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National Cooperative for the
Disposal of Radioactive Waste

TECHNICAL
REPORT 02-22

Project Opalinus Clay

**Radionuclide Concentration
Limits in the Cementitious
Near-Field of an ILW Repository**

February 2003

U. Berner

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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.

PREFACE

The Laboratory for Waste Management of the Nuclear Energy and Safety Research Department at the Paul Scherrer Institut is performing work to develop and test models as well as to acquire specific data relevant to performance assessments of planned Swiss nuclear waste repositories. These investigations are undertaken in close co-operation with, and with the financial support of, the National Cooperative for the Disposal of Radioactive Waste (Nagra). The present report is issued simultaneously as a PSI-Bericht and a Nagra Technical Report.

NOTE: This report contains an addendum written by Nagra.

In this addendum solubility limits are presented that were used in the safety assessment of Project Opalinus Clay. The majority of these solubility limits corresponds to the ones derived in this report. In a few cases modified values or values not given in the report were used in the safety assessment. The rationale for these cases is given in the addendum.

ABSTRACT

The disposal feasibility study currently performed by Nagra includes a succession of quantitative models, aiming at describing the fate of radionuclides potentially escaping from the repository system. In this chain of models the present report provides the so called "solubility limits" (maximum expected concentrations) for safety relevant radionuclides from ILW wastes, disposed of in a chemically reducing, cementitious environment.

From a chemical point of view, the pore waters of hydrated cement matrices provide an exceptional environment. Compared with usual ground waters exhibiting pH-values of around 8, cement pore waters are strongly alkaline with pH-values from 12.5 to13.5 and contain nearly no carbonate and only little sulfate. Oxides and hydroxides mainly determine solubility and speciation of the elements.

Solubility and speciation calculations in cementitious pore waters were performed using the very recently updated Nagra/PSI Chemical Thermodynamic Data Base (TDB) for the majority of the 36 elements addressed as potentially relevant. Wherever possible, maximum concentrations compiled in this report were based on geochemical calculations. In order to ensure full traceability, all thermodynamic data not included in the TDB are explicitly specified in the document. For similar reasons the compilation of results (Table 1) clearly distinguishes between calculated and recommended items. The heading "CALCULATED" lists maximum concentrations based on data fully documented in the TDB; results under the heading "RECOMMENDED" include data from other sources.

The pH sensitivity of the results was examined by performing calculations at pH 13.4, in accordance with the pH of non-altered cement pore water. Solubility increases predominantly for elements that tend to form anionic hydroxide complexes (Sn, Pd, Zr, Ni, Eu, Cd, Mo, Co). Oxidizing conditions around +350 mV might be expected in the environment of nitrate-containing wastes. In this case, significant solubility increases were calculated for U, Np, Pu, Se and Ag.

Special attention is allocated to the uncertainties of the evaluated maximum concentrations, expressed as upper- and lower limits. The conceptual steps to determine these uncertainties are explained in the section 3. Due to lack of data, it was not always possible to assess uncertainties in a manner consistent with that used to assess the solubility limits. For some elements, uncertainties had to be derived from less sharply defined data or even with the help of estimates. Such less rigorous approaches are justified by the fact that in performance assessments particularly the upper limits are as important as are the maximum concentrations themselves. However, appropriate information was available to define an upper limit for nearly all of the relevant nuclides.

ZUSAMMENFASSUNG

Die Abfolge von Modellen zum "Entsorgungsnachweis 2002" der Nagra hat zum Ziel, das Verhalten der aus einem Endlager austretenden Radionuklide quantitativ zu beschreiben. Als ein Glied dieser Modellkette beschreibt die vorliegende Arbeit sogenannte "Löslichkeitslimiten", d.h. die maximalen, in den Porenwässern der Einschlussmaterialien gelösten Mengen sicherheitsrelevanter Nuklide. Das betrachtete chemische System enthält langlebige, mittelaktive Abfälle, welche in Zementmatrizen unter reduzierenden Bedingungen der geologischen Langzeitlagerung unterworfen werden.

Porenwässer von Zementmatrizen stellen aus chemischer Sicht eine extreme Umgebung dar. Im Vergleich zu üblichen Grundwässern (pH um 8) sind Zementporenwässer sehr stark alkalisch (pH im Bereich 12.5 bis 13.5), enthalten fast kein Carbonat und oft nur wenig Sulfat. Löslichkeit und Speziation der Elemente werden hauptsächlich durch Oxide und Hydroxide bestimmt.

Für die meisten der potentiell wichtigen 36 Elemente wurden Löslichkeit und Speziation im Porenwasser des Zementes mit Hilfe der neu überarbeiteten Nagra/PSI chemisch thermodynamischen Datenbank (TDB) evaluiert. Wenn immer möglich, sind die erarbeiteten Maximalkonzentrationen das Resultat einer geochemischen Modellrechnung. Im Sinne der Qualitätssicherung und Nachvollziehbarkeit sind alle thermodynamischen Grunddaten welche nicht in der überarbeiteten TDB enthalten sind, an entsprechender Stelle im Dokument aufgeführt. Aus ähnlichen Gründen unterscheidet die Zusammenstellung der Resultate in Tabelle 1 klar zwischen Rechnungen mit ausschliesslich überarbeiteten Daten (Kolonne "CALCULATED") und Evaluationen die auch "andere" Daten mit einschliessen (Kolonne "RECOMMENDED").

Die pH-Sensitivität der Resultate wurde durch zusätzliche Rechnungen bei pH 13.4, entsprechend dem Porenwasser von nicht gealtertem Zement, überprüft. Wie erwartet steigen vorwiegend die Löslichkeiten jener Elemente stark an, welche zur Bildung anionischer Hydroxokomplexe neigen (Sn, Pd, Zr, Ni, Eu, Cd, Mo, Co). In der näheren Umgebung stark nitrathaltiger Abfälle könnten sich oxidierende Bedingungen im Bereich um +350 mV einstellen. In dieser chemischen Umgebung ergeben sich für U, Np, Pu, Se und Ag signifikante Löslichkeitserhöhungen.

Den Unsicherheiten der berechneten Maximalkonzentrationen, ausgedrückt als obere- und untere Limite, wird ebenfalls spezielle Aufmerksamkeit gewidmet. Die konzeptuellen Schritte zur Bestimmung dieser Unsicherheiten sind im Abschnitt 3 dargelegt. Aus Mangel an Information war es nicht für alle Nuklide möglich, die Unsicherheiten in einer ähnlich strikt nachvollziehbaren Art und Weise zu erarbeiten wie die Maximalkonzentrationen. Für einige Elemente mussten deshalb die Unsicherheiten aus weniger scharf definierten Daten abgeleitet, oder teilweise sogar über Schätzungen festgelegt werden. Dies wird damit gerechtfertigt, dass den Unsicherheiten in der konkreten Anwendung zur Sicherheitsanalyse eine ähnlich wichtige Bedeutung zukommt wie den Maximalkonzentrationen selbst. Für fast alle relevanten Nuklide standen aber angemessene Informationen zur Festlegung des oberen Grenzwertes zur Verfügung.

RÉSUMÉ

L'étude de faisabilité d'entreposage de la Nagra (Cedra), actuellement en cours, inclut une chaîne de modèles quantitatifs visant à décrire le comportement des radionuclides pouvant s'échapper du dépôt. Dans cette chaîne de modèles, le présent rapport fournit les ainsi nommées "solubilités limites" (les concentrations maximales attendues) des radionuclides importants pour la sûreté des dépôts de LMA posés dans un environnement réducteur du ciment.

D'un point de vue chimique les eaux interstitielles des matrices hydratées de ciment fournissent un environnement exceptionnel. Comparé aux eaux souterraines habituelles montrant des valeurs pH autour de 8, les eaux interstitielles de ciment sont fortement alcalines avec des valeurs pH de 12.5 à 13.5 et ne contiennent presque pas de carbonate et seulement peu de sulfate. Les oxydes et les hydroxydes déterminent principalement la solubilité et la spéciation des éléments.

Les calculs de solubilité et de spéciation dans les eaux interstitielles de la bentonite ont été exécutés pour la majorité des 36 éléments réputés potentiellement importants en utilisant la base de données thermodynamique chimique (TDB) de la Nagra et du PSI très récemment mise à jour. Si possible, les concentrations maximales compilées dans ce rapport dépendent des calculs de modélisation géochimique. Toutes les données thermodynamiques non incluent dans la TDB (Nagra/PSI) sont explicitement indiquées dans le rapport afin de fournir une documentation complète garantissant la qualité et bien compréhensible. Pour des raisons analogues la compilation des résultats (tableau 1) distingue clairement entre résultats calculés et recommandés. Les concentrations maximales basées sur des données entièrement documentées dans la TDB remise à jour sont présentées sous le titre "CALCULATED", tandis que les concentrations maximales, incluant des données d'autres sources, sont apparaissent sous la rubrique "RECOMMENDED".

La sensibilité des résultats au pH a été examinée en exécutant des calculs à pH 13.4, le pH de l'eau interstitielle pour ciment non altéré. La solubilité augmente principalement pour les éléments tendant à former des complexes anioniques d'hydroxyde (Sn, Pd, Zr, Ni, Eu, Cd, Mo, Co). Des conditions d'oxydation autour de +350 mV sont prévues dans l'environnement des déchets contenants du nitrate. Dans ce cas, des augmentations significatives de solubilité ont été calculées pour U, Np, Pu, Se et Ag.

Une attention particulière est portée aux incertitudes des concentrations maximales évaluées, exprimées par des limites supérieures et inférieures. Les étapes conceptuelles pour déterminer ces incertitudes sont expliquées dans la section 3. En raison d'un manque de données et de connaissances, il n'a pas toujours été possible d'évaluer les incertitudes d'une manière conforme à celle utilisée pour évaluer les concentrations maximales. Pour quelques éléments il a été nécessaire d'utiliser des informations d'origine moins fiable ou même de se baser sur des estimations pour fournir des incertitudes. Cette approche moins rigoureuse est justifiée par le fait que les incertitudes (en particulier les limites supérieures) sont considérées aussi importantes que les concentrations maximales elles-mêmes dans les analyses de sécurité.

Cependant, information appropriée était disponible en mesure suffisante pour définir la limite supérieure de presque tous les nuclides importants.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

1   INTRODUCTION AND SUMMARY OF RESULTS

The aim of the present work is to provide the so called "solubility limits" (maximum expected concentrations) for safety-relevant radionuclides present in intermediate level wastes (ILW), for a repository in a reducing cementitious environment in Opalinus Clay. The report defines the basis for the actual numerical values needed as input parameters in the ongoing disposal feasibility study (Entsorgungsnachweis).

Solubility limits for spent fuel and vitrified high-level waste (SF/HLW) disposed of in reducing clay environments have been provided very recently (BERNER 2002). Due to large amounts of cementitious matrix, construction, and backfill materials, ILW wastes are present in a completely different chemical environment than the SF/HLW wastes. The most important attribute of cementitious environments is a high to very high pore water pH of 12.5 to 13.5, generated by portlandite- and alkali hydroxide dissolution. Further attributes of the cementitious environment are much lower sulphate concentrations if compared to the Opalinus Clay pore water and the almost complete absence of carbonate. Hence, solubility and speciation will be controlled mainly by hydroxides. These very different chemical conditions require a separate analysis.

Solubility and speciation calculations were performed using the updated Nagra/PSI Chemical Thermodynamic Data Base 01/01 (HUMMEL et al. 2002) for the majority of the 36[1] elements. Since the reference case of the disposal feasibility study rests upon a reference temperature of 25 °C[2], all model calculations performed in this work refer to this reference temperature.

Wherever possible, presented maximum concentrations were based on geochemical calculations. Thus, it is very important that the underlying data and particularly the assumptions are made clear to the reader. Therefore, all thermodynamic data not included in the Nagra/PSI Chemical Thermodynamic Data Base 01/01 are explicitly specified in this report.

Calculations were performed for reference conditions as defined in section 2. In order to clearly distinguish between results derived from data carefully reviewed in the Nagra/PSI Chemical Thermodynamic Data Base 01/01 and results calculated with thermodynamic data from other sources, the summary of

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[1]   Based on scoping calculations with very rough system parameters, Nagra identified 36 elements as potentially relevant nuclides. Using refined system parameters, several were screened out in a later stage of the safety assessment studies.

[2]   The reference temperature at 650 m depth is 38 °C. It may be argued that this is sufficiently close to 25 °C, the usual and general reference temperature of thermodynamic databases.

expected maximum concentrations provided in Table 1 includes two columns. The column headed "CALCULATED" provides maximum concentrations based on data fully documented in the Nagra/PSI Chemical Thermodynamic Data Base 01/01 (HUMMEL et al. 2002). Modelled maximum concentrations that include data from other sources, estimates or conclusions by analogy are given under the heading "RECOMMENDED".

Calculations were also performed for increased pH-values (initial stage pore water, pH 13.4) in order to check the pH-sensitivity of the calculated solubilities. As expected, significant increases were found mainly for elements known to form anionic hydroxide complexes (i.e. Sn, Pd, Zr, Ni, Eu, Cd, Mo, Co, Be). Nitrate dissolving from specific waste products may lead to an oxidising environment (mimicked by +350 mV), which influences the elements U, Np, Pu, Se and Ag.

The present study also pays specific attention to the uncertainties in the evaluated maximum concentrations and represents them as lower- and upper limits. The conceptual steps for deriving uncertainties are outlined in section 3. Due to lack of data/knowledge, it was not always possible to assess uncertainties in strictly the same manner as used in assessing the maximum concentrations. In a number of cases, it was necessary to rely on less well traceable information or even on estimates to provide uncertainties. This (less rigorous) approach is justified by the fact that uncertainties (particularly the upper limits) are deemed as important as the maximum concentrations themselves.

Table 1: Expected maximum radionuclide concentrations in cementitious pore waters at the reference conditions pH 12.55, Eh -230 mV and 25 °C, as CALCULATED with the updated Nagra/PSI Thermochemical Data Base Version 01/01. RECOMMENDED maximum concentrations are provided when "other" thermodynamic data and/or problem specific data including estimates or conclusions by analogy were used to derive limits. Concentrations are given as [mol/l].

Element	CALCULATED			RECOMMENDED			Limiting solid / Comments / Basis for limits
	Lower limit	Maximum solubility	Upper limit	Lower limit	Maximum concentration	Upper limit	
Cm	–	–	–	$3 \cdot 10^{-10}$	$2 \cdot 10^{-9}$	$1 \cdot 10^{-8}$	No data; Am used as analogue
Am	$3 \cdot 10^{-10}$	$2 \cdot 10^{-9}$	$1 \cdot 10^{-8}$	–	–	–	$Am(OH)_3(am)/Am(OH)_3(aq)$; crystalline form not certain (self-irradiation); limits: formal error propagation
Pu	$1 \cdot 10^{-11}$	$4 \cdot 10^{-11}$	$2 \cdot 10^{-10}$	–	–	–	$PuO_2(hyd, aged)$; $Pu(OH)_4(aq)$ dominant; up_limit: Pu(III) formation at low Eh; low_limit: formal error propagation
Np	$3 \cdot 10^{-9}$	$5 \cdot 10^{-9}$	$1 \cdot 10^{-8}$	–	–	–	$NpO_2(hyd, am)$; $Np(OH)_4(aq)$ dominant; limits: formal error propagation
U	–	not limited	–	–	$1 \cdot 10^{-8}$	$5 \cdot 10^{-7}$	Recommendation based on independent exp. findings (BERNER 1999); up_limit: solubility of α-$Na_2U_2O_7$ (GRENTHE et al. 1992)
Pa	–	–	–	–	$\sim 10^{-8}$	–	Estimate, no data available
Th	$8 \cdot 10^{-10}$	$3 \cdot 10^{-9}$	$1 \cdot 10^{-8}$	–	–	–	$ThO_2(s)$; $Th(OH)_4(aq)$ dominant; limits: formal error propagation
Ra	–	$1 \cdot 10^{-5}$	–	$1 \cdot 10^{-6}$	–	$2 \cdot 10^{-2}$	$RaSO_4(s)$; dissolved SO_4^{2-} is critical issue; up_limit: solubility control by $RaCO_3(s)$; low_limit: factor of 10, from potential variation of sulfate
Cs	–	not limited	–	–	–	–	No limiting solid available
I	–	not limited	–	–	–	–	No limiting solid available

Element	CALCULATED			RECOMMENDED			Limiting solid / Comments / Basis for limits
	Lower limit	Maximum solubility	Upper limit	Lower limit	Maximum concentration	Upper limit	
Tc	–	not limited	–	–	–	–	TcO_4^- dominant above -350 mV
Nb	–	not limited	–	–	–	–	Very small database
Se	–	not limited (~0.1)	–	$7 \cdot 10^{-6}$	$1 \cdot 10^{-5}$	$2 \cdot 10^{-5}$	$1 \cdot 10^{-5}$ based on $CaSeO_3(s)$ from SHARMASARKAR et al. (1996); ~0.1 mol/l based on Se(cr); limits: formal error propagation
Cl	–	not limited	–	–	–	–	No limiting solid; system definition $1.6 \cdot 10^{-1}$ derived from Opalinus Clay pore water.
C_{inorg}	–	–	–	–	$9.7 \cdot 10^{-6}$	$2.0 \cdot 10^{-4}$	$CaCO_3(s)$ saturation; $CH_4(g)$ and $C_{organic}$ not considered; up_limit: solubility at pH 13.44
Ac	–	–	–	$4 \cdot 10^{-9}$	$2 \cdot 10^{-6}$	$2 \cdot 10^{-5}$	No data; Eu(III) used as analogue
Sn	$1 \cdot 10^{-7}$	$1 \cdot 10^{-7}$	$2 \cdot 10^{-7}$	–	–	–	$Ca[Sn(OH)_6](s)$; Sn^{2+} not stable; limits: formal error propagation
Pd	–	insignificantly low	–	$8 \cdot 10^{-8}$	$8 \cdot 10^{-7}$	$8 \cdot 10^{-6}$	Calculated: $Pd(0)/Pd(OH)_3^-$; recommended: $Pd(OH)_2(precip.)/Pd(OH)_3^-$; limits: ± 1 log_{10}-units estimated from scatter of exp. data
Zr	–	$6 \cdot 10^{-6}$	–	$6 \cdot 10^{-7}$	–	$6 \cdot 10^{-5}$	$ZrO_2(s)$; limits: ± 1 log_{10}-units estimated from scatter of experimental data
Sr	–	$3 \cdot 10^{-3}$	–	$1 \cdot 10^{-3}$	–	$6 \cdot 10^{-3}$	$SrCO_3(s)$; limits: uncertainty of $\Delta_f G^0$ from ROBIE & HEMINGWAY (1995)
Ni	$1 \cdot 10^{-8}$	$3 \cdot 10^{-7}$	$8 \cdot 10^{-6}$	–	–	–	$Ni(OH)_2(cr)$; $Ni(OH)_3^-$ dominant; limits: formal error propagation
Po	–	–	–	–	–	–	No data available
Pb	–	–	–	–	$3 \cdot 10^{-3}$	$2 \cdot 10^{-2}$	$Pb(OH)_2(s)$; $Pb(OH)_3^-$ dominant; up_limit: solubility calculation at pH 13.44
Hf	–	–	–	$6 \cdot 10^{-7}$	$6 \cdot 10^{-6}$	$6 \cdot 10^{-5}$	No data; Zr used as analogue

Element	CALCULATED			RECOMMENDED			Limiting solid / Comments / Basis for limits
	Lower limit	Maximum solubility	Upper limit	Lower limit	Maximum concentration	Upper limit	
Ho	–	–	–	$4 \cdot 10^{-9}$	$2 \cdot 10^{-6}$	$2 \cdot 10^{-5}$	No data; Eu used as analogue
Eu	–	$2 \cdot 10^{-6}$	$2 \cdot 10^{-5}$	$4 \cdot 10^{-9}$	–	–	$Eu(OH)_3(am)/Eu(OH)_4^-$; crystalline form yields $4 \cdot 10^{-9}$ mol/l; up_limit: $Eu(OH)_3(cr)$; low_limit: formal error propagation
Pm	–	–	–	$4 \cdot 10^{-9}$	$2 \cdot 10^{-6}$	$2 \cdot 10^{-5}$	No data; Eu used as analogue
Sb	–	not limited	–	–	–	–	$Sb(OH)_6^-$ dominant; Sb(cr) stable below -600 mV
Cd	–	–	–	–	$4 \cdot 10^{-6}$	$3 \cdot 10^{-5}$	$Cd(OH)_2(s)$; $Cd(OH)_3^-$ dominant; up_limit: solubility calculation at pH 13.44
Ag	–	–	–	–	insignificantly low	$3 \cdot 10^{-6}$	Ag(cr): HUMMEL (2001); up_limit: solubility of AgCl(s)
Ru	–	–	–	–	–	high	No data available; up_limit: based on BAES & MESMER (1976)
Mo	–	–	–	–	$3 \cdot 10^{-5}$	$2 \cdot 10^{-3}$	$CaMoO_4(s)$; data very sparse; up_limit: solubility calculation at pH 13.44
Co	–	–	–	–	$7 \cdot 10^{-7}$	$8 \cdot 10^{-6}$	$Co(OH)_2(s)$; $Co(OH)_2(aq)$, $Co(OH)_3^-$ and $Co(OH)_4^{2-}$ dominant; up_limit: solubility calculation at pH 13.44
Fe	–	–	–	–	$1 \cdot 10^{-7}$	$1 \cdot 10^{-6}$	$Fe_3O_4(s)$, Fe(II) hydrolysis data from BAES & MESMER (1976); up_limit: control by magnetite and $Fe(OH)_3$(micro-cryst.)
Ca	–	$2 \cdot 10^{-2}$	–	$1.8 \cdot 10^{-2}$	–	$2.2 \cdot 10^{-2}$	$Ca(OH)_2(s)$ / $CaCO_3(s)$ / $CaF_2(s)$; system definition; limits: formal error propagation
Be	–	–	–	–	–	high	No data available; based on BAES & MESMER (1976)

2   REFERENCE CONDITIONS FOR THE PRESENT REPORT

2.1   Pore water compositions

The basic assumptions and compositions for defining the reference cement pore waters used throughout this report were taken from SCHWYN et al. (2003). Detailed underlying information is not repeated here, the reader is referred to the above report and the references therein. Model calculations to obtain the reference water compositions were performed using thermodynamic data given in HUMMEL et al. (2002). The resulting *reference cement pore water*, the *initial stage pore water* and the *oxidising nitrate pore water* are provided in Table 2.

Reference cement pore water: This pore water describes the situation where cementitious matrices have reacted with the Opalinus Clay pore water. Sufficient time has elapsed for the alkali hydroxides to diffuse out of the cement matrix and (sodium-) chloride from the host rock has diffused into the cement pore space. This reference cement pore water was defined by assuming saturation with portlandite, calcite, brucite and fluorite. Its redox conditions range from -750 to -230 mV (see next section).

Initial stage pore water: This pore water describes an early situation of cement degradation, where the hydrated cement is still in equilibrium with its original pore water. Thus, the full cement alkali hydroxide inventory is still present, producing a hyper alkaline pore water of pH 13.4. Since exchanges with the Opalinus Clay pore water have not yet taken place, this pore water does not contain Cl^-.

The reason for considering this initial phase pore water is to study the sensitivity of calculated solubilities against pH. This may be particularly relevant for elements that form anionic complexes. Note that Eh changes associated with this pore water (i.e. -430 mV) were not considered in corresponding solubility calculations.

Oxidising nitrate pore water: A small portion of specific wastes includes substantial amounts of soluble nitrates. Hence, performance assessment has to allow for nitrate concentrations up to 0.5 mol/l in the cement pore water. Such high nitrate concentrations may lead to oxidising conditions. Using available thermodynamic data for the N(V)/N(0) redox couple, WERSIN et al. (2003) suggest an Eh of about +350 mV (to be precise, the formally calculated value was +346 mV), when oxidising conditions need to be considered.

Table 2: Reference cement pore water compositions at 25 °C as used in the present work. Total concentrations are given in [mol/l].

Component	Reference cement pore water	Initial stage pore water	Oxidising nitrate pore water
Na^+	$1.69 \cdot 10^{-1}$	$1.01 \cdot 10^{-1}$	$6.69 \cdot 10^{-1}$
K^+	$5.7 \cdot 10^{-3}$	$3.03 \cdot 10^{-1}$	$5.7 \cdot 10^{-1}$
Mg^{2+}	$1.126 \cdot 10^{-7}$	$1.3 \cdot 10^{-8}$	$1.126 \cdot 10^{-7}$
Ca^{2+}	$2.009 \cdot 10^{-2}$	$8.43 \cdot 10^{-4}$	$2.009 \cdot 10^{-2}$
Al^{3+}	$5.0 \cdot 10^{-6}$	$1 \cdot 10^{-5}$	$5.0 \cdot 10^{-6}$
Cl^-	$1.6 \cdot 10^{-1}$	–	$1.6 \cdot 10^{-1}$
F^-	$1.042 \cdot 10^{-4}$	$7.6 \cdot 10^{-4}$	$1.042 \cdot 10^{-4}$
CO_3^{2-}	$9.74 \cdot 10^{-6}$	$2.04 \cdot 10^{-4}$	$9.74 \cdot 10^{-6}$
SO_4^{2-}	$1.0 \cdot 10^{-4}$	$7.5 \cdot 10^{-4}$	$1.0 \cdot 10^{-4}$
$H_2SiO_4^{2-}$	$1.6 \cdot 10^{-5}$	$5 \cdot 10^{-5}$	$1.6 \cdot 10^{-5}$
NO_3^-	–	–	$5 \cdot 10^{-1}$
Charge balance	$-5.45 \cdot 10^{-2}$	$-4.029 \cdot 10^{-1}$	$-5.45 \cdot 10^{-2}$
pH	12.55	13.44	12.52
Eh	-750 to -230 mV	-430[1] mV	+350 mV
Ionic strength	0.224 mol/l	0.374 mol/l	0.722 mol/l
Saturated phases			
	fluorite	fluorite	fluorite
	brucite	brucite	brucite
	calcite	calcite	calcite
	portlandite	portlandite	portlandite

[1] See note at the end of section 2.2

2.2   Redox conditions in reference cement pore water

The principal assumptions made to define redox conditions in cement pore waters are similar to those used for defining redox conditions in Opalinus Clay environments. Detailed descriptions are provided in WERSIN et al. (2003). The basic assumptions are that

i)   Redox conditions are principally defined through the Fe^{3+}/Fe^{2+} couple, and

ii)   Magnetite is the major corrosion product; it is in equilibrium with the cement pore water and its solubility forms an important part of the definition of Eh.

This leads to a large range of possible redox potentials. A sensitivity analysis revealed that different combinations of iron bearing solids (including sulphides) might produce an Eh range from -750 to -230 mV. It is not clear at present, which of the various possible combinations of iron-bearing phases will actually

form under repository conditions, and which phase assembly will determine redox potentials.

Note the extra use of the following thermodynamic data for Fe(II)-hydrolysis, taken from HUMMEL (2001) and based on BAES & MESMER (1976):

$$Fe^{2+} + 2\ H_2O \Leftrightarrow Fe(OH)_2(aq) + 2\ H^+ \qquad \log_{10}\beta_2° = -20.6 \pm 1.0$$

$$Fe^{2+} + 3\ H_2O \Leftrightarrow Fe(OH)_3^- + 3\ H^+ \qquad \log_{10}\beta_3° = -31 \pm 1.5.$$
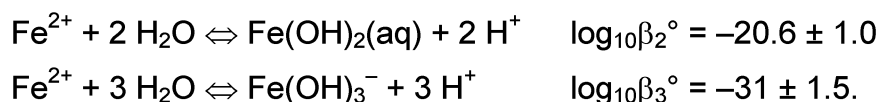
These equilibria are not included in the Nagra/PSI Chemical Thermodynamic Data Base 01/01 (HUMMEL et al. 2002), but in high pH environments it is essential to provide data for the higher hydrolysis complexes.

There is sufficient experimental evidence that very low iron concentrations will be established in cement pore waters, most likely controlled by sparingly soluble calcium-aluminate-ferrite phases. A reliable thermodynamic characterisation of such calcium-aluminate-ferrites is still missing, but there is evidence that total dissolved iron does not exceed about 10^{-7} mol/l (SAROTT et al. 1993). Together with the assumption of magnetite saturation, this restriction of iron solubility helps defending a "reference" redox potential of -230 mV (-226 mV to be very precise), close to the upper limit of the range mentioned above.

Note on redox potential of initial stage pore water: This pore water was calculated to be much more reducing than the reference pore water. Finally, the stability of Fe(III)(OH)$_4^-$ produces an Eh of -430 mV at pH 13.44, when using the same redox model as for the reference pore water. As mentioned above, the *initial pore water composition* was only considered to study the impact of varying pH on solubilities. Hence, and in order to clearly distinguish dependencies on pH from those on Eh, calculations performed with this pore water did not consider the altered redox potential but arbitrarily kept the reference Eh of -230 mV. Variations of Eh at pH 13.44 were not performed within the scope of this work. Although this may lead to some inconsistencies, it has no consequences for Sn, Pd, Zr, Ni, Eu, Cd, Mo, Ca and Be.

2.3   Calculation procedures and how to interpret solubility limits

Establishing solubility limits strongly relies on the updated Nagra/PSI Chemical Thermodynamic Data Base 01/01 (HUMMEL et al. 2002). A clear differentiation is made between "calculated" maximum concentrations and "recommended" maximum concentrations. Results provided in Table 1 belong to either of these categories. If no updated thermodynamic data are available for a particular element, no "calculated" maximum solubility is given. However, in these cases

a maximum concentration in solution is recommended based on other criteria and/or on thermodynamic data specified in the body of the text.

Several of the safety-relevant elements belong to the class of "system defining elements" (e.g. Ca, Cl, Fe). Their maximum concentrations were consequently taken from the corresponding system definition (Table 2).

Calculated maximum concentrations (solubility limits) were derived at the nominal system Eh of -230 mV. Furthermore, the solubility limits were calculated in an extended range from -750 to -230 mV for the redox-sensitive elements Pu, Np, U, Tc, Se, Pd, Sb and Ag. In order to illustrate the potential impact of Eh, the behaviour of Pu, Np, Tc and Se was in addition visualised in the entire redox stability field of aqueous solutions.

Solubility limits were obtained as follows: The geochemical code (MINEQL/PSI) was fed with a given volume of the reference solution as shown in Table 2 and was then "spiked" with increasing amounts of the element in question, using Na^+ or OH^- as counter-ions. The rules of thermodynamics say that the maximum possible concentration (solubility limit) in this chemical system is obtained when, according to the present contents of the database, saturation with the most stable solid appears. If the reference solution itself is not changed to any significant degree by this process, such procedures work well in most cases, and particularly when limits are low. It is clearly presupposed that the thermodynamic database includes sufficiently relevant solids and complexes.

Calculations were performed using the Davies equation for ionic strength corrections (note the restricted applicability of Davies' approach in solutions exceeding I ~ 0.3 mol/l, i.e. the *initial stage* and the *oxidising* pore water).

Eh variations were generated by predefining the redox potential prior to calculations, which means artificially fixing the activity of the "electron-component". Such simplified procedures work when only very low concentrations of redox-sensitive elements are involved (e.g. actinides well below ~10^{-7} mol/l) and when preliminary "what-if" type questions need to be answered.

However, consistency problems with concepts and assumptions concerning the reference chemical system may arise, particularly when full details of all involved redox equilibria need to be studied and varied simultaneously (see note on Eh of initial stage pore water). The "electron-component" often used in geochemical codes is just a very helpful dummy that must not be varied independently. Unlike HCl or KOH, "Eh" cannot be added from a bottle. Varying the redox potential is always associated with varying the principal redox equilibrium (in this case the magnetite/Fe(III)/Fe(II)-system at about 10^{-7} mol/l

of total dissolved iron). Depending on the actual redox potential, the nuclide in question may interfere with this principal redox equilibrium (e.g. U, Tc, Se) when its buffer capacity exceeds the indicated threshold value. In such a case, the underlying information behind the definition of the reference pore water would change accordingly.

2.4   Database

The basic source of data is the updated Nagra/PSI Chemical Thermodynamic Data Base 01/01 (HUMMEL et al. 2002), abbreviated as Nagra/PSI TDB. This database was developed for calculating chemical equilibria under conditions that are relevant for performance assessment studies. After critical appraisal, thermodynamic data for U, Np, Pu, Am and Tc were taken over from corresponding NEA-publications. Extensive in-house reviews were performed for Th, Sn, Eu, Pd, Al, Zr, Ni, Se, for sulphides and for silicates. The data selection procedures for each recommended quantity were fully documented. Empirical and semi-empirical correlations were used to demonstrate the overall chemical consistency of the selected equilibrium constants. Importance was attached to the assessment of the accuracy of the provided values. Conflicting, uncertain and missing data were identified, discussed and complemented where appropriate.

The Nagra/PSI TDB includes formation constants almost exclusively based on experimental findings. Only a few formation constants were estimated using various evaluation methods for a distinct number of inevitable cases. However, it should be pointed out that thermodynamic data for high-pH systems are generally scarce, which is also true for the updated TDB. This should be taken into account when appraising the results provided in this report.

Operational database files are provided in THOENEN (2001) (comprehensive data collections and PHREEQC files) and in BERNER (2001) (MINEQL files) or maybe downloaded from "http://les.web.psi.ch/TDBbook". For elements where no thermodynamic data are included in the database update, older compilations or specifically selected values were used. In all these cases, the relevant equilibria used to perform the calculations are explicitly given in the text body (for T = 25 °C).

Temperature corrections: The Nagra/PSI TDB does not include temperature dependencies of reaction data for all species, minerals and gases. The "official" use of the TDB is therefore restricted to 25 °C. Model calculations performed at temperatures other than 25 °C, although practicable for specific and well selected systems, could introduce into the results significant inconsistencies

that are difficult to control. Based on literature data and relying on extrapolations using isocoulombic reactions, THOENEN et al. (2002) produced a set of equilibrium constants for Am, Pu, Np, U, Th and Tc for use at 50 °C. Unfortunately, this set of constants is restricted for use in bentonite pore waters. A similar set, dedicated for use in cementitious pore waters does not yet exist. Thus, calculations at temperatures other than 25 °C were not performed for this study.

3   UNCERTAINTIES

The present report generally considers two types of uncertainties. A first type is related to the uncertainties of the thermodynamic constants provided in the database. Another type of uncertainty, related to redox-sensitive elements and probably better labelled "results of sensitivity analyses" than "uncertainty", might arise from varying system Eh in the range [-750...-230] mV.

The operational version of the TDB does not include any uncertainties, although uncertainties have been addressed for most of the reviewed equilibria and are provided in HUMMEL et al. (2002). Uncertainties are thus not carried through the geochemical calculation.

In many cases, the maximum concentration of an element may be adequately approximated by a solubility constant and by the formation constant(s) of the major complex(es) in solution. Often, only one complex in solution is relevant and, at most, three to four different complexes need to be considered. As a first approximation, the uncertainty of the calculated maximum concentration may therefore be estimated from the uncertainty of the solubility product and from the uncertainty of the formation constants using the error propagation method proposed by the NEA (GRENTHE et al. 1992).

As a rule, upper and lower limits as provided in Table 1 (and in the text body) are derived from such formal error propagation. However, if uncertainties for thermodynamic equilibria are not available, or if the variation of Eh in the range [-750...-230] mV produces a larger uncertainty bandwidth than the formal error propagation, then this larger range is selected. In principle, the addressed types of "uncertainties" (as well as many others not addressed in this work) are independent of each other and should be accumulated using appropriate error propagation methods. This has not been done in the present report.

Note that all types of "uncertainties" are lumped together under the heading "RECOMMENDED" in Table 1. However, clarifying details are always given in the specific element section and/or may be derived from corresponding figures.

The formal error propagation is not always a straightforward procedure. Uncertainties may be highly correlated. This often reflects the difficulties in deriving independent thermodynamic data from experiments that are not suited to this application. Therefore, a more detailed uncertainty analysis also requires analysing the type of available experimental data and one needs to go far beyond an "inspection" of the database.

Example: Consider the Pu-system at -230 mV, which is fully determined by the solubility of PuO_2(hyd, am) and by the dominant aqueous complex $Pu(OH)_4$(aq). Propagating the formal uncertainties of the two relevant equilibria as provided in the TDB (HUMMEL et al. 2002) would produce an uncertainty of $(1^2 + 1.1^2)^{1/2}$ = ± 1.49 log_{10}-units in the calculated solubility, but the two equilibria were derived from the measured solubility according to PuO_2(hyd, am) + 2 H_2O $\Leftrightarrow$ $Pu(OH)_4$(aq) with $log_{10}K_{s,4}°$ = -10.4 ± 0.5 (NECK & KIM 2001). Hence, the actual uncertainty is only ± 0.5 log_{10}-units and not ± 1.49 log_{10}-units in this particular case.

However, below ~ -700 mV $Pu(III)(OH)_3$(aq) may become important, when the data for trivalent actinides as proposed in BERNER (2002; Table 5 therein) are used in addition to the data given in HUMMEL et al. (2002). Since total dissolved Pu may then increase by a factor of 5, an asymmetric uncertainty range of +0.7/-0.5 log_{10}-units results.

Uncertainties related to pH were only partly considered in this report:

The "initial stage pore water" having a pH of 13.4 was defined in section 2.1, because of the substantial alkali hydroxide inventories of the cements. Solubility limits were also checked at this pH for elements potentially affected by increased hydroxide concentrations (i.e., for Se, C_{inorg}, Sn, Pd, Zr, Ni, Pb, Eu (including Ac, Ho and Pm derived thereof), Cd, Mo and Co). Indeed, increased solubilities were found at elevated pH. In the case of C_{inorg}, Pb, Cd, Mo and Co, the calculated "pH 13.4 solubility" was taken to fix the upper limit.

However, the basic decision of what pH would be an appropriate selection for the "reference cement pore water" depends on the duration of the initial phase, which itself depends on how fast alkali hydroxides are leached from the cement structure. SCHWYN et al. (2003) attempted to mimic the disappearance of alkali hydroxides from the repository with the help of a simple diffusion model using constant concentration boundaries at the clay interface. On this basis, they concluded that an initial stage phase would last a few ten thousand years.

4   EVALUATION OF CONCENTRATION LIMITS

4.1   Curium

Since the Nagra/PSI TDB does not provide data for curium, it is recommended to use the chemically similar Am as an analogue. This is supported by the fact that, vice versa, experimental studies sometimes use Cm(III) to mimic Am(III) (Cm is much more easily accessible through spectroscopic methods).

4.2   Americium

The Am system does not depend on Eh, thus Am(III) is the only relevant redox state. Limiting solids are either Am(OH)$_3$(cr) or Am(OH)$_3$(am), the dominant complex in solution is Am(OH)$_3$(aq) (98.3 %, Table 3). The most stable solid in the system would be Am(OH)$_3$(cr), but there is not enough information to reliably defend a transition from Am(OH)$_3$(am) to Am(OH)$_3$(cr) (HUMMEL et al. 2002). Therefore, the amorphous hydroxide is selected as the limiting solid and the calculated maximum concentration is

$$2.0 \cdot 10^{-9} \text{ mol/l.}$$

Uncertainties arise from the solubility product ($\pm$ 0.6 log$_{10}$-units) and from the formation constant of Am(OH)$_3$(aq) ($\pm$ 0.5 log$_{10}$-units). Propagating the corresponding uncertainty values (HUMMEL et al. 2002) in a formal way, produces an uncertainty of $\pm$ 0.78 log$_{10}$-units (($0.6^2 + 0.5^2$)$^{1/2}$ = 0.78).

upper limit: $1.2 \cdot 10^{-8}$ mol/l
lower limit: $3.3 \cdot 10^{-10}$ mol/l.

The anionic complex Am(OH)$_4{}^-$ does not exist. Therefore, calculations at pH 13.44 were not performed.

Table 3: Am solubility and speciation in cement pore waters.

	pH 12.55
Am(OH)$_3$(cr)	$3.2 \cdot 10^{-11}$ mol/l
Am(OH)$_3$(am)	$2.0 \cdot 10^{-9}$ mol/l
Speciation: [%]	
Am(OH)$_2{}^+$	1.2
Am(OH)$_3$(aq)	98.8

4.3   Plutonium

Plutonium is a redox-sensitive element which may appear in the oxidation states +III, +IV, +V and +VI, but present thermodynamic data favour Pu(IV) species and solids over a very large Eh range (-700 to +350 mV) under cement pore water conditions.

At -230 mV the Pu-system is fully determined by the solubility of $PuO_2(hyd, am)$ and by the dominant complex $Pu(OH)_4(aq)$. The calculated limit is

$$4.0 \cdot 10^{-11} \text{ mol/l.}$$

Propagating the formal uncertainties of the relevant equilibria (HUMMEL et al. 2002) would produce an uncertainty of ± 1.49 $\log_{10}$-units for the calculated total solubility, but the two equilibria were derived from the measured solubility according to $PuO_2(hyd, am) + 2 H_2O \Leftrightarrow Pu(OH)_4(aq)$ with $\log_{10}K_{s,4}° = -10.4 \pm 0.5$ (NECK & KIM 2001). This considerably smaller uncertainty would produce an upper limit of $1.3 \cdot 10^{-10}$ mol/l. However, at Eh values below ~ -700 mV $Pu(III)(OH)_3(aq)$ may become important when, in addition to the data given in HUMMEL et al. (2002), hydrolysis data for trivalent plutonium as proposed by BERNER (2002; Table 5 therein) in analogy to Am(III) are used ($\log\beta_2°(Pu(OH)_2^+)$ = -14.8; $\log\beta_3°(Pu(OH)_3(aq))$ = -25.3). In the case of $Pu(III)(OH)_3(aq)$ formation, total solubility may increase to $2.0 \cdot 10^{-10}$ mol/l, whereas Pu(IV) is dominant and the solubility remains constant in the Eh range -700 to -230 mV, as can be seen from Fig. 1. Independent of whether LEMIRE et al. (2001), and subsequently HUMMEL et al. (2002) do provide formation constants or not, the hydrolysis of Pu^{3+} will undoubtedly take place at high pH. Thus, the upper limit is based on the potential formation of $Pu(III)(OH)_3(aq)$ at very low redox potentials:

upper limit: $2.0 \cdot 10^{-10}$ mol/l
lower limit: $1.3 \cdot 10^{-11}$ mol/l

Increased solubilities are to be expected above ~ +350 mV, where Pu(V) and Pu(VI) become important. Table 4 includes the calculated solubility at +350 mV, but one should recognise that the slope Pu_{tot} vs. Eh is very steep above +350 mV (Fig. 1).
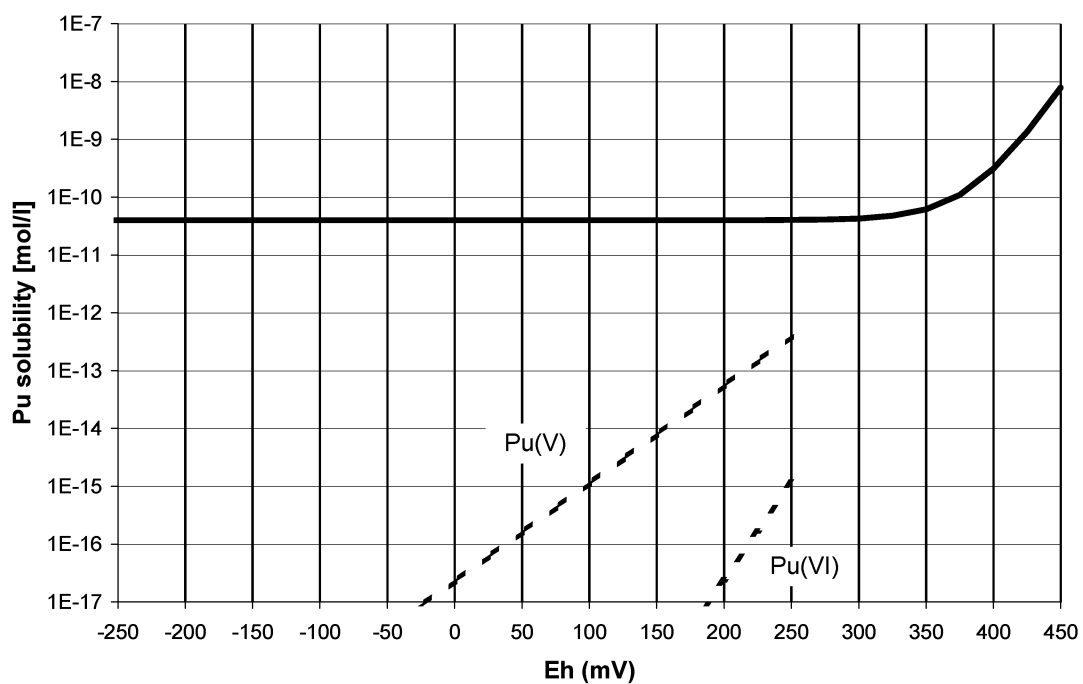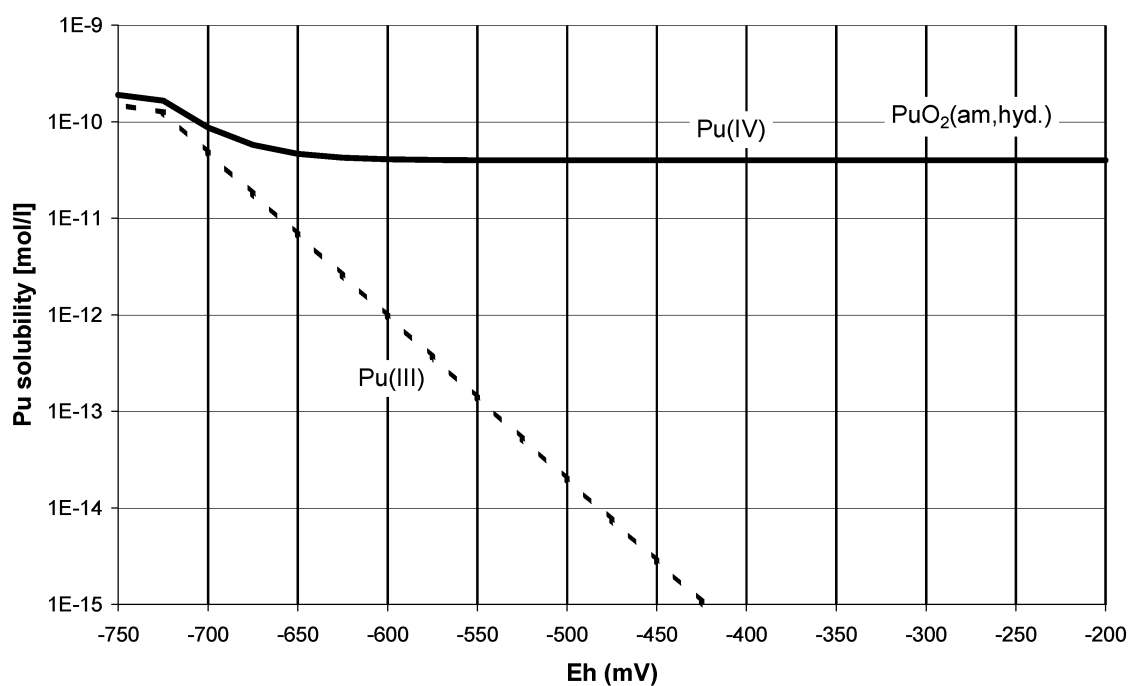
Figure 1: Solubility and redox state of plutonium as a function of system redox potential.

Table 4: Pu solubility and speciation in cement pore waters at pH 12.55.

	$-700 \leq Eh \leq -230$ mV	$Eh < -700$ mV	$Eh = +350$ mV
PuO_2(hyd, aged)	$4.0 \cdot 10^{-11}$ mol/l	$2.0 \cdot 10^{-10}$ mol/l	$6.0 \cdot 10^{-11}$ mol/l
Speciation: [%]			
$Pu(OH)_3$(aq)	–	79	–
$Pu(OH)_4$(aq)	100	21	67
$PuO_2(OH)$(aq)	–	–	29
$PuO_2(OH)_2$(aq)	–	–	4

4.4   Neptunium

At -230 mV the Np-system is fully determined by the solubility of NpO_2(hyd, am) and by the dominant complex $Np(OH)_4$(aq). The calculated limit is

$$5.0 \cdot 10^{-9} \text{ mol/l.}$$

Fig. 2 shows that the solubility of Np is constant in the redox range relevant for the present study. Propagating the uncertainties of the relevant equilibria (HUMMEL et al. 2002) would produce an uncertainty of ± 1.49 $\log_{10}$-units as in the case of Pu. However, also in the case of Np the relevant equilibria were derived from the measured solubility according to NpO_2(hyd, am) + 2 H_2O $\Leftrightarrow$ $Np(OH)_4$(aq) with $\log_{10}K_{s,4}° = -8.3 \pm 0.3$ (LEMIRE et al. 2001). This uncertainty of ± 0.3 $\log_{10}$-units produces the limits:

upper limit: $1.0 \cdot 10^{-8}$ mol/l
lower limit: $2.5 \cdot 10^{-9}$ mol/l.

Note that Np(III) species do not form at low Eh. At pH 12.55, the species $Np(V)O_2(OH)_x^{1-x}$ become important above ~ -150 mV. In a small Eh-range above +50mV the solid $NpO_2(OH)$(aged) controls Np solubility at $1.0 \cdot 10^{-6}$ mol/l, but further oxidation to $Np(VI)O_2(OH)_x^{2-x}$ species leads to concentrations around 10^{-3} mol/l or higher at +350 mV. The uncertainty of the $NpO_2(OH)$(aged)-solubility is moderate (± 0.5 $\log_{10}$-units), but the uncertainty of the formation constants of the oxidised species $Np(VI)O_2(OH)_x^{2-x}$ is not known. Hence, the solubility at +350 mV is considered "not limited".

Table 5:   Np solubility and speciation in cement pore waters at pH 12.55.

	Eh = -230 mV	Eh = + 350 mV
NpO_2(hyd, am)	$5.0 \cdot 10^{-9}$ mol/l	not limited
Speciation: [%]		
$Np(OH)_4$(aq)	100	–
$NpO_2(OH)_3^-$	–	93
$NpO_2(OH)_4^{2-}$	–	7
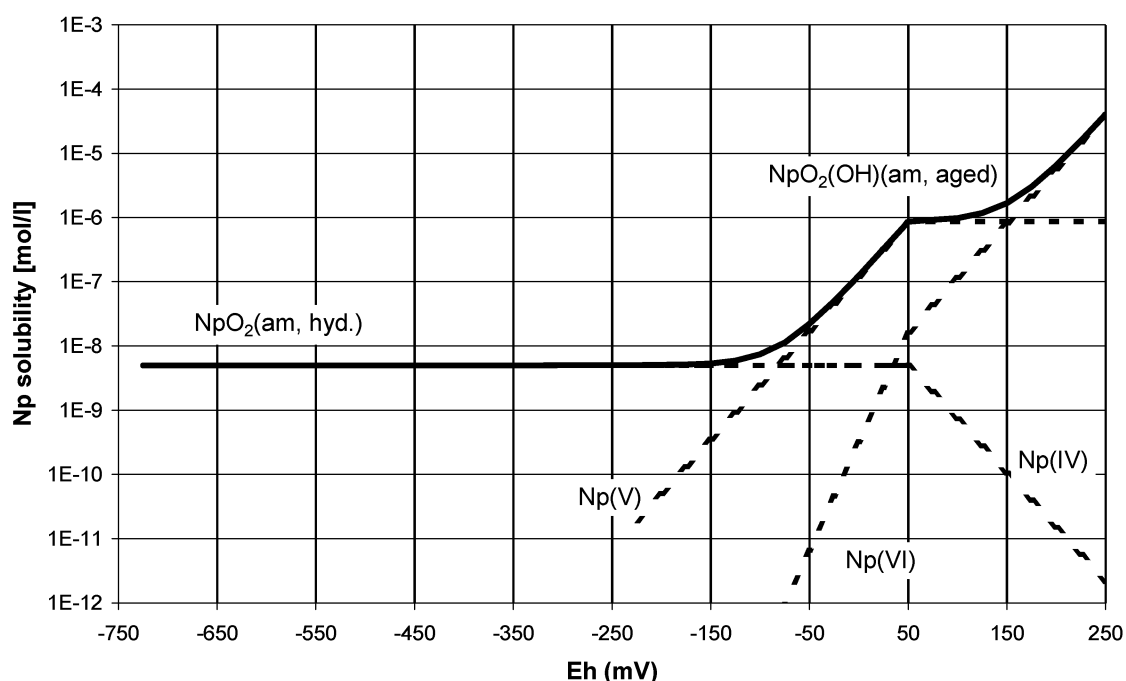
Figure 2:   Solubility and redox state of neptunium as a function of system redox potential.

4.5   Uranium

Uranium is a redox-sensitive element, which in principle may appear in the oxidation states +III, +IV, +V and +VI, but only the +IV and +VI oxidation states are relevant. The distribution of redox states and the total solubility as a function of the redox potential using the TDB as given in HUMMEL et al. (2002) is shown in Fig. 3.

At very low Eh, U(IV) ($U(OH)_4$(aq)) is dominant and a non-specific, amorphous UO_2(s) controls solubility. Around -550 mV, the U(VI)-hydrolysis products

$UO_2(OH)_3^-$ and $UO_2(OH)_4^{2-}$ become dominant, but total U solubility is still controlled by $UO_2(s)$. If Eh is raised above ~ -360 mV, $UO_2(s)$ disappears and there is no other solid phase to control uranium solubility. Therefore, and based on the contents of the updated Nagra/PSI Chemical Thermodynamic Data Base 01/01 (HUMMEL et al. 2002) one is forced to conclude that

uranium is not limited.

This result is clearly a consequence of the fact that the Nagra/PSI TDB includes much less data on solid phases than the NEA-review by GRENTHE et al. (1992). Particularly the types of solids relevant at high pH, i.e. the mixed valency oxides and the alkali and earth alkali uranates are not included in the Nagra/PSI TDB. The reasons for not considering them are discussed in detail by HUMMEL et al. (2002) and are not repeated here. However, in summary it can be said that differences in solid phase data selection between the two databases are conceptually justified. HUMMEL et al. (2002) attached importance to the application of the data and did not select solubility products derived from calculated Gibbs energies (high temperature measurements, thermochemical cycles). Unfortunately, the conclusion as given above contradicts several independent experimental studies that were not (or maybe: not yet) used to derive thermodynamic data for limiting U-solids.

Based on uranium solubility experiments in cementitious systems (MORONY & GLASSER 1995, SERNE et al. 1996), BERNER (1999) recommended using 10^{-8} mol/l as best estimate for dissolved uranium in cementitious systems ($5 \cdot 10^{-7}$ mol/l were recommended for an upper limit). This recommendation was corroborated by recent experimental findings from TITS & WIELAND (2001) and BONHOURE (2002). These authors found that U(VI) solutions at pH 13.3 (artificial cement pore water including ~0.3 mol/l of KOH, no cement present) are not stable above a threshold uranium concentration of $~2 \cdot 10^{-6}$ mol/l (32 days equilibration time). Note that the stability of the dominant solutes decreases with pH and so will also this threshold concentration.

Little is known about the limiting solids which appeared in the experiments of TITS & WIELAND (2001), but from the composition of the solution it is reasonable to assume that they are of the type becquerelite ($Ca(UO_2)_6O_4(OH)_6 \cdot 8H_2O$) and compreignacite ($K_2(UO_2)_6O_4(OH)_6 \cdot 8H_2O$) as earlier found and discussed by SANDINO & GRAMBOW (1994). However, BONHOURE (2002) pursued and completed the experiments of TITS & WIELAND (2001) by utilising spectroscopic methods for analysing the precipitated solids. Based on Ca − U and U − U distances she identified an X-ray-amorphous, not yet specified Ca-uranate by XAFS spectroscopy. Thereby, the formation of the mineral becquerelite could be excluded. Such a phase agrees with (or better: does not contradict) the

findings of SERNE et al. (1996) and with a so-called "phase X" as found by MORONI & GLASSER (1995).

These most recent experimental findings at high pH seem to confirm what has already been proposed in an earlier report on the same subject (BERNER 1999). Other information has not been gathered since then. Hence, the present report follows the arguments given in BERNER (1999) and recommends using a maximum concentration of

$$1 \cdot 10^{-8} \text{ mol/l.}$$

The reader will certainly recognise some inconsistencies between this recommendation and the calculation based on the Nagra/PSI TDB. However, rather strict boundary conditions for producing the cited database report on the one hand and to develop this report on the other hand do not allow for resolving them. One will have to wait for the upcoming uranium update of the NEA review team.

Formal uncertainties of any solubility products that could be applied do not exist. The upper limit of $5 \cdot 10^{-7}$ mol/l as proposed by BERNER (1999) (based on the solubility of α-$Na_2U_2O_7$ as given by GRENTHE et al. 1992) overlaps with the threshold concentration observed by TITS & WIELAND (2001), re-estimated for pH 12.55 conditions. This value is also maintained.

Table 6: U solubility and speciation in cement pore waters.

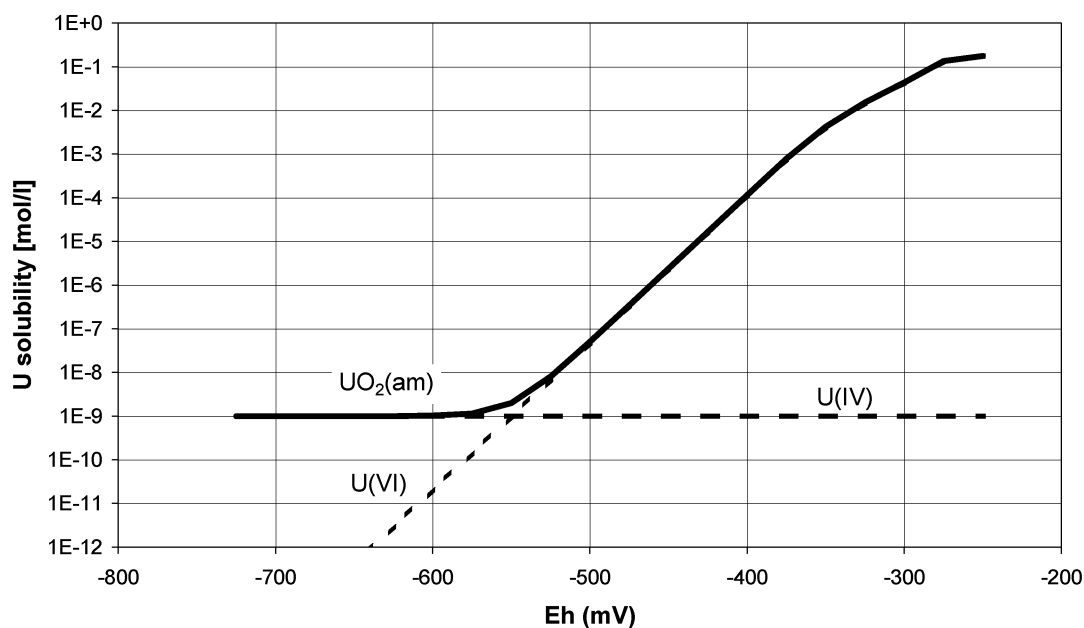|	pH 12.55
	not limited
Speciation: [%]	
$UO_2(OH)_3^-$	88
$UO_2(OH)_4^{2-}$	12

Figure 3: Solubility and redox state of uranium as a function of system redox potential.

4.6   Protactinium

Only few thermodynamic data of unknown quality/reliability are available for protactinium. From the discussion given in BAES & MESMER (1976) it becomes evident that Pa(IV) exhibits hydrolysis properties similar to other An(IV), which would correspond to its position between Th and U in the periodic table of the elements. On the other hand, Pa(IV) seems to be very sensitive to oxidation and is stabilised only in very strong acids at very low Eh. It is much more likely that Pa(V) is the stable oxidation state in present solutions. An estimate obtained using a small collection of Pa-data given by YUI et al. (1999) indicates that the total solubility could be in the order of 10^{-8} mol/l, when $Pa_2O_5(s)$ controls solubility and when $PaO(OH)_3(aq)$ is the dominant complex in solution. The data of YUI et al. (1999) do not include anionic complexes since they are based on older literature that BAES & MESMER (1976) reported on the possible formation of anionic species such as PaO_4^{3-}.

It is completely unclear how to make reliable recommendations based on such limited knowledge. It would be too simplistic to use uranium as a chemical analogue since the tetravalent oxidation state of Pa is almost non-existent under present chemical conditions. It is also not very satisfactory to select Np as an analogue because the hydrolysis of Pa(V) is definitely much stronger

than that of NpO_2^+. Comparing with the calculations/recommendations made for Pu, Np U and Th, $\sim 10^{-8}$ mol/l appears to be a sensible estimate. No upper- and/or lower limits are provided for obvious reasons.

4.7   Thorium

The thorium system does not depend on Eh, thus Th(IV) is the only relevant redox state. Since anionic species do not form, the Th system at pH 12.55 is fully determined by the solubility of a non-specified $ThO_2(s)$ according to $ThO_2(s) + 2\ H_2O \Leftrightarrow Th(OH)_4(aq)$ with $\log_{10}K_{s,4}^\circ = -8.5 \pm 0.6$ (HUMMEL et al. 2002). Hence, the calculated limit is

$$3.2 \cdot 10^{-9}\ mol/l.$$

The uncertainty of the relevant equilibrium produces:

upper limit: $1.3 \cdot 10^{-8}$ mol/l
lower limit: $7.9 \cdot 10^{-10}$ mol/l.

4.8   Radium

The database for Ra is very small. In the present cement pore water, $RaSO_4(s)$ is the limiting solid and Ra^{2+} is the dominating species in solution (more than 90 %). Hence, the calculated Ra solubility inversely depends on total SO_4^{2-} in solution. For present reference conditions ($1 \cdot 10^{-4}$ mol/l of SO_4^{2-}) the calculated limit is

$$9.8 \cdot 10^{-6}\ mol/l.$$

No uncertainties are available for the thermodynamic data of Ra. Alkaline-earth metals are not redox-sensitive, but from a thermodynamic point of view sulphate concentrations may depend on Eh since sulfate may be reduced to sulphide at very low Eh. If sulphate is missing due to reduction, dissolved radium may increase to concentrations controlled by $RaCO_3(s)$ ($1.6 \cdot 10^{-2}$ mol/l). Unfortunately, the question as to what extent the thermodynamic equilibrium SO_4^{2-}/HS^- is established, goes far beyond the scope of this report. Answering this question will address many not yet resolved kinetic issues. Since other criteria are missing, it is proposed that Ra concentrations controlled by $RaCO_3(s)$ serve for the upper limit.

If reduction to sulphide is not a matter of dispute, sulphate concentrations in cementitious systems may well be controlled by ettringite-type phases

$(Ca_6[Al(OH)_6]_2(SO_4)_3 \cdot 26H_2O)$. From the most recent experimental studies dealing with the thermodynamics of ettringites (WARREN & REARDON 1994, MYNENI et al. 1998, PERKINS & PALMER 1999) it is concluded that SO_4^{2-} concentrations in the presence of cement minerals most likely fall in the range $[0.2 \ldots 4] \cdot 10^{-3}$ mol/l, with a peak value around $1 \cdot 10^{-3}$ mol/l. Hence, the present reference pore water underestimates dissolved SO_4^{2-} and consequently overestimates dissolved Ra by a factor of about 10. This factor of ten serves for the lower limit:

upper limit: $1.6 \cdot 10^{-2}$ mol/l
lower limit: $9.8 \cdot 10^{-7}$ mol/l.

Comment: In the Swiss repository concepts radium is present in trace/sub-trace concentrations only (BERNER & CURTI 2002). When regarding the huge amounts of cementitious matrix-, backfill- and construction materials constituting the repository, it is difficult to believe that a limit based on the solubility of pure $RaSO_4(s)$ will establish. Most likely, radium will form a "trace impurity" of the whole variety of alkaline-earth metal bearing solid phases. Therefore, work to substantiate low or even very low Ra concentrations based on formation of solid solutions is in progress (see BERNER & CURTI 2002 for corresponding work in clay systems).

Table 7:   Ra solubility and speciation in cement pore waters.

	pH 12.55	pH 13.44
$RaSO_4(s)$	$9.8 \cdot 10^{-6}$ mol/l	$4.8 \cdot 10^{-8}$ mol/l
$[SO_4^{2-}]$	$1.0 \cdot 10^{-4}$ mol/l	$7.5 \cdot 10^{-4}$ mol/l
Ra^{2+}	92	73
$RaOH^+$	4	25
$RaCl^+$	4	–
$RaSO_4(aq)$	–	2

4.9   Caesium, Iodine

For both elements, the TDB does not include solid phases that could control solute concentrations. Thus, caesium and iodine are considered to be

not limited.

Comment: It is not very satisfying to qualify an important nuclide like iodine as "not solubility limited" in cementitious systems. As a potential sink for iodine, BERNER (1999) discussed the possibility of AFm-type mono-iodide solid phase formation based on experimental work of BROWN & GRUTZECK (1985a, 1985b),

but a quantitative and reliable appraisal was not yet possible at that time. However, solid solution work on the thermodynamics of calcium-aluminium-hydrates with the particular aim of anion fixation in cementitious materials is continued (BERNER & KULIK 2002). Thus, we are convinced that the current "not limited"-qualification as given in Table 1 is of temporary nature only.

4.10   Technetium

Technetium is redox-sensitive and may appear in several redox states. However, available data include the Tc(+IV) and the Tc(+VII) redox states only (Fig. 4). At -230 mV Tc is not limited, TcO_4^- is the only species in solution. Although precipitation of $TcO_2(hyd)$ starts below -300 mV, significant contributions of Tc(VII) are to be expected above -400 mV. At very low redox potentials $TcO(OH)_3^-$ would become the dominant complex in solution. Based on the available thermodynamic data we conclude from the calculation that

technetium is not limited.

The uncertainty of the relevant solubility equilibrium $TcO_2 \cdot 1.6H_2O(s) \Leftrightarrow TcO(OH)_2(aq) + 0.6\ H_2O$ is $\pm\ 0.5\ \log_{10}$-units and the uncertainty of the oxidation

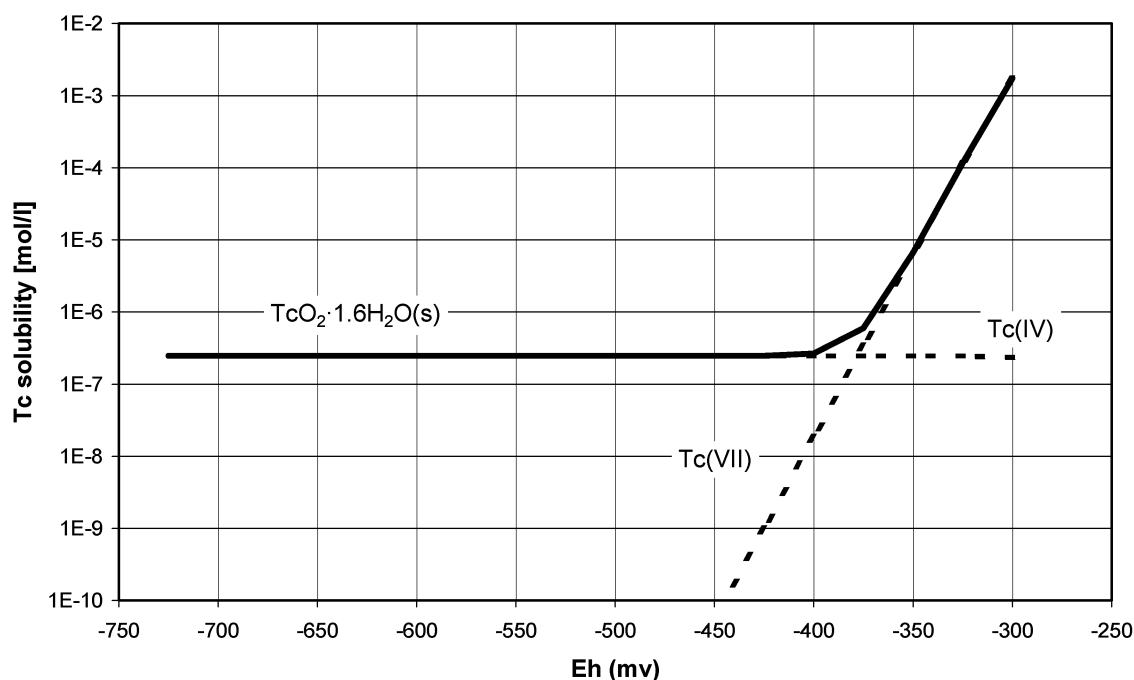**Figure 4:** Technetium solubility in cement pore water as a function of system redox potential. $TcO_2(hyd)$ precipitates when Eh falls below about -300 mV.

equilibrium is ± 0.8 $\log_{10}$-units (HUMMEL et al. 2002). The propagated uncertainty would thus be ± 0.94 $\log_{10}$-units. However, Fig. 4 immediately shows that these uncertainties are not relevant in the case of Tc. Here, the redox potential of the pore solution and its uncertainty is of key importance.

Table 8: Tc solubility and speciation in cement pore waters.

	pH 12.55 Eh –230 mV	pH 13.44 Eh -230 mV	pH 12.52 Eh +350 mV
$TcO_2 \cdot 1.6H_2O(s)$		not limited	
Speciation: [%] TcO_4^-	100	100	100

4.11   Niobium

The database for niobium is very small. With $Nb_2O_5(s)$ being the limiting solid, the complex NbO_3^- (also termed $Nb(OH)_6^-$) produces nearly molar concentrations. Thus, niobium is considered to be

not limited.

Uncertainties are not available.

LOTHENBACH et al. (1999) report some evidence that niobium could be limited by $Ca(NbO_3)_2 \cdot xH_2O(s)$ in Ca-rich solutions, but systematic experiments to confirm this evidence are missing. However, the potential relevance of several calcium-oxo-anion salts demonstrates that defining solubility limits at high pH could benefit from having a closer look to this class of solids (i.e. $CaSeO_3.H_2O(s)$ and $Ca[Sn(OH)_6](s)$, see also sections 4.12 & 4.14).

4.12   Selenium

According to Fig. 5, selenium seems to be very sensitive to Eh, but this might be a consequence of the limited thermodynamic database. Note that the official version of the TDB includes just one single solid phase (Se(cr); HUMMEL et al. 2002), although various solubility studies for many selenites ($M^I_2,M^{II}SeO_3(s)$) can be found in the literature (SÉBY et al. 2001 provide a comprehensive overview). Hence, the "calculated" solubility limit for Se under cement conditions would be around 0.1 mol/l, which is best represented by the term

not limited.

Uncertainties for this estimate are not available/sensible, but as can be seen from Fig. 5, the judgement "not limited" is very sensitive to system Eh. However, the fact that the TDB does not include further limiting solids does not mean that they do not exist. Based on work of SHARMASARKAR et al. (1996), the review of SÉBY et al. (2001) lists $\log_{10}K_{so}{}^{\circ}$ = -7.76 ± 0.18 for the equilibrium

$$CaSeO_3.H_2O(s) \Leftrightarrow Ca^{2+} + SeO_3{}^{2-} + H_2O,$$

among four other determinations for this solubility product. SEBY et al. (2001) prefer this recent work of SHARMASARKAR et al. (1996) because of the well-controlled experimental methods (e. g. 40 weeks of equilibration time and X-ray studies of the solids). In the same work, SHARMASARKAR et al. (1996) have also determined the solubility products of $MnSeO_3(s)$ and $ZnSeO_3(s)$ and could confirm earlier work on this subject. Thus, the present study accepts the preference of SÉBY et al. (2001). At given conditions (i.e. pH 12.55, Eh -230 mV) the above equilibrium limits total dissolved Se at $1.1 \cdot 10^{-5}$ mol/l in the range -275 to +50 mV. The calculated speciation is 100 % $SeO_3{}^{2-}$. It's suggested to use the solubility of

$$\mathbf{1.1 \cdot 10^{-5}\ mol/l}$$
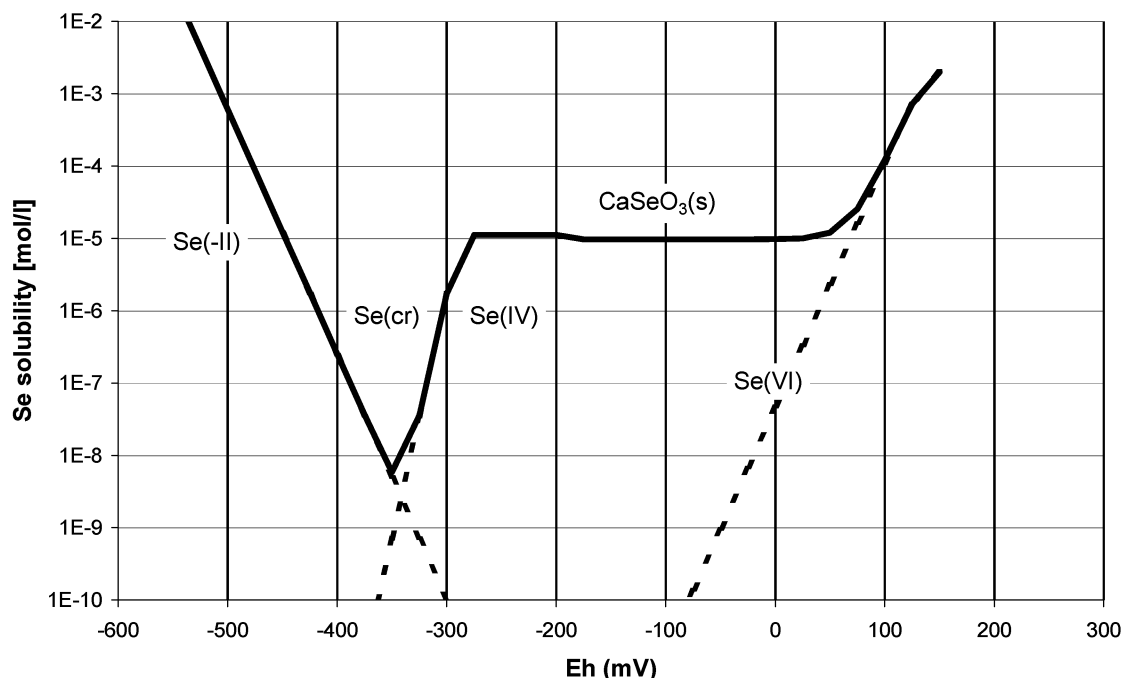
for the "recommended" value in Table 1.

Figure 5:   Solubility and redox state of Se as a function of system redox potential.

Consequently, the limits are given by ±0.18 $\log_{10}$units, or by

upper limit: $1.7 \cdot 10^{-5}$ mol/l
lower limit: $7.3 \cdot 10^{-6}$ mol/l.

Note that SÉBY et al. (2001), based on LIU & NARASIMHAN (1994), provide $\log_{10}K^0 = 3.17$ for the formation of the complex $CaSeO_3(aq)$. Considering this complex would completely change solubility and speciation, but unfortunately, the reference LIU & NARASIMHAN (1994) just provides a number that cannot be traced back.

At pH 13.44, the solubility of Se increases to $7.0 \cdot 10^{-4}$ mol/l. The reason for this increase is the portlandite equilibrium. At pH 12.55 total Ca^{2+} in solution is about $2.0 \cdot 10^{-2}$ mol/l, at pH 13.44 this concentration drops to $8.4 \cdot 10^{-4}$ mol/l. Consequently, SeO_3^{2-} increases accordingly. Above about +75 mV Se(VI) becomes dominant (see Fig. 5). Since other limiting phases for $Se(VI)O_4^{2-}$ are not available, we have to adopt a "not limited" qualification at +350 mV.

Table 9:   Se solubility and speciation in cement pore waters.

	pH 12.55 Eh -230 mV	pH 13.44 Eh -230 mV	pH 12.52 Eh +350 mV
$CaSeO_3.H_2O(s)$	$1.1 \cdot 10^{-5}$ mol/l	$7.0 \cdot 10^{-4}$ mol/l	not limited
SeO_3^{2-}	100	100	–
SeO_4^{2-}	–	–	100

4.13   Chlorine, Carbon, Actinium

<u>Chlorine</u>

Chloride is an essential part of the system definition derived from the reference groundwater (SCHWYN et al. 2003), which has been fixed at $1.6 \cdot 10^{-1}$ mol/l for the pH 12.55 reference pore solution and for the "oxidising" pore solution (Table 2). Note that chloride concentration has not been defined for the initial phase (pH 13.44) pore water. Since no limiting solids are available, chloride is formally marked as

not limited.

<u>Comment</u>: The author believes that comments as made for iodine do also apply for chlorine and that the qualification "not limited" is of temporary nature only and does just reflect the present gaps in chemical knowledge.

Carbon

Inorganic carbon (carbonate) is part of the system definition. Its concentration is given by assuming equilibrium with calcite. At pH 12.55 the geochemical calculation produces

$$9.7 \cdot 10^{-6} \text{ mol/l.}$$

The calcite solubility constant has a negligibly small uncertainty (~0.005 $\log_{10}$-units). Major uncertainties may arise from varying pH, which couples to total dissolved Ca via the portlandite equilibrium. At pH 13.44, the calculation produces $2.0 \cdot 10^{-4}$ mol/l, which may serve as the upper limit.

Note that gaseous (CH_4) and/or organic forms of carbon are not considered. Within Table 1, the limits are therefore indicated as "recommended" values.

Actinium

No thermodynamic data at all are available for Ac. Ac gives the name to the actinide series of elements, but its chemical behaviour is more similar to that of lanthanum (RÖMPP 1989). Thus, Eu-data and solubilities were selected to simulate Ac.


4.14   Tin

In principle, tin may exist in the redox states Sn(II) and Sn(IV), but Sn(II) is not stable in the Eh range from -750 to -230 mV at pH 12.55. At these conditions, the Sn system is fully determined by the solubility of Ca[Sn(OH)$_6$](s) and by the dominant complex $Sn(OH)_6^{2-}$. The calculated limit is

$$1.3 \cdot 10^{-7} \text{ mol/l.}$$

The uncertainty of the relevant equilibrium is only ± 0.1 $\log_{10}$-units (HUMMEL et al. 2002) and produces

upper limit: $1.6 \cdot 10^{-7}$ mol/l
lower limit: $1.0 \cdot 10^{-7}$ mol/l.

Note that the Sn^{2+}/Sn^{4+} redox equilibrium is not included in the updated database. To check for the possible impact of Sn(II), the equilibrium as suggested by HUMMEL et al. (2002) was used:

$$Sn^{2+} + 4H_2O \Leftrightarrow Sn(OH)_4(aq) + 4H^+ + 2e^- \qquad \log_{10}K° = -8.4.$$
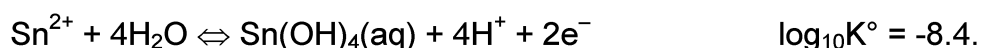
The uncertainty of this redox equilibrium is at least one order of magnitude, but independent of this, Sn(II) does not form to any significant degree, even at very low Eh. If pH is raised to 13.44, a significantly higher tin solubility of $8.1 \cdot 10^{-6}$ mol/l is calculated (Table 10).

Table 10: Sn solubility and speciation in cement pore waters at -230 mV.

	pH 12.55	pH 13.44
$Ca[Sn(OH)_6](s)$	$1.3 \cdot 10^{-7}$ mol/l	$8.1 \cdot 10^{-6}$ mol/l
Speciation: [%]		
$Sn(OH)_6^{2-}$	100	100

4.15   Palladium

Dissolved palladium exists only in the redox state Pd(II) and, provided that elemental Pd is formed as predicted by the thermodynamic calculation, dissolved Pd drops to insignificant levels as shown in Fig. 6. The calculated limit, actually at any Eh below -100 mV, is

insignificantly low.

This is compatible with the assumption that Pd exists in alloy form together with Ru, Tc, etc. and does not dissolve at all. The formal uncertainty of this unspecified "value" is ± 0.8 $\log_{10}$-units (HUMMEL et al. 2002), but this has no meaning in the present case.

Undoubtedly the formation of elemental Pd is thermodynamically favoured due to its noble character, but it is unclear, whether Pd(s) will precipitate from solution or not. In his experiments, WOOD (1991) was not able to show whether Pd(s), which he used as a starting material, or $Pd(OH)_2$(precip), which he expected based on the Eh measurements, was the solubility limiting phase present.

Therefore, Pd solubility was also calculated under the assumption that Pd(s) is not formed by reduction of Pd^{2+} (kinetic hindrance). In this case $Pd(OH)_2$(precip) limits total dissolved Pd at $8.0 \cdot 10^{-7}$ mol/l with $Pd(OH)_3^-$ being the dominant complex (Table 11). Based on a fair amount of solubility data, the

uncertainty of this hydroxide solubility is in the order of ± 1.0 $\log_{10}$-units (HUMMEL et al. 2002; Fig. 5.14.3) at elevated pH. This leads to:

upper limit: $8.0 \cdot 10^{-6}$ mol/l
lower limit: $8.0 \cdot 10^{-8}$ mol/l

Note the solubility increase when pH is raised to 13.44 (Table 11).

Table 11: Pd solubility and speciation in cement pore waters.

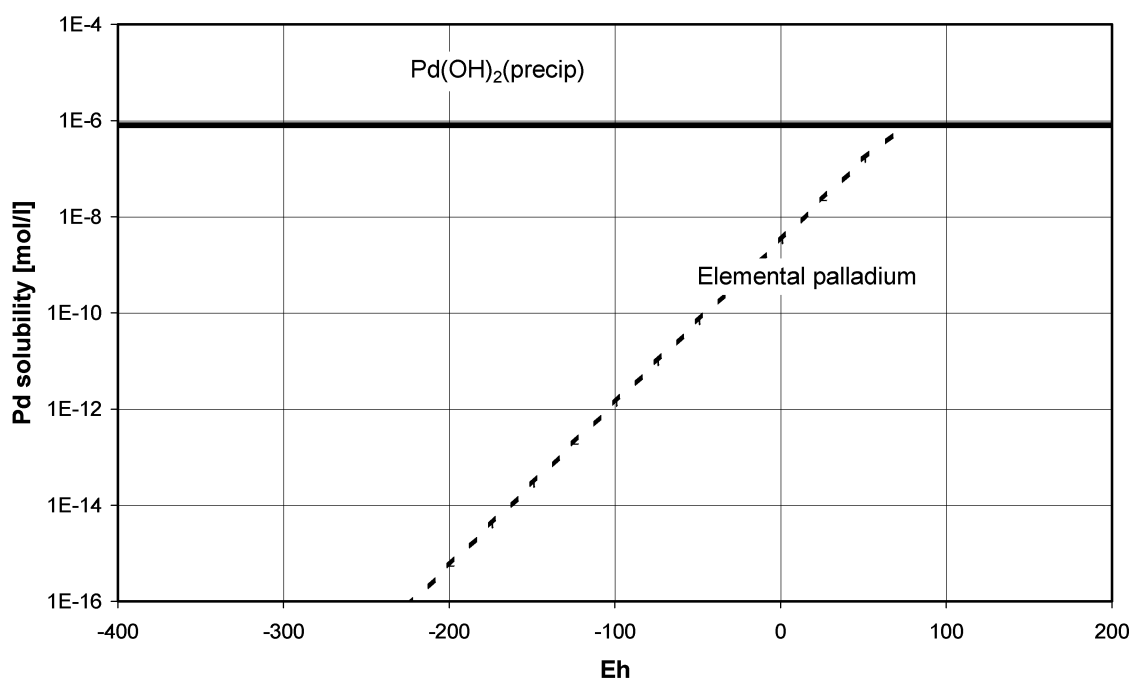|	pH 12.55	pH 13.44
$Pd(OH)_2(precip)$	$8.0 \cdot 10^{-7}$ mol/l	$5.9 \cdot 10^{-6}$ mol/l
Speciation: [%]		
$Pd(OH)_2(aq)$	6	1
$Pd(OH)_3^-$	94	99

Figure 6:   Solubility of palladium as a function of system redox potential.

4.16 Zirconium

Zirconium is not redox-sensitive, thus in solution it appears only in the Zr(IV) oxidation state. At pH 12.55, the system is completely determined by the solubility of ZrO_2(s), the dominant complex in solution is $Zr(OH)_5^-$ and the calculated limit is

$$6.0 \cdot 10^{-6} \text{ mol/l.}$$

Hummel et al. (2002) do not provide uncertainties for the two relevant equilibria. However, from the few experimental data provided in Hummel et al. (2002; Fig. 5.24.1) an uncertainty in the order of ± 1 log_{10}-units might be estimated. This would lead to

upper limit: $6.0 \cdot 10^{-5}$ mol/l
lower limit: $6.0 \cdot 10^{-7}$ mol/l

The solubility increases to $4.7 \cdot 10^{-5}$ mol/l when pH is raised to 13.44.

Other sources for Zr-solubilities at high pH (Kulmala & Hakanen 1993) indicate lower Zr solubilities, but do not allow the extraction of thermodynamic data. At pH 13, very similar results have also been found by other groups (Ochs 2003). As in the case of uranium, one will have to wait for the upcoming zirconium review of the NEA expert team.

4.17 Strontium

The dominant species in solution is Sr^{2+}. With given system parameters the most stable solid is $SrCO_3$(s). Based on the calculated saturation index of strontianite a maximum Sr solubility of

$$2.8 \cdot 10^{-3} \text{ mol/l}$$

is estimated. The TDB (Hummel et al. 2002) does not include uncertainties for this equilibrium, but from Robie & Hemingway (1995) an uncertainty of ± 0.3 log_{10}-units may be estimated for $\Delta_f G^0(SrCO_3(s))$, which is proportional to the solubility product of $SrCO_3$(s). Hence,

upper limit: $5.6 \cdot 10^{-3}$ mol/l
lower limit: $1.4 \cdot 10^{-3}$ mol/l.

If pH is raised, OH^- increases and Ca^{2+} decreases due to portlandite saturation. Consequently, total CO_3^{2-} increases and dissolved Sr decreases to $7.4 \cdot 10^{-5}$ mol/l (Table 12).

The significant differences between the "chemically similar" Sr and Ra are not expected at first sight, but can be attributed to a well-established four orders of magnitude difference in the solubility products of the sulfate solids. In the case of radium, it was argued that traces or sub-traces of Ra would most likely form a "trace impurity" of the whole variety of alkaline-earth metal bearing solid phases. This is no longer valid when considering Sr. Strontium contents in a cement-based repository system are about 10^6 times higher than radium contents (BERNER 1999). Hence, analogy approaches as in the case of Am/Cm should not be followed in the case of Ra/Sr.

Table 12: Sr solubility and speciation in cement pore waters.

	pH 12.55	pH 13.44
$SrCO_3(s)$	$2.8 \cdot 10^{-3}$ mol/l	$7.4 \cdot 10^{-5}$ mol/l
total CO_3^{2-}	$9.9 \cdot 10^{-6}$ mol/l	$2.0 \cdot 10^{-4}$ mol/l
Speciation: [%]		
Sr^{2+}	93	64
$SrOH^+$	7	36

4.18 Nickel

Because nickel does not depend on Eh, Ni(II) is the only relevant redox state that needs to be considered. At pH 12.55 and low carbonate content the Ni system is fully determined by the solubility of $Ni(OH)_2(cr)$ and by the hydrolysis products $Ni(OH)_3^-$ (90 %) and $Ni(OH)_2(aq)$ (10 %). Note that the well-known tetrameric complex $Ni_4(OH)_4^{4-}$ is not relevant at these conditions. The calculated maximum solubility is

$$3.3 \cdot 10^{-7} \text{ mol/l.}$$

HUMMEL et al. (2002) give ± 1.4 log_{10}-units for to the solubility determining equilibrium $Ni(OH)_2(cr) + OH^- \Leftrightarrow Ni(OH)_3^-$, producing the limits

upper limit: $8.3 \cdot 10^{-6}$ mol/l
lower limit: $1.3 \cdot 10^{-8}$ mol/l.

The maximum solubility as established above agrees fairly well with available solubility measurements of Ni in high pH solutions (PILKINGTON & STONE 1990, OCHS et al. 1998, TITS et al. 1998) that had not (or only partly) been used to derive the thermodynamic constants provided in HUMMEL et al. (2002). Note that

also the most recent work on this subject (HUMMEL & CURTI 2003) does not give new views of the system at high pH.

Table 13: Ni solubility and speciation in cement pore waters.

	pH 12.55	pH 13.44
$Ni(OH)_2(s)$	$3.3 \cdot 10^{-7}$ mol/l	$2.4 \cdot 10^{-6}$ mol/l
Speciation: [%]		
$Ni(OH)_2(aq)$	10	1
$Ni(OH)_3^-$	90	96
$Ni_4(OH)_4(aq)^{4-}$	–	3

4.19   Lead

In principle, lead may exist in the redox states Pb(II) and Pb(IV), but Pb(IV) species do not exist in the Eh range considered. Further, it should be pointed up that no data at all are available for Pb(IV) complexes. At pH 12.55, the Pb system is determined by the solubility of $Pb(OH)_2(s)$ and by the hydrolysis products $Pb(OH)_3^-$ (98 %) and $Pb(OH)_2(aq)$ (2 %). The calculated limit is

$$2.8 \cdot 10^{-3} \text{ mol/l.}$$

Uncertainties are not available. The updated Nagra/PSI TDB (HUMMEL et al. 2002) does not include data for lead. Table 14 provides the Pb-data used in the present study. At pH 13.44, the calculated solubility increases to $2.2 \cdot 10^{-2}$ mol/l. This was taken for the upper limit.

Note: Model calculations for lead have been performed under the assumption that sulphate is not reduced to sulphide. Therefore, the HS^- concentration in the reference cement pore water is ignored. When HS^- formation is not ignored, even traces of sulphide are predicted to precipitate galena, PbS(s).

Table 14: Thermodynamic data for lead, taken from a former MINEQL database.

Equilibrium		LOTHENBACH et al. (1999)[1]
$Pb(OH)_2(s) + 2\ H^+ \Leftrightarrow Pb^{2+} + H_2O$	$\log_{10}K_s° = 12.9$	13.1
$PbS(s) + H^+ \Leftrightarrow Pb^{2+} + HS^-$	$\log_{10}K_s° = -13.6$	−12.2
$2PbCO_3.Pb(OH)_2(s) + 2\ H^+ \Leftrightarrow$ $3\ Pb^{2+} + 2\ H_2O + 2\ CO_3^{2-}$	$\log_{10}K_s° = -18.8$	−17.6
$PbCO_3(s) \Leftrightarrow Pb^{2+} + CO_3^{2-}$	$\log_{10}K_s° = -13.13$	-13.2
$PbSO_4(s) \Leftrightarrow Pb^{2+} + SO_4^{2-}$	$\log_{10}K_s° = -7.79$	-7.8
$Pb^{2+} + H_2O \Leftrightarrow Pb(OH)^+ + H^+$	$\log_{10}\beta_1° = -7.7$	-7.5
$Pb^{2+} + 2\ H_2O \Leftrightarrow Pb(OH)_2(aq) + 2\ H^+$	$\log_{10}\beta_2° = -17.1$	-17.0
$Pb^{2+} + 3\ H_2O \Leftrightarrow Pb(OH)_3^- + 3\ H^+$	$\log_{10}\beta_3° = -28.1$	-28.0
$Pb^{2+} + CO_3^{2-} \Leftrightarrow PbCO_3(aq)$	$\log_{10}\beta_1° = 7.0$	7.3
$Pb^{2+} + 2\ CO_3^{2-} \Leftrightarrow Pb(CO_3)_2^{2-}$	$\log_{10}\beta_2° = 10.35$	10.1
$Pb^{2+} + SO_4^{2-} \Leftrightarrow PbSO_4(aq)$	$\log_{10}\beta_1° = 2.75$	2.8
$Pb^{2+} + 2\ SO_4^{2-} \Leftrightarrow Pb(SO_4)_2^{2-}$	$\log_{10}\beta_2° = 4.0$	2.4
$Pb^{2+} + Cl^- \Leftrightarrow PbCl^+$	$\log_{10}\beta_1° = 1.59$	1.6
$Pb^{2+} + 2\ Cl^- \Leftrightarrow PbCl_2(aq)$	$\log_{10}\beta_2° = 1.8$	2.0

[1] For comparison, and in order to help justifying the data selection, thermodynamic constants as recommended in a recent review by LOTHENBACH et al. (1999) are given in this column.

4.20   Polonium, Hafnium, Holmium, Promethium

Polonium

No data are available for Po.

Hafnium

No data are available for Hf. It is recommended to use Zr as an analogue.

Holmium

No data are available for Ho. It is recommended to use Eu as an analogue.

Promethium

No data are available for Pm. It is recommended to use Eu as an analogue.

4.21   Europium

The most stable solid in the system would be $Eu(OH)_3(cr)$, but there is not enough information to reliably defend the required transition from $Eu(OH)_3(am)$ to $Eu(OH)_3(cr)$. Therefore, the amorphous hydroxide is selected as the limiting solid (see also Am). The calculated limit is

$$2.0 \cdot 10^{-6} \text{ mol/l.}$$

The crystalline hydroxide would produce $4.0 \cdot 10^{-9}$ mol/l. Due to the formation of the anionic $Eu(OH)_4^-$, Eu exhibits higher total solubilities at pH 13.44. Note the substantial difference from the so-called "chemically similar" americium.

Uncertainties arise from the solubility product (± 0.8 $\log_{10}$-units) and from the formation constants of $Eu(OH)_3(aq)$ (± 0.1) and $Eu(OH)_4^-$ (± 0.5). Propagating the corresponding uncertainty values (HUMMEL et al. 2002) produces an uncertainty of at most ± 0.9 $\log_{10}$-units. This formal uncertainty was taken for the upper limit. The solubility of the crystalline hydroxide was taken for the lower limit[3].

upper limit: $1.6 \cdot 10^{-5}$ mol/l
lower limit: $4.0 \cdot 10^{-9}$ mol/l.

Eu^{2+}, known as a very strong reductant, is formed at insignificant concentration levels (10^{-14} to 10^{-13} mol/l) only at -700 mV.

Table 15: Eu solubility and speciation in cement pore waters.

	pH 12.55	pH 13.44
$Eu(OH)_3(cr)$	$4.0 \cdot 10^{-9}$ mol/l	$2.0 \cdot 10^{-8}$ mol/l
$Eu(OH)_3(am)$	$2.0 \cdot 10^{-6}$ mol/l	$1.0 \cdot 10^{-5}$ mol/l
Speciation: [%]		
$Eu(OH)_3(aq)$	40	8
$Eu(OH)_4^-$	60	92

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[3]   The lower limit would decrease to $1.2 \cdot 10^{-9}$ mol/l when the formal uncertainty of ± 0.53 $\log_{10}$-units of the crystalline solid is also considered.

4.22   Antimony

In aqueous solutions, antimony exists in the redox states Sb(0), Sb(III) and Sb(V). At redox potentials above -600 mV the system is determined by Sb(V), and $Sb(OH)_6^-$ is by far the dominant complex in solution. Significant contributions from Sb(III) appear only below -600 mV ($Sb(OH)_4^-$, 88 %; $Sb(OH)_3(aq)$, 12 %). Based on the calculated solubility curve shown in Fig. 7, we conclude that antimony is

not limited

at -230 mV. Note that the flattening out of the curve at -600 mV is just a consequence of operatively limiting the maximum concentration to 0.001 mol/l in the system set-up. The updated Nagra/PSI TDB (HUMMEL et al. 2002) does not include data for antimony. Thus, data from a former MINEQL database and from LOTHENBACH et al. (1999) as provided in Table 16 were used. Uncertainties are not available. Based on a single experimental study LOTHENBACH et al. (1999) provide constants for a series of dodecamer Sb(V) hydrolysis products not shown in Table 16. However, the sensitivity analysis reveals that those dodecamers do not contribute at pH 12.55.

Table 16: Thermodynamic data for antimony, taken from a former MINEQL database.

Equilibrium		LOTHENBACH et al. (1999)[1]
$Sb(OH)_5(aq) + 2\ H^+ + 2\ e^- \Leftrightarrow$ $Sb(OH)_3(aq) + 2\ H_2O$	–	$\log_{10}K° = 21.84$
$Sb(OH)_3(aq) + 3\ H^+ + 3\ e^- \Leftrightarrow$ $Sb(cr) + 3\ H_2O$	–	$\log_{10}K° = 11.99$
$Sb(OH)_5(aq) + H_2O \Leftrightarrow Sb(OH)_6^- + H^+$	$\log_{10}K_6° = -2.72$	-2.72
$Sb(OH)_3(aq) + H^+ \Leftrightarrow Sb(OH)_2^+ + H_2O$	$\log_{10}K_2° = 1.42$	1.3
$Sb(OH)_3(aq) + H_2O \Leftrightarrow Sb(OH)_4^- + H^+$	$\log_{10}K_4° = -11.82$	-11.93
$Sb_2O_5(s) + 5\ H_2O \Leftrightarrow 2\ Sb(OH)_5(aq)$	$\log_{10}K_s° = -7.4$	-7.4
$Sb_2O_3(s) + 3\ H_2O \Leftrightarrow 2\ Sb(OH)_3(aq)$	$\log_{10}K_s° = -8.48$	-8.72

[1]   For comparison, and in order to help justifying the data selection, thermodynamic constants as recommended in a recent review by LOTHENBACH et al. (1999) are given in this column.
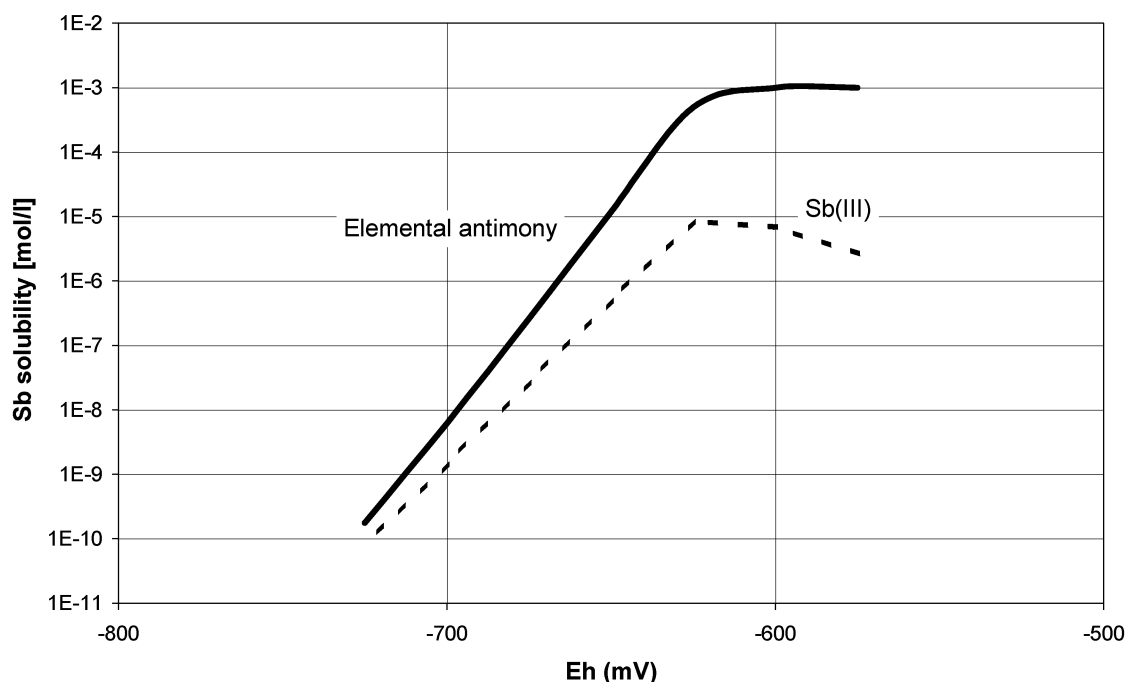
Figure 7:   Antimony solubility in cement pore water as a function of system redox potential. Below ~-600 mV Sb(cr) becomes the limiting solid. Significant contributions from Sb(III) do not appear above -600 mV.

4.23   Cadmium

Cadmium is not redox-sensitive, it exists in the redox state Cd(II). The updated Nagra/PSI TDB (HUMMEL et al. 2002) does not include data for cadmium, but from a former MINEQL database, we used the equilibria provided in Table 17 to perform an estimate for Cd solubility. At -230 mV, $Cd(OH)_2(s)$ limits cadmium solubility at

$$3.6 \cdot 10^{-6} \text{ mol/l.}$$

Relevant complexes in solution are $Cd(OH)_3^-$ (94 %) and $Cd(OH)_2(aq)$ (6 %). Raising pH to 13.44 increases solubility to $2.7 \cdot 10^{-5}$ mol/l and favours higher hydrolysis products. We take this value for the upper limit. Note that CdS(s) may become the limiting solid below ~-500 mV when reduction of sulphate is not suppressed. Uncertainties are not available for the above equilibria.

Table 17: Cd solubility and speciation in cement pore waters.

	pH 12.55	pH 13.44
$Cd(OH)_2(s)$	$3.6 \cdot 10^{-6}$ mol/l	$2.7 \cdot 10^{-5}$ mol/l
Speciation: [%]		
$Cd(OH)_2(aq)$	6	1
$Cd(OH)_3^-$	94	97
$Cd(OH)_4^{2-}$	–	2

Table 18: Thermodynamic data for cadmium as taken from a former MINEQL database.

Equilibrium	
$Cd^{2+} + H_2O \Leftrightarrow CdOH^+ + H^+$	$\log_{10}\beta_1{}^\circ = -10.1$
$Cd^{2+} + 2\ H_2O \Leftrightarrow Cd(OH)_2(aq) + 2\ H^+$	$\log_{10}\beta_2{}^\circ = -20.3$
$Cd^{2+} + 3\ H_2O \Leftrightarrow Cd(OH)_3^- + 3\ H^+$	$\log_{10}\beta_3{}^\circ = -31.8$
$Cd^{2+} + CO_3^{2-} \Leftrightarrow CdCO_3(aq)$	$\log_{10}\beta_1{}^\circ = 4.3$
$Cd^{2+} + SO_4^{2-} \Leftrightarrow CdSO_4(aq)$	$\log_{10}\beta_1{}^\circ = 2.46$
$Cd^{2+} + 2\ SO_4^{2-} \Leftrightarrow Cd(SO_4)_2^{2-}$	$\log_{10}\beta_2{}^\circ = 3.25$
$Cd^{2+} + 3\ SO_4^{2-} \Leftrightarrow Cd(SO_4)_3^{4-}$	$\log_{10}\beta_3{}^\circ = 2.7$
$Cd^{2+} + Cl^- \Leftrightarrow CdCl^+$	$\log_{10}\beta_1{}^\circ = 1.98$
$Cd^{2+} + 2\ Cl^- \Leftrightarrow CdCl_2(aq)$	$\log_{10}\beta_2{}^\circ = 2.6$
$Cd^{2+} + 3\ Cl^- \Leftrightarrow CdCl_3^-$	$\log_{10}\beta_3{}^\circ = 2.4$
$Cd^{2+} + 4\ Cl^- \Leftrightarrow CdCl_4^{2-}$	$\log_{10}\beta_4{}^\circ = 1.7$
$Cd(OH)_2(s) + 2\ H^+ \Leftrightarrow Cd^{2+} + 2\ H_2O$	$\log_{10}K_{so}{}^\circ = 13.65$
$CdCO_3(s) \Leftrightarrow Cd^{2+} + CO_3^{2-}$	$\log_{10}K_{so}{}^\circ = -12.1 \pm 0.2^{1)}$
$CdS(s) + H^+ \Leftrightarrow Cd^{2+} + HS^-$	$\log_{10}K_{so}{}^\circ = -13.1$

[1] GRAUER (1999)

4.24 Silver

The thermodynamic data used to model silver solubility are provided in Table 20. At given Eh conditions elemental Ag shows up as the stable phase and calculated silver concentrations drop to insignificant levels. From Fig. 8 it is concluded that the silver concentration at -230 mV is

insignificantly low.

Compared to the uncertainty of system Eh, the uncertainty of the relevant equilibrium is insignificant. However, concentrations were also modelled under the presumption that elemental silver is not formed. In this case, the dotted curve in Fig. 8 is obtained. AgCl(s) is then the limiting solid, producing $2.6 \cdot 10^{-6}$ mol/l of dissolved silver. Dominant complexes in solution are the silver chlorides (AgCl(aq), 6 %; $AgCl_2^-$, 60 %; $AgCl_3^{2-}$, 18 % and $AgCl_4^{3-}$, 16 %). The uncertainty for the AgCl(s) solubility product is very small, when considering the precise knowledge about the Ag/AgCl electrode. An interesting behaviour is observed when reduction of sulphate to sulphide is enabled. $Ag_2S(s)$ would precipitate below -390 mV and complexes in solution would change from $AgCl_2^-$ to AgS^-.

It is suggested to use the well-known solubility of AgCl(s) for the upper limit, i.e.

upper limit: $2.6 \cdot 10^{-6}$ mol/l.

The definition of a lower limit does not make sense when the solubility is insignificant. Raising pH to 13.44 has no impact on the solubility; total dissolved Ag is still insignificant. When the formation of elemental Ag would be denied, $Ag_2O(s)$ would limit total dissolved Ag at $4.1 \cdot 10^{-6}$ mol/l, with AgOH(aq) being the dominant complex (Table 19).The stability field of elemental Ag disappears under oxidising conditions and AgCl(s) will be the limiting solid (Fig. 8).

Table 19: Ag solubility and speciation in cement pore waters.

	pH 12.55	pH 13.44	Eh +350 mV
Ag(cr)	insignificant	insignificant	
AgCl(s)			$2.6 \cdot 10^{-6}$ mol/l
$Ag_2O(s)$		$(4.1 \cdot 10^{-6}$ mol/l)	
Speciation: [%]			
Ag^+	–	2	–
AgOH(aq)	–	98	–
AgCl(aq)	6	–	6
$AgCl_2^-$	60	–	60
$AgCl_3^{2-}$	18	–	18
$AgCl_4^{3-}$	16	–	16

AgCl(s)

Ag$_2$S(s)

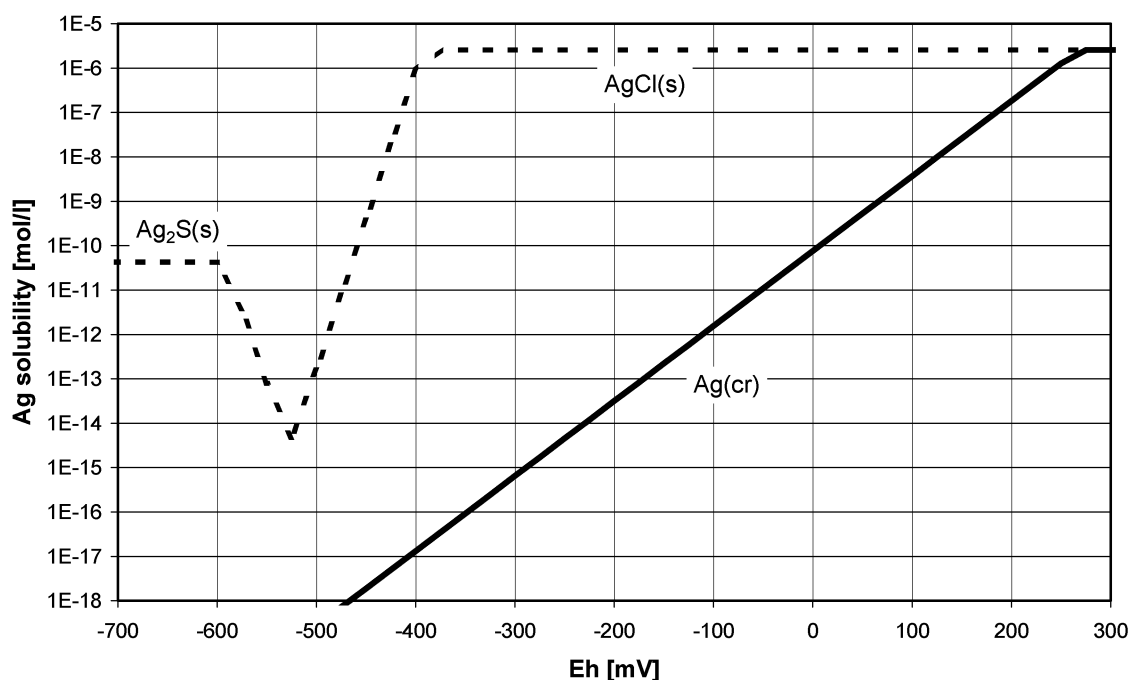Ag(cr)

Ag solubility [mol/l]

Eh [mV]

Figure 8: Solubility of silver as a function of system redox potential. Below +275 mV Ag(cr) is the stable phase, producing insignificant concentrations at -230 mV. The dotted curve represents a sensitivity study, assuming the absence of Ag(cr) as well as the reduction of 10^{-4} mol/l S(VI)O$_4^{2-}$ to HS(-II)$^-$. Below -390 mV AgS$^-$ would become dominant, thus producing the pronounced solubility minimum at -525 mV.

Table 20: Thermodynamic data for silver as taken from a former MINEQL database.

Equilibrium	
Ag$^+$ + H$_2$O $\Leftrightarrow$ AgOH(aq) + H$^+$	Log$_{10}$K$_1$° = −11.7
Ag$^+$ + Cl$^-$ $\Leftrightarrow$ AgCl(aq)	Log$_{10}$K$_1$° = 3.1
Ag$^+$ + 2 Cl$^-$ $\Leftrightarrow$ AgCl$_2^-$	Log$_{10}$β$_2$° = 4.9
Ag$^+$ + 3 Cl$^-$ $\Leftrightarrow$ AgCl$_3^{2-}$	Log$_{10}$β$_3$° = 4.9
Ag$^+$ + 4 Cl$^-$ $\Leftrightarrow$ AgCl$_4^{3-}$	Log$_{10}$β$_4$° = 5.1
Ag$^+$ + HS$^-$ $\Leftrightarrow$ AgS$^-$ + H$^+$	Log$_{10}$K$_1$° = 3.4
AgCl(s) $\Leftrightarrow$ Ag$^+$ + Cl$^-$	Log$_{10}$K$_{so}$° = -9.9
Ag$_2$S(s) + H$^+$ $\Leftrightarrow$ 2 Ag$^+$ + HS$^-$	Log$_{10}$K$_{so}$° = -36.2
Ag(cr) $\Leftrightarrow$ Ag$^+$ + e$^-$	log$_{10}$K$_{so}$° = -13.509±0.014[1]

[1] HUMMEL (2001)

4.25   Molybdenum

Apart from the master species MoO_4^{2-}, the updated Nagra/PSI TDB (HUMMEL et al. 2002) includes only three solids, adopted without change from PEARSON et al. (1992). Together with data for powellite, $CaMoO_4(s)$, and $HMoO_4^-$ from a former MINEQL database, the very small data set compiled in Table 21 is obtained. At -230 mV $CaMoO_4(s)$ is the stable solid. It limits total dissolved Mo at

$$2.6 \cdot 10^{-5} \text{ mol/l.}$$

The dominant complex in solution is MoO_4^{2-}. Uncertainties are not available. The calculation indicates that $MoO_2(s)$ does not become stable above -750 mV. At pH 13.44 calculated solubilities increase to $1.6 \cdot 10^{-3}$ mol/l, which, in the absence of any other information is taken for the upper limit.

Table 21: Thermodynamic data for Molybdenum.

Equilibrium	former MINEQL database	PEARSON et al. (1992)
$MoO_4^{2-} + H^+ \Leftrightarrow HMoO_4^-$	$\log_{10}K_1° = 4.3$	
$CaMoO_4(s) \Leftrightarrow Ca^{2+} + MoO_4^{2-}$	$\log_{10}K_{so}° = -7.4$	
$Mo(s) + 4 H_2O \Leftrightarrow MoO_4^{2-} + 8 H^+ + 6 e^-$	(-19.67)	$\log_{10}K_{so}° = -19.667$
$MoO_2(s) + 2 H_2O \Leftrightarrow MoO_4^{2-} + 4 H^+ + 2 e^-$	(-29.96)	$\log_{10}K_{so}° = -29.956$
$MoO_3(s) + H_2O \Leftrightarrow MoO_4^{2-} + 2 H^+$	(-12.06)	$\log_{10}K_{so}° = -12.055$

4.26   Cobalt

The updated Nagra/PSI TDB (HUMMEL et al. 2002) does not include data for cobalt, but from a former MINEQL database the equilibria as provided in Table 23 were used to perform an estimate for Co solubility. Cobalt may appear in the redox states Co(II) and Co(III), but Co(II) prevails in the Eh range considered. At -230 mV $Co(OH)_2(s)$ limits dissolved Co concentration at

$$7.0 \cdot 10^{-7} \text{ mol/l.}$$

Relevant complexes in solution are the hydroxides. Uncertainties are not available. Note that β-$CoS(s)$ could become the limiting solid below ~-500 mV when potential reduction of sulphate to sulphide is enabled. An increase of total

solubility to $7.7 \cdot 10^{-6}$ mol/l is calculated when pH is increased to 13.44 (Table 22). This value is taken for the upper limit.

Table 22: Co solubility and speciation in cement pore waters.

	pH 12.55	pH 13.44
$Cd(OH)_2(s)$	$7.0 \cdot 10^{-7}$ mol/l	$7.7 \cdot 10^{-6}$ mol/l
Speciation: [%]		
$Co(OH)_2(aq)$	45	4
$Co(OH)_3^-$	43	30
$Co(OH)_4^{2-}$	12	66

Table 23: Thermodynamic data for cobalt as taken from a former MINEQL database.

Equilibrium	
$Co^{2+} + H_2O \Leftrightarrow CoOH^+ + H^+$	$\log_{10}K_1° = -9.7$
$Co^{2+} + 2\ H_2O \Leftrightarrow Co(OH)_2(aq) + 2\ H^+$	$\log_{10}\beta_2° = -19.6$
$Co^{2+} + 3\ H_2O \Leftrightarrow Co(OH)_3^- + 3\ H^+$	$\log_{10}\beta_3° = -32.3$
$Co^{2+} + 4\ H_2O \Leftrightarrow Co(OH)_4^{2-} + 4\ H^+$	$\log_{10}\beta_4° = -45.8$
$Co^{2+} + SO_4^{2-} \Leftrightarrow CoSO_4(aq)$	$\log_{10}\beta_1° = 2.36$
$Co^{2+} + Cl^- \Leftrightarrow CoCl^+$	$\log_{10}\beta_1° = -0.05$
$Co(OH)_2(s) + 2\ H^+ \Leftrightarrow Co^{2+} + 2\ H_2O$	$\log_{10}K_{so}° = 13.1$
$CoS(s) + H^+ \Leftrightarrow Co^{2+} + HS^-$	$\log_{10}K_{so}° = -11.7$
$CoCO_3(s) \Leftrightarrow Co^{2+} + CO_3^{2-}$	$\log_{10}K_{so}° = -11.2 \pm 0.3$[1]

[1] GRAUER (1999)

4.27   Ruthenium, Iron, Calcium, Beryllium

Ruthenium

A short comment on ruthenium is given in BAES & MESMER (1976), saying that "*the hydrolysis of Ru(III) and Ru(IV) is dominated by the insolubility of the oxides* and that *no information is available for Ru(II)*". Due to its noble character, Ru(0) becomes stable when Eh turns negative. $RuO_2(s)$ becomes stable at positive Eh, but solubilities are not available. $Ru(VIII)O_4(s)$ seems to dissolve to $RuO_4(aq)$ and above pH~12 RuO_4OH^- seems to form. However,

Ru(VIII) as well as Ru(VII) compounds (RuO_4^-) are not stable in water. At high pH the formation of $Ru(VI)O_4^{2-}$ could be anticipated, but high concentrations are to be expected. Possibly, Ru has to be compared with Mn(VII,VI,V) under oxidising high-pH conditions.

Iron

The present system Eh of -230 mV was defined under the assumption that total dissolved iron does not exceed 10^{-7} mol/l. Thus, for consistency reasons the limit is:

$$10^{-7} \text{ mol/l.}$$

A maximum concentration of $1.2 \cdot 10^{-6}$ mol/l may be derived under the assumption that magnetite and microcrystalline $Fe(OH)_3$(s) control dissolved iron (WERSIN et al. 2003), but in this case, the system Eh changes accordingly.

Calcium

Calcium is an essential part of the system definition. Its concentration is defined by assuming saturation with portlandite, calcite, and fluorite (Table 2). The calculated concentration is

$$2.0 \cdot 10^{-2} \text{ mol/l.}$$

Formal uncertainties are not available, but it is estimated that the uncertainty of the solubility product of portlandite is in the order of 0.05 log_{10}-units. This translates to

upper limit: $2.2 \cdot 10^{-2}$ mol/l
lower limit: $1.8 \cdot 10^{-2}$ mol/l.

Portlandite solubility decreases with increasing pH. At pH 13.44, total dissolved Ca drops to $8.4 \cdot 10^{-4}$ mol/l.

Beryllium

The Nagra/PSI TDB as well as the former MINEQL database do not include thermodynamic data for beryllium. However, from BAES & MESMER (1976) one learns that Be may form anionic hydroxides ($Be(OH)_3^-$, $Be(OH)_4^{2-}$) above pH ~ 10. Thus, the maximum solubility may well exceed 10^{-3} mol/l in this pH range. A minimum solubility is observed in the pH range [~ 7...~ 10], where saturation with α-$Be(OH)_2$(s) produces Be concentrations not exceeding about 10^{-6} mol/l.

5   CONCLUDING REMARKS

The basic objective, to provide solubility limits for the cementitious environment of ILW wastes based on available thermodynamic data, was achieved. Except for Po, Ru and Be, solubility limits could be calculated or at least estimated. Further, an upper limit for nearly all elements could be provided.

With its very high pH, the cementitious environment creates exceptional chemical conditions, for which thermodynamic data are generally scarce. The high pH environment also forms a region where solubilities usually strongly depend on pH and where even small changes in the chemical system may have severe consequences for the ensemble of dissolved species. Several nuclides had to be qualified as not limited in this exceptional chemical environment (i.e. U, Tc, Nb, Se, Sb). Such behaviour is different from the near-neutral pH region of ordinary groundwaters, where solubilities often do not directly depend on pH, but on carbonate and/or on sulphate concentrations.

The work clearly points out where we still have gaps in the scientific understanding and where additional research activities are necessary. Two large problem areas may be defined ad hoc: the reaction of trace elements with cement minerals and the availability of redox models.

A growing number of recent studies clearly demonstrate the likely irreversible uptake of trace elements by various cement constituting minerals (e.g., KULIK & KERSTEN 2002, TITS et al. 2002, SCHEIDEGGER et al. 2001), but the detailed characterisation, in particularly the thermodynamic characterisation of these new phases, is still missing. Here, a large and scientifically very interesting field opens, which has to be cultivated and explored. The necessary geochemical and spectroscopic tools are either available or developed at present.

To establish a reliable redox model is an unresolved problem since the beginning of investigations on the geochemistry of radioactive waste repositories. Scientists agree on the central role of reduced iron forms and particularly on the importance of magnetite-like reaction products. Unfortu-nately, such agreement is not sufficient. An in-depth analysis of the most likely formed reactive phases, including their morphological and thermodynamic characterisation is missing, but such information alone would not be sufficient. Chemical reactions involving electron transfers are under strong kinetic control. Therefore, it is a priori not clear and predictable, whether a thermodynamically favoured reaction really proceeds in the timeframe considered or not. Classical examples are the reduction of sulphate, which proceeds solely with microbial catalysis, and the kinetically hindered reactions of molecular nitrogen. This

alliance of the redox problem with kinetics and with life cycles and organic chemistry opens an even larger scientific field that goes far beyond the scope of repository investigations. However, an initial goal could be a precise review of the geochemical behaviour of iron under repository conditions. Future safety analyses should not again be limited by these inadequacies.

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REFERENCES

BAES, C.F., JR., MESMER, R.E., (1976): The Hydrolysis of Cations. John Wiley, New York, Reprint Edition, R.E.Krieger Publishing (1986), 490p.

BERNER, U. (1999): Concentration Limits in the Cement Based Swiss Repository for Long-lived Intermediate-level Radioactive Wastes (LMA). PSI Bericht Nr. 99-10, Paul Scherrer Institute, Villigen, Switzerland.

BERNER, U. (2001): Nagra/PSI Thermochemical Database: The MINEQL/PSI-Version 01-01. PSI Internal Report AN-44-01-05, Paul Scherrer Institute, Villigen, Switzerland.

BERNER, U. (2002): Project Opalinus Clay: Radionuclide Concentration Limits in the Near-Field of a Repository for Spent Fuel and Vitrified High-Level Waste. PSI Bericht 02-22, Paul Scherrer Institute, Villigen, Switzerland, and Nagra Technical Report NTB 02-10, Wettingen.

BERNER, U., CURTI, E. (2002): Radium solubilities from SF/HLW wastes using solid solution and co-precipitation models. PSI Technical Report TM-44-02-04, Paul Scherrer Institute, Villigen, Switzerland.

BERNER, U., KULIK, D. (2002): Ca-Al-hydrates: Solid solutions?", Abstract A73, Goldschmidt 2002 Conference, Davos, Switzerland.

BONHOURE, I. (2002): U(VI) immobilization by cementitious phases (working title). Paul Scherrer Institute, Villigen, Switzerland (personal communication).

BROWN, D.R., GRUTZECK, M.W. (1985a): Iodine Waste Forms: Calcium Aluminate Hydrate Analogues. Materials Research Society Symposium Proceedings 44, 911-918.

BROWN D.R., GRUTZECK M.W. (1985b): The Synthesis and Characterisation of Calcium Aluminate Monoiodide. Cement and Concrete Research 15, 1068-1078.

GRAUER, R.[†] (1999): edited and translated by Urs Berner, Solubility Products of M(II) - Carbonates. PSI-Bericht Nr. 99-04, Paul Scherrer Institute, Villigen, Switzerland, and Nagra Technical Report NTB 99-03, Wettingen.

GRENTHE, I., FUGER, J., KONINGS, R.J.M., LEMIRE, R.J., MULLER, A.B., NGUYEN-TRUNG, C., WANNER, H. (1992): Chemical Thermodynamics Vol. 1: Chemical Thermodynamics of Uranium. OECD/NEA, North-Holland Elsevier, 716p.

HUMMEL, W. (2001): The influence of cyanide complexation on the speciation of radionuclides. PSI Technical Report TM-44-01-10, Paul Scherrer Institute, Villigen, Switzerland.

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, Wettingen, Switzerland, and, Universal Publishers/uPublish.com, Parkland, Florida, 565p.

HUMMEL, W., CURTI, E. (2003): Nickel aqueous speciation and solubility at ambient conditions: A thermodynamic elegy. Chemical Monthly (in press).

KULMALA, S., HAKANEN, M. (1993): The solubility of Zr, Nb and Ni in Groundwater and concrete water, and sorption on crushed rock and cement. Voimayhtiöiden Ydinjätetoimikunta (Nuclear Waste Commission of Finnish Power Companies), Report YJT-93-21, 66p.

KULIK, D.A., KERSTEN, M. (2002): Aqueous Solubility Diagrams for Cementitious Waste Stabilization Systems. 4. A Carbonation Model for Zn-Doped Calcium Silicate Hydrate by Gibbs Energy Minimization. Environmental Science & Technology 36, 2926-2931.

LEMIRE, R.J., FUGER, J., NITSCHE, H., POTTER, P., RAND, M.H., RYDBERG, J., SPAHIU, K., SULLIVAN, J.C., ULLMAN, W.J., VITORGE, P., WANNER H. (2001): Chemical Thermodynamics of Neptunium & Plutonium. Elsevier, Amsterdam, 845p.

LIU, C.W., NARASIMHAN, T.N. (1994): Modeling of selenium transport at the Kesterson reservoir, California, U.S.A. J. Contaminant Hydrology 15, 345-366.

LOTHENBACH, B., OCHS, M., WANNER, H., YUI, M. (1999): Thermodynamic Data for the Speciation and Solubility of Pd, Pb, Sn, Sb, Nb and Bi in Aqueous Solution. Japan Nuclear Cycle Development Institute (JNC), Report TN8400 99-011.

MYNENI, S.C.B., TRAINA, S.J., LOGAN, T.J. (1999): Ettringite solubility and geochemistry of the $Ca(OH)_2–Al_2(SO_4)_3–H_2O$ system at 1 atm pressure and 298 K. Chemical Geology 148, 1-19.

MORONY, L.P., GLASSER, F.P. (1995): Reactions between Cement Components and U(VI) Oxide. Waste Management 15/3, 243-403.

NECK, V., KIM, J.I. (2001): Solubility and hydrolysis of tetravalent actinides. Radiochimica Acta 89, 1-16.

OCHS, M. (2003): BMG Engineering Ltd, Zürich, Switzerland, personal communication.

OCHS, M., HAGER, D., HELFER, S., LOTHENBACH, B. (1998): Solubility of radionuclides in fresh and leached cementitious systems at 22 °C and 50 °C. Materials Research Society Symposium Proceedings 506, 773-780.

PILKINGTON, N.J., STONE, N.S. (1990): The solubility and sorption of nickel and niobium under high pH conditions. Harwell Laboratory, UKAEA, NSS/R186, 41p.

PERKINS, R.B., PALMER, C.D. (1999): Solubility of ettringite $(Ca_6[Al(OH)_6]_2(SO_4)_3 \cdot 26H_2O)$ at 5–75 °C. Geochimica et Cosmochimica Acta 63, 1969-1980.

ROBIE, R.A., HEMINGWAY, B.S. (1995): Thermodynamic Properties of Minerals and Related Substances at 298.15 K and 1 Bar (10^5 Pascals) Pressure and at Higher Temperatures. U.S. Geological Survey Bulletin 2131.

RÖMPP (1989): Chemie Lexikon, Band 1 (Falbe, J. & Regitz, M., eds). Georg Thieme Verlag, Stuttgart, 762p.

SANDINO, M.C.A., GRAMBOW, B. (1994): Solubility Equilibria in the U(IV)-Ca-KCl-H_2O System: Transformation of Schoepite into Becquerelite and Compreignacite. Radiochimica Acta 66/67, 37-43.

SAROTT, F.-A., SPIELER, P., PANDOLFO, P. (1995): Artificial ageing of hardened cement paste discs: compilation of experimental data records. PSI Internal, not published document, Paul Scherrer Institute, Villigen, Switzerland.

SCHEIDEGGER, A.M., WIELAND, E., SCHEINOST, A.C., DÄHN, R., TITS, J., SPIELER, P. (2001): Ni Phases Formed in Cement and Cement Systems under Highly Alkaline Conditions: an EXAFS Study. J. Synchrotron Radiation 8, 916-918.

SCHWYN, B., WERSIN, P., BERNER, U., WIELAND, E., NEALL, F. (2003): Near-field chemistry of an ILW repository in Opalinus Clay. Nagra Internal Report, Wettingen, Switzerland.

SÉBY, F., POTIN-GAUTIER, M., GIFFAULT, E., BORGE, G., DONARD, O.F.X. (2001): A critical review of thermodynamic data for selenium species at 25 °C. Chemical Geology 171, 173-194.

SERNE, R.J., RAI, D., MARTIN, P.F., FELMY, A.R., RAO, L., UETA, S. (1996): Leachability of Nd, U, Th and Sr from cements in a CO_2 free atmosphere. Materials Research Society Symposium Proceedings 412, 459-467.

SHARMASARKAR, S., REDDY, K.J., VANCE, G.F. (1996): Preliminary quantification of metal selenite solubility in aqueous solutions. Chemical Geology 132, 165-170.

THOENEN, T. (2001): Nagra/PSI Thermochemical Database Update: PHREEQC Database Version 01-01, Release 30-04-01. PSI Internal Report AN-44-01-06, Paul Scherrer Institute, Villigen, Switzerland.

THOENEN, T., BERNER, U., HUMMEL, W., KULIK, D., (2002): Equilibrium Constants at 50 °C for Solids and Aqueous Species Determining the Solubility of Am, Pu, Np, U, Th and Tc in the Reference Bentonite Porewater. PSI Technical Report TM-44-02-05, Paul Scherrer Institute, Villigen, Switzerland.

TITS, J., BRADBURY, M.H., WIELAND, E., MANTOVANI, M. (1998): The Uptake of Cs, Sr, Ni, Eu and Th by CSH Phases under high pH Cement Pore Water conditions. PSI Technical Report TM-44-98-01, Paul Scherrer Institute, Villigen, Switzerland.

TITS, J., WIELAND, E. (2001): Radionuclide uptake by calcium silicate hydrates (CSH phases): CRIEPI-PSI joint research project - 1st Annual Report. PSI Internal Report AN-44-01-10, Paul Scherrer Institute, Villigen, Switzerland.

TITS, J., STUMPF, T., RABUNG, T., WIELAND, E., FANGHÄNEL, T. (2002): Uptake of trivalent actinides (Cm(III)) and lanthanides (Eu(III)) by calcium silicate hydrates: A wet chemistry and time-resolved laser fluorescence spectroscopy (TRLFS) study. Environmental Science & Technology (submitted).

WARREN, C.J., REARDON, E.J. (1994): The solubility of ettringite at 75 °C. Cement and Concrete Research 24, 1515-1524.

WERSIN, P., JOHNSON, L.H., SCHWYN, B., BERNER, U., CURTI, E., WIELAND, E. (2003): Redox conditions in the near field of a SF/HLW and an ILW repository in Opalinus Clay. Nagra Technical Report NTB 02-13, Wettingen, Switzerland.

WOOD, S.A. (1991): Experimental determination of the hydrolysis constants of Pt^{2+} and Pd^{2+} at 25 °C from the solubility of Pt and Pd in aqueous hydroxide solutions. Geochimica et Cosmochimica Acta 55, 1759-1767.

YUI, M., AZUMA, J., SHIBATA, M. (1999): JNC Thermodynamic Database for Performance Assessment of High-level Radioactive Waste Disposal System. Japan Nuclear Cycle Development Institute (JNC), Report TN8400 99-070.

ADDENDUM WRITTEN BY NAGRA

In the following Table A1 the solubility limits that were used in the transport calculations for the safety assessment of Project Opalinus Clay (NAGRA 2002) are presented. These values were primarily taken from a compilation of BERNER (2002), which represents a predecessor of this final report. The values for the so-called reference case (which represents the most likely chemical conditions) are identical in both compilations. Minor deviations exist for a few elements with regard to the proposed "lower" and "upper" limits. For these cases the differences are highlighted in Table A1.

The values derived by U. Berner were carefully evaluated in terms of their suitability for usage in the transport calculations. Thus, plausibility tests were done by comparisons with other recent safety assessments and by expert judgement. This work is presented in a separate report (SCHWYN & WERSIN 2003).

A small part of the intermediate-level waste (ILW-2) will be physically separated from the main cementitious waste stream (ILW-1) because it contains complexing agents and high amounts of nitrate. As noted in this report, the particular chemistry of ILW-2 might lead to oxidising conditions (WERSIN et al. 2003). Also cyanide complexes with some nuclides might be formed (HUMMEL 2001) which would adversely affect solubility limits. These two aspects are taken into account for the estimation of the solubility limits for ILW-2, which are thus presented separately in Table A1 (see below). For the main ILW-1 repository most of the solubility limits were directly taken from Table 1.

For the elements C_{inorg}, Ni and Co isotopic exchange and shared solubilities with cement-bearing solids were assumed (WIELAND & VAN LOON 2002). Further it was assumed that 1% of these solids are available for isotopic exchange. According to WIELAND & VAN LOON (2002), 1% of the stable inventory per kg of cement is 4×10^{-4} mol for C_{inorg}, 6×10^{-7} mol for Co and 3×10^{-6} mol for Ni.

All the values were rounded to one significant digit. For some elements modified values or values not given in the report were used in the safety assessment (bold face in Table A1). The rationale for selection of these modified values is given in a separate column. The list of radionuclides in Table A1 does not entirely correspond to the one in the main part of the report because during the course of this work the procedure for the selection of safety relevant radionuclides was slightly modified, which led to a modified list.

REFERENCES

BERNER U. (2002): Löslichkeitslimiten für HAA/BEE-Abfälle, Zusammenzug der Zahlenwerte. PSI Aktennotiz AN-44-01-32, PSI, Villigen, Switzerland.

HUMMEL W. (2001): The influence of cyanide complexation on the speciation of radionuclides. PSI Technische Mitteilung TM-44-01-10, PSI, Villigen, Switzerland.

NAGRA (2002): Project Opalinus Clay: Safety report. Demonstration of disposal feasibility for spent fuel, vitrified high-level waste and long-lived intermediate-level waste (Entsorgungsnachweis). Nagra Technical Report NTB 02-05, Wettingen, Switzerland.

SCHWYN B., WERSIN P. (2003) Nagra Technical Report, in preparation.

WERSIN P., JOHNSON L.H., SCHWYN B., BERNER U., CURTI E. (2003): Redox conditions in the near field of a repository for SF/HLW and ILW in Opalinus Clay. Nagra Technical Report NTB 02-13, Nagra, Wettingen, Switzerland.

WIELAND E., VAN LOON L. (2002): Near-field sorption data base for performance assessment of an ILW repository in Opalinus Clay. Nagra Technical Report NTB 02-20, Nagra, Wettingen, Switzerland.

Table A1: Solubility limits (in mol/l) used for safety assessment of ILW. Values are identical to those shown in Tab. A2.5 of the safety report NAGRA (2002).

Bold faced type setting: modified from, or not present in this report. All other values directly taken from Table 1.

"s": same as for ILW-1

element	ILW-1			ILW-2[1]			Rationale for modified or new values
	ref. case rc-v	lower limit ll-v	upper limit ul-v	ref. case	lower limit	upper limit	
H	**high**	**high**	**high**	s	s	s	not present in Table 1
C_{inorg}	2×10^{-4}	1×10^{-4}	4×10^{-4}	s	s	s	initial high-pH stage assumed (Table 2), which is compatible with assumed carbonate inventory in cement and represents more conservative conditions relative to later stage
C_{org}	**high**	**high**	**high**	s	s	s	not present in Table 1
Cl	high	**high**	**high**	s	s	s	not present in Table 1
Co	7×10^{-7}	7×10^{-7}	7×10^{-6}	**high**	**high**	**high**	ll-v: not present in Table 1, conservatively assumed to be same as ref. case ul-v: different rounding procedure ILW-2: complexation with CN⁻ (HUMMEL, 2001)
Ni	3×10^{-7}	1×10^{-8}	8×10^{-6}	**high**	**high**	**high**	ILW-2: complexation with CN⁻ (HUMMEL, 2001)
Se	1×10^{-5}	7×10^{-6}	7×10^{-4}	**high**	**high**	**high**	ul-v: high- pH stage considered (cf. Table 9) ILW-2: oxidised to Se(VI) (cf. Table 9)
Sr	3×10^{-3}	2×10^{-3}	6×10^{-3}	s	s	s	not available in compilation of BERNER (2002), based on slightly different logK error estimation
Zr	6×10^{-6}	6×10^{-7}	6×10^{-5}	s	s	s	
Nb	high	**high**	**high**	s	s	s	not present in Table 1
Mo	3×10^{-5}	3×10^{-6}	2×10^{-3}	s	s	s	not present in Table 1, uncertainty of ±1 in logK of $CaMo_4$ assumed

element	ILW-1			ILW-2[1]			Rationale for modified or new values
Tc	high	3×10^{-7}	**high**	s	**high**	s	not present in Table 1 ll-v: assumed to be reduced to Tc(IV) (Fig. 4) ILW-2: assumed to be in oxidised form
Sn	1×10^{-7}	1×10^{-7}	$\mathbf{8 \times 10^{-6}}$	s	s	s	high- pH stage considered (cf. Table 10)
I	high	**high**	**high**	s	s	s	not present in Table 1
Cs	high	**high**	**high**	s	s	s	not present in Table 1
Sm	$\mathbf{2 \times 10^{-6}}$	$\mathbf{2 \times 10^{-7}}$	$\mathbf{2 \times 10^{-5}}$	s	s	s	missing in Table 1, Eu used as chemical analogue
Eu	2×10^{-6}	$\mathbf{2 \times 10^{-7}}$	2×10^{-5}	s	s	s	taken from BERNER (2002)
Pb	3×10^{-3}	$\mathbf{3 \times 10^{-3}}$	**high**	s	s	s	missing in BERNER (2002) ll-v: conservatively assumed to be same as rc-v ul-v: conservatively "high" assumed
Po	**high**	**high**	**high**	s	s	s	not present in Table 1 "high" selected because of lack of reliable data
Ra	1×10^{-5}	1×10^{-6}	$\mathbf{2 \times 10^{-5}}$	s	s	s	missing in BERNER (2002) assumed uncertainty of factor 2 on $RaSO_4$ solub.
Ac	2×10^{-6}	$\mathbf{2 \times 10^{-7}}$	2×10^{-5}	s	s	s	taken from BERNER (2002)
Th	3×10^{-9}	8×10^{-10}	1×10^{-8}	s	s	s	
Pa	1×10^{-8}	$\mathbf{1 \times 10^{-8}}$	**high**	s	s	s	not present in Table 1 ll-v: conserv. assumed same as rc-v ul-v: conserv. assumed to be "high"
U	1×10^{-8}	$\mathbf{1 \times 10^{-8}}$	5×10^{-7}	s	s	s	not present in Table 1 conserv. assumed same as rc-v
Np	5×10^{-9}	3×10^{-9}	1×10^{-8}	**high**	**high**	**high**	ILW-2: cf. Table 5
Pu	4×10^{-11}	1×10^{-11}	$\mathbf{1 \times 10^{-10}}$	$\mathbf{6 \times 10^{-11}}$	$\mathbf{2 \times 10^{-11}}$	$\mathbf{6 \times 10^{-10}}$	ul-v: taken from BERNER (2002) ILW-2: taken from BERNER (2002)
Am	2×10^{-9}	3×10^{-10}	1×10^{-8}	s	s	s	
Cm	2×10^{-9}	3×10^{-10}	1×10^{-8}	s	s	s	

[1] The ILW-2 values for Se, Tc, U, Np and Pu are also used as conservative estimates for a "what if?" case that assumes oxidising conditions in ILW-1.