

Technical Report 09-03

Sorption Data Bases for Generic Swiss Argillaceous Rock Systems

September 2010

M.H. Bradbury, B. Baeyens and T. Thoenen

Paul Scherrer Institut, Villigen PSI

**National Cooperative
for the Disposal of
Radioactive Waste**

Hardstrasse 73
CH-5430 Wettingen
Switzerland
Tel. +41 56 437 11 11

www.nagra.ch

Technical Report 09-03

Sorption Data Bases for Generic Swiss Argillaceous Rock Systems

September 2010

M.H. Bradbury, B. Baeyens and T. Thoenen

Paul Scherrer Institut, Villigen PSI

**National Cooperative
for the Disposal of
Radioactive Waste**

Hardstrasse 73
CH-5430 Wettingen
Switzerland
Tel. +41 56 437 11 11

www.nagra.ch

This report was prepared on behalf of Nagra. The viewpoints presented and conclusions reached are those of the author(s) and do not necessarily represent those of Nagra.

ISSN 1015-2636

"Copyright © 2010 by Nagra, Wettingen (Switzerland) / All rights reserved.

All parts of this work are protected by copyright. Any utilisation outwith the remit of the copyright law is unlawful and liable to prosecution. This applies in particular to translations, storage and processing in electronic systems and programs, microfilms, reproductions, etc."

Abstract

In Switzerland the site selection procedure for both HLW and L/ILW repositories is specified by the Swiss Federal Office of Energy in the Sectoral Plan for Deep Geological Repositories. In the forthcoming stage 2 of this plan, potential sites will be identified within regions previously selected based on the presence of suitable host rocks, namely Opalinus Clay, 'Brauner Dogger', Effingen Member and Helvetic Marl. Preliminary safety analyses are an integral part of this procedure, and require, amongst other information, the radionuclide sorption properties of the host rock. This report describes a methodology to develop a Generic Rock Sorption Data Base (GR-SDB) for argillaceous rocks. The method will be used to compile specific SDBs for the above mentioned host rocks.

Arguments are presented that the main factor influencing sorption on argillaceous rocks is the phyllosilicate mineral content. These minerals are particularly effective at binding metals to their surfaces by cation exchange and surface complexation. Generally, the magnitude of sorption is directly correlated with the phyllosilicate content (2:1 type clays: illite/smectite/illite-smectite mixed layers), and this parameter best reflects the sorption potential of a given mineral assembly. Consequently, sorption measurements on illite were preferably used as source data for the GR-SDB.

The second component influencing radionuclide sorption is the porewater chemistry. In the present report, generic water compositions were extracted from the analytical ranges of deep ground waters in various sedimentary formations in Switzerland. In order to cover the range of ionic strength (I) and pH values of Swiss ground waters in argillaceous rocks, five types of generic water compositions were defined, combining low, intermediate and high values of ionic strength and pH.

The GR-SDB for in situ conditions was derived using conversion factors (CF). As the name implies, these factors were used to convert the (predominantly) illite sorption values into sorption values valid for the defined generic conditions with regard to mineralogy and porewater composition. Conversion factors were used to adapt sorption values to mineralogy (CF_{\min}), to pH value (CF_{pH}) and to radionuclide speciation (CF_{spec}). Finally, a Lab→Field conversion factor ($CF_{\text{Lab} \rightarrow \text{Field}}$) was applied to adapt sorption data measured in dispersed systems (batch experiments) to intact rock under in-situ conditions.

Calcareous rock is used in safety analyses as being representative of a clay rock which has lost most of its favorable sorption properties due to near-field effects such as alteration by an alkaline plume and subsequent processes. It is assumed that calcareous rocks do not contain any significant quantities of phyllosilicates and that only uptake data on calcite are relevant. Sorption data on calcite are extremely sparse and the uptake mechanisms are not fully understood. However, when the existing sorption data ($\log R_d$ values) are plotted against the ionic radii of the respective metals, an acceptable linear correlation between these two quantities is found. This so-called linear free energy relationship is used to complement the sparse experimental data in the SDB for calcareous systems.

Zusammenfassung

In der Schweiz ist das Auswahlverfahren für geologische Tiefenlager für schwach- und mittelaktive sowie für hochaktive Abfälle durch das Bundesamt für Energie im Sachplan geologische Tiefenlager festgeschrieben. In der bevorstehenden Etappe 2 dieses Sachplans werden innerhalb der früher ausgewählten Standortregionen anhand der vorhandenen geeigneten Wirtgesteine Opalinuston, 'Brauner Dogger', Effinger Schichten und Mergel des Helvetikums potenzielle Standorte identifiziert. Provisorische Sicherheitsanalysen sind integraler Bestandteil des Verfahrens und benötigen unter anderem Informationen über die Sorptionseigenschaften der Wirtgesteine für Radionuklide. In diesem Bericht wird eine Methode zur Erarbeitung einer Generischen Sorptionsdatenbank (GR-SDB) für Tongesteine beschrieben. Diese Methode soll genutzt werden, um spezifische Sorptionsdatenbanken für die erwähnten Wirtgesteine zusammenzustellen.

Es wird argumentiert, dass die Sorption in Tongestein hauptsächlich durch den Gehalt an Schichtsilikaten beeinflusst wird. Diese Minerale können Metalle durch Kationenaustausch und Oberflächenkomplexierung sehr effektiv auf ihren Oberflächen binden. Generell ist die Stärke der Sorption direkt mit dem Gehalt an Schichtsilikaten korreliert (2:1 Tonminerale: Illit, Smektit und Illit-Smektit-Wechselagerungen). Dieser Gehalt beschreibt das Sorptionspotenzial einer Mineralassoziation am besten. Daher stellen Sorptionsmessungen auf Illit eine bevorzugte Datenquelle für die GR-SDB dar.

Eine zweite Komponente, welche die Sorption von Radionukliden beeinflusst, ist die Porenwasserchemie. Im vorliegenden Bericht wurden aus der analytischen Spannweite tiefer Grundwässer verschiedener sedimentärer Formationen der Schweiz generische Wasserzusammensetzungen ausgewählt. Um den Bereich der Ionenstärke (I) und des pH-Wertes der Grundwässer in Tonformationen abzudecken, wurden durch Kombination niedriger, mittlerer und hoher Werte für Ionenstärke und pH-Wert fünf Typen generischer Wasserzusammensetzungen definiert.

Für die Erstellung der GR-SDB für In-situ-Bedingungen wurden Konvertierungsfaktoren (CF) genutzt. Man verwendet diese Faktoren, um unter Berücksichtigung der Mineralogie und der Porenwasserzusammensetzung aus den vorwiegend auf Illit basierenden Sorptionsdaten solche für die definierten generischen Bedingungen zu berechnen. Konkret werden die Konvertierungsfaktoren benutzt, um die Sorptionswerte an die Mineralogie (CF_{Min}), den pH-Wert (CF_{pH}) und die Speziation der Radionuklide (CF_{Spec}) anzupassen. Weiterhin wurde ein Faktor Labor→Feld ($CF_{\text{Lab} \rightarrow \text{Field}}$) verwendet, um die in Suspension (Batchversuche) gemessenen Sorptionsdaten auf intaktes Gestein unter In-situ-Bedingungen zu übertragen.

Kalkstein repräsentiert in der Sicherheitsanalyse eine starke Vereinfachung für einen Tonstein, der durch Nahfeldeffekte, wie Alteration durch eine Hoch-pH-Fahne und dadurch ausgelöste Folgeprozesse, seine günstigen Sorptionseigenschaften verloren hat. Es wird angenommen, dass der Kalkstein keine signifikanten Anteile an Schichtsilikaten enthält und dass nur die Sorptionseigenschaften des Calcit von Bedeutung sind. Es existieren nur wenige Sorptionsdaten für Calcit und die Sorptionsmechanismen sind noch nicht völlig verstanden. Trägt man jedoch die vorhandenen Sorptionsdaten ($\log R_d$) gegen die Ionenradien der jeweiligen Metalle auf, findet man eine akzeptable lineare Korrelation zwischen beiden Grössen. Diese sogenannte Lineare-Freie-Energie-Beziehung wird benutzt, um die wenigen experimentellen Daten in der Sorptionsdatenbank für Kalkstein zu vervollständigen.

Résumé

En Suisse, la procédure de sélection des sites pour le stockage géologique des déchets de haute activité (DHA), ainsi que de faible et moyenne activité (DFMA), a été définie par l'Office fédéral de l'énergie (OFEN) dans la Conception générale du plan sectoriel « Dépôts en couches géologiques profondes ». Au cours de l'étape 2 du plan sectoriel, des sites potentiels seront identifiés au sein des régions d'implantation sélectionnées à l'étape 1 en raison du contexte géologique favorable. Les roches d'accueil jugées adéquates sont les argiles à Opalinus, le 'Brauner Dogger' (« Dogger brun »), les Couches d'Effingen et les formations marneuses de l'Helvétique. Pour les analyses préliminaires de sûreté requises par la procédure de sélection, on a notamment besoin de données sur la rétention des radionucléides par la roche d'accueil. Ce rapport décrit une méthode pour élaborer une base de données de sorption générique (« GR-SDB ») pour des roches argileuses. Cette méthode sera utilisée pour compiler les bases de données de sorption spécifiques aux roches d'accueil potentielles.

La teneur en phyllosilicates est présentée comme le principal facteur influant sur la sorption dans les roches argileuses. Ces minéraux sont particulièrement aptes à retenir les métaux par le biais de mécanismes d'échange cationique et de complexation de surface. D'une façon générale, le degré de sorption est directement lié à la teneur en phyllosilicates (du type 2:1: illite, smectite, interstratifiés illite/smectite). C'est ce paramètre qui traduit le mieux le potentiel de sorption d'un assemblage de minéraux donné. Par conséquent, les valeurs de sorption obtenues pour l'illite ont été utilisées en priorité comme données d'entrée pour la base de données de sorption générique.

Un second facteur ayant un impact sur la sorption est la composition chimique des eaux interstitielles. Dans ce rapport, des compositions d'eaux interstitielles génériques ont été choisies à partir d'une compilation de données analytiques des eaux souterraines de différentes formations géologiques suisses. Afin de couvrir la plage de force ionique (I) et de pH des eaux souterraines suisses pour les différentes roches argileuses, cinq eaux souterraines génériques ont été définies pour chaque type de roche en combinant des valeurs faibles, intermédiaires et élevées de force ionique et de pH.

Les bases de données de sorption génériques pour les conditions in situ ont été élaborées en utilisant des facteurs de conversion (CF). Ces facteurs permettent de convertir les valeurs de sorption obtenues pour l'illite en valeurs de sorption représentatives de la minéralogie et de la chimie des eaux définies pour les conditions génériques données. Les facteurs de conversion sont utilisés pour ajuster les valeurs de sorption en fonction de la minéralogie (CF_{\min}), des valeurs pH (CF_{pH}) et de la spéciation (CF_{spec}) des radionucléides. Un facteur de conversion Laboratoire→Roche ($CF_{\text{Lab} \rightarrow \text{Field}}$) a été introduit afin d'ajuster les données de sorption provenant d'expériences en suspension (« en batch ») aux conditions in situ de la roche intacte.

Dans les analyses de sûreté, on utilise la roche calcaire pour représenter une roche argileuse altérée par des réactions chimiques telles que la perturbation alcaline, et qui a ainsi perdu ses propriétés de sorption. On part du principe que la teneur en phyllosilicates de la roche calcaire est très faible et que seule la rétention par la calcite entre en ligne de compte. Pour la calcite, il existe très peu de données de sorption expérimentales et les mécanismes de rétention sont encore mal compris. Toutefois en confrontant les valeurs de sorption ($\log R_d$) au rayon ionique des métaux respectifs, on trouve entre ces deux mesures une corrélation linéaire acceptable. Cette corrélation linéaire est utilisée afin de compléter le peu de données expérimentales qu'on trouve dans la base de données de sorption pour les roches calcaires.

Table of Contents

Abstract	I
Zusammenfassung	II
Résumé	III
List of Tables.....	VII
List of Figures	VIII
1 Introduction	1
References	1
2 Generic considerations	3
2.1 Main sorption mechanisms	3
2.1.1 Cation exchange	3
2.1.2 Surface complexation	3
2.2 Sorption characteristics of selected radionuclides	4
2.3 Minerals and their uptake characteristics.....	5
2.4 Temperature.....	9
2.5 Competitive sorption effects.....	9
References	9
3 Generic Swiss Water Chemistries for Argillaceous Rock Systems	13
References	14
4 Background Information and Methodologies for the Generation of SDBs for Generic Argillaceous Rock Systems	17
4.1 Aim	17
4.2 Strategy	17
4.3 Conversion factors, CF values.....	18
4.3.1 Mineralogy conversion factor: CF_{min}	19
4.3.2 Water chemistry.....	19
4.3.2.1 pH conversion factors, CF_{pH}	19
4.3.2.2 Speciation conversion factor, CF_{spec}	22
4.3.2.3 Formulation	23
4.3.2.4 Lab→Field conversion factor, $CF_{Lab→Field}$	23
4.3.2.5 Rounding	24
References	24
5 Chemical Analogues, Cation Exchange and Special Cases.....	27
5.1 Chemical analogues	27
5.2 Sorption by cation exchange in argillaceous rocks.....	28
5.3 Special cases: Nb(V), Ru(IV), Sb(V), Tc(IV), Pd(II) and C_{inorg}	29
References	33

6	Source Data for the Compilation of Generic SDBs for Argillaceous Rocks	35
	References	37
7	Generic Argillaceous Rock SDBs	39
8	Generic Calcareous Rock SDB	41
	References	45
	Acknowledgements	46
A1	Generic Groundwater Compositions	A-1
A2	Procedure of Speciation Calculations	A-7
A2.1	Thermodynamic Data	A-9
A3	Generic Reference Water and Speciation Calculations	A-13
A4	Argillaceous Rock Systems: Generic Waters and Speciation Calculations	A-19
A5	Additional Calculations	A-57
A6	Additional Thermodynamic Data	A-61
A6.1	Data estimated by Hummel & Berner (2001), written in PHREEQC format.....	A-61
A6.2	Data by Kalmykow & Choppin (2000), written in PHREEQC format	A-62
A6.3	Data from MINEQL datafile, FEB92.LOGK, version 27.4.1994	A-62
A6.3.1	Data written in PHREEQC format	A-62
A6.3.2	Sources of data from MINEQL datafile, FEB92.LOGK, version 27.4.1994	A-65
A6.4	Data for Co-carbonate complexes written in PHREEQC format	A-67
A6.5	Data for Be written in PHREEQC format	A-67
A6.6	Data for Bi written in PHREEQC format	A-69

List of Tables

Tab. 2.1:	Minerals, surface areas (SA) and cation exchange data (CEC) (Allard et al. 1983).....	8
Tab. 3.1:	Matrix of generic groundwaters defined for argillaceous rocks.	13
Tab. 3.2:	Restrictions and resulting water compositions for generic groundwaters.	15
Tab. 4.1:	Slope values, m in Eq. 4.2, used to calculate pH conversion factors, CF_{pH} , Eq. 4.3.....	21
Tab. 5.1:	Overview of chemical analogues. The log K values are for $I = 0$ and the hydrolysis reaction $Me^{n+} + H_2O \Leftrightarrow MeOH^{(n-1)+} + H^+$	27
Tab. 5.2:	Cation exchange reaction and corresponding selectivity coefficients (K_c) on the planar sites, type-II sites and frayed edge sites of illite (taken from Bradbury & Baeyens 2000, 2005).	29
Tab. 5.3:	Results of R_d ($m^3 kg^{-1}$) calculations for K, Cs, Ca, Sr and Ra for illite in the generic argillaceous water compositions (Tab. 3.2) using the parameters given in Table 5.2.	29
Tab. 5.4:	Sorption data for Nb(V) in a synthetic groundwater on various sediments. (Nb equilibrium concentration $< 10^{-10}$ M). Taken from Legoux et al. (1992).	30
Tab. 6.1:	Source data references.	36
Tab. 6.2:	Source data sets*	37
Tab. 7.1:	Generic argillaceous rock SDBs for the different porewater types given in Table 3.2. (Note that for argillaceous rocks the Lab→field conversion factor is unity. Therefore the sorption values given below apply to the field.)	40
Tab. 8.1:	Experimentally determined sorption values on calcite at pH values near 8 and ionic radii (in Ångstrom units) (Shannon 1976)..	41
Tab. 8.2:	Generic Calcareous Rock SDB ($m^3 kg^{-1}$) for $pH 7.5 < pH < 9$. (Ionic radii of the elements used in the LFER are given in brackets in column 5.) The sorption values given below apply to the field.	44
Tab. A1.1:	Analytical ranges of deep old groundwaters from various geological formations in Switzerland.....	A-1
Tab. A1.2:	Composition ranges of deep old groundwaters from various geological formations in Switzerland. Data from Table A1.1 converted to mol/L.....	A-3
Tab. A2.1:	Overview of speciation calculations.....	A-8
Tab. A3.1:	Generic Reference Water Composition (mol/kg H_2O).....	A-13
Tab. A3.2:	Generic Reference Water, Radionuclide Speciation (mol/kg H_2O).....	A-13
Tab. A4.1:	Argillaceous Rock Systems, $pH = 7.24$, $I = 2.28E-01$, Water Composition (mol/kg H_2O).....	A-19
Tab. A4.2:	Argillaceous Rock Systems, $pH = 7.24$, $I = 2.28E-01$, Radionuclide Speciation (mol/kg H_2O).	A-19
Tab. A4.3:	Argillaceous Rock Systems, $pH = 9$, high I, Water Composition (mol/kg H_2O).....	A-26

Tab. A4.4: Argillaceous Rock Systems, pH = 9, high I, Radionuclide Speciation (mol/kg H ₂ O)	A-26
Tab. A4.5: Argillaceous Rock Systems, pH = 9, low I, Water Composition (mol/kg H ₂ O)	A-33
Tab. A4.6: Argillaceous Rock Systems, pH = 9, low I, Radionuclide Speciation (mol/kg H ₂ O)	A-34
Tab. A4.7: Argillaceous Rock Systems, pH = 6, high I, Water Composition (mol/kg H ₂ O)	A-41
Tab. A4.8: Argillaceous Rock Systems, pH = 6, high I, Radionuclide Speciation (mol/kg H ₂ O)	A-41
Tab. A4.9: Argillaceous Rock Systems, pH = 6, low I, Water Composition (mol/kg H ₂ O)	A-48
Tab. A4.10: Argillaceous Rock Systems, pH = 6, low I, Radionuclide Speciation (mol/kg H ₂ O)	A-48
Tab. A5.1: Groundwater SGS 6, Koss, Winkler & Bütow (1992), Water Composition (mol/kg H ₂ O)	A-57
Tab. A5.2: Groundwater SGS 6, Koss, Winkler & Bütow (1992), Radionuclide Speciation (mol/kg H ₂ O)	A-57
Tab. A5.3: Laboratory Solution, Gorgeon (1994), Water Composition (mol/kg H ₂ O)	A-58
Tab. A5.4: Laboratory Solution, Gorgeon (1994), Radionuclide Speciation (mol/kg H ₂ O)	A-58

List of Figures

Fig. 4.1: Ni sorption edge measured on Na-illite at trace concentration in a 0.1 M NaClO ₄ background electrolyte (Bradbury & Baeyens 2009a)	20
Fig. 4.2: A selenite sorption edge on Na-illite in 0.1 M NaClO ₄ (from Bruggeman 2006). The slope of the broken line is -0.6	21
Fig. 5.1: The speciation of Tc(IV) in 0.1 M NaClO ₄ . Thermodynamic data are taken from Hummel et al. (2002)	31
Fig. 7.1: Flow chart for derivation of generic argillaceous sorption data base $R_{d \text{ arg}}$	39
Fig. 8.1: Linear Free Energy Relation between $\log R_d$ (m ³ kg ⁻¹) and the IR (ionic radii in Å). The least squares relation between $\log R_d$ and IR is given by $\log R_d = (-10.4 \pm 0.6) + (12.0 \pm 0.7) \cdot IR$ ($R^2 = 0.97$)	43
Fig. A1.1: Ranges for onsite pH of deep old groundwaters from various aquifers in Switzerland. Data from Table A1.1	A-5
Fig. A1.2: Calculated ranges for the ionic strength of deep old groundwaters from various aquifers in Switzerland. Calculated from data in Table A1.2	A-6

1 Introduction

In Switzerland, the Nuclear Energy Law requires the disposal of all radioactive waste in deep geological repositories. The Swiss programme foresees the construction of two types of repositories for this purpose: A high-level waste (HLW) and a low- and intermediate-level waste (L/ILW) repository. The Sectoral Plan for Deep Geological Repositories (Sachplan Geologische Tiefenlager), which was issued by the Swiss Federal Office of Energy in April 2008, defines the site selection procedure for both the HLW and L/ILW repositories. The Sectoral Plan specifies that site selection shall be conducted in three stages: In Stage 1, potential geological siting regions are identified. In Stage 2, at least two potential sites for each type of repository are determined. In Stage 3, sites for both the HLW and L/ILW repository are selected and the licensing procedure is carried through.

During Stage 1, Nagra, on behalf of the Swiss waste producers, proposed several potential siting regions based on the occurrence of suitable host rock formations. Opalinus Clay was selected as the host rock for the HLW repository. For the L/ILW repository, Opalinus Clay, "Brauner Dogger", Effingen Member and Helvetic Marl were selected. As part of the above mentioned selection procedure, a generic method was developed to derive sorption properties of radionuclides for all potential host rock formations in Switzerland. In the subsequent evaluation of the state of knowledge for the provisional safety analyses in Stage 2 of the Sectoral Plan, test calculations have been carried out (Nagra, 2010). To this end, sorption data sets for all host rocks mentioned above have been derived adopting a simplified methodology from Stage 1 (Bradbury et al. 2008).

The provisional safety analyses in Stage 2 of the Sectoral Plan are an integral part of the procedure used to identify potential sites. Again, radionuclide sorption properties for all host rocks considered need to be derived. For this purpose, the procedures utilised in Stage 1 were further developed. The resulting generic methodology is reported in the present document. Further, batch sorption measurements on selected samples of the different host rocks will be carried out to verify the data sets derived by the methodology described in this report.

The sorption of radionuclides by solid phases depends mainly on the minerals present in a rock and the porewater chemistry.

For many mineral systems cation exchange and surface complexation are the main sorption mechanisms governing the extent of the uptake on solid phases, especially for sorbates at trace concentrations, which is of most relevance in radioactive waste disposal. These two sorption mechanisms will be at the focus of the discussions given here.

The other focal point of the present report concerns the influence of porewater chemistry on radionuclide sorption. The most important parameters are pH and speciation for radionuclides sorbing by surface complexation, and ionic strength and speciation for those sorbing by cation exchange. The redox conditions are only important for a limited number of radionuclides for example U, Pu, Np, Tc, Se.

References

- Bradbury, M., Baeyens, B., Thoenen, T. (2008): Sorption Data Bases for Generic Swiss Argillaceous, Crystalline and Calcareous Rock Systems. Nagra Working Rep.
- Nagra (2010): Beurteilung der geologischen Unterlagen für die provisorischen Sicherheitsanalysen in SGT Etappe 2 – Klärung der Notwendigkeit ergänzender geologischer Untersuchungen. Nagra Tech. Rep. NTB 10-01.

2 Generic considerations

2.1 Main sorption mechanisms

2.1.1 Cation exchange

When certain solid minerals come into contact with aqueous solutions, ions bound electrostatically at the surface may undergo exchange with ions of the same sign in solution. Depending on whether the species involved are positively or negatively charged the phenomenon is called cation exchange or anion exchange respectively. This exchange is an adsorption process in which so called "outer sphere complexes" are formed. The exchanging ions do not have to be in the same charge or valence state, but the exchange has to be stoichiometric.

Cation exchange on clay minerals has been extensively studied (see for example Grim 1953; Bolt 1979; Bolt & Bruggenwert 1979; Bruggenwert & Kamphorst 1982) and can contribute significantly to radionuclide sorption depending on the conditions. Sorption by this mechanism is characterised by a strong dependency on ionic strength/solution composition and a weak dependency on pH and sorbate concentration and is usually of the Langmuir type. Amongst the major rock forming minerals, clay minerals and zeolites have particularly high cation exchange capacities and are thus the most effective ion exchangers and are responsible for most ion exchange reactions in geological systems.

A cation exchange sorption model has been developed to describe the sorption of Cs on argillaceous rock types where the major sorbing mineral component is illite (Bradbury & Baeyens 2000). Selectivity coefficient data have also been deduced for K-Na, Ca-Na, Sr-Na, Mg-Na and Al-Na exchange equilibria from experimental data on argillaceous rocks and illite (Baeyens & Bradbury 1994; Bradbury & Baeyens 1998a, 2005a). A high degree of confidence exists in these models and parameters since they have been tested over a wide range of different conditions. Thus, sorption values for clay mineral containing rocks for the alkaline and alkaline-earth metals can be calculated specifically for the reference water compositions using sorption models, taking into account the natural background element concentrations.

2.1.2 Surface complexation

Many radionuclides can be taken up on the amphoteric hydroxyl surface functional groups ($\equiv\text{SOH}$) of iron, silica and alumina phases (see for example Stumm et al. 1970; Schindler et al. 1976; Sposito 1984; Davis & Kent 1990; Dzombak & Morel 1990) and on phosphates and sulphides and on silanol and aluminol sites of aluminosilicates i.e. on the edge sites of clay minerals (Bradbury & Baeyens 2005).

Surface complexation of aqueous species on clay minerals involves the formation of tightly bound "inner sphere complexes" and is characterised by a strong dependency on pH, a weak dependency on ionic strength and a strong dependency on sorbate concentration. Generally, the sorption of metal species tends to increase with increasing pH in the range ~5 to ~9 and sorption exhibits a Freundlich type behaviour. Generally speaking, pH is probably the single most important parameter influencing the uptake of aqueous metal species via a surface complexation mechanism and can have a very significant influence on the magnitude of sorption. Exactly how sorption varies with pH is strongly dependent on sorbent and sorbate (see for example Baeyens & Bradbury 1995a,b, 1997; Bradbury & Baeyens 1995, 1997, 2002, 2005a,b).

Anions can sorb on the same type of amphoteric hydroxyl surface function groups by a ligand exchange mechanism. (Goldberg & Glaubig 1988; Davis & Kent 1990). Their sorption behaviour shows two clear features: (i) sorption tends to increase with decreasing pH and (ii) sorption exhibits a Langmuir type behaviour (Motta & Miranda 1989). Again, the parameter of most importance is the pH.

Cations such as Ca, Sr, Mg, Na, K are not generally competitive with the specifically sorbing heavy metals, transition metals, lanthanides and actinides for the surface sites. Thus major groundwater cations do not usually influence sorption by surface complexation.

For other mechanisms such as surface precipitation, incorporation in the sorbent matrix and solid solution formation hardly any data are available and generally these processes often follow on from a sorption step. It could therefore be argued that just considering adsorption processes is conservative.

2.2 Sorption characteristics of selected radionuclides

As stated previously, the rock mineralogy and the water chemistry are the two most important factors determining the uptake in any system. Whether the conditions are reducing or oxidizing will only be important for a limited number of radionuclides namely U, Pu, Np, Tc, Se. A brief overview is given below of the sorption characteristics expected for the main radionuclides included in a performance assessment assuming reducing conditions. At the end some comments will be given for the influence of oxidizing conditions on those radionuclides affected.

Surface complexation on amphoteric hydroxyl sites is a major uptake mechanism for clay minerals, micas, zeolites, oxides and sulphides (possibly). In general, those elements which exhibit strong hydrolysis behaviour also exhibit strong sorption when the uptake mechanism is surface complexation. Cation exchange will only be relevant for a few metals (see below) and only when the CEC is significant. Aqueous phase complexation with carbonate and to a lesser extent with sulphate, silicate and chloride tends to lead to a reduction in sorption in most cases.

Reducing conditions

HTO, C_{org}, Cl(-I), Se(-II) Ag(I), I(-I)

Irrespective of the rock mineralogy and water composition it is expected that the above elements will exhibit zero sorption.

Cs, K, Ca, Sr, Ra

In the pH range 6 - 9 these elements will exist principally as cations and their sorption is expected to be independent of pH. Also, since they all sorb by cation exchange, the magnitude of sorption will decrease with increasing salt concentration. Their sorption will be highly dependent on the CECs of the rock, i.e. on the rock mineralogy.

C_{inorg}

It is assumed that ¹⁴C_{inorg} is present in solution as carbonate species. The sorption value can be calculated from the aqueous inorganic carbon concentration and the quantity of calcite present. The magnitude of ¹⁴C_{inorg} sorption is therefore dependent on the pH (carbonate concentration) and the quantity of calcite present (see also section 5.3).

Nb(V), Mo(VI), Po(IV), Se(IV), Ru(IV)

The above elements form oxy-anionic species in solution, and experimental data indicate that sorption generally increases with decreasing pH, but the values near pH = 8 are very low. Se(IV) is often used as a chemical analogue for Po(IV) for which there are no sorption values existing. Sorption values for these metals are low. The water composition has little influence on the sorption but the mineralogy will play a role.

Be(II), Ni(II), Co(II), Cd(II), Pd(II), Pb(II)

The uptake of the transition metals (Ni, Co, Cd, Pd) and the heavy metal Pb by surface complexation is moderate to strong. Therefore the magnitude of the sorption will depend primarily on pH and the mineralogy and less on the water composition. Ni(II) is taken as chemical analogue for Be(II).

Sb(III), Bi(III), lanthanides (Ce(III), Pm(III), Sm(III), Eu(III), Ho(III)) and trivalent actinides (Ac(III), Am(III), Cm(III), Pu(III))

The tendency for this grouping of elements is towards strong to very strong sorption where surface complexation is the uptake mechanism. Hence the sorption can be strongly pH dependent, less directly dependent on the ionic strength of the water but dependent on speciation and mineralogy.

Tetravalent metals (Sn(IV), Zr(IV), Tc(IV) and Hf(IV)) and actinides (U(IV), Np(IV), Pu(IV), Th(IV))

The sorption of the tetravalent metals and actinides can be extremely strong and in some cases where the dominant aqueous species is the neutral hydroxy complex the sorption is high and constant over a wide range of pH. The mineralogy plays an important role.

Pentavalent metals Pa(V) and Np(V)

The sorption of Pa(V) is stronger than Np(V) due the stronger hydrolysis behaviour.

Oxidising conditions

Oxidising conditions will influence the sorption of the redox sensitive elements Se, Tc, Sb, U, Np and Pu. In general an increase in the oxidation state leads to reduced sorption, sometimes by orders of magnitude compared to the values under reducing conditions. Tc(VII) and Se(VI) – oxidising conditions – are considered not to sorb whereas Se(IV) exhibits slight sorption.

2.3 Minerals and their uptake characteristics

In trying to gain a general picture of which mineral phases may be of most importance in the uptake of radioactive species, the cation exchange capacity (CEC) and/or the specific (external) surface area (SA) provide excellent guides. For an element where the main adsorption mechanism is cation exchange, the CEC is clearly a major factor in determining how high the adsorption is. In systems where surface complexation is the dominant uptake mechanism, many studies have shown that high specific surface areas (N_2 BET) tend to lead to high sorption values because the amphoteric sites are situated at the edges of the structures and the capacities are proportional to the areas of the edges.

A broad listing of the main primary and secondary minerals found in many rock systems is given in Table 2.1, grouped according to their mineral classes and groups. The corresponding cation exchange capacities and specific surface areas are given wherever possible. With this information, these minerals are discussed very generally below with respect to their importance for adsorption (after Bolt & Bruggenwert 1978). The minerals listed in Table 2.1 can be divided up into four groups:

1. minerals with very high solubility (*halides*) and low CECs and SAs
2. minerals with high solubility (*carbonates, sulphates*) and low CECs and SAs
3. minerals with low solubility, low CECs and low to moderate SAs (*neso-/soro-/inosilicates/feldspars, oxides/hydroxides, sulfides*)
4. minerals with low solubility and high to very high CECs and SAs (*phyllosilicates and zeolites*).

Neither cation exchange nor surface complexation are relevant for the minerals grouped under 1 and 2 (halides, sulphates and carbonates). Halides and sulphates (anhydrite/gypsum) have very low CECs and SAs and are likely to exhibit little or no sorption. (Carbonates are discussed below). Group 3 mainly comprises silicates and oxide type minerals with low solubility. The former are considered as the (metastable) left-overs from parent materials, i.e., minerals derived from rock formations, whereas the latter may be considered as the stable end members of the weathering processes. If coarse grained they constitute the inert matrix of major rock type systems and are essentially of no significance with regard to sorption (low specific surface area). On the other hand, the Fe- and Al-(hydr)oxides exhibit high SA and have high affinities for many cationic and anionic species. However, they are secondary minerals present only at low levels in natural rock systems.

The phyllosilicates (and to a lesser extent the zeolites) play a dominant role in almost all soil and rock systems (Brown et al. 1978). This is mainly due to their (often) very large surface areas, which are connected in turn with their lattice structure. This group of minerals can be divided into two sub-groups based on their CEC and SA characteristics. The most important ones are the clay minerals (very high CECs and SAs) which are dominant in argillaceous rocks.

Alternatively, Table 2.1 can be viewed in terms of the major rock forming minerals occurring in Swiss argillaceous rock systems, and their sorption properties. These minerals are:

- clay minerals
- quartz
- feldspars
- carbonates (calcite, dolomite)
- sulphates (anhydrite, gypsum)

Anhydrite and gypsum are minerals with high solubilities and essentially nothing can be expected from these minerals in terms of sorption (extremely low CECs).

Even though quartz and feldspars are present in argillaceous rocks, sometimes at relatively high levels, their extremely low SAs and low CECs lead to the conclusion that they will make only a very minor contribution to the uptake of radionuclides.

Carbonates are omnipresent in almost all sedimentary rocks. In whatever form they appear, CECs and SAs are low (comparable to quartz, and lower than many feldspars) and even in the

rare cases where they constitute almost the whole of the rock, their sorption is expected to be generally low. The sorption mechanisms for solid carbonates are likely to be a combination of surface exchange reactions with Ca and solid solution formation. There is little quantitative knowledge about these processes, but it is not unreasonable to assume that they could depend on ionic radii and steric considerations.

Clay minerals have moderate to high SAs and moderate to very high CECs. Therefore they are expected to contribute strongly to the sorption of rocks in which they are present. This would be particularly so for illites, smectites and illite-smectite mixed layers.

Minerals in Table 2.1 which can be classified as "minor" are:

- neso/soro/inosilicates
- oxides/hydroxides
- sulphides

Minor minerals are present on the few percent scale and unless they exhibit very high sorption, will not contribute to any significant extent to the overall sorption. From the SAs and CECs of the above minerals this would not be expected. Some iron oxides do have very high surface areas but these are ferric oxides, and under reducing conditions are not anticipated to be present in the rock. On the other hand the presence of Fe-minerals such as pyrite and siderite (Fe(II)) at low levels may be important for controlling the redox conditions within the rock.

The main conclusion from this brief overview regarding the main factors influencing the sorption characteristics of the primary and secondary minerals constituting argillaceous and calcareous rocks is simple and clear, namely, the silicate mineral content is decisive. More specifically, the phyllosilicates (clay minerals) are particularly effective at binding metals to their surfaces either by surface complexation or cation exchange. Generally, the magnitude of sorption is directly correlated with the phyllosilicate content. The cation exchange capacity clearly reflects the uptake potential for those radionuclides sorbing by cation exchange. In the case of minerals where the major uptake mechanism is surface complexation, then the magnitude of the external surface area is usually indicative of the amphoteric surface site capacities.

The exception to the above is calcareous rocks, which are often devoid of silicates and therefore have low surface areas and essentially no exchange capacity. However, these rocks are known to exhibit sorption. Their uptake mechanism is not cation exchange or surface complexation. A procedure for estimating sorption in such systems will be presented in Chapter 8.

Tab. 2.1: Minerals, surface areas (SA) and cation exchange data (CEC) (Allard et al. 1983).

Mineral group	Mineral	BET (m ² g ⁻¹)	CEC (pH 8) (meq. kg ⁻¹)
Silicates			
Nesosilicates	olivine	-	1.8
	zircon	-	3.5
Sorosilicate	epidote	0.38 ¹	6.0
Inosilicates	augite	-	8.0
	hornblende	4.3	2.5
Phyllosilicates			
	kaolinite	11; 15.5 ² ; 10.5-23.5 ³	28; 30-150 ² ; 20-49 ³
	serpentine	15.7	1.0
	illite	24.8 ⁴ ; 97.1 ² ; 101 ³	225 ⁵ ; 100-400 ² ; 266 ³ ; 122-264 ⁶
	montmorillonite	15.5 ² ; 31.8-97.4 ³	800; 800-1500 ² ; 764-1200 ³
	illite-smectite ML	25.6 ⁴	594 ⁶
	palygorskite	136.4 ⁷	80
	attapulgitite	190	85
	chlorite	0.9-2.9 ⁸	50; 100-400 ²
	muscovite	7.2	52; 105 ² ; 59 ⁶
	biotite	7.0	17; 30 ²
	prehnite	-	25
Tectosilicates			
<i>feldspars</i>			
	albite (Na)	1.3 ⁹ ; 2.2 ¹⁰	3.7; 33.7 ⁶
	K-feldspar	0.16 ⁴	-
	anorthite (Ca)	0.08-0.42 ¹³	5.0
	microcline	1.1	3.7
	bytownite	-	9.0
<i>zeolites</i>			
	analcime	-	180
	stilbite	-	640
	laumontite	-	35
	chabazite	500-800 ¹¹	4000-4200 ¹¹
Oxides/Hydroxides			
Si-oxides	quartz	0.3	0.2
Fe-(hydr)oxides	goethite	46.0 ¹²	
	hematite	0.9	0.5
	magnetite	1.5; 0.094 ³	0.4
	limonite	13	6.3
Al-(hydr)oxides	gibbsite	13-16 ¹³ ; 7.3 ³	-
	corundum	0.5	0.4
Manganese oxide	pyrolusite	2.5 ¹⁴	8
Sulphides			
	pyrite (FeS ₂)	0.24 ¹⁵ ; 41.7 ¹⁶	1.5
	chalcopyrite	1.0	2.6
	galena (PbS)	-	1.1
	sphalerite	-	1.4
	pyrrhotite	-	1.5
Carbonates			
	calcite	0.6; 0.067 ³	0.2
	dolomite/ankarite	-	0.2
	siderite (FeCO ₃)	2.8 ¹⁷ ; 2.2 ¹⁸	-
Sulphates	anhydrite/gypsum	0.075 ³	0.8
Halides	fluorite (NaF)	-	0.2

¹)Ticknor (1993); ²)Grim (1953); ³)Van Olphen & Fripiat (1979); ⁴)Bradbury & Baeyens (1998); ⁵)Baeyens & Bradbury (2004); ⁶)De Preter (1990); ⁷)Ticknor (1994); ⁸) Bradbury & Baeyens (Unpubl. data); ⁹)Blum & Lasaga (1991); ¹⁰)Walthert et al. (2005); ¹¹)Valcke & Cremers (1994); ¹²)Davis & Kent (1990); ¹³)Hodson (2006); ¹⁴)Powell et al. (2006); ¹⁵)Borah & Senapati (2006); ¹⁶)Bostick et al. (2003); ¹⁷)Pokrovsky et al. (1999); ¹⁸)Charlet et al. (1990).

2.4 Temperature

The temperature considered in this work is 25 °C. That is to say, the sorption values in the SDB and the constants in the TDB used in speciation calculations refer to this temperature. The OPA formation temperature at the considered depth is approximately 40 °C.

There is little or no information available in the open literature on temperature effects. Their potential influence was not considered in the report.

2.5 Competitive sorption effects

The majority of sorption data originates from batch type experiments in which it is usual to measure the sorption behaviour of a single metal at a time. In complex systems, such as a deep underground radioactive waste repository, many radionuclides and inactive metal contaminants will be simultaneously present at different concentrations in the aqueous phase. Under such circumstances, competitive sorption effects may be an important issue.

In a recent study (Bradbury and Baeyens 2005c), competitive effects on the uptake of metals on montmorillonite (as a model 2:1 clay mineral) were investigated at trace concentrations in the presence of different metals at high concentrations. One of the main findings from this experimental work was that all metals are not mutually competitive, but rather competition is selective. Metals with similar chemistries (valence state, hydrolysis behaviour) compete with one another but metals with dissimilar chemistries do not compete e.g. divalent transition metals with trivalent lanthanides, or Th(IV) with U(VI).

The influence of competitive sorption effects on the sorption values given in this report is a priori not included. For the derivation of the sorption databases for the host rocks, Opalinus Clay, Effingen Member, 'Brauner Dogger' and Helvetic Marl sorption competition effects on radionuclide uptake will be considered.

References

- Allard, B., Karlsson, M., Tullbory, E.L. & Larson S.A. (1983): Ion exchange capacities and surface areas of some major components and common fracture filling materials of igneous rocks. SKBF/KBS Tech. Rep. 83-64.
- Baeyens, B. & Bradbury, M.H. (1994): Physico-Chemical Characterisation and Calculated In Situ Porewater Chemistries for Low Permeability Palfris Marl from Wellenberg. PSI-Bericht Nr. 94-19, Nagra Tech. Rep. 94-22.
- Baeyens, B. & Bradbury, M.H. (1995a) A quantitative mechanistic description of Ni, Zn and Ca sorption on Na-montmorillonite. Part I: Titration measurements., PSI Bericht Nr. 95-10, Nagra Tech. Rep. NTB 95-04.
- Baeyens, B. & Bradbury, M.H. (1995b): A quantitative mechanistic description of Ni, Zn and Ca sorption on Na-montmorillonite. Part II: Sorption measurements., PSI Bericht Nr. 95-11, Nagra Tech. Rep. NTB 95-05.
- Baeyens, B. & Bradbury, M.H. (1997): A mechanistic description of Ni and Zn sorption on Na-montmorillonite. Part I: Titration and sorption measurements. J. Cont. Hydrol. 27, 199-222.

- Baeyens, B. & Bradbury, M.H. (2004): Cation exchange capacity measurements of illite using the sodium and cesium isotope dilution technique: Effects of the index-cation, electrolyte concentration and competition: *Modeling. Clays Clay Min.* 52, 421-431.
- Blum, A.E., Lasaga, A.C. (1991): The role of surface speciation in the dissolution of albite. *Geochim. Cosmochim. Acta* 55, 2193-2201.
- Bolt, G.H. (1979): Surface interaction between the soil solid phase and the soil solution. In *Soil Chemistry A: Basic elements* (eds. G.H. Bolt and M.G.M. Bruggenwert). Vol. 5A, Chap. 3, 43-53. Elsevier.
- Bolt, G.H. & Bruggenwert, M.G.M. (1979): *Soil Chemistry A. Basic Elements*. Elsevier, Amsterdam.
- Borah, D, Senapati, K. (2006): Adsorption of Cd(II) from aqueous solution onto pyrite. *FUEL* 85, 1929-1034.
- Bostick, B.C., Fendorf, S., Helz, G.R. (2003): Differential adsorption of molybdate and tetrathiomolybdate on pyrite (FeS₂). *Environ. Sci. Technol.* 37, 285-291.
- Bradbury, M.H. & Baeyens, B., (1995): A quantitative mechanistic description of Ni, Zn and Ca sorption on Na-montmorillonite. Part III: Modelling., PSI Bericht Nr. 95-12, Nagra Tech. Rep. NTB 95-06.
- Bradbury, M.H. & Baeyens, B. (1997a): A mechanistic description of Ni and Zn sorption on Na-montmorillonite. Part II: Modelling. *J. Cont. Hydrol.* 27, 223-248.
- Bradbury, M.H. & Baeyens, B. (1997b): Derivation of in situ Opalinus Clay porewater compositions from experimental and geochemical modelling studies. PSI Bericht Nr. 97-14, Nagra Tech. Rep. NTB 97-07.
- Bradbury, M.H. & Baeyens, B. (1998a): A physico-chemical characterisation and geochemical modelling approach for determining porewater chemistries in argillaceous rocks. *Geochim. Cosmochim. Acta* 62, 783-795.
- Bradbury, M.H. & Baeyens, B. (1998b): N₂-BET surface area measurements on crushed and intact minerals and rocks: A proposal for estimating transfer factors. *Nuclear Technology* 122, 250-253.
- Bradbury, M.H. & Baeyens, B. (2000): A generalised sorption model for the concentration dependent uptake of Cs by argillaceous rock. *J. Contam Hydrol.* 42, 141-163.
- Bradbury, M.H. & Baeyens, B. (2002a): Porewater chemistry in compacted re-saturated MX-80 bentonite: Physico-chemical characterisation and geochemical modelling PSI Bericht Nr. 02-10, Nagra Tech. Rep. NTB 01-08.
- Bradbury, M.H. & Baeyens, B. (2002b): Sorption of Eu on Na- and Ca-montmorillonites: Experimental investigations and modelling with cation exchange and surface complexation. *Geochim. Cosmochim. Acta* 66, 2325-2334.
- Bradbury, M.H. & Baeyens, B. (2005a): Experimental and modelling investigations on Na-illite: Acid-base behaviour and the sorption of strontium, nickel, europium and uranyl. PSI Bericht Nr. 05-02, Nagra Tech. Rep. NTB 04-02.

- Bradbury, M.H. & Baeyens, B. (2005b): Modelling the sorption of Mn(II), Co(II), Ni(II), Zn(II), Cd(II), Eu(III), Am(III), Sn(IV), Th(IV), Np(V) and U(VI) on montmorillonite: Linear free energy relationships and estimates of surface binding constants for some selected heavy metals and actinides. *Geochim. Cosmochim. Acta* 69, 875-892 and Erratum 69, 5391-5392.
- Brown, G., Newman, A.C.D., Rayner, J.H. & Weir, A.H. (1978): Chapter 2 in: *The Chemistry of Soil Constituents* (Eds. Greenland D.J. and Hayes M.H.B.) Wiley Interscience.
- Bruggenwert, M.G.M. & Kamphorst, A. (1982): Survey of experimental information on cation exchange in soil systems. In *Soil Chemistry B. Physico-chemical Models*. (ed. G. H. Bolt), Vol. 5B, Chap. 5, Elsevier.
- Charlet, L., Wersin, P., Stumm, W. (1990): Surface charge of MnCO₃ and FeCO₃. *Geochim. Cosmochim. Acta* 54, 2329-2336.
- Davis, J.A. & Kent, D.B. (1990): Surface complexation modelling in aqueous geo-chemistry. In *Mineral-Water Interface Geochemistry* (M.F. Hochella and White, A.F., Eds.) *Reviews in Mineralogy* 23, pp. 177-260.
- De Preter, P. (1990): Radiocesium retention in the aquatic terrestrial and urban environment: A quantitative and unifying analysis. Ph.D Thesis. Catholic University Leuven.
- Dzombak, D.A. & Morel, F.M.M. (1990): *Surface Complexation Modelling: Hydrous Ferric Oxides*. John Wiley and Sons, New York, NY.
- Goldberg, S. & Glaubig, R.A. (1988): Anion sorption on a calcareous, montmorillonite soil-selenium. *Soil Sci. Soc. Amer. J.* 49, 954-958.
- Grim, R.E. (1953): *Clay Mineralogy*. Mc Graw-Hill, New York.
- Hodson, M.E. (2006): Does reactive surface area depend on grain size? Results from pH 3, 25 °C far-from-equilibrium flow-through dissolution experiments on anorthite and biotite. *Geochim. Cosmochim. Acta* 70, 1655-1667.
- Motta, M.M. & Miranda, C.F. (1989): Molybdate adsorption on kaolinite, montmorillonite and illite: Constant capacitance modelling. *Soil Sci. Soc. Am. J.* 53, 380-385.
- Pokrovsky, O.S., Schott, J., Thomas, F. (1999): Dolomite surface speciation and reactivity in aquatic systems. *Geochim. Cosmochim. Acta* 63, 3133-3143.
- Powell, B.A., Duff, M.C., Kaplan, D.I., Fjeld, R.A., Newville, M., Hunter, D.B., Bertsch, P.M., Coates, J.T., Eng, P., Rivers, M.L., Serkiz, S.M., Sutton, S.R., Triay, I.R., Vaniman, D.T. (2006): Plutonium oxidation and subsequent reduction by Mn(IV) minerals in Yucca Mountain tuff. *Environ. Sci. Technol.* 40, 3508-3514.
- Schindler, P.W., Furst, B., Dick, R. & Wolf, P.U. (1976): Ligand properties of surface silanol groups. I Surface complex formation with Fe³⁺, Cu²⁺, Cd²⁺ and Pb²⁺. *J. Colloid Interface Sci.* 55, 469-475.
- Sposito, G. (1984): *The Surface Chemistry of Soils*. Oxford University Press, New York, NY.
- Stumm, W., Huang, C.P. & Jenkins, S.R. (1970): Specific chemical interactions affecting the stability of dispersed systems. *Croat. Chem. Acta* 42, 223-244.
- Ticknor, K.V. (1993): Actinide sorption by fracture-infilling minerals. *Radiochim. Acta* 60, 33-42.

- Ticknor, T.V. (1994): Uranium sorption on geological materials. *Radiochim. Acta* 64, 229-236.
- Valcke, E. & Cremers, A. (1994): Sorption of radionuclides by natural zeolites: A critical literature survey on the sorption properties of seven selected zeolites. *Nagra Int. Rep. NIB 95-06*.
- Van Olphen, H. & Fripiat, J.J. (1979): *Data Handbook for Clay Minerals and other Non-metallic Minerals*. Pergamon Press, Oxford.
- Walter, M., Arnold, T., Geipel, G., Scheinost, A., Bernhard, G. (2005): An EXAFS and TRLFS investigation on uranium(VI) sorption to pristine and leached albite surfaces. *J. Coll. Interface Sci.* 282, 293-305.

3 Generic Swiss Water Chemistries for Argillaceous Rock Systems

For the development of generic sorption databases for argillaceous rocks, generic groundwater compositions need to be defined. They should cover the expected range of pore water compositions in argillaceous rocks in Switzerland. The idea is to keep these "generic waters" as simple as possible. The most important parameters relevant for sorption are ionic strength, pH and radionuclide speciation (mainly carbonate and hydroxide complexation and to a lesser extent complexation with sulphate and chloride). In order to cover the range of ionic strengths (*I*) and pHs of Swiss groundwaters for argillaceous rocks, 5 types of generic groundwaters were defined, combining high *I* with high pH, low *I* with high pH, high *I* with low pH, low *I* with low pH, and intermediate *I* with intermediate pH (see Tab. 3.1).

Tab. 3.1: Matrix of generic groundwaters defined for argillaceous rocks.

	Argillaceous Rocks		
	high <i>I</i>	intermediate <i>I</i>	low <i>I</i>
high pH	Argh9		Argl9
intermediate pH		Argint	
low pH	Argh6		Argl6

The starting point for the derivation of generic groundwater compositions was a list of the analytical ranges (maximum, median and minimum) of deep groundwaters from various argillaceous formations in Switzerland, compiled by Dr. H.N. Waber (Rock-Water Interaction Group, University of Bern, Switzerland) from the Nagra Hydrodatenbank 2007 (see Tables A1.1 and A1.2 in Appendix A1). The variations in measured pH values are given in Fig. A1.1. All pH values are within the range from 6 to 9 (with the exception of the maximum value of 9.2 for the Palfris formation). Consequently, for argillaceous generic groundwaters a lower bound pH value of 6 and an upper bound value 9 was chosen.

The ionic strength values shown in Fig. A1.2 were calculated from the concentration data in Table A1.1 by performing speciation calculations with PHREEQC (Parkhurst & Appelo, 1999), version 2.12.1-669 for Mac OS X, using the Nagra/PSI Thermochemical Database 01/01 (Hummel et al. 2002). For the generic argillaceous groundwaters, the low *I* was chosen to be 0.13 mol kg⁻¹ and the high *I* to be 0.4 mol/kg H₂O, corresponding to the variations found within Opalinus Clay formations.

Intermediate values of pH and ionic strength were chosen to be 7.2 and 0.23 mol kg⁻¹ H₂O, respectively, for the generic argillaceous groundwater.

With these upper, intermediate and lower values for ionic strength and pH, compositions were defined for the generic groundwaters. The following assumptions were made for all generic groundwaters:

- Groundwaters are saturated with quartz and calcite
- pH is controlled by the carbonate system
- Ionic strength is controlled by NaCl
- Fixed molar ratio of chloride/sulphate

The restrictions for calculating the compositions of the generic groundwaters with PHREEQC were the following: The groundwaters are saturated with quartz and calcite, pH is adjusted to the desired value by adjusting $p\text{CO}_2$, the total chloride concentration is fixed, the total sulphate concentration is fixed (at a given molar ratio of chloride and sulphate), the total sodium concentration is calculated from the charge balance. The molar ratio of 13 for chloride/sulphate for all generic argillaceous groundwaters was taken from the median concentrations of the Opalinus Clay in Table A1.2. Given these restrictions, for each generic groundwater a speciation calculation was done with an initial composition in terms of chloride and sulphate. Chloride and sulphate compositions were adjusted until the desired ionic strength was obtained. The final generic groundwater compositions are listed in Table 3.2.

However, although the aim was to produce simple water chemistries for the "generic water types", the compositions arising from the above procedure would have been too simple in certain respects. The aim in the derivation of the generic rock sorption data bases is to calculate sorption values for those metals whose main uptake mechanism is cation exchange, using previously determined selectivity coefficients. In order to make these calculations, the groundwaters have to contain some Na and some K, which in fact are always present. An average Na/K ratio of 212 was deduced from the data in Table A1.2 and was used to calculate K concentrations. The Na and K values introduced into the different waters in the above manner are given in Table 3.2 in italics.

References

- Hummel, W., Berner, U., Curti, E., Pearson, F.J. & Thoenen, T. (2002): Nagra/PSI Thermochemical Database 01/01. Nagra Technical Report, NTB 02-16, Nagra, Wettingen, Switzerland; and Universal Publishers, Parkland, Florida, USA, 589 pp.
- Mäder, U. (2009a) Reference pore water for the Effingen Members (Standortregion Südjura) for the provisional safety-analysis in the framework of the sectorial plan-interim results (SGT-ZE) Nagra Internal Report NAB 09-13.
- Mäder, U. (2009b): Reference pore water for the Opalinus Clay and "Brown Dogger" for the provisional safety-analysis in the framework of the sectorial plan-interim results (SGT-ZE) Nagra Internal Report NAB 09-14.
- Parkhurst, D.L. & Appelo, C.A.J. (1999): User's guide to PHREEQC (Version 2) - A computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations. Water-Resources Investigations Report 99-4259, U.S. Geological Survey, Denver, Colorado, U.S.A. 312 pp.

Tab. 3.2: Restrictions and resulting water compositions for generic groundwaters.

Abbreviations: SI (saturation index), I (ionic strength).

			Argint Argillaceous <i>I: intermediate</i> pH: intermediate	Argh9 Argillaceous <i>I: high</i> pH: high	Argl9 Argillaceous <i>I: low</i> pH: high	Argh6 Argillaceous <i>I: high</i> pH: low	Argl6 Argillaceous <i>I: low</i> pH: low
Restrictions	T	[°C]	25	25	25	25	25
	Quartz SI		0.0	0.0	0.0	0.0	0.0
	Calcite SI		0.0	0.0	0.0	0.0	0.0
	pH		7.2	9.00	9.00	6.00	6.00
	pe		-2.00	-2.00	-2.00	-2.00	-2.00
	Na	[mol/kg H ₂ O]	charge balance	charge balance	charge balance	charge balance	charge balance
	Na / K	molar ratio	212	212	212	212	212
	Cl / S(VI)	molar ratio	13	13	13	13	13
	Cl	[mol/kg H ₂ O]	0.184	0.33865	0.1066	0.3107	0.0806
S(VI)	[mol/kg H ₂ O]	0.142	0.02605	0.0082	0.0239	0.0062	
Resulting Water Composition	I*	[mol/kg H ₂ O]	0.23	0.4	0.13	0.4	0.13
	C_{inorg}	[mol/kg H ₂ O]	7.50E-03	9.99E-04	7.97E-04	7.89E-02	6.87E-02
	Ca	[mol/kg H ₂ O]	3.46E-3	6.50E-04	4.85E-04	1.61E-02	1.32E-02
	Cl	[mol/kg H ₂ O]	1.84E-01	3.39E-01	1.07E-01	3.11E-01	8.06E-02
	Na	[mol/kg H ₂ O]	2.12E-01	3.91E-01	1.23E-01	3.59E-01	9.30E-02
	K	[mol/kg H ₂ O]	1.00E-03	1.84E-03	5.80E-04	1.69E-03	4.39E-04
	S(VI)	[mol/kg H ₂ O]	1.42E-02	2.61E-02	8.20E-03	2.39E-02	6.20E-03
	Si	[mol/kg H ₂ O]	1.78E-04	2.12E-04	2.14E-04	1.75E-04	1.78E-04

* Recently defined new reference porewaters for certain argillaceous rocks in Stage 2 of the SGT exhibit higher ionic strength than the range considered in this table (Mäder 2009a,b)

4 Background Information and Methodologies for the Generation of SDBs for Generic Argillaceous Rock Systems

4.1 Aim

The aim in this part of the report is to produce generic rock sorption data bases (GR-SDBs) for argillaceous host rock formations for the disposal of radioactive waste in Switzerland, taking into account the spread in their associated pore water chemistries. In contrast, calcareous rock is considered a model for a clay rock affected by an alkaline plume and subsequent processes during which most of the favorable sorption properties are lost. This rock type will be treated separately in Chapter 8. The sorption values contained in the data bases are expressed as solid to liquid distribution ratios (R_d values) defined as the ratio of the quantity of radionuclide sorbed on the solid phase per unit mass to the total equilibrium radionuclide concentration in the liquid phase.

In the following chapters, the stepwise procedures to achieve this aim are described.

4.2 Strategy

One of the main conclusions drawn in section 1.3 was that, from a mineralogical viewpoint, the phyllosilicate component in any rock system was the one main single specific factor determining its sorption characteristics. Also, since the aim of the work is to create generic rock SDBs, the source data should ideally be as "generic" as possible. For most radionuclides the main sorbing phases in argillaceous rocks are 2:1 type clay minerals (illite + smectite + illite/smectite mixed layers).

In a series of investigations on montmorillonite and illite Bradbury and Baeyens (1997, 2009a) have shown clearly that the surface complexation behaviour of these two important clay minerals is similar. The results from modelling titration experiments using the 2 site protolysis non electrostatic surface complexation and cation exchange model yielded the same edge sorption site capacities. Further, the Linear Free Energy Relationships derived between metal surface complexation constants and the corresponding hydrolysis constants (Bradbury and Baeyens 2005, 2009b) for a wide variety of metals in different valence states are similar. The extension to these observations is that structural mixtures of illite and montmorillonite i.e. illite –smectite mixed layers are also very likely to exhibit very similar surface complexation characteristics as their component clay minerals. However, to the authors knowledge, there are no surface complexation data on illite –smectite mixed layers in the open literature, so the above statement must be viewed as an assumption in the development of the following SDBs. In very general terms it is considered that the generic sorption properties of argillaceous rocks can best be represented by illite. (Illite was chosen rather than montmorillonite since the latter is hardly ever present in argillaceous rocks in Switzerland, and if so, only at low levels.) Kaolinite and chlorite are often present in argillaceous rocks but are a 1:1 type clay mineral and a 2:1:1 mineral, respectively, and therefore have different properties from 2:1 clay minerals. The potential contribution from kaolinite and chlorite to the overall sorption was not taken into account in the following (a conservative approximation). Thus the approach taken to produce a generic rock SDB will be to use illite source sorption data wherever possible and scale this data over the wt.% of the 2:1 type clay minerals (illite + smectite + illite/smectite mixed layers) of the argillaceous rock in question. A simple set of reference conditions for the illite source data has been chosen; pH = 7 and 0.1 M NaClO₄. The illite CEC is taken to be 225 meq kg⁻¹ (Baeyens and Bradbury 2004).

Thus, wherever possible, the source sorption data chosen for the GR-SDB are values measured on illite. The preferred selection sequence will be "in house" data followed by literature data. In the majority of cases the measured data are in the form of sorption edges measured at trace concentrations under well defined conditions. However, an important constraint on developing SDBs is the availability of reliable sorption measurements for the wide range of radionuclides required and these will not all be provided from illite systems.

At the next level in the selection hierarchy preference is given to sorption measurements on argillaceous rocks and sediments. Isotherm data are preferred to single point measurements. Isotherm determinations which yield a consistent picture of sorption over a range of concentrations bring with them a confidence in the measurements which cannot be there to the same degree when only single point values are measured. In most cases, selections of R_d values have been made at "trace concentrations" (generally $< 10^{-6}$ M) in the linear part of the sorption isotherm.

Sometimes reliable sorption data for a particular radionuclide are not available at all. The only option then is to select a chemical analogue for which sorption data are available and make a selection on this basis. Generally, two nuclides are taken to be chemically analogous when they belong to the same group in the periodic table and exhibit similar aqueous speciation behaviour. This is then taken to imply that they also exhibit a similar sorption behaviour.

4.3 Conversion factors, CF values

In setting up SDBs of any kind, it is almost always necessary to modify the available data, whether "in house" or literature, to the mineralogy/water chemistry conditions defined for the particular system under consideration. The following sections describe proposals for making such modifications. In general, it is important to try to identify the most probable dominant sorption mechanism for each particular radionuclide, since the influence of water chemistry on sorption is strongly linked to the mechanism. A mechanistic approach and the development of thermodynamic sorption models are used (at the moment) predominantly to interpret laboratory experiments, gain insights into the processes occurring and as a tool to better understand sorption and the main factors which influence it (e.g. see Bradbury & Baeyens 1997b, 2004, 2009a,b, Davis et al. 2005). A (quasi) mechanistic approach to sorption enables the selection of values for SDBs to be better justified and defended through an increased understanding of the underlying processes. By viewing sorption in terms of these uptake models, trends and insights into the important processes can be identified, which in turn allow deductions to be made concerning how sorption depends on some key system parameters.

In the following, the uptake of radionuclides at (generally) trace concentrations ($< 10^{-6}$ M) is interpreted in terms of one of two mechanisms: (i) cation exchange and (ii) surface complexation. Sorption values are selected at trace concentrations since under these conditions the uptake of sorbates tend to a Langmuir type behaviour, i.e., at low enough concentrations sorption becomes linear.

Generally, any set of selected sorption values measured under a given set of mineralogical/water chemistry conditions is converted or "tailored" to those of the required system using a series of conversion factors which take into consideration mineralogy, pH, aqueous speciation and finally the fact that measurements are mostly made on dispersed systems in batch type experiments whereas the application in performance assessments is to intact rock.

4.3.1 Mineralogy conversion factor: CF_{\min}

The conversion factor, which takes into account the differences in mineralogy, is given by an equation of the form:

Argillaceous rocks

$$CF_{\min, \text{arg}} = \frac{MIN_{GR, \text{arg}}}{MIN_{\text{illite}}} \quad (4.1)$$

where,

$CF_{\min, \text{arg}}$ = mineralogy conversion factor for argillaceous rocks.

$MIN_{GR, \text{arg}}$ = fractional weight content of 2:1 type clay minerals (illite + illite/smectite ML + smectite) in the argillaceous rock.

$MIN_{\text{illite}} = 1$, when illite is the source data.

4.3.2 Water chemistry

4.3.2.1 pH conversion factors, CF_{pH}

When metal sorption at trace concentrations is investigated in clay mineral systems in simple background electrolytes at moderate concentrations as a function of pH, many metals sorb by surface complexation which gives rise to a strong increase in sorption in the pH range from ~ 5 to ~ 7-8. (The exception to this is the alkaline and alkaline-earth metals which sorb predominantly by cation exchange.) Above pH ~7-8 either a plateau is observed (constant sorption) or a decrease in sorption occurs due to the formation of non sorbing negatively charged hydrolysed species.

In certain cases for very strongly hydrolysing metals, the sorption is high and constant over the whole pH range from ~ 4 to ~ 10.

For metal uptake by surface complexation, corrections for the differences in pH when converting sorption values from one system to another can be significant. Thus it is important to define this conversion factor carefully. For generating SDBs, the selection of the source sorption values were made at a pH of 7 whenever possible.

In many cases the source data were "in house" and literature sorption edge measurements. In these cases, CF_{pH} values could be calculated directly from the measured sorption edge curves. (As an illustration, the calculation of a CF_{pH} relation for Ni is given later.) Listed below are the metals for which the above approach was taken:

Transition and heavy metals: Ni(II); Co(II), Bi(III), Sn(IV)

Lanthanides: Eu(III)

Actinides: Am(III), Th(IV); Pa(V); Np(V); U(VI)

Oxyanions: Se(IV); Mo(VI)

As indicated above, a procedure needs to be developed for taking into account the differences in pH between the source and the generic rock SDB conditions. The strategy followed in this work

is to use sorption edges of metals and anions on illite and derive a pH conversion factor from the experimental data. This procedure is illustrated for 2 cases, a metal (Ni) and an oxyanion (SeO_3^{2-}).

As can be seen in Fig. 4.1, the log of the Ni distribution ratio increases linearly as a function of pH in the range ~4 to ~8. Below and above these pH values the sorption remains approximately constant. The slope (m) of the dotted line drawn through the experimental data is given by:

$$m = \frac{\log R_{d2} - \log R_{d1}}{pH_2 - pH_1} \quad (4.2)$$

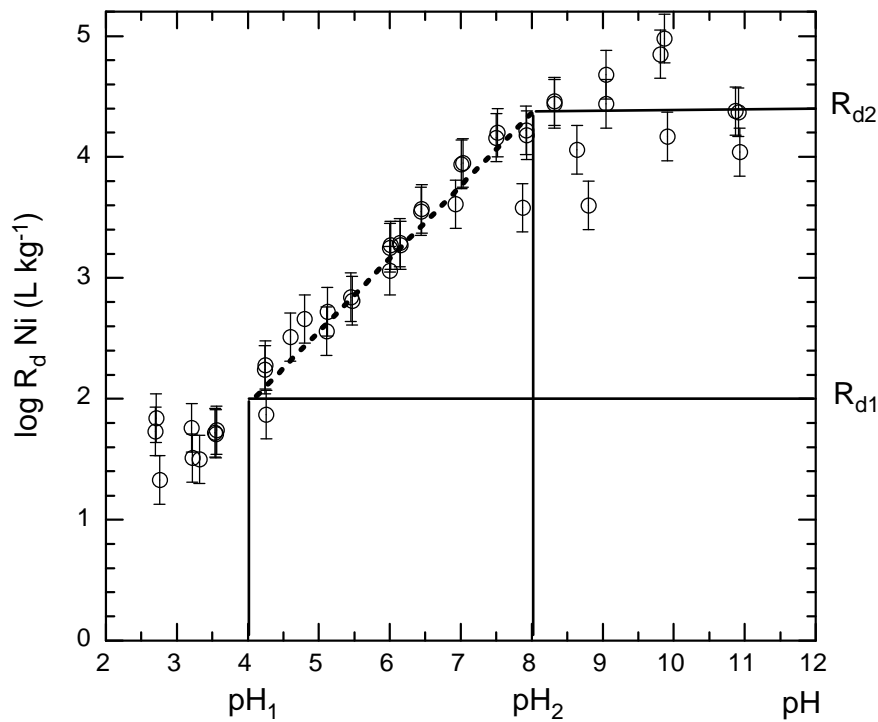


Fig. 4.1: Ni sorption edge measured on Na-illite at trace concentration in a 0.1 M NaClO_4 background electrolyte (Bradbury & Baeyens 2009a).

Equation 4.2 can be re-arranged to give:

$$CF_{pH} = \frac{R_{d2}}{R_{d1}} = 10^{m(pH_2 - pH_1)} \quad (4.3)$$

For the measured sorption edge of each element on illite, the slope m , and the pH range where this slope is constant, can be evaluated. Eq. 4.3 can then be used to calculate the corresponding CF_{pH} value.

A summary of the radionuclides for which a slope and pH range was derived from experimental sorption edge data is given below.

In Fig. 4.2 an example of an oxyanion (Se(IV)) sorption edge on Na-illite is shown (Bruggeman 2006). The same expression as given in Eq. 4.3 can be used to evaluate the pH conversion factor.

No pH corrections are needed for K(I), Cs(I), Ca(II), Sr(II) and Ra(II) since the sorption mechanism for these elements is cation exchange and the sorption values are calculated, see section 5.2.

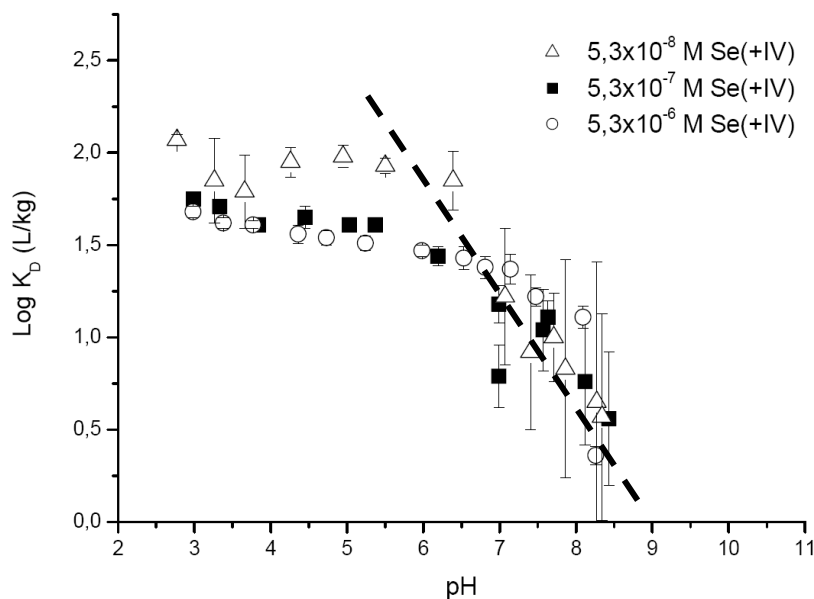


Fig. 4.2: A selenite sorption edge on Na-illite in 0.1 M NaClO₄ (from Bruggeman 2006). The slope of the broken line is -0.6.

Tab. 4.1: Slope values, m in Eq. 4.2, used to calculate pH conversion factors, CF_{pH} , Eq. 4.3.

Radionuclide	slope	pH range	Source
Ni(II)	0.6	4 – 8	Bradbury & Baeyens (2009a)
Co(II)	0.8	6 – 9	Bradbury & Baeyens (2009a)
Bi(III)	0.6	5 – 7	Ulrich & Degueldre (1992)
Eu(III)	0.8	4 – 8	Bradbury & Baeyens (2009a)
Am(III)	0.9	4 – 7	Bradbury & Baeyens (2009a)
Np(V)	0.5	6 – 11	Gorgeon (1994)
U(VI)	1.0	3 – 6	Bradbury & Baeyens (2009b)
Se(IV)	-0.6	6 – 9	Bruggeman (2006)
Mo(VI)	-0.3	4 – 8	Theng (1971)

4.3.2.2 Speciation conversion factor, CF_{spec}

The complexation of radionuclides with inorganic and organic ligands can influence sorption, and therefore corrections need to be made to reflect the variations in aqueous speciation in the different water chemistries considered. A rigorous correction is only possible when a verified sorption model is available, and this is generally not the case. Nevertheless some plausible procedures are given below.

In oxide and clay mineral systems it is widely observed that the formation of positively charged or neutral hydrolysed species does not adversely influence sorption behaviour. Indeed, very high metal sorption is often measured in regions where neutral hydroxy species dominate. (See for example Schultess & Huang 1990; Gorgeon 1994; Turner et al. 1998.) Whether or not other neutral and positively charged complexes can also be taken up by sorbents is less clear, but must remain a possibility.

In order to make a correction to sorption values taking into account the differences in radionuclide speciation in different water chemistries, species which sorb and those which do not sorb have to be distinguished. The proposal put forward for metals is to define free cation, positively charged and neutral hydrolysed species as being sorbing. All other species are treated as being non-sorbing.

For elements such as Se(IV) and Mo(VI), the sorbing species in the range of pH values considered are taken to be the oxyanion and the protonated oxyanion (see Fig. 4.2).

The conversion factor used for modifying sorption values according to the speciation in different water chemistries is simply:

$$CF_{\text{spec}} = \frac{F_{\text{GR}}}{F_{\text{source}}} \quad (4.4)$$

where

CF_{spec} is the speciation conversion factor.

F_{GR} is the fraction of the radionuclide concentration calculated to be present in the aqueous phase as sorbing species in the generic rock water chemistry.

F_{source} is the fraction of the radionuclide concentration calculated to be present in the aqueous phase as sorbing species in the source sorption measurements.

Attempts to correct for speciation differences in this manner are of course sensitively dependent on the quality and consistency of the stability constants in the thermodynamic data bases. The Nagra/PSI thermodynamic data base (Hummel et al. 2002) has been used throughout this report. Speciation calculations were carried out in a redox decoupled mode. That is to say the speciation was calculated for a single valence state of an element (decoupled) and not for systems where an element existed in a number of valence states (coupled). A compilation of the results of all the speciation calculations is given in the Appendices A3 to A4.

It was noted in some previous work (Bradbury & Baeyens 2003a,b) that the above scheme was not appropriate for tetravalent actinides. Speciation calculations using the stability constants in Hummel et al. (2002), indicated that negatively charged hydroxy-carbonato complexes become very important in the pH ranges of interest in calcite saturated solutions. However, sorption measurements of Th(IV) on clay mineral containing systems in such solutions showed that the

expected reductions in sorption based on the above hypothesis were orders of magnitude greater than found experimentally (Lauber et al. 2000). In view of this discrepancy, which, incidentally, highlights a deficit of understanding for this important group of safety relevant radionuclides, a simplifying assumption was made, i.e., for tetravalent metals a speciation factor of unity was taken. This assumption was more or less in accord with the experimental findings (see also Lauber et al. 2000).

4.3.2.3 Formulation

The above procedures can be summarised as follows. Consider that a measured source data set for a radionuclide RN needs to be transposed to the GR-SDB conditions. The source data are:

$R_{d,illite}$, MIN_{illite} , pH_{illite} , F_{illite} and variation of the distribution coefficient with pH from the sorption edge data is given by: $10^{m(pH_{GR} - pH_{illite})}$.

The distribution ratio, $R_{d,GR}$, is required for the generic rock sorption data base conditions: MIN_{GR} , pH_{GR} , F_{GR}

Then,

$$R_{d,GR} = R_{d,illite} \cdot CF_{min} \cdot CF_{pH} \cdot CF_{spec}$$

where:

$$CF_{min} = \frac{MIN_{GR}}{MIN_{illite}}$$

$$CF_{pH} = 10^{m(pH_{GR} - pH_{illite})}$$

$$CF_{spec} = \frac{F_{GR}}{F_{illite}}$$

4.3.2.4 Lab→Field conversion factor, $CF_{Lab \rightarrow Field}$

The general applicability of batch sorption data obtained on dispersed systems to intact rock systems, and proposals how to modify such measurements so that they are applicable to the "in situ" case have been addressed in Bradbury & Baeyens (1997) Chapter 7, and in Bradbury & Baeyens (1998). In this latter work the Lab→Field conversion factor is used to convert laboratory sorption data measured on dispersed systems to values appropriate for intact rock. This factor was calculated from N₂-BET surface area data measured on intact rock and then again on the same sample but in a crushed state. The conversion factor was then defined as:

$$CF_{Lab \rightarrow Field} = \frac{(N_2 - BET \text{ area})_{intact \text{ rock}}}{(N_2 - BET \text{ area})_{crushed \text{ rock}}} \quad (4.5)$$

Since this procedure was first proposed in 1998 (Bradbury & Baeyens 1998) no new information on this topic has been published which changes the general conclusions. Consequently, Lab→Field conversion factors of unity for argillaceous rocks and 0.05 for calcareous rocks have been chosen in the generic rock SDBs given later in Chapter 6.

4.3.2.5 Rounding

The R_d values given are the product of the individual selected R_d values and their respective conversion factors. For transparency and traceability reasons these calculated values have not been rounded.

References

- Bradbury, M.H. & Baeyens, B. (1997a): Far-Field Sorption Data Bases for Performance Assessment of a L/ILW Repository in an Undisturbed Palfris Marl Host Rock PSI Bericht Nr. 97-15, Nagra Tech. Rep. NTB 96-06.
- Bradbury, M.H. & B. Baeyens, B.(1997b): "A mechanistic description of Ni and Zn Sorption on Na-montmorillonite. Part II: Modelling." *Journal of Contaminant Hydrology*, 27, 223-248.
- Bradbury, M.H. & Baeyens, B. (1998): N_2 -BET surface area measurements on crushed and intact minerals and rocks: A proposal for estimating transfer factors. *Nuclear Technology* 122, 250-253.
- Bradbury, M.H. & Baeyens, B. (2003) Far-field sorption data bases for performance assessment of a high-level radioactive waste repository in an undisturbed Opalinus Clay host rock. PSI Bericht Nr. 03-08, Nagra Tech. Rep. NTB 02-19.
- Bradbury, M.H. and Baeyens, B. (2004): Modelling the sorption of Mn(II), Co(II), Ni(II), Zn(II), Cd(II), Eu(III), Am(III), Sn(IV), Th(IV), Np(V) and U(VI) on montmorillonite: Linear free energy relationships and estimates of surface binding constants for some selected heavy metals and actinides *Geochimica et Cosmochimica Acta* 69, 875-892 and Erratum 69 5391-5392.
- Bradbury, M.H. & Baeyens, B. (2005): Experimental and modelling investigations on Na-illite: Acid-base behaviour and the sorption of strontium, nickel, europium and uranyl. PSI Bericht Nr. 05-02, Nagra Tech. Rep. NTB 04-02.
- Bradbury, M.H., Baeyens, B. (2009a): Sorption modeling on illite Part I: Titration measurements and the sorption of Ni, Co, Eu and Sn. *Geochimica et Cosmochimica Acta* 73, 990-1003.
- Bradbury, M.H., Baeyens, B. (2009b): Sorption modeling on illite Part II: Actinide sorption and linear free energy relationships. *Geochimica et Cosmochimica Acta* 73, 1004-1013.
- Bruggeman, C. (2006): Assessment of the geochemical behaviour of selenium oxyanions under Boom Clay geochemical conditions. *Dissertationes de Agricultura*, PhD Nr. 733, Catholic University Leuven, Belgium.
- Davis, J.A., Ochs, M., Olin, M., Payne, T.E., and Tweed, C.J., (2005): Interpretation and prediction of radionuclide sorption onto substrates relevant for radioactive waste disposal using thermodynamic sorption models. Nuclear Energy Agency, Paris. 286 pp.
- Gorgeon, L. (1994): Contribution à la modélisation physico-chimique de la rétention de radioéléments à vie longue par des matériaux argileux. Unpublished PhD Thesis. Université Paris 6.

- Hummel, W., Berner, U., Curti, E., Pearson, F.J. & Thoenen, T. (2002): Nagra/PSI Chemical Thermodynamic Data Base 01/01. Nagra Tech. Rep. NTB 02-16, and Universal Publishers/uPublish.com, Parkland, Florida, USA.
- Lauber, M., Baeyens, B. & M. H. Bradbury (2000): Sorption of Cs, Sr, Ni, Eu, Th, Sn and Se on Mont Terri Opalinus Clay: Physico-chemical characterisation and sorption measurements. PSI Bericht Nr. 00-10, Nagra Tech. Rep. NTB 00-11.
- Schultess, C.P. & Huang, C.P. (1990): Adsorption of heavy metals by silicon and aluminium oxide surfaces on clay minerals. *Soil Sci. Soc. Am. J.* 54, pp. 679-688.
- Theng, B.K.G. (1971): Adsorption of molybdate by some crystalline and amorphous soil clays. *New Zealand J. Sci.* 14, pp. 1040-1056.
- Turner, D.R., Pabalan, R.T. & Bertetti, F.P. (1998): Neptunium (V) sorption on montmorillonite: An experimental and surface complexation modelling study. *Clays and Clay Minerals* 4, pp. 256-269.
- Ulrich, H.J. & Degueldre, C. (1992): The sorption of ^{210}Pb , ^{210}Bi and ^{210}Po on montmorillonite: A study with emphasis on reversibility aspects and on the effect of radioactive decay of adsorbed nuclides. *Radiochimica Acta* 62, pp. 81-90.

5 Chemical Analogues, Cation Exchange and Special Cases

5.1 Chemical analogues

Sometimes there is no or only unreliable sorption data available for particular radionuclides and then the only option is to select chemical analogues for which sorption data are available.

In this report the choice of an appropriate chemical analogue is based upon:

- the valence state
- the hydrolysis behaviour

In some previous work it has been shown that there is a linear relationship between surface complexation constants and the corresponding hydrolysis constants, so called Linear Free Energy Relations, for radionuclides uptake on both illite and montmorillonite (Bradbury & Baeyens 2005, 2009b). Thus, chemical analogues are chosen primarily on the basis of the similarity of the first hydrolysis constant as illustrated for the metals in Table 5.1.

Tab. 5.1: Overview of chemical analogues. The log K values are for $I = 0$ and the hydrolysis reaction $Me^{n+} + H_2O \Leftrightarrow MeOH^{(n-1)+} + H^+$.

	Element	Chemical analogue		
<i>Transition metals</i> log K_1 ^{a)}	Ni ²⁺ -9.86	Cd ²⁺ -10.08		
<i>Lanthanides</i> log K_1 ^{a)}	Eu ³⁺ -7.8	Ce ³⁺ -8.3	Sm ³⁺ -7.9	Ho ³⁺ -8.0
<i>Trivalent actinides</i> log K_1 ^{b)}	Am ³⁺ -7.2	Ac ^{3+a)} <-10.4	Pu ³⁺ -6.9	Cm ³⁺ -7.2
<i>Tetravalent actinides</i> log K_1 ^{b)}	Th ⁴⁺ -2.5	U ⁴⁺ -0.54	Np ⁴⁺ 0.55	Pu ⁴⁺ 0.0
<i>Pentavalent actinides</i> log K_1 ^{b)}	NpO ₂ ⁺ -11.3	PuO ₂ ⁺ ≤ -9.73		
<i>Tetravalent elements</i> log K_1 ^{a)}	Sn ⁴⁺ -0.8	Zr ⁴⁺ 0.3	Hf ⁴⁺ -0.3	

^{a)} Baes & Mesmer (1976)

^{b)} Nagra/PSI TDB 2010 (T. Thoenen, pers. comm.)

In the cases of Be(II) (log $K_1 = -5.4$) and Pd(II) (log $K_1 = -2.0$ at $I = 1$ M) there are no obvious choices of chemical analogues based on the criteria of similar first hydrolysis constants. However, for both Be(II) and Pd(II) lead has been chosen because the log K_1 value of - 7.7 is the nearest to those of Be(II) and Pd(II) of all divalent metals for which sorption data exist. The hydrolysis constants for Be(II) and Pd(II) are much greater than that of Pb(II) which implies that the choice is a conservative one.

Bi(III) is taken as a chemical analogue for Sb(III) and Se(IV) for Po(IV), because their respective speciations in the pH range of interest are similar and sorption data for Bi(III) and Se(IV) are available.

The hydrolysis behaviour of U(IV), Np(IV) and Pu(IV) is much stronger than Th(IV). On the basis of the arguments given in section 4.3.2.2 and the Linear Free Energy relationships presented in Bradbury & Baeyens (2005, 2009b), U(IV), Np(IV) and Pu(IV) would be expected in general to form stronger surface complexes. Therefore, taking Th(IV) as the chemical analogue for these tetravalent actinides is a rather conservative choice.

In cases where chemical analogy is invoked, the sorption value for the analogue element in the generic rock sorption data base is taken, i.e., $R_{d \text{ ANALOG GR}}$. The only further correction factor which needs to be applied to obtain the $R_{d \text{ RN GR}}$ value for the radionuclide in question is one which takes into account any differences in aqueous speciation between the two in the appropriate reference waters, i.e.,

$$CF_{\text{SPEC (ANALOG)}} = F_{\text{SPEC RN GR}} / F_{\text{SPEC ANALOG GR}} \quad (5.1)$$

where

$F_{\text{SPEC RN GR}}$ is the fraction of the radionuclide concentration calculated to be present in the aqueous phase as sorbing species in the generic rock porewater.

$F_{\text{SPEC ANALOG GR}}$ is the fraction of the chemical analogue concentration calculated to be present in the aqueous phase as sorbing species in the generic rock porewater.

$$R_{d \text{ RN GR}} = R_{d \text{ ANALOG GR}} \times CF_{\text{SPEC (ANALOG)}} \quad (5.2)$$

5.2 Sorption by cation exchange in argillaceous rocks

The sorption values for K, Cs, Ca, Sr and Ra on illite in the generic water compositions (Table 3.2) are calculated using the generalised Cs sorption model developed by Bradbury & Baeyens (2000) for illitic systems. The cation exchange reactions and corresponding selectivity coefficients are given in Table 5.2. The selectivity coefficient for Sr-Na was taken from Bradbury & Baeyens (2005) and the selectivity coefficients for Ca-Na and Ra-Na were assumed to be the same. The model calculations yield fractional occupancies from which R_d values for illite can be calculated. For Cs and Ra the calculations were performed at trace concentrations, $\sim 10^{-8}$ M; K, Ca and Sr concentrations are fixed by the porewater composition. The results presented in Table 5.3 are the source data for illite (see Chapter 6) for the alkaline and alkaline earth metals. These values are then converted to those corresponding to argillaceous rocks (Table 7.1) using the mineralogical conversion factors given in section 4.3.1.

Tab. 5.2: Cation exchange reaction and corresponding selectivity coefficients (K_c) on the planar sites, type-II sites and frayed edge sites of illite (taken from Bradbury & Baeyens 2000, 2005).

Cation exchange reactions:	log K_c	Site capacity
Planar sites (PS)		1.6×10^{-1} Eq kg ⁻¹
Na-PS + K ⁺ \rightleftharpoons K-PS + Na ⁺	1.1	
Na-PS + Cs ⁺ \rightleftharpoons Cs-PS + Na ⁺	1.6	
2Na-PS + Me ²⁺ \rightleftharpoons Me-PS + 2Na ⁺	1.05	
Type II sites (II-S)		4.0×10^{-2} Eq kg ⁻¹
Na-II-S + K ⁺ \rightleftharpoons K-II-S + Na ⁺	2.1	
Na-II-S + Cs ⁺ \rightleftharpoons Cs-II-S + Na ⁺	3.6	
Frayed edge sites (FES)		5.0×10^{-4} Eq kg ⁻¹
Na-FES + K ⁺ \rightleftharpoons K-FES + Na ⁺	2.4	
Na-FES + Cs ⁺ \rightleftharpoons Cs-FES + Na ⁺	7	

Me = Ca or Sr or Ra

Tab. 5.3: Results of R_d (m³ kg⁻¹) calculations for K, Cs, Ca, Sr and Ra for illite in the generic argillaceous water compositions (Tab. 3.2) using the parameters given in Table 5.2.

System	K	Cs	Ca	Sr	Ra
Argint	2.2×10^{-2}	9.6	5.1×10^{-3}	5.1×10^{-3}	3.9×10^{-3}
Argl6	4.1×10^{-2}	18.2	4.3×10^{-3}	4.2×10^{-3}	4.0×10^{-3}
Arg6	1.3×10^{-2}	6.1	1.4×10^{-3}	1.4×10^{-3}	1.1×10^{-3}
Argl9	4.1×10^{-2}	15.1	2.2×10^{-2}	2.2×10^{-2}	1.7×10^{-2}
Arg9	1.3×10^{-2}	5.8	2.2×10^{-3}	2.2×10^{-3}	1.5×10^{-3}

5.3 Special cases: Nb(V), Ru(IV), Sb(V), Tc(IV), Pd(II) and C_{inorg}

Nb(V)

In the case of Nb(V), the only data available are those from Legoux et al. (1992). The "one off" sorption results measured at different pH values by Legoux et al. (1992) for four sediments with different clay mineral contents are given in Table 5.4. The illite/glaucanite and smectite values are given. The presence of the other minerals (kaolinite, < 2 wt. % and palygorskite, 1.4 wt. % in sediment A) has been neglected.

Tab 5.4: Sorption data for Nb(V) in a synthetic groundwater on various sediments. (Nb equilibrium concentration $< 10^{-10}$ M). Taken from Legoux et al. (1992).

Solid phase	Clay content (wt. %)	pH_{source}	R_d measured (m³ kg⁻¹)
Sediment A	7.2	7.6	2.6
Sediment B	12.6	5.9	1.5
Sediment C	15.3	6.6	1.7
Sediment D	8.0	8.0	2.1

The Legoux et al. (1992) data for the sorption of Nb(V) at different pH values (5.9 to 8) on sediments with different 2:1 clay mineral contents (7.2 to 15.3 wt%) seem to be independent of both of these parameters i.e. a sorption value of around 2 m³ kg⁻¹ is measured in all cases, and this is somewhat difficult to understand.

The sorption mechanism for Nb(V) is not known, and there is no sorption model to guide the selection of sorption values under different conditions. If the main sorbing species is taken to be Nb(OH)₅⁰, then at pH ~ 6 the negatively charged Nb(OH)₆⁻ species already begins to form, and this is taken to be non-sorbing. Further, nothing is known about the complexation of Nb(V) with carbonate. Again, in the range of water chemistries investigated by Legoux et al. (1992), these factors do not seem to have played an important role.

Thus, there are considerable difficulties in applying this data for Nb(V) to other systems. However, Legoux et al.'s experiments do at least indicate that Nb(V) sorbs, and some credit should be taken for this; but Nb(V) needs to be treated as a special case.

The following is recommended on the basis of conservatism. A sorption value of 1 m³ kg⁻¹ is taken for any systems which lie in the range of the main parameters in Legoux et al.'s experiments i.e. for average clay mineral contents of approximately 10 wt. % and pH values in the range 6 to 8.

For any systems with a pH > 8, the sorption of Nb(V) is set to zero for speciation reasons. If the 2:1 clay mineral content in an argillaceous rock is > 10 wt. %, then, on a conservative approach, no additional credit is taken for this. However, for 2:1 clay mineral contents > 0 and < 10 wt. %, sorption will occur, and in such cases the sorption value of 1 m³ kg⁻¹ should be reduced proportionally, i.e. by a reduction factor of X/10, where "X" is the 2:1 clay mineral wt. % content.

Ru(IV)

No sorption data at all could be found for Ru(IV). The thermodynamic data available are sparse and uncertain and no chemical analogue for which reliable sorption data are available readily suggests itself. Considering its position in the Periodic Table, Ru(IV) could be taken to behave similarly to Tc(IV) and/or the platinum metals. However, sorption data for these metals is also practically non-existent. Because of this extreme lack of information, Ru(IV) has been taken as non sorbing.

Sb(V)

Under oxidising conditions antimony occurs in the pentavalent state. No sorption data for this element could be found in the open literature and because the hydrolysed species above pH 4 is the negatively charged $\text{Sb}(\text{OH})_6^-$ (Baes & Mesmer 1976), a sorption value of zero has been attributed to Sb(V).

Tc(IV)

Tc(IV) is another of those metals for which reliable sorption data are not available. Speciation calculations indicate that the solubility is very low, and that the neutral $\text{TcO}(\text{OH})_2^0$ species is dominant in simple 1:1 electrolyte solutions from pH ~ 3 to ~ 10, see Fig. 5.1.

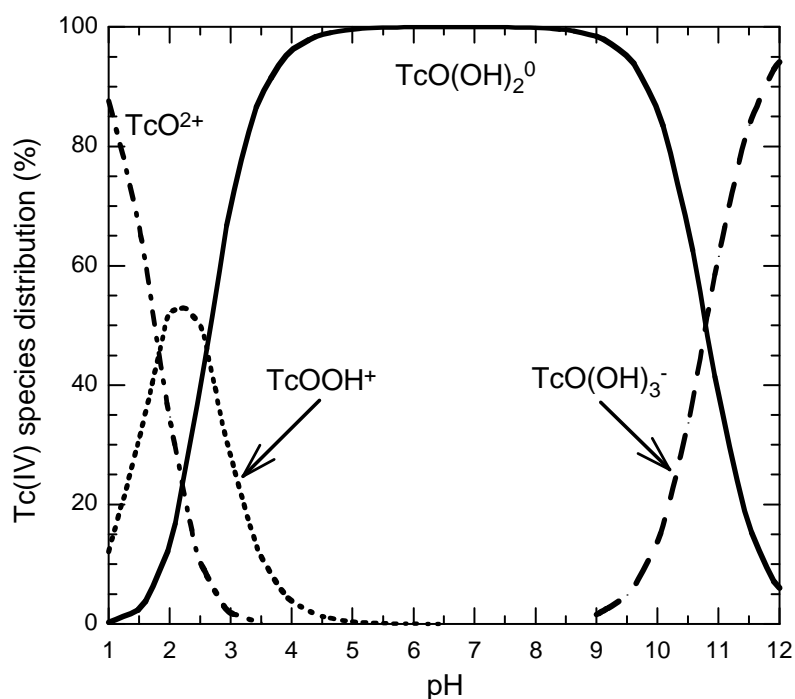


Fig. 5.1: The speciation of Tc(IV) in 0.1 M NaClO_4 . Thermodynamic data are taken from Hummel et al. (2002).

In the cases of Th(IV) and Sn(IV) the dominant aqueous species in the pH range ~4 to ~10 is the neutral tetrahydroxy complex and the sorption of these two elements on clay minerals (illite, montmorillonite) is very high and constant in this pH range (Bradbury & Baeyens 2005a, 2009a,b). If it is accepted that the key sorption indicators are the presence of hydroxy ions in an overall neutral species, a similar sorption behaviour between a neutral tetrahydroxy complex and a neutral $\text{TcO}(\text{OH})_2^0$ species might be expected. Given the lack of reliable quantitative experimental data, a nominal sorption value for Tc(IV) on illite of 2 orders of magnitude below that of Sn(IV) and Th(IV) is given i.e. $2.5 \text{ m}^3 \text{ kg}^{-1}$. (The speciation factor corresponding to the ground waters for Tc(IV) is applied.)

Pd(II)

No sorption data exist for Pd(II).

Based on their hydrolysis behaviour (Baes & Mesmer 1976) and their relative positions in the Periodic Table, metals such as Co(II), Ni(II), Cd(II) and Pb(II), for which sorption data exist, might suggest themselves as chemical analogues for Pd(II). However, Pd(II) would be expected to be much more strongly sorbing than any of these metals because of its considerably greater tendency to hydrolyse. Lead is chosen as the most suitable chemical analogue for Pd(II) because it is the most strongly hydrolysable of the group (Co(II), Ni(II), Cd(II), Pb(II)) but will almost certainly yield very conservative R_d values for Pd(II). No pH conversion factor is used for Pd(II) since the neutral $\text{Pd}(\text{OH})_2^0$ species dominates in the pH range 3 to 10 and it is anticipated that the sorption edge would be a plateau in this pH region.

Inorganic carbon, C_{inorg}

A sorption value for C_{inorg} is not given in the GR-SDB since any value for inorganic carbon containing ^{14}C is system dependent and is calculated individually from the inorganic carbon concentration in the groundwater and the calcite content in the rock. The procedure is described in section 9.4.2 in Bradbury & Baeyens (1997), but is worth briefly describing here for completeness.

The most likely removal mechanism for any ^{14}C existing in solution as $\text{H}^{14}\text{CO}_3^- / ^{14}\text{CO}_3^{2-}$, is isotopic exchange with the surface layers of carbonate minerals, particularly CaCO_3 . A difficult question to answer is how much of the calcite present is available to take part in this exchange. An estimate can be made on the basis of the work of Stipp et al. (1994, 1996) who showed that the calcium in the first approximately 30 monolayers, i.e., to a depth of $\sim 10^{-8}$ m, is readily accessible on time scales of the order of a few months. If we take this value of 10^{-8} m and the accessible surface area in intact calcite ($\sim 0.1 \text{ m}^2 \text{ g}^{-1}$) then the volume of calcite available for exchange is $\sim 10^{-6} \text{ m}^3 \text{ kg}^{-1}$. For a calcite density of 2700 kg m^{-3} , this converts to $\sim 2.7 \times 10^{-3} \text{ kg kg}^{-1}$, or $\sim 0.27 \text{ wt. \%}$ of the total calcite. This estimate is almost certainly conservative, since more calcite is likely to become available over longer times. Note also that the above value is an in situ estimate since the surface area for intact calcite was used.

In the generic rock SDBs, a calcite content in the argillaceous rock of 16 wt. % was taken. If required, the calculations can easily be carried out with other values.

If 0.27 wt.% of the bulk calcite is taken to be available for exchange with $^{14}\text{C}_{\text{inorg}}$ ($\text{H}^{14}\text{CO}_3^- / ^{14}\text{CO}_3^{2-}$), then the total moles of exchangeable CO_3^{2-} in calcite is $2.7 \times 10^{-2} \text{ mol kg}^{-1}$. The available exchangeable $^{14}\text{C}_{\text{inorg}}$ in argillaceous rocks is $4.3 \times 10^{-3} \text{ mol CO}_3$ per kg.

Thus, the $^{14}\text{C}_{\text{inorg}}$ sorption values in the generic rock SDBs can be readily obtained using the above values together with the respective aqueous concentrations given in Table 3.2. The results are given in Table 7.1.

Non sorbing elements

HTO, C_{org} , Cl(-I), I(-I), Ag(I), Se(-II), Ru(IV), Sb(V), Se(VI), Tc(VII) are considered to be non-sorbing.

References

- Baes, C.F. & Mesmer, R.E. (1976): *The Hydrolysis of Cations*. John Wiley and Sons, New York.
- Bradbury, M.H. & Baeyens, B. (1997): Far-Field Sorption Data Bases for Performance Assessment of a L/ILW Repository in an Undisturbed Palfris Marl Host Rock PSI Bericht Nr. 97-15, Nagra Tech. Rep. NTB 96-06.
- Bradbury, M.H. & Baeyens, B. (2003): Far-field sorption data bases for performance assessment of a HLW repository in an undisturbed Opalinus Clay host rock. PSI Bericht Nr. 03-08 and Nagra NTB 02-19.
- Bradbury, M.H. & Baeyens, B. (2005): Experimental and modelling investigations on Na-illite: Acid-base behaviour and the sorption of strontium, nickel, europium and uranyl. PSI Bericht Nr. 05-02, Nagra Tech. Rep. NTB 04-02.
- Hummel, W., Berner, U., Curti, E., Pearson, F.J. & Thoenen, T. (2002): Nagra/PSI Chemical Thermodynamic Data Base 01/01. Nagra Technical Report NTB 02-16, Nagra, Wetingen, Switzerland, and Universal Publishers/uPublish.com, Parkland, Florida, USA.
- Legoux, Y., Blain, G., Guillaumont, R., Ouzounizian, G., Brillard, L. & Hussonnois, M. (1992): K_d measurements of activation, fission and heavy elements in water/solid phase systems. *Radiochimica Acta* 58/59, 211-218.
- Stipp, S.L.S., Eggleston, C.M. & Nielsen, B.S. (1994): Calcite surface structure observed at microtopographic and molecular scales with atomic force microscopy (AFM). *Geochimica et Cosmochimica Acta* 58, 3023-3033.
- Stipp, S.L.S., Gutmannsbauer, W. & Lehmann, T. (1996): The dynamic nature of calcite surfaces in air. *American Mineralogist* 81, 1-18.

6 Source Data for the Compilation of Generic SDBs for Argillaceous Rocks

The references for the source data used in the compilation of GR-SDBs are given in Table 6.1. Also the chemical analogues used in the GR-SDBs to derive values for metals for which no sorption data were available are also given in Table 6.1. In addition see section 5.1 on chemical analogues.

On the basis of the source data selected from the references given in Table 6.1, the columns $R_{d-source}$, $F_{spec.-source}$ and pH_{source} were completed in Table 6.2. The pH plateau ranges are also indicated, i.e., pH ranges where the sorption is effectively constant. The "sorbing mineral content" is 100 % in all cases. The values for F-source were obtained from the tabulated speciation calculation results given in Appendix A3.2.

Note that no sorption values are given for the alkali metals K and Cs, and the alkali earth metals Ca, Sr and Ra since they are all calculated according to cation exchange models and depend on the specific water chemistries and mineralogies (CEC values) considered. The sorption of these radionuclides will be calculated for the individual conditions for the generic rock SDBs for argillaceous rocks.

Tab. 6.1: Source data references.

Radionuclide	Source data reference
H(HTO)	Sorption set to zero; Bradbury Baeyens (2003)
Be(II)	Ni(II) analogue
C(inorg.)	Sorption calculated from isotopic exchange with calcite
C(org.)	Sorption set to zero; Bradbury Baeyens (2003)
Cl(-I)	Sorption set to zero; Bradbury Baeyens (2003)
K(I)	Illite sorption model; Bradbury & Baeyens (2000, 2005)
Ca(II)	Illite sorption model; Bradbury & Baeyens (2000, 2005)
Co(II)	Illite: Bradbury & Baeyens (2009a)
Ni(II)	Illite: Bradbury & Baeyens (2009a)
Se(-II)	Sorption set to zero; Bradbury Baeyens (2003)
Se(IV)	Illite: Bruggeman (2006)
Se(VI)	Sorption set to zero, see Bruggeman (2006)
Sr(II)	Illite sorption model; Bradbury & Baeyens (2000, 2005)
Zr(IV)/Hf(IV)	Sn(IV) analogue
Nb(V)	Sedimentary rocks: Legoux et al. (1992),
Mo(VI)	Illite: Motta & Miranda (1989)
Tc(IV)	Expert judgement (see section 4.3)
Tc(VII)	Sorption set to zero; Bradbury Baeyens (2003)
Ru(IV)	Sorption set to zero (see section 4.3)
Pd(II)	Pb(II) analogue
Ag(I)	Sorption set to zero; Bradbury Baeyens (2003)
Cd(II)	Ni(II) analogue
Sn(IV)	Illite: Bradbury & Baeyens (2009a)
Bi(III)	Montmorillonite: Ulrich & Degueldre (1992)
Sb(III)	Bi(III) analogue
I(-I)	Sorption set to zero, Bradbury & Baeyens (unpublished data)
Cs(I)	Model calculations; Bradbury & Baeyens (2000)
Eu(III)	Illite: Bradbury & Baeyens (2009a)
Ce(III), Pm(III), Ln(III), Ho(III)	Eu(III) analogue
Pb(II)	montmorillonite; Ulrich & Degueldre (1992)
Po(IV)	Se(IV) analogue
Ra(II)	Illite sorption model; Bradbury & Baeyens (2000, 2005)
Th(IV)	Illite: Bradbury & Baeyens (2009b)
Pa(V)	Illite: Bradbury & Baeyens (2009b)
U(IV), Np(IV), Pu(IV)	Th(IV) analogue
U(VI)	Illite: Bradbury & Baeyens (2009b)
Np(V)	Illite: Gorgeon (1994)
Pu(III)	Am(III) analogue
Pu(V)	Np(V) analogue
Am(III)	Illite: Bradbury & Baeyens (2009b)
Ac(III), Cm(III)	Am(III) analogue

Tab. 6.2: Source data sets*

Element	R_d, source ($\text{m}^3 \text{kg}^{-1}$)	$F_{\text{spec. source}}$	$\text{pH}_{\text{source}}$	Plateau: pH range
Co(II)	1.6	1.00	7.00	9 to 10
Ni(II)	4.0	1.00	7.00	8 to 10
Se(IV)	1.8×10^{-2}	1.00	7.00	3 to 6
Nb(V)	1	-	-	
Mo(VI)	1.6×10^{-2}	1.00	8.20	
Tc(IV)	2.5	1.00	7.00	plateau
Sn(IV)	250	0.89	7.00	3 to 10
Bi(III)	32	1.00	7.00	> 7
Eu(III)	100	1.00	7.00	8 to 10
Pb(II)	32	0.93	7.00	8 to 10
Th(IV)	250	1.00	7.00	5 to 10
Pa(V)	50	1.00	7.00	4 to 10
U(VI)	63	0.70	7.00	6 to 10
Np(V)	1.6×10^{-2}	1.00	7.00	
Am(III)	300	1.00	7.00	7 to 10

* The R_d values for K, Cs, Ca, Sr and Ra are calculated for illite in the respective reference waters (see Tables 5.2 and 5.3), and C_{inorg} as described in section 5.2. These elements are therefore not included in this table.

The analogues listed in Table 5.1 are treated as described in section 5.1.

For the elements HTO, C_{org} , Cl(-I), Se(-II), Se(VI), Tc(VII), Ru(IV), Ag(I), I(-I) the sorption values were taken to be zero, and are not included in this table.

References

- Bradbury, M.H. & Baeyens, B. (1997): Far-Field Sorption Data Bases for Performance Assessment of a L/ILW Repository in an Undisturbed Palfris Marl Host Rock PSI Bericht Nr. 97-15 and Nagra Technical Report NTB 96-06.
- Bradbury, M.H. & Baeyens B. (2000): A generalised sorption model for the concentration dependent uptake of Cs by argillaceous rock. Journal of Contaminant Hydrology 42, pp. 141-163.
- Bradbury, M.H. & Baeyens, B. (2001): In Smith, P.A., Alexander, W.R., Heer, W., Fierz, T., Meier, P.M., Baeyens, B., Bradbury, M.H., Mazurek, M., & McKinley, I.G. (2001): Grimsel Test Site Investigation Phase IV (1994-1996). The Nagra-JNC in situ study of safety relevant radionuclide retardation in fractured crystalline rock. I: Radionuclide Migration Experiment - Overview 1990-1996. Nagra Tech. Rep. NTB 00-09.

- Bradbury, M.H. & Baeyens, B. (2003): Far-field sorption data bases for performance assessment of a HLW repository in an undisturbed Opalinus Clay host rock. PSI Bericht Nr. 03-08, Nagra Tech. Rep. NTB 02-19.
- Bradbury, M.H. & Baeyens, B. (1998b): A physico-chemical characterisation and geochemical modelling approach for determining porewater chemistries in argillaceous rocks. *Geochim. Cosmochim. Acta* 62, 783-795.
- Bradbury, M.H., Baeyens, B. (2009a): Sorption modeling on illite Part I: Titration measurements and the sorption of Ni, Co, Eu and Sn *Geochimica et Cosmochimica Acta* 73, 990-1003.
- Bradbury, M.H., Baeyens, B. (2009b): Sorption modeling on illite Part II: Actinide sorption and linear free energy relationships *Geochimica et Cosmochimica Acta* 73, 1004-1013.
- Bruggeman, C. (2006): Assessment of the geochemical behaviour of selenium oxyanions under Boom Clay geochemical conditions. *Dissertationes de Agricultura*, Ph.D. Nr. 733, Catholic University Leuven, Belgium.
- Legoux, Y., Blain, G., Guillaumont, R., Ouzounizian, G., Brillard, L. & Hussonnois, M. (1992): K_d measurements of activation, fission and heavy elements in water/solid phase systems. *Radiochimica Acta* 58/59, 211-218.
- Gorgeon, L. (1994): Contribution à la modélisation physico-chimique de la rétention de radioéléments à vie longue par des matériaux argileux. Unpublished Ph.D. Thesis. Université Paris 6.
- Koss, V., Winkler, A. & Bütow, E. (1992): Experimental investigation and modelling of the migration of radionuclides from the Ellweiler uranium mill tails. *Radiochimica Acta* 58/59, 447-451.
- Motta, M.M. & Miranda, C.F. (1989): Molybdate adsorption on kaolinite, montmorillonite and illite: Constant capacitance modelling. *Soil Sci. Soc. Am. J.* 53, 380-385.
- Ulrich, H.J. & Degueldre, C. (1992): The sorption of ^{210}Pb , ^{210}Bi and ^{210}Po on montmorillonite: A study with emphasis on reversibility aspects and on the effect of radioactive decay of adsorbed nuclides. *Radiochimica Acta* 62, 81-90.

7 Generic Argillaceous Rock SDBs

In Chapter 3 arguments were presented which bounded the types of groundwater to be expected in argillaceous rock formations in Switzerland. Basically, four types of generic groundwaters were defined, a high and low ionic strength water at a lower bound pH of 6, and a high and low ionic strength water at an upper bound pH of 9. In addition, a generic groundwater with intermediate ionic strength and pH was specified. For each of these generic groundwaters, see Tab. 3.2, speciation factors (F-values), as defined in section 4.4.2.2, were calculated for all of the radionuclides (and valence states) listed in Table 6.1. These values are given in Appendix 4 Tables A4.2, A4.4, A4.6, A4.8 and A4.10.

A 2:1 clay mineral content of 25 wt. % was chosen for a generic argillaceous rock mineralogy. The exact value selected is somewhat arbitrary but is considered to be realistic. If the need arises to consider argillaceous rock systems with different 2:1 clay mineral contents, it is a simple matter to re-calculate sorption values.

The basis for the generation of a generic argillaceous rock sorption data base for a given water chemistry (Tab. 3.2) has been described in Chapters 4, 5 and 6. The procedure is illustrated in the flow diagram shown in Fig. 7.1. The CF values for converting the sorption values given in Table 6.2 to sorption values appropriate to argillaceous rocks at the five different water chemistries are calculated as shown in Chapters 4 and 5. The data required for the calculations are given in Chapter 6 and in Appendix 4 Tables A4.2, A4.4, A4.6, A4.8 and A4.10 for the argillaceous rocks.

A summary of the $R_{d,Arg}$ values corresponding to the five generic argillaceous rock systems is given in Table 7.1.

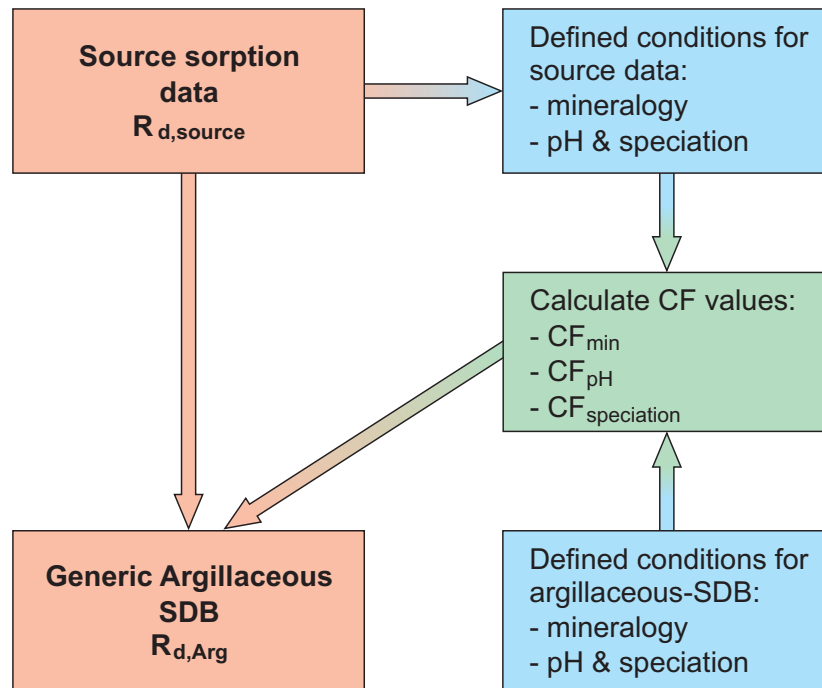


Fig. 7.1: Flow chart for derivation of generic argillaceous sorption data base $R_{d,Arg}$.

Tab. 7.1: Generic argillaceous rock SDBs for the different porewater types given in Table 3.2. (Note that for argillaceous rocks the Lab→field conversion factor is unity. Therefore the sorption values given below apply to the field.)

Element	Argint	Argl6	Argh6	Argl9	Argh9
H (HTO)	0	0	0	0	0
Be(II)	1.3	2.0×10^{-1}	1.9×10^{-1}	3.2	3.1
C (inorg.)	5.7×10^{-4}	6.2×10^{-5}	5.4×10^{-5}	5.4×10^{-3}	4.3×10^{-3}
C (org.)	0	0	0	0	0
Cl(-I)	0	0	0	0	0
K(I)	5.5×10^{-3}	1.0×10^{-2}	3.3×10^{-3}	1.0×10^{-2}	3.3×10^{-3}
Ca(II)	1.3×10^{-3}	1.1×10^{-3}	3.5×10^{-4}	5.5×10^{-3}	5.5×10^{-4}
Co(II)	4.8×10^{-1}	5.1×10^{-2}	4.4×10^{-2}	12	11
Ni(II)	9.8×10^{-1}	1.9×10^{-1}	1.5×10^{-1}	3.2	2.6
Se(-II)	0	0	0	0	0
Se(IV)	3.2×10^{-3}	1.8×10^{-2}	1.8×10^{-2}	2.8×10^{-4}	2.8×10^{-4}
Se(VI)	0	0	0	0	0
Sr(II)	1.3×10^{-3}	1.1×10^{-3}	3.5×10^{-4}	5.5×10^{-3}	5.5×10^{-4}
Zr(IV)/Hf(IV)	5.5	42	42	1.0×10^{-1}	1.0×10^{-1}
Nb(V)	1.0	1.0	1.0	0	0
Mo(VI)	7.8×10^{-3}	1.8×10^{-2}	1.8×10^{-2}	2.3×10^{-3}	2.3×10^{-3}
Tc(IV)	4.9×10^{-1}	3.3×10^{-2}	3.1×10^{-2}	6.1×10^{-1}	6.1×10^{-1}
Tc(VII)	0	0	0	0	0
Ru(IV)	0	0	0	0	0
Pd(II)	8.2	5.8	1.4×10^{-1}	8.5	8.5
Ag(I)	0	0	0	0	0
Cd(II)	1.5×10^{-1}	5.8×10^{-2}	1.5×10^{-2}	6.8×10^{-1}	2.1×10^{-1}
Sn(IV)	57	70	70	4.6	44
Bi(III)	8.0	2.0	2.0	8.0	8.0
Sb(III)	8.0	2.0	2.0	8.0	8.0
Sb(V)	0	0	0	0	0
I(-I)	0	0	0	0	0
Cs(I)	2.4	4.6	1.5	3.8	1.5
Eu(III)/Ln(III)	7.4×10^{-1}	2.3×10^{-1}	2.5×10^{-1}	24	22
Pb(II)	7.8×10^{-1}	3.6×10^{-1}	2.2×10^{-1}	3.8	3.8
Po(IV)	3.2×10^{-3}	1.8×10^{-2}	1.8×10^{-2}	2.8×10^{-4}	2.8×10^{-4}
Ra(II)	9.8×10^{-4}	1.0×10^{-3}	2.8×10^{-4}	4.3×10^{-3}	3.8×10^{-4}
Th(IV)	63	63	63	63	63
Pa(V)	13	13	13	13	13
U(IV)	63	63	63	63	63
U(VI)	2.7×10^{-4}	1.4×10^{-4}	1.1×10^{-4}	6.1×10^{-3}	2.9×10^{-3}
Np(IV)	63	63	63	63	63
Np(V)	4.2×10^{-3}	1.1×10^{-3}	1.1×10^{-3}	1.4×10^{-2}	1.3×10^{-2}
Pu(III)	2.6	9.7×10^{-1}	9.8×10^{-1}	11	11
Pu(IV)	63	63	63	63	63
Pu(V)	3.5×10^{-3}	1.1×10^{-3}	1.1×10^{-3}	1.2×10^{-2}	1.2×10^{-2}
Am(III)	2.2	1.0	1.0	5.1	4.7
Ac(III)/Cm(III)	2.2	1.0	1.0	5.1	4.7

source data	set to zero	cation exchange	chemical analogue
-------------	-------------	-----------------	-------------------

8 Generic Calcareous Rock SDB

In the derivation of a generic calcareous rock SDB it is assumed that such rocks do not contain any significant quantities of phyllosilicates and that only uptake data on calcite are relevant. (If calcareous rocks do contain phyllosilicates, then these are likely to dominate the sorption characteristics of the rock and a procedure similar to that given in Chapters 5 and 6 would be more appropriate.)

The sparse source data used in developing a generic rock SDB for jointed calcareous marl/limestone layers in marl formations can be found in Bradbury & Baeyens (1997). The data pool available today has changed little since then except for new data for Pb(II), Eu(III), Np(V) and Pu(IV)/(V) (see Tab. 8.1). The situation is exacerbated by a lack of understanding on the sorption mechanisms for calcite. Exchange with calcium ions in the matrix, the formation of metal-calcium-vacancy complexes at the surface and in the bulk of calcite, incorporation in the matrix, solid solution formation are amongst a number of proposals which have been made. The sorption data available are summarised in Table 8.1.

Tab. 8.1: Experimentally determined sorption values on calcite at pH values near 8 (see Bradbury & Baeyens 1997, Chapter 9) and ionic radii (in Ångstrom units) (Shannon 1976). (Note: ionic radii are for hexagonal coordination number).

Element	Ionic Radii (Å)	$\log R_{d \text{ calcite}}$ ($\text{m}^3 \text{kg}^{-1}$)	Source
Mn(II)	0.83	-0.8	Zachara et al. (1991)
Co(II)	0.745	-1.4	Zachara et al. (1991)
Ni(II)	0.69	-2.0	Zachara et al. (1991)
Zn(II)	0.74	0.0 -0.1	Zachara et al. (1991) Zachara et al. (1988)
Cd(II)	0.95	0.6 1.0	Zachara et al. (1991) Papadopoulos & Rowell (1988)
Sr(II)	1.18 (>1)	-3.0	Zachara et al. (1991)
Pb(II)	1.19 (>1)	-0.4	Rouff et al. (2005)
Eu(III)	0.95	0.86	Zavarin et al. (2005)
Th(IV)	0.94	1.15	Maite et al. (1989)
Np(V)	0.75	-1.4 -0.66 -0.1	Herberling et al. (2008) Zavarin et al. (2005) Allard (1982)
Pu(IV)	0.86	0.04	Zavarin et al. (2005)
Pu(V)	0.76	-1.7	Zavarin et al. (2005)
Am(III)	0.975	1.3	Allard & Beall (1979)
Se(IV)	0.50	-3.1	Cowan et al. (1990)

The lack of data and understanding of the sorption processes on calcite makes it intrinsically difficult to develop a SDB for calcareous rocks. In view of this situation, and in order to complement the information given in Bradbury & Baeyens (1997, Chapter 9), a means of estimating (missing) sorption data was sought. It was found that if the sorption data ($\log R_d$ values) were plotted against the ionic radii (IR) in Å of the respective metals (Shannon 1976), an acceptable linear correlation was found between these two quantities, a so-called linear free energy relationship, LFER, Fig. 8.1. (The ionic radii were chosen for the VI coordination number and for Co(II) and Mn(II) for high-spin states.)

The experimental data for Zn(II) (Zachara et al. 1991) and Np(V) (Allard 1982) and Zavarin et al. (2005)) are not consistent with the correlation in Fig. 8.1. These data points are not shown in Fig. 8.1 and are not included in the linear regression equation. The anomalous behaviour of Zn(II) has been noted previously by Zachara et al. (1991), see Fig. 8a in this reference. These authors postulated that other factors, perhaps related to the electronic environment of the metallic cation, were important. For Np(V) three different data sources are available. The isotherm measurements from Heberling et al. (2008) are considered as being the most reliable since the other two sources only report single point values.

There is no clear theoretical support for why such a correlation should exist, except that if the uptake processes involves exchange with calcium and/or incorporation in the calcite lattice, then steric considerations (the size of the ions involved) might be one of the factors influencing "sorption". Despite this somewhat tenuous connection between "sorption" on calcite and the ionic radius of the sorbate, the LFER given in Fig. 8.1 was used to estimate sorption values in the generic calcareous SDB. Where sorption values have been estimated in this way, they are indicated as such in Table 8.2. Elements with an IR greater than 1.00 (equal to that of Ca) have not been considered in the carbonate-LFER since it is well known that these elements sorb/incorporate very weakly on calcite (e.g. Curti 1997). Also, the carbonate-LFER is not used for elements with an IR below the lowest value given in Fig. 8.1. The conservative assumption was made that such elements have zero sorption.

The $R_{d \text{ calc}}$ values given in Table 8.1 are considered to be valid in the pH range 7.5 to 9 (see Bradbury & Baeyens 1997, Chapter 9). At pH values < 7.5 the sorption of alkali, alkali earth metals and transition metals tends to decrease so that at pH = 6 the sorption of these classes of metals is effectively zero. For trivalent and tetravalent metals measurements indicate that the sorption is approximately constant over the pH range 6 to 9 (Allard & Beall 1979; Cowan et al. 1990). The situation with respect to pentavalent (Np(V), Nb(V)) and hexavalent metals (U(VI)) at pH values down to 6 is unclear. Because there is even more uncertainty here, their sorption values are conservatively set to zero at pH = 6.

Again, because of the uncertainties associated with the sorption mechanisms on calcite, no corrections for water chemistries were attempted. The Lab→Field conversion factor for calcareous systems is taken to be 0.05, section 4.3.2.4.

For ^{14}C as $\text{H}^{14}\text{CO}_3^-$ or $^{14}\text{CO}_3^{2-}$, the most likely removal mechanism from solution is isotopic exchange in the surface layers of calcite. The method for calculating an R_d value for inorganic carbon is described in section 5.3 (see also Bradbury & Baeyens 1997, section 9.4.2).

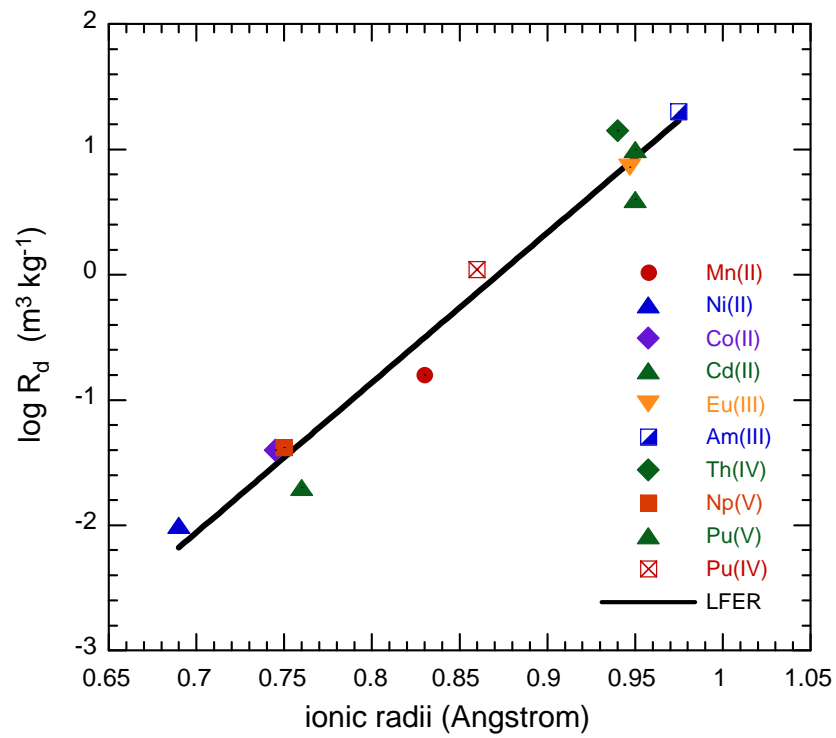


Fig. 8.1: Linear Free Energy Relation between $\log R_d$ ($\text{m}^3 \text{kg}^{-1}$) and the IR (ionic radii in \AA). The least squares relation between $\log R_d$ and IR is given by $\log R_d = (-10.4 \pm 0.6) + (12.0 \pm 0.7) \cdot \text{IR}$ ($R^2 = 0.97$).

Tab. 8.2: Generic Calcareous Rock SDB ($\text{m}^3 \text{kg}^{-1}$) for $\text{pH } 7.5 < \text{pH} < 9$. (Ionic radii of the elements used in the LFER are given in brackets in column 5.) The sorption values given below apply to the field.

Element	R_d -source	Lab->Field	R_d -gen calc	Source Data
H (HTO)	0	0.05	0	Set = 0
Be(II)	0	0.05	0	Set = 0 (IR = 0.45)
C (inorg.)	1.6E-03	na	1.6E-03	Calculated (see text)
C (org.)	0	0.05	0	Bradbury & Baeyens (1997)
Cl(-I)	0	0.05	0	Bradbury & Baeyens (1997)
K(I)	0	0.05	0	Bradbury & Baeyens (1997)
Ca(II)	1.0E-03	0.05	5.0E-05	Sr analogue
Co(II)	4.0E-02	0.05	2.0E-03	Bradbury & Baeyens (1997)
Ni(II)	1.0E-02	0.05	5.0E-04	Bradbury & Baeyens (1997)
Se(-II)	0	0.05	0	Bradbury & Baeyens (1997)
Se(IV)	8.0E-04	0.05	4.0E-05	Bradbury & Baeyens (1997)
Se(VI)	0	0.05	0	Set = 0
Sr(II)	1.0E-03	0.05	5.0E-05	Bradbury & Baeyens (1997)
Zr(IV)/Hf(IV)	1.7E-02	0.05	8.5E-04	Carbonate-LFER (IR = 0.72/0.71 Å)
Nb(V)	0	0.05	0	Set to zero (IR = 0.64 Å)
Mo(VI)	0	0.05	0	Set = 0 (Se(VI) chem. analogue)
Tc(IV)	0	0.05	0	Set to zero (IR = 0.645 Å)
Tc(VII)	0	0.05	0	Set = 0
Ru(IV)	0	0.05	0	Set to zero (IR = 0.62 Å)
Pd(II)	8.3E-01	0.05	4.2E-02	Carbonate-LFER (IR = 0.86 Å)
Ag(I)	0	0.05	0	Bradbury & Baeyens (1997)
Cd(II)	4	0.05	2.0E-01	Zachara et al. (1991)
Sn(IV)	7.6E-03	0.05	3.8E-04	Carbonate-LFER (IR = 0.69 Å)
Sb(III)	5.2E-02	0.05	2.6E-03	Carbonate-LFER (IR = 0.76 Å)
Sb(V)	0	0.05	0	Set = 0 (IR = 0.60)
I(-I)	0	0.05	0	Bradbury & Baeyens (1997)
Cs(I)	0	0.05	0	Bradbury & Baeyens (1997)
Eu(III)/Ln(III)	7.2	0.05	3.6E-01	Zavarin et al. (2005)
Pb(II)	0.4	0.05	2.0E-02	Rouff et al. (2005)
Po(IV)	8.0E-04	0.05	4.0E-05	Se(IV) analogue
Ra(II)	1.00E-03	0.05	5.0E-05	Sr analogue
Th(IV)	14	0.05	4.5E-02	Bradbury & Baeyens (1997)
Pa(V)	9.1E-02	0.05	4.6E-03	Carbonate-LFER (IR = 0.78 Å)
U(IV)	1.9	0.05	9.5E-02	Carbonate-LFER (IR = 0.89 Å)
U(VI)	2.3E-02	0.05	1.2E-03	Carbonate-LFER (IR = 0.73 Å)
Np(IV)	1.1	0.05	5.5E-02	Carbonate-LFER (IR = 0.87 Å)
Np(V)	4.0E-02	0.05	2.0E-03	Heberling et al. (2008)
Pu(III)	40	0.05	2.0E+00	Carbonate-LFER (IR = 1.00 Å)
Pu(IV)	1.1	0.05	5.5E-02	Zavarin et al. (2005)
Pu(V)	2.0E-02	0.05	1.0E-03	Zavarin et al. (2005)
Am(III)	20	0.05	1.0E+00	Bradbury & Baeyens (1997)
Ac(III)	0	0.05	0	Set to zero (IR = 1.12)
Cm(III)	17	0.05	8.7E-01	Carbonate-LFER (IR = 0.97 Å)

References

- Allard, B. & Beall, G.W. (1979): Sorption of americium on geologic media. *J. Environ. Sci. Health A1* (6), 507-518.
- Bradbury, M.H. & Baeyens, B. (1997): Far-Field Sorption Data Bases for Performance Assessment of a L/ILW Repository in an Undisturbed Palfris Marl Host Rock PSI Bericht and Nagra Tech. Rep. NTB 96-06.
- Curti, E. (1997): Coprecipitation of radionuclides: basic concepts, literature review and first applications. PSI Report 97-10, Nagra Tech. Rep. NTB 97-08.
- Cowan, et al. (1990): Solution ion effects on the surface exchange of selenite on calcite. *Geochim. Cosmochim. Acta* 54, 2223-2234.
- Heberling, F., Brendebach, B. & Bosbach, D. (2008): Neptunium(V) adsorption to calcite. *J. Contam. Hydrol.* 102, 246-252.
- Maite, T.C., Smith, M.R. & Laul, J.C. (1989): Sorption of uranium, thorium, and radium on matrices under oxic environments. *Radioactive Waste Management and the Nuclear Fuel Cycle*, Vol. 11(3), 269-278.
- Papadopoulos, P. & Rowell, D.L. (1988): The reactions of cadmium with calcium carbonate surfaces. *J. Soil Sci.* 39, 23-36.
- Rouff, A.A., Reeder, R.J., Fisher, N.S. (2005): Electrolyte and pH effects on Pb(II)-calcite sorption processes: the role of the $\text{PbCO}_3(\text{aq})$ complex. *J. Colloid Interface Sci.* 286, 61-67.
- Shannon, R.D. (1976): Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides. *Acta Cryst.* A32, 751-767.
- Zachara, J.M., Kittrick, J.A. & Harsh J.B. (1988): The mechanism of Zn^{2+} adsorption on calcite. *Geochim. Cosmochim. Acta* 52, 2281-2291.
- Zachara, J.M., Cowan, C.E. & Resch, C.T. (1991): Sorption of divalent metals on calcite. *Geochim. Cosmochim. Acta* 55, 1549-1562.
- Zavarin, M., Roberts, S.K., Hakem, N., Sawvel, A.M. & Kersting, A.B. (2005): Eu(III), Sm(III), Np(V), Pu(V), and Pu(IV) sorption to calcite. *Radiochim. Acta* 93, 93-102.

Acknowledgements

We would like to express our gratitude to Drs. J. Mibus, B. Schwyn and P. Zuidema (Nagra) for their constructive and helpful comments on the report. Special thanks are extended to Dr. V. Brendler (FZ Dresden-Rossendorf, Germany) for reviewing the manuscript. The final layout of the report was carried out by B. Gschwend. Partial financial support was provided by Nagra.

A1 Generic Groundwater Compositions

Tab. A1.1: Analytical ranges of deep old groundwaters from various geological formations in Switzerland.

Source: Nagra Hydrodatenbank 2007, data kindly provided by H.N. Waber, Rock-Water Interaction Group, University of Bern, Switzerland

Geological Formation	Statistics	T	El. Cond	TDS	pH	pH Cc-	Eh	Li	Na	K	NH4	Mg	Ca	Sr
		°C	µS/cm	mg/L	onsite	Equil.	(Ag/AgCl) mV	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L
Upper Meeres-Molasse	Samples	23	23	23	23	3	4	20	23	20	23	23	23	19
	Median	23	1330	1040	8.58	7.86	0	0.07	328	2	0.3	1	3	0.5
	Stdev	2	1634	1248	0.34	0.49	241	0.07	415	3	0.4	9	18	2.9
	Maximum	30	5254	3724	8.90	8.67	200	0.19	1224	10	1.3	22	46	7.8
	Minimum	22	921	858	7.84	7.79	-340	<0.1	255	2	0.1	1	2	0.1
Lower Süßwasser-Molasse	Samples	61	63	66	65	22	25	47	66	66	41	67	67	45
	Median	16	5100	3294	8.18	8.10	-140	0.40	1184	5	0.4	19	40	3.4
	Stdev	1	2110	1372	0.38	0.28	97	0.36	497	3	0.4	13	32	3.9
	Maximum	18	13785	8810	8.76	8.33	120	1.90	3035	20	2.6	69	211	20.4
	Minimum	12	538	510	7.10	7.15	-360	<0.1	4	1	<0.1	4	17	0.5
Palfris-Formation	Samples	11	17	17	17		10	16	17	17	17	17	17	16
	Median	11	1840	1810	8.55		-299	0.11	527	2	0.5	2	6	0.6
	Stdev	6	4275	3178	0.55		132	0.39	1181	5	1.1	25	60	16.4
	Maximum	22	12910	10771	9.24		76	1.00	3600	19	3.6	78	239	57.0
	Minimum	0	950	966	7.20		-340	<0.1	45	1	<0.1	1	2	<0.1
Malm, various limestone formations	Samples	22	24	24	22	15	16	15	24	24	17	24	24	19
	Median	20	986	983	7.82	7.89	-190	0.12	241	10	0.9	9	16	0.6
	Stdev	4	4221	2633	0.26	0.24	152	0.06	836	13	0.6	34	69	4.5
	Maximum	21	16226	10406	7.94	8.20	190	0.15	3290	56	2.9	145	275	15.4
	Minimum	10	238	249	7.10	7.22	-275	<0.1	0.1	0.4	<0.01	5	14	0.1
Hauptrogenstein	Samples	10	10	10	10	8	8	7	10	10	7	10	10	8
	Median	24	2272	1976	6.72	6.49	100	2.40	352	13	2.4	51	207	5.2
	Stdev	11	2447	2053	0.69	0.55	199	1.47	471	16	1.5	51	155	2.7
	Maximum	40	6030	4687	7.76	7.39	310	3.70	979	35	4.4	115	420	5.9
	Minimum	12	319	320	6.06	6.05	-220	0.01	1	0.4	0.1	4	66	0.1
Opalinus clay	Samples	23	14	35	19		12	24	35	35	15	35	35	34
	Median	13	24635	13800	7.92		-90	0.83	4280	34	8.3	311	500	35.7
	Stdev	3	6058	3980	0.41		119	0.27	1234	30	2.6	123	214	11.9
	Maximum	20	30200	20400	8.80		150	1.16	6320	133	10.5	538	853	67.4
	Minimum	13	14550	7451	7.20		-120	0.34	2300	20	1.1	91	43	2.2
Stuben- & Schilfsandstein	Samples	2	2	2	2	1	2	2	2	2	2	2	2	2
	Median	19	13742	12944	8.55	7.56	-292	1.73	3532	43	6.7	136	398	9.2
	Stdev	5	3043	3660	0.21		144	0.04	1034	15	3.5	96	265	2.4
	Maximum	23	15894	15532	8.70	7.56	-190	1.75	4263	54	9.1	203	585	10.9
	Minimum	16	11590	10355	8.40	7.56	-394	1.70	2800	33	4.2	68	210	7.5
Trigonodus-Dolomite	Samples	27	27	27	27	14	16	22	27	27	19	27	27	22
	Median	26	2360	2494	6.85	6.90	-294	0.11	29	4	0.1	129	500	7.5
	Stdev	6	4585	3529	0.28	0.15	101	1.63	1151	40	1.4	38	127	3.6
	Maximum	43	19822	15339	8.12	7.24	-47	6.20	4490	132	6.1	210	874	16.9
	Minimum	16	750	768	6.51	6.62	-442	0.04	14	4	<0.01	41	118	2.1
Buntsandstein	Samples	9	11	11	11	5	8	9	11	11	9	11	11	11
	Median	18	13800	11557	7.03	6.92	-187	4.70	3665	77	0.6	65	462	10.8
	Stdev	7	5498	5742	0.63	0.48	131	4.58	1552	40	2.0	29	195	6.2
	Maximum	32	18907	16329	8.48	7.93	-94	14.40	4955	132	6.5	87	532	17.8
	Minimum	13	793	383	6.59	6.71	-505	0.64	181	5	<0.01	1	13	0.2

Tab. A1.1: (continued)

Geological Formation	Statistics	F	Cl	Br	SO ₄	NO ₃	HCO ₃	TOC	DOC	H ₂ SiO ₃ direct	H ₂ SiO ₃ filtr.	H ₃ BO ₃	Fe _{tot}	Mn _{tot}
		mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L
Upper Meeres-Molasse	Samples	22	23	15	23	19	23	1	4	22	1	18	7.00	11.00
	Median	3.1	164	0.6	135	<0.1	371	0.9	0.6	15.3	14.8	4.0	0.09	0.01
	Stdev	0.3	482	1.8	358		51		0.3	11.9		4.0	0.05	0.02
	Maximum	3.7	1200	4.4	935	<0.1	431	0.9	0.9	68.0	14.8	12.6	0.14	0.04
	Minimum	2.3	34	<0.5	109	<0.1	274	0.9	0.3	9.3	14.8	1.9	0.00	<0.05
Lower Süßwasser-Molasse	Samples	47	66	44	66	27	67	1	23	64	11	46	39	46
	Median	1.4	1603	4.3	245	<0.2	238	2.6	0.5	12.0	11.7	6.4	0.10	0.02
	Stdev	0.5	864	3.1	94		70		1.0	5.0	7.6	2.8	3.12	0.07
	Maximum	2.7	5224	20.3	410	4	450	2.6	4.6	36.8	36.7	13.4	19.40	0.36
	Minimum	<0.1	1	<0.1	<0.1	<0.2	110	2.6	0.1	5.8	9.9	<0.5	0.01	<0.01
Palfris-Formation	Samples	16	17	17	17	17	17	10	14	7	11	16	10	16
	Median	20.0	27	0.8	12	<0.1	968	5.7	4.9	6.3	11.2	5.5	1.50	0.04
	Stdev	10.8	2137	27.1	60	<0.1	635	29.2	80.3	8.0	5.2	2.8	10.88	0.15
	Maximum	32.0	5800	75.0	232	2	2430	93.0	302.0	16.0	24.6	11.7	35.00	0.62
	Minimum	1.0	1	<0.1	1	<0.1	113	1.0	0.7	<0.5	6.0	2.1	<0.02	0.00
Malm, various limestone formations	Samples	19	24	14	24	9	24	2	17	23	6	19	17	18
	Median	5.1	55	0.2	85	0.4	538	157.0	0.6	14.8	14.7	5.8	0.98	0.01
	Stdev	2.2	1234	2.5	394	5	120	1.4	33.3	3.4	2.2	6.0	13.69	0.23
	Maximum	6.0	4550	7.0	1462	13	548	158.0	107.0	22.1	17.2	23.0	49.00	0.88
	Minimum	<0.1	2	<0.1	3	<0.1	176	156.0	0.2	5.3	10.8	<0.03	0.03	<0.01
Hauptrogenstein	Samples	8	10	7	10	4	10	0	8	10	0	8	6	6
	Median	0.7	696	5.9	134	3	493		0.2	15.9		2.5	0.66	0.03
	Stdev	0.6	916	3.8	127	3	312		0.5	8.5		1.7	0.86	0.01
	Maximum	1.7	1961	9.3	314	7	962		1.4	25.2		4.4	2.00	0.04
	Minimum	0.1	2	<0.1	16	1	218		0.1	4.4		0.1	0.01	0.01
Opalinus clay	Samples	25	35	29	34	29	30	14	13	29	6	7	20.00	18.00
	Median	0.6	6720	24.0	1400	<0.1	179	70.4	16.0	2.1	3.0	2.4	0.58	0.38
	Stdev	2.1	2277	7.3	352		255	170.8	70.0	3.9	1.5	4.8	1.65	0.54
	Maximum	5.3	10800	36.3	2168	<0.2	1098	448.0	250.0	17.0	4.6	12.0	6.80	2.65
	Minimum	0.1	3580	14.3	840	<0.1	41	9.5	3.5	0.6	0.6	1.4	<0.1	0.26
Stuben- & Schilfsandstein	Samples	2	2	2	2	2	2	2	2	2	1	2	2	2
	Median	1.4	1648	3.3	6607	<0.1	287	3.7	2.1	114.0	190.0	36.4	10.25	0.23
	Stdev	0.6	1595	4.6	1000		117	0.8	0.9	142.9		20.3	8.41	0.21
	Maximum	1.8	2775	6.6	7314	<0.1	369	4.2	2.7	215.0	190.0	50.8	16.20	0.38
	Minimum	1.0	520	0.1	5900	<0.1	204	3.1	1.4	12.9	190.0	22.0	4.30	0.08
Trigonodus-Dolomite	Samples	22	27	17	27	9	27	5	15	27	8	22	21	22
	Median	2.6	42	0.1	1500	<0.1	259	4.4	0.9	24.0	23.0	1.4	1.80	0.02
	Stdev	0.4	1661	1.6	638	0.2	54	13.9	8.5	9.9	12.7	9.6	5.41	0.09
	Maximum	3.9	6400	6.6	3011	0.6	429	34.0	34.0	58.9	53.0	36.4	24.40	0.35
	Minimum	2.2	7	<0.1	211	<0.1	214	1.1	0.4	17.8	17.8	0.5	0.02	<0.01
Buntsandstein	Samples	11	11	9	11	3.0	11	6	10	10	5	11	11	11
	Median	1.0	2568	2.2	3083	2.5	552	1.3	1.3	19.3	27.0	18.8	36.00	0.54
	Stdev	5.1	1724	4.3	2316	1.6	220	43.6	29.6	10.5	9.6	17.6	44.25	0.55
	Maximum	17.0	6405	11.6	6235	2.9	845	109.0	95.0	35.7	33.3	55.7	125.0 0	1.70
	Minimum	<0.1	26	0.2	155	<0.1	192	0.3	0.3	5.2	11.6	1.4	0.65	0.05

Tab. A1.2: Composition ranges of deep old groundwaters from various geological formations in Switzerland. Data from Table A1.1 converted to mol/L

Geological Formation	Statistics	Li	Na	K	NH4	Mg	Ca	Sr	F	Cl
		mol/L	mol/L	mol/L	mol/L	mol/L	mol/L	mol/L	mol/L	mol/L
Upper Meeres-Molasse	Median	1.01E-05	1.43E-02	6.01E-05	1.55E-05	4.53E-05	6.99E-05	6.16E-06	1.63E-04	4.63E-03
	Stdev	9.90E-06	1.81E-02	8.53E-05	2.35E-05	3.83E-04	4.52E-04	3.32E-05	1.45E-05	1.36E-02
	Maximum	2.74E-05	5.32E-02	2.53E-04	7.21E-05	9.01E-04	1.15E-03	8.90E-05	1.95E-04	3.38E-02
	Minimum	<1.44E-05	1.11E-02	4.42E-05	2.77E-06	2.88E-05	4.74E-05	9.13E-07	1.21E-04	9.59E-04
Lower Süss-wasser-Molasse	Median	5.76E-05	5.15E-02	1.15E-04	2.44E-05	7.69E-04	1.00E-03	3.93E-05	7.37E-05	4.52E-02
	Stdev	5.20E-05	2.16E-02	8.15E-05	2.42E-05	5.29E-04	8.02E-04	4.43E-05	2.78E-05	2.44E-02
	Maximum	2.74E-04	1.32E-01	4.99E-04	1.44E-04	2.83E-03	5.25E-03	2.33E-04	1.42E-04	1.47E-01
	Minimum	<1.44E-05	1.74E-04	1.53E-05	<5.54E-06	1.48E-04	4.24E-04	5.48E-06	<5.26E-06	2.82E-05
Palfris-Formation	Median	1.58E-05	2.29E-02	5.88E-05	2.72E-05	8.64E-05	1.45E-04	7.19E-06	1.05E-03	7.62E-04
	Stdev	5.60E-05	5.14E-02	1.34E-04	5.93E-05	1.01E-03	1.51E-03	1.87E-04	5.67E-04	6.03E-02
	Maximum	1.44E-04	1.57E-01	4.86E-04	2.00E-04	3.21E-03	5.96E-03	6.51E-04	1.68E-03	1.64E-01
	Minimum	<1.44E-05	1.96E-03	2.30E-05	<5.54E-06	2.47E-05	3.99E-05	<1.14E-06	5.26E-05	3.95E-05
Malm, various limestone formations	Median	1.73E-05	1.05E-02	2.51E-04	4.99E-05	3.64E-04	3.88E-04	7.30E-06	2.66E-04	1.55E-03
	Stdev	9.23E-06	3.64E-02	3.43E-04	3.49E-05	1.40E-03	1.72E-03	5.19E-05	1.14E-04	3.48E-02
	Maximum	2.16E-05	1.43E-01	1.43E-03	1.61E-04	5.97E-03	6.86E-03	1.76E-04	3.16E-04	1.28E-01
	Minimum	<1.44E-05	4.35E-06	1.02E-05	<5.54E-07	1.89E-04	3.49E-04	1.14E-06	<5.26E-06	4.23E-05
Haupt-rogenstein	Median	3.46E-04	1.53E-02	3.26E-04	1.33E-04	2.08E-03	5.15E-03	5.90E-05	3.87E-05	1.96E-02
	Stdev	2.12E-04	2.05E-02	3.99E-04	8.15E-05	2.10E-03	3.86E-03	3.03E-05	2.92E-05	2.58E-02
	Maximum	5.33E-04	4.26E-02	8.95E-04	2.44E-04	4.73E-03	1.05E-02	6.73E-05	9.00E-05	5.53E-02
	Minimum	1.44E-06	3.04E-05	1.10E-05	3.33E-06	1.73E-04	1.65E-03	1.37E-06	4.74E-06	6.68E-05
Opalinus clay	Median	1.19E-04	1.86E-01	8.80E-04	4.58E-04	1.28E-02	1.25E-02	4.07E-04	3.11E-05	1.90E-01
	Stdev	3.83E-05	5.37E-02	7.69E-04	1.43E-04	5.07E-03	5.35E-03	1.36E-04	1.09E-04	6.42E-02
	Maximum	1.67E-04	2.75E-01	3.40E-03	5.82E-04	2.21E-02	2.13E-02	7.69E-04	2.79E-04	3.05E-01
	Minimum	4.96E-05	1.00E-01	5.01E-04	6.10E-05	3.72E-03	1.08E-03	2.45E-05	5.26E-06	1.01E-01
Stuben- & Schilfsandstein	Median	2.49E-04	1.54E-01	1.11E-03	3.69E-04	5.58E-03	9.92E-03	1.05E-04	7.37E-05	4.65E-02
	Stdev	5.09E-06	4.50E-02	3.74E-04	1.92E-04	3.94E-03	6.62E-03	2.74E-05	2.98E-05	4.50E-02
	Maximum	2.52E-04	1.85E-01	1.38E-03	5.04E-04	8.37E-03	1.46E-02	1.24E-04	9.47E-05	7.83E-02
	Minimum	2.45E-04	1.22E-01	8.47E-04	2.33E-04	2.79E-03	5.24E-03	8.56E-05	5.26E-05	1.47E-02
Trigo-nodus-Dolomite	Median	1.58E-05	1.26E-03	1.10E-04	4.43E-06	5.31E-03	1.25E-02	8.50E-05	1.37E-04	1.18E-03
	Stdev	2.34E-04	5.01E-02	1.02E-03	7.73E-05	1.56E-03	3.18E-03	4.16E-05	2.20E-05	4.68E-02
	Maximum	8.93E-04	1.95E-01	3.38E-03	3.38E-04	8.64E-03	2.18E-02	1.93E-04	2.07E-04	1.81E-01
	Minimum	5.33E-06	5.92E-04	9.46E-05	<5.54E-07	1.70E-03	2.94E-03	2.35E-05	1.16E-04	2.03E-04
Buntsandstein	Median	6.77E-04	1.59E-01	1.96E-03	3.55E-05	2.67E-03	1.15E-02	1.23E-04	5.47E-05	7.24E-02
	Stdev	6.59E-04	6.75E-02	1.02E-03	1.12E-04	1.18E-03	4.87E-03	7.03E-05	2.67E-04	4.86E-02
	Maximum	2.07E-03	2.16E-01	3.38E-03	3.60E-04	3.58E-03	1.33E-02	2.03E-04	8.95E-04	1.81E-01
	Minimum	9.22E-05	7.87E-03	1.18E-04	<5.54E-07	4.53E-05	3.24E-04	2.62E-06	<5.26E-06	7.33E-04

Tab. A1.2: (continued)

Geological Formation	Statistics	Br	SO ₄	NO ₃	HCO ₃	H ₂ SiO ₃ direct	H ₂ SiO ₃ filtr.	H ₃ BO ₃	Fe _{tot}	Mn _{tot}
		mol/L	mol/L	mol/L	mol/L	mol/L	mol/L	mol/L	mol/L	mol/L
Upper Meeres-Molasse	Median	7.51E-06	1.41E-03	<1.61E-06	6.08E-03	1.95E-04	1.90E-04	6.39E-05	1.61E-06	9.10E-08
	Stdev	2.26E-05	3.73E-03		8.38E-04	1.53E-04		6.49E-05	9.84E-07	4.06E-07
	Maximum	5.51E-05	9.73E-03	<1.61E-06	7.07E-03	8.71E-04	1.90E-04	2.04E-04	2.51E-06	7.64E-07
	Minimum	6.26E-06	1.13E-03	<1.61E-06	4.49E-03	1.20E-04	1.90E-04	3.06E-05	3.37E-08	<9.10E-07
Lower Süßwasser-Molasse	Median	5.41E-05	2.55E-03	<3.23E-06	3.90E-03	1.54E-04	1.50E-04	1.03E-04	1.74E-06	3.37E-07
	Stdev	3.87E-05	9.76E-04		1.14E-03	6.40E-05	9.75E-05	4.60E-05	5.59E-05	1.36E-06
	Maximum	2.54E-04	4.26E-03	5.64E-05	7.38E-03	4.71E-04	4.70E-04	2.17E-04	3.47E-04	6.55E-06
	Minimum	<1.25E-06	<1.04E-06	<3.23E-06	1.80E-03	7.36E-05	1.27E-04	<8.09E-06	1.79E-07	<1.82E-07
Palfris-Formation	Median	9.51E-06	1.25E-04	<1.61E-06	1.59E-02	8.07E-05	1.43E-04	8.81E-05	2.69E-05	7.10E-07
	Stdev	3.39E-04	6.21E-04	<1.61E-06	1.04E-02	1.02E-04	6.62E-05	4.52E-05	1.95E-04	2.80E-06
	Maximum	9.39E-04	2.42E-03	2.90E-05	3.98E-02	2.05E-04	3.15E-04	1.89E-04	6.27E-04	1.13E-05
	Minimum	<1.25E-06	8.33E-06	<1.61E-06	1.85E-03	<6.40E-06	7.68E-05	3.40E-05	<3.58E-07	0.00E+00
Malm, various limestone formations	Median	2.00E-06	8.82E-04	6.45E-06	8.82E-03	1.90E-04	1.88E-04	9.35E-05	1.75E-05	1.73E-07
	Stdev	3.12E-05	4.10E-03	8.13E-05	1.96E-03	4.38E-05	2.87E-05	9.74E-05	2.45E-04	4.26E-06
	Maximum	8.76E-05	1.52E-02	2.10E-04	8.98E-03	2.83E-04	2.20E-04	3.72E-04	8.77E-04	1.60E-05
	Minimum	<1.25E-06	2.71E-05	<1.61E-06	2.88E-03	6.79E-05	1.38E-04	<4.85E-07	4.83E-07	<1.82E-07
Hauptrogenstein	Median	7.37E-05	1.40E-03	5.43E-05	8.08E-03	2.03E-04		4.04E-05	1.18E-05	5.10E-07
	Stdev	4.78E-05	1.33E-03	4.26E-05	5.12E-03	1.09E-04		2.72E-05	1.54E-05	2.13E-07
	Maximum	1.16E-04	3.26E-03	1.11E-04	1.58E-02	3.23E-04		7.12E-05	3.58E-05	7.64E-07
	Minimum	<1.25E-06	1.62E-04	2.10E-05	3.57E-03	5.63E-05		8.09E-07	1.79E-07	2.18E-07
Opalinus clay	Median	3.00E-04	1.46E-02	<1.61E-06	2.93E-03	2.73E-05	3.87E-05	3.84E-05	1.03E-05	6.88E-06
	Stdev	9.14E-05	3.66E-03		4.18E-03	4.98E-05	1.94E-05	7.77E-05	2.95E-05	9.83E-06
	Maximum	4.54E-04	2.26E-02	<3.23E-06	1.80E-02	2.18E-04	5.89E-05	1.94E-04	1.22E-04	4.82E-05
	Minimum	1.79E-04	8.74E-03	<1.61E-06	6.72E-04	8.04E-06	8.17E-06	2.28E-05	<1.79E-06	4.77E-06
Stuben- & Schilfsandstein	Median	4.16E-05	6.88E-02	<1.61E-06	4.70E-03	1.46E-03	2.43E-03	5.88E-04	1.84E-04	4.20E-06
	Stdev	5.80E-05	1.04E-02		1.91E-03	1.83E-03		3.29E-04	1.51E-04	3.85E-06
	Maximum	8.26E-05	7.61E-02	<1.61E-06	6.05E-03	2.75E-03	2.43E-03	8.21E-04	2.90E-04	6.92E-06
	Minimum	6.26E-07	6.14E-02	<1.61E-06	3.34E-03	1.65E-04	2.43E-03	3.56E-04	7.70E-05	1.47E-06
Trigonodus-Dolomite	Median	8.76E-07	1.56E-02	1.61E-06	4.24E-03	3.07E-04	2.94E-04	2.18E-05	3.22E-05	3.00E-07
	Stdev	2.01E-05	6.64E-03	3.68E-06	8.83E-04	1.27E-04	1.63E-04	1.55E-04	9.69E-05	1.55E-06
	Maximum	8.26E-05	3.13E-02	8.87E-06	7.03E-03	7.54E-04	6.79E-04	5.89E-04	4.37E-04	6.37E-06
	Minimum	<1.25E-06	2.20E-03	<1.61E-06	3.51E-03	2.28E-04	2.28E-04	8.25E-06	4.30E-07	<1.82E-07
Buntsandstein	Median	2.75E-05	3.21E-02	4.03E-05	9.05E-03	2.46E-04	3.46E-04	3.03E-04	6.45E-04	9.83E-06
	Stdev	5.32E-05	2.41E-02	2.63E-05	3.60E-03	1.35E-04	1.23E-04	2.85E-04	7.92E-04	9.93E-06
	Maximum	1.45E-04	6.49E-02	4.68E-05	1.38E-02	4.57E-04	4.26E-04	9.01E-04	2.24E-03	3.09E-05
	Minimum	2.50E-06	1.61E-03	<1.61E-06	3.15E-03	6.66E-05	1.49E-04	2.26E-05	1.16E-05	9.10E-07

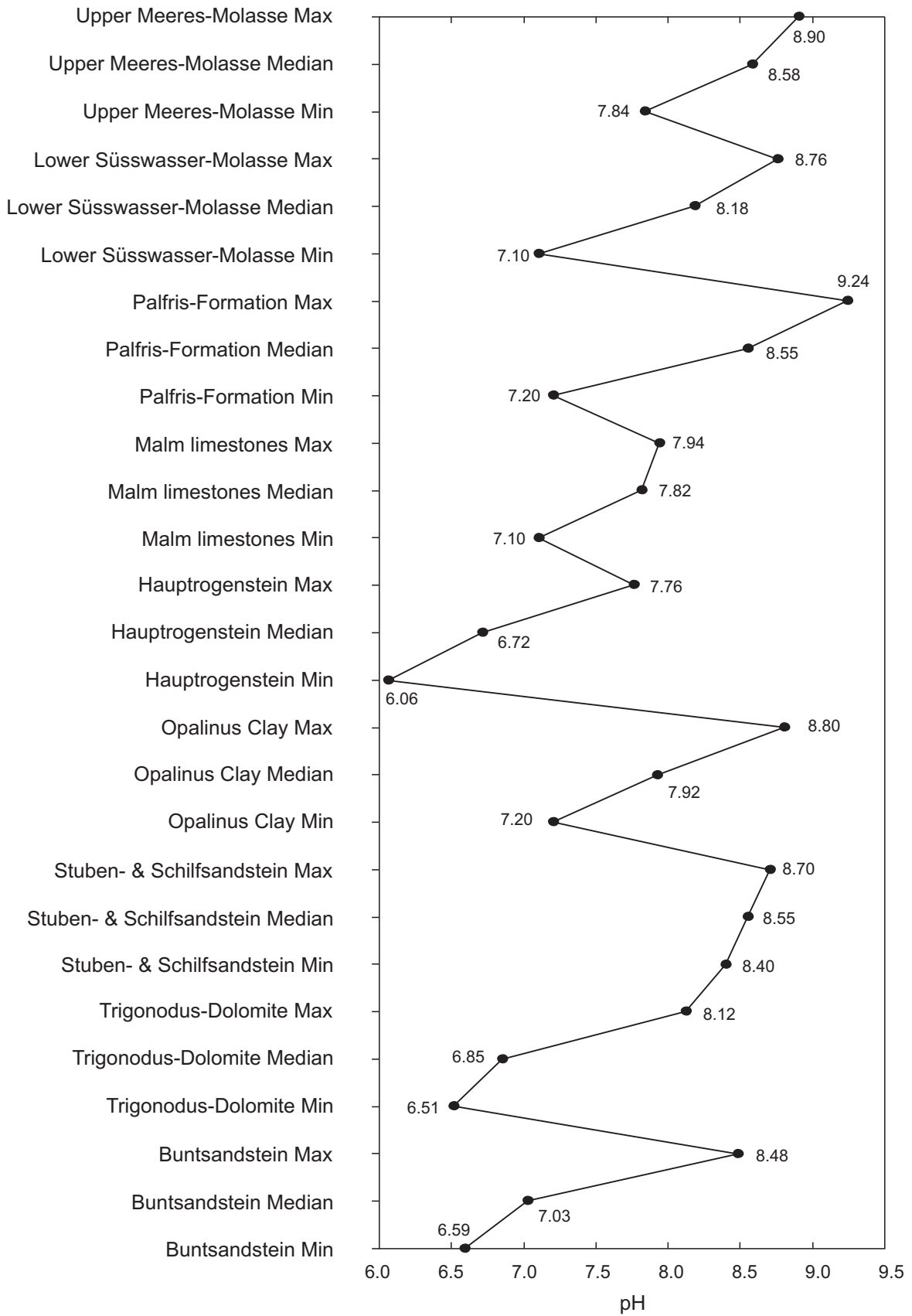


Fig. A1.1: Ranges for onsite pH of deep old groundwaters from various aquifers in Switzerland. Data from Table A1.1

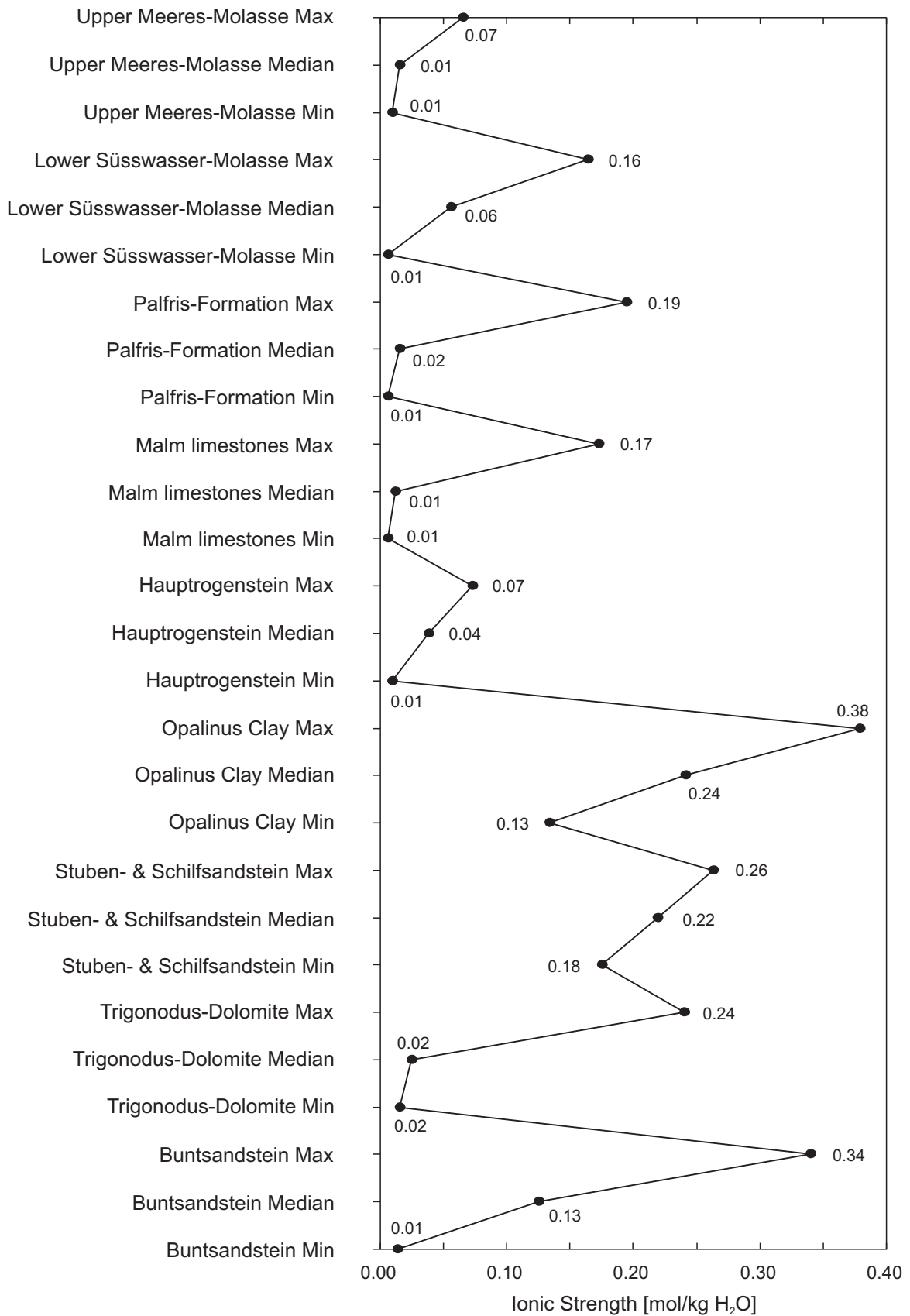


Fig. A1.2: Calculated ranges for the ionic strength of deep old groundwaters from various aquifers in Switzerland. Calculated from data in Table A1.2

A2 Procedure of Speciation Calculations

Speciation calculations were performed with the code PHREEQC (Parkhurst & Appelo 1999), version 2.12.1-669 for Mac OS X, using the Davies equation for activity coefficients of charged aqueous species:

$$\log_{10} \gamma_i = -Az_i^2 \left(\frac{\sqrt{I}}{1 + \sqrt{I}} - 0.3I \right)$$

where γ_i is the activity coefficient of species i , z_i the ionic charge of species i and I the ionic strength of the aqueous solution. Activity coefficients of neutral species were assumed to be one.

For the speciation calculations 13 different water types were considered. Their compositions are given in Appendices A3 through A6. For each water type the speciation of several radionuclides was considered (see Table A2.1 for an overview). Speciation calculations were performed as follows: A trace amount of a specific radionuclide (the speciation of each radionuclide was calculated separately) was added to the composition of the water under consideration and the speciation was calculated. As a rule, a total radionuclide concentration of 10^{-9} mol/kg H₂O was assumed in the speciation calculations to represent trace amounts. In some cases, lower concentrations were assumed when the calculation predicted the precipitation of a solid phase containing the specific radionuclide (e.g., Zr and Co). However, this was not done in each case of potential precipitation, as the relative amounts of the different species of a radionuclide do not change with a variation in the total concentration of the radionuclide (except in the case of polynuclear complexes, which are, however, irrelevant at trace concentrations). Furthermore, the precipitation of oversaturated solids was not actually modelled (only saturation indices were calculated) leaving the composition of the aqueous solution unchanged. As a consequence, the relative amounts of the different radionuclide species are not affected. The results of the speciation calculations are presented in tables in the Appendices A3 through A5.

Tab. A2.1: Overview of speciation calculations.

Water	pH	<i>I</i>	Water Composition	Radionuclides	Radionuclide Speciation	Reference (original water)
Generic reference groundwater	7.0	0.1	Table A3.1	Be(II), Co(II), Ni(II), Se(IV), Zr(IV), Nb(V), Mo(VI), Tc(IV), Pd(II), Cd(II), Sn(IV), Bi(III), Sb(III), Eu(III), Pb(II), Th(IV), Pa(V), U(IV, V, VI), Np(III, IV, V, VI), Pu(III, IV, V, VI), Am(III)	Table A3.2	this study
Argint Generic argillaceous groundwater	7.24	2.28E-01	Table A4.1	Be(II), Co(II), Ni(II), Se(IV), Zr(IV), Nb(V), Mo(VI), Tc(IV), Pd(II), Cd(II), Sn(IV), Bi(III), Sb(III), Eu(III), Pb(II), Th(IV), Pa(V), U(IV, V, VI), Np(III, IV, V, VI), Pu(III, IV, V, VI), Am(III)	Table A4.2	this study
Argh9 Generic argillaceous groundwater	9.0	0.4	Table A4.3	Be(II), Co(II), Ni(II), Se(IV), Zr(IV), Nb(V), Mo(VI), Tc(IV), Pd(II), Cd(II), Sn(IV), Bi(III), Sb(III), Eu(III), Pb(II), Th(IV), Pa(V), U(IV, V, VI), Np(III, IV, V, VI), Pu(III, IV, V, VI), Am(III)	Table A4.4	this study
Argl9 Generic argillaceous groundwater	9.0	0.13	Table A4.5	Be(II), Co(II), Ni(II), Se(IV), Zr(IV), Nb(V), Mo(VI), Tc(IV), Pd(II), Cd(II), Sn(IV), Bi(III), Sb(III), Eu(III), Pb(II), Th(IV), Pa(V), U(IV, V, VI), Np(III, IV, V, VI), Pu(III, IV, V, VI), Am(III)	Table A4.6	this study
Argh6 Generic argillaceous groundwater	6.0	0.4	Table A4.7	Be(II), Co(II), Ni(II), Se(IV), Zr(IV), Nb(V), Mo(VI), Tc(IV), Pd(II), Cd(II), Sn(IV), Bi(III), Sb(III), Eu(III), Pb(II), Th(IV), Pa(V), U(IV, V, VI), Np(III, IV, V, VI), Pu(III, IV, V, VI), Am(III)	Table A4.8	this study
Argl6 Generic argillaceous groundwater	6.0	0.13	Table A4.9	Be(II), Co(II), Ni(II), Se(IV), Zr(IV), Nb(V), Mo(VI), Tc(IV), Pd(II), Cd(II), Sn(IV), Bi(III), Sb(III), Eu(III), Pb(II), Th(IV), Pa(V), U(IV, V, VI), Np(III, IV, V, VI), Pu(III, IV, V, VI), Am(III)	Table A4.10	this study
Groundwater SGS 6	6.68	3.97E-02	Table A6.1	Pb(II)	Table A6.2	Koss et al. (1992)
Laboratory solution	7.24	0.1	Table A6.3	Np(III, IV, V, VI)	Table A6.4	Gorgeon (1994)

A2.1 Thermodynamic Data

Calculations were made for the following radionuclides:

Be(II), Co(II), **Ni(II)**, **Se(IV)**, **Zr(IV)**, **Nb(V)**, **Mo(VI)**, **Tc(IV)**, **Pd(II)**, Cd(II), **Sn(IV)**, Bi(III), Sb(III), **Eu(III)**, Pb(II), **Th(IV)**, Pa(V), U(IV, V, VI), **Np(III, IV, V, VI)**, **Pu(III, IV, V, VI)**, **Am(III)**.

For the elements listed above in boldface type the Nagra/PSI Thermochemical Database 01/01 (Hummel et al. 2002) provided reviewed data. The PHREEQC datafile used, NAPSI_300401DAV.DAT, was derived from the Nagra/PSI Thermochemical Database 01/01 (release of 30-04-01) and is listed in Thoenen (2001). For calculations involving Sn(IV) the PHREEQC datafile NAPSI_300401TNDV.DAT was used. This file was obtained from NAPSI_300401DAV.DAT by replacing the following entry in the SOLUTION_MASTER_SPECIES data block

```
Tin          Sn(OH)4          0.0          Sn(OH)4          186.739 #          Ma(P)          PSI TM-44-00-05
```

with

```
Tn          Tn(OH)4          0.0          Tn(OH)4          186.739 #          Ma(P)          PSI TM-44-00-05
```

In addition, the following entries in the SOLUTION_SPECIES data block

```
Sn(OH)4          = Sn(OH)4
log_k            0.0
-gamma          0.00  0.00

+1.000Sn(OH)4          +1.000H2O          -1.000H+          = Sn(OH)5-
log_k            -8.0000
# delta_h        0.0000
# -a_e          -8.000000E+00  0.000000E+00  0.000000E+00  0.000000E+00  0.000000E+00
# -gamma        4.00  0.00

+1.000Sn(OH)4          +2.000H2O          -2.000H+          = Sn(OH)6-2
log_k            -18.4000
# delta_h        0.0000
# -a_e          -1.840000E+01  0.000000E+00  0.000000E+00  0.000000E+00  0.000000E+00
# -gamma        4.00  0.00
```

were replaced with

```
Tn(OH)4          = Tn(OH)4
log_k            0.0
-gamma          0.00  0.00

+1.000Tn(OH)4          +1.000H2O          -1.000H+          = Tn(OH)5-
log_k            -8.0000
# delta_h        0.0000
# -a_e          -8.000000E+00  0.000000E+00  0.000000E+00  0.000000E+00  0.000000E+00
# -gamma        4.00  0.00

+1.000Tn(OH)4          +2.000H2O          -2.000H+          = Tn(OH)6-2
log_k            -18.4000
# delta_h        0.0000
# -a_e          -1.840000E+01  0.000000E+00  0.000000E+00  0.000000E+00  0.000000E+00
# -gamma        4.00  0.00
```

and the following entries in the PHASES data block

```
Cassiterite
SnO2          = +1.000Sn(OH)4          -2.000H2O
log_k            -8.0000
# delta_h        -0.0000
# -a_e          -8.000000E+00  -0.000000E+00  -0.000000E+00  -0.000000E+00  -0.000000E+00

SnO2(am)
SnO2          = +1.000Sn(OH)4          -2.000H2O
log_k            -7.3000
# delta_h        -0.0000
# -a_e          -7.300000E+00  -0.000000E+00  -0.000000E+00  -0.000000E+00  -0.000000E+00

CaSn(OH)6(s)
CaSn(OH)6          = +1.000Sn(OH)4          +2.000H2O          +1.000Ca+2
-2.000H+
log_k            8.7000
# delta_h        -0.0000
# -a_e          8.700000E+00  -0.000000E+00  -0.000000E+00  -0.000000E+00  -0.000000E+00
```

were replaced with

```

Cassiterite
TnO2          = +1.000Tn(OH)4          -2.000H2O
#   log_k      -8.0000
#   delta_h    -0.0000
#   -a_e       -8.000000E+00 -0.000000E+00 -0.000000E+00 -0.000000E+00 -0.000000E+00

TnO2 (am)
TnO2          = +1.000Tn(OH)4          -2.000H2O
#   log_k      -7.3000
#   delta_h    -0.0000
#   -a_e       -7.300000E+00 -0.000000E+00 -0.000000E+00 -0.000000E+00 -0.000000E+00

CaTn(OH)6 (s)
CaTn(OH)6     = +1.000Tn(OH)4          +2.000H2O          +1.000Ca+2
-2.000H+
#   log_k      8.7000
#   delta_h    -0.0000
#   -a_e       8.700000E+00 -0.000000E+00 -0.000000E+00 -0.000000E+00 -0.000000E+00

```

In order to calculate the speciation of U(IV), U(V), U(VI), Np(III), Np(IV), Np(V), Np(VI), Pu(III), Pu(IV), Pu(V), Pu(VI), Se(IV), and Tc(IV) decoupled from the redox state, a separate PHREEQC datafile was created from NAPSI_300401DAV.DAT for each of these species. In the case of U(IV) the procedure was as follows:

The entry for U in the SOLUTION_MASTER_SPECIES block:

U	UO2+2	0.0	U	238.029	#	92	Ele	PSI TM-44-00-03
U(4)	U+4	0.0	U		#		Ma (S)	PSI TM-44-00-03
U(5)	UO2+	0.0	U		#		Ma (S)	PSI TM-44-00-03
U(6)	UO2+2	0.0	UO2		#		Ma (P)	PSI TM-44-00-03

was replaced by

U	U+4	0.0	U	238.029	#	92	Ele	PSI TM-44-00-03
#U(4)	U+4	0.0	U		#		Ma (S)	PSI TM-44-00-03
#U(5)	UO2+	0.0	U		#		Ma (S)	PSI TM-44-00-03
#U(6)	UO2+2	0.0	UO2		#		Ma (P)	PSI TM-44-00-03

The entry for U in the SOLUTION_SPECIES (PMATCH MASTER SPECIES) block

```

UO2+2          = UO2+2
#   log_k      0.0
#   -gamma     4.00  0.00

```

was replaced by

```

U+4            = U+4
#   log_k      0.0
#   -gamma     4.00  0.00

```

Finally, all data for reactions involving UO2+ and UO2+2 were commented out by inserting # at the beginning of the appropriate lines. The resulting PHREEQC datafile was called NAPSI_300401_U_IV_DAV.DAT.

Similar procedures were used for the other redox decoupled species.

In addition to the data from the Nagra/PSI Thermochemical Database 01/01, the estimates by Hummel & Berner (2001) for the formation constants of

Np(III): Np(OH)₂⁺, Np(OH)₃(aq), NpCO₃⁺, Np(CO₃)₂⁻, Np(CO₃)₃³⁻, NpSO₄⁺, Np(SO₄)₂⁻,
NpSiO(OH)₃²⁺
Pu(III): Pu(OH)₂⁺, Pu(OH)₃(aq), PuCO₃⁺, Pu(CO₃)₂⁻, Pu(CO₃)₃³⁻, PuSiO(OH)₃²⁺
U(IV): U(CO₃)(OH)₃⁻
Np(IV): Np(CO₃)(OH)₃⁻
Pu(IV): Pu(CO₃)(OH)₃⁻

were also used and were included in the PHREEQC inputfiles, where appropriate. These data are listed in PHREEQC format in Appendix A6.1.

The formation constant for Ca₂UO₂(CO₃)₃(aq) reported by Kalmykow & Choppin (2000), but not considered in the Nagra/PSI Thermochemical Database 01/01, is listed in PHREEQC format in Appendix A6.2 and was included in the PHREEQC inputfiles, where appropriate.

Thermodynamic data for

Co(II), Cd(II), Sb(III), Pb(II), Pa(V)

are not included in the Nagra/PSI Thermochemical Database 01/01. Speciation calculations for these elements were made with unreviewed data taken from the MINEQL datafile, FEB92.LOGK, Version 27.4.1994. These data, listed in Appendix A6.3 in PHREEQC format, were included in the PHREEQC inputfiles, where appropriate.

There are no thermodynamic data for $\text{CoCO}_3(\text{aq})$, $\text{Co}(\text{CO}_3)_2^{2-}$ and CoHCO_3^+ included in the Nagra/PSI Thermochemical Database 01/01 and in the MINEQL database. As an estimate, values for equilibrium constants were substituted by the corresponding values for Ni-Carbonate complexes from the Nagra/PSI Thermochemical Database 01/01 (note that the equilibrium constants for $\text{Ni}(\text{CO}_3)_2^{2-}$ and NiHCO_3^+ are only approximations). These data, listed in Appendix A6.4 in PHREEQC format, were included in the PHREEQC inputfiles, where appropriate.

There are also no data for Be(II) in the Nagra/PSI Thermochemical Database 01/01. Unreviewed data were taken from the MINTEQ Version 4 database (HydroGeoLogic Inc. & Allison Geoscience Consultants Inc. 1999), distributed with the PHREEQC package. These data, listed in Appendix A6.5 in PHREEQC format, were included in the PHREEQC inputfiles, where appropriate.

Unreviewed data for Bi(III) were taken from Baes & Mesmer (1974). These data, listed in Appendix A6.6 in PHREEQC format, were included in the PHREEQC inputfiles, where appropriate.

Perchlorate is not contained in the Nagra/PSI Thermochemical Database 01/01. The generic reference groundwater (see Tab. A3.1) and the laboratory solution by Gorgeon (1994) (see Tab. A5.1) both require NaClO_4 as constant ionic strength medium. Therefore, the species ClO_4^- was considered in the appropriate PHREEQC inputfiles by adding the following lines:

```
SOLUTION_MASTER_SPECIES
Per      Per-          0.0 Per 99.45 # Perchlorate ClO4-

SOLUTION_SPECIES
Per- = Per-
      log_k 0.0
```

No reactions with ClO_4^- were considered.

References

- Baes, C.F., Jr. & Mesmer, R.E. (1976): *The Hydrolysis of Cations*. John Wiley & Sons, New York, 489 pp.
- Gorgeon, L. (1994): *Contribution à la modélisation physico-chimique de la rétention de radioéléments à vie longue par des matériaux argileux*. Unpublished Ph.D. thesis, Université Paris VI, Paris, France.
- Hummel, W. & Berner, U. (2001): *Application of the Nagra/PSI Thermochemical Data Base 01/01: Solubility and Sorption of Th, U, Np and Pu*. PSI Internal Report TM-44-01-04, Paul Scherrer Institut, Villigen, Switzerland.
- Hummel, W., Berner, U., Curti, E., Pearson, F.J. & Thoenen, T. (2002): *Nagra/PSI Thermochemical Database 01/01*. Nagra Technical Report, NTB 02-16, Nagra, Wettingen, Switzerland; and Universal Publishers, Parkland, Florida, USA, 589 pp.
- HydroGeoLogic Inc. & Allison Geoscience Consultants Inc. (1999): *MINTEQA2/PRODEFA2, a geochemical assessment model for environmental systems: user manual supplement for version 4.0*, EPA report, Athens, GE, USA. 76 pp.
- Kalmykow, S.N. & Choppin, G.R. (2000): Mixed $\text{Ca}^{2+}/\text{UO}_2^{2+}/\text{CO}_3^{2-}$ complex formation at different ionic strengths. *Radiochimica Acta*, 88, 603-606.
- Koss, V., Winkler, A. & Bütow, E. (1992): Experimental investigation and modelling of the migration of radionuclides from the Ellweiler uranium mill tailings. *Radiochimica Acta*, 58/59, 447-451
- Parkhurst, D.L. & Appelo, C.A.J. (1999): *User's guide to PHREEQC (Version 2) - A computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations*. Water-Resources Investigations Report 99-4259, U.S. Geological Survey, Denver, Colorado, U.S.A. 312 pp.
- Pearson, F.J. (2002): *Benken Reference Water Geochemistry*. Internal Report, Nagra, Wettingen, Switzerland.
- Stenhouse, M.J. (1995): *Sorption Databases for Crystalline, Marl and Bentonite for Performance Assessment*, Nagra Technical Report, NTB 93-06, Nagra, Wettingen, Switzerland.
- Thoenen, T. (2001): *Nagra/PSI Thermochemical Database Update: PHREEQC Database Version 01-01, Release 30-4-01*. PSI Internal Report AN-44-01-06, Paul Scherrer Institut, Villigen, Switzerland. 80 pp.

A3 Generic Reference Water and Speciation Calculations

Tab. A3.1: Generic Reference Water Composition (mol/kg H₂O)

Na	1.000e-01
ClO ₄	1.000e-01
temp	25°C
pH	7.0
I	0.1

Tab. A3.2: Generic Reference Water, Radionuclide Speciation (mol/kg H₂O).

Element	Species	Concentration [m]	Distribution [%]	Output File	Data File
Be(II)	BeOH+	9.05E-10	90.52	Synth_Ref_Be.out	NAPSI_300401DAV.DAT Be: Inputfile (Minteq.v4)
	Be+2	4.87E-11	4.87		
	Be(OH) ₂	4.59E-11	4.59		
	Be(OH) ₃ ⁻	1.45E-13	0.01		
	Be ₂ OH ₃	1.60E-17	0.00		
	Be ₃ (OH) ₃₊₃	6.77E-20	0.00		
	Be(OH) ₄₋₂	1.78E-20	0.00		
		1.00E-09	100		
Co(II)	Co+2	9.99E-10	99.91	Synth_Ref_CoNi.out	NAPSI_300401DAV.DAT Co: Inputfile (Mineql)
	CoOH+	9.48E-13	0.09		
	Co(OH) ₂	9.30E-16	0.00		
	Co(OH) ₃ ⁻	2.37E-21	0.00		
	Co ₂ OH ₃	6.38E-23	0.00		
	Co(OH) ₄₋₂	1.56E-27	0.00		
	Co ₄ (OH) ₄₊₄	3.91E-39	0.00		
		1.00E-09	100		
Ni(II)	Ni+2	9.99E-10	99.85	Synth_Ref_Ni.out	NAPSI_300401DAV.DAT
	NiOH+	1.50E-12	0.15		
	Ni(OH) ₂	3.70E-14	0.00		
	Ni(OH) ₃ ⁻	9.41E-19	0.00		
	Ni ₂ OH ₃	2.02E-21	0.00		
	Ni(OH) ₄₋₂	1.24E-26	0.00		
	Ni ₄ (OH) ₄₊₄	1.23E-36	0.00		
		1.00E-09	100		
Se(IV) decoupled	HSeO ₃ ⁻	9.23E-10	92.30	Synth_Ref_Se_IV.out	NAPSI_300401_SE_IV_DAV.DAT only Se(IV) considered
	SeO ₃ ⁻²	7.70E-11	7.70		
	H ₂ SeO ₃	4.55E-14	0.00		
		1.00E-09	100		

Zr(IV)	Zr(OH)5-	8.65E-12	86.47	Synth_Ref_Zr.out	NAPSI_300401DAV.DAT
	Zr(OH)4	1.35E-12	13.53		
	ZrOH+3	1.26E-22	0.00		
	Zr+4	3.55E-29	0.00		
		1.00E-11	100		
Nb(V)	Nb(OH)5	6.32E-10	63.15	Synth_Ref_Nb.out	NAPSI_300401DAV.DAT
	NbO3-	3.69E-10	36.85		
	Nb(OH)4+	2.89E-17	0.00		
		1.00E-09	100		
Mo(VI)	MoO4-2	1.00E-09	100.00	Synth_Ref_Mo.out	NAPSI_300401DAV.DAT
		1.00E-09	100		
Tc(IV) decoupled	TcO(OH)2	1.00E-09	99.98	Synth_Ref_Tc_IV.out	NAPSI_300401_TC_DAV.DAT only Tc(IV) considered
	TcO(OH)3-	1.61E-13	0.02		
	TcO(OH)+	4.06E-14	0.00		
	TcO+2	2.70E-19	0.00		
		1.00E-09	100		
Pd(II)	Pd(OH)2	1.00E-09	100.00	Synth_Ref_Pd.out	NAPSI_300401DAV.DAT
	Pd(OH)3-	4.03E-14	0.00		
	Pd+2	2.70E-19	0.00		
		1.00E-09	100		
Cd(II)	Cd+2	1.00E-09	99.96	Synth_Ref_Cd.out	NAPSI_300401DAV.DAT Cd: Inputfile (Mineql)
	CdOH+	3.78E-13	0.04		
	Cd(OH)2	1.86E-16	0.00		
	Cd(OH)3-	7.48E-21	0.00		
	Cd2OH+3	5.07E-21	0.00		
	Cd(OH)4-2	4.94E-29	0.00		
	Cd4(OH)4+4	0.00E+00	0.00		
		1.00E-09	100		
Sn(IV) decoupled	Tn(OH)4	8.87E-10	88.68	Synth_Ref_Tn.out	NAPSI_300401TNDV.DAT only Sn(IV)=Tn considered
	Tn(OH)5-	1.13E-10	11.31		
	Tn(OH)6-2	9.40E-14	0.01		
		1.00E-09	100		
Bi(III)	Bi(OH)3	9.91E-10	99.08	Synth_Ref_Bi.out	NAPSI_300401DAV.DAT Bi: Inputfile (Baes & Mesmer 1976)
	Bi(OH)2+	9.22E-12	0.92		
	BiOH+2	1.58E-15	0.00		
	Bi(OH)4-	1.45E-15	0.00		
	Bi+3	6.67E-21	0.00		
		1.00E-09	100		

Sb(III) decoupled	Sb(OH)3	1.00E-09	100.00	Synth_Ref_Sb_III.out	NAPSI_300401DAV.DAT
	Sb(OH)4-	1.93E-14	0.00		Sb: Inputfile (Mineql)
	Sb(OH)2+	3.38E-15	0.00		only Sb(III) considered
		1.00E-09	100		
Eu(III)	Eu+3	9.28E-10	92.79	Synth_Ref_Eu.out	NAPSI_300401DAV.DAT
	EuOH+2	6.17E-11	6.17		
	Eu(OH)2+	1.02E-11	1.02		
	Eu(OH)3	1.99E-13	0.02		
	Eu(OH)4-	8.03E-19	0.00		
	1.00E-09	100			
Pb(II)	Pb+2	9.13E-10	91.31	Synth_Ref_Pb.out	NAPSI_300401DAV.DAT
	PbOH+	8.67E-11	8.66		Pb: Inputfile (Mineql)
	Pb(OH)2	2.69E-13	0.03		
	Pb(OH)3-	3.43E-17	0.00		
	Pb2(OH)+3	4.23E-18	0.00		
	Pb3(OH)4+2	1.32E-24	0.00		
	Pb4(OH)4+4	8.63E-30	0.00		
	1.00E-09	100			
Th (IV)	Th(OH)4	1.00E-09	99.99	Synth_Ref_Th.out	NAPSI_300401DAV.DAT
	ThOH+3	9.29E-14	0.01		
	Th+4	1.32E-17	0.00		
	1.00E-09	100			
Pa(V) decoupled	PaO2OH	9.96E-10	99.60	Synth_Ref_Pa.out	NAPSI_300401DAV.DAT
	PaO2+	4.04E-12	0.40		Pa: Inputfile (Mineql)
	PaOOH+2	2.68E-18	0.00		only Pa(V) considered
	1.00E-09	100			
U(IV) decoupled	U(OH)4	1.00E-09	100.00	Synth_Ref_U_IV_est.out	NAPSI_300401_U_IV_DAV.DAT
	UOH+3	2.68E-21	0.00		U: Inputfile (TM-44-01-04)
	U+4	5.24E-27	0.00		only U(IV) considered
	1.00E-09	100			
U(V) decoupled	UO2+	1.00E-09	100.00	Synth_Ref_U_V.out	NAPSI_300401_U_V_DAV.DAT
		1.00E-09	100		only U(V) considered
U(VI) decoupled	UO2(OH)2	3.79E-10	37.85	Synth_Ref_U_VI.out	NAPSI_300401_U_VI_DAV.DAT
	UO2OH+	3.07E-10	30.67		only U(VI) considered
	UO2(OH)3-	3.05E-10	30.46		
	UO2+2	1.02E-11	1.02		
	(UO2)2(OH)2+2	9.28E-15	0.00		
	(UO2)3(OH)5+	1.96E-15	0.00		
	UO2(OH)4-2	1.01E-16	0.00		

	(UO ₂) ₃ (OH) ₇ ⁻	6.92E-17	0.00		
	(UO ₂) ₂ OH ₃	2.66E-18	0.00		
	(UO ₂) ₃ (OH) ₄ ⁺²	1.84E-18	0.00		
	(UO ₂) ₄ (OH) ₇ ⁺	3.32E-19	0.00		
		1.00E-09	100		
Np(III)	Np ⁺³	6.72E-10	67.21	Synth_Ref_Np_III_est.out	NAPSI_300401_NP_III_DAV.DAT
decoupled	NpOH ₂	3.09E-10	30.94		Np: Inputfile (TM-44-01-04)
	Np(OH) ₂ ⁺	1.85E-11	1.85		only Np(III) considered
	Np(OH) ₃	4.56E-15	0.00		
		1.00E-09	100		
Np(IV)	Np(OH) ₄	1.00E-09	100.00	Synth_Ref_Np_IV_est.out	NAPSI_300401_NP_IV_DAV.DAT
decoupled	NpOH ₃	3.01E-20	0.00		Np: Inputfile (TM-44-01-04)
	Np ⁺⁴	3.31E-26	0.00		only Np(IV) considered
		1.00E-09	100		
Np(V)	NpO ₂ ⁺	1.00E-09	100.00	Synth_Ref_Np_V.out	NAPSI_300401_NP_V_DAV.DAT
decoupled	NpO ₂ (OH)	3.90E-14	0.00		only Np(V) considered
	NpO ₂ (OH) ₂ ⁻	2.50E-19	0.00		
		1.00E-09	100		
Np(VI)	NpO ₂ (OH) ₃ ⁻	5.49E-10	54.92	Synth_Ref_Np_VI.out	NAPSI_300401_NP_VI_DAV.DAT
decoupled	NpO ₂ OH ⁺	4.39E-10	43.92		only Np(VI) considered
	NpO ₂ ⁺²	1.16E-11	1.16		
	(NpO ₂) ₂ (OH) ₂ ⁺²	2.69E-15	0.00		
	NpO ₂ (OH) ₄ ⁻²	1.15E-16	0.00		
	(NpO ₂) ₃ (OH) ₅ ⁺	7.78E-17	0.00		
		1.00E-09	100		
Pu(III)	Pu ⁺³	7.21E-10	72.07	Synth_Ref_Pu_III_est.out	NAPSI_300401_PU_III_DAV.DAT
decoupled	PuOH ₂	2.64E-10	26.35		Pu: Inputfile (TM-44-01-04)
	Pu(OH) ₂ ⁺	1.58E-11	1.58		only Pu(III) considered
	Pu(OH) ₃	3.89E-15	0.00		
		1.00E-09	100		
Pu(IV)	Pu(OH) ₄	1.00E-09	100.00	Synth_Ref_Pu_IV_est.out	NAPSI_300401_PU_IV_DAV.DAT
decoupled	PuOH ₃	3.87E-22	0.00		Pu: Inputfile (TM-44-01-04)
	Pu ⁺⁴	1.32E-27	0.00		only Pu(IV) considered
		1.00E-09	100		
Pu(V)	PuO ₂ ⁺	9.99E-10	99.86	Synth_Ref_Pu_V.out	NAPSI_300401_PU_V_DAV.DAT
decoupled	PuO ₂ OH	1.45E-12	0.14		only Pu(V) considered
		1.00E-09	100		

Pu(VI) decoupled	PuO ₂ OH ⁺	8.18E-10	81.84	Synth_Ref_Pu_VI.out	NAPSI_300401_PU_VI_DAV.DAT only Pu(VI) considered
	PuO ₂ (OH) ₂	1.27E-10	12.72		
	PuO ₂ + ₂	5.44E-11	5.44		
	(PuO ₂) ₂ (OH) ₂ + ₂	3.47E-15	0.00		
		1.00E-09	100		
Am(III)	Am+ ₃	8.66E-10	86.63	Synth_Ref_Am.out	NAPSI_300401DAV.DAT
	AmOH+ ₂	1.26E-10	12.61		
	Am(OH) ₂ + ₂	7.55E-12	0.76		
	Am(OH) ₃	1.86E-15	0.00		
		1.00E-09	100		

A4 Argillaceous Rock Systems: Generic Waters and Speciation Calculations

Tab. A4.1: Argillaceous Rock Systems, pH = 7.24, I = 2.28E-01, Water Composition (mol/kg H₂O)

Na	2.124E-01
Ca	3.458E-03
C	7.497E-03
Cl	1.840E-01
S	1.420E-02
Si	1.776E-04
temp	25°C
pH	7.24
I	2.28E-01
log pCO ₂	-1.74

Tab. A4.2: Argillaceous Rock Systems, pH = 7.24, I = 2.28E-01, Radionuclide Speciation (mol/kg H₂O).

Element	Species	Concentration [m]	Distribution [%]	Output File	Data File
Be(II)	BeOH+	8.30E-10	83.02	Argint_Be.out	NAPSI_300401DAV.DAT Be: Inputfile (Minteq.v4)
	Be(OH)2	6.90E-11	6.90		
	BeCO3	6.29E-11	6.29		
	Be+2	3.01E-11	3.00		
	BeSO4	4.43E-12	0.44		
	BeCl+	2.70E-12	0.27		
	Be(OH)3-	3.97E-13	0.04		
	Be(SO4)2-2	3.32E-13	0.03		
	Be2OH+3	1.15E-17	0.00		
	Be(OH)4-2	1.00E-19	0.00		
	Be3(OH)3+3	7.30E-20	0.00		
		1.00E-09	100		
Co(II)	Co+2	7.69E-12	76.93	Argint_CoNi.out	NAPSI_300401DAV.DAT Co: Inputfile (Mineql)
	CoSO4	1.68E-12	16.76		
	CoCl+	3.82E-13	3.82		
	CoHCO3+	1.48E-13	1.48		
	CoCO3	8.96E-14	0.90		
	CoOH+	1.08E-14	0.11		
	Co(CO3)2-2	1.14E-16	0.00		
	Co(OH)2	1.74E-17	0.00		
	Co(OH)3-	8.09E-23	0.00		
	Co2OH+3	6.90E-27	0.00		
	Co(OH)4-2	1.08E-28	0.00		

	CoS2O3	9.80E-34	0.00		
	Co4(OH)4+4	0.00E+00	0.00		
		1.00E-11	100		
Ni(II)	Ni+2	6.97E-10	69.71	Argent_Ni.out	NAPSI_300401DAV.DAT
	NiSO4	1.35E-10	13.54		
	NiCl+	9.76E-11	9.75		
	NiCl2	3.59E-11	3.59		
	NiHCO3+	1.34E-11	1.34		
	Ni(SO4)2-2	1.09E-11	1.09		
	NiCO3	8.12E-12	0.81		
	NiOH+	1.55E-12	0.16		
	Ni(OH)2	6.28E-14	0.01		
	Ni(CO3)2-2	1.03E-14	0.00		
	Ni(OH)3-	2.92E-18	0.00		
	Ni2OH+3	1.79E-21	0.00		
	NiHS+	9.85E-23	0.00		
	Ni(OH)4-2	7.78E-26	0.00		
	Ni(HS)2	3.19E-35	0.00		
	Ni4(OH)4+4	2.64E-36	0.00		
		1.00E-09	100		
Se(IV) decoupled	HSeO3-	8.55E-15	85.51	Argent_Se_IV.out	NAPSI_300401_SE_IV_DAV.DAT
	SeO3-2	1.45E-15	14.49		only Se(IV) considered
	H2SeO3	2.30E-19	0.00		
		1.00E-14	100		
Zr(IV)	Zr(OH)5-	9.21E-10	92.10	Argent_Zr.out	NAPSI_300401DAV.DAT
	Zr(OH)4	7.90E-11	7.90		
	ZrOH+3	2.26E-21	0.00		
	ZrSO4+2	4.64E-25	0.00		
	Zr+4	5.32E-28	0.00		
	ZrCl+3	2.84E-28	0.00		
		1.00E-09	100		
Nb(V)	NbO3-	5.18E-10	51.83	Argent_Nb.out	NAPSI_300401DAV.DAT
	Nb(OH)5	4.82E-10	48.17		
	Nb(OH)4+	1.34E-17	0.00		
		1.00E-09	100		
Mo(VI)	MoO4-2	1.00E-09	100.00	Argent_Mo.out	NAPSI_300401DAV.DAT
		1.00E-09	100		
Tc(IV) decoupled	TcO(OH)2	7.78E-10	77.75	Argent_Tc_IV.out	NAPSI_300401_TC_DAV.DAT
	TcCO3(OH)2	1.99E-10	19.91		only Tc(IV) considered
	TcCO3(OH)3-	2.32E-11	2.32		
	TcO(OH)3-	2.28E-13	0.02		

	TcO(OH)+	1.92E-14	0.00		
	TcO+2	8.63E-20	0.00		
		1.00E-09	100		
Pd(II)	Pd(OH)2	9.71E-10	97.06	Argent_Pd.out	NAPSI_300401DAV.DAT
	PdCl4-2	1.87E-11	1.87		
	PdCl3-	8.88E-12	0.89		
	PdCl3OH-2	1.49E-12	0.15		
	PdCl2	1.21E-13	0.01		
	Pd(OH)3-	7.14E-14	0.01		
	PdCl2(OH)2-2	5.97E-14	0.01		
	PdCl+	7.55E-16	0.00		
	Pd+2	1.08E-19	0.00		
		1.00E-09	100		
Cd(II)	CdCl+	5.81E-10	58.08	Argent_Cd.out	NAPSI_300401DAV.DAT
	CdCl2	2.45E-10	24.52		Cd: Inputfile (Mineql)
	Cd+2	1.09E-10	10.92		
	CdSO4	2.99E-11	2.99		
	CdCl3-	2.85E-11	2.85		
	CdCO3	2.54E-12	0.25		
	Cd(SO4)2-2	1.92E-12	0.19		
	CdCl4-2	1.90E-12	0.19		
	Cd(SO4)3-4	6.11E-14	0.01		
	CdOH+	6.11E-14	0.01		
	Cd(OH)2	4.93E-17	0.00		
	Cd(OH)3-	3.63E-21	0.00		
	CdSO3	3.48E-22	0.00		
	Cd2OH+3	1.10E-22	0.00		
	Cd(OH)4-2	4.85E-29	0.00		
	CdS2O3	1.11E-30	0.00		
	Cd4(OH)4+4	0.00E+00	0.00		
		1.00E-09	100		
Sn(IV)	Tn(OH)4	8.11E-10	81.10	Argent_Tn.out	NAPSI_300401TNDV.DAT
decoupled	Tn(OH)5-	1.89E-10	18.87		only Sn(IV)=Tn considered
	Tn(OH)6-2	3.18E-13	0.03		
		1.00E-09	100		
Bi(III)	Bi(OH)3	9.94E-10	99.44	Argent_Bi.out	NAPSI_300401DAV.DAT
decoupled	Bi(OH)2+	5.63E-12	0.56		Bi: Inputfile (Baes &
	Bi(OH)4-	2.66E-15	0.00		Mesmer 1976)
	BiOH+2	6.50E-16	0.00		
	Bi+3	2.06E-21	0.00		
		1.00E-09	100		

Sb(III) decoupled	Sb(OH)3	1.00E-09	100.00	Argent_Sb_III.out	NAPSI_300401DAV.DAT Sb: Inputfile (Mineql) only Sb(III) considered
	Sb(OH)4-	3.52E-14	0.00		
	Sb(OH)2+	2.06E-15	0.00		
		1.00E-09	100		
Eu(III)	EuCO3+	7.49E-10	74.87	Argent_Eu.out	NAPSI_300401DAV.DAT
	EuSiO(OH)3+2	1.43E-10	14.32		
	EuSO4+	4.33E-11	4.33		
	Eu(CO3)2-	2.88E-11	2.88		
	Eu+3	1.69E-11	1.69		
	Eu(SO4)2-	7.64E-12	0.76		
	EuCl+2	6.51E-12	0.65		
	Eu(SiO(OH)3)2+	2.21E-12	0.22		
	EuOH+2	1.50E-12	0.15		
	EuCl2+	9.11E-13	0.09		
	Eu(OH)2+	3.66E-13	0.04		
	Eu(OH)3	1.18E-14	0.00		
	Eu(OH)4-	8.64E-20	0.00		
		1.00E-09	100		
Pb(II)	PbCO3	7.13E-10	71.30	Argent_Pb.out	NAPSI_300401DAV.DAT Pb: Inputfile (Mineql)
	PbCl+	1.33E-10	13.26		
	Pb+2	6.12E-11	6.12		
	PbSO4	3.27E-11	3.27		
	PbCl2	2.18E-11	2.18		
	Pb(CO3)2-2	2.03E-11	2.03		
	PbOH+	8.60E-12	0.86		
	Pb(SO4)2-2	6.04E-12	0.60		
	PbCl3-	3.18E-12	0.32		
	PbCl4-2	5.34E-13	0.05		
	Pb(OH)2	4.38E-14	0.00		
	Pb(OH)3-	1.02E-17	0.00		
	Pb2(OH)+3	3.47E-20	0.00		
	Pb3(OH)4+2	2.34E-27	0.00		
	PbS2O3	1.24E-28	0.00		
	Pb4(OH)4+4	1.57E-33	0.00		
	Pb(S2O3)2-2	0.00E+00	0.00		
		1.00E-09	100		
	Th (IV)	ThCO3(OH)3-	9.98E-10		
Th(OH)4		1.66E-12	0.17		
Th(CO3)5-6		1.18E-15	0.00		
Th(SO4)2		1.85E-16	0.00		
ThOH+3		4.77E-17	0.00		
ThSO4+2		1.95E-17	0.00		
Th(SO4)3-2		1.21E-17	0.00		
Th+4		5.61E-21	0.00		
	1.00E-09	100.00			

Pa(V) decoupled	PaO ₂ OH	9.98E-10	99.75	Argent_Pa_V.out	NAPSI_300401DAV.DAT Pa: Inputfile (Mineql) only Pa(V) considered
	PaO ₂ ⁺	2.47E-12	0.25		
	PaOOH+2	1.10E-18	0.00		
		1.00E-09	100		
U(IV) decoupled	UCO ₃ (OH)3-	7.51E-10	75.04	Argent_U_IV_est.out	NAPSI_300401_U_IV_DAV.DAT U: Inputfile (TM-44-01-04) only U(IV) considered
	U(OH) ₄	2.50E-10	24.96		
	U(CO ₃) ₄ -4	1.22E-14	0.00		
	U(CO ₃) ₅ -6	1.40E-18	0.00		
	UOH+3	2.06E-22	0.00		
	U(SO ₄) ₂	8.99E-25	0.00		
	USO ₄ +2	1.11E-25	0.00		
	U+4	3.35E-28	0.00		
	UCI+3	2.97E-28	0.00		
	1.00E-09	100			
U(V) decoupled	UO ₂ ⁺	1.00E-09	100.00	Argent_U_V.out	NAPSI_300401_U_V_DAV.DAT only U(V) considered
	UO ₂ (CO ₃) ₃ -5	1.90E-15	0.00		
		1.00E-09	100		
U(VI) decoupled	UO ₂ (CO ₃) ₃ -4	7.05E-10	70.53	Argent_U_VI_Kal_Cho.out	NAPSI_300401_U_VI_DAV.DAT Ca ₂ UO ₂ (CO ₃) ₃ : Inputfile, Kalmykow & Choppin (2000) only U(VI) considered
	Ca ₂ UO ₂ (CO ₃) ₃	1.83E-10	18.29		
	UO ₂ (CO ₃) ₂ -2	1.11E-10	11.13		
	UO ₂ CO ₃	4.70E-13	0.05		
	UO ₂ (OH) ₃ -	1.14E-14	0.00		
	UO ₂ (OH) ₂	7.77E-15	0.00		
	UO ₂ OH ⁺	3.83E-15	0.00		
	UO ₂ SO ₄	1.16E-16	0.00		
	UO ₂ +2	8.63E-17	0.00		
	UO ₂ (SO ₄) ₂ -2	1.18E-17	0.00		
	UO ₂ Cl ⁺	7.11E-18	0.00		
	(UO ₂) ₂ CO ₃ (OH) ₃ -	2.51E-18	0.00		
	UO ₂ Cl ₂	3.86E-20	0.00		
	UO ₂ (OH) ₄ -2	7.65E-21	0.00		
	(UO ₂) ₃ (CO ₃) ₆ -6	2.71E-24	0.00		
	(UO ₂) ₂ (OH) ₂ +2	1.61E-24	0.00		
	(UO ₂) ₂ OH+3	3.45E-28	0.00		
	(UO ₂) ₃ (OH) ₅ ⁺	1.04E-29	0.00		
	(UO ₂) ₃ (OH) ₇ -	1.09E-30	0.00		
	(UO ₂) ₃ (OH) ₄ +2	6.56E-33	0.00		
	(UO ₂) ₃ O(OH) ₂ HCO ₃ ⁺	2.17E-33	0.00		
(UO ₂) ₄ (OH) ₇ ⁺	3.59E-38	0.00			
	1.00E-09	100			
Np(III) decoupled	NpCO ₃ ⁺	5.21E-10	52.12	Argent_Np_III_est.out	NAPSI_300401_NP_III_DAV.DAT Np: Inputfile (TM-44-01-04) only Np(III) considered
	NpSiO(OH) ₃ +2	3.15E-10	31.53		
	Np(CO ₃) ₂ -	6.34E-11	6.34		

	NpSO4+	5.36E-11	5.36		
	Np+3	2.34E-11	2.34		
	NpOH+2	1.44E-11	1.44		
	Np(SO4)2-	5.32E-12	0.53		
	Np(CO3)3-3	2.12E-12	0.21		
	Np(OH)2+	1.28E-12	0.13		
	Np(OH)3	5.16E-16	0.00		
		<hr/>	<hr/>		
		1.00E-09	100		
Np(IV) decoupled	Np(OH)4	8.34E-10	83.41	Argent_Np_IV_est.out	NAPSI_300401_NP_IV_DAV.DAT
	NpCO3(OH)3-	1.58E-10	15.83		Np: Inputfile (TM-44-01-04)
	Np(CO3)4-4	7.60E-12	0.76		only Np(IV) considered
	Np(CO3)5-6	9.78E-16	0.00		
	NpOH+3	7.73E-21	0.00		
	Np(SO4)2	6.57E-23	0.00		
	NpSO4+2	4.36E-24	0.00		
	Np+4	7.07E-27	0.00		
	NpCl+3	3.77E-27	0.00		
		<hr/>	<hr/>		
		1.00E-09	100		
Np(V) decoupled	NpO2+	7.35E-10	73.51	Argent_Np_V.out	NAPSI_300401_NP_V_DAV.DAT
	NpO2CO3-	2.58E-10	25.81		only Np(V) considered
	NpO2SO4-	6.36E-12	0.64		
	NpO2(CO3)2-3	4.03E-13	0.04		
	NpO2(OH)	4.72E-14	0.00		
	NpO2(CO3)2OH-4	8.32E-17	0.00		
	NpO2(CO3)3-5	1.72E-17	0.00		
	NpO2(OH)2-	5.50E-19	0.00		
		<hr/>	<hr/>		
		1.00E-09	100		
Np(VI) decoupled	NpO2(CO3)2-2	9.06E-10	90.60	Argent_Np_VI.out	NAPSI_300401_NP_VI_DAV.DAT
	NpO2(CO3)3-4	8.90E-11	8.90		only Np(VI) considered
	NpO2CO3	4.50E-12	0.45		
	NpO2(OH)3-	3.87E-13	0.04		
	NpO2OH+	1.03E-13	0.01		
	NpO2SO4	3.35E-15	0.00		
	NpO2+2	1.85E-15	0.00		
	NpO2(SO4)2-2	9.14E-16	0.00		
	NpO2Cl+	2.59E-16	0.00		
	(NpO2)2CO3(OH)3-	1.13E-17	0.00		
	NpO2(OH)4-2	1.64E-19	0.00		
	(NpO2)2(OH)2+2	1.65E-22	0.00		
	(NpO2)3(CO3)6-6	1.84E-24	0.00		
	NpO2(CO3)2-2	9.06E-10	90.60		
		<hr/>	<hr/>		
		1.00E-09	100		

Pu(III) decoupled	PuCO ₃ ⁺	5.14E-10	51.43	Argint_Pu_III_est.out	NAPSI_300401_PU_III_DAV.DAT Pu: Inputfile (TM-44-01-04) only Pu(III) considered
	PuSiO(OH) ₃ ⁺	3.11E-10	31.11		
	Pu(CO ₃) ₂ ⁻	6.26E-11	6.26		
	PuSO ₄ ⁺	5.29E-11	5.28		
	Pu ⁺³	2.31E-11	2.31		
	PuOH ₂	1.13E-11	1.13		
	PuCl ₂	1.12E-11	1.12		
	Pu(SO ₄) ₂ ⁻	1.05E-11	1.05		
	Pu(CO ₃) ₃ ⁻³	2.09E-12	0.21		
	Pu(OH) ₂ ⁺	9.99E-13	0.10		
	Pu(OH) ₃	4.05E-16	0.00		
	<hr/>	<hr/>			
	1.00E-09	100			
Pu(IV) decoupled	PuCO ₃ (OH) ₃ ⁻	9.87E-10	98.69	Argint_Pu_IV_est.out	NAPSI_300401_PU_IV_DAV.DAT Pu: Inputfile (TM-44-01-04) only Pu(IV) considered
	Pu(OH) ₄	1.31E-11	1.31		
	Pu(CO ₃) ₄ ⁻⁴	7.68E-16	0.00		
	Pu(CO ₃) ₅ ⁻⁶	4.63E-20	0.00		
	PuOH ₃	1.56E-24	0.00		
	Pu(SO ₄) ₂	5.04E-26	0.00		
	PuSO ₄ ⁺²	2.98E-27	0.00		
	PuCl ₃	4.69E-30	0.00		
	Pu ⁺⁴	4.41E-30	0.00		
	<hr/>	<hr/>			
	1.00E-09	100			
Pu(V) decoupled	PuO ₂ ⁺	6.62E-10	66.23	Argint_Pu_V.out	NAPSI_300401_PU_V_DAV.DAT only Pu(V) considered
	PuO ₂ CO ₃ ⁻	3.36E-10	33.61		
	PuO ₂ OH	1.58E-12	0.16		
	PuO ₂ (CO ₃) ₃ ⁻⁵	4.90E-18	0.00		
	<hr/>	<hr/>			
	1.00E-09	100			
Pu(VI) decoupled	PuO ₂ (CO ₃) ₂ ⁻²	6.35E-10	63.52	Argint_Pu_VI.out	NAPSI_300401_PU_VI_DAV.DAT only Pu(VI) considered
	PuO ₂ CO ₃	2.51E-10	25.05		
	PuO ₂ (CO ₃) ₃ ⁻⁴	1.11E-10	11.09		
	PuO ₂ OH ⁺	2.40E-12	0.24		
	PuO ₂ (OH) ₂	6.13E-13	0.06		
	PuO ₂ SO ₄	2.46E-13	0.02		
	PuO ₂ ⁺²	1.08E-13	0.01		
	PuO ₂ Cl ⁺	3.01E-14	0.00		
	PuO ₂ (SO ₄) ₂ ⁻²	2.67E-14	0.00		
	PuO ₂ Cl ₂	1.53E-16	0.00		
(PuO ₂) ₂ (OH) ₂ ⁺²	3.31E-20	0.00			
	<hr/>	<hr/>			
	1.00E-09	100			
Am(III)	AmCO ₃ ⁺	5.26E-10	52.57	Argint_Am.out	NAPSI_300401DAV.DAT
	AmSiO(OH) ₃ ⁺	3.18E-10	31.80		
	Am(CO ₃) ₂ ⁻	6.40E-11	6.40		
	AmSO ₄ ⁺	4.81E-11	4.81		

Am ³⁺	2.36E-11	2.36
AmCl ²⁺	8.12E-12	0.81
Am(SO ₄) ₂ ⁻	5.37E-12	0.54
AmOH ²⁺	4.59E-12	0.46
Am(CO ₃) ₃ ³⁻	2.13E-12	0.21
Am(OH) ₂ ⁺	4.07E-13	0.04
Am(OH) ₃	1.65E-16	0.00
	1.00E-09	100

Tab. A4.3: Argillaceous Rock Systems, pH = 9, high I,
Water Composition (mol/kg H₂O)

Na	3.908E-01
Ca	6.498E-04
C	9.989E-04
Cl	3.387E-01
S	2.605E-02
Si	2.121E-04
temp	25°C
pH	9.0
I	0.4
log pCO ₂	-4.48

Tab. A4.4: Argillaceous Rock Systems, pH = 9, high I,
Radionuclide Speciation (mol/kg H₂O).

Element	Species	Concentration [m]	Distribution [%]	Output File	Data File
Be(II)	Be(OH) ₂	6.40E-10	63.98	Argh9_Be.out	NAPSI_300401DAV.DAT Be: Inputfile (Minteq.v4)
	Be(OH) ₃ ⁻	2.19E-10	21.91		
	BeOH ⁺	1.40E-10	13.99		
	BeCO ₃	1.06E-12	0.11		
	Be ²⁺	9.04E-14	0.01		
	BeSO ₄	1.91E-14	0.00		
	BeCl ⁺	1.46E-14	0.00		
	Be(SO ₄) ₂ ²⁻	4.52E-15	0.00		
	Be(OH) ₄ ²⁻	3.54E-15	0.00		
	Be ₂ OH ³⁺	7.47E-21	0.00		
	Be ₃ (OH) ₃ ³⁺	4.40E-22	0.00		
	1.00E-09	100			
Co(II)	Co ²⁺	6.45E-12	64.50	Argh9_CoNi.out	NAPSI_300401DAV.DAT Co: Inputfile (Mineql)
	CoSO ₄	2.02E-12	20.16		
	CoCl ⁺	5.55E-13	5.55		

	CoOH+	4.96E-13	4.96		
	CoCO3	4.23E-13	4.23		
	Co(OH)2	4.50E-14	0.45		
	CoHCO3+	1.23E-14	0.12		
	Co(CO3)2-2	3.41E-15	0.03		
	Co(OH)3-	1.21E-17	0.00		
	Co(OH)4-2	9.71E-22	0.00		
	Co2OH+3	2.82E-25	0.00		
	Co4(OH)4+4	6.55E-40	0.00		
	CoS2O3	0.00E+00	0.00		
		<hr/>	<hr/>		
		1.00E-11	100		
Ni(II)	Ni+2	4.58E-10	45.76	Argh9_Ni.out	NAPSI_300401DAV.DAT
	NiSO4	1.28E-10	12.75		
	Ni(OH)2	1.27E-10	12.72		
	NiCl+	1.11E-10	11.10		
	NiCl2	7.29E-11	7.29		
	NiOH+	5.58E-11	5.58		
	NiCO3	3.00E-11	3.00		
	Ni(SO4)2-2	1.66E-11	1.66		
	NiHCO3+	8.75E-13	0.09		
	Ni(OH)3-	3.43E-13	0.03		
	Ni(CO3)2-2	2.42E-13	0.02		
	Ni(OH)4-2	5.47E-19	0.00		
	Ni2OH+3	4.48E-20	0.00		
	Ni4(OH)4+4	5.24E-30	0.00		
	NiHS+	1.39E-38	0.00		
	Ni(HS)2	0.00E+00	0.00		
		<hr/>	<hr/>		
		1.00E-09	100		
Se(IV) decoupled	SeO3-2	9.11E-14	91.07	Argh9_Se_ox.out	NAPSI_300401_SE_IV_DAV.DAT
	HSeO3-	8.93E-15	8.93		only Se(IV) considered
	H2SeO3	4.12E-21	0.00		
		<hr/>	<hr/>		
		1.00E-13	100		
Zr(IV)	Zr(OH)5-	9.99E-10	99.85	Argh9_Zr.out	NAPSI_300401DAV.DAT
	Zr(OH)4	1.48E-12	0.15		
	ZrOH+3	2.58E-28	0.00		
	ZrSO4+2	1.31E-33	0.00		
	Zr+4	1.18E-36	0.00		
	ZrCl+3	1.02E-36	0.00		
		<hr/>	<hr/>		
		1.00E-09	100		
Nb(V)	NbO3-	9.85E-10	98.45	Argh9_Nb.out	NAPSI_300401DAV.DAT
	Nb(OH)5	1.55E-11	1.55		
	Nb(OH)4+	7.65E-21	0.00		
		<hr/>	<hr/>		
		1.00E-09	100		

Mo(VI)	MoO4-2	1.00E-10	100.00	Argh9_Mo.out	NAPSI_300401DAV.DAT
		1.00E-10	100		
Tc(IV) decoupled	TcO(OH)2	9.80E-10	97.98	Argh9_Tc_IV.out	NAPSI_300401_TC_DAV.DAT only Tc(IV) considered
	TcO(OH)3-	1.67E-11	1.67		
	TcCO3(OH)3-	3.08E-12	0.31		
	TcCO3(OH)2	4.55E-13	0.05		
	TcO(OH)+	4.29E-16	0.00		
	TcO+2	3.52E-23	0.00		
		1.00E-09	100		
Pd(II)	Pd(OH)2	9.95E-10	99.53	Argh9_Pd.out	NAPSI_300401DAV.DAT
	Pd(OH)3-	4.25E-12	0.43		
	PdCl2(OH)2-2	2.14E-13	0.02		
	PdCl3OH-2	1.69E-13	0.02		
	PdCl4-2	6.73E-14	0.01		
	PdCl3-	1.68E-14	0.00		
	PdCl2	1.25E-16	0.00		
	PdCl+	4.35E-19	0.00		
	Pd+2	3.58E-23	0.00		
		1.00E-09	100		
Cd(II)	CdCl+	4.74E-10	47.42	Argh9_Cd.out	NAPSI_300401DAV.DAT Cd: Inputfile (Mineql)
	CdCl2	3.58E-10	35.75		
	CdCl3-	7.64E-11	7.64		
	Cd+2	5.14E-11	5.14		
	CdSO4	2.02E-11	2.02		
	CdCl4-2	9.67E-12	0.97		
	CdCO3	6.72E-12	0.67		
	Cd(SO4)2-2	2.09E-12	0.21		
	CdOH+	1.57E-12	0.16		
	Cd(SO4)3-4	1.22E-13	0.01		
	Cd(OH)2	7.16E-14	0.01		
	Cd(OH)3-	3.06E-16	0.00		
	Cd2OH+3	1.42E-21	0.00		
	Cd(OH)4-2	2.45E-22	0.00		
	CdSO3	7.15E-26	0.00		
	Cd4(OH)4+4	1.05E-38	0.00		
	CdS2O3	0.00E+00	0.00		
		1.00E-09	100		
	Sn(IV) decoupled	Tn(OH)5-	8.51E-10		
Tn(OH)6-2		8.57E-11	8.57		
Tn(OH)4		6.30E-11	6.30		
	1.00E-09	100			

Bi(III) decoupled	Bi(OH) ₃	1.00E-09	99.97	Argh9_Bi.out	NAPSI_300401DAV.DAT Bi: Inputfile (Baes & Mesmer 1976)
	Bi(OH) ₄ ⁻	1.55E-13	0.02		
	Bi(OH) ₂ ⁺	1.00E-13	0.01		
	BiOH ₂	2.12E-19	0.00		
	Bi ⁺³	1.27E-26	0.00		
		<hr/>	<hr/>		
		1.00E-09	100		
Sb(III) decoupled	Sb(OH) ₃	9.98E-14	99.80	Argh9_Sb_red.out	NAPSI_300401DAV.DAT Sb: Inputfile (Mineql) only Sb(III) considered
	Sb(OH) ₄ ⁻	2.04E-16	0.20		
	Sb(OH) ₂ ⁺	3.64E-21	0.00		
		<hr/>	<hr/>		
		1.00E-13	100		
Eu(III)	EuSiO(OH) ₃ ⁺²	3.44E-10	34.43	Argh9_Eu.out	NAPSI_300401DAV.DAT
	Eu(SiO(OH) ₃) ₂ ⁺	2.89E-10	28.92		
	EuCO ₃ ⁺	1.81E-10	18.06		
	Eu(OH) ₃	8.76E-11	8.76		
	Eu(OH) ₂ ⁺	4.83E-11	4.83		
	Eu(CO ₃) ₂ ⁻	4.15E-11	4.15		
	EuOH ₂	3.62E-12	0.36		
	EuSO ₄ ⁺	2.66E-12	0.27		
	Eu ⁺³	7.68E-13	0.08		
	Eu(SO ₄) ₂ ⁻	7.16E-13	0.07		
	EuCl ₂ ⁺	4.98E-13	0.05		
	EuCl ₂ ⁺	1.21E-13	0.01		
	Eu(OH) ₄ ⁻	3.74E-14	0.00		
			<hr/>		
		1.00E-09	100		
Pb(II)	PbCO ₃	6.93E-10	69.33	Argh9_Pb.out	NAPSI_300401DAV.DAT Pb: Inputfile (Mineql)
	Pb(CO ₃) ₂ ⁻²	1.25E-10	12.50		
	PbOH ⁺	8.13E-11	8.13		
	PbCl ⁺	3.98E-11	3.98		
	Pb(OH) ₂	2.34E-11	2.34		
	PbCl ₂	1.17E-11	1.17		
	Pb ⁺²	1.06E-11	1.06		
	PbSO ₄	8.12E-12	0.81		
	PbCl ₃ ⁻	3.14E-12	0.31		
	Pb(SO ₄) ₂ ⁻²	2.42E-12	0.24		
	PbCl ₄ ⁻²	9.97E-13	0.10		
	Pb(OH) ₃ ⁻	3.16E-13	0.03		
	Pb ₂ (OH) ₃ ⁺	6.02E-20	0.00		
	Pb ₃ (OH) ₄ ⁺²	1.15E-22	0.00		
	Pb ₄ (OH) ₄ ⁺⁴	1.50E-29	0.00		
	PbS ₂ O ₃	0.00E+00	0.00		
	Pb(S ₂ O ₃) ₂ ⁻²	0.00E+00	0.00		
			<hr/>		
		1.00E-09	100		

Th (IV)	ThCO ₃ (OH) ₃ -	9.85E-10	98.45	Argh9_Th.out	NAPSI_300401DAV.DAT
	Th(OH) ₄	1.55E-11	1.55		
	Th(CO ₃) ₅₋₆	1.33E-17	0.00		
	ThOH+ ₃	2.71E-21	0.00		
	Th(SO ₄) ₂	3.73E-22	0.00		
	Th(SO ₄) ₃₋₂	3.95E-23	0.00		
	ThSO ₄ + ₂	2.74E-23	0.00		
	Th+ ₄	6.19E-27	0.00		
	<hr/>	1.00E-09	100.00		
Pa(V) decoupled	PaO ₂ OH	1.00E-09	100.00	Argh9_Pa.out	NAPSI_300401DAV.DAT Pa: Inputfile (Mineql) only Pa(V) considered
	PaO ₂ + ₂	4.38E-14	0.00		
	PaOOH+ ₂	3.55E-22	0.00		
	<hr/>	1.00E-09	100		
U(IV) decoupled	U(OH) ₄	7.59E-10	75.85	Argh9_U_IV_est.out	NAPSI_300401_U_IV_DAV.DAT U: Inputfile (TM-44-01-04) only U(IV) considered
	UCO ₃ (OH) ₃ -	2.42E-10	24.15		
	U(CO ₃) ₄₋₄	5.58E-18	0.00		
	U(CO ₃) ₅₋₆	5.15E-21	0.00		
	UOH+ ₃	3.82E-27	0.00		
	U(SO ₄) ₂	5.91E-31	0.00		
	USO ₄ + ₂	5.09E-32	0.00		
	UCl+ ₃	1.74E-34	0.00		
U+ ₄	1.21E-34	0.00			
	<hr/>	1.00E-09	100		
U(V) decoupled	UO ₂ + ₂	9.99E-10	99.94	Argh9_U_V.out	NAPSI_300401_U_V_DAV.DAT only U(V) considered
	UO ₂ (CO ₃) ₃₋₅	5.79E-13	0.06		
	<hr/>	1.00E-09	100		
U(VI) decoupled	UO ₂ (CO ₃) ₃₋₄	9.62E-10	96.206	Argh9_U_VI_Kal_Cho.out	NAPSI_300401_U_VI_DAV.DAT Ca ₂ UO ₂ (CO ₃) ₃ : Inputfile, Kalmykow & Choppin (2000) only U(VI) considered
	UO ₂ (CO ₃) ₂₋₂	2.13E-11	2.126		
	UO ₂ (OH) ₃ -	1.10E-11	1.096		
	Ca ₂ UO ₂ (CO ₃) ₃	5.52E-12	0.552		
	UO ₂ (OH) ₂	1.29E-13	0.013		
	UO ₂ CO ₃	1.42E-14	0.001		
	UO ₂ OH+ ₂	1.12E-15	0.000		
	UO ₂ (OH) ₄₋₂	4.39E-16	0.000		
	(UO ₂) ₂ CO ₃ (OH) ₃ -	7.26E-17	0.000		
	UO ₂ SO ₄	8.91E-19	0.000		
	UO ₂ + ₂	4.62E-19	0.000		
	UO ₂ (SO ₄) ₂₋₂	1.46E-19	0.000		
	UO ₂ Cl+ ₂	6.61E-20	0.000		
	UO ₂ Cl ₂	6.42E-22	0.000		
	(UO ₂) ₃ (OH) ₇ -	2.87E-25	0.000		
	(UO ₂) ₂ (OH) ₂ + ₂	1.43E-25	0.000		
(UO ₂) ₃ (CO ₃) ₆₋₆	2.70E-26	0.000			

	(UO ₂) ₃ (OH) ₅ ⁺	8.29E-28	0.000		
	(UO ₂) ₂ OH ₃	5.76E-31	0.000		
	(UO ₂) ₃ (OH) ₄ ⁺ ₂	9.61E-33	0.000		
	(UO ₂) ₃ O(OH) ₂ HCO ₃ ⁺	3.17E-34	0.000		
	(UO ₂) ₄ (OH) ₇ ⁺	4.76E-35	0.000		
		<hr/>	<hr/>		
		1.00E-09	100		
Np(III) decoupled	NpSiO(OH) ₃ ⁺ ₂	6.28E-10	62.76	Argh9_Np_III_est.out	NAPSI_300401_NP_III_DAV.DAT
	Np(OH) ₂ ⁺	1.40E-10	13.97		Np: Inputfile (TM-44-01-04)
	NpCO ₃ ⁺	1.04E-10	10.41		only Np(III) considered
	Np(CO ₃) ₂ ⁻	7.57E-11	7.56		
	NpOH ₂	2.88E-11	2.88		
	Np(CO ₃) ₃ ⁻³	1.70E-11	1.70		
	Np(OH) ₃	3.19E-12	0.32		
	NpSO ₄ ⁺	2.73E-12	0.27		
	Np ⁺³	8.83E-13	0.09		
	Np(SO ₄) ₂ ⁻	4.13E-13	0.04		
		<hr/>	<hr/>		
		1.00E-09	100		
Np(IV) decoupled	Np(OH) ₄	9.80E-10	98.03	Argh9_Np_IV_est.out	NAPSI_300401_NP_IV_DAV.DAT
	NpCO ₃ (OH) ₃ ⁻	1.97E-11	1.97		Np: Inputfile (TM-44-01-04)
	Np(CO ₃) ₄ ⁻⁴	1.34E-15	0.00		only Np(IV) considered
	Np(CO ₃) ₅ ⁻⁶	1.39E-18	0.00		
	NpOH ₃	5.54E-26	0.00		
	Np(SO ₄) ₂	1.67E-29	0.00		
	NpSO ₄ ⁺²	7.73E-31	0.00		
	Np ⁺⁴	9.84E-34	0.00		
	NpCl ₃	8.57E-34	0.00		
		<hr/>	<hr/>		
		1.00E-09	100		
Np(V) decoupled	NpO ₂ CO ₃ ⁻	6.69E-10	66.85	Argh9_Np_V.out	NAPSI_300401_NP_V_DAV.DAT
	NpO ₂ ⁺	3.19E-10	31.90		only Np(V) considered
	NpO ₂ (CO ₃) ₂ ⁻³	7.02E-12	0.70		
	NpO ₂ SO ₄ ⁻	4.20E-12	0.42		
	NpO ₂ (OH)	1.15E-12	0.12		
	NpO ₂ (CO ₃) ₂ OH ₄	9.20E-14	0.01		
	NpO ₂ (CO ₃) ₃ ⁻⁵	2.27E-15	0.00		
	NpO ₂ (OH) ₂ ⁻	7.81E-16	0.00		
		<hr/>	<hr/>		
		1.00E-09	100		
Np(VI) decoupled	NpO ₂ (OH) ₃ ⁻	5.58E-10	55.80	Argh9_Np_VI.out	NAPSI_300401_NP_VI_DAV.DAT
	NpO ₂ (CO ₃) ₂ ⁻²	2.60E-10	25.97		only Np(VI) considered
	NpO ₂ (CO ₃) ₃ ⁻⁴	1.82E-10	18.21		
	NpO ₂ CO ₃	2.03E-13	0.02		
	NpO ₂ OH ⁺	4.55E-14	0.00		
	NpO ₂ (OH) ₄ ⁻²	1.41E-14	0.00		
	(NpO ₂) ₂ CO ₃ (OH) ₃ ⁻	7.33E-16	0.00		
	NpO ₂ SO ₄	3.86E-17	0.00		

	NpO ₂ (SO ₄) ₂₋₂	1.70E-17	0.00		
	NpO ₂ + ₂	1.49E-17	0.00		
	NpO ₂ Cl ⁺	3.60E-18	0.00		
	(NpO ₂) ₂ (OH) ₂₊₂	3.30E-23	0.00		
	(NpO ₂) ₃ (OH) ₅₊	7.41E-25	0.00		
	(NpO ₂) ₃ (CO ₃) ₆₋₆	6.20E-26	0.00		
		<hr/>	<hr/>		
		1.00E-09	100		
Pu(III) decoupled	PuSiO(OH) ₃₊₂	6.50E-12	64.98	Argh9_Pu_red_est.out	NAPSI_300401_PU_III_DAV.DAT
	Pu(OH) ₂₊	1.15E-12	11.49		Pu: Inputfile (TM-44-01-04)
	PuCO ₃ ⁺	1.08E-12	10.78		only Pu(III) considered
	Pu(CO ₃) ₂₋	7.83E-13	7.83		
	PuOH ₂	2.37E-13	2.37		
	Pu(CO ₃) ₃₋₃	1.76E-13	1.76		
	PuSO ₄ ⁺	2.83E-14	0.28		
	Pu(OH) ₃	2.62E-14	0.26		
	Pu ⁺³	9.14E-15	0.09		
	Pu(SO ₄) ₂₋	8.53E-15	0.09		
	PuCl ₂	7.47E-15	0.07		
		<hr/>	<hr/>		
		1.00E-11	100		
Pu(IV) decoupled	PuCO ₃ (OH) ₃₋	8.89E-12	88.89	Argh9_Pu_IV_est.out	NAPSI_300401_PU_IV_DAV.DAT
	Pu(OH) ₄	1.11E-12	11.11		Pu: Inputfile (TM-44-01-04)
	Pu(CO ₃) ₄₋₄	9.83E-21	0.00		only Pu(IV) considered
	Pu(CO ₃) ₅₋₆	4.76E-24	0.00		
	PuOH ₃	8.10E-31	0.00		
	Pu(SO ₄) ₂	9.28E-34	0.00		
	PuSO ₄ + ₂	3.82E-35	0.00		
	PuCl ₃	7.72E-38	0.00		
	Pu ⁺⁴	4.44E-38	0.00		
		<hr/>	<hr/>		
		1.00E-11	100		
Pu(V) decoupled	PuO ₂ CO ₃₋	7.28E-12	72.75	Argh9_Pu_V.out	NAPSI_300401_PU_V_DAV.DAT
	PuO ₂ ⁺	2.40E-12	24.02		only Pu(V) considered
	PuO ₂ OH	3.23E-13	3.23		
	PuO ₂ (CO ₃) ₃₋₅	5.41E-18	0.00		
		<hr/>	<hr/>		
		1.00E-11	100.00		
Pu(VI) decoupled	PuO ₂ (CO ₃) ₃₋₄	5.20E-12	51.98	Argh9_Pu_VI.out	NAPSI_300401_PU_VI_DAV.DAT
	PuO ₂ (CO ₃) ₂₋₂	4.17E-12	41.70		only Pu(VI) considered
	PuO ₂ (OH) ₂	3.48E-13	3.48		
	PuO ₂ CO ₃	2.59E-13	2.59		
	PuO ₂ OH ⁺	2.42E-14	0.24		
	PuO ₂ SO ₄	6.49E-17	0.00		
	PuO ₂ + ₂	1.98E-17	0.00		
	PuO ₂ (SO ₄) ₂₋₂	1.14E-17	0.00		
	PuO ₂ Cl ⁺	9.60E-18	0.00		
	PuO ₂ Cl ₂	8.71E-20	0.00		

	(PuO ₂) ₂ (OH) ₂ + ₂	3.46E-24	0.00		
		1.00E-11	100		
Am(III)	AmSiO(OH) ₃ + ₂	7.11E-10	71.09	Argh9_Am.out	NAPSI_300401DAV.DAT
	AmCO ₃ +	1.18E-10	11.79		
	Am(CO ₃) ₂ -	8.57E-11	8.57		
	Am(OH) ₂ +	5.00E-11	5.00		
	Am(CO ₃) ₃ - ₃	1.92E-11	1.92		
	AmOH+ ₂	1.03E-11	1.03		
	AmSO ₄ +	2.75E-12	0.28		
	Am(OH) ₃	1.14E-12	0.11		
	Am+ ₃	1.00E-12	0.10		
	AmCl+ ₂	5.79E-13	0.06		
	Am(SO ₄) ₂ -	4.68E-13	0.05		
		1.00E-09	100		

Tab. A4.5: Argillaceous Rock Systems, pH = 9, low I,
Water Composition (mol/kg H₂O)

Na	1.230E-01
Ca	4.853E-04
C	7.972E-04
Cl	1.066E-01
S	8.200E-03
Si	2.140E-04
temp	25°C
pH	9.0
I	0.13
log pCO ₂	-4.48

Tab. A4.6: Argillaceous Rock Systems, pH = 9, low I,
Radionuclide Speciation (mol/kg H₂O)

Element	Species	Concentration [m]	Distribution [%]	Output File	Data File
Be(II)	Be(OH)2	6.57E-10	65.69	Argl9_Be.out	NAPSI_300401DAV.DAT Be: Inputfile (Minteq.v4)
	Be(OH)3-	2.10E-10	21.01		
	BeOH+	1.32E-10	13.18		
	BeCO3	1.08E-12	0.11		
	Be+2	7.50E-14	0.01		
	BeSO4	9.38E-15	0.00		
	BeCl+	4.41E-15	0.00		
	Be(OH)4-2	2.72E-15	0.00		
	Be(SO4)2-2	3.01E-16	0.00		
	Be2OH+3	3.84E-21	0.00		
	Be3(OH)3+3	2.32E-22	0.00		
		1.00E-09	100		
Co(II)	Co+2	7.15E-10	71.45	Argl9_CoNi.out	NAPSI_300401DAV.DAT Co: Inputfile (Mineql)
	CoSO4	1.32E-10	13.22		
	CoOH+	6.42E-11	6.42		
	CoCO3	5.74E-11	5.74		
	CoCl+	2.35E-11	2.35		
	Co(OH)2	6.17E-12	0.62		
	CoHCO3+	1.60E-12	0.16		
	Co(CO3)2-2	3.84E-13	0.04		
	Co(OH)3-	1.60E-15	0.00		
	Co(OH)4-2	1.11E-19	0.00		
	Co2OH+3	3.32E-21	0.00		
	Co4(OH)4+4	1.02E-31	0.00		
	CoS2O3	0.00E+00	0.00		
			1.00E-09		
Ni(II)	Ni+2	5.38E-10	53.83	Argl9_Ni.out	NAPSI_300401DAV.DAT
	Ni(OH)2	1.85E-10	18.51		
	NiSO4	8.87E-11	8.87		
	NiOH+	7.66E-11	7.66		
	NiCl+	5.00E-11	5.00		
	NiCO3	4.33E-11	4.33		
	NiCl2	1.14E-11	1.14		
	Ni(SO4)2-2	4.63E-12	0.46		
	NiHCO3+	1.20E-12	0.12		
	Ni(OH)3-	4.80E-13	0.05		
	Ni(CO3)2-2	2.89E-13	0.03		
	Ni(OH)4-2	6.67E-19	0.00		
	Ni2OH+3	5.96E-20	0.00		
	Ni4(OH)4+4	1.04E-29	0.00		

	NiHS+	8.92E-39	0.00		
	Ni(HS)2	0.00E+00	0.00		
		1.00E-09	100		
Se(IV)	SeO3-2	8.98E-14	89.81	Argl9_Se_ox.out	NAPSI_300401_SE_IV_DAV.DAT
	HSeO3-	1.02E-14	10.19		only Se(IV) considered
	H2SeO3	4.94E-21	0.00		
		1.00E-13	100		
Zr(IV)	Zr(OH)5-	9.99E-10	99.85	Argl9_Zr.out	NAPSI_300401DAV.DAT
	Zr(OH)4	1.54E-12	0.15		
	ZrOH+3	1.68E-28	0.00		
	ZrSO4+2	5.25E-34	0.00		
	Zr+4	5.41E-37	0.00		
	ZrCl+3	2.19E-37	0.00		
		1.00E-09	100		
Nb(V)	NbO3-	9.84E-10	98.35	Argl9_Nb.out	NAPSI_300401DAV.DAT
	Nb(OH)5	1.65E-11	1.65		
	Nb(OH)4+	7.71E-21	0.00		
		1.00E-09	100		
Mo(VI)	MoO4-2	1.00E-09	100.00	Argl9_Mo.out	NAPSI_300401DAV.DAT
		1.00E-09	100		
Tc(IV) decoupled	TcO(OH)2	9.81E-10	98.06	Argl9_Tc_IV.out	NAPSI_300401_TC_DAV.DAT
	TcO(OH)3-	1.60E-11	1.60		only Tc(IV) considered
	TcCO3(OH)3-	2.96E-12	0.30		
	TcCO3(OH)2	4.55E-13	0.05		
	TcO(OH)+	4.06E-16	0.00		
	TcO+2	2.85E-23	0.00		
		1.00E-09	100		
Pd(II)	Pd(OH)2	9.96E-10	99.59	Argl9_Pd.out	NAPSI_300401DAV.DAT
	Pd(OH)3-	4.09E-12	0.41		
	PdCl2(OH)2-2	1.92E-14	0.00		
	PdCl3OH-2	4.99E-15	0.00		
	PdCl4-2	6.50E-16	0.00		
	PdCl3-	5.69E-16	0.00		
	PdCl2	1.34E-17	0.00		
	PdCl+	1.35E-19	0.00		
	Pd+2	2.90E-23	0.00		
		1.00E-09	100		
Cd(II)	CdCl+	5.92E-10	59.24	Argl9_Cd.out	NAPSI_300401DAV.DAT
	Cd+2	1.68E-10	16.78		Cd: Inputfile (Mineql)
	CdCl2	1.55E-10	15.50		

	CdSO4	3.91E-11	3.91		
	CdCO3	2.69E-11	2.69		
	CdCl3-	1.04E-11	1.04		
	CdOH+	6.00E-12	0.60		
	Cd(SO4)2-2	1.62E-12	0.16		
	CdCl4-2	3.77E-13	0.04		
	Cd(OH)2	2.89E-13	0.03		
	Cd(SO4)3-4	2.55E-14	0.00		
	Cd(OH)3-	1.19E-15	0.00		
	Cd2OH+3	1.46E-20	0.00		
	Cd(OH)4-2	8.28E-22	0.00		
	CdSO3	1.37E-25	0.00		
	Cd4(OH)4+4	1.24E-36	0.00		
	CdS2O3	0.00E+00	0.00		
		1.00E-09	100		
Sn(IV) decoupled	Tn(OH)5-	8.59E-10	85.85	Argl9_Tn.out	NAPSI_300401TNDV.DAT
	Tn(OH)6-2	7.53E-11	7.53		only Sn(IV)=Tn considered
	Tn(OH)4	6.62E-11	6.62		
		1.00E-09	100		
Bi(III) decoupled	Bi(OH)3	1.00E-09	99.98	Argl9_Bi.out	NAPSI_300401DAV.DAT
	Bi(OH)4-	1.49E-13	0.01		Bi: Inputfile (Baes &
	Bi(OH)2+	9.48E-14	0.01		Mesmer 1976)
	BiOH+2	1.71E-19	0.00		
	Bi+3	7.95E-27	0.00		
		1.00E-09	100		
Sb(III) decoupled	Sb(OH)3	9.98E-13	99.81	Argl9_Sb_red.out	NAPSI_300401DAV.DAT
	Sb(OH)4-	1.96E-15	0.20		Sb: Inputfile (Mineql)
	Sb(OH)2+	3.44E-20	0.00		only Sb(III) considered
		1.00E-12	100		
Eu(III)	EuSiO(OH)3+2	3.10E-10	31.02	Argl9_Eu.out	NAPSI_300401DAV.DAT
	Eu(SiO(OH)3)2+	3.07E-10	30.70		
	EuCO3+	1.87E-10	18.68		
	Eu(OH)3	9.68E-11	9.68		
	Eu(OH)2+	5.04E-11	5.04		
	Eu(CO3)2-	4.33E-11	4.33		
	EuOH+2	3.23E-12	0.32		
	EuSO4+	1.33E-12	0.13		
	Eu+3	5.32E-13	0.05		
	Eu(SO4)2-	1.74E-13	0.02		
	EuCl+2	1.46E-13	0.01		
	Eu(OH)4-	3.97E-14	0.00		
	EuCl2+	1.35E-14	0.00		
		1.00E-09	100		

Pb(II)	PbCO ₃	7.49E-10	74.94	Argl9_Pb.out	NAPSI_300401DAV.DAT Pb: Inputfile (Mineql)		
	Pb(CO ₃) ₂ -2	1.12E-10	11.21				
	PbOH+	8.37E-11	8.37				
	Pb(OH) ₂	2.55E-11	2.55				
	PbCl+	1.34E-11	1.34				
	Pb+ ₂	9.32E-12	0.93				
	PbSO ₄	4.23E-12	0.42				
	PbCl ₂	1.37E-12	0.14				
	Pb(SO ₄) ₂ -2	5.06E-13	0.05				
	Pb(OH) ₃ -	3.31E-13	0.03				
	PbCl ₃ -	1.16E-13	0.01				
	PbCl ₄ -2	1.05E-14	0.00				
	Pb ₂ (OH) ₃ +3	4.49E-20	0.00				
	Pb ₃ (OH) ₄ +2	1.21E-22	0.00				
	Pb ₄ (OH) ₄ +4	9.36E-30	0.00				
	PbS ₂ O ₃	0.00E+00	0.00				
	Pb(S ₂ O ₃) ₂ -2	0.00E+00	0.00				
		<hr/>	<hr/>				
		1.00E-09	100				
Th (IV)	ThCO ₃ (OH) ₃ -	9.84E-10	98.37	Argl9_Th.out	NAPSI_300401DAV.DAT		
	Th(OH) ₄	1.63E-11	1.63				
	Th(CO ₃) ₅ -6	2.42E-18	0.00				
	ThOH+ ₃	1.78E-21	0.00				
	Th(SO ₄) ₂	8.96E-23	0.00				
	ThSO ₄ + ₂	1.11E-23	0.00				
	Th(SO ₄) ₃ -2	3.80E-24	0.00				
	Th+ ₄	2.87E-27	0.00				
		<hr/>	<hr/>				
	1.00E-09	100					
Pa(V) decoupled	PaO ₂ OH	1.00E-09	100.00	Argl9_Pa.out	NAPSI_300401DAV.DAT Pa: Inputfile (Mineql) only Pa(V) considered		
	PaO ₂ + ₂	4.14E-14	0.00				
	PaOOH+ ₂	2.90E-22	0.00				
		<hr/>	<hr/>				
	1.00E-09	100					
U(IV) decoupled	U(OH) ₄	7.67E-10	76.73	Argl9_U_IV_est.out	NAPSI_300401_U_IV_DAV.DAT U: Inputfile (TM-44-01-04) only U(IV) considered		
	UCO ₃ (OH) ₃ -	2.33E-10	23.27				
	U(CO ₃) ₄ -4	2.58E-18	0.00				
	U(CO ₃) ₅ -6	9.07E-22	0.00				
	UOH+ ₃	2.43E-27	0.00				
	U(SO ₄) ₂	1.37E-31	0.00				
	USO ₄ + ₂	1.99E-32	0.00				
	U+ ₄	5.39E-35	0.00				
	UCl+ ₃	3.63E-35	0.00				
		<hr/>	<hr/>				
	1.00E-09	100					

U(V)	UO ₂ ⁺	1.00E-09	99.98	Argl9_U_V.out	NAPSI_300401_U_V_DAV.DAT
decoupled	UO ₂ (CO ₃) ₃₋₅	1.84E-13	0.02		only U(V) considered
		1.00E-09	100		
U(VI)	UO ₂ (CO ₃) ₃₋₄	9.30E-10	92.971	Argl9_U_VI_Kal_Cho.out	NAPSI_300401_U_VI_DAV.DAT
decoupled	UO ₂ (CO ₃) ₂₋₂	3.66E-11	3.658		Ca ₂ UO ₂ (CO ₃) ₃ : Inputfile,
	UO ₂ (OH) ₃₋	2.20E-11	2.202		Kalmykow & Choppin (2000)
	Ca ₂ UO ₂ (CO ₃) ₃	1.14E-11	1.144		only U(VI) considered
	UO ₂ (OH) ₂	2.69E-13	0.027		
	UO ₂ CO ₃	2.94E-14	0.003		
	UO ₂ OH ⁺	2.22E-15	0.000		
	UO ₂ (OH) ₄₋₂	7.69E-16	0.000		
	(UO ₂) ₂ CO ₃ (OH) ₃₋	3.03E-16	0.000		
	UO ₂ SO ₄	8.92E-19	0.000		
	UO ₂ + ₂	7.82E-19	0.000		
	UO ₂ (SO ₄) ₂₋₂	5.85E-20	0.000		
	UO ₂ Cl ⁺	4.27E-20	0.000		
	UO ₂ Cl ₂	1.44E-22	0.000		
	(UO ₂) ₃ (OH) ₇₋	2.52E-24	0.000		
	(UO ₂) ₂ (OH) ₂₊₂	5.04E-25	0.000		
	(UO ₂) ₃ (CO ₃) ₆₋₆	4.26E-26	0.000		
	(UO ₂) ₃ (OH) ₅₊	7.17E-27	0.000		
	(UO ₂) ₂ OH+ ₃	1.58E-30	0.000		
	(UO ₂) ₃ (OH) ₄₊₂	7.12E-32	0.000		
	(UO ₂) ₃ O(OH) ₂ HCO ₃ ⁺	2.72E-33	0.000		
	(UO ₂) ₄ (OH) ₇₊	8.61E-34	0.000		
		1.00E-09	100		
Np(III)	NpSiO(OH) ₃₊₂	6.01E-10	60.09	Argl9_Np_III_est.out	NAPSI_300401_NP_III_DAV.DAT
decoupled	Np(OH) ₂₊	1.55E-10	15.48		Np: Inputfile (TM-44-01-04)
	NpCO ₃ ⁺	1.14E-10	11.44		only Np(III) considered
	Np(CO ₃) ₂₋	8.39E-11	8.38		
	NpOH+ ₂	2.73E-11	2.73		
	Np(CO ₃) ₃₋₃	1.28E-11	1.28		
	Np(OH) ₃	3.74E-12	0.37		
	NpSO ₄ ⁺	1.45E-12	0.14		
	Np+ ₃	6.51E-13	0.07		
	Np(SO ₄) ₂₋	1.07E-13	0.01		
		1.00E-09	100		
Np(IV)	Np(OH) ₄	9.81E-10	98.12	Argl9_Np_IV_est.out	NAPSI_300401_NP_IV_DAV.DAT
decoupled	NpCO ₃ (OH) ₃₋	1.88E-11	1.88		Np: Inputfile (TM-44-01-04)
	Np(CO ₃) ₄₋₄	6.15E-16	0.00		only Np(IV) considered
	Np(CO ₃) ₅₋₆	2.42E-19	0.00		
	NpOH+ ₃	3.48E-26	0.00		
	Np(SO ₄) ₂	3.83E-30	0.00		
	NpSO ₄ + ₂	2.99E-31	0.00		

	Np+4	4.35E-34	0.00		
	NpCl+3	1.76E-34	0.00		
		1.00E-09	100		
Np(V) decoupled	NpO2CO3-	6.73E-10	67.34	Argl9_Np_V.out	NAPSI_300401_NP_V_DAV.DAT
	NpO2+	3.19E-10	31.85		only Np(V) considered
	NpO2(CO3)2-3	4.82E-12	0.48		
	NpO2SO4-	2.04E-12	0.20		
	NpO2(OH)	1.22E-12	0.12		
	NpO2(CO3)2OH-4	4.54E-14	0.00		
	NpO2(OH)2-	7.94E-16	0.00		
	NpO2(CO3)3-5	7.22E-16	0.00		
		1.00E-09	100		
Np(VI) decoupled	NpO2(OH)3-	6.43E-10	64.27	Argl9_Np_VI.out	NAPSI_300401_NP_VI_DAV.DAT
	NpO2(CO3)2-2	2.56E-10	25.62		only Np(VI) considered
	NpO2(CO3)3-4	1.01E-10	10.08		
	NpO2CO3	2.42E-13	0.02		
	NpO2OH+	5.15E-14	0.01		
	NpO2(OH)4-2	1.42E-14	0.00		
	(NpO2)2CO3(OH)3-	1.00E-15	0.00		
	NpO2SO4	2.22E-17	0.00		
	NpO2+2	1.44E-17	0.00		
	NpO2(SO4)2-2	3.91E-18	0.00		
	NpO2Cl+	1.34E-18	0.00		
	(NpO2)2(OH)2+2	3.83E-23	0.00		
	(NpO2)3(OH)5+	1.21E-24	0.00		
	(NpO2)3(CO3)6-6	1.84E-26	0.00		
		1.00E-09	100		
Pu(III) decoupled	PuSiO(OH)3+2	6.25E-12	62.45	Argl9_Pu_red_est.out	NAPSI_300401_PU_III_DAV.DAT
	Pu(OH)2+	1.28E-12	12.78		Pu: Inputfile (TM-44-01-04)
	PuCO3+	1.19E-12	11.89		only Pu(III) considered
	Pu(CO3)2-	8.72E-13	8.72		
	PuOH+2	2.26E-13	2.26		
	Pu(CO3)3-3	1.34E-13	1.34		
	Pu(OH)3	3.09E-14	0.31		
	PuSO4+	1.50E-14	0.15		
	Pu+3	6.76E-15	0.07		
	PuCl+2	2.33E-15	0.02		
	Pu(SO4)2-	2.21E-15	0.02		
		1.00E-11	100		
Pu(IV) decoupled	PuCO3(OH)3-	8.84E-12	88.40	Argl9_Pu_IV_est.out	NAPSI_300401_PU_IV_DAV.DAT
	Pu(OH)4	1.16E-12	11.60		Pu: Inputfile (TM-44-01-04)
	Pu(CO3)4-4	4.70E-21	0.00		only Pu(IV) considered
	Pu(CO3)5-6	8.65E-25	0.00		

	PuOH+3	5.31E-31	0.00		
	Pu(SO4)2	2.22E-34	0.00		
	PuSO4+2	1.54E-35	0.00		
	Pu+4	2.05E-38	0.00		
	PuCl+3	1.66E-38	0.00		
		<hr/>	<hr/>		
		1.00E-11	100		
Pu(V) decoupled	PuO2CO3-	7.28E-12	72.79	Argl9_Pu_V.out	NAPSI_300401_PU_V_DAV.DAT
	PuO2+	2.38E-12	23.82		only Pu(V) considered
	PuO2OH	3.39E-13	3.39		
	PuO2(CO3)3-5	1.71E-18	0.00		
		<hr/>	<hr/>		
		1.00E-11	100.00		
Pu(VI) decoupled	PuO2(CO3)2-2	5.31E-12	53.11	Argl9_Pu_VI.out	NAPSI_300401_PU_VI_DAV.DAT
	PuO2(CO3)3-4	3.72E-12	37.17		only Pu(VI) considered
	PuO2(OH)2	5.39E-13	5.39		
	PuO2CO3	3.98E-13	3.98		
	PuO2OH+	3.53E-14	0.35		
	PuO2SO4	4.81E-17	0.00		
	PuO2+2	2.48E-17	0.00		
	PuO2Cl+	4.60E-18	0.00		
	PuO2(SO4)2-2	3.38E-18	0.00		
	PuO2Cl2	1.45E-20	0.00		
	(PuO2)2(OH)2+2	6.70E-24	0.00		
		<hr/>	<hr/>		
		1.00E-11	100		
Am(III)	AmSiO(OH)3+2	6.88E-10	68.83	Argl9_Am.out	NAPSI_300401DAV.DAT
	AmCO3+	1.31E-10	13.10		
	Am(CO3)2-	9.61E-11	9.61		
	Am(OH)2+	5.61E-11	5.61		
	Am(CO3)3-3	1.47E-11	1.47		
	AmOH+2	9.90E-12	0.99		
	AmSO4+	1.48E-12	0.15		
	Am(OH)3	1.36E-12	0.14		
	Am+3	7.45E-13	0.07		
	AmCl+2	1.82E-13	0.02		
	Am(SO4)2-	1.22E-13	0.01		
		<hr/>	<hr/>		
		1.00E-09	100		

Tab. A4.7: Argillaceous Rock Systems, pH = 6, high I,
Water Composition (mol/kg H₂O)

Na	3.586E-01
Ca	1.610E-02
C	7.885E-02
Cl	3.108E-01
S	2.391E-02
Si	1.748E-04
temp	25°C
pH	6.0
I	0.4
log pCO ₂	0.14

Tab. A4.8: Argillaceous Rock Systems, pH = 6, high I,
Radionuclide Speciation (mol/kg H₂O)

Element	Species	Concentration [m]	Distribution [%]	Output File	Data File
Be(II)	BeOH+	4.54E-10	45.41	Argh6_Be.out	NAPSI_300401DAV.DAT Be: Inputfile (Minteq.v4)
	Be+2	2.94E-10	29.34		
	BeCO ₃	1.45E-10	14.45		
	BeSO ₄	5.22E-11	5.22		
	BeCl+	4.35E-11	4.34		
	Be(SO ₄) ₂₋₂	1.04E-11	1.04		
	Be(OH) ₂	2.08E-12	0.21		
	Be(OH) ₃₋	7.11E-16	0.00		
	Be ₂ OH+ ₃	7.89E-17	0.00		
	Be ₃ (OH) ₃₊₃	1.51E-20	0.00		
	Be(OH) ₄₋₂	1.15E-23	0.00		
		1.00E-09	100		
Co(II)	Co+2	7.02E-12	70.19	Argh6_CoNi.out	NAPSI_300401DAV.DAT Co: Inputfile (Mineql)
	CoSO ₄	1.85E-12	18.46		
	CoHCO ₃ ⁺	5.61E-13	5.61		
	CoCl+	5.55E-13	5.55		
	CoCO ₃	1.92E-14	0.19		
	CoOH+	5.40E-16	0.01		
	Co(CO ₃) ₂₋₂	6.47E-18	0.00		
	Co(OH) ₂	4.90E-20	0.00		
	CoS ₂ O ₃	3.58E-21	0.00		
	Co(OH) ₃₋	1.32E-26	0.00		
	Co ₂ OH+ ₃	3.34E-28	0.00		
	Co(OH) ₄₋₂	1.06E-33	0.00		
	Co ₄ (OH) ₄₊₄	0.00E+00	0.00		
			1.00E-11		

Ni(II)	Ni+2	5.79E-10	57.91	Argh6_Ni.out	NAPSI_300401DAV.DAT
	NiSO4	1.36E-10	13.57		
	NiCl+	1.29E-10	12.90		
	NiCl2	7.77E-11	7.77		
	NiHCO3+	4.63E-11	4.63		
	Ni(SO4)2-2	1.49E-11	1.49		
	NiHS+	1.49E-11	1.49		
	NiCO3	1.59E-12	0.16		
	Ni(HS)2	8.98E-13	0.09		
	NiOH+	7.06E-14	0.01		
	Ni(CO3)2-2	5.34E-16	0.00		
	Ni(OH)2	1.61E-16	0.00		
	Ni(OH)3-	4.34E-22	0.00		
	Ni2OH+3	7.18E-23	0.00		
	Ni(OH)4-2	6.92E-31	0.00		
Ni4(OH)4+4	0.00E+00	0.00			
	1.00E-09	100			
Se(IV) decoupled	HSeO3-	9.90E-11	98.94	Argh6_Se_ox.out	NAPSI_300401_SE_IV_DAV.DAT only Se(IV) considered
	SeO3-2	1.01E-12	1.01		
	H2SeO3	4.56E-14	0.05		
	1.00E-10	100			
Zr(IV)	Zr(OH)4	5.97E-13	59.64	Argh6_Zr.out	NAPSI_300401DAV.DAT
	Zr(OH)5-	4.04E-13	40.36		
	ZrOH+3	1.04E-19	0.00		
	ZrSO4+2	4.45E-22	0.00		
	Zr+4	4.76E-25	0.00		
	ZrCl+3	3.81E-25	0.00		
	1.00E-12	100			
Nb(V)	Nb(OH)5	9.40E-10	94.02	Argh6_Nb.out	NAPSI_300401DAV.DAT
	NbO3-	5.99E-11	5.98		
	Nb(OH)4+	4.65E-16	0.00		
	1.00E-09	100			
Mo(VI)	MoO4-2	1.00E-10	100.00	Argh6_Mo.out	NAPSI_300401DAV.DAT
		1.00E-10	100		
Tc(IV) decoupled	TcCO3(OH)2	9.45E-10	94.49	Argh6_Tc_IV.out	NAPSI_300401_TC_DAV.DAT only Tc(IV) considered
	TcO(OH)2	4.87E-11	4.87		
	TcCO3(OH)3-	6.40E-12	0.64		
	TcO(OH)+	2.14E-14	0.00		
	TcO(OH)3-	8.28E-16	0.00		
	TcO+2	1.75E-18	0.00		
	1.00E-09	100			

Pd(II)	PdCl4-2	7.71E-10	77.03	Argh6_Pd.out	NAPSI_300401DAV.DAT
	PdCl3-	2.10E-10	20.98		
	Pd(OH)2	1.61E-11	1.60		
	PdCl3OH-2	2.11E-12	0.21		
	PdCl2	1.70E-12	0.17		
	PdCl+	6.45E-15	0.00		
	PdCl2(OH)2-2	2.90E-15	0.00		
	Pd(OH)3-	6.85E-17	0.00		
	Pd+2	5.78E-19	0.00		
		1.00E-09	100		
Cd(II)	CdCl+	4.99E-12	49.88	Argh6_Cd.out	NAPSI_300401DAV.DAT Cd: Inputfile (Mineql)
	CdCl2	3.45E-12	34.51		
	CdCl3-	6.77E-13	6.77		
	Cd+2	5.89E-13	5.89		
	CdSO4	1.95E-13	1.95		
	CdCl4-2	7.86E-14	0.79		
	Cd(SO4)2-2	1.70E-14	0.17		
	CdCO3	3.22E-15	0.03		
	Cd(SO4)3-4	8.29E-16	0.01		
	CdOH+	1.80E-17	0.00		
	CdS2O3	2.39E-20	0.00		
	Cd(OH)2	8.21E-22	0.00		
	CdSO3	6.90E-22	0.00		
	Cd(OH)3-	3.50E-27	0.00		
	Cd2OH+3	1.87E-28	0.00		
	Cd(OH)4-2	2.80E-36	0.00		
	Cd4(OH)4+4	0.00E+00	0.00		
		1.00E-11	100		
Sn(IV) decoupled	Tn(OH)4	9.87E-10	98.67	Argh6_Tn.out	NAPSI_300401TNDV.DAT only Sn(IV)=Tn considered
	Tn(OH)5-	1.33E-11	1.33		
	Tn(OH)6-2	1.34E-15	0.00		
	1.00E-09	100			
Bi(III)	Bi(OH)3	9.09E-10	90.85	Argh6_Bi.out	NAPSI_300401DAV.DAT Bi: Inputfile (Baes & Mesmer 1976)
	Bi(OH)2+	9.13E-11	9.13		
	BiOH+2	1.93E-13	0.02		
	Bi(OH)4-	1.41E-16	0.00		
	Bi+3	1.15E-17	0.00		
	1.00E-09	100			
Sb(III) decoupled	Sb(OH)3	1.00E-12	100.00	Argh6_Sb.out	NAPSI_300401DAV.DAT Sb: Inputfile (Mineql) only Sb(III) considered
	Sb(OH)2+	3.65E-17	0.00		
	Sb(OH)4-	2.04E-18	0.00		
	1.00E-12	100			

Eu(III)	EuCO ₃ ⁺	6.27E-10	62.68	Argh6_Eu.out	NAPSI_300401DAV.DAT		
	EuSO ₄ ⁺	1.86E-10	18.60				
	Eu ⁺³	6.38E-11	6.38				
	Eu(SO ₄) ₂ ⁻	4.21E-11	4.21				
	EuCl ₂ ⁺	3.80E-11	3.80				
	EuSiO(OH) ₃ ⁺²	2.86E-11	2.86				
	EuCl ₂ ⁺	8.46E-12	0.85				
	Eu(CO ₃) ₂ ⁻	6.02E-12	0.60				
	EuOH ₂ ⁺	3.01E-13	0.03				
	Eu(SiO(OH) ₃) ₂ ⁺	2.40E-14	0.00				
	Eu(OH) ₂ ⁺	4.01E-15	0.00				
	Eu(OH) ₃	7.27E-18	0.00				
	Eu(OH) ₄ ⁻	3.10E-24	0.00				
		1.00E-09	100				
Pb(II)	PbCl ⁺	3.73E-13	37.30	Argh6_Pb.out	NAPSI_300401DAV.DAT Pb: Inputfile (Mineql)		
	PbCO ₃	2.96E-13	29.61				
	Pb ⁺²	1.08E-13	10.82				
	PbCl ₂	1.00E-13	10.04				
	PbSO ₄	6.98E-14	6.98				
	PbCl ₃ ⁻	2.48E-14	2.48				
	Pb(SO ₄) ₂ ⁻²	1.75E-14	1.75				
	PbCl ₄ ⁻²	7.23E-15	0.72				
	Pb(CO ₃) ₂ ⁻²	2.23E-15	0.22				
	PbOH ⁺	8.31E-16	0.08				
	PbS ₂ O ₃	8.75E-19	0.00				
	Pb(OH) ₂	2.39E-19	0.00				
	Pb(OH) ₃ ⁻	3.22E-24	0.00				
	Pb ₂ (OH) ₃ ⁺	6.29E-27	0.00				
	Pb(S ₂ O ₃) ₂ ⁻²	1.09E-27	0.00				
	Pb ₃ (OH) ₄ ⁺²	1.23E-40	0.00				
	Pb ₄ (OH) ₄ ⁺⁴	0.00E+00	0.00				
		1.00E-12	100				
	Th (IV)	ThCO ₃ (OH) ₃ ⁻	9.92E-10			99.20	Argh6_Th.out
Th(SO ₄) ₂		6.38E-12	0.64				
Th(SO ₄) ₃ ⁻²		5.68E-13	0.06				
ThSO ₄ ⁺²		5.56E-13	0.06				
Th(OH) ₄		3.74E-13	0.04				
ThOH ₃ ⁺		6.54E-14	0.01				
Th(CO ₃) ₅ ⁻⁶		4.08E-14	0.00				
Th ⁺⁴		1.50E-16	0.00				
	1.00E-09	100					
Pa(V) decoupled	PaO ₂ OH	9.58E-10	95.80	Argh6_Pa.out	NAPSI_300401DAV.DAT Pa: Inputfile (Mineql) only Pa(V) considered		
	PaO ₂ ⁺	4.20E-11	4.20				
	PaOOH ₂ ⁺	3.40E-16	0.00				
	1.00E-09	100					

U(IV)	UCO ₃ (OH) ₃ -	9.29E-10	92.87	Argh6_U_IV_est.out	NAPSI_300401_U_IV_DAV.DAT
decoupled	U(OH) ₄	6.98E-11	6.98		U: Inputfile (TM-44-01-04)
	U(CO ₃) ₄ -4	1.57E-12	0.16		only U(IV) considered
	U(CO ₃) ₅ -6	6.05E-17	0.00		
	UOH+3	3.52E-19	0.00		
	U(SO ₄) ₂	3.85E-20	0.00		
	USO ₄ +2	3.95E-21	0.00		
	UCl+3	1.48E-23	0.00		
	U+4	1.11E-23	0.00		
		<hr/>	<hr/>		
		1.00E-09	100		
U(V)	UO ₂ +	1.00E-09	100.00	Argh6_U_V.out	NAPSI_300401_U_V_DAV.DAT
decoupled	UO ₂ (CO ₃) ₃ -5	4.23E-17	0.00		only U(V) considered
		<hr/>	<hr/>		
		1.00E-09	100		
U(VI)	Ca ₂ UO ₂ (CO ₃) ₃	6.81E-10	68.10858	Argh6_U_VI_Kal_Cho.out	NAPSI_300401_U_VI_DAV.DAT
decoupled	UO ₂ (CO ₃) ₃ -4	2.08E-10	20.74348		Ca ₂ UO ₂ (CO ₃) ₃ : Inputfile,
	UO ₂ (CO ₃) ₂ -2	1.10E-10	10.96655		Kalmykow & Choppin (2000)
	UO ₂ CO ₃	1.75E-12	0.17504		only U(VI) considered
	UO ₂ OH+	3.32E-15	0.00033		
	UO ₂ SO ₄	2.22E-15	0.00022		
	UO ₂ +2	1.37E-15	0.00014		
	UO ₂ (OH) ₂	3.80E-16	0.00004		
	UO ₂ (SO ₄) ₂ -2	3.05E-16	0.00003		
	UO ₂ Cl+	1.79E-16	0.00002		
	UO ₂ (OH) ₃ -	3.24E-17	0.00000		
	UO ₂ Cl ₂	1.60E-18	0.00000		
	(UO ₂) ₂ CO ₃ (OH) ₃ -	2.65E-20	0.00000		
	(UO ₂) ₃ (CO ₃) ₆ -6	3.71E-24	0.00000		
	UO ₂ (OH) ₄ -2	1.30E-24	0.00000		
	(UO ₂) ₂ (OH) ₂ +2	1.25E-24	0.00000		
	(UO ₂) ₂ OH+3	5.03E-27	0.00000		
	(UO ₂) ₃ (OH) ₅ +	2.14E-32	0.00000		
	(UO ₂) ₃ O(OH) ₂ HCO ₃ +	3.42E-34	0.00000		
	(UO ₂) ₃ (OH) ₄ +2	2.48E-34	0.00000		
	(UO ₂) ₃ (OH) ₇ -	7.39E-36	0.00000		
	(UO ₂) ₄ (OH) ₇ +	0.00E+00	0.00000		
		<hr/>	<hr/>		
		1.00E-09	100		
Np(III)	NpCO ₃ +	5.05E-10	50.52	Argh6_Np_III_est.out	NAPSI_300401_NP_III_DAV.DAT
decoupled	NpSO ₄ +	2.67E-10	26.66		Np: Inputfile (TM-44-01-04)
	Np+3	1.03E-10	10.26		only Np(III) considered
	NpSiO(OH) ₃ +2	7.29E-11	7.28		
	Np(SO ₄) ₂ -	3.39E-11	3.39		
	Np(CO ₃) ₂ -	1.54E-11	1.53		
	NpOH+2	3.34E-12	0.33		

	Np(CO ₃) ₃₋₃	1.44E-13	0.01		
	Np(OH) ₂₊	1.62E-14	0.00		
	Np(OH) ₃	3.70E-19	0.00		
		1.00E-09	100		
Np(IV)	Np(CO ₃) ₄₋₄	6.95E-10	69.45	Argh6_Np_IV_est.out	NAPSI_300401_NP_IV_DAV.DAT
decoupled	Np(OH) ₄	1.66E-10	16.60		Np: Inputfile (TM-44-01-04)
	NpCO ₃ (OH) ₃₋	1.40E-10	13.95		only Np(IV) considered
	Np(CO ₃) ₅₋₆	3.01E-14	0.00		
	NpOH ₃	9.40E-18	0.00		
	Np(SO ₄) ₂	2.01E-18	0.00		
	NpSO ₄ ₂	1.11E-19	0.00		
	Np ₄	1.67E-22	0.00		
	NpCl ₃	1.34E-22	0.00		
		1.00E-09	100		
Np(V)	NpO ₂ ₊	9.11E-10	91.02	Argh6_Np_V.out	NAPSI_300401_NP_V_DAV.DAT
decoupled	NpO ₂ CO ₃₋	7.97E-11	7.97		only Np(V) considered
	NpO ₂ SO ₄₋	1.01E-11	1.01		
	NpO ₂ (CO ₃) ₂₋₃	3.50E-14	0.00		
	NpO ₂ (OH)	3.29E-15	0.00		
	NpO ₂ (CO ₃) ₃₋₅	4.73E-19	0.00		
	NpO ₂ (CO ₃) _{2OH-4}	4.58E-19	0.00		
	NpO ₂ (OH) ₂₋	2.23E-21	0.00		
		1.00E-09	100		
Np(VI)	NpO ₂ (CO ₃) ₂₋₂	9.54E-10	95.39	Argh6_Np_VI.out	NAPSI_300401_NP_VI_DAV.DAT
decoupled	NpO ₂ (CO ₃) ₃₋₄	2.80E-11	2.79		only Np(VI) considered
	NpO ₂ CO ₃	1.79E-11	1.79		
	NpO ₂ OH ₊	9.57E-14	0.01		
	NpO ₂ SO ₄	6.84E-14	0.01		
	NpO ₂ ₂	3.13E-14	0.00		
	NpO ₂ (SO ₄) ₂₋₂	2.54E-14	0.00		
	NpO ₂ Cl ₊	6.96E-15	0.00		
	NpO ₂ (OH) ₃₋	1.17E-15	0.00		
	(NpO ₂) ₂ CO ₃ (OH) ₃₋	1.35E-19	0.00		
	(NpO ₂) ₂ (OH) ₂₊₂	1.46E-22	0.00		
	NpO ₂ (OH) ₄₋₂	2.97E-23	0.00		
	(NpO ₂) ₃ (CO ₃) ₆₋₆	3.07E-24	0.00		
	(NpO ₂) ₃ (OH) ₅₊	6.89E-30	0.00		
		1.00E-09	100		
Pu(III)	PuCO ₃ ₊	4.55E-10	45.53	Argh6_Pu_III_est.out	NAPSI_300401_PU_III_DAV.DAT
decoupled	PuSO ₄ ₊	2.40E-10	24.01		Pu: Inputfile (TM-44-01-04)
	Pu ₃	9.24E-11	9.24		only Pu(III) considered
	PuCl ₂	6.93E-11	6.93		
	PuSiO(OH) ₃₊₂	6.56E-11	6.56		

	Pu(SO4)2-	6.10E-11	6.10		
	Pu(CO3)2-	1.38E-11	1.38		
	PuOH+2	2.39E-12	0.24		
	Pu(CO3)3-3	1.30E-13	0.01		
	Pu(OH)2+	1.16E-14	0.00		
	Pu(OH)3	2.65E-19	0.00		
		<hr/>			
		1.00E-09	100		
Pu(IV) decoupled	PuCO3(OH)3-	9.97E-10	99.69	Argh6_Pu_IV_est.out	NAPSI_300401_PU_IV_DAV.DAT
	Pu(OH)4	2.98E-12	0.30		Pu: Inputfile (TM-44-01-04)
	Pu(CO3)4-4	8.05E-14	0.01		only Pu(IV) considered
	Pu(CO3)5-6	1.63E-18	0.00		
	PuOH+3	2.18E-21	0.00		
	Pu(SO4)2	1.77E-21	0.00		
	PuSO4+2	8.65E-23	0.00		
	PuCl+3	1.90E-25	0.00		
	Pu+4	1.19E-25	0.00		
		<hr/>			
		1.00E-09	100		
Pu(V) decoupled	PuO2+	8.88E-10	88.75	Argh6_Pu_V.out	NAPSI_300401_PU_V_DAV.DAT
	PuO2CO3-	1.12E-10	11.24		only Pu(V) considered
	PuO2OH	1.19E-13	0.01		
	PuO2(CO3)3-5	1.46E-19	0.00		
		<hr/>			
		1.00E-09	100.00		
Pu(VI) decoupled	PuO2CO3	5.83E-10	58.23	Argh6_Pu_VI.out	NAPSI_300401_PU_VI_DAV.DAT
	PuO2(CO3)2-2	3.91E-10	39.11		only Pu(VI) considered
	PuO2(CO3)3-4	2.04E-11	2.04		
	PuO2SO4	2.94E-12	0.29		
	PuO2OH+	1.30E-12	0.13		
	PuO2+2	1.07E-12	0.11		
	PuO2Cl+	4.74E-13	0.05		
	PuO2(SO4)2-2	4.34E-13	0.04		
	PuO2(OH)2	1.87E-14	0.00		
	PuO2Cl2	3.94E-15	0.00		
	(PuO2)2(OH)2+2	9.98E-21	0.00		
		<hr/>			
		1.00E-09	100		
Am(III)	AmCO3+	4.94E-10	49.39	Argh6_Am.out	NAPSI_300401DAV.DAT
	AmSO4+	2.32E-10	23.22		
	Am+3	1.00E-10	10.02		
	AmSiO(OH)3+2	7.12E-11	7.12		
	AmCl+2	5.33E-11	5.32		
	Am(SO4)2-	3.32E-11	3.32		
	Am(CO3)2-	1.50E-11	1.50		
	AmOH+2	1.03E-12	0.10		
	Am(CO3)3-3	1.41E-13	0.01		

Am(OH) ₂ ⁺	5.01E-15	0.00
Am(OH) ₃	1.14E-19	0.00
	1.00E-09	100

Tab. A4.9: Argillaceous Rock Systems, pH = 6, low I, Water Composition (mol/kg H₂O).

Na	9.302E-02
Ca	1.319E-02
C	6.871E-02
Cl	8.062E-02
S	6.202E-03
Si	1.779E-04

temp	25°C
pH	6.0
I	0.13
log pCO ₂	0.09

Tab. A4.10: Argillaceous Rock Systems, pH = 6, low I, Radionuclide Speciation (mol/kg H₂O).

Element	Species	Concentration [m]	Distribution [%]	Output File	Data File
Be(II)	BeOH ⁺	5.11E-10	51.06	Argl6_Be.out	NAPSI_300401DAV.DAT Be: Inputfile (Minteq.v4)
	Be ⁺²	2.91E-10	29.06		
	BeCO ₃	1.59E-10	15.92		
	BeSO ₄	2.36E-11	2.36		
	BeCl ⁺	1.29E-11	1.29		
	Be(OH) ₂	2.54E-12	0.25		
	Be(SO ₄) ₂ ⁻²	4.94E-13	0.05		
	Be(OH) ₃ ⁻	8.13E-16	0.00		
	Be ₂ OH ₃	5.77E-17	0.00		
	Be ₃ (OH) ₃ ⁺³	1.35E-20	0.00		
	Be(OH) ₄ ⁻²	1.05E-23	0.00		
		1.00E-09	100		
Co(II)	Co ⁺²	8.11E-12	81.11	Argl6_CoNi.out	NAPSI_300401DAV.DAT Co: Inputfile (Mineql)
	CoSO ₄	9.75E-13	9.75		
	CoHCO ₃ ⁺	6.87E-13	6.87		
	CoCl ⁺	2.02E-13	2.02		
	CoCO ₃	2.47E-14	0.25		
	CoOH ⁺	7.28E-16	0.01		
	Co(CO ₃) ₂ ⁻²	6.27E-18	0.00		
	Co(OH) ₂	7.00E-20	0.00		
	CoS ₂ O ₃	6.81E-22	0.00		

	Co(OH)3-	1.81E-26	0.00		
	Co2OH+3	4.28E-28	0.00		
	Co(OH)4-2	1.26E-33	0.00		
	Co4(OH)4+4	0.00E+00	0.00		
		<hr/>	<hr/>		
		1.00E-11	100		
Ni(II)	Ni+2	7.74E-10	77.40	Argl6_Ni.out	NAPSI_300401DAV.DAT
	NiSO4	8.29E-11	8.29		
	NiHCO3+	6.56E-11	6.56		
	NiCl+	5.43E-11	5.43		
	NiCl2	9.36E-12	0.94		
	NiHS+	8.35E-12	0.83		
	Ni(SO4)2-2	2.81E-12	0.28		
	NiCO3	2.36E-12	0.24		
	Ni(HS)2	1.92E-13	0.02		
	NiOH+	1.10E-13	0.01		
	Ni(CO3)2-2	5.99E-16	0.00		
	Ni(OH)2	2.66E-16	0.00		
	Ni(OH)3-	6.89E-22	0.00		
	Ni2OH+3	1.23E-22	0.00		
	Ni(OH)4-2	9.58E-31	0.00		
	Ni4(OH)4+4	0.00E+00	0.00		
		<hr/>	<hr/>		
		1.00E-09	100		
Se(IV) decoupled	HSeO3-	9.91E-11	99.08	Argl6_Se_ox.out	NAPSI_300401_SE_IV_DAV.DAT
	SeO3-2	8.73E-13	0.87		only Se(IV) considered
	H2SeO3	4.80E-14	0.05		
		<hr/>	<hr/>		
		1.00E-10	100		
Zr(IV)	Zr(OH)4	6.06E-13	60.59	Argl6_Zr.out	NAPSI_300401DAV.DAT
	Zr(OH)5-	3.94E-13	39.41		
	ZrOH+3	6.66E-20	0.00		
	ZrSO4+2	1.35E-22	0.00		
	Zr+4	2.14E-25	0.00		
	ZrCl+3	6.56E-26	0.00		
		<hr/>	<hr/>		
		1.00E-12	100		
Nb(V)	Nb(OH)5	9.44E-10	94.38	Argl6_Nb.out	NAPSI_300401DAV.DAT
	NbO3-	5.62E-11	5.62		
	Nb(OH)4+	4.41E-16	0.00		
		<hr/>	<hr/>		
		1.00E-09	100		
Mo(VI)	MoO4-2	1.00E-10	100.00	Argl6_Mo.out	NAPSI_300401DAV.DAT
		<hr/>	<hr/>		
		1.00E-10	100		
Tc(IV) decoupled	TcCO3(OH)2	9.41E-10	94.05	Argl6_Tc_IV.out	NAPSI_300401_TC_DAV.DAT
	TcO(OH)2	5.34E-11	5.34		only Tc(IV) considered
	TcCO3(OH)3-	6.12E-12	0.61		

	TcO(OH)+	2.21E-14	0.00		
	TcO(OH)3-	8.72E-16	0.00		
	TcO+2	1.55E-18	0.00		
		1.00E-09	100		
Pd(II)	Pd(OH)2	6.80E-10	67.99	Argl6_Pd.out	NAPSI_300401DAV.DAT
	PdCl3-	1.68E-10	16.81		
	PdCl4-2	1.45E-10	14.53		
	PdCl2	5.24E-12	0.52		
	PdCl3OH-2	1.48E-12	0.15		
	PdCl+	6.96E-14	0.01		
	PdCl2(OH)2-2	7.51E-15	0.00		
	Pd(OH)3-	2.79E-15	0.00		
	Pd+2	1.98E-17	0.00		
		1.00E-09	100		
Cd(II)	CdCl+	6.09E-12	60.85	Argl6_Cd.out	NAPSI_300401DAV.DAT
	Cd+2	2.28E-12	22.80		Cd: Inputfile (Mineql)
	CdCl2	1.20E-12	12.04		
	CdSO4	3.45E-13	3.45		
	CdCl3-	6.13E-14	0.61		
	CdCO3	1.39E-14	0.14		
	Cd(SO4)2-2	9.30E-15	0.09		
	CdCl4-2	1.67E-15	0.02		
	Cd(SO4)3-4	9.53E-17	0.00		
	CdOH+	8.15E-17	0.00		
	CdS2O3	1.52E-20	0.00		
	Cd(OH)2	3.93E-21	0.00		
	CdSO3	1.21E-21	0.00		
	Cd(OH)3-	1.61E-26	0.00		
	Cd2OH+3	2.69E-27	0.00		
	Cd(OH)4-2	1.12E-35	0.00		
	Cd4(OH)4+4	0.00E+00	0.00		
		1.00E-11	100		
Sn(IV) decoupled	Tn(OH)4	9.87E-10	98.72	Argl6_Tn.out	NAPSI_300401TNDV.DAT
	Tn(OH)5-	1.28E-11	1.28		only Sn(IV)=Tn considered
	Tn(OH)6-2	1.12E-15	0.00		
		1.00E-09	100		
Bi(III)	Bi(OH)3	9.14E-10	91.32	Argl6_Bi.out	NAPSI_300401DAV.DAT
	Bi(OH)2+	8.66E-11	8.66		Bi: Inputfile (Baes &
	BiOH+2	1.57E-13	0.02		Mesmer 1976)
	Bi(OH)4-	1.36E-16	0.00		
	Bi+3	7.28E-18	0.00		
		1.00E-09	100		

Sb(III) decoupled	Sb(OH)3	1.00E-12	100.00	Argl6_Sb.out	NAPSI_300401DAV.DAT Sb: Inputfile (Mineql) only Sb(III) considered
	Sb(OH)2+	3.44E-17	0.00		
	Sb(OH)4-	1.96E-18	0.00		
		1.00E-12	100		
Eu(III)	EuCO3+	7.83E-10	78.30	Argl6_Eu.out	NAPSI_300401DAV.DAT
	EuSO4+	9.55E-11	9.54		
	Eu+3	5.89E-11	5.89		
	EuSiO(OH)3+2	3.43E-11	3.43		
	EuCl+2	1.22E-11	1.22		
	Eu(SO4)2-	8.13E-12	0.81		
	Eu(CO3)2-	6.89E-12	0.69		
	EuCl2+	8.56E-13	0.09		
	EuOH+2	3.57E-13	0.04		
	Eu(SiO(OH)3)2+	3.39E-14	0.00		
	Eu(OH)2+	5.57E-15	0.00		
	Eu(OH)3	1.07E-17	0.00		
	Eu(OH)4-	4.39E-24	0.00		
		1.00E-09	100		
	Pb(II)	PbCO3	5.47E-13		
PbCl+		1.95E-13	19.53		
Pb+2		1.80E-13	17.96		
PbSO4		5.30E-14	5.30		
PbCl2		1.50E-14	1.50		
Pb(SO4)2-2		4.12E-15	0.41		
Pb(CO3)2-2		3.11E-15	0.31		
PbOH+		1.61E-15	0.16		
PbCl3-		9.63E-16	0.10		
PbCl4-2		6.61E-17	0.01		
Pb(OH)2		4.90E-19	0.00		
PbS2O3		2.39E-19	0.00		
Pb(OH)3-		6.36E-24	0.00		
Pb2(OH)+3		1.67E-26	0.00		
Pb(S2O3)2-2		3.33E-29	0.00		
Pb3(OH)4+2		8.61E-40	0.00		
Pb4(OH)4+4		0.00E+00	0.00		
		1.00E-12	100		
Th (IV)		ThCO3(OH)3-	9.99E-10	99.83	Argl6_Th.out
	Th(SO4)2	1.01E-12	0.10		
	Th(OH)4	4.35E-13	0.04		
	ThSO4+2	1.93E-13	0.02		
	ThOH+3	4.78E-14	0.00		
	Th(SO4)3-2	2.80E-14	0.00		
	Th(CO3)5-6	5.11E-15	0.00		
	Th+4	7.70E-17	0.00		
		1.00E-09	100		

Pa(V)	PaO2OH	9.61E-10	96.03	Argl6_Pa.out	NAPSI_300401DAV.DAT
decoupled	PaO2+	3.98E-11	3.97		Pa: Inputfile (Mineql)
	PaOOH+2	2.78E-16	0.00		only Pa(V) considered
		<hr/>	<hr/>		
		1.00E-09	100		
U(IV)	UCO3(OH)3-	9.20E-10	91.96	Argl6_U_IV_est.out	NAPSI_300401_U_IV_DAV.DAT
decoupled	U(OH)4	7.99E-11	7.99		U: Inputfile (TM-44-01-04)
	U(CO3)4-4	5.59E-13	0.06		only U(IV) considered
	U(CO3)5-6	7.46E-18	0.00		
	UOH+3	2.53E-19	0.00		
	U(SO4)2	6.03E-21	0.00		
	USO4+2	1.35E-21	0.00		
	U+4	5.64E-24	0.00		
	UCI+3	2.86E-24	0.00		
		<hr/>	<hr/>		
		1.00E-09	100		
U(V)	UO2+	1.00E-09	100.00	Argl6_U_V.out	NAPSI_300401_U_V_DAV.DAT
decoupled	UO2(CO3)3-5	1.01E-17	0.00		only U(V) considered
		<hr/>	<hr/>		
		1.00E-09	100		
U(VI)	Ca2UO2(CO3)3	8.06E-10	80.57408	Argl6_U_VI_Kal_Cho.out	NAPSI_300401_U_VI_DAV.DAT
decoupled	UO2(CO3)2-2	9.78E-11	9.78007		Ca2UO2(CO3)3: Inputfile,
	UO2(CO3)3-4	9.44E-11	9.44113		Kalmykow & Choppin (2000)
	UO2CO3	2.07E-12	0.20706		only U(VI) considered
	UO2OH+	4.12E-15	0.00041		
	UO2+2	1.45E-15	0.00015		
	UO2SO4	1.08E-15	0.00011		
	UO2(OH)2	4.99E-16	0.00005		
	UO2Cl+	6.00E-17	0.00001		
	UO2(SO4)2-2	4.60E-17	0.00000		
	UO2(OH)3-	4.09E-17	0.00000		
	UO2Cl2	1.53E-19	0.00000		
	(UO2)2CO3(OH)3-	3.96E-20	0.00000		
	(UO2)2(OH)2+2	1.74E-24	0.00000		
	UO2(OH)4-2	1.43E-24	0.00000		
	(UO2)3(CO3)6-6	8.17E-25	0.00000		
	(UO2)2OH+3	5.46E-27	0.00000		
	(UO2)3(OH)5+	4.59E-32	0.00000		
	(UO2)3O(OH)2HCO3+	6.60E-34	0.00000		
	(UO2)3(OH)4+2	4.55E-34	0.00000		
	(UO2)3(OH)7-	1.61E-35	0.00000		
	(UO2)4(OH)7+	0.00E+00	0.00000		
		<hr/>	<hr/>		
		1.00E-09	100		
Np(III)	NpCO3+	6.45E-10	64.52	Argl6_Np_III_est.out	NAPSI_300401_NP_III_DAV.DAT
decoupled	NpSO4+	1.40E-10	13.99		Np: Inputfile (TM-44-01-04)

	Np+3	9.68E-11	9.68		only Np(III) considered
	NpSiO(OH)3+2	8.93E-11	8.93		
	Np(CO3)2-	1.80E-11	1.79		
	Np(SO4)2-	6.70E-12	0.67		
	NpOH+2	4.06E-12	0.41		
	Np(CO3)3-3	1.04E-13	0.01		
	Np(OH)2+	2.30E-14	0.00		
	Np(OH)3	5.56E-19	0.00		
		1.00E-09	100.00		
Np(IV) decoupled	Np(CO3)4-4	4.30E-10	43.01	Argl6_Np_IV_est.out	NAPSI_300401_NP_IV_DAV.DAT
	Np(OH)4	3.30E-10	33.01		Np: Inputfile (TM-44-01-04)
	NpCO3(OH)3-	2.40E-10	23.98		only Np(IV) considered
	Np(CO3)5-6	6.44E-15	0.00		
	NpOH+3	1.18E-17	0.00		
	Np(SO4)2	5.45E-19	0.00		
	NpSO4+2	6.56E-20	0.00		
	Np+4	1.47E-22	0.00		
	NpCl+3	4.50E-23	0.00		
		1.00E-09	100		
Np(V) decoupled	NpO2+	9.22E-10	92.22	Argl6_Np_V.out	NAPSI_300401_NP_V_DAV.DAT
	NpO2CO3-	7.40E-11	7.40		only Np(V) considered
	NpO2SO4-	3.85E-12	0.38		
	NpO2(CO3)2-3	2.01E-14	0.00		
	NpO2(OH)	3.53E-15	0.00		
	NpO2(CO3)2OH-4	1.89E-19	0.00		
	NpO2(CO3)3-5	1.14E-19	0.00		
	NpO2(OH)2-	2.30E-21	0.00		
		1.00E-09	100		
Np(VI) decoupled	NpO2(CO3)2-2	9.62E-10	96.15	Argl6_Np_VI.out	NAPSI_300401_NP_VI_DAV.DAT
	NpO2CO3	2.39E-11	2.39		only Np(VI) considered
	NpO2(CO3)3-4	1.44E-11	1.44		
	NpO2OH+	1.34E-13	0.01		
	NpO2+2	3.76E-14	0.00		
	NpO2SO4	3.76E-14	0.00		
	NpO2(SO4)2-2	4.32E-15	0.00		
	NpO2Cl+	2.64E-15	0.00		
	NpO2(OH)3-	1.68E-15	0.00		
	(NpO2)2CO3(OH)3-	2.59E-19	0.00		
	(NpO2)2(OH)2+2	2.60E-22	0.00		
	NpO2(OH)4-2	3.69E-23	0.00		
	(NpO2)3(CO3)6-6	9.78E-25	0.00		
	(NpO2)3(OH)5+	2.13E-29	0.00		
		1.00E-09	100		

Pu(III) decoupled	PuCO ₃ ⁺	6.26E-10	62.57	Argl6_Pu_III_est.out	NAPSI_300401_PU_III_DAV.DAT Pu: Inputfile (TM-44-01-04) only Pu(III) considered
	PuSO ₄ ⁺	1.36E-10	13.57		
	Pu ⁺³	9.39E-11	9.39		
	PuSiO(OH) ₃₊₂	8.66E-11	8.66		
	PuCl ⁺²	2.45E-11	2.45		
	Pu(CO ₃) ₂ ⁻	1.74E-11	1.74		
	Pu(SO ₄) ₂ ⁻	1.30E-11	1.30		
	PuOH ⁺²	3.13E-12	0.31		
	Pu(CO ₃) ₃₋₃	1.01E-13	0.01		
	Pu(OH) ₂ ⁺	1.77E-14	0.00		
	Pu(OH) ₃	4.28E-19	0.00		
	<hr/>	<hr/>			
	1.00E-09	100			
Pu(IV) decoupled	PuCO ₃ (OH) ₃₋	9.97E-10	99.65	Argl6_Pu_IV_est.out	NAPSI_300401_PU_IV_DAV.DAT Pu: Inputfile (TM-44-01-04) only Pu(IV) considered
	Pu(OH) ₄	3.45E-12	0.34		
	Pu(CO ₃) ₄₋₄	2.90E-14	0.00		
	Pu(CO ₃) ₅₋₆	2.03E-19	0.00		
	PuOH ⁺³	1.58E-21	0.00		
	Pu(SO ₄) ₂	2.79E-22	0.00		
	PuSO ₄ ⁺²	2.99E-23	0.00		
	Pu ⁺⁴	6.11E-26	0.00		
	PuCl ⁺³	3.73E-26	0.00		
	<hr/>	<hr/>			
	1.00E-09	100			
Pu(V) decoupled	PuO ₂ ⁺	8.96E-10	89.60	Argl6_Pu_V.out	NAPSI_300401_PU_V_DAV.DAT only Pu(V) considered
	PuO ₂ CO ₃ ⁻	1.04E-10	10.39		
	PuO ₂ OH	1.28E-13	0.01		
	PuO ₂ (CO ₃) ₃₋₅	3.52E-20	0.00		
	<hr/>	<hr/>			
	1.00E-09	100.00			
Pu(VI) decoupled	PuO ₂ CO ₃	6.55E-10	65.53	Argl6_Pu_VI.out	NAPSI_300401_PU_VI_DAV.DAT only Pu(VI) considered
	PuO ₂ (CO ₃) ₂₋₂	3.32E-10	33.17		
	PuO ₂ (CO ₃) ₃₋₄	8.82E-12	0.88		
	PuO ₂ OH ⁺	1.53E-12	0.15		
	PuO ₂ SO ₄	1.36E-12	0.14		
	PuO ₂ ⁺²	1.08E-12	0.11		
	PuO ₂ Cl ⁺	1.51E-13	0.02		
	PuO ₂ (SO ₄) ₂₋₂	6.21E-14	0.01		
	PuO ₂ (OH) ₂	2.34E-14	0.00		
	PuO ₂ Cl ₂	3.59E-16	0.00		
(PuO ₂) ₂ (OH) ₂₊₂	1.26E-20	0.00			
	<hr/>	<hr/>			
	1.00E-09	100			
Am(III)	AmCO ₃ ⁺	6.46E-10	64.53	Argl6_Am.out	NAPSI_300401DAV.DAT
	AmSO ₄ ⁺	1.25E-10	12.47		
	Am ⁺³	9.69E-11	9.68		
	AmSiO(OH) ₃₊₂	8.93E-11	8.93		
	Am(CO ₃) ₂ ⁻	1.80E-11	1.79		

AmCl ₂	1.79E-11	1.79
Am(SO ₄) ₂ ⁻	6.70E-12	0.67
AmOH ₂	1.29E-12	0.13
Am(CO ₃) ₃ ⁻³	1.04E-13	0.01
Am(OH) ₂ ⁺	7.28E-15	0.00
Am(OH) ₃	1.76E-19	0.00
	<hr/>	
	1.00E-09	100

A5 Additional Calculations

Tab. A5.1: Groundwater SGS 6, Koss, Winkler & Bütow (1992),
Water Composition (mol/kg H₂O)

Al	2.520E-05	
C	1.000E-03	
Ca	5.740E-03	
Cl	3.300E-03	
F	3.050E-05	
K	4.090E-04	
Mg	6.170E-04	
N(-3)	4.150E-03	
N(5)	1.300E-02	
Na	1.590E-02	
Ni	8.550E-07	
P	3.550E-05	
Pb	1.500E-08	
S	6.950E-03	
Si	1.860E-04	quartz saturation
U	4.110E-07	
temp	25°C	
pH	6.68	
pe	13.923	O ₂ (g) saturation
I	3.972E-02	
log pCO ₂	-2.09	

Tab. A5.2: Groundwater SGS 6, Koss, Winkler & Bütow (1992),
Radionuclide Speciation (mol/kg H₂O).

Element	Species	Concentration [m]	Distribution [%]	Output File	Data File
Pb(II)	Pb+2	5.69E-09	37.94	Ko_PbMineql.outDAV	NAPSI_300401DAV.DAT
	PbSO4	4.09E-09	27.26		Pb: Inputfile (Mineql)
	PbCO3	3.61E-09	24.08		
	PbNO3+	5.31E-10	3.54		
	Pb(SO4)2-2	3.95E-10	2.63		
	PbCl+	3.54E-10	2.36		
	PbOH+	3.16E-10	2.10		
	Pb(NO3)2	8.16E-12	0.05		
	Pb(CO3)2-2	2.18E-12	0.01		
	PbCl2	1.32E-12	0.01		
	Pb(OH)2	5.01E-13	0.00		
	PbCl3-	3.46E-15	0.00		
	Pb2(OH)+3	7.39E-17	0.00		
	Pb(OH)3-	2.87E-17	0.00		
	PbCl4-2	8.22E-18	0.00		

Pb3(OH)4+2	2.86E-23	0.00
Pb4(OH)4+4	6.91E-28	0.00
Pb(P2O7)2-6	4.33E-29	0.00
PbS2O3	0.00E+00	0.00
Pb(S2O3)2-2	0.00E+00	0.00
	1.50E-08	100

Tab. A5.3: Laboratory Solution, Gorgeon (1994),
Water Composition (mol/kg H₂O)

C	7.403E-05	
K	6.373E-05	(KOH was added in the calculations in order to obtain the required pH)
Na	1.000E-01	
ClO4	1.000E-01	
Si	1.786E-04	quartz saturation
temp	25°C	
pH	7.0	
pe	13.6	atmospheric O ₂ (g) saturation
I	1.0E-01	
log pCO ₂	-3.50	atmospheric CO ₂ (g) saturation

Tab. A5.4: Laboratory Solution, Gorgeon (1994),
Radionuclide Speciation (mol/kg H₂O).

Element	Species	Concentration [m]	Distribution [%]	Output File	Data File
Np(III)	NpSiO(OH)3+2	0.00E+00	0.00	Go_70_2007_Np_est.out	NAPSI_300401DAV.DAT Np: Inputfile (TM-44-01-04)
	Np+3	0.00E+00	0.00		
	NpOH+2	0.00E+00	0.00		
	NpCO3+	0.00E+00	0.00		
	Np(OH)2+	0.00E+00	0.00		
	Np(CO3)2-	0.00E+00	0.00		
	Np(OH)3	0.00E+00	0.00		
Np(IV)	Np(CO3)3-3	0.00E+00	0.00		
	Np(OH)4	4.96E-23	0.00		
	NpCO3(OH)3-	8.99E-26	0.00		
	Np(CO3)4-4	2.01E-33	0.00		
	NpOH+3	1.49E-33	0.00		
	Np+4	1.64E-39	0.00		
Np(V)	Np(CO3)5-6	5.32E-40	0.00		
	NpO2+	9.98E-10	99.77		
	NpO2CO3-	2.04E-12	0.20		
	NpO2(OH)	3.89E-14	0.00		

	NpO ₂ (CO ₃) ₂ -3	1.22E-17	0.00
	NpO ₂ (OH) ₂ -	2.49E-19	0.00
	NpO ₂ (CO ₃) ₂ OH-4	1.01E-21	0.00
	NpO ₂ (CO ₃) ₃ -5	1.32E-24	0.00
Np(VI)	NpO ₂ (OH) ₃ -	1.02E-13	0.01
	NpO ₂ OH+	8.15E-14	0.01
	NpO ₂ CO ₃	3.76E-14	0.00
	NpO ₂ (CO ₃) ₂ -2	3.58E-14	0.00
	NpO ₂ +2	2.16E-15	0.00
	NpO ₂ (CO ₃) ₃ -4	1.09E-17	0.00
	(NpO ₂) ₂ CO ₃ (OH) ₃ -	2.48E-20	0.00
	NpO ₂ (OH) ₄ -2	2.13E-20	0.00
	(NpO ₂) ₂ (OH) ₂ +2	9.26E-23	0.00
	(NpO ₂) ₃ (OH) ₅ +	4.97E-28	0.00
	(NpO ₂) ₃ (CO ₃) ₆ -6	3.25E-38	0.00
		<hr/>	
		1.00E-09	100

A6 Additional Thermodynamic Data

A6.1 Data estimated by Hummel & Berner (2001), written in PHREEQC format

+1.000Np+3 log_k	+2.000H2O -14.7000	-2.000H+	= Np(OH)2+	
+1.000Pu+3 log_k	+2.000H2O -14.8000	-2.000H+	= Pu(OH)2+	
+1.000Np+3 log_k	+3.000H2O -25.2000	-3.000H+	= Np(OH)3	
	-gamma 0.00 0.00			
+1.000Pu+3 log_k	+3.000H2O -25.3000	-3.000H+	= Pu(OH)3	
	-gamma 0.00 0.00			
+1.000Np+3 log_k	+1.000CO3-2 7.8000	= NpCO3+		
+1.000Pu+3 log_k	+1.000CO3-2 7.8000	= PuCO3+		
+1.000Np+3 log_k	+2.000CO3-2 12.3000	= Np(CO3)2-		
+1.000Pu+3 log_k	+2.000CO3-2 12.3000	= Pu(CO3)2-		
+1.000Np+3 log_k	+3.000CO3-2 15.2000	= Np(CO3)3-3		
+1.000Pu+3 log_k	+3.000CO3-2 15.2000	= Pu(CO3)3-3		
+1.000Np+3 log_k	+1.000SO4-2 3.9000	= NpSO4+		
+1.000Np+3 log_k	+2.000SO4-2 5.4000	= Np(SO4)2-		
+1.000Np+3 log_k	+1.000SiO(OH)3- 8.1000	= NpSiO(OH)3+2		
+1.000Pu+3 log_k	+1.000SiO(OH)3- 8.1000	= PuSiO(OH)3+2		
+1.000U+4 log_k	+1.000CO3-2 4.0000	-3.000H+	+3.000H2O	= UCO3(OH)3-
+1.000Np+4 log_k	+1.000CO3-2 2.0000	-3.000H+	+3.000H2O	= NpCO3(OH)3-
+1.000Pu+4 log_k	+1.000CO3-2 6.0000	-3.000H+	+3.000H2O	= PuCO3(OH)3-

References

Hummel, W. & Berner, U. (2001): Application of the Nagra/PSI Thermochemical Data Base 01/01: Solubility and Sorption of Th, U, Np and Pu. PSI Internal Report TM-44-01-04, Paul Scherrer Institut, Villigen, Switzerland.

A6.2 Data by Kalmykow & Choppin (2000), written in PHREEQC format

```
+1.000UO2+2      +2.000Ca+2      +3.000CO3-2      = Ca2UO2(CO3)3
log_k           29.22
-gamma          0.00      0.00
```

References

Kalmykow, S.N. & Choppin, G.R. (2000): Mixed Ca²⁺/UO₂²⁺/CO₃²⁻ complex formation at different ionic strengths. *Radiochimica Acta*, 88, 603-606.

A6.3 Data from MINEQL datafile, FEB92.LOGK, version 27.4.1994

A6.3.1 Data written in PHREEQC format

Cd Cadmium

```
SOLUTION_MASTER_SPECIES
Cd      Cd+2      0.0      Cd      112.411      #      Mineql
SOLUTION_SPECIES
Cd+2      = Cd+2
log_k      0.0
+1.000Cd+2      +1.000CO3-2      = CdCO3
log_k      4.3000
-gamma      0.00      0.00
+1.000Cd+2      +1.000SO4-2      = CdSO4
log_k      2.4600
-gamma      0.00      0.00
+1.000Cd+2      +2.000SO4-2      = Cd(SO4)2-2
log_k      3.2500
+1.000Cd+2      +3.000SO4-2      = Cd(SO4)3-4
log_k      2.7000
+1.000Cd+2      +1.000Cl-      = CdCl+
log_k      1.9800
+1.000Cd+2      +2.000Cl-      = CdCl2
log_k      2.6000
-gamma      0.00      0.00
+1.000Cd+2      +3.000Cl-      = CdCl3-
log_k      2.4000
+1.000Cd+2      +4.000Cl-      = CdCl4-2
log_k      1.7000
+1.000Cd+2      +1.000F-      = CdF+
log_k      1.1000
+1.000Cd+2      +1.000Br-      = CdBr+
log_k      2.1000
+1.000Cd+2      +2.000Br-      = CdBr2
log_k      2.9000
-gamma      0.00      0.00
+1.000Cd+2      +3.000Br-      = CdBr3-
log_k      3.0000
+1.000Cd+2      +4.000Br-      = CdBr4-2
log_k      3.1000
+1.000Cd+2      +1.000S2O3-2      = CdS2O3
log_k      3.9000
-gamma      0.00      0.00
+1.000Cd+2      +1.000SO3-2      = CdSO3
log_k      5.4000
-gamma      0.00      0.00
+1.000Cd+2      +1.000H2O      -1.000H+      = CdOH+
log_k      -10.1000
+1.000Cd+2      +2.000H2O      -2.000H+      = Cd(OH)2
log_k      -20.3000
-gamma      0.00      0.00
+1.000Cd+2      +3.000H2O      -3.000H+      = Cd(OH)3-
log_k      -31.8000
+1.000Cd+2      +4.000H2O      -4.000H+      = Cd(OH)4-2
log_k      -47.3000
+2.000Cd+2      +1.000H2O      -1.000H+      = Cd2OH+3
log_k      -9.4000
+4.000Cd+2      +4.000H2O      -4.000H+      = Cd4(OH)4+4
log_k      -32.8000
PHASES
CdCO3(s)      = +1.000Cd+2      +1.000CO3-2
CdS(s)      = +1.000Cd+2      +1.000HS-      -1.000H+
log_k      -13.7400
Cd(OH)2(s)      = +1.000Cd+2      +2.000H2O      -2.000H+
log_k      -13.1000
log_k      13.6500
```


Co Cobalt

SOLUTION_MASTER_SPECIES				Co	58.933	#		Mineql
Co	Co+2	0.0		Co				Mineql
Co(2)	Co+2	0.0		Co				Mineql
Co(3)	Co+3	0.0		Co				Mineql
SOLUTION_SPECIES								
Co+2			= Co+2					
	log_k	0.0						
+1.000Co+2			-1.000e-			= Co+3		
	log_k	-31.6000						
+1.000Co+2			+1.000SO4-2			= CoSO4		
	log_k	2.3600						
	-gamma	0.00	0.00					
+1.000Co+2			+1.000Cl-			= CoCl+		
	log_k	-0.0500						
+1.000Co+2			+1.000Br-			= CoBr+		
	log_k	0.6000						
+1.000Co+2			+1.000S2O3-2			= CoS2O3		
	log_k	2.0000						
	-gamma	0.00	0.00					
+1.000Co+2			+1.000H2O			-1.000H+		= CoOH+
	log_k	-9.7000						
+1.000Co+2			+2.000H2O			-2.000H+		= Co(OH)2
	log_k	-19.6000						
	-gamma	0.00	0.00					
+1.000Co+2			+3.000H2O			-3.000H+		= Co(OH)3-
	log_k	-32.3000						
+1.000Co+2			+4.000H2O			-4.000H+		= Co(OH)4-2
	log_k	-45.8000						
+2.000Co+2			+1.000H2O			-1.000H+		= Co2OH+3
	log_k	-11.3000						
+4.000Co+2			+4.000H2O			-4.000H+		= Co4(OH)4+4
	log_k	-30.4000						
+1.000Co+3			+1.000F-			= CoF+2		
	log_k	5.2000						
+1.000Co+3			+2.000F-			= CoF2+		
	log_k	9.1000						
+1.000Co+3			+3.000F-			= CoF3		
	log_k	12.0000						
	-gamma	0.00	0.00					
PHASES								
CoCO3(s)			= +1.000Co+2			+1.000CO3-2		
CoCO3								
	log_k	-10.0000						
CoS(alpha)			= +1.000Co+2			+1.000HS-		-1.000H+
CoS								
	log_k	-7.4000						
CoS(beta)			= +1.000Co+2			+1.000HS-		-1.000H+
CoS								
	log_k	-11.7000						
Co(OH)2(s)			= +1.000Co+2			+2.000H2O		-2.000H+
Co(OH)2								
	log_k	13.1000						
Co2O3(s)			= +2.000Co+3			+3.000H2O		-6.000H+
Co2O3								
	log_k	-7.4000						

Cs Caesium

SOLUTION_SPECIES							
+1.000Cs+			+1.000Cl-			= CsCl	
	log_k	-0.1000					
	-gamma	0.00	0.00				
+1.000Cs+			+1.000F-			= CsF	
	log_k	0.0000					
	-gamma	0.00	0.00				

Pa Protactinium(V)

SOLUTION_MASTER_SPECIES				Pa	231.036	#		Mineql
Pa	PaO2+	0.0		Pa				Mineql
SOLUTION_SPECIES								
PaO2+			= PaO2+					
	log_k	0.0						
+1.000PaO2+			+1.000H+			= PaOOH+2		
	log_k	0.5000						
+1.000PaO2+			+1.000H2O			-1.000H+		= PaO2OH
	log_k	-4.5000						
	-gamma	0.00	0.00					

Pb Lead

SOLUTION_MASTER_SPECIES	Pb	Pb+2	0.0	Pb	207.2	#	Mineq1
SOLUTION_SPECIES							
Pb+2							
log_k		0.0					
+1.000Pb+2				+1.000CO3-2		= PbCO3	
log_k		7.0000					
-gamma		0.00	0.00				
+1.000Pb+2				+2.000CO3-2		= Pb(CO3)2-2	
log_k		10.3500					
+1.000Pb+2				+1.000SO4-2		= PbSO4	
log_k		2.7500					
-gamma		0.00	0.00				
+1.000Pb+2				+2.000SO4-2		= Pb(SO4)2-2	
log_k		4.0000					
+1.000Pb+2				+1.000Cl-		= PbCl+	
log_k		1.5900					
+1.000Pb+2				+2.000Cl-		= PbCl2	
log_k		1.8000					
-gamma		0.00	0.00				
+1.000Pb+2				+3.000Cl-		= PbCl3-	
log_k		1.7000					
+1.000Pb+2				+4.000Cl-		= PbCl4-2	
log_k		1.4000					
+1.000Pb+2				+1.000Br-		= PbBr+	
log_k		1.6000					
+1.000Pb+2				+2.000Br-		= PbBr2	
log_k		2.2000					
-gamma		0.00	0.00				
+1.000Pb+2				+3.000Br-		= PbBr3-	
log_k		3.0000					
+1.000Pb+2				+1.000S2O3-2		= PbS2O3	
log_k		6.2000					
-gamma		0.00	0.00				
+1.000Pb+2				+2.000S2O3-2		= Pb(S2O3)2-2	
log_k		7.5000					
+1.000Pb+2				+1.000H2O		-1.000H+	= PbOH+
log_k		-7.7000					
+1.000Pb+2				+2.000H2O		-2.000H+	= Pb(OH)2
log_k		-17.1000					
-gamma		0.00	0.00				
+1.000Pb+2				+3.000H2O		-3.000H+	= Pb(OH)3-
log_k		-28.1000					
+2.000Pb+2				+1.000H2O		-1.000H+	= Pb2(OH)+3
log_k		-6.4000					
+3.000Pb+2				+4.000H2O		-4.000H+	= Pb3(OH)4+2
log_k		-23.9000					
+4.000Pb+2				+4.000H2O		-4.000H+	= Pb4(OH)4+4
log_k		-20.9000					
+1.000Pb+2				+1.000NO3-		= PbNO3+	
log_k		1.17					
+1.000Pb+2				+2.000NO3-		= Pb(NO3)2	
log_k		1.40					
-gamma		0.00	0.00				
+2.000PO4-3				-1.000H2O		+2.000H+	= P2O7-4
log_k		21.26					
+1.000Pb+2				+2.000P2O7-4		= Pb(P2O7)2-6	
log_k		5.2000					
PHASES							
PbCO3(s)							
PbCO3				+1.000Pb+2		+1.000CO3-2	
log_k		-13.1300					
Pb3(CO3)2(OH)2(s)							
Pb3(CO3)2(OH)2				+3.000Pb+2		+2.000CO3-2	+2.000H2O
-2.000H+							
log_k		-18.8000					
PbSO4(s)							
PbSO4				+1.000Pb+2		+1.000SO4-2	
log_k		-7.7900					
PbF2(s)							
PbF2				+1.000Pb+2		+2.000F-	
log_k		-7.6000					
PbS(s)							
PbS				+1.000Pb+2		+1.000HS-	-1.000H+
log_k		-13.6000					
Pb2SiO4(s)							
Pb2SiO4				+2.000Pb+2		+1.000SiO2(OH)2-2	-2.000H+
log_k		-3.5000					
PbO(s)							
PbO				+1.000Pb+2		+1.000H2O	-2.000H+
log_k		12.9000					
Pb2O(OH)2(s)							
Pb2O(OH)2				+2.000Pb+2		+3.000H2O	-4.000H+
log_k		26.2000					

Sb Antimony

SOLUTION_MASTER_SPECIES						
Sb	Sb(OH)3	0.0	Sb	121.757	#	Mineql
Sb(3)	Sb(OH)3	0.0	Sb		#	Mineql
Sb(5)	Sb(OH)5	0.0	Sb		#	Mineql
SOLUTION_SPECIES						
Sb(OH)3	= Sb(OH)3					
log_k	0.0					
-gamma	0.00	0.00				
+1.000Sb(OH)3		+2.000H2O		-2.000H+		-2.000e-
= Sb(OH)5						
log_k	-17.1900					
-gamma	0.00	0.00				
+1.000Sb(OH)3		+1.000H+		-1.000H2O		= Sb(OH)2+
log_k	1.4200					
+1.000Sb(OH)3		+1.000H2O		-1.000H+		= Sb(OH)4-
log_k	-11.8200					
+1.000Sb(OH)5		+1.000H2O		-1.000H+		= Sb(OH)6-
log_k	-2.7200					
PHASES						
Sb2O3(s)		= +2.000Sb(OH)3		-3.000H2O		
log_k	-8.4800					
Sb2O5(s)		= +2.000Sb(OH)5		-5.000H2O		
log_k	-7.4000					

A6.3.2 Sources of data from MINEQL datafile, FEB92.LOGK, version 27.4.1994**Cd Cadmium**

CdCO3	M. Schweingruber, personal estimate (1983)
CdSO4	Smith & Martell (1976)
Cd(SO4)2-2	Smith & Martell (1976)
Cd(SO4)3-4	Smith & Martell (1976)
CdCl+	Smith & Martell (1976)
CdCl2	Smith & Martell (1976)
CdCl3-	Smith & Martell (1976)
CdCl4-2	Smith & Martell (1976)
CdF+	source unknown
CdBr+	source unknown
CdBr2	source unknown
CdBr3-	source unknown
CdBr4-2	source unknown
CdS2O3	source unknown
CdSO3	source unknown
CdOH+	Smith & Martell (1976)
Cd(OH)2	Smith & Martell (1976)
Cd(OH)3-	M. Schweingruber, personal estimate (1983)
Cd(OH)4-2	Smith & Martell (1976)
Cd2OH+3	Smith & Martell (1976)
Cd4(OH)4+4	Smith & Martell (1976)
CdCO3(s)	Smith & Martell (1976)
CdS(s)	Smith & Martell (1976)
Cd(OH)2(s)	Smith & Martell (1976)

Co Cobalt

Co+3	source unknown
CoSO4	Smith & Martell (1976)
CoCl+	Smith & Martell (1976)
CoBr+	source unknown
CoS2O3	source unknown
CoOH+	Smith & Martell (1976)
Co(OH)2	Smith & Martell (1976)
Co(OH)3-	Smith & Martell (1976)
Co(OH)4-2	Smith & Martell (1976)
Co2OH+3	Smith & Martell (1976)
Co4(OH)4+4	Smith & Martell (1976)
CoF+2	source unknown

CoF ₂ ⁺	source unknown
CoF ₃	source unknown
CoCO ₃ (s)	Smith & Martell (1976)
CoS(alpha)	Smith & Martell (1976)
CoS(beta)	Smith & Martell (1976)
Co(OH) ₂ (s)	Smith & Martell (1976)
Co ₂ O ₃ (s)	source unknown
Cs Caesium	
CsCl	source unknown
CsF	source unknown
Pa Protactinium(V)	
PaO ₂ ⁺	Baes & Mesmer (1976)
PaOOH ⁺ 2	Baes & Mesmer (1976)
PaO ₂ OH	Baes & Mesmer (1976)
Pb Lead	
PbCO ₃	Phillips (1982)
Pb(CO ₃) ₂ -2	Phillips (1982)
PbSO ₄	Smith & Martell (1976)
Pb(SO ₄) ₂ -2	M. Schweingruber, personal estimate (1983)
PbCl ⁺	Smith & Martell (1976)
PbCl ₂	Smith & Martell (1976)
PbCl ₃ ⁻	Smith & Martell (1976)
PbCl ₄ -2	Smith & Martell (1976)
PbBr ⁺	source unknown
PbBr ₂	source unknown
PbBr ₃ ⁻	source unknown
PbS ₂ O ₃	source unknown
Pb(S ₂ O ₃) ₂ -2	source unknown
PbOH ⁺	Smith & Martell (1976)
Pb(OH) ₂	Smith & Martell (1976)
Pb(OH) ₃ ⁻	Smith & Martell (1976)
Pb ₂ (OH) ⁺ 3	Smith & Martell (1976)
Pb ₃ (OH) ⁺ 4+2	Phillips (1982)
Pb ₄ (OH) ⁺ 4+4	Smith & Martell (1976)
PbNO ₃ ⁺	Smith & Martell (1976)
Pb(NO ₃) ₂	Smith & Martell (1976)
P ₂ O ₇ -4	NEA ?
Pb(P ₂ O ₇) ₂ -6	source unknown
PbCO ₃ (s)	Smith & Martell (1976)
Pb ₃ (CO ₃) ₂ (OH) ₂ (s)	Stumm & Morgan (1970)
PbSO ₄ (s)	Smith & Martell (1976)
PbF ₂ (s)	source unknown
PbS(s)	Smith & Martell (1976)
Pb ₂ SiO ₄ (s)	source unknown
PbO(s)	Smith & Martell (1976)
Pb ₂ O(OH) ₂ (s)	Smith & Martell (1976)
Sb Antimony	
Sb(OH) ₅	Latimer (1952)
Sb(OH) ₂ ⁺	Baes & Mesmer (1976)
Sb(OH) ₄ ⁻	Baes & Mesmer (1976)
Sb(OH) ₆ ⁻	Baes & Mesmer (1976)
Sb ₂ O ₃ (s)	Baes & Mesmer (1976)
Sb ₂ O ₅ (s)	Baes & Mesmer (1976)

References

- Baes, C.F., Jr. & Mesmer, R.E. (1976): The Hydrolysis of Cations. John Wiley & Sons, New York. 489 pp.
- Latimer, W.M. (1952): Oxidation Potentials, 2nd edition. Prentice-Hall, Englewood Cliffs, N.J., U.S.A. 392 pp.
- Phillips, S.L. (1982): Hydrolysis and formation constants at 25°C. Report LBL-14313/UC-70, Lawrence Berkeley Laboratory, 65 pp.
- Smith, R.M. & Martell, A.E. (1976): Critical Stability Constants, Volume 4: Inorganic Complexes. Plenum Press, New York and London. 257 pp.
- Stumm, W. & Morgan, J.J. (1970): Aquatic Chemistry. Wiley Interscience, New York.

A6.4 Data for Co-carbonate complexes written in PHREEQC format

There are no thermodynamic data for $\text{CoCO}_3(\text{aq})$, $\text{Co}(\text{CO}_3)_2^{2-}$ and CoHCO_3^+ in the Nagra/PSI Thermochemical Database 01/01 and in the MINEQL database. As an estimate, values for equilibrium constants were substituted by the corresponding values for Ni-carbonate complexes from the Nagra/PSI Thermochemical Database 01/01. Note that some of these constants are only approximations themselves.

```
+1.000Co+2          +1.000CO3-2          = CoCO3
log_k              4.0000
-gamma            0.00    0.00
+1.000Co+2          +2.000CO3-2          = Co(CO3)2-2
log_k              6.0000    ##### log_k < 6 !
+1.000Co+2          +1.000HCO3-          = CoHCO3+
log_k              1.0000    ##### log_k ca. 1 !
```

A6.5 Data for Be written in PHREEQC format

There are no data for Be in the Nagra/PSI Thermochemical Database 01/01. Unreviewed data were taken from the MINTEQ Version 4 database (HydroGeoLogic Inc. & Allison Geoscience Consultants Inc. 1999), distributed with the PHREEQC package. Where indicated, the log K values refer to NIST46.6, which means Smith et al. (1997).

```
SOLUTION_MASTER_SPECIES
Be          Be+2          0.0    Be          9.0122

SOLUTION_SPECIES
Be+2 = Be+2
log_k 0

Be+2 + H2O = BeOH+ + H+
log_k -5.397
delta_h 0    kJ
-gamma 6.5    0
# Id: 1103301
# log K source: NIST46.4
# Delta H source: MTQ3.11
#T and ionic strength: 0.00 25.0

Be+2 + 2H2O = Be(OH)2 + 2H+
log_k -13.594
delta_h 0    kJ
-gamma 6.5    0
# Id: 1103302
# log K source: NIST46.4
# Delta H source: MTQ3.11
#T and ionic strength: 0.00 25.0

Be+2 + 3H2O = Be(OH)3- + 3H+
log_k -23.191
```

```

delta_h 0      kJ
-gamma  6.5    0
#
#           Id: 1103303
#           log K source: NIST46.4
#           Delta H source: MTQ3.11
#T and ionic strength: 0.00 25.0
Be+2 + 4H2O = Be(OH)4-2 + 4H+
log_k    -37.388
delta_h  0      kJ
-gamma  6.5    0
#
#           Id: 1103304
#           log K source: NIST46.4
#           Delta H source: MTQ3.11
#T and ionic strength: 0.00 25.0
2Be+2 + H2O = Be2OH+3 + H+
log_k    -3.177
delta_h  0      kJ
-gamma  6.5    0
#
#           Id: 1103305
#           log K source: NIST46.4
#           Delta H source: MTQ3.11
#T and ionic strength: 0.10 25.0
3Be+2 + 3H2O = Be3(OH)3+3 + 3H+
log_k    -8.8076
delta_h  0      kJ
-gamma  6.5    0
#
#           Id: 1103306
#           log K source: NIST46.4
#           Delta H source: MTQ3.11
#T and ionic strength: 0.10 25.0

Be+2 + F- = BeF+
log_k    5.249
delta_h  0      kJ
-gamma  0      0
#
#           Id: 1102701
#           log K source: NIST46.4
#           Delta H source: NIST46.4
#T and ionic strength: 0.50 25.0
Be+2 + 2F- = BeF2
log_k    9.1285
delta_h  -4     kJ
-gamma  0      0
#
#           Id: 1102702
#           log K source: NIST46.4
#           Delta H source: NIST46.4
#T and ionic strength: 0.50 25.0
Be+2 + 3F- = BeF3-
log_k    11.9085
delta_h  -8     kJ
-gamma  0      0
#
#           Id: 1102703
#           log K source: NIST46.4
#           Delta H source: NIST46.4
#T and ionic strength: 0.50 25.0

Be+2 + Cl- = BeCl+
log_k    0.2009
delta_h  0      kJ
-gamma  5      0
#
#           Id: 1101801
#           log K source: NIST46.4
#           Delta H source: MTQ3.11
#T and ionic strength: 0.70 20.0

Be+2 + Br- = BeBr+
log_k    0.1009
delta_h  0      kJ
-gamma  5      0
#
#           Id: 1101301
#           log K source: NIST46.4
#           Delta H source: MTQ3.11
#T and ionic strength: 0.70 20.0

Be+2 + SO4-2 = BeSO4
log_k    2.19
delta_h  29     kJ
-gamma  0      0
#
#           Id: 1107321
#           log K source: NIST46.4
#           Delta H source: NIST46.4
#T and ionic strength: 0.00 25.0
Be+2 + 2SO4-2 = Be(SO4)2-2
log_k    2.596
delta_h  0      kJ
-gamma  0      0
#
#           Id: 1107322
#           log K source: NIST46.4
#           Delta H source: MTQ3.11
#T and ionic strength: 1.00 25.0

Be+2 + CO3-2 = BeCO3
log_k    6.2546
delta_h  0      kJ

```

```

-gamma 0 0
# Id: 1101401
# log K source: NIST46.4
# Delta H source: MTQ3.11
#T and ionic strength: 3.00 25.0

```

PHASES

BeS

```

BeS + H+ = Be+2 + HS-
log_k 19.38
delta_h -0 kJ

```

Be (OH) 2 (am)

```

Be (OH) 2 + 2H+ = Be+2 + 2H2O
log_k 7.194
delta_h -0 kJ

```

Be (OH) 2 (alpha)

```

Be (OH) 2 + 2H+ = Be+2 + 2H2O
log_k 6.894
delta_h -0 kJ

```

Be (OH) 2 (beta)

```

Be (OH) 2 + 2H+ = Be+2 + 2H2O
log_k 6.494
delta_h -0 kJ

```

References

HydroGeoLogic Inc. & Allison Geoscience Consultants Inc. (1999): MINTEQA2/PRODEFA2, a geochemical assessment model for environmental systems: user manual supplement for version 4.0, EPA report, Athens, GE, USA. 76 pp.

Smith, R.M., Martell, A.E. & Motekaitis, R.J. (1997): NIST Standard Reference Database 46, NIST Critically Selected Stability Constants of Metal Complexes Database, Version 4.0. National Institute of Standards and Technology Standard Reference Data Program, Gaithersburg, MD, USA.

A6.6 Data for Bi written in PHREEQC format

There are no data for Bi in the Nagra/PSI Thermochemical Database 01/01. Unreviewed data for Bi were taken from Baes & Mesmer (1976).

SOLUTION_MASTER_SPECIES

```

Bi Bi+3 0.0 Bi 208.98

```

SOLUTION_SPECIES

```

Bi+3 = Bi+3
log_k 0.0
+1.000Bi+3 +1.000H2O -1.000H+ = BiOH+2
log_k -1.09
+1.000Bi+3 +2.000H2O -2.000H+ = Bi (OH) 2+
log_k -4.0
+1.000Bi+3 +3.000H2O -3.000H+ = Bi (OH) 3
log_k -8.86
-gamma 0.00 0.00
+1.000Bi+3 +4.000H2O -4.000H+ = Bi (OH) 4-
log_k -21.8

```

References

Baes, C.F., Jr. & Mesmer, R.E. (1976): The Hydrolysis of Cations. John Wiley & Sons, New York, 489 pp.