

Technical Report 14-06

**Solubility of Radionuclides in
a Bentonite Environment for
Provisional Safety Analyses
for SGT-E2**

August 2014

U. Berner

Paul Scherrer Institut, Villigen PSI

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

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ISSN 1015-2636

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Summary

Within stage 2 of the sectoral plan for deep geological repositories for radioactive waste in Switzerland provisional safety analyses are carried out. In the case of the repository for spent fuel and vitrified high level waste considered retention mechanisms include the concentration limits of safety relevant elements in the pore water of the buffer material (bentonite).

The present work describes the solubility limits of the safety relevant elements Be, C_{inorg}, Cl, K, Ca, Co, Ni, Se, Sr, Zr, Nb, Mo, Tc, Pd, Ag, Sn, I, Cs, Sm, Eu, Ho, Pb, Po, Ra, Ac, Th, Pa, U, Np, Pu, Am and Cm in the pore water of bentonite after diffusive solution exchange with the host rock Opalinus Clay.

The term solubility limit denotes the maximum amount of an element dissolving in the pore solution of the considered chemical reference system. Chemical equilibrium thermodynamics is the classical tool used for quantifying such considerations. For a given solid phase equilibrium thermodynamics predict the amount of substance dissolving in the solution and describe the speciation of the considered element in solution. The principles of chemical equilibrium will also be the primary work hypothesis in the present work.

Solubility calculations were performed with the most recent version of GEMS/PSI (GEMS3.2 v.890) using the PSI/Nagra Chemical Thermodynamic Data Base 12/07, which is an update of the former Nagra/PSI Chemical Thermodynamic Data Base 01/01. The database was complemented with datasets from the ThermoChimie v. 7b for elements that were not considered in the mentioned update (Ag, Co, Sm, Ho, Pa, Be), with data from IUPAC (Pb) and with data from the literature (Mo). Differing sources for thermodynamic data are noted.

Reference values as well as lower and upper guideline values are evaluated. For many formation constants of solids and solutes uncertainties are known and allow conveying lower and upper guideline values. In many cases it is not clear whether the most stable solid is formed. In such cases the (kinetically driven) formation of alternative solid phases is included in the derivation of reference and guideline values. This procedure is based on expert judgment. Corresponding justifications are given for the individual elements and are an integral part of this work.

A similar report for an almost identical chemical environment has been produced in 2002, based on the PSI/Nagra Thermodynamic Data Base 01/01. A comparison of the solubility limits illustrates that for most of the elements the difference to this former work is below one order of magnitude.

Zusammenfassung

Innerhalb der Etappe 2 des Sachplans geologische Tiefenlager werden provisorische Sicherheitsanalysen durchgeführt. Beim Lager für abgebrannte Brennelemente und verglaste radioaktive Abfälle wird dabei auch die Konzentrationslimitierung durch die Löslichkeiten der sicherheitsrelevanten Radionuklide (Elemente) im Porenwasser des Verfüllmaterials (Bentonit) berücksichtigt.

Die vorliegende Arbeit beschreibt die sogenannten Löslichkeitslimiten der sicherheitsrelevanten Elemente Be, C_{inorg}, Cl, K, Ca, Co, Ni, Se, Sr, Zr, Nb, Mo, Tc, Pd, Ag, Sn, I, Cs, Sm, Eu, Ho, Pb, Po, Ra, Ac, Th, Pa, U, Np, Pu, Am und Cm im Porenwasser des Barrierenmaterials Bentonit nach diffusivem Wasseraustausch mit dem Wirtgestein Opalinuston.

Unter dem Begriff Löslichkeitslimite versteht man die maximale Menge eines chemischen Elements, die sich im Porenwasser des betrachteten Referenzsystems aufzulösen vermag. Als klassisches Werkzeug wird für solche Betrachtungen die Gleichgewichtsthermodynamik angewendet. Diese sagt aus, welche Stoffmenge sich im Gleichgewicht mit einem Festkörper in der zugehörigen flüssigen Phase befindet und wie sich das untersuchte Element auf die verschiedenen gelösten Spezies verteilt. Die Gleichgewichtsthermodynamik wurde auch im vorliegenden Bericht als zentrale Arbeitshypothese verwendet.

Die Löslichkeitsberechnungen wurden mit dem GEMS/PSI Programm (GEMS3.2 v.890) durchgeführt. Die notwendigen thermodynamischen Daten entstammen hauptsächlich der PSI/Nagra Chemical Thermodynamic Database 12/07, einer Aktualisierung der PSI/Nagra Chemical Thermodynamic Database 01/01. Daten für Elemente welche in der erwähnten Datenbank nicht zur Verfügung stehen (Ag, Co, Sm, Ho, Pa, Be, Pb, Mo), wurden der ThermoChimie v.7b Datenbank, der UPAC Datensammlung oder der Literatur entnommen. Abweichende Datenquellen sind jeweils vermerkt.

Neben Referenzwerten werden auch untere und obere Eckwerte evaluiert. Oft sind für die Formationskonstanten der Festkörper und gelösten Spezies Bandbreiten verfügbar, mit welchen die unteren und oberen Eckwerte abgeschätzt werden können. In vielen Fällen ist aber ungewiss, ob wirklich der thermodynamisch stabilste Festkörper gebildet wird. Dann wird die (kinetische) Bildung von alternativen Festkörpern in die Herleitung der Referenz- und Eckwerte mit einbezogen. Dieses Verfahren verlangt Expertenwissen. Die entsprechenden Begründungen sind unter den jeweiligen Elementen aufgeführt und sind ein zentraler Bestandteil dieser Arbeit.

Eine ähnliche Arbeit unter fast gleichen chemischen Bedingungen wurde bereits im Jahre 2002, mit der PSI/Nagra Chemical Thermodynamic Database 01/01, durchgeführt. Der Vergleich der Löslichkeitslimiten zeigt auf, dass für die meisten Elemente die Differenz zur früheren Arbeit unterhalb einer Grössenordnung liegt.

Résumé

Dans le cadre de l'étape 2 du plan sectoriel «Dépôts en couches géologiques profondes», mis en œuvre pour sélectionner les sites de stockage pour déchets radioactifs en Suisse, il est prévu de réaliser des analyses de sûreté provisoires. Pour le dépôt destiné à accueillir les éléments combustibles usés et les déchets de haute activité vitrifiés, on prend notamment en compte, en tant que mécanisme de rétention, la limitation de la concentration des radionucléides importants pour la sûreté du dépôt (ci-dessous: les «éléments») en solution dans l'eau interstitielle du matériau de remplissage (bentonite).

La présente étude décrit les «limites de solubilité» des éléments d'intérêt Be, C_{inorg}, Cl, K, Ca, Co, Ni, Se, Sr, Zr, Nb, Mo, Tc, Pd, Ag, Sn, I, Cs, Sm, Eu, Ho, Pb, Po, Ra, Ac, Th, Pa, U, Np, Pu, Am et Cm dans l'eau interstitielle de la bentonite utilisée comme barrière ouvragée après échange diffusif avec la roche d'accueil (les Argiles à Opalinus).

La notion de « limite de solubilité » désigne la concentration maximale d'un élément donné dans l'eau interstitielle du système de référence étudié. Pour déterminer ce type de donnée, on fait généralement appel aux principes de la thermodynamique d'équilibre chimique. Pour une phase solide donnée, la thermodynamique d'équilibre permet de déterminer la quantité de matière dissoute et la spéciation de l'élément étudié dans la solution. Dans le cadre de la présente étude, on a également utilisé les principes de la thermodynamique d'équilibre comme principale hypothèse de travail.

Les calculs de solubilité ont été réalisés avec le logiciel GEMS/PSI (GEMS3.2 v.890). Les données thermodynamiques nécessaires proviennent principalement de la PSI/Nagra Chemical Thermodynamic Database 12/07, une version mise à jour de la PSI/Nagra Chemical Thermodynamic Database 01/01. Pour les éléments ne figurant pas dans la mise à jour (Ag, Co, Sm, Ho, Pa, Be, Pb, Mo), on a utilisé des données provenant de la base ThermoChimie v.7b, ainsi que de l'IUCA ou de la littérature existante. Toute autre source a été mentionnée.

En plus des valeurs de référence, on a aussi estimé les valeurs limites inférieure et supérieure. Pour de nombreuses constantes de formation des corps solides et liquides, on dispose d'un spectre qui permet d'estimer les valeurs limites inférieure et supérieure. Cependant, dans de nombreux cas, il n'est pas certain que se forme le corps solide le plus stable du point de vue thermodynamique. Dans ce cas, on fait intervenir la formation (cinétique) de corps solides alternatifs pour dériver les valeurs de référence et les valeurs limites. Cette procédure fait appel aux connaissances d'experts. Les justifications correspondantes figurent dans la description des différents éléments. Elles constituent une contribution importante au travail présenté ici.

Une étude similaire avait déjà été effectuée en 2002 dans des conditions chimiques presque identiques, en utilisant la PSI/Nagra Chemical Thermodynamic Database 01/01. La comparaison des limites de solubilité montre que, pour la plupart des éléments, la différence par rapport à l'étude de 2002 est inférieure à un ordre de grandeur.

Table of Contents

Summary	I
Zusammenfassung	III
Résumé	V
Table of Contents	VII
List of Tables	VIII
List of Figures	VIII
1 Introduction	1
2 Basic Data, Chemical Conditions and Methods	3
2.1 Database and Code	3
2.2 Pore Water Compositions	3
2.3 Operational Approach for Deriving Limits	5
2.4 Lower and Upper Guideline Values and Recommended Values	6
2.5 Additional Comments	8
3 Evaluated Element Solubilities	9
4 Comments on Individual Elements	15
5 Concluding Remarks	45
6 References	47
Appendix: Solubility Limits used for Dose Calculations	A-1
A.1 Introduction	A-1
A.2 Adjusted solubility values	A-1
A.3 Solubility Limits in the SF/HLW Near Field for Dose Calculations	A-2
A.4 References	A-2

List of Tables

Tab. 1:	Composition of the chemical system for calculating solubility limits, taken in the middle of the bentonite layer after 10'000 years solution exchange between bentonite and Opalinus Clay (298.15 K, 1 bar), as taken from Kosakowski & Berner (2011).....	4
Tab. 2:	Summary of recommended element concentration including lower and upper guideline values, calculated at 25 °C, 1 bar.	11
Tab. A-1:	Solubility limits of safety relevant elements in the SF/HLW near field (bentonite).....	A-3

List of Figures

Fig. 1:	Comparison of present solubility limits (yellow) with those evaluated in Berner (2002) (blue) (25 °C, 1 bar).....	10
Fig. 2:	Solubility data for Pd(OH) _{2(s)} published by Van Middlesworth & Wood (1999) and Wood (1991) measured at various temperatures, ionic strengths and pH-values.	26

1 Introduction

As part of Stage 1 of the Sectoral Plan for Deep Geological Repositories, Nagra has proposed six regions which are suitable for hosting a repository for low- and intermediate-level waste (L/ILW) and three regions for high-level (HLW) radioactive waste (Nagra 2008). In the current Stage 2 of the Sectoral Plan, Nagra will propose at least two siting regions each for the L/ILW repository and for the HLW repository for further consideration. Provisional safety analyses for all siting regions are part of the procedure and support the evaluation and selection process. The present work aims at providing the "solubility limits" (or maximum expected concentrations) for safety relevant elements in the buffer (bentonite) of a deep geological repository for spent fuel and vitrified high level radioactive waste in Switzerland.

A multi-barrier system is responsible for the retention of the radionuclides on their way from the near field of a repository to the biosphere (see for example (Nagra 2002)), including various processes like slow transport through the geological system, radioactive decay, sorption on backfill and host rock minerals, limited solubilities or precipitation of secondary minerals. The present report specifically deals with solubility limits or maximum expected concentrations of chemical elements in the near field buffer material (bentonite). The formation of solids is an important chemical retention mechanism for many radionuclides.

The principles of equilibrium thermodynamics are well established and have already been used in a former report (Berner 2002). The maximum concentrations of thirty-one relevant elements presented in this report were also evaluated based on these principles. The evaluations, however, may also have to include kinetic processes. Thermodynamic principles demand, that the least soluble solid phase (associated to the particular element) is formed. This is, however, not always the case since very stable solids may form under specific conditions only (e.g. at elevated temperature, high pressure, extremely slow kinetics). This implies that calculated individual solubilities need to be interpreted for their plausibility and often supporting information is needed to select appropriate solubility limiting phases.

The provisional safety analyses require not only reference but also upper guideline values (obere Eckwerte) (ENSI 2010). Here, for each element, upper and lower guideline values are provided in addition to the reference solubility limit. Supporting arguments for selecting all these values have been adopted either from a former report (Berner 2002), from available numerical uncertainties of solubility constants or are based on expert judgment. Comments and advice from a review of this former report by ENSI (Wanner 2003) have been taken into account where appropriate.

2 Basic Data, Chemical Conditions and Methods

2.1 Database and Code

Solubility calculations were performed with the most recent version of GEMS/PSI package (GEMS3.1 v.868, <http://gems.web.psi.ch>) (Kulik et al. 2013) using the PSI/Nagra Chemical Thermodynamic Data Base 12/07 (Thoenen 2012a, Thoenen 2014), including additions for the not yet reviewed elements Ag, Be, Co, Ho, Pa, Pb and Sm (Thoenen 2012b) and data for Mo.

2.2 Pore Water Compositions

Solubility calculations were performed in bentonite pore water described in Bradbury et al. (2014), Curti (2012), Berner & Kosakowski (2011a), Berner & Kosakowski (2011b), Curti (2011), Berner (2010), Berner (2011). The reference bentonite composition (pore water and minerals) in Tab. 1 was evaluated based on the following conditions:

Starting from the basic bentonite system according to Berner (2011) a diffusive pore water exchange with Opalinus Clay during 10'000 years was modelled and the composition in the middle of the 0.73 m thick bentonite layer was taken (for details see (Bradbury et al. 2014), (Berner & Kosakowski 2011a)). Besides the longevity of the steel canisters, during which the radioactive material is hermetically enclosed, the reasons for selecting such pore water conditions were:

- a) Consider and allow for the back diffusion of electrolytes from the basic bentonite system to the less concentrated Opalinus Clay pore water in the combined system waste-bentonite-Opalinus Clay
- b) Consider the timely evolved and thus changed occupancy of the ion exchange phase (montmorillonite)

An optional 0.15 m thick low-pH shotcrete liner was not included in the derivation of the reference chemical bentonite composition since its impact on the chemical conditions was found to be small due to the limited amount of cementitious material.

Tab. 1: Composition of the chemical system for calculating solubility limits, taken in the middle of the bentonite layer after 10'000 years solution exchange between bentonite and Opalinus Clay (298.15 K, 1 bar), as taken from Kosakowski & Berner (2011).

Inert is an operationally defined, non-reacting phase having the physical/chemical properties of quartz. It mainly preserves weight and volume in coupled processes and includes all those non-specified solid phases considered to be non-reactive.

Element	[mol]	Solution species [mol/kg H ₂ O]*)	Main species in solution
Al	112.078	1.472×10^{-8}	Al(OH) ₄ ⁻ 97 %, Al(OH) _{3(aq)} 3 %
Ba	0.00756917	1.119×10^{-7}	Ba ²⁺ 52 %, BaSO _{4(aq)} 48 %
C	4.6829	8.994×10^{-4}	HCO ₃ ⁻ 87 %, NaHCO _{3(aq)} 5 %, CO _{2(aq)} 2 %, CaHCO ₃ ⁺ 2 %, MgHCO ₃ ⁺ 1 %, NaCO ₃ ⁻ 1 %, CO ₃ ²⁻ 1 %, CaCO _{3(aq)} 1 %
Ca	4.56119	8.997×10^{-3}	Ca ²⁺ 73 %, CaSO _{4(aq)} 27 %
Cl	0.16032	1.607×10^{-1}	Cl ⁻ 100 %
Fe	16.16	3.698×10^{-5}	Fe ²⁺ 70 %, FeSO _{4(aq)} 23 %, FeHCO ₃ ⁺ 2 %, Fe(III) _{tot} 3.5 x 10 ⁻¹⁶
K	0.513764	1.217×10^{-3}	K ⁺ 96 %, KSO ₄ ⁻ 4 %
Mg	20.9565	5.126×10^{-3}	Mg ²⁺ 70 %, MgSO _{4(aq)} 30 %
Na	20.6657	1.919×10^{-1}	Na ⁺ 97 %, NaSO ₄ ⁻ 3 %
S	1.78715	3.005×10^{-2}	SO ₄ ²⁻ 68 %, NaSO ₄ ⁻ 19 %, CaSO _{4(aq)} 8 %, MgSO _{4(aq)} 5 %, S(-II) _{tot} 1.4 x 10 ⁻¹¹ .
Si	374.996	1.820×10^{-4}	SiO _{2(aq)} 99 %, HSiO ₃ ⁻ 1 %
Sr	0.0131178	5.606×10^{-5}	Sr ²⁺ 74 %, SrSO _{4(aq)} 26 %
O	1,456.23	--	
H	947.593	--	
N	3.99×10^{-5}	8.028×10^{-5}	N _{2(g)} 100 %, (NH _{3(aq)} +NH ₄ ⁺) 1.0 x 10 ⁻⁸
Inert (SiO ₂)	50.605	--	
Phases	[mol]	[kg]	Comments
Solution		1.008	
Montmorillonite units of charge -1	27.124	32.84	The upper part of Column 2 represents the full elemental composition (43.042 [kg]) as taken from Kosakowski & Berner (2011) leading to 18.97 [L] of solid phases and 1.001[L] of solution. The calculated solid phase assembly is provided in Columns 2 & 3.
Quartz	90.92	5.463	
Inert (SiO ₂)	50.61	3.041	
Siderite	2.230	0.2584	
Calcite	2.452	0.2454	
Pyrite	0.8748	0.1050	
Hydrous Magnetite	0.2987	7.992×10^{-2}	
Barite	7.64×10^{-3}	1.775×10^{-3}	

Tab. 1: (continued)

System characteristics			
pH		7.79	
Ionic strength		0.239 [mol/kg]	
Eh		-0.204 [V]	
$\log_{10}(p\text{CO}_2)$		-3.20	
Equiv. CEC		0.63 [mol/kg]	The cation exchange capacity (CEC) refers to moles per kg of system. The present system in total includes 43.042 [kg].
Occupancy	Na	75.4 %	
	Ca	15.5 %	
	Mg	7.1 %	
	K	1.9 %	
	Sr	0.1 %	
	Fe	0.05 %	

* A simplified recipe of the solution presented in Tab. 1 would be 1.0 kg of water, 159.8 mmoles of NaCl, 15.6 mmoles of Na₂SO₄, 9.0 mmoles of CaSO₄, 5.1 mmoles of MgSO₄, 0.8 mmoles of KHCO₃, 0.2 mmoles of K₂SO₄ and 0.2 mmoles of SiO₂.

Concerning bentonite the present study considers a closed system because the exchange with the surrounding rock system may be very slow. The pH of the solution is primarily determined and also buffered by the amphoteric sites of the montmorillonite phase; the site concentration is about 2 [mol/kg H₂O] (for details see Berner et al. (2013)). The carbonate system ($\sim 9 \times 10^{-4}$ [mol/kg H₂O]) is determined by pH and the solubility of calcite and siderite and fixes $\log_{10}(p\text{CO}_2)$ at -3.20. The redox potential of the system (Eh = -204 [mV]) is determined by the Fe(II)/Fe(III) and S(VI)/S(-II) couples. Relevant solid phases determining Eh are the montmorillonite solid solution phase, including structurally bound Fe(II) and Fe(III) (Berner et al. 2013), siderite, pyrite and hydrous magnetite (Berner 2009).

The sensitivity of such types of pore waters against changes of total anion concentration, sulfate/chloride-ratio and also $\log_{10}(p\text{CO}_2)$ have been discussed in Berner & Kosakowski (2011a). There, it was concluded that such pore water compositions behave remarkably robust, i.e. are buffered with respect to chemical changes.

2.3 Operational Approach for Deriving Limits

Deriving solubility limits is a multi-stage process. The procedure outlined below was used for each of the 32 elements included in the list of safety relevant elements (Be, C, Cl, K, Ca, Co, Ni, Se, Sr, Zr, Nb, Mo, Tc, Pd, Ag, Sn, I, Cs, Sm, Eu, Ho, Pb, Po, Ra, Ac, Th, Pa, U, Np, Pu, Am, Cm).

The solubility calculations (Tab. 2) were started with the same full system (including all solids and the pore solution) as was used to calculate the pore water composition presented in Tab. 1. This system is buffered with respect to the major solutes and with respect to selected minor species (i.e. sulfide species). For all relevant elements to be assessed (cf. list of safety relevant elements above), a minimum amount of 1×10^{-8} [mol/kg H₂O] was simultaneously added to the reference composition provided in Tab. 1. In a first simulation step the mentioned elements were added as chlorides, hydroxides, oxides, likewise also as acids or as alkali salts, in order not

to disturb the basic chemical system. Inspecting calculated saturation indices then allowed deciding on the least soluble solid phase with respect to a particular element. In the progress of the solubility limit evaluation this first step addition was then replaced/completed by adding appropriate amounts of the least soluble solid to the chemical system. This approach produces the minimum solubility of the element in question for the least soluble solid by assuming full validity of thermodynamic principles.

However, this approach does not answer the question of whether the selected solid phase really is the limiting solid or not, because thermodynamics do not answer questions related to kinetic aspects (i.e. precipitation kinetics, issues of over-saturation, temperature range of formation etc.). It may, for example, well be that the most stable solid producing the lowest solubility never forms at ambient temperature because this solid is a high temperature phase exclusively forming under different environmental conditions. Such difficulties imperatively need to be assessed when evaluating solubility limits on the basis of thermodynamic equilibrium calculations.

Therefore, the next steps in the evaluation of element-specific solubility limits proceeded as follows: Using corresponding operational constraints in the code system, the least soluble solid phase was excluded from being considered and the above mentioned procedure was applied to the "next" stable solid. In this way all potentially limiting solids available from the thermodynamic database were processed. One obtains a series of distinct "solubility limits" increasing in numerical value and depending on the solid phase. This series of distinct limits finally forms a range.

As indicated above, the finally given solubility limit is not necessarily identical with the absolutely lowest calculated concentration as this would be inferred from thermodynamic principles. Moreover, the recommended value as provided in Tab. 2 is an individual selection out of the mentioned range. This individual selection is finally based on expert opinion. Notes and comments associated with particular numerical values are an integrated part of this value because they indicate/explain why a certain value has been selected.

2.4 Lower and Upper Guideline Values and Recommended Values

It is part of the ongoing safety assessment procedure to accompany recommended parameter values (solubility limits) by bounding values (obere und untere Eckwerte, ENSI 2010). These bounding values should provide a sensible and justifiable range of expectable maximum concentrations including the recommended solubility limit. In earlier reports (Berner 2002, Berner 2003) such bounding values had been denoted as lower and upper limits or sometimes even as "uncertainties". The term "uncertainties" appears to be a too sloppy expression for this type of bounding values and also the term lower limit is actually not correct. This work prefers to use the term guideline values (lower and upper) as synonyms for ENSI's *obere und untere Eckwerte*, because these bounding values should guide the reader to a range of reasonable values, rather than implying a pure mathematical reasoning behind the limiting values.

The evaluation of such guideline values is much more challenging than just selecting/ calculating the recommend solubility limits.

The approach to obtain upper and lower guideline values includes the analysis of the series of potentially limiting solids and provides the associated numerical values. The formation constant of each limiting solid may or may not have an uncertainty bandwidth which, when evaluated, leads to an individual solid phase dependent concentration bandwidth. Further, each dissolved element exhibits a certain speciation, describing the distribution of the total dissolved concentra-

tion over the different complexes in solution. Complexes comprising more than about 30 to 40 % of the total dissolved concentration are called dominant complexes. If a selected element shows only one dominant complex, the overall uncertainty can be evaluated more or less straightforwardly by combining the uncertainty of the complex formation constant (if available) with the one of the limiting solid formation constant. *Note* that the concentration of the complexing agent itself (typically Cl^- , OH^- , CO_3^{2-} , SO_4^{2-} , HSiO_3^-) may vary in a certain range, but this is neglected in the present work. If the element exhibits two or three dominant complexes in solution, the evaluation of solid phase dependent borderline values becomes much more difficult because Monte Carlo-type analyses of all relevant parameters had to be performed in principle.

The thermodynamic database does not provide uncertainties for all parameters (solid phase formation constant; dominant complex formation constant), but sometimes a parameter uncertainty may be estimated based on chemically similar elements or based on other information. This will be noted in the summarizing table or under the comments associated with each particular element.

The general approach for establishing the lower and upper guideline values and the recommended solubilities was as follows:

Lower guideline value: Evaluate the solubility using the formation constants of the most stable solid and of the least stable dominant complex from the available ranges of formation constant uncertainties. Perform this evaluation using the least soluble solid from the series of available solid phases.

Upper guideline value: Evaluate the solubility using the formation constants of the least stable solid and the most stable dominant complex from the available ranges of formation constant uncertainties. Perform this evaluation using the most soluble solid from the series of available solid phases.

Recommended (reference) value: As outlined above, the band width bordered by upper- and lower guideline values was evaluated using well-confirmed and documented thermodynamic data including uncertainties. The recommended solubility (reference value) for the safety relevant elements is evaluated from the same calculations using the same data as well as the same chemical system. The recommended value is usually located between the lower and the upper guideline value, in some cases it may lay on the borderline. The calculated speciation in solution is perfectly traceable based on the available thermodynamic data, but selecting the nature of the limiting solid or fixing a certain concentration needs expert judgment, when no other clear indications are available (a clear indication may for example be the fact that only one limiting solid phase is available in the database). This shall be illustrated using americium as an example:

For Am the thermodynamic database (Section 2.1) includes the solid phases $\text{AmOHCO}_3 \cdot 0.5\text{H}_2\text{O}(\text{cr})$ (4.0×10^{-8} [mol/kg H_2O]), $\text{NaAm}(\text{CO}_3)_2 \cdot 0.5\text{H}_2\text{O}(\text{cr})$ (2.8×10^{-6} [mol/kg H_2O]), $\text{AmOHCO}_3(\text{am,hyd})$ (6.3×10^{-6} [mol/kg H_2O]), $\text{Am}_2(\text{CO}_3)_3(\text{cr})$ (9.5×10^{-6} [mol/kg H_2O]) und $\text{Am}(\text{OH})_3(\text{cr})$ (1.8×10^{-5} [mol/kg H_2O]). In parentheses calculated solubilities in the reference solution (Tab. 1) are provided. The dominant complex in solution is AmHSiO_3^{2+} , which comprises about 70 % of dissolved Am. Individual uncertainties of solid phase formation constants range from ± 0.5 up to ± 2.2 \log_{10} -units. Applying evaluated solubilities and individual uncertainties leads to a range from 8.3×10^{-9} [mol/kg H_2O] up to 5.4×10^{-5} [mol/kg H_2O] for the solubility of Am. Hence, lower and upper guideline values can be defined by these figures, but what should be recommended/selected for the limiting solid phase? Experimental evidences measured in the present reference solution are not available.

It seems that the hydroxide carbonates are more stable than the pure carbonates. Does the most stable phase $\text{AmOHCO}_3 \cdot 0.5\text{H}_2\text{O}(\text{cr})$ directly precipitate from solution? Or does a hydrated, amorphous modification precipitate first, which gradually converts to the crystalline form? What is the kinetics of such a process? The double salt $\text{NaAm}(\text{CO}_3)_2 \cdot 0.5\text{H}_2\text{O}(\text{cr})$ is a factor of only 2 less soluble than the amorphous $\text{AmOHCO}_3(\text{am,hyd})$, seems to form in alkali-rich solutions and its equilibrium with the solution seems to be well characterised when looking at its formation constant uncertainty of $\pm 0.5 \log_{10}$ -units. Hence, expert opinion suggests to select $\text{NaAm}(\text{CO}_3)_2 \cdot 0.5\text{H}_2\text{O}(\text{cr})$ as the limiting solid.

2.5 Additional Comments

The approach of simultaneously calculating all solubility limits is novel. It produces on the one hand very complex solution systems (about 700 solute species) and makes high demands on the code system and its numerical accuracy. On the other hand such an approach reflects realistic system behaviour and highlights potential interdependencies among the different elements to be assessed. It also necessitates, in principle, a full appraisal of (relative) mass balances¹. In the present state of work such interdependencies and potential impacts of mass balances are not worked out in detail, but are used to indicate problem areas to be addressed in a future version of the data base presented here.

Curti (2012) has modelled bentonite pore waters under different conceptual- and constraints assumptions (i.e. $\log_{10}\text{pCO}_2$ from -1.8 to -2.5, total porosity from 0.36 to 0.48, accessible anion porosity from 0.05 to 0.145). Differences in resulting total major element concentrations and solution parameters (pH, pe, I, $\log_{10}\text{pCO}_2$) from the present pore water seem not critical in the sense of evaluated solubilities and particularly in the sense of lower- and upper guideline values. An exception may be the high salinity pore water, originally tracing back to a work of Mäder (2009), where the chloride concentration is as high as 0.66 [mol/kg H₂O]. *Note* that such exceptions are for example discussed in the case of $\text{AgCl}(\text{s})$ or $\text{Pd}(\text{OH})_2$ solubility.

The present work, different from earlier works on the same subject (Berner 2002, Berner 2003) does not explicitly rely on uncertainties in the composition of the basic pore solution but considers a (potentially more robust with respect to pH and $\log_{10}\text{pCO}_2$) single pore water modelled under improved concepts (thermodynamic equilibrium of clay minerals, amphoteric surface sites and ion exchange processes). Uncertainties in the resulting recommendations may arise from the choice of the limiting phase, from uncertainties in corresponding solubility constants, from incomplete knowledge of complexes in solution including their formation constants or from mutual interactions with other elements on the basis of relative overall mass balances (see for example silver or nickel). It is strongly believed that uncertainties arising from differences in pore water compositions are, in most cases, only of minor importance.

¹ Consider for example the formation of a limiting solid like Ag_2Se . Depending on the relative amounts either Ag or Se might be exhausted by forming this solid. The remaining element will then be controlled by another solid phase at higher concentration levels.

3 Evaluated Element Solubilities

Element solubilities evaluated in the pore water shown in Tab. 1 are presented in this section. Fig. 1 provides a visual representation of the ranges from the lower to the upper guideline value (yellow horizontal bars). The recommended solubility limit is visualised with a black vertical bar, indicating not only the numerical value but also the position of the recommended value within the range. For comparison, solubility values evaluated 10 years before for a very similar pore water system (Berner 2002) are presented using light blue bars.

Tab. 2 provides a summary of the numerical values of recommended solubilities, and of lower and upper guideline values (Columns 2 to 4). A comparison with an earlier evaluation (Berner 2002) and with recommendations from Wanner (2003) (indicated by an asterisk) is also given (Columns 5 to 7). Tab. 2 includes individual comments (last column), summarizing relevant information leading to the recommended values or to the lower and upper guideline values. A more comprehensive description of the evaluated element solubilities, including the speciation in solution at the recommended value and at the upper guideline value, is provided in Section 4.

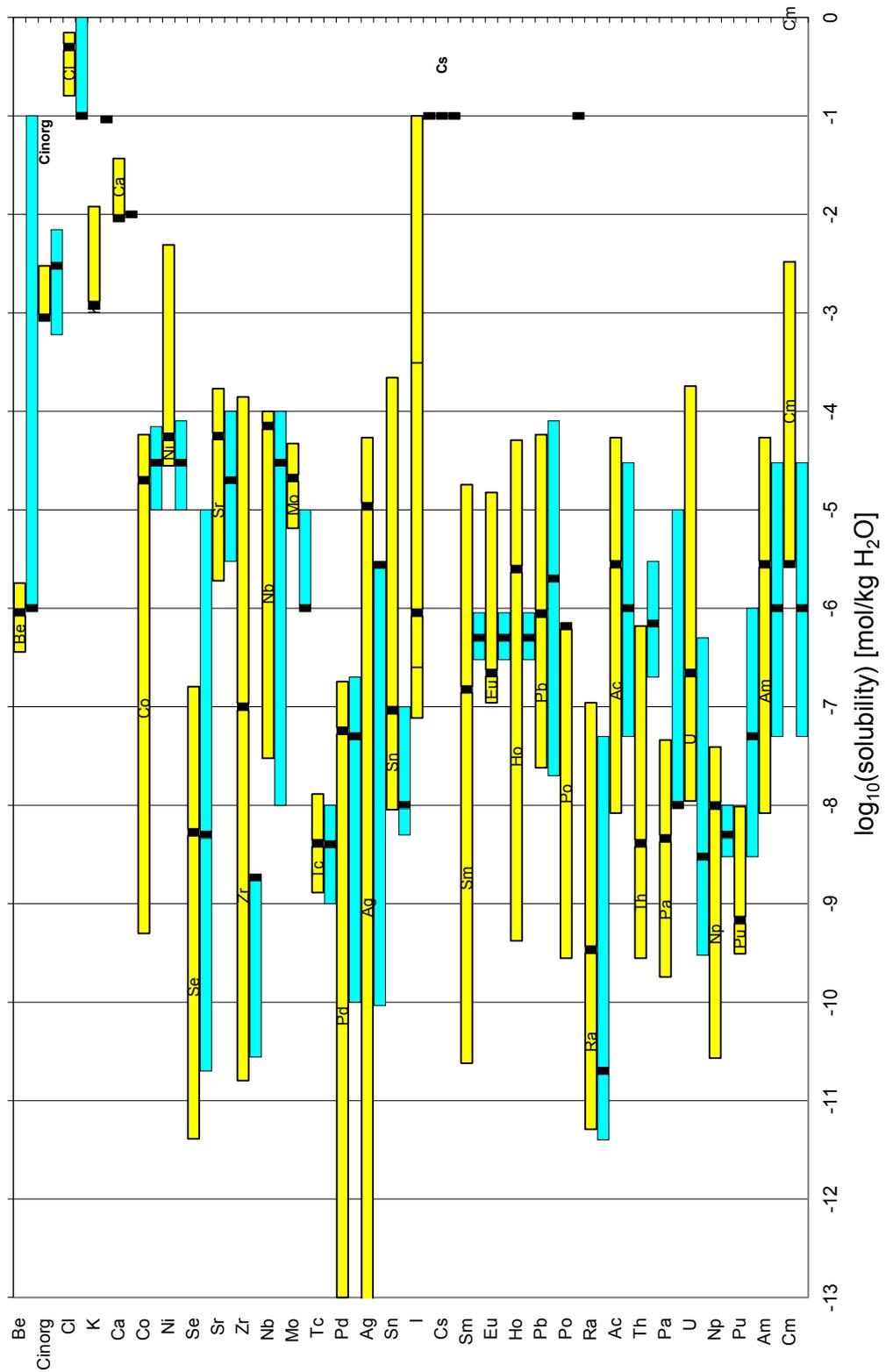


Fig. 1: Comparison of present solubility limits (yellow) with those evaluated in Berner (2002) (blue) (25 °C, 1 bar).

Black vertical bars indicate the recommended value. Colored horizontal bars indicate lower & upper guideline values. Vertical bars at the -1 position indicate non-values.

Tab. 2: Summary of recommended element concentration including lower and upper guideline values, calculated at 25 °C, 1 bar.

For a detailed description of Tab. 2, see Chapter 3.

Bentonite pore water without liner (after 10,000 years)				(Berner 2002) ^{*/6} (Wanner 2003)			Limiting solid(s)/comments
Element	Recommended value [mol/kg]	Lower guideline value [mol/kg]	Upper guideline value [mol/kg]	Reference case [mol/l]	Lower limit [mol/l]	Upper limit [mol/l]	
Be	9.1×10^{-7}	3.6×10^{-7}	1.8×10^{-6}	1×10^{-6}	1×10^{-6}	high	Be(OH) _{2(a,β,or am)}
C _{inorg}	8.9×10^{-4}	8.9×10^{-4}	3.0×10^{-3}	3×10^{-3}	6×10^{-4}	7×10^{-3}	Calcite, siderite; basic solution composition. See text for guideline values.
Cl	Not limited	1.6×10^{-1}	7.0×10^{-1}	High	High	High	Not limited; basic solution composition
K	1.2×10^{-3}	1.1×10^{-3}	1.2×10^{-2}	--	--	--	Controlled by ion exchange equilibria on montmorillonite solid solution; potential control by illite (upper guideline). Recommended value taken from Tab. 1
Ca	9.1×10^{-3}	8.7×10^{-3}	3.7×10^{-2}	1×10^{-2}	1×10^{-2}	1×10^{-2}	Calcite, also controlled by ion exchange equilibria on montmorillonite solid solution.
Co	2.0×10^{-5}	5.0×10^{-10}	5.8×10^{-5}	3×10^{-5}	1×10^{-5}	7×10^{-5}	Spherochalcite (CoCO _{3(er)}); the complex CoHSiO ₃ ⁺ , an analogue to NiHSiO ₃ ⁺ , is missing.
Ni	5.5×10^{-5}	2.8×10^{-5}	4.9×10^{-3}	3×10^{-5}	1×10^{-5}	8×10^{-5}	NiCO _{3(er)} limiting phase with uncertainty of $\pm 0.18 \log_{10}$ -units. Complex NiHSiO ₃ ⁺ ; comprises ~50 % of dissolved Ni.
Se	5.3×10^{-9}	4.1×10^{-12}	1.6×10^{-7}	5×10^{-9}	2×10^{-11}	1×10^{-5}	Se(-II) is predominant at given redox potential and HSe ⁻ is dominant complex; Se _(er) is controlling phase. Lower guideline value: CoSe _{2(er)} , upper guideline value based on Sr _(er) by applying maximum uncertainties (Se ₄ ²⁻ becomes dominant complex). Above about +200 mV not solubility limited anymore and Se(IV) species dominant.
Sr	5.6×10^{-5}	1.9×10^{-6}	1.4×10^{-4}	2×10^{-5} * 1×10^{-4}	3×10^{-6}	1×10^{-4}	Basic solution composition; controlled by ion exchange equilibria on montmorillonite solid solution; upper guideline value controlled by celestite.
Zr	1.0×10^{-7}	1.6×10^{-11}	1.1×10^{-4}	2×10^{-9}	3×10^{-11}	2×10^{-9} * 2×10^{-8}	Lower guideline value: Baddeleyite (ZrO ₂) including $\pm 1.6 \log_{10}$ -units of uncertainty. Upper guideline value: Zr(OH) _{4(am,fr)} including $\pm 0.1 \log_{10}$ -units of uncertainty. See text for recommended value (based on experimental study).

Tab. 2: (continued)

Bentonite pore water without liner (after 10,000 years)				(Berner 2002)/*(Wanner 2003)			Limiting solid(s)/comments
Element	Recommended value [mol/kg]	Lower guideline value [mol/kg]	Upper guideline value [mol/kg]	Reference case [mol/l]	Lower limit [mol/l]	Upper limit [mol/l]	
Nb	7.1×10^{-5}	3×10^{-8}	1×10^{-4}	3×10^{-5}	1×10^{-8}	1×10^{-4}	Based on arguments provided in former report on same subject; see text.
Mo	2.1×10^{-5}	6.5×10^{-6}	4.7×10^{-5}	1×10^{-6}	1×10^{-6}	1×10^{-5}	Data on Mo very scarce. Lower guideline value based on solubility of tugarnovite. Recommended value based on powellite ($\text{CaMoO}_4(\text{s})$), using $\log K_s$ taken from Felmy et al. (1992). Upper guideline value considers uncertainty of $\pm 0.3 \log_{10}$ -units for powellite and $\pm 0.3 \log_{10}$ -units for complex $\text{CaMoO}_4(\text{aq})$.
Tc	4.1×10^{-9}	1.3×10^{-9}	1.3×10^{-8}	4×10^{-9}	1×10^{-9}	1×10^{-8}	TcO_2 , $1.6\text{H}_2\text{O}(\text{s})$ unique solid phase. Dominant solute is $\text{Tc(IV)O}(\text{OH})_2(\text{aq})$. Uncertainty of solubility reaction is $\pm 0.5 \log_{10}$ -units. System is redox sensitive. Above -40 mV the pertechnetate ion TcO_4^- will become stable and dominant.
Pd	5.7×10^{-8}	Unsignif. low	1.8×10^{-7}	5×10^{-8}	1×10^{-10}	2×10^{-7}	Recommended value based on $\text{Pd}(\text{OH})_2(\text{s})$ and on experimental data.
Ag	1.0×10^{-5}	7.7×10^{-14}	5.0×10^{-5}	3×10^{-6}	1×10^{-10}	3×10^{-6}	Limiting solid is $\text{AgCl}(\text{s})$, dominant complex in solution is AgCl_2^- . Uncertainties presently not available. Upper guideline value evaluated in 0.7 M Cl^- .
Sn	9.2×10^{-8}	9.0×10^{-9}	2.2×10^{-4}	1×10^{-8}	5×10^{-9}	1×10^{-7} * 1×10^{-5}	Lower guideline value based on cassiterite ($\text{SnO}_{2(\text{cr})}$), upper guideline value based on $\text{CaSn}(\text{OH})_6(\text{s})$. Dominant complex $\text{Sn}(\text{OH})_4(\text{aq})$ or $\text{Sn}(\text{OH})_5^-$, depending on applied uncertainty. Recommended value: calculated solubility of $\text{SnO}_{2(\text{am})}$.
I	9.0×10^{-7}	7.7×10^{-8}	High	High	High	High	Limiting solid $\text{AgI}(\text{s})$ defines recommended value. Co-existence of $\text{AgI}(\text{s})$ and $\text{AgCl}(\text{s})$ defines lower guideline value. Not limited when (local) inventory of $\text{I} >$ inventory of Ag .
Cs	Not limited	--	--	High	High	High	No limiting solids available; potential control via ion exchange. Maximum concentrations to be defined via inventories.

Tab. 2: (continued)

Bentonite pore water without liner (after 10,000 years)				(Berner 2002) ^{*/*} (Wanner 2003)			Limiting solid(s)/comments
Element	Recommended value [mol/kg]	Lower guideline value [mol/kg]	Upper guideline value [mol/kg]	Reference case [mol/l]	Lower limit [mol/l]	Upper limit [mol/l]	
Sm	1.5×10^{-7}	2.4×10^{-11}	1.8×10^{-5}	5×10^{-7}	3×10^{-7}	9×10^{-7} $*5 \times 10^{-6}$	Several carbonate solids available. Lower guideline value based on $\text{SmPO}_{4(\text{cr})}$. No uncertainties available.
Eu	2.2×10^{-7}	1.1×10^{-7}	1.5×10^{-5}	5×10^{-7}	3×10^{-7}	9×10^{-7} $*5 \times 10^{-6}$	Solubility limiting phase is $\text{EuOHCO}_{3(\text{cr})}$ with uncertainty $\pm 0.1 \log_{10}$ -units. Dominant complex in solution is $\text{EuH}_3\text{SiO}_4^{2+}$ with uncertainty $\pm 0.4 \log_{10}$ -units.
Ho	2.5×10^{-6}	4.2×10^{-10}	5.1×10^{-5}	5×10^{-7}	3×10^{-7}	9×10^{-7} $*5 \times 10^{-6}$	Several carbonate solids available. Lower guideline value based on $\text{HoPO}_{4(\text{cr})}$. No uncertainties available.
Pb	8.8×10^{-7}	2.4×10^{-8}	6.5×10^{-5}	2×10^{-6}	2×10^{-8}	8×10^{-5}	New Pb data evaluation by Powell et al. (2009). Limiting solid $\text{PbCO}_{3(\text{s})}$ with uncertainty $\pm 0.07 \log_{10}$ -units. No clearly dominant complex, see text.
Po	(6.6×10^{-7})	(2.8×10^{-10})	(6.6×10^{-7})	High	High	High	Indications that probably $\text{Th}(\text{IV})$ could act as surrogate for Po.
Ra	3.4×10^{-10}	5.1×10^{-12}	1.1×10^{-7}	2×10^{-11} $*5 \times 10^{-8}$	4×10^{-12}	5×10^{-8}	Upper guideline value based on calculated solubility of $\text{RaSO}_{4(\text{s})}$ applying an uncertainty of $0.2 \log_{10}$ -units. Lower guideline value and recommended value based on solid solution formation and relative inventories (Ra/Ba), see text.
Ac	2.8×10^{-6}	8.3×10^{-9}	5.4×10^{-5}	1×10^{-6}	5×10^{-8}	3×10^{-5}	No new data. As in former report data in analogy to Am selected.
Th	4.1×10^{-9}	2.8×10^{-10}	6.6×10^{-7}	7×10^{-7}	2×10^{-7}	3×10^{-6}	$\text{ThO}_{2(\text{am,hyd,aged})}$ uncertainty $\pm 0.9 \log_{10}$ -units. Dominant complex $\text{Th}(\text{OH})_3(\text{CO}_3)$; uncertainty $\pm 0.7 \log_{10}$ -units.
Pa	4.6×10^{-9}	1.8×10^{-10}	4.6×10^{-8}	1×10^{-8} $*1 \times 10^{-5}$	1×10^{-8}	1×10^{-5}	Thermodynamic data on Pa are still scarce. Present data and uncertainty estimates were taken over from Duro et al. (2006). Limiting solid is $\text{Pa}_2\text{O}_{5(\text{s})}$ and dominant complex is $\text{PaO}_2(\text{CO}_3)$ when hypothetical carbonate complexes in analogy to Np(V) are taken into account; see text.

Tab. 2: (continued)

Element	Bentonite pore water without liner (after 10,000 years)			(Berner 2002)/*(Wanner 2003)			Limiting solid(s)/comments
	Recommended value [mol/kg]	Lower guideline value [mol/kg]	Upper guideline value [mol/kg]	Reference case [mol/l]	Lower limit [mol/l]	Upper limit [mol/l]	
U	2.2×10^{-7}	1.1×10^{-8}	1.8×10^{-4}	3×10^{-9}	3×10^{-10}	5×10^{-7}	Recommended value: solubility of $\text{UO}_2(\text{am})$; lower guideline value: uncertainty of $\text{UO}_2(\text{am})$ and dominant complex $\text{CaUO}_2(\text{CO}_3)_3^{2-}$; upper guideline value: Na-Boltwoodite at extreme conditions for solid stability and dominant complex serve for upper guideline value.
Np	9.9×10^{-9}	2.7×10^{-11}	3.9×10^{-8}	5×10^{-9}	3×10^{-9}	1×10^{-8}	Under present conditions $\text{Np}(\text{IV})\text{O}_2(\text{am,hyd})$ only sensible limiting solid; uncertainty $\pm 0.5 \log_{10}$ -units; nearly exclusive solute is $\text{Np}(\text{OH})_4(\text{aq})$ with uncertainty $\pm 1.1 \log_{10}$ -units. Recommended value close to upper border considering both uncertainty bands.
Pu	6.8×10^{-10}	3.1×10^{-10}	9.7×10^{-9}	5×10^{-8}	3×10^{-9}	1×10^{-6}	$\text{PuO}_2(\text{am,hyd})$ with uncertainty of $\pm 0.52 \log_{10}$ -units. Dominant complex is PuHSiO_3^{2+} with estimated uncertainty of max $\pm 0.5 \log_{10}$ -units.
Am	2.8×10^{-6}	8.3×10^{-9}	5.4×10^{-5}	1×10^{-6}	5×10^{-8}	3×10^{-5}	Relevant solids will most likely be mixed hydroxides/carbonates exhibiting variable amounts of chemically bound water. One double salt ($\text{NaAm}(\text{CO}_3)_2$) produces an intermediate solubility, which is taken for the recommended value.
Cm	2.8×10^{-6}	--	3.3×10^{-3}	1×10^{-6}	5×10^{-8}	3×10^{-5}	Only solid phase in database is $\text{Cm}(\text{OH})_3(\text{am,coll})$ with uncertainty of $\pm 0.4 \log_{10}$ -units. Its solubility including uncertainty of dominant complex CmHSiO_3^{2+} ($\pm 0.6 \log_{10}$ -units) is taken for upper guideline value. Recommended value selected in analogy to americium; see text.

4 Comments on Individual Elements

As indicated in Section 2.3, a multitude of solubility calculations were performed for each individual element, including at least one calculation for each solid phase in the database. Further, the necessary number of calculations to explore the impact of uncertainties of solid formation and dominant complex formation constants as well as combinations thereof was also performed.

In general, the present section therefore provides element-specific tables, including the limiting solid selected to calculate solubility, the solubility and the speciation of the element in solution. Depending on available information, individual arguments, reasons or comments for selecting lower- or upper guideline values may be specified in addition.

ENSI (2010) requires that, apart from the recommended value, upper guideline values should also be given. Where appropriate, a second element-specific table is provided, giving concentration and speciation at the upper guideline value.

Beryllium

The chemistry of beryllium is determined by oxides/hydroxides, although minor amounts of carbonate, sulfate and chloride complexes are formed in solution. Dominant complex in solution is BeOH^+ (76 %), followed by $\text{Be(OH)}_{2(\text{aq})}$ (22 %). The limiting phase is one of the hydroxides $\text{Be(OH)}_{2(\alpha, \beta \text{ or am})}$. The lower guideline value was taken from the solubility of $\text{Be(OH)}_{2(\beta)}$, the recommended value was calculated from $\text{Be(OH)}_{2(\alpha)}$ and the upper guideline value was taken from the solubility of $\text{Be(OH)}_{2(\text{am})}$. No uncertainties for individual equilibria were available.

Be-speciation at recommended solubility:

Limiting phase	Calculated solubility [mol/kg H ₂ O]	Distribution of solute components
$\text{Be(OH)}_{2(\alpha)}$	9.1×10^{-7}	BeOH^+ (76.0 %) $\text{Be(OH)}_{2(\text{aq})}$ (21.9 %) Be^{2+} (0.8 %) $\text{BeCO}_{3(\text{aq})}$ (0.7 %) Be(OH)_3^- (0.5 %) $\text{BeSO}_{4(\text{aq})}$ (0.2 %) BeCl^+ (0.1 %)

Be-speciation at upper guideline concentration:

Limiting phase	Upper guideline value [mol/kg H ₂ O]	Distribution of solute components
$\text{Be(OH)}_{2(\text{am})}$	1.8×10^{-6}	BeOH^+ (76.0 %) $\text{Be(OH)}_{2(\text{aq})}$ (21.9 %) Be^{2+} (0.8 %) $\text{BeCO}_{3(\text{aq})}$ (0.7 %) Be(OH)_3^- (0.5 %) $\text{BeSO}_{4(\text{aq})}$ (0.2 %) BeCl^+ (0.1 %)

Carbon

Inorganic carbon, present as CO_3^{2-} is a key constituent of the basic solution. Modelling the different bentonite pore waters to be considered in contemporary solubility studies (Curti 2012a) shows a rather narrow range between 8.9×10^{-4} and 3.0×10^{-3} [mol/kg H_2O] (upper and lower guideline value). The study of Berner & Kosakowski (2011b) shows for Opalinus Clay pore waters a likewise narrow range between 1.3×10^{-3} and 4.0×10^{-3} [mol/kg H_2O] of total dissolved inorganic carbon. Total dissolved carbonate as given in Tab. 1 is taken for the recommended value. Organic carbon (i.e. arising from the corrosion of carbon steel) is not considered in the present study. However, the impact of organic complexing agents on safety relevant elements is discussed in a similar report on solubilities in a concrete environment (Berner 2014).

C-speciation at specified concentration:

Limiting phases	Used value [mol/kg H_2O]	Distribution of solute components
Calcite, Siderite	8.9×10^{-4}	HCO_3^- (87.1 %) $\text{Na}(\text{HCO}_3)_{(\text{aq})}$ (5.0 %) $\text{CO}_{2(\text{aq})}$ (2.4 %) $\text{Ca}(\text{HCO}_3)^+$ (2.2 %) $\text{Mg}(\text{HCO}_3)^+$ (1.1 %) NaCO_3^- (0.6 %) CO_3^{2-} (0.6 %) $\text{CaCO}_{3(\text{aq})}$ (0.6 %) $\text{MgCO}_{3(\text{aq})}$ (0.2 %) $\text{Fe}(\text{HCO}_3)^+$ (0.1 %)

The relevant radionuclide ^{14}C , arising from nitrogen in activated steel, is (most likely) only a small part of the total carbon in solution. Implicitly it is assumed that ^{14}C is determined by isotopic dilution. This also holds for the part of organic carbon not considered here.

Chlorine

Chlorine is a system defining element, given by the definition of ionic strength through the concentration of NaCl , i.e., in the range 0.16 to 0.7 [mol/kg H_2O]. A potential limiting solid would be $\text{AgCl}_{(\text{s})}$, but since the inventory of chlorine by far exceeds that of silver, chloride is never controlled by silver.

Note that for silver we may have a reversed situation (see also discussion below).

Cl-speciation at specified concentration: Cl^- (100 %)

Potassium

Potassium is a system defining element. In the present setup its concentration is controlled by exchange equilibria on the montmorillonite solid solution phase. An upper guideline value is potentially given by the solubility of illite. In a sensitivity analysis Berner & Kosakowski (2011b) did not find a large bandwidth for K concentrations in Opalinus Clay pore waters (1 to 5×10^{-3} [mol/kg H₂O]).

K-speciation at specified concentration:

Limiting process	Used value [mol/kg H ₂ O]	Distribution of solute components
Ion exchange on montmorillonite	1.2×10^{-3}	K ⁺ (95.9 %) KSO ₄ ⁻ (4.1 %)

Calcium

Calcium is a major element comprising the chemical system. Its concentration is controlled by calcite/siderite and by ion exchange on the montmorillonite solid solution phase. Lower and upper guideline values were taken from a range of bentonite pore water definitions provided by Curti (2012). A study investigating benchmark figures in similar Opalinus Clay porewaters (Berner & Kosakowski 2011b) revealed that dissolved Ca may vary from 0.4×10^{-3} to 56×10^{-3} [mol/kg H₂O], depending on various system parameters. The recommended value was taken from Tab. 1.

Ca-speciation at specified solubility:

Limiting phase	Calculated solubility [mol/kg H ₂ O]	Distribution of solute components
Calcite	9.1×10^{-3}	Ca ²⁺ (73.2 %) CaSO _{4(aq)} (26.5 %) Ca(HCO ₃) ⁺ (0.2 %) CaCO _{3(aq)} (0.1 %)

Cobalt

A series of sparingly soluble cobalt selenides and sulfides is known, producing calculated concentrations from 5×10^{-10} [mol/kg H₂O] up to 1×10^{-6} [mol/kg H₂O]. CoSe_(s) and Co₂SiO_{4(s)} seem to be co-existent and fix the cobalt solubility at very low Co-concentration (5.0×10^{-10} [mol/kg H₂O]), a value which was taken for the lower guideline value. The available formation constant of Co(Fe^{III}O₂)_{2(s)} would produce an even lower concentration (2×10^{-18} [mol/kg H₂O]), but the quality of this data seems questionable. The recommended value was taken from the solubility of spherocobaltite (CoCO_{3(s)}). This solid had originally been discussed/recommended by Grauer (1999) and was used in a former study (Berner 2002). It was incorporated in the SKB data base (Duro et al. 2006), from where the full set of present Co-data was taken over. The present set of thermodynamic data does, however, not include the species CoHSiO₃⁺, an analogue to NiHSiO₃⁺. Introducing this silicate complex (taking the same formation constant as for the Ni-complex) to the database and considering an uncertainty of log₁₀K ±0.2 in the solubility constant produced the calculated upper guideline value of 5.8×10^{-5} [mol/kg H₂O].

Note the problem with the missing selenide(-II) complexes. In contrast to the dataset for silver, no aqueous cobalt selenide complexes are included in the database. Hence, the low solubilities calculated for the Co_xSe_y phases may well be an artefact of an incomplete database. That was the reason for selecting the carbonate as the limiting phase. Selecting the sulfides (CoS , Co_3S_4 , CoS_2) as limiting phases would be an option (producing solubilities in the range 7.8×10^{-8} to 1.1×10^{-6} [mol/kg H_2O]), but searching the literature for corresponding solubility experiments is still an open issue.

Co-speciation at specified solubility:

Limiting phase	Calculated solubility [mol/kg H_2O]	Distribution of solute components
$\text{CoCO}_3(\text{s})$ Sphero-cobaltite	2.0×10^{-5}	Co^{2+} (63.0 %) $\text{CoSO}_4(\text{aq})$ (22.8 %) CoCl^+ (11.3 %) CoHCO_3^+ (1.1 %) $\text{Co}(\text{OH})^+$ (0.9 %) $\text{CoCO}_3(\text{aq})$ (0.5 %) $\text{CoCl}_2(\text{aq})$ (0.3 %)

Co-speciation at upper guideline concentration, when introducing CoHSiO_3^+ to the database (in analogy to NiHSiO_3^+):

Limiting phase	Calculated solubility [mol/kg H_2O]	Distribution of solute components
$\text{CoCO}_3(\text{s})$ Sphero-cobaltite, 0.2 \log_{10} -units less stable	5.8×10^{-5}	CoHSiO_3^+ (44.7 %) Co^{2+} (34.8 %) $\text{CoSO}_4(\text{aq})$ (12.7 %) CoCl^+ (6.2 %) CoHCO_3^+ (0.6 %) $\text{Co}(\text{OH})^+$ (0.95 %) $\text{CoCO}_3(\text{aq})$ (0.3 %) $\text{CoCl}_2(\text{aq})$ (0.2 %)

Nickel

$\text{NiCO}_3(\text{cr})$ is the limiting solid (uncertainty of solubility constant $\pm 0.18 \log_{10}\text{K}$ -units) and NiHSiO_3^+ (estimated uncertainty of formation constant $\pm 0.3 \log_{10}\text{K}$ -units) is the dominant complex in solution (the other ~ 50 % of solutes consist of Ni^{2+} (36 %) and $\text{NiSO}_4(\text{aq})$ (15 %)). The calculated solubility limit is 5.5×10^{-5} [mol/kg H_2O]. Other potential solids are the hydroxide $\text{Ni}(\text{OH})_{2(\text{cr},\text{beta})}$ (2.5×10^{-4} [mol/kg H_2O]) and the oxide $\text{NiO}(\text{cr})$ (4.9×10^{-3} [mol/kg H_2O]). This soluble oxide was used to define the upper guideline value. The lower limit was calculated using $\text{NiCO}_3(\text{cr})$ at the more stable end of the uncertainty range ($-0.18 \log_{10}\text{K}$ -units, as indicated above) in combination with a less stable dominant complex according to given uncertainties.

Noteworthy is an interesting interdependency between Ni and silica. Close to the upper guideline value the dominant NiHSiO_3^+ has a concentration of 2.6×10^{-3} [mol/kg H_2O], which is about 15 times the concentration of silica in the reference solution! Hence, Ni might have a strong impact on total dissolved silica and consequently on the phase composition related to dissolved silica.

Ni-speciation at specified solubility:

Limiting phase	Calculated solubility [mol/kg H_2O]	Distribution of solute components
$\text{NiCO}_3(\text{cr})$	5.5×10^{-5}	NiHSiO_3^+ (46.5 %) Ni^{2+} (36.1 %) $\text{NiSO}_4(\text{aq})$ (14.7 %) NiCl^+ (2.1 %) $\text{NiCO}_3(\text{aq})$ (0.3 %) NiOH^+ (0.3 %) NiHCO_3^+ (0.1 %)

Ni-speciation at upper guideline concentration:

Limiting phase	Calculated solubility [mol/kg H_2O]	Distribution of solute components
$\text{NiO}(\text{cr})$	4.9×10^{-3}	NiHSiO_3^+ (53.2 %) Ni^{2+} (31.5 %) $\text{NiSO}_4(\text{aq})$ (12.8 %) NiCl^+ (1.8 %) $\text{NiCO}_3(\text{aq})$ (0.3 %) NiOH^+ (0.3 %) $\text{Ni(OH)}_2(\text{aq})$ (0.1 %)

Note that system Eh changes to -229 [mV] at upper guideline concentration. Strongly increased dissolved silica impacts on montmorillonite and consequently on its Fe(III)/Fe(II) balance.

Selenium

Preliminary comment: Due to its predominant occurrence as anionic species selenium may be strongly related to the chemistry and to the available inventory of other elements. Examples are ($\text{Ag}_2\text{Se}(\text{aq})$, $\text{Ag}_2\text{Se}(\text{cr})$, $\text{CoSe}_2(\text{s})$, $\text{Co}_{0.84}\text{Se}(\text{s})$ and M^+ , M^{2+} (selenites, selenates)). Consequently, the relation extends to other elements, which themselves are related to the mentioned elements (i.e. iodine ($\text{AgI}(\text{s})$), sulfur ($\text{Ag}_2\text{S}(\text{s})$) and maybe others). Such interdependencies are not worked out in detail in the present work but are mentioned where appropriate.

At -204 mV selenium is present in the oxidation state Se(-II). Se(IV) and Se(VI) complexes and solids will become stable above $\sim +200$ mV, where the element is no longer solubility limited.

$\text{CoSe}_2(\text{cr})$ is the least soluble solid, producing insignificant concentrations of 4×10^{-12} [mol/kg H_2O]. Dominant complex in solution is HSe^- . This value serves for the lower guideline value. According to the present status of thermodynamic data, $\text{Se}(\text{cr})$ dominates the chemistry under slightly reducing conditions and produces calculated solubilities of 5.3×10^{-9} [mol/kg H_2O].

This concentration forms the recommended value. HSe^- is still the dominant complex in solution, although the tetramer Se_4^{2-} becomes co-dominant at these concentrations. The upper guideline value of 1.6×10^{-7} [mol/kg H_2O] was also calculated using $\text{Se}_{(\text{cr})}$ by associating the extreme end of the uncertainty band for the solubility constant and the dominant complex formation constants. The increase in solubility by a factor of 30 completely modifies the speciation (at $\text{Se}_{\text{tot}} > 1 \times 10^{-7}$ [mol/kg H_2O] Se_4^{2-} clearly dominates HSe^-).

Note that in the presence of sufficient amounts of silver, crystalline $\text{Ag}_2\text{Se}_{(\text{cr})}$ and the complex $\text{Ag}_2\text{Se}_{(\text{aq})}$ would completely dominate the "combined" system at a concentration level of 2.2×10^{-8} [mol/kg H_2O] of dissolved selenium (and consequently 4.4×10^{-8} [mol/kg H_2O] of Ag). See also footnote on Page 8.

Se-speciation at specified solubility:

Limiting phase	Calculated solubility [mol/kg H_2O]	Distribution of solute components
$\text{Se}_{(\text{cr})}$	5.3×10^{-9}	HSe^- (80.3 %) Se_4^{2-} (16.1 %) Se_3^{2-} (3.6 %) Se_2^{2-} (0.2 %)

Se-speciation at upper guideline concentration (extreme end of uncertainty band for dominant complex):

Limiting phase	Calculated solubility [mol/kg H_2O]	Distribution of solute components
$\text{Se}_{(\text{cr})}$, at extreme end of uncertainty band	1.6×10^{-7}	Se_4^{2-} (92.9 %) HSe^- (6.1 %) Se_3^{2-} (1.0 %)

Perspectives in aqueous thermodynamics of selenium: Justified analogies of Se with sulfur and a well-established solubility of elemental sulfur in aqueous systems ($\text{S}(0)_{8(\text{aq})}$) = $(2.6 \pm 0.1) \times 10^{-8}$ [mol/kg H_2O], (Boulegue 1979), (Kamyshny 2009), (Wang & Tessier 2009) lead to the hypothesis that the solubility of elemental selenium should be situated in a similar range. Indeed, ongoing experimental studies (Tits, pers. comm.) seem to indicate $\text{Se}(0)$ -solubilities in the range of 10^{-7} to 10^{-6} [mol/kg H_2O]. Once confirmed, such results would favour selecting selenium concentrations close to the upper guideline value. However, confirmations are still missing and the present review prefers to rely on available thermodynamic data for the upper limit.

Strontium

Strontium is an element that is controlled by ion exchange equilibria on the montmorillonite phase. The lower guideline value was taken from the range of bentonite pore water compositions specified in Bradbury et al. (2014), Curti (2012). If $\text{SrSO}_{4(\text{aq})}$ concentration in solution increases, the system will be buffered by the precipitation of celestite at $[\text{Sr}]_{\text{tot}} = 1.4 \times 10^{-4}$ [mol/kg H_2O]. This value is taken for the upper guideline value. The recommended value corresponds to the concentration of Sr^{2+} displayed in Tab. 1.

Sr-speciation at specified concentration:

Limiting phase	Concentration [mol/kg H_2O]	Distribution of solute components
Control by ion exchange equilibria on montmorillonite	5.6×10^{-5}	Sr^{2+} (73.7 %) $\text{SrSO}_{4(\text{aq})}$ (26.1 %) $\text{Sr}(\text{HCO}_3)^+$ (0.3 %)

Sr-speciation at upper guideline concentration:

Limiting phase	Concentration [mol/kg H_2O]	Distribution of solute components
$\text{SrSO}_4(\text{cr})$, celestite	1.4×10^{-4}	Sr^{2+} (67.4 %) $\text{SrSO}_{4(\text{aq})}$ (32.4 %) $\text{Sr}(\text{HCO}_3)^+$ (0.2 %)

The precipitation of celestite may also occur at the recommended Sr-concentration of 5.6×10^{-5} [mol/kg H_2O] at free $[\text{SO}_4^{2-}]$ -concentrations $> 3.0 \times 10^{-2}$ [mol/kg H_2O]. Hence, there is not a single answer to the question of an upper guideline value because the concentration of sulfate may be of importance. However, the present study does not consider $[\text{SO}_4^{2-}]$ -uncertainties in the basic pore water composition.

Zirconium

There are no other solid phases than ZrO_2 (cr & amorphous) present in the database. The uncertainty of the solubility product of the crystalline phase is $\pm 1.7 \log_{10}$ -units, the uncertainty of the amorphous phase is only $\pm 0.1 \log_{10}$ -units. This rather strange fact is, however, not the key point here. An essential uncertainty originates from the existence of the polymeric hydroxide $\text{Zr}_4(\text{OH})_{16(\text{aq})}$, which has been derived by the NEA reviewers based on solubility and hydrolysis data from a series of research studies. Unfortunately this determination had been performed at low pH values. Scoping calculations revealed that the polymeric species may become dominant when total dissolved Zr exceeds a concentration of about 1×10^{-7} [mol/kg H_2O], but this statement strongly depends on the actually selected formation constant for $\text{Zr}_4(\text{OH})_{16(\text{aq})}$. Hence, specifying a recommended value based on "calculated" values including uncertainty bands is largely speculation because the mentioned tetrameric complex depends on the fourth power of $\text{Zr}(\text{OH})_{4(\text{aq})}$. What seems evident from the calculations is that neither sulfate- nor carbonate species play any role under given conditions. Even much higher carbonate or sulfate concentrations would not produce significant concentrations of these complexes.

Fortunately, there is one study covering the solubility of "Zr(OH)_{4(s)}" (an amorphous solid) over the whole pH range (Ekberg et al. 2004), on Page 427 of the NEA review on Zirconium (Brown et al. 2005). These measurements are nicely fitted with the proposed hydrolysis model and form the basis of the proposed "recommended value" of 1×10^{-7} [mol/kg H₂O].

Note that dissolution measurements on crystalline products produce much lower solubilities in the range of 1×10^{-10} to 1×10^{-8} [mol/kg H₂O], whereas precipitation experiments exhibiting an unknown status of oversaturation produce much higher total Zr concentrations (Brown et al. 2005, Fig. D-2, Page 409). The upper guideline value corresponds to the solubility calculated with Zr(OH)_{4(am,fr.)} and the then dominating tetrameric complex Zr₄(OH)_{16(aq)}.

Zr-speciation at specified solubility:

Limiting phase	Calculated solubility [mol/kg H ₂ O]	Distribution of solute components
Zr(OH) _{4(s)}	1×10^{-7}	Zr(OH) _{4(aq)} (100 %)

Zr-speciation at upper guideline concentration:

Limiting phase	Calculated solubility [mol/kg H ₂ O]	Distribution of solute components
Zr(OH) _{4(am,fr.)}	1.1×10^{-4}	Zr ₄ (OH) _{16(aq)} (96.6 %) Zr(OH) _{4(aq)} (3.3 %) Zr ₄ (OH) _{15⁺} (0.03 %)

Niobium

The situation on available data since the last evaluation of Nb solubility (Berner 2002) has not changed. The database is very small and data on potential carbonate complexes are still missing. The recommended value represents the calculated solubility of Nb₂O_{5(s)}. Wanner (2003) commented on the solubility of Nb presented in Berner (2002) and advised considering the existence of carbonate complexes (*nothing is known about Nb-carbonates but their existence is likely*). The present evaluation follows this suggestion and assumes that complexes of the form Nb(OH)_x(CO₃)_y^{5-x-2y} may form in the presence of carbonate. However, carbonate complexes of Nb will not be dominant and considering a concentration level similar to twice the concentration of Nb(OH)_{5(aq)} seems appropriate. This leads to an upper guideline value of 1×10^{-4} [mol/kg H₂O].

Note that Lothenbach et al. (1999) do neither consider nor report on any formation of Nb-carbonate complexes. Reported Nb solubility increases with increasing pH. This increase seems to fade away above pH 10, a fact which does not specifically support the formation of (strong) carbonate complexes.

A lower guideline value around 10^{-8} [mol/kg H₂O] under near neutral pH conditions (pH ~7) can be derived from experimental work reported in Lothenbach et al. (1999). The reported pH dependency of the Nb₂O_{5(cr)} solubility would approximately shift the lower guideline value at pH ~7 to the presented value of 3×10^{-8} [mol/kg H₂O] at pH 7.8.

Nb-speciation at specified solubility:

Limiting phase	Calculated solubility [mol/kg H ₂ O]	Distribution of solute components
Nb ₂ O _{5(cr)}	7.1×10^{-5}	Nb(OH) ₆ ⁻ (79.0 %) Nb(OH) _{5(aq)} (21.0 %)

Nb-speciation at upper guideline concentration, assuming that niobium may form (non-specified) carbonate complexes:

Limiting phase	Concentration [mol/kg H ₂ O]	Distribution of solute components
Nb ₂ O _{5(cr)}	1×10^{-4}	Nb(OH) ₆ ⁻ (55 %) Nb(OH) _x (CO ₃) _y (30 %) Nb(OH) _{5(aq)} (15 %)

Molybdenum

The data situation on molybdenum has only slightly changed since the last study on this subject (Berner 2002). The solubility of powellite (CaMoO_{4(s)}) and the complex CaMoO_{4(aq)}, taken from (Felmy et al. 1992) were added to the operational database. Uncertainties for the two equilibria were estimated to be $\pm 0.3 \log_{10}$ -units (powellite) and $\pm 0.5 \log_{10}$ -units (solute complex), respectively. The calculated solubility was 2.1×10^{-5} [mol/kg H₂O], which serves as the recommended value. The upper guideline value is based on the uncertainties of the powellite formation constant and the complex CaMoO_{4(aq)} formation constant. Further available solids (Mo_(s), Mo(IV)O_{2(s)} (tugarinovite), Mo(VI)O_{3(s)}, BeMoO_{4(s)}, Ag₂MoO_{4(s)}), taken over from Pearson et al. (1992) and Thoenen (2012) have solubility constants of questionable quality. The equilibrium $\text{Mo(IV)O}_2(\text{s}) + 2\text{H}_2\text{O} \rightleftharpoons \text{Mo(VI)O}_4^{2-} + 4\text{H}^+ + 2\text{e}^-$ produces Mo(IV)O₄²⁻ concentrations similar to those of powellite and is sensitive to pH and Eh.

Hence, a comment made in the former report (Berner 2002) (relying on tugarinovite as the limiting solid at that time) may still be valid and is thus repeated here: *According to the (potentially) relevant equilibrium $\text{MoO}_2(\text{s}) + 2\text{H}_2\text{O} \rightleftharpoons \text{MoO}_4^{2-} + 4\text{H}^+ + 2\text{e}^-$, total dissolved Mo is sensitive to pH and Eh and may increase with both, pH and Eh. Further, the mandatory redox reaction between Mo(IV) and Mo(VI) may well interfere with the redox determining iron system, since both redox couples appear at comparable concentration levels in the dissolved state. In other words, Mo(VI)/Mo(IV) instead of Fe(III)/Fe(II) may become the redox determining couple and the underlying conceptual redox model could potentially depend on the availability of molybdenum.*

This statement implies that the inventory of molybdenum relative to that of iron may become important in the case Mo-dominated wastes.

Mo-speciation at specified solubility:

Limiting phase	Calculated solubility [mol/kg H ₂ O]	Distribution of solute components
CaMoO _{4(s)} Powellite	2.1×10^{-5}	MoO ₄ ²⁻ (94.2 %) CaMoO _{4(aq)} (5.8 %)

Mo-speciation at upper guideline concentration (powellite 0.3 log₁₀-units less stable, species CaMoO_{4(aq)} 0.5 log₁₀-units more stable):

Limiting phase	Calculated solubility [mol/kg H ₂ O]	Distribution of solute components
CaMoO _{4(s)} Powellite	4.7×10^{-5}	MoO ₄ ²⁻ (83.6 %) CaMoO _{4(aq)} (16.4 %)

Tchnetium

TcO₂.1.6H₂O_(s) is the only solid phase available from the database. TcO(OH)_{2(aq)} is the dominant complex in solution (99 %). Tc(VII) (i.e. TcO₄⁻) is not yet stable at -204 mV. The uncertainty of the limiting solid (± 0.5 log₁₀-units) is directly linked with the uncertainty of the dominant complex. This implies that the two uncertainties cannot be applied independently. The calculated solubility of 4.1×10^{-9} [mol/kg H₂O] was used for defining the recommended value, and the given uncertainty for defining the upper- and lower guideline values.

Emanating from TcO(OH)_{2(aq)}, the formation of TcO₄⁻ strongly depends on Eh. Under given pH-conditions and assuming the same limiting solid, the very soluble pertechnetate TcO₄⁻ has a negligible concentration of 2×10^{-17} [mol/kg H₂O], but would become stable and dominant (4×10^{-9} [mol/kg H₂O]) at ~ -40 mV. Hence, above this threshold Eh value the solubility of TcO₂.1.6H₂O_(s) will increase with about one order of magnitude per 20 mV.

Tc-speciation at specified solubility:

Limiting phase	Calculated solubility [mol/kg H ₂ O]	Distribution of solute components
TcO ₂ .1.6H ₂ O	4.1×10^{-9}	TcO(OH) _{2(aq)} (98.6 %) Tc(CO ₃)(OH) _{2(aq)} (0.9 %) Tc(CO ₃)(OH) ₃ ⁻ (0.4 %) TcO(OH) ₃ ⁻ (0.1 %)

Tc-speciation at upper guideline concentration (TcO₂.1.6H₂O_(s) 0.5 log₁₀-units less stable) does not change.

Palladium

At -204 mV elemental Pd is identified as the limiting solid and produces an absolutely insignificant concentration of 5×10^{-27} [mol/kg H₂O] (uncertainty $\sim \pm 0.8 \log_{10}$ -units). In Tab. 2 this was translated to "insignificantly low". However, very recently Hummel (2013) demonstrated for silver that applying the equilibrium $\text{Ag}_{(s)} \rightleftharpoons \text{Ag}_{(aq)}$ having a constant in the order of 10^{-7} [mol/kg H₂O] could be a feasible way to describe the solubility of elemental silver at low redox potentials (at higher redox potentials silver will be oxidised to Ag⁺). This may also be true for other B-type elements like Pd, Pt, Au, Hg. Confirming such behaviour is ongoing and will help to replace very small numbers (e.g. 5×10^{-27} [mol/kg H₂O]).

A fair amount of solubility data for Pd(OH)_{2(s)} were published by Van Middlesworth & Wood (1999) and Wood (1991) and allow establishing a solubility constant for this hydroxide (Hummel et al. 2002, Hummel & Berner 2000). The experimental data (see Fig. 2) form the basis for the recommended value and for the upper guideline value.

Pd-speciation at specified solubility:

Limiting phase	Calculated solubility [mol/kg H ₂ O]	Distribution of solute components
Pd(OH) _{2(s)}	5.7×10^{-8}	Pd(OH) _{2(aq)} (99.8 %) PdCl ₄ ²⁻ (0.1 %) PdCl _x (OH) _y ^{2-x-y} (0.1 %)

Pd-speciation at upper guideline concentration (based on experimental data from Van Middlesworth & Wood (1999), Wood (1991), Pd(OH)_{2(s)} 0.5 log₁₀-units less stable) produces the same speciation.

Note: The solubility of Pd may be influenced by the concentration of chloride because the importance of the complex PdCl₄²⁻ will increase with the 4th power of the chloride concentration. A scoping calculation evaluated in 0.7 [mol/kg H₂O] M⁺Cl⁻ (an alternative reference water (Curti 2012a)) reveals that dissolved Pd does not exceed a concentration of 8×10^{-8} [mol/kg H₂O].

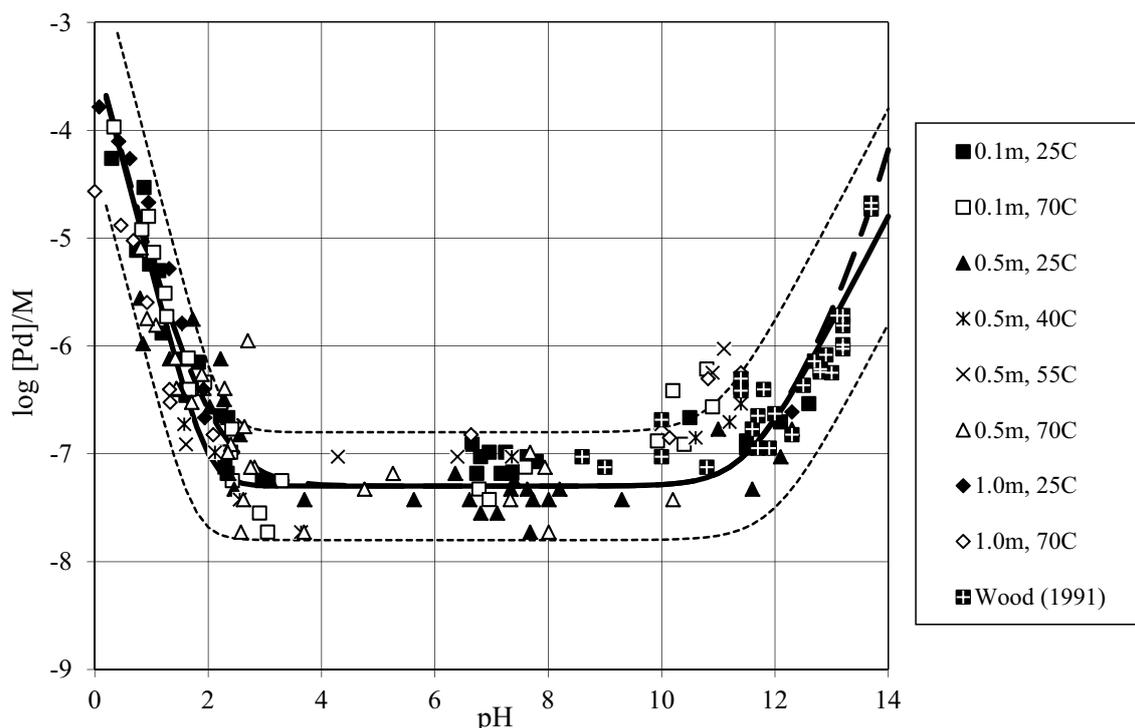


Fig. 2: Solubility data for $\text{Pd}(\text{OH})_{2(s)}$ published by Van Middlesworth & Wood (1999) and Wood (1991) measured at various temperatures, ionic strengths and pH-values.

Details are given in Hummel & Bermer (2000).

Silver

The silver speciation in solution is determined by the chloride complexes AgCl_2^- , AgCl_3^{2-} , AgCl_4^{3-} , $\text{AgCl}_{(aq)}$ (in this sequence), but also the species $\text{AgHS}_{(aq)}$ contributes to about 15 % of total dissolved silver. Prevailing redox conditions would, in principle, favour the presence of elemental silver $\text{Ag}_{(cr)}$, which would produce a calculated insignificant solubility of 8×10^{-14} [mol/kg H_2O]. This calculated solubility of $\text{Ag}_{(cr)}$ serves as the lower guideline value. Silver sulfide ($\text{Ag}_2\text{S}_{(s)}$, Acanthite) would also produce a nearly insignificant solubility (2.6×10^{-13} [mol/kg H_2O]). For $\text{AgI}_{(s)}$ the calculation produces a solubility of 9.3×10^{-7} [mol/kg H_2O], and finally, 1.0×10^{-5} [mol/kg H_2O] was obtained for the solubility of $\text{AgCl}_{(s)}$. The solubility of silver chloride is probably one of the most accurately established equilibrium in analytical chemistry (note an uncertainty of the silver/silver chloride electrode potential of only 0.014 \log_{10} -units). The solubility of $\text{AgCl}_{(s)}$ serves as the recommended value. The concentration for the upper guideline value was estimated using an alternative reference water composition (Curti 2012a) exhibiting increased chloride concentration of 0.7 [mol/kg H_2O]. Operationally this was achieved by adding 0.54 [mol/kg H_2O] of M^+Cl^- to the reference water from Tab. 1 and re-evaluating the solubility of $\text{AgCl}_{(s)}$. Total dissolved Ag was found to increase to 5.0×10^{-5} [mol/kg H_2O] at increased Cl^- concentration due to the favoured formation of AgCl_4^{3-} .

Ag-speciation at specified solubility:

Limiting phase	Calculated solubility [mol/kg H ₂ O]	Distribution of solute components
AgCl _(s)	1.0×10^{-5}	AgCl ₂ ⁻ (51.3 %) AgCl ₃ ²⁻ (15.9 %) AgHS _(aq) (15.4 %) AgCl ₄ ³⁻ (14.2 %) AgCl _(aq) (3.2 %)

Ag-speciation at upper guideline value (Solubility of AgCl_(s) in 0.7 [mol/kg H₂O] Cl⁻):

Limiting phase	Calculated solubility [mol/kg H ₂ O]	Distribution of solute components
AgCl _(s)	5.0×10^{-5}	AgCl ₄ ³⁻ (65.9 %) AgCl ₃ ²⁻ (18.6 %) AgCl ₂ ⁻ (14.5 %) AgHS _(aq) (0.7 %) AgCl _(aq) (0.2 %)

Note 1: Uncertainties for individual equilibria are presently not available from the database, but an uncertainty estimate for the solubility of AgCl_(s) of about $\pm 0.014 \log_{10}$ -units may be derived from the NEA series. From a recent NEA thermodynamic data publication (Olin et al. 2005) we learn that the silver selenide Ag₂Se_(s, α) is extremely stable and insoluble. On the other hand, the corresponding complex Ag₂Se_(aq) would absolutely dominate the silver speciation in solution in the presence of selenium(-II) and the maximum calculated concentration would be 2.2×10^{-8} [mol/kg H₂O]. However, the interdependency between silver and selenium was not evaluated further.

Note 2: Selecting AgCl_(s) as the limiting solid phase (thereby neglecting AgI_(s)) is a decision driven by conservatism. Selecting the well-known AgI_(s), as selected in case of evaluating the iodine solubility (see below), would result in an order of magnitude lower silver solubility. Why does the present evaluation not select AgI_(s)? A few comments to clarify this inconsistency seem necessary: When relying on pure thermodynamic principles the relative available/accessible amounts of the relevant elements Ag, I, Cl play a key role in evaluating the maximum concentration.

If $I_{\text{total}} > Ag_{\text{total}}$, then AgI_(s) will precipitate to the point where Ag is exhausted. Dissolved Ag will be limited around 1×10^{-6} [mol/kg H₂O], depending on the given concentration of Cl⁻ (speciation in solution). Dissolved iodine may increase to unlimited values.

If $Ag_{\text{total}} > I_{\text{total}}$, then AgI_(s) will precipitate to the point where iodine is exhausted. Remaining dissolved Ag will be limited at a level of 1×10^{-5} [mol/kg H₂O] by AgCl_(s) (considering that total dissolved Cl⁻ = 0.161 [mol/kg H₂O]).

There are other safety relevant elements (sulfur, selenium, see above) that may interact/precipitate with silver and create a lot more interdependencies among safety relevant elements. As indicated in Section 2.5, such interdependencies are not worked out in the present report, mainly because the relative mass balances are not (yet) accessible and may further depend on the heterogeneity of waste emplacement.

Very recently Hummel (2013) has demonstrated that elemental silver may exhibit a solubility ($\text{Ag}_{(s)} \rightleftharpoons \text{Ag}_{(aq)}$) of about 10^{-7} [mol/kg H₂O] under reducing conditions. These indications are not yet fully assured and are not considered in the present evaluation, but they justify identifying the present selection as conservative.

Tin

Available solid phases in the database are crystalline and amorphous SnO₂ having uncertainties of ± 0.2 and ± 0.3 log₁₀-units, respectively in their solubility constant. The database also lists the stannate CaSn(OH)_{6(s)} (Lothenbach et al. (2000), producing a much higher solubility of 2.2×10^{-4} [mol/kg H₂O] (including the uncertainty of ± 0.3 log₁₀-units of the co-dominant complex Sn(OH)₅⁻). The solubility of this latter solid produces the upper guideline value. At this upper guideline value, using the highest possible formation constant of the co-dominant complex Sn(OH)₅⁻ the speciation changes and Sn(OH)₅⁻ becomes absolutely dominant.

Note that the uncertainty of the dominant complex Sn(OH)_{4(aq)} is related to the uncertainty of the corresponding solubility constant. Only hydroxide solutes are formed in the present chemical environment. The fact that Sn(OH)₅⁻ is a co-dominant complex implies that the log₁₀-value of tin solubility is directly proportional to pH (7.79 in the present system). Sn(II) species are completely irrelevant at given Eh of -204 mV, the speciation is dominated by Sn(IV).

The solubility of crystalline cassiterite (SnO_{2(cr)}), using the lowest possible stability formation constant of the co-dominant complex Sn(OH)₅⁻ was used to define the lower guideline value. The recommended value of 9.2×10^{-8} [mol/kg H₂O] was based on the solubility of amorphous SnO_{2(am)}. The recommended solubility roughly corresponds to measurements of Amaya et al. (1997) on poorly crystalline SnO_{2(s)}.

Sn-speciation at specified solubility:

Limiting phase	Calculated solubility [mol/kg H ₂ O]	Distribution of solute components
SnO _{2(am)}	9.2×10^{-8}	Sn(OH) _{4(aq)} (54.6 %) Sn(OH) ₅ ⁻ (45.2 %) Sn(OH) ₆ ²⁻ (0.3 %)

Sn-speciation at upper guideline concentration considering 0.3 log₁₀-units higher stability of co-dominant complex Sn(OH)₅⁻:

Limiting phase	Calculated solubility [mol/kg H ₂ O]	Distribution of solute components
CaSn(OH) _{6(s)}	2.2×10^{-4}	Sn(OH) ₅ ⁻ (62.3 %) Sn(OH) _{4(aq)} (37.5 %) Sn(OH) ₆ ²⁻ (0.2 %)

Iodine

Preliminary comments: Iodine data present in the current database had been taken over from a former database without additional re-evaluation. In the mean time it was recognised that some inconsistencies occurred when transforming from the former to the current database. In particular, much too big stabilities had been associated to the species $I_{2(aq)}$ and I_3^- , resulting in erroneous iodine speciation and in much too high calculated iodine solubilities. In the course of evaluating data for calcium-aluminate-sulfate-iodide solid solutions Aimoz (2012) made a preliminary re-evaluation of iodine thermodynamic data based on corresponding literature data and proposed using the following $\Delta_f G^0$ values: I^- : -51'723.4 J/mol; $I_{2(aq)}$: -108.0 J/mol; I_3^- : -51'463.0 J/mol; IO_3^- : -128'050.0 J/mol; $HIO_{3(aq)}$: -132'632.9 J/mol. These values were used in the present work for modelling the solubility of $AgI_{(s)}$ and the speciation of iodine in solution.

$AgI_{(s)}$ is the only solid available in the database and produces a calculated total iodine solubility of 9.0×10^{-7} [mol/kg H_2O]. I^- is the dominant complex in solution. This calculated solubility is used for the recommended value. Uncertainties are not available for the solubility constant of $AgCl_{(s)}$. Since the recommended value for silver is based on the solubility of $AgCl_{(s)}$ and the only available solid to fix iodine is $AgI_{(s)}$, we consequently should also consider a situation when both solids are saturated. This is the case when total dissolved iodine $[I]_{tot} = 7.7 \times 10^{-8}$ [mol/kg H_2O] at $[Cl^-]_{tot} = 0.161$ [mol/kg H_2O]. The calculated $[I]_{tot}$ concentration when both, $AgCl_{(s)}$ and $AgI_{(s)}$ are stable is taken for the lower guideline concentration.

Note that total dissolved Ag under these conditions is 1.0×10^{-5} [mol/kg H_2O]. Once the available silver is exhausted iodine is no more solubility limited (see also notes under "silver").

I-speciation at specified solubility:

Limiting phase	Calculated solubility [mol/kg H_2O]	Distribution of solute components
$AgI_{(s)(cr)}$	9.0×10^{-7}	I^- (100.0 %) $AgI_{(aq)}$ (0.04 %)

Cesium

There are neither limiting solid phases nor complexes of Cs available from the database. In nature Cs is found in the rare mineral pollucite which is related to analcime (a zeolithe phase). Solubilities for this mineral phase are presently not known and its potential precipitation from hydro-geochemical systems seems unlikely.

Cs is strongly sorbed on various materials and huge amounts of sorption data are available in the literature on radioactive waste management. Hence, sorption processes in the individual systems under consideration should be used to justify reduced Cs concentrations in aqueous systems. This work qualifies Cs as not solubility limited in terms of distinct solid phases. Restricted inventories may potentially limit concentrations in solution.

Cs-speciation at specified solubility:

Limiting phase	Evaluated concentration [mol/kg H_2O]	Distribution of solute components
Not limited	--	Cs^+ (100.0 %)

Samarium

Based on the available data the calculated behaviour is very similar to that of europium, but uncertainties for individual equilibria/formation constants are not available. The lower guideline value of 2.4×10^{-11} [mol/kg H₂O] is based on a crystalline SmPO_{4(cr)}. A similar value is calculated for an amorphous phosphate. Phosphate is not considered in the present reference system but there is no doubt that phosphate is an ubiquitous ligand in environmental and underground systems. The potential concentration level of phosphate remains an open question. The present evaluation considers phosphate in the sense of a placeholder and assigns a concentration level of 1×10^{-8} [mol/kg H₂O] to [PO₄³⁻]_{tot}. This was done to check for potential formation of phosphate solids.

A series of carbonate phases produces solubility limits from 1.5×10^{-7} [mol/kg H₂O] to 8.5×10^{-7} [mol/kg H₂O] (SmOHCO₃.0.5H₂O_(cr), Sm₂(CO₃)_{3(s)}, NaSm(CO₃)_{2(s)}, see also calculations for Am) and an unspecified hydroxide (Sm(OH)_{3(s)}) would produce concentrations of 1.8×10^{-5} [mol/kg H₂O]. This latter phase was used to define the upper guideline value. In analogy to Eu and Am the hydroxide-carbonate SmOHCO₃.0.5H₂O_(cr), exhibiting a solubility of 1.5×10^{-7} [mol/kg H₂O] served for defining the recommended value.

The dominant complex in solution, different from calculated Am and Eu speciation, is SmCO₃⁺. The silicate complex M(III)H₃SiO₄⁺, characteristic for the trivalent ions, is relevant (~30 %) but not dominant.

Sm-speciation at specified solubility:

Limiting phase	Calculated solubility [mol/kg H ₂ O]	Distribution of solute components
SmOHCO ₃ .0.5H ₂ O _(cr)	1.5×10^{-7}	SmCO ₃ ⁺ (46.4 %) SmH ₃ SiO ₄ ²⁺ (28.4 %) SmSO ₄ ⁺ (8.5 %) Sm(CO ₃) ₂ ⁻ (7.7 %) Sm ³⁺ (4.9 %) Sm(SO ₄) ₂ ⁻ (2.6 %) SmOH ²⁺ (0.8 %) SmCl ²⁺ (0.7 %) Sm(OH) ₂ ⁺ (0.3 %) Sm(HCO ₃) ₂ ⁺ (0.1 %)

Sm-speciation at upper guideline value:

Limiting phase	Calculated solubility [mol/kg H ₂ O]	Distribution of solute components
Sm(OH) _{3(s)}	1.8×10^{-5}	SmCO ₃ ⁺ (46.0 %) SmH ₃ SiO ₄ ²⁺ (28.5 %) SmSO ₄ ⁺ (8.5 %) Sm(CO ₃) ₂ ⁻ (7.6 %) Sm ³⁺ (4.9 %) Sm(SO ₄) ₂ ⁻ (2.6 %) SmOH ²⁺ (0.8 %) SmCl ²⁺ (0.7 %) Sm(OH) ₂ ⁺ (0.3 %) Sm(HCO ₃) ₂ ⁺ (0.1 %)

Note: the database also includes data for a non-hydrated hydroxide-carbonate SmOHCO_{3(s)}. However, its solubility constant is not consistent with constants for the corresponding Eu- and Am-phases (about 5 orders of magnitude off) and will need further re-evaluation.

Europium

Using the combination of lowest possible solubility of the least soluble solid (EuOHCO_{3(cr)}) with the least stable dominant complex (and vice versa for the solid phase with the highest solubility) we calculated a guideline range from 1.1×10^{-7} [mol/kg] (lower guideline value) to 1.5×10^{-5} [mol/kg] (upper guideline value).

Note that in contrast to Sm and Ho no phosphate solid is available from the database. Therefore, the lower guideline value for Eu is higher than those for Sm and Ho.

Potential limiting solid phases are the hydroxide (Eu(OH)_{3(cr)}), the carbonate (Eu₂(CO₃)_{3(cr)}) and the mentioned hydroxide-carbonate (EuOHCO_{3(cr)}). The speciation in solution includes carbonates, sulfates, hydroxides and chlorides, apart from the most dominant complex EuH₃SiO₄²⁺. In such a system it makes sense, at least from a chemical point of view, to select the mixed solid as the solubility limiting phase (simple phases, i.e. the hydroxide and the carbonate reveal slightly higher individual solubilities). The recommended value based on the hydroxide-carbonate is 3×10^{-7} [mol/kg H₂O]. Adopted uncertainties for calculating upper- and lower guideline values were EuOHCO_{3(cr)}: $\pm 0.1 \log_{10}$ -units, Eu(OH)_{3(cr)}: $\pm 0.3 \log_{10}$ -units and EuH₃SiO₄²⁺: $\pm 0.4 \log_{10}$ -units.

Eu-speciation at specified solubility:

Limiting phase	Calculated solubility [mol/kg H ₂ O]	Distribution of solute components
EuOHCO ₃ ·0.5H ₂ O _(cr)	2.2×10^{-7}	EuH ₃ SiO ₄ ²⁺ (63.3 %) EuCO ₃ ⁺ (25.0 %) EuSO ₄ ⁺ (6.5 %) Eu(SO ₄) ₂ ⁻ (2.2 %) Eu ³⁺ (1.3 %) EuCl ²⁺ (0.4 %) Eu(CO ₃) ₂ ⁻ (0.4 %) EuOH ²⁺ (0.4 %) Eu(OH) ₂ ⁺ (0.4 %) EuCl ₂ ⁺ (0.1 %)

Eu-speciation at upper guideline value (considering uncertainty of formation constant of solid and of dominant complex):

Limiting phase	Calculated solubility [mol/kg H ₂ O]	Distribution of solute components
Eu(OH) _{3(cr)}	1.5×10^{-5}	EuH ₃ SiO ₄ ²⁺ (81.3 %) EuCO ₃ ⁺ (12.8 %) EuSO ₄ ⁺ (3.3 %) Eu(SO ₄) ₂ ⁻ (1.1 %) Eu ³⁺ (0.7 %) EuCl ²⁺ (0.2 %) Eu(CO ₃) ₂ ⁻ (0.2 %) EuOH ²⁺ (0.2 %) Eu(OH) ₂ ⁺ (0.2 %)

Holmium

Based on the available data (and consistent with its position in the periodic table of the elements) the calculated behaviour is very similar to that of europium and samarium, but uncertainties for individual equilibria/formation constants are not available. The lower guideline value of 4.2×10^{-10} [mol/kg H₂O] is based on a crystalline HoPO_{4(cr)}, assuming total dissolved phosphate of 1×10^{-8} [mol/kg H₂O] (see section samarium). A twenty times higher value is calculated for an amorphous phosphate.

Two different carbonate phases and a hydroxide phase produce solubilities from 2.5×10^{-6} [mol/kg H₂O] to 5.1×10^{-6} [mol/kg H₂O] (Ho₂(CO₃)_{3(cr)}, NaHo(CO₃)_{2(s)} and Ho(OH)_{3(s)}). The latter phase was used to define the upper guideline value. A hydroxide-carbonate phase as in the case of Sm and Eu is not included in the database (the source for the presently used Ho-data is specified in Thoenen (2012)). Therefore, the pure carbonate phase served for defining the recommended value of 2.5×10^{-6} [mol/kg H₂O].

As in the case of Sm, HoCO_3^+ is the dominant complex in solution. The silicate complex $\text{HoH}_3\text{SiO}_4^{2+}$ is relevant (~ 20 %) but not dominant as in the case of europium.

Ho-speciation at specified solubility:

Limiting phase	Calculated solubility [mol/kg H ₂ O]	Distribution of solute components
$\text{Ho}_2(\text{CO}_3)_3(\text{cr})$	2.5×10^{-6}	HoCO_3^+ (51.9 %) $\text{HoH}_3\text{SiO}_4^{2+}$ (20.2 %) $\text{Ho}(\text{CO}_3)_2^-$ (17.2 %) HoSO_4^+ (4.8 %) Ho^{3+} (3.5 %) $\text{Ho}(\text{SO}_4)_2^-$ (0.9 %) HoOH^{2+} (0.6 %) HoCl^{2+} (0.5 %) $\text{Ho}(\text{OH})_2^+$ (0.2 %) HoHCO_3^{2+} (0.1 %) $\text{HoPO}_4(\text{aq})$ (0.1 %)

Ho-speciation at upper guideline value:

Limiting phase	Calculated solubility [mol/kg H ₂ O]	Distribution of solute components
$\text{Ho}(\text{OH})_3(\text{s})$	5.1×10^{-5}	Corresponds to the speciation given at solubility of 2.5×10^{-6} [mol/kg H ₂ O]

Lead

Powell et al. (2009) published a careful evaluation on lead solubility using the SIT approach. With one exception ($\text{PbCO}_3(\text{aq})$; uncertainty $\pm 0.72 \log_{10}$ -units) the evaluated complex and solid formation constants have uncertainties below $\pm 0.1 \log_{10}$ -units. This dataset, complemented with published solubilities from Lothenbach et al. (1999) (hydro-cerussite ($\text{Pb}_3(\text{CO}_3)_2(\text{OH})_2(\text{cr})$), $\text{Pb}(\text{OH})_2(\text{pr})$, $\text{PbS}(\text{s})$) was used for evaluating solubilities and speciation. Under given chemical conditions there is no really dominant complex in solution. All of the complexes PbCl^+ , $\text{PbCO}_3(\text{aq})$, Pb^{2+} , $\text{PbSO}_4(\text{aq})$, and PbOH^+ contribute between 13 % and 23 % to totally dissolved lead.

Galena (PbS) exhibits the lowest solubility and produces 2.4×10^{-8} [mol/kg H₂O] of dissolved Pb, which was taken as the lower guideline value. The highest solubility (6.5×10^{-5} [mol/kg H₂O]) is produced when evaluating $\text{PbSO}_4(\text{s})$ including its uncertainty of $\pm 0.05 \log_{10}$ -units. It serves as the upper guideline value. The recommended value is based on the solubility of $\text{PbCO}_3(\text{s})$ (8.8×10^{-7} [mol/kg H₂O]) (potential uncertainty $\pm 0.07 \log_{10}$ -units).

Note an inconsistency with the potential solubility of hydro-cerrusite: This phase is not stable with respect to $\text{PbCO}_3(\text{s})$ under given chemical conditions. However, hydro-cerrusite may have its stability field at slightly increased pH.

Pb-speciation at specified solubility:

Limiting phase	Calculated solubility [mol/kg H ₂ O]	Distribution of solute components
$\text{PbCO}_3(\text{s})$	8.8×10^{-7}	PbCl^+ (23.0 %) $\text{PbCO}_3(\text{aq})$ (21.1 %) Pb^{2+} (14.9 %) $\text{PbSO}_4(\text{aq})$ (14.4 %) PbOH^+ (12.9 %) $\text{PbCl}_2(\text{aq})$ (8.1 %) PbHCO_3^+ (3.8 %) PbCl_3^- (1.0 %) $\text{Pb}(\text{CO}_3)_2^{2-}$ (0.6 %) $\text{Pb}(\text{OH})_2(\text{aq})$ (0.2 %)

Pb-speciation at upper guideline value:

Limiting phase	Calculated solubility [mol/kg H ₂ O]	Distribution of solute components
$\text{PbSO}_4(\text{s})$	6.5×10^{-5}	PbCl^+ (22.9 %) $\text{PbCO}_3(\text{aq})$ (21.1 %) Pb^{2+} (15.1 %) $\text{PbSO}_4(\text{aq})$ (14.4 %) PbOH^+ (12.9 %) $\text{PbCl}_2(\text{aq})$ (8.0 %) PbHCO_3^+ (3.8 %) PbCl_3^- (1.0 %) $\text{Pb}(\text{CO}_3)_2^{2-}$ (0.6 %) $\text{Pb}(\text{OH})_2(\text{aq})$ (0.2 %)

Polonium

Data on Polonium are very scarce, solubility data are absent and hydrolysis data, at the best, seem to be conflicting. There are indications that Po(IV) is the dominant redox state under given conditions and that Po(IV) hydrolyses at low pH values (Treiman & Treiman 1953). It is assumed that probably Th(IV) could act as surrogate to make an estimate on the behaviour of polonium². Consequently, the present work used the upper guideline value of Th (i.e. 6.6×10^{-7} [mol/kg H₂O]) as a recommendation (and as an upper guideline value). Consistently, the lower guideline value is also taken from Th. However, in Tab. 2 the values are put into parentheses to indicate their speculative character.

² Earlier reports on similar subjects promoted using Se(IV) as a proxy for Po. In the opinion of the author and based on [1953TRE/TRE] this view should be revised.

Radium

The database includes $\text{RaSO}_{4(s)}$ and $\text{RaCO}_{3(s)}$ as potential limiting solids. The solubility of $\text{RaSO}_{4(s)}$, including an uncertainty of $\pm 0.2 \log_{10}$ -units in the solubility constant serves as the upper guideline value. Dominant complexes/species in solution are $\text{RaSO}_{4(aq)}$ and Ra^{2+} , each comprising about 50 % of total dissolved Ra.

Based on the low inventories, and as already outlined and recommended in Berner (2002), a solid solution approach was traced to define the limiting concentrations in this work. In the meantime, Curti et al. (2010) have experimentally shown that radium forms solid solutions with barite at fast kinetic rates and in complete thermodynamic equilibrium with the aqueous solutions. The present evaluation decided to use a ternary, non-ideal solid solution comprised of $(\text{Ba,Ca,Ra})\text{SO}_{4(s)}$ to investigate the impact on calculated Ra-solubilities (regular Margules parameters taken from Glynn (2000)). This is justified by the fact that in the present chemical system barite is saturated and gypsum is very close to saturation. If the solubility calculation is performed using the solid solution instead of the three individual sulfates ($\text{BaSO}_{4(s)}$, $\text{CaSO}_{4(s)}$, $\text{RaSO}_{4(s)}$), the full amount of barite (7.6×10^{-3} [mol], according to Tab. 1) is transferred from pure barite to the ternary solid solution. The ternary solid solution also includes traces of $\text{CaSO}_{4(s)}$ (7.4×10^{-5} [mol]) and $\text{RaSO}_{4(s)}$. The trace of $\text{CaSO}_{4(s)}$ is a consequence of the general system composition, the amount of $\text{RaSO}_{4(s)}$ in the ternary solid solution is a priori unclear because a distinct mass balance is not available. In a first step it is assumed that the trapped amount of $\text{RaSO}_{4(s)}$ corresponds to the solubility of pure $\text{RaSO}_{4(s)}$ (6.2×10^{-8} [mol/kg H_2O]). Under such conditions the solubility of Ra drops, as expected when solid solutions form instead of individual phases, from 6.2×10^{-8} [mol/kg H_2O] to 5.1×10^{-12} [mol/kg H_2O]. This latter value serves as the lower guideline value.

When accepting that solid solutions form instead of individual limiting solids, the evaluation of a recommended value for Ra-solubility mainly depends on the ratio of $\text{RaSO}_4/\text{BaSO}_4$ in the solid solution ($6.2 \times 10^{-8}/7.6 \times 10^{-3}$ in the above example) and partly also on the non-ideality parameters of the solid solution.

At this point a short excursion to inventory and volume considerations seems necessary:

The absolute maximum radium inventory for a single spent fuel canister (diameter 1.05 m, length 4.6 m) after 200'000 years is about 3×10^{-2} mol, estimated from uranium inventories and decay chains (Hummel 2012), see also (Nagra 2010). The present reference water is calculated at a distance of 0.36 m from the canister, which means that the associated volume of bentonite is 14.82 m³ (including 742.5 kg of solution), when considering an interval of 3 m between canisters. When assuming a homogeneous distribution of Ra in this volume we estimate a maximum inventory of 4×10^{-5} mol of Ra per 1 kg of bentonite pore water. The inventory of barium, taken from Tab. 1, represents a minimum value, based solely on the content of exchangeable Ba associated with the montmorillonite phase. It does not yet include other sources of Ba from the bentonite, nor does it include the inventory in the spent fuel canister. This spent fuel canister inventory was estimated (Curti 2012b) to be 48.5 mol of Ba/canister, including ingrowths from decay chains. Assuming a homogeneous distribution of all available Ba in the same volume as for Ra leads to an additional Ba inventory of 6.5×10^{-2} [mol/kg H_2O] (compared to the 7.6×10^{-3} [mol/kg H_2O] as indicated in Tab. 1) and consequently to a $\text{RaSO}_4/\text{BaSO}_4$ ratio of $4 \times 10^{-5}/7.3 \times 10^{-2}$ in the solid solution.

Using the estimated inventories the resulting ternary solid solution includes 99.0 % of BaSO_4 , 0.94 % of CaSO_4 and 0.055 % of RaSO_4 . The calculated Ra concentration of 3.4×10^{-10} [mol/kg H_2O] is selected as the recommended value. Based on the Ra/Ba-ratio provided above and on

the solubility of phase pure $\text{RaSO}_{4(s)}$ one would expect a linearly scaled Ra concentration of 3.3×10^{-11} [mol/kg H_2O] for an ideal solid solution. The increase of one order of magnitude is a consequence of the non-ideality parameters taken from Glynn (2000).

Ra-speciation at recommended solubility:

Limiting phase	Calculated solubility [mol/kg H_2O]	Distribution of solute components
(Ba,Ca,Ra) $\text{SO}_{4(ss)}$; non-ideal solid solution $x_{\text{BaSO}_4} = 0.9901$ $x_{\text{CaSO}_4} = 0.0094$ $x_{\text{RaSO}_4} = 0.00055$	3.4×10^{-10}	$\text{RaSO}_{4(aq)}$ (49.6 %) Ra^{2+} (48.5 %) RaCl^+ (1.9 %)

Ra-speciation at upper guideline concentration:

Limiting phase	Calculated solubility [mol/kg H_2O]	Distribution of solute components
Single phase $\text{RaSO}_{4(s)}$ solid 0.2 \log_{10} -units less stable	1.1×10^{-7}	$\text{RaSO}_{4(aq)}$ (49.6 %) Ra^{2+} (48.5 %) RaCl^+ (1.9 %)

Actinium

Since the last assessment of solubility limits (Berner 2002) no new data or findings have been elaborated for actinium. The present report relies on analogy with tri-valent elements to simulate actinium. Recommended values for Eu, Am and Cm in the present report are 2.2×10^{-7} , 2.8×10^{-6} , and 2.8×10^{-6} [mol/kg H_2O], respectively. In order to stay on a safe side, 2.8×10^{-6} [mol/kg H_2O] as evaluated for Am is also recommended for Ac. Upper and lower guideline values are also taken from Am, although the upper guideline value for Cm is 2 orders of magnitude higher (see comments in the curium section).

Thorium

The relevant solid phase determining the solubility will be an amorphous, hydrated ThO_2 . Additional phases available from the database are $\text{ThF}_{4(cr,hyd)}$, $\text{Na}_6\text{Th}(\text{CO}_3)_5 \cdot 12\text{H}_2\text{O}_{(cr)}$ and $\text{Th}_3(\text{PO}_4)_3(s)$, but all these phases are under-saturated by many orders of magnitude and the thermodynamic data are partly of questionable quality (e.g. $\text{Th}_3(\text{PO}_4)_3(s)$). Dominant complexes in solution are the mixed hydroxide-carbonate complex $\text{Th}(\text{OH})_3(\text{CO}_3)^-$ and the neutral hydroxide $\text{Th}(\text{OH})_{4(aq)}$. The lower guideline value is based on the combined uncertainties of the solubility constant ($\pm 0.9 \log_{10}$ -units) for $\text{ThO}_{2(am,hyd,aged)}$ and of the dominant complex ($\pm 0.7 \log_{10}$ -units). For the upper guideline value the same uncertainty bands were applied to the solubility of $\text{ThO}_{2(am,hyd,fresh)}$. The recommended value corresponds to the calculated solubility of $\text{ThO}_{2(am,hyd,aged)}$.

Th-speciation at recommended solubility:

Limiting phase	Calculated solubility [mol/kg H ₂ O]	Distribution of solute components
ThO _{2(am,hyd,aged)}	4.1×10^{-9}	Th(OH) ₃ (CO ₃) ⁻ (56.3 %) Th(OH) _{4(aq)} (30.6 %) Th(OH) ₂ (CO ₃) ₂ ²⁻ (12.0 %) Th(OH) ₂ CO _{3(aq)} (1.1 %)

Th-speciation at upper guideline concentration:

Limiting phase	Calculated solubility [mol/kg H ₂ O]	Distribution of solute components
ThO _{2(am,hyd,aged)} solid: 0.9 log ₁₀ -units less stable, dominant complex 0.7 log ₁₀ -units more stable	6.6×10^{-7}	Th(OH) ₃ (CO ₃) ⁻ (86.6 %) Th(OH) _{4(aq)} (9.4 %) Th(OH) ₂ (CO ₃) ₂ ²⁻ (3.7 %) Th(OH) ₂ CO _{3(aq)} (0.3 %)

Protactinium

Thermodynamic data on protactinium are still scarce. The present work uses a collection of data given by Duro et al. (2006). Compared to the earlier study (Berner 2002) this recent data collection also includes sulfate complexes but they do not become important under given solution conditions. The only relevant solid is Pa(V)₂O_{5(s)}, leading to a calculated solubility of 1.25×10^{-9} [mol/kg H₂O] of dissolved Pa. The dominant complex in solution is Pa(V)O₂(OH)_(aq) (80 %). Estimates for uncertainties are available for the dominant complex (± 0.2 log₁₀-units (Duro et al. 2006)) but this value seems rather optimistic. The present study instead adopts a value of ± 0.5 log₁₀-units, in analogy to other dominant actinide complexes. No uncertainty is available for the limiting solid but Duro et al. (2006) proposes ± 1 log₁₀-unit for Pa(IV)O_{2(s)}, which is also adopted for Pa(V)₂O_{5(s)}. Using the combination lower solubility/less stable dominant complex produced the lower guideline value of 1.8×10^{-10} [mol/kg H₂O].

Earlier work on the same subject (Berner 2002) in a very similar chemical environment had been criticised by Wanner (2003) because potential carbonate complexes for protactinium were not considered. The hypothesis of relevant carbonate complexes was therefore tested in this work by introducing carbonate complexes to the operational database. Estimated data for the complexes PaO₂(CO₃)⁻, PaO₂(CO₃)₂³⁻, PaO₂(CO₃)₃⁵⁻ and PaO₂(CO₃)₂(OH)⁴⁻, in analogy to the thermodynamic data for Np(V) were introduced into the operational thermodynamic database and the very same formation constants (log₁₀K-value) as for the Np-complexes were used. Calculated solubility increased insignificantly from 1.25×10^{-9} to 1.28×10^{-9} [mol/kg H₂O].

The present work also tested the hypothesis that potential Pa(V)-carbonate complexes are much more stable (a factor of 100 was selected to test sensitivity) than corresponding Np(V) complexes. With these increased Pa(V)-carbonate stabilities the calculated Pa solubility increased from 1.3×10^{-9} to 4.6×10^{-9} [mol/kg H₂O] and displayed, as expected, PaO₂(CO₃)⁻ to be the dominant complex. Using this procedure the criticism about the missing carbonate complexes is sufficiently considered.

The present work recommends using a calculated solubility including carbonate complexes 100 times more stable than those reported for the Np(V) "analogue". A potential impact of carbonate complexation will almost certainly lead to lower solubilities.

The upper guideline value was derived by further adopting the proposed uncertainty for the solubility constant ($\pm 1 \log_{10}$ -unit). The solution at the upper guideline value exhibits the same speciation and is therefore not explicitly reported, below.

Pa-speciation at specified solubility, including hypothetical carbonate complexes:

Limiting phase	Calculated solubility [mol/kg H ₂ O]	Distribution of solute components
Pa ₂ O _{5(s)}	4.6×10^{-9}	PaO ₂ (CO ₃) ⁻ (72.7 %) PaO ₂ (OH) _{aq} (21.7 %) PaO ₂ ⁺ (4.8 %) PaO ₂ (OH) ₂ ⁻ (0.7 %) PaO ₂ (CO ₃) ₂ ³⁻ (0.1 %)

Uranium

A lower guideline value is estimated from the solubility of UO_{2(am,hyd)} by applying the lower value of the uncertainty band of the solubility ($\pm 1.0 \log_{10}$ -units) as well as the lowest stability of the dominant complex (CaUO₂(CO₃)₃²⁻; $\pm 0.5 \log_{10}$ -units). The recommended value corresponds to the calculated solubility of UO_{2(am,hyd)}. Noticeable differences to a previous evaluation (Berner 2002) can be traced back to the difference in the re-evaluated solubility product of UO_{2(am,hyd)}, to the nature and stability of the dominant complex and to the presence of the mixed M(II)UO₂(CO₃)_x(OH)_y-complexes (Thoenen 2012a), based on Guillaumont et al. (2003). Thermodynamic data on the present dominant complex were not available for the former evaluation. The upper guideline is based on the solubility of Na-boltwoodite (Na(H₃O)UO₂SiO₄·H₂O) by considering the extremes of the solubility uncertainty band ($\pm 1.0 \log_{10}$ -units) and of the dominant complex stability band ($\pm 0.5 \log_{10}$ -units).

U-speciation at specified solubility:

Limiting phase	Calculated solubility [mol/kg H ₂ O]	Distribution of solute components
UO _{2(am, hyd)}	2.2×10^{-7}	CaUO ₂ (CO ₃) ₃ ²⁻ (77.1 %) UO ₂ (CO ₃) ₃ ⁴⁻ (6.7 %) U(IV)(CO ₃)(OH) ₃ ⁻ (5.2 %) Ca ₂ UO ₂ (CO ₃) _{3(aq)} (5.0 %) MgUO ₂ (CO ₃) ₃ ²⁻ (3.5 %) U(OH) _{4aq} (1.4 %) UO ₂ (CO ₃) ₂ ²⁻ (0.6 %) SrUO ₂ (CO ₃) ₃ ²⁻ (0.2 %) U(V)O ₂ ⁺ (0.2 %)

U-speciation at upper guideline concentration:

Limiting phase	Calculated solubility [mol/kg H ₂ O]	Distribution of solute components
Na-boltwoodite (Na(H ₃ O)UO ₂ SiO ₄ .H ₂ O)	1.8×10^{-4}	CaUO ₂ (CO ₃) ₃ ²⁻ (91.3 %) UO ₂ (CO ₃) ₃ ⁴⁺ (2.5 %) U(IV)(CO ₃)(OH) ₃ ⁻ (1.9 %) Ca ₂ UO ₂ (CO ₃) _{3(aq)} (1.9 %) MgUO ₂ (CO ₃) ₃ ²⁻ (1.3 %) U(OH) _{4aq} (0.5 %) UO ₂ (CO ₃) ₂ ²⁻ (0.2 %) U(V)O ₂ ⁺ (0.1 %) (UO ₂) ₂ CO ₃ (OH) ₃ ⁻ (0.1 %) SrUO ₂ (CO ₃) ₃ ²⁻ (0.1 %)

Neptunium

The only sensible limiting solid under present conditions is NpO_{2(am,hyd)} with an uncertainty in the solubility constant of $\pm 0.5 \log_{10}$ -units and the exclusive solute is Np(OH)_{4(aq)}, whose formation constant has an uncertainty of $\pm 1.1 \log_{10}$ -units. The calculated and recommended solubility is 9.9×10^{-9} [mol/kg H₂O]. The lower guideline value of 2.7×10^{-11} [mol/kg H₂O] was calculated at the lowest value of the solubility uncertainty bandwidth. The upper guideline value of 3.9×10^{-8} [mol/kg H₂O] originates from the most stable end of the uncertainty bandwidth of the Np(OH)_{4(aq)} stability and the least stability of NpO_{2(am,hyd)}.

Note that the solubility of Np will increase with increasing Eh. Above +200 mV it is expected that Np(V) exhibiting the species Np(V)O₂⁺ and NpO₂CO₃⁻ will stabilise.

Np-speciation at specified solubility:

Limiting phase	Selected solubility [mol/kg H ₂ O]	Distribution of solute components
NpO _{2(am, hyd)}	9.9×10^{-9}	Np(OH) _{4aq} (99.2 %), Np(OH) ₃ ⁺ (0.7 %) NpCO ₃ (OH) ₃ ⁻ (0.1 %)

Note that the speciation in solution at the upper guideline value is similar to the speciation at the recommended solubility.

Plutonium

With PuO_{2(am,hyd)} and PuPO_{4(s)} the database reports two solid phases that might be responsible for limiting Pu-solubility. It is interesting to note that Pu(III)HSiO₃²⁺ is the dominant complex (~48 %), followed by Pu(IV)(CO₃)(OH)₃⁻ (~25 %) and by Pu(III)(CO₃)⁺ (~15 %). The uncertainty for the solubility of PuO_{2(am,hyd)} is $\pm 0.52 \log_{10}$ -units, that for PuPO_{4(s)} is about $\pm 0.8 \log_{10}$ -units. The uncertainty for the dominant silicate complex is unclear. Thoenen (2012) discusses a variety of silicate complexes with bi-, tri- and tetravalent metals and generally associates uncertainties in the range ± 0.1 to $\pm 0.3 \log_{10}$ -units to the formation constant of such

complexes. In order to stay on the safe side the present work assumes an uncertainty of ± 0.5 \log_{10} -units for the dominant complex $\text{Pu(III)HSiO}_3^{2+}$. The uncertainty for the co-dominant complex $\text{Pu(IV)CO}_3(\text{OH})_3^-$ is estimated to be ± 1 \log_{10} -unit. Using $\text{PuO}_{2(\text{am,hyd})}$ as the limiting solid and considering the most pessimistic border of the uncertainty ranges of the solid and the two dominant complexes, the upper guideline concentration of 9.7×10^{-9} [mol/kg H_2O] is calculated. In a similar way, using the most optimistic range borders the lower guideline value was calculated to be 3.1×10^{-10} [mol/kg H_2O] based on the limiting solid $\text{PuO}_{2(\text{am,hyd})}$. The recommended value of 6.8×10^{-10} [mol/kg H_2O] represents the calculated solubility of $\text{PuO}_{2(\text{am,hyd})}$ without considering uncertainties.

Neck et al. (2007) report on rather constant concentrations of colloidal $\text{Pu(IV)}_{(\text{coll,hyd})}$ in the presence of $\text{PuO}_{2(\text{am,hyd})}$ in the pH range 6 to 13. Their measured amounts of colloidal Pu in solution (5×10^{-10} to 5×10^{-8} [mol/kg H_2O]) are in good agreement with the concentrations based on thermodynamic calculations.

Using $\text{PuPO}_{4(\text{s})}$ as the limiting solid a concentration of 3.7×10^{-9} [mol/kg H_2O] is calculated.

Note that phosphate is not considered in the definition of the basic chemical bentonite system, but in the presence of Pu(III) even traces of phosphate may be relevant. The present evaluation considers phosphate in the sense of a placeholder and assigns a concentration level of 1×10^{-8} [mol/kg H_2O] to $[\text{PO}_4^{3-}]_{\text{tot}}$. This was done to check for potential formation of phosphate solids. Total dissolved phosphate concentrations significantly above 10^{-8} [mol/kg H_2O] would decrease the solubility of $\text{PuPO}_{4(\text{s})}$.

With $\text{Pu(OH)}_{3(\text{cr})}$ there exists another potential solid phase in the database. Neglecting other phases (i.e., particularly $\text{PuO}_{2(\text{am,hyd})}$) this hydroxide would produce a Pu solubility of 4.2×10^{-5} [mol/kg H_2O].

Pu-speciation at specified solubility:

Limiting phase	Calculated solubility [mol/kg H_2O]	Distribution of solute components
$\text{PuO}_{2(\text{am, hyd})}$	6.8×10^{-10}	$\text{Pu(III)HSiO}_3^{2+}$ (47.9 %) $\text{Pu(IV)CO}_3(\text{OH})_3^-$ (25.0 %) $\text{Pu(III)(CO}_3)^+$ (15.1 %) $\text{Pu(III)(SO}_4)^+$ (4.4 %) $\text{Pu(III)(CO}_3)_2^-$ (2.0 %) Pu(III)(OH)^{2+} (1.7 %) $\text{Pu(IV)(SO}_4)_2^-$ (1.7 %) Pu^{3+} (1.0 %) Pu(III)(OH)_2^+ (0.5 %) Pu(III)Cl^{2+} (0.4 %) $\text{Pu(IV)(OH)}_{4(\text{aq})}$ (0.3 %)

Pu-speciation at upper guideline value, using border values of uncertainty range for solid and both dominant complexes:

Limiting phase	Calculated solubility [mol/kg H ₂ O]	Distribution of solute components
PuO _{2(am, hyd)}	9.7×10^{-9}	Pu(IV)CO ₃ (OH) ₃ ⁻ (58.3 %) Pu(III)HSiO ₃ ²⁺ (35.4 %) Pu(III)(CO ₃) ⁺ (3.5 %) Pu(III)(SO ₄) ⁺ (1.0 %) Pu(III)(CO ₃) ₂ ⁻ (0.5 %) Pu(III)(OH) ₂ ²⁺ (0.4 %) Pu(IV)(SO ₄) ₂ ⁻ (0.4 %) Pu ³⁺ (0.2 %) Pu(III)(OH) ₂ ⁺ (0.1 %) Pu(III)Cl ²⁺ (0.1 %) Pu(IV)(OH) _{4(aq)} (0.1 %)

Americium

Limiting solid in the americium system will be a hydroxide/carbonate solid phase. The least soluble solid is a crystalline hydroxide carbonate including chemically bound water (AmOH(CO₃).0.5H₂O) and exhibiting an uncertainty of ± 0.5 log₁₀-units in the formation constant. A corresponding, amorphous/hydrated phase has an about two orders of magnitude higher solubility. The pure carbonate- and the pure hydroxide phases show a twofold higher solubility. The dominant species in solution (about 70 %) is the silicate complex AmHSiO₃²⁺ with an associated uncertainty of about ± 0.6 log₁₀-units in the formation constant. In alkali-rich solution the mixed and hydrated salt NaAm(CO₃)₂.5H₂O_(s) exhibiting a total solubility of 2.8×10^{-6} [mol/kg H₂O] may become stable. Its solubility is selected as the recommended value (see also the discussion on selecting the limiting solid in Section 2.4). The lower guideline value is based on the solubility of AmOH(CO₃).0.5H₂O_(cr) (8.3×10^{-9} [mol/kg H₂O]) including the most optimistic uncertainty borders and the upper guideline value is based on the solubility of Am(OH)_{3(cr)} using the most pessimistic uncertainty borders (5.4×10^{-5} [mol/kg H₂O]). The database includes an amorphous hydroxide (Am(OH)_{3(am)}), exhibiting a calculated solubility of about 1.3 orders of magnitude (a factor of 20) above the crystalline modification. This could, in the present solution system, potentially lead to millimolar AmHSiO₃²⁺ solutions and would strongly influence total dissolved silica (see also the comment on nickel and the potential impact of silica on Cm).

The author is not aware of any experimental evidence of such behaviour but recommends further exploring the potential complexation of di- and trivalent cations with silicate anions. However, the present study does not consider (Am(OH)_{3(am)}) being a realistic limiting solid.

Am-speciation at specified solubility:

Limiting phase	Calculated solubility [mol/kg H ₂ O]	Distribution of solute components
NaAm(CO ₃) ₂ ·5H ₂ O	2.8×10^{-6}	AmHSiO ₃ ²⁺ (70.1 %) AmCO ₃ ⁺ (22.0 %) Am(CO ₃) ₂ ⁻ (2.9 %) AmSO ₄ ⁺ (1.6 %) Am ³⁺ (1.5 %) AmOH ²⁺ (1.3 %) Am(OH) ₂ ⁺ (0.4 %) Am(HCO ₃) ₂ ⁺ (0.2 %) AmCl ²⁺ (0.1 %)

Am-speciation at upper guideline value:

Limiting phase	Calculated solubility [mol/kg H ₂ O]	Distribution of solute components
Am(OH) _{3(cr)}	5.4×10^{-5}	AmHSiO ₃ ²⁺ (90.4 %) AmCO ₃ ⁺ (7.1 %) Am(CO ₃) ₂ ⁻ (0.9 %) AmSO ₄ ⁺ (0.5 %) Am ³⁺ (0.5 %) AmOH ²⁺ (0.4 %) Am(OH) ₂ ⁺ (0.1 %) Am(HCO ₃) ₂ ⁺ (0.1 %)

Curium

The speciation of Cm is usually taken identical to the speciation of Am. This assumption is nearly "classical" and also reflects the fact that today measurements on Am speciation are performed using the analogue Cm (i.e. TRLFS measurements). Unfortunately, for Cm there is only one solid phase listed in the database (Cm(OH)_{3(am, coll)}). The formation constant is very similar to the formation constant of the corresponding amorphous americium solid, except for the addition "coll". Hence, the curium solid seems to have colloidal properties.

The present work used Cm(OH)_{3(am, coll)}, including its uncertainty of $\pm 0.4 \log_{10}$ -units and the uncertainty of the dominant complex CmHSiO₃²⁺ ($\pm 0.6 \log_{10}$ -units) to evaluate the upper guideline value of 3.3×10^{-3} [mol/kg H₂O]. The recommended value of 2.8×10^{-6} [mol/kg H₂O] is solely justified by the analogy with americium. This justification (for the recommended value) is the reason why no lower guideline value is provided for Cm. One could, of course and in analogy with Am, set the lower guideline value similar to the corresponding Am value. Conversely, this would imply the existence of a solid like CmOH(CO₃)₂·0.5H₂O, which in fact is nowhere reported and not included in the database. The present study abstains from setting a lower guideline value.

Note that also the upper guideline value is a formally calculated number which should be taken with great care. Since CmHSiO₃²⁺ is the dominant complex, its concentration of about 3.0×10^{-3} [mol/kg H₂O] would fully dominate the speciation of dissolved silicon in the system (present

values is 1.8×10^{-4} [mol/kg H₂O]) and consequently would affect a major system component. It is highly unlikely that such a high concentration can ever be reached. From total inventories an amount of 2.2×10^{-2} [mol curium/canister] is estimated. This translates (see also section on radium) to a maximum Cm concentration of $\sim 3 \times 10^{-5}$ [mol/kg H₂O].

Cm-speciation at specified solubility:

Limiting phase	Selected solubility [mol/kg H ₂ O]	Distribution of solute components
Analogy to Am	2.8×10^{-6}	CmHSiO ₃ ²⁺ (71.0 %) CmCO ₃ ⁺ (21.2 %) Cm(CO ₃) ₂ ⁻ (2.8 %) CmSO ₄ ⁺ (1.5 %) Cm ³⁺ (1.4 %) CmOH ²⁺ (1.3 %) Cm(OH) ₂ ⁺ (0.4 %) Cm(HCO ₃) ₂ ²⁺ (0.2 %) CmCl ²⁺ (0.1 %)

Cm-speciation at upper guideline value:

Limiting phase	Selected solubility [mol/kg H ₂ O]	Distribution of solute components
Cm(OH) _{3(am,coll)}	3.3×10^{-3}	CmHSiO ₃ ²⁺ (91.8 %) CmCO ₃ ⁺ (5.9 %) Cm(CO ₃) ₂ ⁻ (0.8 %) CmSO ₄ ⁺ (0.4 %) CmOH ²⁺ (0.4 %) Cm ³⁺ (0.4 %) Cm(OH) ₂ ⁺ (0.2 %) Cm(HCO ₃) ₂ ²⁺ (0.1 %)

5 Concluding Remarks

The presented approach is a well-established, world-wide accepted and state-of-the-art approach to establish maximum concentrations and one recognises that the values evaluated by different organisations are converging over the past decades. The approach is based on the most recent collection of thermodynamic data and on a careful and rather conservative selection of limiting solid phases. The results reveal that in 20 cases (Be, C_{inorg}, Cl, K, Ca, Co, Se, Sr, Tc, Pd, I, Cs, Sm, Eu, Pb, Po, Ra, Th, Pa and Pu) the evaluated maximum concentration is much lower, lower or similar than in a former study. Slightly increased recommended values (within a factor of 3.2 (0.5 log₁₀-units)) were evaluated for 8 elements (Ni, Nb, Ag, Ho, Ac, Np, Am, and Ca). This demonstrates a substantial improvement in evaluating solubility limits. In only four cases (Zr, Mo, Sn and U) improved thermodynamic data (Zr, U) or revised considerations (Mo, Sn) lead to higher recommended values. Compared to earlier studies on solubility limits the number of available thermodynamic data as well as their quality has increased. In addition, the process of assessing recommended values and bounding ranges has improved over the last decade. Present results clearly indicate the robustness of the approach.

The method to evaluate maximum expected concentrations of relevant elements is based on a "single element approach", meaning that an individual calculation in a given solution is performed for each element in question. Compared to earlier code systems, the present chemical solver (i.e. GEMS) exhibits a strongly improved performance and allows for solving much more complex and particularly much larger chemical systems³. Elements in question may form solid solutions (e.g. Ra/Ba) or may mutually interact (e.g. Ag, Se, Co, I, Cl), leading tentatively to lower recommended concentrations. Presently, the improved performance of the chemical solver is not yet fully exploited. It is strongly supposed that forcing a "multi element approach" (i.e. considering the full chemical system including all relevant elements in one run) will lead to improved system understanding and potentially to even lower recommended solubilities in distinct cases. This is certainly valid for elements forming solid solutions with system determining solid phases.

Outlook

To apply a "multi element approach" as indicated above may have consequences for setting up the basic chemical system. It will be necessary to include relevant system-defining solid phases and their masses. It will also be necessary to include the radioelement comprising solid phases and, particularly important, their inventories, keeping in mind that they might be heterogeneously distributed within the waste. This is certainly an ambitious task but it may be essential in cases where elements mutually interact. This principle may be compared with the principle of buffer capacity in solution, where the most abundant acid/base couple defines pH. The knowledge of relative masses in a system is also essential when applying approaches including solid solutions (e.g. the Ra/Ba issue or cementitious phases).

A well-known and periodic task is the determination of the limiting solid phase. The key issue here is the question as to whether the solid phase actually forms under given conditions. High temperature phases, also hardly soluble at ambient conditions, probably never form at lower temperature. Certain phases may have extremely slow precipitation kinetics (e.g. dolomite) and for some complex mixed phases (for example in the cement subsystem) the conditions leading

³ For calculations in the present report we simultaneously considered more than 700 species and solids. The mentioned "single element approach" was enforced by operationally setting mass balance constraints of other elements to insignificant values.

to their formation need to be studied further. Such considerations call for investigations on dissolution and precipitation kinetics. In this area the knowledge basis is still behind the knowledge basis on thermodynamics. Indeed, a fair amount of data is available on the dissolution kinetics of solid phases but considerably less is known about precipitation kinetics. This issue becomes particularly important when maximum solubilities or the chemical evolution is being investigated using reactive transport models. It is well conceivable that potentially stable solid phases are not able to form because the time scales for precipitation are affected by transport in/through the system.

Present thermodynamic concepts evaluate Eh on the basis of reference volumes exhibiting a homogeneous distribution of chemical masses. Sharp redox fronts observed in natural systems indicate evidence that many redox reactions primarily "happen" close to surfaces and not in the homogeneous bulk solution. Vice versa, redox determining surfaces (e.g. metals) may be "shielded" by reaction products, leading to a spatial separation of potential reactants. This is certainly an area deserving further studies.

All these considerations, although summarised in a very brief and fragmentary manner, indicate directions for further improvements on evaluating limiting concentrations for relevant elements. Apart from ongoing work on filling gaps in the grid of thermodynamic data, research on the presented topic should in addition concentrate on investigating mutual inventories, on spatial heterogeneities in the elemental distribution, on geometrical aspects of pore distributions, on the kinetics of precipitation reactions and, last but not least, on time scale aspects imposed by simultaneously ongoing transport processes.

Acknowledgements

I very much appreciate many fruitful discussions with my colleagues Wolfgang Hummel, Tres Thoenen and Enzo Curti and I thank for their help in finding and assessing a lot of literature data on specific elements. I experienced a lot of support from Dmitrii Kulik in operating and improving the GEMS code system. I would like to thank Bernhard Schwyn and Veerle Cloet, Nagra, for their careful review of the first manuscript and for the many helpful supporting comments. Partial financial support from Nagra is acknowledged.

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Appendix: Solubility Limits used for Dose Calculations

Cloet, V. & Schwyn, B. (Nagra)

A.1 Introduction

The present report compiles solubility limits for safety relevant elements in a bentonite environment of a SF/HLW repository. This appendix presents the values that are selected for transport/dose calculations for the provisional safety analyses within the Sectoral Plan for Deep Geological Repositories. These values are taken from the main part of the present report (cf. columns 2 – 4 in Tab. 2) and are in single cases adapted to the needs of the safety analysis. Requirements of the regulator (ENSI 2010) are considered.

A.2 Adjusted solubility values

The majority of the elements and their solubility values (reference and upper guideline values) are taken directly from this report and used in the dose calculations for SGT E2. For a few elements however, slight adaptations are made for the safety assessment. For those elements, a motivation for change is given below.

Cl

In this report, the Cl⁻-range of the pore water composition is considered for upper guideline values. However, for safety assessment Cl is assumed to be "not limited".

Co, Eu and K

These elements are not safety-relevant in an SF/HLW repository (Table A3.1-2 in Nagra 2008). These elements are removed for the dose calculations in SGT E2.

Sr

The ion exchange equilibrium with bentonite is used as reference value in this report. However, this is already considered for the derivation of the sorption value in argillaceous rock and bentonite (Baeyens 2014). For safety assessment the upper guideline value (SrSO₄(s)) is also used as reference value.

I

In this report, AgI is used as the concentration limiting solid. However, when taking into account the inventory of Ag⁺ and I⁻ in the SF/HLW waste, as it is currently known, the solubility limit should be adjusted.

The inventories of Ag⁺ and I⁻ can be derived from Häner et al. (2014). Neither Ag⁺ nor I⁻ are initially present as standard material in the fuel. Both activated nuclides are formed during the use of the fuel and are present in the SF:

Ag: 0.11g/kg SF = 1.0×10^{-3} mol/kg SF

I: 0.25g/kg SF = 2.0×10^{-3} mol/kg SF

The activated nuclides Ag^+ and I^- are contained in comparable amounts in SF. 100 % of Ag is assumed to be bound in the matrix and will only be released by very slow SF corrosion. It is questionable whether sufficient Ag^+ will ever be present in the near-field pore water to allow the precipitation of AgI. In contrast, around 10 % of I^- is contained in the instant release fraction and will therefore be in the near-field pore water before significant amounts of Ag will be released. For safety assessment I is therefore assumed to be "not limited".

Po

The analogy with Th(IV) is used in this report to describe the solubility of Po. As reference value the upper guideline value is taken. Since the analogy is speculative (the values are put in parentheses in this report) we use "not limited" as an upper guideline value instead.

Complexation with borate released from HLW glass

Because of the lack of thermodynamic data for borate complexes, silicate complexes are taken as analogues for Am, Cm, Eu, Ho, which are expected to form strong complexes. Considering borate complexes with $[\text{B}]_{\text{tot}}=10^{-4}\text{M}$, the solubility limit for Eu increases by a factor 2 (Bradbury et al. 2014). This increase is covered by the considered bandwidth of the solubility limits.

A.3 Solubility Limits in the SF/HLW Near Field for Dose Calculations

The solubility limits for a bentonite near field to be used for dose calculations within the provisional safety assessments are listed in Tab. A-1. The values are rounded to one significant figure. For conservative reasons, the solubility limits for Ho (ref.) and Pb (upper limit) were rounded to the next higher integer.

A.4 References

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Tab. A-1: Solubility limits of safety relevant elements in the SF/HLW near field (bentonite).

Element	Reference value [mol/kg H₂O]	Upper bound value [mol/kg H₂O]
Be	9×10^{-7}	2×10^{-6}
C _{inorg}	9×10^{-4}	3×10^{-3}
Cl	Not limited	Not limited
Ca	9×10^{-3}	4×10^{-2}
Ni	6×10^{-5}	5×10^{-3}
Se	5×10^{-9}	2×10^{-7}
Sr	1×10^{-4}	1×10^{-4}
Zr	1×10^{-7}	1×10^{-4}
Nb	7×10^{-5}	1×10^{-4}
Mo	2×10^{-5}	5×10^{-5}
Tc	4×10^{-9}	1×10^{-8}
Pd	6×10^{-8}	2×10^{-7}
Ag	1×10^{-5}	5×10^{-5}
Sn	9×10^{-8}	2×10^{-4}
I	Not limited	Not limited
Cs	Not limited	Not limited
Sm	2×10^{-7}	2×10^{-5}
Ho	3×10^{-6}	5×10^{-5}
Pb	9×10^{-7}	7×10^{-5}
Po	7×10^{-7}	Not limited
Ra	3×10^{-10}	1×10^{-7}
Ac	3×10^{-6}	5×10^{-5}
Th	4×10^{-9}	7×10^{-7}
Pa	5×10^{-9}	5×10^{-8}
U	2×10^{-7}	2×10^{-4}
Np	1×10^{-8}	4×10^{-8}
Pu	7×10^{-10}	1×10^{-8}
Am	3×10^{-6}	5×10^{-5}
Cm	3×10^{-6}	3×10^{-3}