102  1                      5 7602                 17/2/83
20810     7.60  15  1 104  2                      5                       V4   85
20820    13.6   15  1 108  1  50 -1               5 7602  PbS   SULPH     21.3.91
20830    12.60  15  1 109  1  50  1               5                       V4   87
20840    43.00  15  3 109  2                      5                       V4   88
20850    60.90  15  5 109  3  50 -1           1.0 5                       V4   89
20860     3.50  15  2 112  1  50 -2               5                       V4   90
20870     9.20  15  1 118  1                      5                       V4   91
20880    13.00  15  1 152  1                      5                       V4   92
20890    36.30  15  3 154  2                      5                       V4   93
20900    11.50  15  1 156  1                      5                       V4   94
20910   -12.90  15  1  50 -2                  1.0 5 7602  PbO            17/2/83
20911   -26.20  15  2  50 -4                  3.0 5 7602  PbO.Pb(OH)2    26.10.90
20920    10.00  16  1 101  1                      5 7602                 18.3.83
20930      7.4  16  1 108  1  50 -1               5 7602  a-CoS   SULPH   21.3.91
20931     11.7  16  1 108  1  50 -1               5 7602  b-CoS   SULPH   21.3.91
20940    32.80  16  3 154  2                      5                       V4   98
20950     7.10  16  1 156  1                      5                       V4   99
20960   -13.10  16  1  50 -2                  2.0 5 7602  Co(OH)2        18.3.83
20970     7.40  17  2  50 -6                  3.0 5       Co2O3          26.10.90
20980    10.90  18  2 101  1                      5                       V4  102
20990     4.90  18  2 102  1                      5                       V4  103
21000     9.90  18  1 103  1                      5                       V4  104
21010    12.30  18  1 105  1                      5                       V4  105
21020    16.08  18  1 106  1                      5 7602                  V4  106
21030    36.2   18  2 108  1  50 -1               5 7602  Ag2S   SULPH    21.3.91
21040    16.00  18  3 109  1                      5                       V4  108
21050     2.30  18  1 115  1                      5                       V4  109
21060    10.40  18  2 118  1                      5                       V4  110
21070    11.90  18  1 150  1                      5                       V4  111
21080    11.40  18  2 152  1                      5                       V4  112
21090    11.20  18  2 153  1                      5                       V4  113
21100    19.30  18  3 154  1                      5                       V4  114
21110    14.90  18  2 156  1                      5                       V4  115
21120   -12.60  18  2  50 -2                  1.0 5       Ag2O           26.10.90
21130    20.90  19  1 154  1                      5                       V4  117
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21140   -11.80   19  1  50 -3                      3.0 5 7602  Cr(OH)3 .aq      14.2.84
21144    33.84   20  1   5  3 104  6                   5 STAND CRYOLITE           1.6.90
21150    22.50   20  1 109  1                          5                        V4  119
21160   38.845   20  2 112  2  50 -2               1.0 5 9001  KAOLINITE          1.6.90
21170    16.60   20  1 154  1                          5                        V4  121
21180    -8.11   20  1  50 -3                      3.0 5 9001  GIBBSITE cr.       1.6.90
21181    -9.35   20  1  50 -3                      3.0 5 9001  GIBBS. microcr.    1.6.90
21182   -10.80   20  1  50 -3                      3.0 5 9001  Al(OH)3            1.6.90
21190    38.60   23  3 109  2                          5                        V4  123
21200    -6.7    23  1  50 -2                      2.0 5 7601                     2.9.90
21210    -5.60   24  1 103  1  50 -2               2.0 5                        V4  125
21220     0.71   25  1  50 -2                      1.0 5 7601  TiO2 (act.)        2.9.90
21230     12.0   26  1 108  1  50 -1                   5 7602  SnS   SULPH       21.3.91
21232    40.86   26  2 108  3  50 -3  99 -2            5 SUPPL 9102                Sn2S3
21235    23.93   26  1 102  1                          5 SUPPL 9102                SnSO4
21240    -1.76   26  1  50 -2                      1.0 5 SUPPL 7601                  SnO
21250     5.     27  1  50 -4                      2.0 5 SUPPL 7601                 SnO2
21255   -16.11   27  1 102  2                          5 SUPPL 9102             Sn(SO4)2
21260    33.40   28  2 101  3                          5 7602                   17/2/83
21280    -28.1   28  2 108  3  50 -3                   5 7602  La2S3   SULPH     21.3.91
21290    25.20   28  1 109  1                          5                        V4  133
21310   -19.7    28  1  50 -3                      3.0 5 7804                   26.10.90
21319    33.4    29  2 101  3                          5 9004                   26.10.90
21320    -30.6   29  2 108  3  50 -3                   5 7602  Ce2S3    SULPH    21.3.91
21330    22.10   29  1 109  1                          5                        V4  137
21340    25.30   29  2 156  3                          5                        V4  138
21350   -20.1    29  1  50 -3                      3.0 5 7804                   26.10.90
21360    31.60   30  1  50 -1                      1.0 5                        V4  140
21440    27.12   50  2 112  1                     -2.0 5 CORE  QUARTZ     (3.98)  1.6.90
21441    25.85   50  2 112  1                     -2.0 5 CORE  SiO2 am.  (2.71)  1.6.90
21442   26.691   50  2 112  1                     -2.0 5 CORE  CHALCED.  (3.55)  1.6.90
21450     17.5    7  1 108  2  99 -2  50 -2            5       PYRITE  SULPH    21.3.91
21460    -4.10    6  2   7  1  50 -8               4.0 5 8104  MAGNETITE        14.2.84
21470   -42.00    8  1  50 -4  99 -2               2.0 5       MnO2 (cf.21491)  V4  209
21480   -61.03    8  3  50 -8  99 -2               4.0 5 STAND HAUSMANNITE        1.6.90
21490   -25.34    8  1  50 -3  99 -1               2.0 5 STAND MANGANITE          1.6.90
21491   -41.38    8  1  50 -4  99 -2               2.0 5 STAND PYROLUSITE         1.6.90
21500   -49.20   15  1  50 -4  99 -2               2.0 5                        V4  212
21520    28.70   14  1  99  2                          5       Hg(0)            V4  214
21530     2.14  108  1  50 -1  99 -2                   5 STAND SULPH S-rhomb    21.3.91
21540    32.15  101  1  50  6  99  4                   5 SUPPL                     C(0)
21550  -13.823    7  1  99  1                          5 SUPPL                    Fe(0)
21555    19.67  152  1  50  8  99  6              -4.0 5 SUPPL                    Mo(0)
21560    11.40    9  1  99  2                          5       Cu(0)            V4  213
21570    30.93   52  1  99  2                          5 8208  Pd(0)            21.3.91
21580     7.71  177  1  50 -1  99 -2                   5 SUPPL 8208               Se(0)
21590    -7.78   13  1  99  2                          5 8402  Ni(0)            21.3.91
21595    -4.77   26  1  99  2                          5 SUPPL 9102               Sn(0)
22000    19.90  160  2  50  2                     -1.0 5                       10.02.84
22500     6.78  156  1  50  2                     -1.0 5 7402  SeO2             21.3.91
22501   -19.2   178  1  50  2                     -1.0 5 7402  SeO3             21.3.91
22502    19.6   156  1  50  6  99  2              -3.0 5 7402  Se2O5            21.3.91
22505   -14.42  156  1  50  6 103  4              -3.0 5 7402  SeCl4            21.3.91
22510   -25.47    1  1 177  1  50 -1                   5 7402  CaSe             21.3.91
22511     5.44    1  1 156  1                      2.0 5 8208  CaSeO2.2H2O      21.3.91
22512     3.09    1  1 178  1                      2.0 5 8208  CaSeO4.2H2O      21.3.91
22520   -21.57    2  1 177  1  50 -1                   5 7402  MgSe             21.3.91
22530   -22.37    3  1 177  1  50 -1                   5 7402  SrSe             21.3.91
22540   -26.47    4  2 177  1  50 -1                   5 7402  K2Se             21.3.91
22541    -9.96    4  2 156  1                          5 8106  K2SeO3           21.3.91
22542     0.64    4  2 178  1                          5 8106  K2SeO4           21.3.91
22550   -26.77    5  2 177  1  50 -1                   5 7402  Na2Se            21.3.91
22551   -11.54    5  2 177  2  50 -2  99 -2            5 7402  Na2Se2           21.3.91
22552    -3.93    5  2 156  1                          5 8106  Na2SeO3          21.3.91
22553    -0.51    5  2 178  1                          5 8106  Na2SeO4          21.3.91
22560    18.66    7  1 177  2  50 -2  99 -2            5 7402  FeSe2            21.3.91
22570   -22.37   10  1 177  1  50 -1                   5 7402  BaSe             21.3.91
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22571      6.58  10 1 156  1                       5 8208  BaSeO3           21.3.91
22572      7.47  10 1 178  1                       5 8208  BaSeO4           21.3.91
22580    -26.17  22 2 177  1  50 -1                5 7402  Li2Se            21.3.91
22581      2.41  22 2 156  1                       5 8106  Li2SeO3          21.3.91
22582     -1.25  22 2 178  1                       5 8106  Li2SeO4          21.3.91
22590      0.5  112 1 177  1  50  4           -4.0 5 7402  SiSe2            21.3.91
22600     -5.94  50 1 159  1                       5 SUPPL 9102          HTc(VII)O4
22610      2.22   4 1 159  1                       5 SUPPL 9102          KTc(VII)O4
22620     -1.56   5 1 159  1                       5 SUPPL 9102         NaTc(VII)O4
22700     29.96 152 1  50  4  99  2           -2.0 5 SUPPL 8208            MoO2(cr)
22701     12.06 152 1  50  2                  -1.0 5 SUPPL 8208            MoO3(cr)
22710     24.34 161 2  50  2                  -1.0 5 SUPPL 8208           Nb2O5(cr)
22711      7.98 161 1  50  2  99  1           -1.0 5 SUPPL 8208            NbO2(cr)
31501     -6.30  31 1  50 -4                   2.0 5 7602  ThO2            V4   141
31502    -13.80  31 1  50 -4                   4.0 5 7801  Th(OH)4         V4   142
31503     30.10  31 1 104  4                       5 8002                  V4   143
31504     33.10  31 1 104  4                   2.5 5 8002U ThF4 .2.5H2O    V4   144
31505     51.50  31 1 109  2  50  2            4.0 5 8002  Th(HPO4)2 .4H2O V4   145
31506     20.50  31 1 149  2                       5                       V4   146
32502     -8.64  32 1  50 -2                   1.0 5 NEA  a-UO3     (NEW  ) 20.7.90
32503     -5.00  32 1  50 -2                   1.9 5 NEA  a-UO3     (NEW  ) 20.7.90
32505     -8.31  32 1  50 -2                   1.0 5 NEA  b-UO3     (NEW  ) 20.7.90
32508     -7.72  32 1  50 -2                   1.0 5 NEA  g-UO3     (32009) 20.7.90
32515     -4.82  32 1  50 -2                   3.0 5 NEA  UO3.2H2O  (32011) 20.7.90
32516     -4.94  32 1  50 -2                   2.0 5 NEA  b-UO2(OH)2(32010)20.7.90
32520      3.60  32 1  41  2  50 -4            2.0 5 NEA  A-U3O8    (32057) 20.7.90
32530     14.44  32 1 101  1                       5 NEA  UO2CO3    (32028) 20.7.90
32560     -1.89  32 1 102  1                       5 NEA  UO2SO4    (32015) 20.7.90
32562      1.59  32 1 102  1                   2.5 5 NEA  UO2SO4    (NEW  ) 20.7.90
32563      1.50  32 1 102  1                   3.0 5 NEA  UO2SO4    (NEW  ) 20.7.90
32564      1.58  32 1 102  1                   3.5 5 NEA  UO2SO4    (NEW  ) 20.7.90
32590    -12.12  32 1 103  2                       5 NEA  UO2Cl2    (NEW  ) 20.7.90
32591     -8.26  32 1 103  2                   1.0 5 NEA  UO2Cl2    (NEW  ) 20.7.90
32593     -5.57  32 1 103  2                   3.0 5 NEA  UO2Cl2    (NEW  ) 20.7.90
32600     -2.28  32 1 103  1  50 -1            3.0 5 NEA  UO2ClOH   (NEW  ) 20.7.90
32605    -55.05  32 1 103  6  50  4           -2.0 5 NEA  UCl6      (NEW  ) 20.7.90
32610    -12.69  32 1 103  3  41  1                5 NEA  (UO2)2Cl3 (NEW  ) 20.7.90
32620      7.31  32 1 104  2                       5 NEA  UO2F2     (NEW  ) 20.7.90
32622      7.48  32 1 104  2                   3.0 5 NEA  UO2F2     (NEW  ) 20.7.90
32626      2.33  32 1 104  1  50 -1            2.0 5 NEA  UO2FOH    (NEW  ) 20.7.90
32627      2.71  32 1 104  1  50 -1            3.0 5 NEA  UO2FOH    (NEW  ) 20.7.90
32630     -4.41  32 1 104  4  50  2           -1.0 5 NEA  UOF4      (NEW  ) 20.7.90
32632    -17.31  32 1 104  6  50  4           -2.0 5 NEA  UF6(cr)   (NEW  ) 20.7.90
32635      2.95  32 2 104  6  50  2           -1.0 5 NEA  U2O3F6    (NEW  ) 20.7.90
32638      2.95  32 3 104  8  50  2           -1.0 5 NEA  U3O5F8    (NEW  ) 20.7.90
32640    -16.47  32 1 105  2                       5 NEA  UO2Br2    (NEW  ) 20.7.90
32641    -12.08  32 1 105  2                   1.0 5 NEA  UO2Br2    (NEW  ) 20.7.90
32643     -9.34  32 1 105  2                   3.0 5 NEA  UO2Br2    (NEW  ) 20.7.90
32645     -4.16  32 1 105  1  50 -1            3.0 5 NEA  UO2BrOH   (NEW  ) 20.7.90
32680     24.21  32 1 109  1  50  1            4.0 5 NEA  UO2HPO4   (NEW  ) 20.7.90
32690     36.34  32 3 109  2                       5 NEA  UO23PO42  (NEW  ) 20.7.90
32692     49.37  32 3 109  2                   4.0 5 NEA  UO23PO42  (32023) 20.7.90
32693     50.21  32 3 109  2                   6.0 5 NEA  UO23PO42  (NEW  ) 20.7.90
32710     15.65  32 2 110  1                       5 NEA  UO22P2O7  (NEW  ) 20.7.90
32720      7.90  32 1 175  2                       5 NEA  UO2(IO3)2 (NEW  )  2.9.90
32750     15.83  32 1 149  1                       5 NEA  UO2SO3    (NEW  ) 20.7.90
32760    -11.93  32 1 157  2                       5 NEA  UO2(NO3)2 (NEW  ) 20.7.90
32761     -8.47  32 1 157  2                   1.0 5 NEA  UO2(NO3)2 (NEW  ) 20.7.90
32762     -4.90  32 1 157  2                   2.0 5 NEA  UO2(NO3)2 (NEW  ) 20.7.90
32763     -3.67  32 1 157  2                   3.0 5 NEA  UO2(NO3)2 (NEW  ) 20.7.90
32764     -2.25  32 1 157  2                   6.0 5 NEA  UO2(NO3)2 (NEW  ) 20.7.90
32800    -16.04  32 1   1  1  50 -4            2.0 5 NEA  CaUO4     (32059) 20.7.90
32805    -23.30  32 1   2  1  50 -4            2.0 5 NEA  MgUO4     (32060) 20.7.90
32810    -19.16  32 1   3  1  50 -4            2.0 5 NEA  b-SrUO4   (NEW  ) 20.7.90
32820    -47.58  32 1   5  2  50 -4            2.0 5 NEA  a-Na2UO4  (32058) 20.7.90
32821    -22.62  32 2   5  2  50 -6            3.0 5 NEA  Na2U2O7   (NEW  ) 20.7.90
32822     26.93  32 1   5  4 101  3                5 NEA  Na4UO2CO33(NEW ) 20.7.90
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 32830    -16.68  32  1  10  1  50 -4              2.0 5 NEA  BaUO4     (NEW  ) 20.7.90
 32835    -29.8   32  2  21  2  50 -6              3.0 5 NEA  Cs2U2O7   (NEW  ) 20.7.90
 32836    -18.5   32  2  21  2  41  2  50 -8       4.0 5 NEA  Cs2U4O12  (NEW  ) 20.7.90
 32840    -29.12  32  1  22  2  50 -4              2.0 5 NEA  Li2UO4    (NEW  ) 20.7.90
 32850    -35.83  32  1  68  2  50 -4              2.0 5 NEA  Rb2UO4    (NEW  )  2.9.90
 34006    -18.7   34  1  50 -3                     3.0 5 7804                  26.10.90
 34011     33.00  34  2 101  3                         5 7602                  V4  174
 35004     -3.50  35  1  50 -2                     1.0 5 SUPPL 8004               PuO3
 35010     14.00  35  1 101  1                         5 7801B                 V4  176
 35021     21.40  35  1 101  2 107  2  50  2           5 7801B                 V4  177
 35024     25.40  35  1 109  1  50  1                  5 8004                  V4  178
 36002     -5.50  36  1  50 -1                     1.0 5 8004                  V4  179
 37005      7.00  37  1  50 -4                     2.0 5 8004  PuO2            V4  180
 37006     -1.00  37  1  50 -4                     4.0 5 8004U Pu(OH)4         V4  181
 37015     13.00  37  1 104  4                         5 8004                  V4  182
 37017     52.70  37  1 109  2  50  2                  5 8004 7801             V4  183
 37018     18.00  37  1   4  4 102  4                  5 7801                  V4  184
 38005    -48.10  38  2  50 -6                     3.0 5 8004 7702 Pu2O3       V4  185
 38006    -22.30  38  1  50 -3                     3.0 5 8004 8001 7401 Pu(OH)3 V4 186
 38013     11.40  38  1 103  3                         5 7801                  V4  187
 38014     10.00  38  1 104  3                         5 8004                  V4  188
 39500    -10.11  39  1 103  1  50 -2              1.0 5 NEA  UOCl      (NEW  ) 20.7.90
 39590    -12.24  39  1 103  3                         5 NEA  UCl3      (NEW  ) 20.7.90
 39591    -14.21  39  1 103  2 105  1                  5 NEA  UBrCl2    (NEW  ) 20.7.90
 39592    -17.47  39  1 103  1 105  2                  5 NEA  UBr2Cl    (NEW  ) 20.7.90
 39620     19.90  39  1 104  3                         5 NEA  UF3       (NEW  ) 20.7.90
 39630    -19.92  39  1 105  3                         5 NEA  UBr3      (NEW  ) 20.7.90
 39640    -28.66  39  1 106  3                         5 NEA  UI3       (NEW  ) 20.7.90
 40500      4.94  40  1  50 -4                     2.0 5 NEA  UO2       (40007) 20.7.90
 40502     -0.10  40  1  50 -4                     2.0 5 NEA  UO2-am.   (NEW  ) 20.7.90
 40560     11.67  40  1 102  2                         5 NEA  U(SO4)2   (NEW  ) 20.7.90
 40562     11.71  40  1 102  2                     4.0 5 NEA  U(SO4)2   (NEW  ) 20.7.90
 40564     12.77  40  1 102  2                     8.0 5 NEA  U(SO4)2   (NEW  ) 20.7.90
 40570      3.17  40  1 102  1  50 -2              2.0 5 NEA  USO4(OH)2(40022) 20.7.90
 40590    -21.92  40  1 103  4                         5 NEA  UCl4      (NEW  ) 20.7.90
 40592     -5.84  40  1 103  2  50 -2              1.0 5 NEA  UOCl2     (NEW  ) 20.7.90
 40595     17.66  40  1 103  1 104  3                  5 NEA  UClF3     (NEW  ) 20.7.90
 40596    -29.02  40  1 103  1 105  3                  5 NEA  UClBr3    (NEW  ) 20.7.90
 40597    -25.11  40  1 103  1 106  3                  5 NEA  UClI3     (NEW  ) 20.7.90
 40600      3.63  40  1 103  2 104  2                  5 NEA  UCl2F2    (NEW  ) 20.7.90
 40601    -26.14  40  1 103  2 105  2                  5 NEA  UCl2Br2   (NEW  ) 20.7.90
 40602    -30.19  40  1 103  2 106  2                  5 NEA  UCl2I2    (NEW  ) 20.7.90
 40605    -10.23  40  1 103  3 104  1                  5 NEA  UCl3F     (NEW  ) 20.7.90
 40606    -23.46  40  1 103  3 105  1                  5 NEA  UCl3Br    (NEW  ) 20.7.90
 40607    -25.45  40  1 103  3 106  1                  5 NEA  UCl3I     (NEW  ) 20.7.90
 40620     29.37  40  1 104  4                         5 NEA  UF4       (40016) 20.7.90
 40622     33.56  40  1 104  4                     2.5 5 NEA  UF4 .aq   (40032) 20.7.90
 40624      9.98  40  1 104  1  50 -3              2.0 5 NEA  UOF(OH)   (NEW  ) 20.7.90
 40625      9.44  40  1 104  1  50 -3              2.5 5 NEA  UOF(OH)aq(NEW  ) 20.7.90
 40626     18.23  40  1 104  2  50 -2              1.0 5 NEA  UOF2      (NEW  ) 20.7.90
 40627     18.80  40  1 104  2  50 -2              2.0 5 NEA  UOF2 aq   (NEW  ) 20.7.90
 40630    -31.18  40  1 105  4                         5 NEA  UBr4      (NEW  ) 20.7.90
 40632     -7.92  40  1 105  2  50 -2              1.0 5 NEA  UOBr2     (NEW  ) 20.7.90
 40640    -39.16  40  1 106  4                         5 NEA  UI4       (NEW  ) 20.7.90
 40680     55.23  40  1 109  2  50  2              4.0 5 NEA  U(HPO4)2  (40017) 20.7.90
 40710     33.97  40  1 110  1                         5 NEA  UP2O7     (NEW  ) 20.7.90
 40715     27.75  40  1 110  1                    20.0 5 NEA  UP2O7 aq  (NEW  ) 20.7.90
 40756     36.44  40  1 149  2                         5 NEA  U(SO3)2   (NEW  ) 20.7.90
 40760     30.97  40  1 112  1  50 -2                  5 NEA  USiO4     (40038) 20.7.90
 41505     13.74  41  2  40  1  50 -6              3.0 5 NEA  b-U3O7    (NEW  ) 20.7.90
 41510     19.35  41  2  40  2  50-10              5.0 5 NEA  b-U4O9    (40039) 20.7.90
 41590      0.54  41  1 103  1                         5 NEA  UO2Cl     (NEW  ) 20.7.90
 41593     -8.53  41  1 103  3  50  2             -1.0 5 NEA  UOCl3     (NEW  ) 20.7.90
 41595    -33.82  41  1 103  5  50  4             -2.0 5 NEA  UCl5      (NEW  ) 20.7.90
 41600     18.81  41  5 103  1  50 -4              2.0 5 NEA  U5O12Cl   (NEW  ) 20.7.90
 41610    -19.21  41  1  40  1 103  5                  5 NEA  U2O2Cl5   (NEW  ) 20.7.90
 41620     13.04  41  1 104  5  50  4             -2.0 5 NEA  a-UF5     (NEW  ) 20.7.90
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41621     13.38  41  1 104  5  50  4          -2.0 5 NEA  b-UF5     (NEW  ) 20.7.90
41625     45.88  41  1 104  9  40  1  50  4   -2.0 5 NEA  U2F9      (NEW  ) 20.7.90
41629    105.48  41  1 104 17  40  3  50  4   -2.0 5 NEA  U4F17     (NEW  ) 20.7.90
41633    -23.49  41  1 105  3  50  2          -1.0 5 NEA  UOBr3     (NEW  ) 20.7.90
41635    -41.51  41  1 105  5  50  4          -2.0 5 NEA  UBr5      (NEW  ) 20.7.90
41750    -56.31  41  1   5  3  50 -4           2.0 5 NEA  Na3UO4    (41004) 20.7.90
42005    -22.00  42  1  50 -3                  3.0 5 7401 8001*             V4  201
43006      2.70  43  1  50 -4                  2.0 5 7801                   V4  202
43007     -0.80  43  1  50 -4                  4.0 5 7801 8001              V4  203
44002     -4.90  44  1  50 -1                  1.0 5 7801 7601 8001*        V4  204
45004     -5.30  45  1  50 -2                  2.0 5 7801 8001              V4  205
47500     24.06  47  1  50  2  99  4          -1.0 5 SUPPL 9102               Tc(0)
47510    -13.1  159  2  50  2                 -1.0 5 SUPPL 9102          Tc(VII)2O7
47520     57.0   47  3  50 -2  99  4           1.0 5 SUPPL 9102       Tc(II,III)3O4
47530     36.8   47  4  50 -6  99  2           3.0 5 SUPPL 9102       Tc(III,IV)4O7
47540      4.2   47  1  50 -2                  3.0 5 SUPPL 9102            TcO2(am)
47550     23.2  163  1  50  2                 -1.0 5 SUPPL 9102                TcO3
47551    241.05 159  2 108  7  50  9          -8.0 5 SUPPL 9102 !!!           Tc2S7
47552     65.91  47  1 108  2                 -1.0 5 SUPPL 9102            Tc(IV)S2
47553     82.47 163  1 108  3  50  5          -4.0 5 SUPPL 9102                TcS3
47559     23.54  47  1  99  2                      5 SUPPL 9102                 TcO
47560     21.63  47  1  99  2                  1.0 5 SUPPL 9102             Tc(OH)2
47570      8.41  56  1  50 -1                  2.0 5 SUPPL 9102             Tc(OH)3
48500    -18.0   48  1  50 -3                  3.0 5 7804                  26.10.90
48510     32.5   48  2 101  3                      5 9004                  26.10.90
49100     32.5   49  2 101  3                      5 7602                  26.10.90
49110    -18.5   49  1  50 -3                  3.0 5 7804                  26.10.90
51500      1.9   51  1  50 -4                  2.0 5 SUPPL 9102                ZrO2
51530    -37.53  51  1 103  4                      5 SUPPL 9102               ZrCl4
52500      1.6   52  1  50 -2                  2.0 5 SUPPL 7003             Pd(OH)2
52505      4.4   52  1  50 -2                  1.0 5 7601 PdO               21.3.91
52590      7.09  52  1 103  2                      5 7903 PdCl2             21.3.91
52630     13.31  52  1 105  2                      5 5201 PdBr2             21.3.91
52640     23.77  52  1 106  2                      5 7903 PdI2              21.3.91
52670     39.31  52  1 108  1  50 -1               5 SUPPL 7402                 PdS
52671     37.3   52  1 108  2  50 -2  99 -2        5 SUPPL 7402                PdS2
52672    132.34  52  4 108  1  50 -1  99  6        5 SUPPL 7402  !!!           Pd4S
52770     16.7   52  1 150  2                      5 8208 Pd(SCN)2          21.3.91
53500     -0.6   53  1  50 -4                  2.0 5 7601                      PaO2
55006    -18.70  55  1  50 -3                  3.0 5 7601*                 12/0/83
57500      8.48  57  2                        -3.0 5 7601                     Sb2O3
58500     7.4    58  2                        -5.0 5 7601                     Sb2O5
59500     10.8   59  2                        -3.0 5 7601                   a-Bi2O3
69510     8.3    69  1 101  1                      5 8501                     RaCO3
69520    10.261  69  1 102  1                      5 8501                     RaSO4
  19
25000    18.149  50  2 101  1                 -1.0 6 CORE  CO2-gas           1.6.90
25001      8.0   50  1 108  1                      6 7602  H2S-gas          21.3.91
25002      9.00  50  2 149  1                 -1.0 6 7602  SO2-gas          V4    3
25003     3.106 199  1                             6 CORE  H2-gas (7401)     1.6.90
25004     2.894 200  1                             6 CORE  O2-gas (7401)     1.6.90
25005     3.186 198  1                             6 CORE  N2-gas            1.6.90
25006     2.856 197  1                             6 STAND CH4-gas           1.6.90
25022    52.585 154  1  50  8  99  5          -4.0 6 STAND As(0)             1.6.90
25101    38.177 197 -1 101  1  50 10  99  8   -3.0 6 STAND CO3-2/CH4(aq)     1.6.90
25157    109.90 107 -1 157  1  50  9  99  8   -3.0 6 STAND NO3-/NH3(aq)      1.6.90
25198     12.52 107 -2 198  1  50  6  99  6        6 STAND N2(aq)/NH3(aq)    1.6.90
32521     -2.48  32  2  40  1  50 -8           4.0 6 NEA  A-U3O8 CF.32520  20.7.90
37008     41.    37  1 101  1                      6 8004U moved to 6 on 24.4.92
41506      7.71  32  1  40  2  50-10           5.0 6 NEA  B-U3O7 CF.41505  20.7.90
41511     13.27  32  1  40  3  50-14           7.0 6 NEA  B-U4O9 CF.41510  20.7.90
55500     -51.7  55  2  50 -6                  3.0 6 9102 ?????               Am2O3
55505      7.03  55  1 101  1  50 -1           1.0 6 9102                   AmOHCO3
55510      37.6  55  2 101  3                      6 9102                 Am2(CO3)3
55700      23.0  55  1 109  1                      6 9102                     AmPO4
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E.3 *Table of $\Delta_r H$ and $\Delta_r C_p$ Data*

Enthalpy and heat capacity data are known for some of the complex species given in the table of Appendix E.2. These data are listed in the following table. Units are kcal/mol ($\Delta_r H^\circ$) and cal/(K.mol) ($\Delta_r C_p^\circ$), respectively. The information in the columns "Ref." concerns the value directly in front of it and refers to entries in the reference list, cf. Appendix E.4. Please note that care is required when modeling equilibria at temperatures different from the reference temperature of 298.15 K, because enthalpy data may not be available for all significant species in the calculation. This can lead to errors in the results.

ID	$\Delta_r H$ [kcal/mol]	Ref.	$\Delta_r C_p$ [cal/(K.mol)]	Ref.	Information	last update
1000	3.54	CORE			/ UPDATE 10.3.92	451 ITEMS
1010	-0.87	CORE			/	1.6.90
1020	1.65	CORE			/	1.6.90
1030	4.12	STAND			/	1.6.90
1080	-0.5	7602			/	14.2.84
1081	3.0	7602U			/	14.2.84
1082	-1.3	7602U			/	14.2.84
1350	15.90	CORE			/	1.6.90
1360	2.71	CORE			/	1.6.90
1370	-2.78	CORE			/	1.6.90
1380	4.55	CORE			/	1.6.90
1390	3.20	STAND			/	1.6.90
1440	-0.5	7602			/	14.2.84
1749	2.49	CORE			/	1.6.90
1950	14.5	CORE			/	17.2.83
1951	5.22	CORE			/	1.6.90
1952	2.08	CORE			/	1.6.90
1960	2.25	CORE			/	1.6.90
1999	0.0	CORE			/	1.6.90
2000	8.91	CORE			/	1.6.90
2001	-3.56	CORE			/	1.6.90
2010	1.12	CORE			/	1.6.90
2070	3.91	STAND			/	1.6.90
2075	3.85	STAND			/	1.6.90
2080	4.60	STAND			/	1.6.90
2090	1.48	STAND			/	1.6.90
2120	2.70	STAND			/	1.6.90
2130	4.80	STAND			/	1.6.90
2140	5.40	STAND			/	1.6.90
2670	10.40	STAND			/	1.6.90
2680	17.10	STAND			/	1.6.90
2690	24.80	STAND			/	1.6.90
2700	31.90	STAND			/	1.6.90
2710	13.50	STAND			/	1.6.90
2711	14.3	SUPPL			/ Fe3(OH)4+5	
2716	-3.56	STAND			/	1.6.90
2720	3.23	STAND			/	1.6.90
2725	3.85	STAND			/	1.6.90
3280	13.20	STAND			/	1.6.90
3290	-3.56	STAND			/	1.6.90
3300	3.37	STAND			/	1.6.90
3900	14.40	STAND			/	1.6.90
4851	3.55	CORE			/	1.6.90

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 4852      2.00 CORE                                   /                        1.6.90
 6770      3.34 8208                                   /                       21.3.91
 6820     -7.57 SUPPL                                  / 8208  Ni(NH3)2+2
 6860    -22.42 SUPPL                                  / 8208  Ni(NH3)6+2
 6900    -43.16 8208                                   /                       21.3.91
 7540     13.14 8208                                   /                       21.3.91
 7590     12.41 8208                                   /                       21.3.91
10030      2.15 CORE                                   /                        1.6.90
10035      3.85 STAND                                  /                        1.6.90
10040      2.84 CORE                                   /                        1.6.90
10050      1.06 CORE                                   /                        1.6.90
10060      1.96 CORE                                   /                        1.6.90
10070      2.16 CORE                                   /                        1.6.90
10080      2.20 CORE                                   /                        1.6.90
10090      1.84 CORE                                   /                        1.6.90
10100     -1.67 CORE                                   /                        1.6.90
10340     11.49 STAND                                  /                        1.6.90
10341     26.90 STAND                                  /                        1.6.90
10342     39.89 STAND                                  /                        1.6.90
10350     42.30 STAND                                  /                        1.6.90
10480      0.0  CORE                                   /                        1.6.90
11005      0.64 SUPPL                                  / 9102  SnCl+
11006      0.77 SUPPL                                  / 9102  SnCl2
11007      1.33 SUPPL                                  / 9102  SnCl3-
11101      0.48 SUPPL                                  / 9102  SnOH+
11120      4.4  7602                                   /                      26.10.90
11121      5.7  7602                                   /                      26.10.90
11480      4.6  7602                                   /                      26.10.90
11481      6.2  7602                                   /                      26.10.90
12530  -3.561   CORE                                   /                        1.6.90
12540  -5.738   CORE                                   /                        1.6.90
12550     3.85  CORE       81.30 8004                  /                       21.3.91
12560     3.18  CORE       38.50 8004                  /                       21.3.91
12561     3.9   CORE                                   /                       21.3.91
12570   -12.46  CORE                                   /                        1.6.90
12590    -5.33  CORE             NEA                   /                       21.3.91
12600     -3.49 NEA                                    /                       21.3.91
12610     -4.71 NEA                                    /                        1.6.90
12620     -2.68 NEA                                    /                        1.6.90
12710    -11.81 CORE                                   /                        1.6.90
12720    -17.93 CORE                                   /                        1.6.90
12725    -34.19 STAND                                  /                        1.6.90
12730      3.82 NEA                                    /                        2.9.90
13490     -3.36 CORE                                   /                        1.6.90
13500     15.77 NEA                                    /                        2.9.90
13501     19.60 NEA                                    /                        2.9.90
13540     -4.35 CORE                                   /                       21.3.91
13550     -5.12 CORE                                   /                        1.6.90
13555     -3.43 CORE                                   /                        1.6.90
13570      1.20 NEA                                    /                        2.9.90
13571      2.89 NEA                                    /                        2.9.90
13576     -4.54 NEA                                    /                        2.9.90
13578     -7.17 NEA                                    /                        2.9.90
13580      0.79 SUPPL                                  /  H2Se
13581      4.18 SUPPL                                  /  HSeO4-
13582     -3.59 NEA                                    /                        2.9.90
13583     -2.72 NEA                                    /                        2.9.90
13592     -6.53 CORE                                   /                       21.3.91
13594     11.5  SUPPL                                  /  Se-2
13595     13.36 CORE      -55.50 8004                  /                        1.6.90
15000     -9.68 CORE                                   /                       21.3.91
15040    -33.91 CORE                              SULPH.DEP.                    1.6.90
15041     -2.78 SUPPL                                  / 9201 8208              2.3 92
15042    -56.16 SUPPL                                  / 9201 8208              2.3 92
15050    -26.90 CORE                                   /                       21.3.91
15156    -46.8  8208                                   /                       21.3.91
15177   -126.27 8208                                   /                       21.3.91
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20000      2.30 CORE                             CALCITE (107.70 8301*)     1.6.90
20001      2.59 CORE                             ARAGONITE                  1.6.90
20010      0.11 CORE                             GYPSUM    (57.20 8301*)    1.6.90
20011      1.71 CORE                             ANHYDRITE  (4.40 8301*)    1.6.90
20020     -4.70 STAND                            FLUORITE  (74.40 8301*)    1.6.90
20030     25.60 8301*    510.00 8301*                /                     14.2.84
20031     -1.90 8301*    559.00 8301*                /                     14.2.84
20050     -4.50 7602*                                /                     14.2.84
20070     41.2  8301*    -11.00 8301*                /                     14.2.84
20130     31.00 CORE                             PORTLANDITE                1.6.90
20140      6.20 8301*     98.00 8301*                /                     14.2.84
20145      9.44 CORE                             DOLOMITEord.(200.00 8301 21.3.91
20149     11.09 CORE                             DOLOMITE disord.          21.3.91
20150      2.0  7602                                 /                     17.2.83
20200     27.10 CORE                             BRUCITE                    1.6.90
20210      0.40 CORE                             STRONTIANITE               1.6.90
20220      1.04 CORE                             CELESTITE                  1.6.90
20230     -1.0  7602                                 /                     17.2.83
20311     19.5  8301*    -67.    8301*               /                     14.2.84
20312     14.3  8301*    -23.    8301*           Goethite-B (old dH kept) 24.4.92
20313     30.6  8301*    -31.0   8301*               /                    26.10.90
20320      2.48 STAND                            SIDERITE (100.00 8301*)    1.6.90
20325     -4.91 STAND                            MELANTERITE                1.6.90
20350     21.7  8301*    -34.00 8301*                /                     14.2.84
20360     21.8  5201                                 /                     17.2.83
20370      1.43 STAND                            RHODOCHROSI. 102.008301*   1.6.90
20510     -0.70 CORE                             WITHERITE                  1.6.90
20520     -6.35 CORE                             BARITE                    21.3.91
20710      9.1  7102                             NiCO3                     21.3.91
20711     21.6  8208                             NiSO4                     21.3.91
20712     -1.1  7805                             NiSO4.6H2O                21.3.91
20713     -2.9  7805                             NiSO4.7H2O                21.3.91
20715     19.3  7903                             NiCl2                     21.3.91
20716      9.0  8208                             NiCl2.2H2O                21.3.91
20717      3.6  8208                             NiCl2.4H2O                21.3.91
20723     -3.16 7805                             NiS MILLERITE             21.3.91
20724    -12.9  7402                             NiS2                      21.3.91
20725      3.1  8208                             Ni3S2 HAEZLEWOODITE       21.3.91
20726      2.2  7402                             Ni3S4                     21.3.91
20731     15.7  7903                             NiF2                      21.3.91
20733     19.8  7903                             NiBr2                     21.3.91
20734     20.9  7903                             NiI2                      21.3.91
20735     36.4  7703                             Ni3(PO4)2                 21.3.91
20738     23.1  8403                             NiSiO4 OLIVINE            21.3.91
20739     24.7  8403                             NiSiO4 SPINEL             21.3.91
20745     -2.53 SUPPL                            NiFe2O4 TREVORITE 7805
20750     22.93 8208                             Ni(OH)2                   21.3.91
20751     23.93 8208                             NiO                       21.3.91
20818      0.02 8208                             NiCl2.6H2O                21.3.91
21144     -9.09 STAND                            CRYOLITE                   1.6.90
21160     -0.56 CORE                             KAOLINITE                  1.6.90
21180     22.80 STAND                            GIBBSITE cryst.            1.6.90
21181     24.50 STAND                            GIBBSITE microcryst.       1.6.90
21182     26.50 STAND                            Al(OH)3                    1.6.90
21232     89.06 SUPPL                            Sn2S3 9102
21233    113.37 SUPPL                            Sn3S4 9102
21440    -23.92 CORE       0.00 8301*            QUARTZ                     1.6.90
21441    -21.28 CORE       0.00 8301*            SiO2 am.                   1.6.90
21442   -22.652 CORE       0.00 8301*            CHALCEDONY                 1.6.90
21460     50.   8301*    -44.    8301*               /                     14.2.84
21480    100.64 STAND                            HAUSMANNITE                1.6.90
21491     65.11 STAND                            PYROLUSITE                 1.6.90
21530      3.89 CORE                             SULPH.DEP                 21.3.91
21540    -43.54 SUPPL                            C(0)
21550     21.30 SUPPL                            Fe(0)
21555    -34.76 SUPPL                            Mo(0)
21570    -35.6  8208                             Pd(0)                     21.3.91
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21580    -3.8  SUPPL            Se(0)   8208
21590    12.45 8402             Ni(0)                       21.3.91
22500    -0.4  7402             SeO2                        21.3.91
22501    34.2  7402             SeO3                        21.3.91
22502   -17.4  7402             Se2O5                       21.3.91
22505    31.4  7402             SeCl4                       21.3.91
22510    38.0  7402             CaSe                        21.3.91
22512     1.65 8208             CaSeO4.2H2O                 21.3.91
22520    28.0  7402             MgSe                        21.3.91
22530    33.0  7402             SrSe                        21.3.91
22540    25.0  7402             K2Se                        21.3.91
22541    11.2  8105             K2SeO3                      21.3.91
22542    -5.9  8105             K2SeO4                      21.3.91
22550    29.1  7402             Na2Se                       21.3.91
22551    14.5  7402             Na2Se2                      21.3.91
22552     7.2  8105             Na2SeO3                     21.3.91
22553    -0.05 8105             Na2SeO4                     21.3.91
22560   -10.9  7402             FeSe2                       21.3.91
22570    30.8  7402             BaSe                        21.3.91
22571     1.5  8208             BaSeO3                      21.3.91
22572    -2.3  8208             BaSeO4                      21.3.91
22580    33.5  7402             K2Se                        21.3.91
22581     2.0  8105             Li2SeO3                     21.3.91
22582     4.3  8105             Li2SeO4                     21.3.91
22590    17.3  7402             SiSe                        21.3.91
22700   -38.9  SUPPL            MoO2(cr)
22701    -7.89 SUPPL            MoO3(cr)
25000    -0.962 CORE            CO2 - GAS(90.70 8004)        1.6.90
25003     0.965 CORE            H2 - GAS                     1.6.90
25004     2.882 CORE            O2 - GAS                     1.6.90
25005     2.49  CORE            N2 - GAS                    21.3.91
25006     3.30  STAND           CH4 - GAS                    1.6.90
25022   -60.99  STAND           AS(O)                        1.6.90
25101   -64.72  STAND           CO32-/CH4                   21.3.91
25157  -174.9   STAND           NO3-/NH3                    21.3.91
25198   -36.3   STAND           N2/NH3                      21.3.91
31001     5.95 8002U                /                       17.2.83
31002    13.8  8002U                /                       17.2.83
31003    20.4  8002U                /                       17.2.83
31004    24.7  8002U                /                       17.2.83
31005    14.8  8002U                /                       17.2.83
31006    57.8  8002U                /                       17.2.83
31007   108.4  8002U                /                       17.2.83
31008    -1.4  8002                 /                       17.2.83
31009    -2.1  8002                 /                       17.2.83
31010    -3.   8002                 /                       17.2.83
31011    -3.8  8002                 /                       17.2.83
31012     -.2  8002                 /                       17.2.83
31013    20.9  8002                 /                       17.2.83
31014    15.75 8002                 /                       17.2.83
31015    12.3  8002                 /                       17.2.83
31016     3.7  8002                 /                       17.2.83
31017     7.5  8002                 /                       17.2.83
31018    11.7  8002                 /                       17.2.83
31019    13.1  8002                 /                       17.2.83
31020    -3.6  8002U                /                       17.2.83
31021   -10.25 8002U                /                       17.2.83
31022   -15.7  8002                 /                       17.2.83
31023    12.9  8002                 /                       17.2.83
31024    -3.8  8002                 /                       17.2.83
31025    13.7  8002                 /                       17.2.83
31501    27.2  8002                 /                       17.2.83
31502     7.5  8002U                /                       17.2.83
31503     2.8  8002                 /                       17.2.83
31504    -7.15 8002U                /                       17.2.83
31505    -2.   8002U                /                       17.2.83
32001    10.31 NEA                  /               (32001) 20.7.90
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32008     9.00 NEA          /               (32003) 20.7.90
32015    23.20 NEA          /               (32005) 20.7.90
32030     1.20 NEA          /               (32036) 20.7.90
32031     4.41 NEA          /               (32026) 20.7.90
32032    -9.15 NEA          /               (32027) 20.7.90
32045   -16.42 NEA          /               (NEW  ) 20.7.90
32060     4.65 NEA          /               (32012) 20.7.90
32061     8.37 NEA          /               (32013) 20.7.90
32090     1.91 NEA          /               (32016) 20.7.90
32091     3.59 NEA          /               (NEW  ) 20.7.90
32120     0.41 NEA          /               (32017) 20.7.90
32121     0.50 NEA          /               (32018) 20.7.90
32122     0.56 NEA          /               (32019) 20.7.90
32123     0.07 NEA          /               (32020) 20.7.90
32220     2.34 NEA          /                        2.9.90
32270     0.77 NEA          /               (NEW  ) 20.7.90
32271     2.13 NEA          /               (NEW  ) 20.7.90
32272     1.43 NEA          /               (NEW  ) 20.7.90
32502    20.87 NEA          /     A-UO3     (NEW  ) 20.7.90
32503    13.33 NEA          /     A-UO3     (NEW  ) 20.7.90
32505    20.20 NEA          /     B-UO3     (NEW  ) 20.7.90
32508    19.37 NEA          /     G-UO3     (32009) 20.7.90
32515    12.04 NEA          /     UO3.2H2O  (32011) 20.7.90
32516    13.59 NEA          /     UO2(OH)2  (32010) 20.7.90
32520    15.79 NEA          /     A-U3O8    (32057) 20.7.90
32521    47.26 NEA          /     A-U3O8 CF.32520   20.7.90
32530     1.12 NEA          /     UO2CO3    (32028) 20.7.90
32560    19.88 NEA          /     UO2SO4    (32015) 20.7.90
32562     8.45 NEA          /     UO2SO4    (NEW  ) 20.7.90
32563     7.29 NEA          /     UO2SO4    (NEW  ) 20.7.90
32564     6.48 NEA          /     UO2SO4    (NEW  ) 20.7.90
32590    26.20 NEA          /     UO2CL2    (NEW  ) 20.7.90
32591    18.94 NEA          /     UO2CL2    (NEW  ) 20.7.90
32593    11.16 NEA          /     UO2CL2    (NEW  ) 20.7.90
32600     7.93 NEA          /     UO2CLOH   (NEW  ) 20.7.90
32605    85.55 NEA          /     UCL6      (NEW  ) 20.7.90
32610    33.68 NEA          /     (UO2)2CL3 (NEW  ) 20.7.90
32620     8.65 NEA          /     UO2F2     (NEW  ) 20.7.90
32622     3.06 NEA          /     UO2F2     (NEW  ) 20.7.90
32626     7.53 NEA          /     UO2FOH    (NEW  ) 20.7.90
32627     5.15 NEA          /     UO2FOH    (NEW  ) 20.7.90
32630    35.84 NEA          /     UOF4      (NEW  ) 20.7.90
32632    62.72 NEA          /     UF6(cr)   (NEW  ) 20.7.90
32635    43.95 NEA          /     U2O3F6    (NEW  ) 20.7.90
32638    60.83 NEA          /     U3O5F8    (NEW  ) 20.7.90
32640    29.74 NEA          /     UO2BR2    (NEW  ) 20.7.90
32641    21.93 NEA          /     UO2BR2    (NEW  ) 20.7.90
32643    14.65 NEA          /     UO2BR2    (NEW  ) 20.7.90
32645     9.54 NEA          /     UO2BROH   (NEW  ) 20.7.90
32680    -5.92 NEA          /     UO2HPO4   (NEW  ) 20.7.90
32690    31.43 NEA          /     UO23PO42  (NEW  ) 20.7.90
32692     6.46 NEA          /     UO23PO42  (32023) 20.7.90
32760    19.55 NEA          /     UO2(NO3)2 (NEW  ) 20.7.90
32761    13.06 NEA          /     UO2(NO3)2 (NEW  ) 20.7.90
32762     6.16 NEA          /     UO2(NO3)2 (NEW  ) 20.7.90
32763     2.36 NEA          /     UO2(NO3)2 (NEW  ) 20.7.90
32764    -4.71 NEA          /     UO2(NO3)2 (NEW  ) 20.7.90
32800    31.54 NEA          /     CAUO4     (32059) 20.7.90
32805    47.96 NEA          /     MGUO4     (32060) 20.7.90
32810    36.32 NEA          /     B-SRUO4   (NEW  ) 20.7.90
32820    41.19 NEA          /     A-NA2UO4  (32058) 20.7.90
32821    41.20 NEA          /     NA2U2O7   (NEW  ) 20.7.90
32830    30.13 NEA          /     BAUO4     (NEW  ) 20.7.90
32835    44.19 NEA          /     CS2U2O7   (NEW  ) 20.7.90
32836    41.71 NEA          /     CS2U4O12  (NEW  ) 20.7.90
32840    44.48 NEA          /     LI2UO4    (NEW  ) 20.7.90
32850    42.99 NEA          /     RB2UO4             2.9.90
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34007     4.7  7602                          /                    26.10.90
34008     8.0  7602                          /                    26.10.90
35001    10.81 8004     -3.90 8004           /                     17.2.83
35004     8.58 8004    -11.80 8004           /                     17.2.83
35006    13.83 8004    -53.90 8004           /                     17.2.83
35007    33.40 8004    -97.30 8004           /                     17.2.83
35009     6.47 8004     34.50 8004           /                     17.2.83
35014     2.77 8004    131.30 8004           /                     17.2.83
35016    -4.97 8004    114.40 8004           /                     17.2.83
35017    -1.29 8004     48.30 8004           /                     17.2.83
35018    -3.67 8004     55.80 8004           /                     17.2.83
35019    -6.97 8004     20.00 8004           /                     17.2.83
35020    -9.61 8004     96.20 8004           /                     17.2.83
35023     4.80 8004    125.70 8004           /                     17.2.83
35024    -0.96 8004    142.40 8004           /                     17.2.83
36000   -22.08 SUPPL    17.37 8004           /                     2.3.92
36001    16.57 8004    -41.40 8004           /                     17.2.83
36002    10.20 8004    -20.80 8004           /                     17.2.83
37000   -46.24 SUPPL    -5.93 8004           /                     2.3.92
37001    11.54 8004    -19.40 8004           /                     17.2.83
37002    17.81 8004    -24.70 8004           /                     17.2.83
37003    23.07 8004    -24.80 8004           /                     17.2.83
37004    26.11 8004    -56.90 8004           /                     17.2.83
37005    12.45 8004     -5.10 8004           /                     17.2.83
37006    16.47 8004    -25.60 8004           /                     17.2.83
37008   -44.62 8004    110.9  8004           / old Pu(CO3)+2 set to typ 6
37009     2.98 8004     78.40 8004           /                     17.2.83
37010     9.88 8004     99.70 8004           /                     17.2.83
37012     4.16 8004    108.60 8004           /                     17.2.83
37014     5.90 8004     27.80 8004           /                     17.2.83
37015    23.90 8004    159.7  8004           /                     17.2.83
37017     1.26 8004    282.40 8004           /                     17.2.83
37019     6.22 8004    117.60 8004           /                     17.2.83
37020     -.61 8004    229.10 8004           /                     17.2.83
37025    30.08 8004    -90.70 8004           /                     17.2.83
37026   -11.69 8004    407.10 8004           /                     17.2.83
37027   -31.68 8004    540.10 8004           /                     17.2.83
38000   -13.29 SUPPL    -2.93 8004           /                     2.3.92
38001    12.82 8004     -1.30 8004           /                     17.2.83
38005    86.12 8004      4.80 8004           /                     17.2.83
38006    35.45 8004    -14.30 8004           /                     17.2.83
38010     3.49 8004     83.90 8004           /                     17.2.83
38014    11.07 8004    123.40 8004           /                     17.2.83
38016     3.48 8004    102.00 8004           /                     17.2.83
39000    24.40 SUPPL                         /                      2.3.92
39500    26.08 NEA                           /   UOCL     (NEW  ) 20.7.90
39590    29.71 NEA                           /   UCL3     (NEW  ) 20.7.90
39591    31.69 NEA                           /   UBRCL2   (NEW  ) 20.7.90
39592    35.47 NEA                           /   UBR2CL   (NEW  ) 20.7.90
39620    -1.66 NEA                           /   UF3      (NEW  ) 20.7.90
39630    36.96 NEA                           /   UBR3     (NEW  ) 20.7.90
39640    45.90 NEA                           /   UI3      (NEW  ) 20.7.90
40000   -32.93 NEA                           /                    20.7.90
40001    11.21 NEA                           /            (40001) 20.7.90
40034    -4.78 NEA                           /            (NEW  ) 20.7.90
40060     1.90 NEA                           /            (40009) 20.7.90
40061     7.79 NEA                           /            (40010) 20.7.90
40090    -4.54 NEA                           /            (40011) 20.7.90
40120    -1.35 NEA                           /            (40013) 20.7.90
40121    -0.84 NEA                           /            (40014) 20.7.90
40122     0.12 NEA                           /            (40015) 20.7.90
40123    -0.87 NEA                           /            (40029) 20.7.90
40290    -6.45 NEA                           /            (NEW  ) 20.7.90
40291    -4.30 NEA                           /            (NEW  ) 20.7.90
40500    18.61 NEA                           /   UO2      (40007) 20.7.90
40560    23.95 NEA                           /   U(SO4)2  (NEW  ) 20.7.90
40562    16.71 NEA                           /   U(SO4)2  (NEW  ) 20.7.90
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40564     8.09 NEA                                      /   U(SO4)2   (NEW   ) 20.7.90
40590    57.55 NEA                                      /   UCL4      (NEW   ) 20.7.90
40592    34.50 NEA                                      /   UOCL2     (NEW   ) 20.7.90
40595    17.77 NEA                                      /   UCLF3     (NEW   ) 20.7.90
40596    64.59 NEA                                      /   UCLBR3    (NEW   ) 20.7.90
40597    68.08 NEA                                      /   UCLI3     (NEW   ) 20.7.90
40600    31.09 NEA                                      /   UCL2F2    (NEW   ) 20.7.90
40601    62.22 NEA                                      /   UCL2BR2   (NEW   ) 20.7.90
40602    64.75 NEA                                      /   UCL2I2    (NEW   ) 20.7.90
40605    44.18 NEA                                      /   UCL3F     (NEW   ) 20.7.90
40606    59.94 NEA                                      /   UCL3BR    (NEW   ) 20.7.90
40607    59.99 NEA                                      /   UCL3I     (NEW   ) 20.7.90
40620     4.40 NEA                                      /   UF4       (40016) 20.7.90
40622    -5.81 NEA                                      /   UF4       (40032) 20.7.90
40624    17.09 NEA                                      /   UOF(OH)   (NEW   ) 20.7.90
40625    15.54 NEA                                      /   UOF(OH)   (NEW   ) 20.7.90
40626    10.31 NEA                                      /   UOF2      (NEW   ) 20.7.90
40627     7.54 NEA                                      /   UOF2      (NEW   ) 20.7.90
40630    65.66 NEA                                      /   UBR4      (NEW   ) 20.7.90
40632    34.95 NEA                                      /   UOBR2     (NEW   ) 20.7.90
40640    71.59 NEA                                      /   UI4       (NEW   ) 20.7.90
40680    -8.26 NEA                                      /   U(HPO4)2  (40017) 20.7.90
41000    -1.46 NEA                                      /                     20.7.90
41505    17.42 NEA                                      /   B-U3O7    (NEW   ) 20.7.90
41506    48.65 NEA                                      /   B-U3O7 CF.41505   20.7.90
41510    35.50 NEA                                      /   B-U4O9    (40039) 20.7.90
41511    66.97 NEA                                      /   B-U4O9 CF.41510   20.7.90
41590     5.31 NEA                                      /   UO2CL     (NEW   ) 20.7.90
41593    18.54 NEA                                      /   UOCL3     (NEW   ) 20.7.90
41595    55.05 NEA                                      /   UCL5      (NEW   ) 20.7.90
41600     2.38 NEA                                      /   U5O12CL   (NEW   ) 20.7.90
41610    60.80 NEA                                      /   U2O2CL5   (NEW   ) 20.7.90
41620    13.12 NEA                                      /   A-UF5     (NEW   ) 20.7.90
41621    11.23 NEA                                      /   B-UF5     (NEW   ) 20.7.90
41625    11.21 NEA                                      /   U2F9      (NEW   ) 20.7.90
41629    18.71 NEA                                      /   U4F17     (NEW   ) 20.7.90
41633    35.73 NEA                                      /   UOBR3     (NEW   ) 20.7.90
41635    59.77 NEA                                      /   UBR5      (NEW   ) 20.7.90
41750    70.22 NEA                                      /   NA3UO4    (41004) 20.7.90
42000     6.91 SUPPL                                    /                     2.3.92
43000    35.75 SUPPL                                    /                     2.3.92
44000   -28.11 SUPPL                                    /                     2.3.92
47500   -56.38 SUPPL                                    /   Tc(0)
47520    -8.1  SUPPL                                    /   Tc(II,III)3O4  9102
47552    48.6  SUPPL                                    /   Tc(IV)S2  9102
47559   -16.11 SUPPL                                    /   TcO  9102
47560    -8.1  SUPPL                                    /   Tc(OH)2  9102
48020     4.9  7602                                     /                   26.10.90
48021     7.1  7602                                     /                   26.10.90
49030     4.9  7602                                     /                   26.10.90
49031     7.0  7602                                     /                   26.10.90
52090    -4.74 8208                                     /                     21.3.91
52093    -7.30 8208                                     /                     21.3.91
52133   -11.4  8208                                     /                     21.3.91
52500     6.6  7003                                     /   Pd(OH)2           21.3.91
52505    12.3  7601                                     /   PdO /             21.3.91
52590     2.9  7903                                     /   PdCl2             21.3.91
52630    -2.7  5201                                     /   PdBr2             21.3.91
52640   -23.7  7903                                     /   PdI2              21.3.91
52670   -49.2  7402                                     /   PdS               21.3.91
52671   -47.6  7402                                     /   PdS2              21.3.91
52770   -61.3  8208                                     /   Pd(SCN)2          21.3.91
55500   -95.3  9102                                     /   Am2O3(s) ?????
55505    13.1  9102                                     /   AmOHCO3(s)
55510    10.5  9102                                     /   Am2(CO3)3(s)
69001    14.46 8501                                     /   RaOH+
69010     1.07 CORE                                     /   RaCO3 8501
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69015      1.30 CORE                                /     RaSO4 8501
69020      0.5  8501                                /     RaCl+
69510     -2.8  8501                                /     RaCO3(s)
69520     -9.40 CORE                                /     RaSO4(s) 8501
99199    -0.965 CORE                                /     H2(AQ)/H+            1.6.90
99200  -133.75  CORE                                /     O2/H2O               1.6.90
```

E.4 List of References Cited in the Data Files of Appendix E.2 and Appendix E.3

This Appendix presents the reference list supplied with the database of the code MIN_SURF (Berner, 1993). The data files in Appendix E.2 ($\log_{10} K^\circ$) and Appendix D.3 ($\Delta_r H^\circ$ and $\Delta_r C_p{}^\circ$) contain a column with a reference code consisting of 4 digits plus a 1-digit qualifier. The first 2 digits of the reference code refer to the year of publication. The qualifier contains information on deviations from standard and/or reference conditions (A-I), on the quality of the value (U, X, *) if it has been assessed, or on ionic strength corrections performed on the original data (Z, Y), see the list below. Reference codes consisting of letters, e.g. `CORE`, `SUPPL`, `STAND`, `NEA`, etc., are explained at the end of this Appendix.

THE FOLLOWING QUALIFIERS 'Q' ARE USED IN THE THERMODYNAMIC DATABASE (X = IONIC STRENGHT, T = TEMPERATURE) IN THE FIFTH POSITION OF THE REFERENCE FIELD:

	X = 0	X ≤ 0.5	X = 1.0	X = 2.0	X = 3.0
T = 25	BLANK	A	B	C	D
T ≠ 25	E	F	G	H	I

AND:
U - UNCERTAIN
X - LACK OF X/T - INDICATION
* - GUESS

NEW:
Z - VALUES ARE CORRECTED TO IONIC STRENGHT I=0 USING THE DAVIES EQUATION.

Y - VALUES ARE CORRECTED TO IONIC STRENGHT I=0 USING THE SPECIFIC ION-INTERACTION THEORY (SIT).
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***** I = 7 !!!

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OR I=0.5 TO I=0 WITH S.I.T (SPECIFIC ION INTERACTION THEORY)
USING E (AM+3, CLO4-) = 0.47
E (SO4-2,NA+) =-0.12
E (AMSO4+,CLO4-) = 0.31
E (EU(SO4)2-, NA+) = 0.0
E (F-, NA+) = 0.02
E (AMF+2, CLO4-) = 0.3
E (AMF2+, CLO4-) = 0.3
E: ION INTERACTION COEFFICIENT
SEE PSI-REPORT NO. ?? (TO BE PUBLISHED)

7602Z VALUES FROM REFERENCE 7602; IONIC STRENGHT CORRECTION
TO ZERO IONIC STRENGHT MADE BY APPLYING THE
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TO ZERO IONIC STRENGHT MADE BY APPLYING THE
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CONCERNS ONLY CITRATE EQUILIBRIA

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TO I=0 WITH S.I.T (SPECIFIC ION INTERACTION THEORY)
USING E (EU+3, CLO4-) = 0.49
E (CO3-2,NA+) =-0.05
E (EUCO3+,CLO4-) = 0.31
E (EU(CO3)2-, NA+) = 0.0
FOR EU+3, SM+3, ND+3, CE+3, LA+3
E (AMCO3+,CLO4-) = 0.31
E (AM(CO3)2-,NA+) = 0.0
E (AM+3, CLO4-) = 0.47
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SEE PSI-REPORT NO. ?? (TO BE PUBLISHED)

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GEOCHMIM. COSMOCHIM. ACTA, **49** (1985) 1593.

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USING
E (AM+3, CLO4-) = 0.47
E (OH-, NA+) = 0.04
E (AMOH+2,CLO4-) = 0.4
E (AM(OH)2+,CLO4-) = 0.3
E (CO3-2,NA+) =-0.05
E (AMOH(CO3)2-2,NA+) = 0.06
E (AM(OH)2CO3-,NA+) = 0.0
E (AMCO3+,CLO4-) = 0.31
E (AM(CO3)2-,NA+) = 0.0
E (AM(CO3)3-3,NA+) =-0.25
E: ION INTERACTION COEFFICIENT
SEE PSI-REPORT NO. ?? (TO BE PUBLISHED)

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IN: MELCHIOR D.C. AND BASSET R.L. EDS., CEMICAL MODELING OF AQUEOUS SYSTEMS II: WASHINGTON, D.C.
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THESE DATA SERVE AS A BASIS FOR THE DATA COMPILED IN REF. 9101

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9005 EIKENBERG J.,
ON THE PROBLEM OF SILICA SOLUBILITY AT HIGH PH

PSI REPORT NR. 74, WUERENLINGEN/VILLIGEN, 1990.

THE RECOMMENDED USE OF THE SILICA EQUILIBRIA
IN THE PRESENT DATABASE DEPENDS ON THE CONCENTRATION
LEVEL OF SILICA IN SOLUTION AND ON THE PH-VALUE:

AT PH-LEVELS BELOW 10 IT IS SUFFICIENT TO USE THE EQUILIBRIA
NUMBERED WITH 12710 AND 12720 (H4SIO4, H3SIO4-).

IT IS PROPOSED TO INCLUDE THE EQUILIBRIA NUMBERED WITH
12712, 12713, 12715, 12716, 12718, 12719, SIMULTANEOUSLY IN ORDER
TO DESCRIBE THE SPECIATION OF SILICA UP TO A PH OF 11.2 IF
AMORPHOUS SILICA IS THE SOLUBILITY LIMITING PHASE. (POLYMERIC
SPECIES)

THE (POLYMERIC) EQUILIBRIA MAY BE USED UP TO A PH
OF 12.2 IF QUARTZ LIMITS SILICA SOLUBILITY.

AT SILICA LEVELS AROUND 10**-5 TO 10**-6 (FOR EXAMPLE
CSH-GEL OF HYDRATED CEMENT) THE POLYMERIC EQUILIBRIA MAY BE USED
UP TO A PH OF 13.

9006 VAN LOON L.R., KOPAJTIC Z.
COMPLEXATION OF CU2+, NI2+ AND UO22+ BY RADIOLYTIC DEGRADATION
PRODUCTS OF BITUMEN
PSI-BERICHT NO 66, 39 P., WUERENLINGEN UND VILLIGEN 1990.

9101 PEARSON, JR. F.J., BERNER U.
NAGRA THERMOCHEMICAL DATABASE, I. CORE DATA
NATIONAL COOPERATIVE FOR THE DISPOSAL OF RADIOACTIVE WASTE (NAGRA)
REPORT NTB 91-17, WETTINGEN/SWITZERLAND, 1991.
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NATIONAL COOPERATIVE FOR THE DISPOSAL OF RADIOACTIVE WASTE (NAGRA)
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HATCHES - A THERMODYNAMIC DATABASE AND MANAGEMENT SYSTEM
RADIOCHIMICA ACTA 52/53 421 (1991)
HATCHES DATABASE VERSION 3.0

UPDATED JUNE 1990 BY U.BERNER
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DURING THIS UPDATING PROCEDURE A QUALITY ASPECT HAS BEEN
INTRODUCED INTO THE PRESENT VERSION OF THE DATABASE.
ITS ASSUMED THAT THE DATA DESCRIBING THE BASIC
GROUNDWATER CHEMISTRY ARE NOW SUFFICIENTLY WELL KNOWN
AND ARE AVAILABLE IN A GOOD QUALITY. THESE DATA ARE
REFERENCED WITH "CORE" AND ARE MAINLY TAKEN FROM
REFERENCES 9001 (MAIN SOURCE), 9101 AND "NEA".

UPDATED MARCH 1991 BY U.BERNER
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THIS UPDATE OF THE DATABASE HAS SEVERAL REASONS:

1. THE SULPHIDE SYSTEM IS NOW EXPRESSED WITH HS- AS THE BASIC

COMPONENT. THEREFORE, ALL EQUILIBRIA CONTAINING S-2 HAVE LOG K-VALUES DIFFERING FROM FORMER VERSIONS OF THE DATABASE.

2. DATA ON PD, NI AND SE FROM REFERENCE 8902 ARE INCLUDED IN THE DATABASE. REFERENCE 8902 IS NOT CITED IN THE DATABASE, SINCE THE ORIGINAL REFERENCE IS GIVEN FOR PARTICUALR EQUILIBRIA.
3. SOME OF THE "CORE"-EQULIBRIA HAD TO BE CHANGED (DIGIT CORRECTIONS) IN ORDER TO ACHIEVE COMPLETE AGREEMENT WITH THE VALUES GIVEN IN REFERENCE 9101.
4. FINAL CHANGES IN THE QUALITY PARAMETERS "CORE" AND "SUPPL"
5. CLEARING OF TYPOGRAPHICAL ERRORS

CORE	DATA FROM REFERENCE 9001, 9101 OR "NEA" WHICH ARE ASSUMED TO BE OF GOOD QUALITY. THESES DATA WILL NOT BE SUBJECT OF FURTHER UPDATING DURING AN APPROPRIATE PERIOD OF TIME (SAY 5 YEARS).
SUPPL	DATA FROM REFERENCE 9101.
STAND	SAME SOURCES AS "CORE" BUT NOT INCLUDED IN THE BASIC CORE DATA. A MODERATE TO GOOD QUALITY IS ASSIGNED TO THESE DATA. DATA WITH THE REFERENCE "STAND" ARE THE SOURCE FOR THE "SUPPL" DATA. AFTER FINAL REVISION "STAND" WILL BE CHANGED TO "SUPPL"
DEP.	EQUILIBRIA CHANGED DUE TO DEPENDENCY ON CHANGED CORE DATA (CONCERNS MAINLY CHANGES IN PROTONATION CONSTANTS OF ANIONS). THIS CHANGE KEEPS THE DEPENDENT DATA CONSISTENT WITH FORMER VERSIONS OF THE DATABASE SEE ALSO THE FILE "DEPENDENT.EQUILIBRIA".
NEA	GRENTHE I., FUGER J., LEMIRE R.J., MULLER A.B., NGUYEN-TRUNG C., WANNER H. NEA -TDB, CHEMICAL THERMODYNAMICS OF URANIUM NUCLEAR ENERGY AGENCY (OECD), GIF-SUR-YVETTE, FRANCE FINAL DRAFT OF MARCH 1990.
NEA1	GRENTHE I., FUGER J., LEMIRE R.J., MULLER A.B., NGUYEN-TRUNG C., WANNER H. NEA -TDB, CHEMICAL THERMODYNAMICS OF URANIUM NUCLEAR ENERGY AGENCY (OECD), GIF-SUR-YVETTE, FRANCE DRAFT VERSION OF JUNE 1991.
SULPH	DURING THE UPDATE OF 23.3.91 THE BASIC SPECIES FOR THE SULPHIDE SYSTEM HAS BEEN CHANGED FROM S-2 TO HS- . IN A FORMER VERSION (OCTOBER 1990) ALL SULPHIDE EQUILIBRIA HAD BEEN CHANGED BY 5.1 LOG K UNITS PER S-2 BASED ON A 5.1 LOG K - CHANGE IN THE EQUILIBRIUM S-2 + H+ = HS- . THIS CHANGE IS BACK-CORRECTED IN THE 1991-VERSION OF THE DATABASE. ALL SUPLPHIDE EQUILIBRIA ARE NOW EXPRESSED USING HS- AS THE BASIC SULPHIDE SPECIES. TO PERFORM THE CORRECTION IT WAS ASSUMED THAT ALL EQUILIBRIA CONTAINING THE SULPHIDE ION S-2 WERE ORIGINALLY BASED ON LOG K = 13.9 FOR THE REACTION S-2 + H+ = HS- AS GIVEN IN REFERENCE 7602.