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Technical Report 14-07

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

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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 long-lived intermediate level waste (ILW) considered retention mechanisms include the concentration limits of safety relevant elements in the pore water of the engineered concrete system.

The present work describes the evaluation of solubility limits for the 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 and Cm in the pore water of a concrete system corresponding to a degradation stage characterised by portlandite (Ca(OH)$_2$) saturation and by the absence of (Na,K)OH solutes.

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 for hydrated cement phases from CEMDATA07, with data from IUPAC (Pb) and with data from the literature (Mo). Differing sources for thermodynamic data are noted.

Reference values solubilities 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 important part of this work.

A similar report for an almost identical chemical environment has been produced in 2002, based on the PSI/Nagra Thermodynamic database 01/01. A comparison of the solubility limits with results from this former report and with regulatory recommendations to the values in this former report was made and is illustrated. With the criterion of a threshold value of ±0.5 log$_{10}$-units (a factor of 3.2) the evaluated solubilities were classified within this comparison into lower, similar, and higher recommended values. With this classification 14 elements fall into the class of lower recommended solubilities (Be, C$_{inorg}$, Se, Zr, Mo, Tc, I, Sm, Ho, Po, Ra, Np, Pu, Am) and 15 elements (Cl, K, Ca, Co, Sr, Nb, Pd, Sn, Cs, Eu, Pb, Ac, Th, U, Cm) into the class of similar recommended solubilities. Only three elements (Ni with a factor of 10, u with a factor of 70, Pa with a factor of 200 and Ag with a factor "high") exhibit higher recommended solubilities than evaluated in the former report.

A specific request concerned the potential impact of isosccharinic acid (ISA) on the solubility of the elements. ISA is at elevated pH a stronly complexing product of cellulose degradation. The isosaccharininate anion (ISA$^-$) is known to form strong complexes with di-, tri- and tetravalent cations and therefore to stabilise increased concentrations in solution. Thermodynamic complex formation data for relevant elements were collected from a recent NEA review (Hummel et al. 2005). Solubility calculations were repeated for these elements in the presence of 5×10^{-3} [mol/kg H$_2$O] of ISA$^-$ and a solubility enhancement factor was established. Low solubility enhancement factors were found for Ca (1.1), Ni (1.2), Pa (1.3), U (1.2), Np (3.5) and Pu (3.5). Considerable enhancement factors were found for Zr (109), Sm (630), Eu (263), Ho (632), Po (731), Ac (263), Th (731), Am (165) and Cm (165), where the ISA$^-$-complexes strongly dominate the speciation in solution. Since rather high ISA$^-$ concentrations were selected to study their impact on solubility, it can be concluded that in the worst case dissolved ISA has a detrimental impact on solubilites of tri-valent elements as well as Po and Th.

Zusammenfassung

Innerhalb der Etappe 2 des Sachplans geologische Tiefenlager (SGT) für radioaktive Abfälle in der Schweiz werden provisorische Sicherheitsanalysen durchgeführt. Beim Lager für langlebige mittelaktive Abfälle (LMA) wird dabei auch die Konzentrationslimitierung durch die Löslichkeiten der sicherheitsrelevanten Radionuklide (Elemente) im Porenwasser des Zement-/Betonsystems der Lagerkammern berücksichtigt.

Die vorliegende Arbeit beschreibt die sogenannten Löslichkeitslimiten der sicherheitsrelevanten Elemente 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 und Cm im Porenwasser eines Zement-/Betonsystems welches durch die Sättigung von Portlandit (Ca(OH)$_2$) und das Fehlen der ursprünglichen Alkalihydroxide charakterisiert ist.

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 im Gleichgewicht 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. Die Daten für hydratisierten Zement entstammen der CEMDATA07 Datenbank. Davon abweichende Datenquellen sind jeweils vermerkt.

Neben Referenzwerten werden auch untere und obere Eckwerte evaluiert. Oft sind für Formationskonstanten der Festkörper und gelösten Spezies Bandbreiten verfügbar, mit welchen die unteren und oberen Eckwerte abgeschätzt werden können. In vielen Fällen ist auch 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 erwähnten PSI/Nagra Chemical Thermodynamic Database 01/01 durchgeführt. Der Vergleich der Löslichkeitslimiten mit denjenigen dieser älteren Arbeit wird auch bildhaft aufgezeigt. Mit dem Kriterium eines Schwellenwerts von ± 0.5 log$_{10}$-Einheiten (ein Faktor 3.2) wurden die evaluierten Zahlenwerte in diesem Vergleich als weniger, gleich oder höher löslich eingestuft. Mit dieser Einstufung fallen 14 Elemente (Be, C$_{inorg}$, Se, Zr, Mo, Tc, I, Sm, Ho, Po, Ra, Np, Pu, Am) in die Klasse "weniger löslich", 15 Elemente (Cl, K, Ca, Co, Sr, Nb, Pd, Sn, Cs, Eu, Pb, Ac, Th, U, Cm) in die Klasse "gleich löslich" und nur 3 Elemente in die Klasse "höher löslich" als in der früheren Arbeit (Ni mit einem Faktor 10, Pa mit einem Faktor 200 und Ag mit einem Faktor "hoch").

Eine spezifische Anforderung an diese Arbeit betraf den Einfluss von Isosaccharinsäure (ISA) auf die Löslichkeit der Elemente. ISA ist bei hohem pH-Wert ein stark komplexierendes Zersetzungsprodukt der Zellulose. Das Isosaccharinat-Anion (ISA⁻) ist dafür bekannt, mit zwei-, drei- und vierwertigen Kationen starke Komplexe zu bilden und damit gegebenenfalls erhöhte Konzentrationen in Lösung zu stabilisieren. Entsprechende thermodynamische Konstanten für einige relevante Elemente wurden einer neueren Review der NEA (Hummel et al. 2005) entnommen. Für diese Elemente wurden die Löslichkeitsberechnungen in Anwesenheit von 5×10^{-3} [mol/kg H$_2$O] ISA⁻ wiederholt und die Erhöhung der Löslichkeiten ermittelt. Kleine Erhöhungsfaktoren wurden für Ca (1.1), Ni (1.2), Pa (1.3), U (1.2), Np (3.5) und Pu (3.5) festgestellt. Erhebliche Erhöhungsfaktoren wurden für Zr (109), Sm (630), Eu (263), Ho (632), Po (731), Ac (263), Th (731), Am (165) and Cm (165) gefunden, bei welchen die Speziation in Lösung durch den Isosaccharinatkomplex dominiert wird. Mit 5×10^{-3} [mol/kg H$_2$O] ISA⁻ wurde für diese Einflussstudie aber eine ziemlich hohe Konzentration des Komplexbildners gewählt. ISA hat also schlimmstenfalls auf die tri-valenten Elemente sowie Po und Th einen löslichkeitserhöhenden Einfluss.

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 déchets de moyenne activité à vie longue (DMAVL), 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 système de ciment / béton de l'infrastructure souterraine de stockage.

La présente étude décrit les «limites de solubilité» des éléments d'intérêt 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 et Cm dans l'eau interstitielle du système de ciment / béton, caractérisé par la saturation de la portlandite ($Ca(OH)_2$) et l'absence de l'hydroxyde d'alcali d'origine.

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 cette 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'IUCPA ou de la littérature existante. Les données relatives au ciment hydraté sont issues de la base CEMDATA 07. 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. Souvent, 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 mentionnée plus haut. Les limites de solubilité obtenues ici ont été comparées à celles de 2002. En fixant un seuil de ±0.5 $\log_{10}$-units (un facteur de 3.2), on a réparti les éléments dans trois catégories, selon que les valeurs de solubilité obtenues étaient inférieures, similaires et supérieures aux valeurs estimées en 2002. Sur cette base, la catégorie «valeurs de solubilité inférieures» comprend 14 éléments (Be, C_{inorg}, Se, Zr, Mo, Tc, I, Sm, Ho, Po, Ra, Np, Pu, Am), tandis que 15 éléments figurent dans la catégorie «valeurs similaires» (Cl, K, Ca, Co, Sr, Nb, Pd, Sn, Cs, Eu, Pb, Ac, Th, U, Cm). Pour trois éléments seulement (Ni avec un facteur 10, Pa avec un facteur 200 et Ag avec un facteur "élevé"), on a constaté des solubilités plus élevées que celles obtenues dans l'étude précédente.

Dans le cadre de la présente étude, l'impact potentiel de l'acide iso-saccharinique (ISA) sur la solubilité des éléments a fait l'objet d'une attention particulière. L'ISA, au fort pouvoir complexant, est issu de la dégradation de la cellulose dans un environnement caractérisé par un pH élevé. On sait que l'anion d'isosaccharinate (ISA⁻) forme des complexes forts avec des cations di-, tri- and tétravalents et qu'il a par conséquent un effet stabilisateur en cas d'élévation de la concentration dans une solution. Une étude récente réalisée par l'AEN (Hummel et al. 2005) comprend les constantes thermodynamiques correspondantes pour certains éléments d'intérêt. Les calculs ont été répétés pour ces éléments en présence de 5×10^{-3} [mol/kg H₂O] d'ISA⁻, afin de calculer le taux d'augmentation de la solubilité. Pour Ca (1.1), Ni (1.2), Pa (1.3), U (1.2), Np (3.5) et Pu (3.5), l'augmentation est restée faible. En revanche, on a observé une solubilité supérieure pour Zr (109), Sm (630), Eu (263), Ho (632), Po (731), Ac (263), Th (731), Am (165) et Cm (165), où la spéciation en solution est dominée par le complexe d'ISA⁻. Du fait que la concentration d'ISA⁻ choisie pour cette étude (5×10^{-3} [mol/kg H₂O]) est assez élevée, on peut en conclure que, dans le pire des cas, l'ISA dissous augmentera la solubilité des éléments tri-valents, ainsi que celle de Po et Th.

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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 (L/ILW) and three regions for high-level 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 "solubility limits" (or maximum expected concentrations) of safety relevant elements for the provisional safety analysis.

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 cementitious near field.

The principles of equilibrium thermodynamics are well established and have already been used in a former report (Berner 2002b). The maximum concentrations of thirty-two 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 recommended solubility limit. Supporting arguments for selecting all these values have been adopted either from the mentioned former report (Berner 2002b), 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 2004) have been taken into account where appropriate.

For the elements Ca, Ni, Zr, Sm, Eu, Ho, Po, Ac, Th, Pa, U, Np, Pu, Am and Cm thermo-dynamic data on complexation with the isosaccharinic acid anion (ISA$^-$) are either available from literature or were estimated based on chemical analogy. The impact of a maximum concentration of ISA$^-$ present in the concrete system on the solubility of these elements was investigated and solubility enhancement factors were derived.

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) combined with the CEMDATA07 Thermodynamic Data Base (Lothenbach et al. 2008), (Matschei et al. 2007), (Möschner et al. 2008), (Babushkin et al. 1985) (which had been evaluated using data from (Hummel et al. 2002), (Thoenen & Kulik 2003)), including additions for the not yet reviewed elements Ag, Be, Co, Ho, Pa, Pb and Sm (Duro et al. 2006, Colàs et al. 2007, Thoenen 2012b) and data for Mo (Felmy et al. 1992). Additional sources for thermodynamic data are indicated in the text at appropriate positions. Note that Thoenen (2012b) amongst other refers directly to a PHREEQC (Parkhurst & Appelo 1999) version of the ThermoChimie v.7.b database distributed with PHREEQC version 2.17.4137_modified, since there was no access to the corresponding documentation file.

2.2   Pore water compositions

The solubility calculations were performed in concrete pore water defined by Berner & Kosakowski (2011). This concrete pore water was based on following conditions:

The "basic" cement/concrete system according to Berner (2009) was equilibrated with Opalinus Clay for 10'000 years using a fully coupled model under a regime of diffusion (for details see (Kosakowski & Berner 2013), (Kosakowski & Berner 2011)). The selection of this particular type of cement/concrete pore water was discussed in Kosakowski et al. (2011), according to earlier reports on this topic (Nagra 1994), (Nagra 2002). The three classical stages of cement/concrete degradation are:

The fresh cement/concrete stage is characterised by high pH (>13) values caused by alkali hydroxides solutes. An exchange with adjacent host rocks has not yet occurred.

The portlandite stage, characterised by the domination of portlandite ($Ca(OH)_2$). Highly soluble alkali hydroxides have reacted/exchanged with the surrounding host rock. Compared to stage A the pore water exhibits a decreased ionic strength and a pH around 12.5.

The low-pH stage is characterised by the absence of portlandite as a consequence of leaching of portlandite and/or reaction with silicates, aluminates and other host rock components. As a result of such processes, the Ca/Si ratio of the C-S-H phases decreases and the pH of the pore water reaches values around 11 or even below.

In the present report maximum solubilities were evaluated for type B) pore water. The details of the pore water defining chemical system as well as the pore solution composition are provided in Tab. 1. The total volume (5.000 L) includes aggregates (62.1 %), hydrated cement minerals (17.9 %) and pore solution (20.0 %). The total mass is 11.257 kg, including 73.1 % of aggregates, 18.0 % of hydrated cement minerals and 8.9 % of pore solution.

Note on the calculated redox potential of the pore water: The calculated redox potential of the system (-498 [mV]) indicates that the porewater constitutes a reducing environment. This potential is established by thermodynamic equilibrium with the phases Fe-monocarbonate ($Ca_4Fe^{III}_2(CO_3)(OH)_{12}(H_2O)_5$), Fe-ettringite ($Ca_6Fe^{III}_2(SO_4)_3(OH)_{12}(H_2O)_{26}$), Fe-hydrotalcite (($MgO)_4Fe^{III}_2O_3(H_2O)_{10}$) and hydrous magnetite ($Fe_3O_4.2H_2O$). The former three phases are

members of the corresponding cementitious Al,Fe-solid solutions. They exclusively include iron in the trivalent state. Corresponding thermodynamic data were taken from [2007MAT/LOT]. Hydrous magnetite (see Berner 2009) is the single Fe(II)-bearing phase in the system since phases like pyrite (Fe(II)S$_2$), troilite (Fe(II)S) or siderite (Fe(II)CO$_3$) are strongly under saturated in the resulting water composition. Total dissolved iron is very low (5.6×10^{-8} [mol/kg H$_2$O]), with Fe(III)(OH)$_4^-$ being the dominant Fe-species in solution. Hence, the thermodynamic formation constants of the four Fe-bearing solids constrain the calculated redox potential in the present chemical system.

2.3   Operational approach for deriving limits

The solubility calculations (Tab. 3) were started with a "full chemical system" including all potentially forming solids and the pore solution. This system is buffered with respect to the major solutes and with respect to selected minor species (i.e. sulfide species). For each element to be assessed, a minimum amount of 1×10^{-8} [mol/kg H$_2$O] was concurrently 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 allowed deciding on the least soluble solid phase for each element. In the progress of the solubility limit evaluation the first step addition was replaced/completed by adding appropriate amounts of the ultimately relevant limiting solid to the chemical system. Such an approach produces the minimum dissolved concentration solubility of the element in question for the least soluble solid assuming full validity of thermodynamic properties/values. It further should have the least possible impact on the basic chemical system because the applied procedure ensures minimum amounts of mass fluxes from/to the solution.

However, the approach does not answer the question whether the selected solid 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). It may 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 solubility limits proceeded as follows: Using corresponding operational constraints in the code system the least soluble solid phase was excluded from being considered in the equilibrium calculation and the above mentioned procedure was applied to the second most stable solid. In this way all potential limiting solids available from the thermodynamic database were processed.

Tab. 1: Composition of chemical system for concrete degradation stage B): HTS reference system (Berner 2009) after 10'000 years of diffusive exchange with Opalinus Clay (298.15 K, 1 bar) (Kosakowski & Berner 2013), (Kosakowski & Berner 2011).

The system includes 4.000 L of solids (10.257 kg) and 1.000 L of solution (1.001 kg). Inert (8.227 kg) is an operationally defined, non-reacting phase having the physical properties of quartz. It represents the non-reacting/kinetically hindered aggregates of the concrete system and ist given for the sake of completeness in system mass.

Element	Moles*	Dissolved element [mol/kg H_2O]	Speciation in solution**
Al	0.8247	6.912×10^{-6}	$Al(OH)_4^-$
Ba	0.00025	2.658×10^{-5}	Ba^{2+}, $BaOH^+$
C	0.5661	8.064×10^{-6}	$CaCO_{3(aq)}$, CO_3^{2-}, $Na(CO_3)^-$, $SrCO_{3(aq)}$
Ca	18.3846	1.806×10^{-2}	Ca^{2+}, $CaOH^+$
Cl	0.0374	3.752×10^{-2}	Cl^-
Fe	0.37525	5.589×10^{-8}	$Fe(III)(OH)_4^-$
K	0.0033	3.310×10^{-3}	K^+, $KOH_{(aq)}$
Mg	0.32845	1.107×10^{-8}	$MgOH^+$, Mg^{2+}
Na	0.04214	4.228×10^{-2}	Na^+, $NaOH_{(aq}$
S	0.42735	4.711×10^{-5}	SO_4^{2-}, $Ca(SO_4)_{(aq)}$, $Na(SO_4)^-$, $Sr(SO_4)_{(aq)}$
Si	5.77955	3.432×10^{-5}	$Ca(H_2SiO_4)_{(aq)}$, $H_3SiO_4^-$, $H_2SiO_4^{2-}$
Sr	0.0263	2.486×10^{-3}	Sr^{2+}, $SrOH^+$
O	117.918	--	*OH^-: 4.892×10^{-2}* *OH^-, $CaOH^+$, $NaOH_{(aq)}$*
H	166.804	--	
Inert (quartz, SiO_2)	136.9285	--	
Phases		**[moles]**	**[kg]**
Solution			1.001
Solid solution phases			
Tobermorite-Jennite solid solution			1.061
Tobermorite-II $(SiO_2)(CaO)_{0.8333}(H_2O)_{1.333}$		5.0389	
Jennite $(SiO_2)(CaO)_{1.6667}(H_2O)_{2.1}$		0.74059	
Al,Fe-monocarbonate solid solution			0.2235
Monocarbonate $Ca_4Al_2(CO_3)(OH)_{12}(H_2O)_5$		0.21945	
Fe-monocarbonate $Ca_4Fe^{III}_2(CO_3)(OH)_{12}(H_2O)_5$		0.15535	
Al,Fe-ettringite solid solution			0.1787
Ettringite $Ca_6Al_2(SO_4)_3(OH)_{12}(H_2O)_{26}$		0.14236	
Fe-ettringite $Ca_6Fe^{III}_2(SO_4)_3(OH)_{12}(H_2O)_{26}$		(1.7×10^{-7})	

Tab. 1:   (continued)

Phases	[moles]	[kg]
OH-hydrotalcite solid solution		0.03822
Fe-hydrotalcite $(MgO)_4Fe^{III}_2O_3(H_2O)_{10}$	0.03158	
Inert (quartz)	136.9285	8.2273
Portlandite	6.8364	0.5065
Calcite	0.16947	0.01696
Strontianite	0.02382	3.517×10^{-3}
Hydrous Magnetite	0.0018	4.82×10^{-4}
Barite	2.10×10^{-4}	4.90×10^{-5}
System characteristics		
pH		12.54
Ionic strength		0.098 [mol/kg]
Eh***		-0.498 [V]
$\log_{10}(pCO_2)$		-13.1

*   Mole numbers of elements represent full system mass balance.
**   List includes those species (in descending order) that contribute > 1 % to total dissolved element.
***   See note in Section 2.2

One obtains a series of distinct potential "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 it would be inferred from thermodynamic principles. Moreover, the recommended value as provided in Tab. 3 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 therefore an integrated part of this value because they indicate/explain why a certain value has been selected or why other values/phases/processes seem less plausible.

2.4   Lower and upper guideline 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 between the bounding values. In earlier reports (Berner 2002a and 2002b) 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 bounding values is much more challenging than just selecting the recommended solubility limits calculated from available solid phase formation constants.

The approach to obtain the guideline values includes the analysis of the series of potentially limiting solids and provides the associated numerical values. The formation constant of each potential limiting solid may or may not have an uncertainty bandwidth which, when evaluated, leads to a concentration bandwidth depending on individual solid phases. Each dissolved element exhibits a certain speciation, describing the distribution of the total dissolved concentration over the different complexes in solution. Complexes comprising more than about 30 to 40 % of the total 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 its formation constant (if available) with the one of the limiting solid formation constant. If the element exhibits two or three dominant complexes, the evaluation of bounding 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 in all cases (solid phase formation constant; dominant complex formation constant). Sometimes a parameter uncertainty may be estimated based on chemically similar entities or based on other information. This will be noted in Tab. 3 or under the comments associated with the element in question.

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

Lower guideline value: evaluate the solubility using the formation constant 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 constant of the least stable solid and of 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.

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 would necessitate, in principle, a full appraisal of (relative) mass balances for all relevant elements because many different elements may share the same complexing anion[1] (or cation). 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 future versions of the data base presented here.

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[1]   This argument is less important for high pH solutions because the complexing anion is nearly exclusively hydroxide (OH^-), which is buffered by portlandite ($Ca(OH)_2$). As a consequence, the formation of significant amounts of hydroxide solutes will increase dissolved Ca^{2+} and may thus affect the solid phase assembly. Such problems are minimised by including the full reactive system mass (2.07 kg (excluding the 8.22 kg inert aggregates), see Tab. 1) into the equilibrium calculation.

In some solubility evaluations (e.g. C, Ca, Co) several solids may be involved. This is consistent with the principles of the Gibbs' phase rule when components with differing counter-ions are involved (e.g. Ca).

Uncertainties arising from using cement pore waters different from the selected stage B) pore water (e.g. stage A) or C)) are not considered in the present report. In most cases oxides/ hydroxides are the relevant limiting phases and the evaluated solubilities depend on the formation of (anionic) hydroxide complexes or polynuclear species (Zr). The potential impact of a stage A) pore water (pH 13.1) is about a factor of three (when the speciation is dominated by an anionic hydroxide complex), which is included in the upper guideline value. The impact of a stage C) pore water (pH 11.1) tends towards lower solubilities (about a factor of 30, provided that the speciation is fully dominated by an anionic hydroxide complex) because of lower [OH^-] concentrations. Corresponding impacts from pH-differences can easily be estimated from the given element-specific speciation.

Experimental information on solubilities in cementitious or cement-like systems at elevated pH is not very common in literature. Exceptions like Moroni & Glasser (1995), Ochs et al. (1998), (Wieczinski et al. (1998), Lothenbach et al. (2000), Ochs et al. (2002), Talerico et al. (2004) and Wieland et al. (2006) were partly considered in the judgement of recommended limits (Ni, Sn).

The present report does not provide solubilities for specific isotopes (e.g. ^{14}C, ^{79}Se….) but lists elemental solubilities. Isotope solubilities are worked out later in the overall safety assessment procedure, based on inventories and on the principles of isotopic dilution.

3   Impact of Isosaccharinic Acid Complexes on Element Solubilities

Organic ligands that form strong complexes with cationic species may increase the solubility of elements. Usually the speciation in solution above pH 12 is determined by the hydroxide ion OH-. However, isosaccharinic acid, a reaction product of cellulose degradation processes at elevated pH is known to form strong complexes, particularly with di-, tri- and tetravalent cations at elevated pH. According to Wieland & Berner (2012), isosaccharinic acid concentrations in the millimolar range could be found in cement/concrete environments due to the hydrolysis of cellulosic waste components. Therefore, the impact of isosaccharinic acid (HISA) on the solubility of selected elements was investigated. Thermodynamic data on complex formation with the isosaccharinic anion ISA- were taken from Hummel et al. (2005; see Tab. 2). There is a more recent review on actinide complexation with ISA from Gaona et al. (2008), exhibiting slightly different formation constants, particularly for the tetravalent actinides. The differences between the works of Hummel et al. (2005) and Gaona et al. (2008) have not yet been assessed in detail. This work therefore relies entirely on the values provided by Hummel et al. (2005) and may be subject to change, depending on the assessment of the data from Gaona et al. (2008).

Operational procedure to investigate the impact of ISA: The maximum concentration of ISA$^-$ in cementitious pore waters is expected to be 3.7×10^{-3} [mol/kg H$_2$O] (Wieland & Berner 2012). The present study considers a total of 5×10^{-3} [mol/kg H$_2$O] of ISA$^-$ being dissolved in the pore water and further considers ISA$^-$ being in equilibrium with dissolved Ca. Attributable to the formation of Ca-ISA complexes, total dissolved Ca increases from 18.1×10^{-3} [mol/kg H$_2$O] to 19.6×10^{-3} [mol/kg H$_2$O], where dissolved Ca-ISA complexes make up 11.4 % (2.23×10^{-3} [mol/kg H$_2$O]) of totally dissolved Ca. The complexation with Ca^{2+} reduces the "free" ISA$^-$ concentration in the inventory of 5×10^{-3} [mol/kg H$_2$O] down to 2.78×10^{-3} [mol/kg H$_2$O] (55.5 %).

Note that a further increase of ISA$^-$ leads to a nearly invariant system when Ca(ISA)$_{2(cr)}$ starts precipitating besides portlandite (the term nearly invariant refers to Ca and ISA; dissolved OH$^-$ may still be subject to variations). In this case (i.e. Ca(ISA)$_{2(cr)}$ precipitates) total dissolved Ca increases to 28.5×10^{-3} [mol/kg H$_2$O] and total dissolved ISA to 20.3×10^{-3} [mol/kg H$_2$O] (ionic strength increases to 0.11 [mol/kg H$_2$O]). In this nearly invariant system Ca-ISA complexes contribute with 33 % to totally dissolved Ca (9.3×10^{-3} [mol/kg H$_2$O]) and with 46 % to totally dissolved ISA.

The impact of ISA$^-$ on individual elements were always modeled under the assumption that ISA$^-$ (5×10^{-3} [mol/kg H$_2$O]) competes with the Ca-system.

A second model calculation was performed under the assumption that solid Ca(ISA)$_{2(cr)}$ is present in the system. Such model calculations produce maximum conceivable impacts of ISA$^-$ on the selected element solubility for a given solid phase. In Tab. 3 the corresponding numerical value is therefore noted under the heading "upper guideline value" (in rows denoted with "ISA b").

Tab. 2:   Complexes and solids of the isosaccharinic anion ISA- with selected elements used to investigate the potential of organic ligands as taken from Hummel et al (2005)

Where possible, $\log_{10}K$ of reaction was selected from investigations made in high pH environments.

Equilibrium reaction	Log$_{10}$K of reaction
$H^+ + ISA^- \iff HISA(aq)$*	4.0 ± 0.5
$Ca^{2+} + ISA^- \iff CaISA^+$	1.7 ± 0.3
$Ca^{2+} + ISA^- + H_2O \iff Ca(OH)ISA_{(aq)} + H^+$	-10.4 ± 0.5
$Ca^{2+} + 2ISA^- \iff Ca(ISA)_{2(cr)}$	-6.4 ± 0.2
$Ni^{2+} + ISA^- \iff NiISA^+$	$1.99 \pm$ n.d.
$2Ni^{2+} + ISA^- + 4OH^- \iff Ni_2(OH)_4ISA^-$	29.85 ± 0.89
$Eu(OH)_{3(aq)} + ISA^- \iff Eu(OH)_3ISA^-$	5.4 ± 0.2
$Th(OH)_{4(aq)} + ISA^- \iff Th(OH)_4ISA^-$	5.4 ± 0.2
$Th(OH)_{4(aq)} + Ca^{2+} + 2ISA^- \iff CaTh(OH)_4(ISA)_{2(aq)}$	9.4 ± 0.3
$U^{4+} + ISA^- + 4OH^- \iff U(OH)_4ISA^-$	50 ± 0.1
$UO_2^{2+} + ISA^- \iff UO_2ISA^+$	2.91 ± 0.15
$UO_2^{2+} + 2ISA^- \iff UO_2(ISA)_{2(aq)}$	5.37 ± 0.07
$UO_2^{2+} + 3ISA^- \iff UO_2(ISA)_3^-$	7.25 ± 0.18
$Np^{4+} + ISA^- + 3OH^- \iff Np(OH)_3ISA_{(aq)}$	(43.47) 43.87**
$Np^{4+} + 2ISA^- + 3OH^- \iff Np(OH)_3(ISA)_2^-$	(45.58) 45.98**
$Np^{4+} + ISA^- + 4OH^- \iff Np(OH)_4ISA^-$	(50.14) 50.54**
$Np^{4+} + 2ISA^- + 4OH^- \iff Np(OH)_4(ISA)_2^{2-}$	52.0
$Am(OH)_{3(aq)} + ISA^- \iff Am(OH)_3ISA^-$	4.8 ± 1.1

*   HISA(aq)* denotes the sum of HISA(aq) and $ISA_{L(aq)}$, the lactonised form of isosaccharinic acid (HISA(aq) $\iff ISA_{L(aq)} + H_2O$; see comprehensive discussion in Hummel et al. (2005). At pH 12.5 isosaccharinic acid is completely dissociated and the protonation constant is given for completeness only.

**   Neptunium complex formation constants (values in parentheses) were evaluated by Hummel et al. (2005) based on log10Ks,0 (NpO2(am,hyd)) = -54.9. The present value of this constant in the database (Thoenen 2012a) is log10Ks,0 (NpO2(am,hyd)) = -55.3. Constants for Np-ISA complexes have been adapted accordingly.

4   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 earlier for a very similar pore water system (Berner 2002b) are presented using light blue bars.

Tab. 3 provides a summary of the numerical values of recommended solubilities, lower guideline values and upper guideline values (Columns 2 to 4). A comparison with an earlier evaluation (Berner 2002b, Nagra 2002) and with recommendations from Wanner (2004) (indicated by an asterisk) is also given (columns 5 to 7). Rows denoted with "ISA a)" indicate calculations including 5×10^{-3} [mol/kg H_2O] of $(K^+)ISA^-$ and rows denoted with "ISA b)" indicate calculations where solid $Ca(ISA)_2(cr)$ is present. For redox-sensitive elements the dominant redox state in solution is given. Tab. 3 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 5.
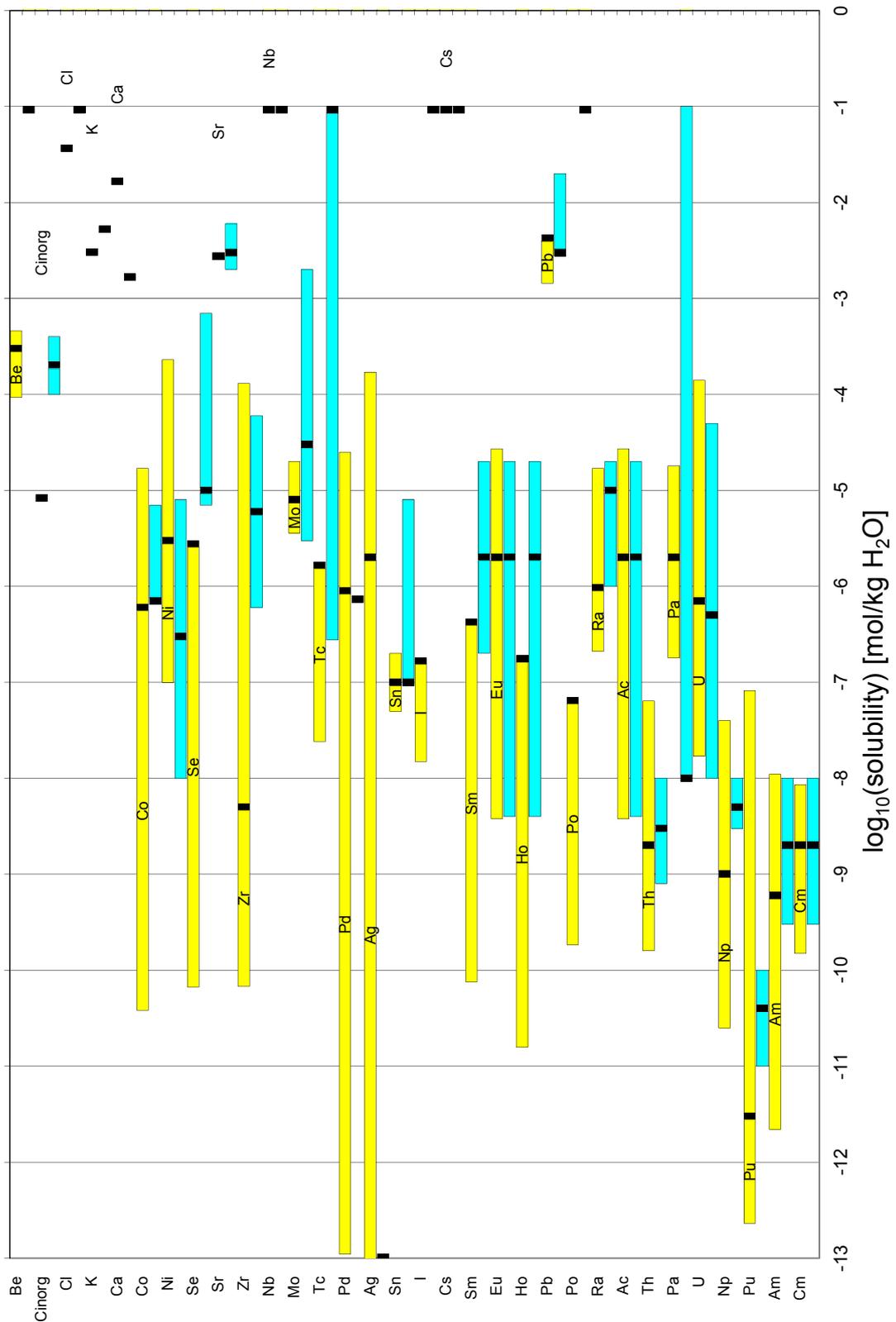
Fig. 1:   Comparison of present solubility limits (yellow) with those from Berner (2003)
            (blue) (25 ºC, 1 bar).

            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. 3: Summary of element solubilities including lower- and upper guideline values, calculated at 25 ºC, 1 bar.

For a more detailed description of Tab. 3 see Chapter 4.

| | Concrete pore water B), portlandite stage, pH 12.54 | | | (Berner 2002a), (Wanner 2004), (Nagra 2002) | | | |
Element	Recommended value [mol/kg H$_2$O]	Lower guideline value [mol/kg H$_2$O]	Upper guideline value [mol/kg H$_2$O]	Reference case [mol/l]	Lower limit [mol/l]	Upper limit [mol/l]	Limiting solid(s)/Comments
Be	2.3×10^{-4}	9.3×10^{-5}	4.6×10^{-4}	--	--	High	K_{sp} values for three modifications of Be(OH)$_2$ (alpha, beta or am) listed in the database. Quality is unknown, no uncertainties are available. Recommended value: Be(OH)$_{2(alpha)}$; lower guideline value: Be(OH)$_{2(beta)}$; upper guideline value: Be(OH)$_{2(am)}$.
C$_{inorg}$	8.1×10^{-6}			2×10^{-4}	1×10^{-4}	4×10^{-4}	Limiting solids: calcite, strontianite, Al,Fe-monocarbonate solid solutions; basic solution composition.
Cl	3.8×10^{-2}			High		High	Not limited; basic solution composition
K	3.3×10^{-3}			5.7×10^{-3}	High	High	Not limited by solid phases.
Ca	1.8×10^{-2}			1.8×10^{-3}	-	-	Concrete system; controlled by portlandite, calcite, CSH and several Calcium–Aluminate-phases.
ISA a)	2.0×10^{-2}						Addition of 5×10^{-3} [mol/kg H$_2$O] of ISA$^-$. Complexes CaISA$^+$ (3.6 %) and Ca(OH)ISA$_{(aq)}$ (7.8 %).
ISA b)			2.9×10^{-2}				Addition of 5×10^{-3} [mol/kg H$_2$O] of ISA$^-$ and of solid Ca(ISA)$_{2(cr)}$. Complexes CaISA$^+$ (10.6 %) and Ca(OH)ISA$_{(aq)}$ (22.1 %), Ca(ISA)$_{2(cr)}$ saturated. Total dissolved ISA increases to 20.3×10^{-3} [mol/kg H$_2$O].
Co	5.4×10^{-7}	3.8×10^{-11}	1.7×10^{-5}	7×10^{-7}	7×10^{-7}	7×10^{-6}	Recommended value; solubility of Co(OH)$_2$(s, rose); no uncertainties available. Lower guideline value: Solubility of Co$_2$SiO$_4$(s). Upper guideline value: solubility of Co(OH)$_{2(s,blue)}$. Dominant complexes Co(OH)$_{2(aq)}$(73.7 %) and Co(OH)$_3^-$ (25.9 %).

Tab. 3: (continued)

Concrete pore water B), portlandite stage, pH 12.54				(Berner 2002a), (Wanner 2004), (Nagra 2002)			
Element	Recommended value [mol/kg H2O]	Lower guideline value [mol/kg H2O]	Upper guideline value [mol/kg H2O]	Reference case [mol/l]	Lower limit [mol/l]	Upper limit [mol/l]	Limiting solid(s)/Comments
Ni	3.0×10^{-6}	1.0×10^{-7}	2.3×10^{-4}	3×10^{-7}	1×10^{-8}	8×10^{-6}	$Ni(OH)_{2(cr)}$ (theophrastite) limiting phase with uncertainty of ±0.2 log_{10}-units. Complex $Ni(OH)_3^-$ dominant (96.5 %; uncertainty ±1.7 log_{10}-units). Upper & lower guideline values: extremes of two uncertainty bandwidths.
ISA a)	3.5×10^{-6}						Addition of 5×10^{-3} [mol/kg H2O] of ISA. CalSA-complexes competitive. $Ni(OH)_{2(cr)}$ limiting phase with uncertainty of ±0.2 log_{10}-units. Complex $Ni(OH)_3^-$ dominant (84.9 %), $Ni_2(OH)_4ISA^-$ (6.1 %).
ISA b)			4.7×10^{-6}				Addition of 5×10^{-3} [mol/kg H2O] of ISA^- and of solid $Ca(ISA)_{2(cr)}$. CalSA-complexes competitive. $Ni(OH)_{2(cr)}$ limiting phase. Complex $Ni(OH)_3^-$ dominant (61.5 %), $Ni_2(OH)_4ISA^-$ (18.2 %).
Se(-II)	2.1×10^{-6}	7.2×10^{-11}	High	1×10^{-5}	7×10^{-6}	7×10^{-4} *High	Se(-II) is predominant at given redox potential and HSe^- is dominant complex at low concentrations. $CoSe_2(cr)$ (uncertainty ±2.6 log_{10}-units) limiting phase, used for lower guideline value (HSe^- dominant complex). Recommended value based on $CoSe_2(cr)$ using increased solubility (+2.6 log_{10}-units). Necessary condition: Co limited by $Co_2SiO_{4(s)}$. Elemental $Se_{(cr)}$ not stable due to formation of highly soluble polynuclear Se_x^{2-} (Se_2^{2-}, Se_3^{2-}, Se_4^{2-}). See text.
Sr	2.4×10^{-3}	--	--	3×10^{-3}	2×10^{-3}	6×10^{-3}	Limiting solid is strontianite; basic system definition.

Tab. 3:   (continued)

	Concrete pore water B), portlandite stage, pH 12.54			(Berner 2002a), (Wanner 2004), (Nagra 2002)			
Element	Recommended value [mol/kg H_2O]	Lower guideline value [mol/kg H_2O]	Upper guideline value [mol/kg H_2O]	Reference case [mol/l]	Lower limit [mol/l]	Upper limit [mol/l]	Limiting solid(s)/Comments
Zr	4.5×10^{-9}	6.8×10^{-11}	1.3×10^{-4}	6×10^{-6}	6×10^{-7}	6×10^{-5} *6×10^{-4} (100 times ref. value)	Lower guideline value: solubility of baddeleyite (ZrO_2) including uncertainty of 1.7 log_{10}-units and of 0.3 log_{10}-units for $Ca_2Zr(OH)_6^{2+}$. Upper guideline value: solubility of $Zr(OH)_{4(am,fresh)}$. Recommended value is based on the solubility of baddeleyite.
ISA a)	(4.9×10^{-7})						Exclusively based on hypothetical complex $Zr(OH)_4ISA^-$ in analogy to thorium.
Nb(V)	High	High	High	High	High	High	Data on Nb very scarce. Solute species $Nb(V)(OH)_6^-$.
Mo(VI)	7.2×10^{-6}	3.6×10^{-6}	2.0×10^{-5}	3×10^{-5}	3×10^{-6}	2×10^{-3}	Solubility and upper/lower guideline values based on powellite ($CaMoO_{4(s)}$), taken from Felmy et al. (1992) (uncertainty ± 0.3 log_{10}-units). Dominant complex $Mo(VI)O_4^{2-}$ (83 %), minor complex $CaMoO_{4(aq)}$ (estimated uncertainty ± 0.5 log_{10}-units).
Tc(IV)	1.8×10^{-6}	2.9×10^{-8}	1.8×10^{-6}	High	3×10^{-7}	High	Only available limiting solid is $TcO_2.1.6H_2O(s)$. with uncertainty of ± 0.5 log_{10}-units. Dominant solute is $Tc(IV)O(OH)_3^-$ having uncertainty of ± 0.4 log_{10}-units. System is redox- & pH sensitive. Above about -370 mV (at pH 12.5) the pertechnetate ion $Tc(VII)O_4^-$ will become stable and dominant (alternatively: pH >14.6 at -98 mV). Calculation leads to 2.3×10^{-7} [mol/kg H_2O]. Lower and upper guideline values based on uncertainty of $TcO_2.1.6H_2O_{(s)}$ and $Tc(IV)O(OH)_3^-$. No thermodynamic data available for potential Tc(V) and Tc(VI) complexes at elevated pH. Decision: take upper guideline concentration for the recommended value, bearing the Eh/pH sensitivity in mind.

Tab. 3:   (continued)

| Concrete pore water B), portlandite stage, pH 12.54 | | | | (Berner 2002a), (Wanner 2004), (Nagra 2002) | | | |
Element	Recommended value [mol/kg H₂O]	Lower guideline value [mol/kg H₂O]	Upper guideline value [mol/kg H₂O]	Reference case [mol/l]	Lower limit [mol/l]	Upper limit [mol/l]	Limiting solid(s)/Comments
Pd	8.5×10^{-7}	insignificant	2.5×10^{-5}	8×10^{-7}	--	--	Recommended value based on $Pd(OH)_{2(s)}$ and on experimental data from Middlesworth & Wood (1999) and Wood (1991). Uncertainty of ±0.5 $\log_{10}K_s$ and ±1.0 $\log_{10}$-units for $Pd(OH)_3^-$ defines upper guideline value. Lower guideline value based on solubility of $Pd_{(cr)}$.
Ag	1.8×10^{-6}	2.9×10^{-14}	1.7×10^{-4}	insignificant	--	--	Limiting solid assumed to be $AgCl_{(s)}$, dominant complex in solution is $AgCl_2^-$. Uncertainties presently not available, but very low for $AgCl_{(s)}$. $Ag_{(cr)}$ potentially stable ($\sim 1 \times 10^{-20}$ [mol/kg H₂O]). Lower guideline value: solubility of acanthite ($Ag_2S_{(s)}$). The solubility of $AgOH_{(s)}$ serves for the upper guideline value.
Sn(IV)	1.0×10^{-7}	5.0×10^{-8}	2.0×10^{-7}	1×10^{-7}	1×10^{-7}	8×10^{-6}	Recommended value: calculated solubility for $CaSn(OH)_{6(precip)}$ (uncertainty ±0.3 $\log_{10}K_s$). Lower guideline value: applying -0.3 $\log_{10}K_s$. Dominant complex $Sn(OH)_6^{-2}$. Upper guideline value: applying $+0.3$ $\log_{10}K_s$. Neglecting the stannate phase would lead to concentrated solutions (0.1 [mol/kg H₂O], cassiterite ($SnO_{2(cr)}$)). Tin solubility inverse to Ca concentration.
I	1.8×10^{-7}	1.8×10^{-8}	1.8×10^{-7}	High	High	High	Only limiting solid for iodine is $AgI_{(s)}$, uncertainties are not available. Calculated $AgI_{(s)}$ solubility serves for recommended and upper guideline value. Note: if $AgCl_{(s)}$ is assumed to control solubility of silver (see also under heading "silver"), then $AgI_{(s)}$ becomes stable at 1.8×10^{-8} [mol/kg H₂O] of total dissolved iodine (serves for lower guideline value). For corrected thermodynamic data on iodine species see text.

Tab. 3: (continued)

| Concrete pore water B), portlandite stage, pH 12.54 | | | | (Berner 2002a), (Wanner 2004), (Nagra 2002) | | | |
Element	Recommended value [mol/kg H$_2$O]	Lower guideline value [mol/kg H$_2$O]	Upper guideline value [mol/kg H$_2$O]	Reference case [mol/l]	Lower limit [mol/l]	Upper limit [mol/l]	Limiting solid(s)/Comments
Cs	High	High	High	High	High	High	No limiting solids available. Potential control by inventories or by sorption equilibria.
Sm	4.6×10^{-7}	8.9×10^{-11}	4.6×10^{-7}	2×10^{-6}	2×10^{-7}	2×10^{-5}	Sm(OH)$_{3(am,cr)}$ considered to be limiting solid. Uncertainty ± 1.0 log$_{10}$-units each (estimate from (Duro et al. 2006). Solubility of Sm(OH)$_{3(cr)}$ serves for lower guideline value. The upper guideline value is based on the solubility of Sm(OH)$_{3(am)}$ including simultaneously the uncertainties of the solid and the dominating complex. Samarium data not compatible with homologous europium. Hence, the upper guideline value was selected for the recommendation.
ISA a)	2.9×10^{-4}						Based exclusively on analogy to Eu, assuming that Sm(OH)$_{3(aq)}$ + ISA$^-$ <=>Sm(OH)$_3$ISA$^-$, log$_{10}$K = 5.4.
Eu	1.9×10^{-6}	3.8×10^{-9}	2.7×10^{-5}	2×10^{-6}	4×10^{-9} $*2 \times 10^{-7}$	2×10^{-5}	Solubility limiting phase is assumed to be Eu(OH)$_{3(am)}$ (uncertainty ± 0.8 log$_{10}$-units is used to define upper guideline value); dominant complex is Eu(OH)$_4^-$ (58.3 %, uncertainty ± 0.5 log$_{10}$-units). Limiting phase Eu(OH)$_{3(cr)}$ with uncertainty ± 0.3 log$_{10}$-units produces $3.8 \cdot 10^{-9}$ [mol/kg H$_2$O] (used for lower guideline value).
ISA a)	5.0×10^{-4}	1.1×10^{-6}					Addition of 5×10^{-3} [mol/kg H$_2$O] of ISA$^-$. CaISA-complexes competitive. Eu(OH)$_{3(am)}$ limiting phase. Complex Eu(OH)$_2$ISA$^-$ dominant (99.7 %) solute. Lower guideline value based on more stable Eu(OH)$_{3(cr)}$.

Tab. 3:   (continued)

Concrete pore water B), portlandite stage, pH 12.54				(Berner 2002a), (Wanner 2004), (Nagra 2002)			
Element	Recommended value [mol/kg H$_2$O]	Lower guideline value [mol/kg H$_2$O]	Upper guideline value [mol/kg H$_2$O]	Reference case [mol/l]	Lower limit [mol/l]	Upper limit [mol/l]	Limiting solid(s)/Comments
ISA b)			2.2×10^{-3}				Addition of 5×10^{-3} [mol/kg H$_2$O] of ISA$^-$ and of solid Ca(ISA)$_{2(cr)}$. CaISA-complexes competitive. Eu(OH)$_{3(am)}$ limiting phase. Eu(OH)$_2$ISA$^-$ dominant (99.9 %) solute.
Ho	1.9×10^{-7}	1.8×10^{-11}	1.9×10^{-7}	2×10^{-6}	4×10^{-9}	2×10^{-5}	Ho(OH)$_{3(am,cr)}$ considered to be type of limiting solid. Uncertainty of ±0.1 log$_{10}$-units each (estimate from Duro et al. (2006)) seems too low compared with Sm. Solubility of Ho(OH)$_{3(cr)}$ including uncertainty serves for lower guideline value. Upper guideline value based on solubility of Ho(OH)$_{3(am)}$ including increased uncertainty (taken similar to Sm). Holmium data not compatible with homologous europium. Hence, upper guideline value selected for recommendation. Solubility of HoPO$_{4(cr)}$ would lead to 4.7×10^{-7} [mol/kg H$_2$O].
ISA a)	1.2×10^{-4}				--		Based exclusively on analogy to Eu, assuming that Sm(OH)$_{3(aq)}$ + ISA$^-$ <=>Sm(OH)$_3$ISA$^-$, log$_{10}$K = 5.4.
Pb	4.6×10^{-3}	1.7×10^{-3}	4.6×10^{-3}	3×10^{-3}	--	2×10^{-2}	Data from(Powell et al. (2009) and Lothenbach et al. (1999). PbO$_{(red)}$ (±0.07 log$_{10}$-units), Pb$_3$(PO$_4$)$_{2(pr)}$ (±1.0 log$_{10}$-units) and Pb(OH)$_{2(pr)}$ (no uncertainty) produce solubilities of 1.7·10^{-3}, 2.5×10^{-3} and 4.6×10^{-3} [mol/kg H$_2$O], respectively. In case of Pb$_3$(PO$_4$)$_{2(pr)}$: pH decreases to 12.51, IS increases to 0.111 [mol/kg] and PO$_4^{3-}$ $_{total}$ to 1.68×10^{-3} [mol/kg H$_2$O]. Dominant complex always Pb(OH)$_3^-$. Decision: recommended value and upper guideline value: solubility of Pb(OH)$_{2(pr)}$. Lower guideline value: solubility of PbO$_{(red)}$. Galena (PbS) is undersaturated by 4 orders of magnitude.

Tab. 3:   (continued)

Concrete pore water B), portlandite stage, pH 12.54				(Berner 2002a), (Wanner 2004), (Nagra 2002)			
Element	**Recommended value** [mol/kg H$_2$O]	**Lower guideline value** [mol/kg H$_2$O]	**Upper guideline value** [mol/kg H$_2$O]	**Reference case** [mol/l]	**Lower limit** [mol/l]	**Upper limit** [mol/l]	**Limiting solid(s)/Comments**
Po(IV)	6.4×10^{-8}	1.6×10^{-10}	6.4×10^{-8}	High	High	High	Evidence that Th(IV) could act as surrogate for Po. Use upper guideline value of Th as recommendation and consequently use lower guideline value from Th. Analogy with Th is not extended to ISA in this table.
Ra	9.7×10^{-7}	2.1×10^{-7}	1.7×10^{-5}	1×10^{-5}	1×10^{-6}	2×10^{-5} $*2 \times 10^{-2}$	The formation of (Ra,Ba)SO$_{4(ss)}$ in scales from geothermal energy production is a fact. The recommended value is thus calculated from solid solution formation based on appropriate inventories (see text). The upper guideline value is based on calculated solubility of RaSO4$_{(s)}$, applying an uncertainty of 0.2 log$_{10}$-units for the solubility constant. For lower guideline value see text.
Ac	(1.9×10^{-6})	(3.8×10^{-9})	(2.7×10^{-5})	2×10^{-6}	4×10^{-9}	2×10^{-5}	No new data. Use principle adopted in (Berner 2014) and select recommended value in analogy to Eu. Upper and lower guideline values also taken from Eu.
ISA a)	(5.0×10^{-4})						Analogy with Eu.
Th	1.3×10^{-9}	1.6×10^{-10}	6.4×10^{-8}	3×10^{-9}	8×10^{-10}	1×10^{-8}	ThO$_{2(am,hyd,aged)}$ is limiting solid and dominant complex in solution is Th(OH)$_{4(aq)}$ (99.4 %). including 0.9 log$_{10}$-units of uncertainty would produce 1.6×10^{-10} [mol/kg H$_2$O], which serves for lower guideline value.. Upper guideline value: ThO$_{2(am,hyd,fresh)}$, including 0.9 log$_{10}$-units of uncertainty.

Tab. 3: (continued)

Concrete pore water B), portlandite stage, pH 12.54				(Berner 2002a), (Wanner 2004), (Nagra 2002)			
Element	Recommended value [mol/kg H$_2$O]	Lower guideline value [mol/kg H$_2$O]	Upper guideline value [mol/kg H$_2$O]	Reference case [mol/l]	Lower limit [mol/l]	Upper limit [mol/l]	Limiting solid(s)/Comments
ISA a)	9.5×10^{-7}		6.0×10^{-6}				Addition of 5×10^{-3} [mol/kg H$_2$O] of ISA. CaISA-complexes in competition. ThO$_{2(am,hyd,aged)}$ limiting phase. Complex Th(OH)$_4$(ISA)$^-$ dominant (92.1 %), ThCa(OH)$_4$(ISA)$_{2(aq)}$ (7.8 %). Upper guideline value: use ThO$_{2(am,hyd,fresh)}$ instead of ThO$_{2(am,hyd,aged)}$.
ISA b)			3.0×10^{-5}				Addition of 5×10^{-3} [mol/kg H$_2$O] of ISA and of solid Ca(ISA)$_{2(cr)}$. Upper guideline value: ThO$_{2(am,hyd,fresh)}$ assumed to be limiting solid. Speciation: Th(OH)$_4$ISA$^-$ dominant (73.4 %), ThCa(OH)$_4$(ISA)$_{2(aq)}$ (26.6 %).
Pa(V)	1.8×10^{-6}	1.8×10^{-7}	1.8×10^{-5}	1×10^{-8}	1×10^{-8}	High	Thermodynamic data on Pa are still scarce. Present data and uncertainty estimates were taken over from Duro et al. (2006). Limiting solid is Pa$_2$O$_{5(s)}$, dominant complex is Pa(V)O$_2$(OH)$_2^-$. Estimated uncertainties of Pa$_2$O$_{5(s)}$ (±1 log$_{10}$-units) and Pa(V)O$_2$(OH)$_2^-$ (±0.5 log$_{10}$-units) serve for upper and lower guideline value.
ISA a)	(2.3×10^{-6})						Addition of 5×10^{-3} mol/kg of ISA. CaISA-complexes in competition. Pa$_2$O$_{5(s)}$ limiting phase. Pa(OH)$_5$ISA$^-$ formation constant based on chemical analogy (see text).
U(VI)	7.0×10^{-7}	1.7×10^{-8}	1.4×10^{-4}	1×10^{-8} *5×10^{-7}	1×10^{-8}	5×10^{-7} *5×10^{-5}	Limiting solid UO$_{2(am)}$ (uncertainty ±1.0 log$_{10}$-units). Dominant complexes UO$_2$(OH)$_4^{2-}$ (83.3 %; ±0.68 log$_{10}$-units) and UO$_2$(OH)$_3^-$ (16.3 %; ±0.42 log$_{10}$-units) =>recommended value. Lower guideline value based on uncertainty of UO$_{2(am)}$, UO$_2$(OH)$_4^{2-}$ (±0.68 log$_{10}$-units) and UO$_2$(OH)$_3^-$ (±0.42 log$_{10}$-units). Upper guideline value based on becquerelite (Ca(UO$_2$)$_6$O$_4$(OH)$_6$.8H$_2$O).

Tab. 3: (continued)

Concrete pore water B), portlandite stage, pH 12.54				(Berner 2002a), (Wanner 2004), (Nagra 2002)			
Element	Recommended value [mol/kg H$_2$O]	Lower guideline value [mol/kg H$_2$O]	Upper guideline value [mol/kg H$_2$O]	Reference case [mol/l]	Lower limit [mol/l]	Upper limit [mol/l]	Limiting solid(s)/Comments
ISA a)	8.4×10^{-7}						Addition of 5×10^{-3} [mol/kg H$_2$O] of ISA. CaISA-complexes in competition. UO$_{2(am,hyd)}$ limiting phase. Complex U(OH)$_4$ISA$^-$ (10.4 %), UO$_2$(OH)$_4^{2-}$ still dominant (75.1 %).
ISA b)			1.1×10^{-6}				Addition of 5×10^{-3} [mol/kg H$_2$O] of ISA$^-$ and of solid Ca(ISA)$_{2(cr)}$. UO$_{2(am,hyd)}$ limiting phase. UO$_2$(OH)$_4^{2-}$ dominant (56.1 %), U(OH)$_4$ISA$^-$ (32.7 %).
Np(IV)	1.0×10^{-9}	2.5×10^{-11}	4.0×10^{-8}	5×10^{-9}	3×10^{-9}	1×10^{-8}	Under present conditions Np(IV)O$_{2(am,hyd)}$ only sensible limiting solid with uncertainty of ±0.5 log$_{10}$-units; exclusive solute is Np(OH)$_{4(aq)}$ with uncertainty of ±1.1 log$_{10}$-units. Upper and lower guideline value according to given uncertainties.
ISA a)	3.5×10^{-9}						Addition of 5×10^{-3} [mol/kg H$_2$O] of ISA. CaISA-complexes in competition. NpO$_{2(am,hyd)}$ limiting phase. Complex Np(OH)$_4$ISA$^-$ (54.0 %), and Np(OH)4(ISA)$_2^{2-}$ (17.9 %) make up 72 % of dissolved Np.
ISA b)			1.9×10^{-8}				Addition of 5×10^{-3} [mol/kg H$_2$O] of ISA and of solid Ca(ISA)$_{2(cr)}$. NpO$_{2(am,hyd)}$ limiting phase. Np(OH)$_4$(ISA)$_2^{2-}$ (53.9 %), Np(OH)$_4$ISA$^-$ (40.7 %).

Tab. 3:   (continued)

Concrete pore water B), portlandite stage, pH 12.54				(Berner 2002a), (Wanner 2004), (Nagra 2002)			
Element	**Recommended value** [mol/kg H_2O]	**Lower guideline value** [mol/kg H_2O]	**Upper guideline value** [mol/kg H_2O]	**Reference case** [mol/l]	**Lower limit** [mol/l]	**Upper limit** [mol/l]	**Limiting solid(s)/Comments**
Pu(IV)	2.3×10^{-12}	2.3×10^{-13}	8.2×10^{-8}	4×10^{-11}	1×10^{-11}	1×10^{-10}	$PuO_{2(am,hyd)}$ has uncertainty of ± 0.52 $\log_{10}$-units. Dominant complex is $Pu(OH)_{4(aq)}$ with estimated uncertainty of ± 0.5 $\log_{10}$-units. Note that $Pu(III)(OH)_{3(cr)}$ would produce 8.2×10^{-8} mol/kg of totally dissolved Pu, also with $Pu(IV)(OH)_{4(aq)}$ being the dominant complex.
(ISA a)	(8.1×10^{-12})						Data for Pu-ISA complexes are not available. In analogy to Np(IV), the present study estimates a similar increase in solubility at 5×10^{-3} [mol/kg H_2O] of ISA, resulting in 8.1×10^{-12} [mol/kg H_2O] of totally dissolved Pu.
(ISA a)			(4.4×10^{-11})				Data for Pu-ISA complexes are not available. In analogy to Np(IV) the present study estimates a similar solubility increase at 5×10^{-3} [mol/kg H_2O] of ISA and presence of solid $Ca(ISA)_2$, resulting in 4.4×10^{-11} [mol/kg H_2O] of totally dissolved Pu.
Am	5.4×10^{-10}	2.2×10^{-12}	1.1×10^{-8}	2×10^{-9}	3×10^{-10}	1×10^{-8}	Limiting solid will be either $Am(OH)_{3(cr)}$ or $Am(OH)_{3(am)}$, differing by factor of 20 in solubility. Recommended value is based on $Am(OH)_{3(am)}$ and upper guideline value is based on uncertainties of $Am(OH)_{3(am)}$ (± 0.8 $\log_{10}$-units), $Am(OH)_{3(aq)}$ (± 0.5 $\log_{10}$-units) and $Am(OH)_2^+$ (± 0.7 $\log_{10}$-units). Lower guideline value is based on $Am(OH)_{3(cr)}$ including corresponding uncertainties. Dominant complex is $Am(OH)_{3(am)}$.

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Tab. 3: (continued)

Concrete pore water B), portlandite stage, pH 12.54				(Berner 2002a), (Wanner 2004), (Nagra 2002)			
Element	Recommended value [mol/kg H2O]	Lower guideline value [mol/kg H2O]	Upper guideline value [mol/kg H2O]	Reference case [mol/l]	Lower limit [mol/l]	Upper limit [mol/l]	Limiting solid(s)/Comments
ISA a)	8.9×10^{-8}	4.4×10^{-9}					Addition of 5×10^{-3} [mol/kg H2O] of ISA. CaISA-complexes in competition. $Am(OH)_{3(am)}$ assumed to be limiting phase. Complex $Am(OH)_3ISA^-$ dominant (99.4 %). $Am(OH)_{3(cr)}$ would produce 4.4×10^{-9} [mol/kg H2O], which is taken as lower guideline value. Am-ISA complex becomes significant when $\log_{10}K(Am(OH)_3ISA^-)$ exceeds 2.56.
ISA b)			3.5×10^{-7}				Addition of 5×10^{-3} [mol/kg H2O] of ISA^- and of solid $Ca(ISA)_{2(cr)}$. $Am(OH)_{3(am)}$ assumed to be limiting phase. $Am(OH)_3ISA^-$ dominant (99.8 %).
Cm	1.1×10^{-9}	1.5×10^{-10}	8.6×10^{-9}	2×10^{-9}	3×10^{-10}	1×10^{-8}	Only solid phase in database is $Cm(OH)_{3(am,coll.)}$, including an uncertainty of ± 0.4 $\log_{10}$-units. Dominant complexes in solution $Cm(OH)_{3(aq)}$ (93.6 %, uncertainty ± 0.5 $\log_{10}$-units) and $Cm(OH)_2^+$ (4.4 %, uncertainty ± 0.7 $\log_{10}$-units). Upper and lower guideline values are based on these uncertainties.
(ISA a)	(1.8×10^{-7})						Data on Cm-ISA complexes are not available. An estimate based on the analogy with Am (solubility increase by a factor of ~165 when 5×10^{-3} [mol/kg H2O] of ISA is present) produces value given in parentheses.
(ISA b)			(7.1×10^{-7})				Data on Cm-ISA complexes are not available. An estimate based on the analogy with Am (solubility increase by factor of ~650 when 5×10^{-3} [mol/kg H2O] of ISA and solid $Ca(ISA)_{2(cr)}$ is present) produces value given in parentheses.

5   Comments on Individual Elements

Beryllium

The chemistry of beryllium is determined by oxides/hydroxides. Carbonates, sulfates or chlorides are not significant at pH 12.5. Dominant complex in solution is $Be(OH)_3^-$ (95.5 %). The solubility limiting phase is one of the hydroxides $Be(OH)_{2(\alpha, \beta \text{ or am})}$. The lower guideline value was based on the solubility of $Be(OH)_{2(\beta)}$, the recommended value was calculated from $Be(OH)_{2(\alpha)}$ and the upper guideline value was taken from the solubility of $Be(OH)_{2(am)}$. No uncertainties for individual equilibria were available.

Be-speciation at specified solubility:

Limiting Phase	Calculated solubility [mol/kg H_2O]	Distribution of solute components
$Be(OH)_{2(alpha)}$	2.3×10^{-4}	$Be(OH)_3^-$ (95.5 %) $Be(OH)_4^{2-}$ (4.4 %) $Be(OH)_{2(aq)}$ (0.1 %)

The Be-speciation at the upper guideline value is identical.

Carbon

Inorganic carbon, present as CO_3^{2-} is a non-relevant anion in the reference solution provided in Tab. 1. Its concentration is determined by the interplay of calcite, strontianite and Al,Fe-monocarbonate solid solutions. The actually calculated value depends on the relative masses of the actual phase assembly. Siderite ($FeCO_3$) is another potential carbonate limiting solid phase which is not stable in the present reference system. Lower and upper guideline values are not provided since they would be valid for an alternative phase composition. Note that the phase assembly may be subject to change when time dependent systems in reactive transport models need to be considered. With the exception of Sr (and to a much lesser extent Th) the elements considered in the present report do not form significant amounts of carbonate complexes at pH 12.5. The potential solubility of organic forms of carbon is not considered here but the potential impact of the complexing agent isosaccharinic acid on the selected elements has been investigated.

C-speciation at specified solubility:

Limiting Phase(s)	Calculated solubility [mol/kg H_2O]	Distribution of solute components
Calcite, strontianite, Al,Fe-mono-carbonate solid solution	8.1×10^{-6}	$CaCO_{3(aq)}$ (68.8 %) CO_3^{2-} (20.8 %) $NaCO_3^-$ (6.0 %) $SrCO_{3(aq)}$ (4.3 %) HCO_3^- (0.06 %) $FeCO_{3(aq)}$ (0.04 %)

Chlorine

Chlorine is a system defining element, not limited by a solid phase. Its concentration represents a snapshot after 10'000 years of exchange between concrete and Opalinus Clay (Kosakowski & Berner 2013). A potential limiting solid for chloride would be $AgCl_{(s)}$, which would induce interdependency between silver and chlorine. In the present setup the chemical system includes 37.5 mmoles of Cl^- per 10.26 kg of solid phases. Hence, $AgCl_{(s)}$ could become a relevant solid phase above 400 ppm of Ag when referring to the solid system mass, i.e., for silver-bearing wastes. Note that for other types of host rocks the concentration of chloride could be as high as 0.66 [mol/kg H_2O] (Mäder 2009). As outlined in Berner (2014), this could potentially have less significant consequences for the solubility of Ag. Under concrete conditions and at high Cl^- loadings Friedel's salt ($3CaO.Al_2O_3.CaCl_2.10H_2O$) could potentially be a limiting solid. However, Friedel's salt is not stable against carbonate and sulfate (formation of Ca-monocarbonate and ettringite).

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

Potassium

Potassium is a system defining element. In the present setup its concentration is controlled by the inventory of the cement and by 10'000 years of diffusive exchange with Opalinus Clay (Kosakowski & Berner 2013).

K-speciation at specified concentration:

Control	Modelled value [mol/kg H_2O]	Distribution of solute components
Cement inventory, diffusive exchange with Opalinus Clay	3.3×10^{-3}	K^+ (99.1 %) KOH(aq) (0.9 %)

Calcium

Calcium is a major element of the chemical system. Its solubility is controlled by portlandite, calcite, CSH and several calcium-aluminate-phases and depends on the actual phase assembly and on the distribution of anions in solution. Upper and lower guideline values are not provided; these depend simultaneously on variations of the basic chemical setup which is controlled by the inventory of the cement and by 10'000 years of diffusive exchange with Opalinus Clay

Ca-speciation at specified solubility:

Limiting Phase	Calculated solubility [mol/kg H_2O]	Distribution of solute components
Portlandite, CSH, calcite, calcium-aluminate-phases	1.8×10^{-2}	Ca^{2+} (78.3 %) $CaOH^+$ (21.4 %) $CaSiO_{3(aq)}$ (0.2 %) $CaSO_{4(aq)}$ (0.1 %)

There is no upper guideline value specified. However, considering a solution saturated with $Ca(ISA)_2$ the speciation will include significant parts (33 %) of Ca-ISA complexes (see below).

Impact of Isosaccharinic acid on solubility of Calcium

Isosaccharinic acid	Calculated solubility [mol/kg H_2O]	Distribution of solute components for Ca	Distribution of solute components for ISA
ISA^-_{tot} 5×10^{-3} [mol/kg H_2O] Portlandite, CSH, calcite, calcium-aluminate-phases	2.0×10^{-2}	Ca^{2+} (69.1 %) $CaOH^+$ (19.3 %) $Ca(OH)ISA_{(aq)}$ (7.8 %) $CaISA^+$ (3.6 %) $CaSiO_{3(aq)}$ (0.2 %) $CaSO_{4(aq)}$ (0.1 %)	ISA^- (55.5 %) $Ca(OH)ISA_{(aq)}$ (30.6 %) $CaISA^+$ (13.9 %)
$Ca(ISA)_2$ saturated ISA^-_{tot} 2.0×10^{-2} [mol/kg H_2O]	2.9×10^{-2}	Ca^{2+} (53.2 %) $Ca(OH)ISA_{(aq)}$ (22.1 %) $CaOH^+$ (14.0 %) $CaISA^+$ (10.6 %) $CaSiO_{3(aq)}$ (0.1 %)	ISA^- (54.1 %) $Ca(OH)ISA_{(aq)}$ (31.0 %) $CaISA^+$ (14.9 %)

Cobalt

$Co_2SiO_{4(s)}$ fixes cobalt solubility at very low Co-concentration (3.8×10^{-11} [mol/kg H_2O]). This value was taken for the lower guideline value, although a potential formation of $Co_2SiO_{4(s)}$ from homogeneous solutions needs verification. The recommended value of 5.4×10^{-7} [mol/kg H_2O] was based on the solubility of $Co(OH)_{2(s,rose)}$. Two other Co-hydroxides, $Co(OH)_{2(s,rose2)}$ and $Co(OH)_{2(s,blue)}$ produce solubilities increased by a factor of 10 and 32, respectively. The solubility of $Co(OH)_{2(s,blue)}$ was selected to represent the upper guideline value. The speciation in solution is dominated by hydroxide complexes. Other ligands, i.e., $HSiO_3^-$, SO_4^{2-} or Cl^- are not significant. Thermodynamic data for Co were taken from Duro et al. (2006). No uncertainties are provided in Duro et al. (2006).

Co-speciation at specified solubility:

Limiting phase	Calculated solubility [mol/kg H_2O]	Distribution of solute components
$Co(OH)_2$(s,rose)	5.4×10^{-7}	$Co(OH)_{2(aq)}$ (73.7 %) $Co(OH)_3^-$ (25.9 %) $Co(OH)_4^{2-}$ (0.4 %) $Co(OH)^+$ (0.1 %)

The speciation at the upper guideline value of 1.7×10^{-5} [mol/kg H_2O] is similar.

Nickel

The recommended solubility of Ni is determined by $Ni(OH)_{2(cr)}$ (theophrastite) and the dominant complex in solution is $Ni(OH)_3^-$ at pH 12.5. Solute complexes other than hydroxides are not significant (i.e. carbonates, sulfates, silicates). Available uncertainties are ± 0.2 log_{10}-units for

the formation constant of the solid phase and ± 1.7 $\log_{10}$-units for the formation constant of the dominant complex. With $NiO_{(cr)}$ the database displays another potential limiting phase. With 8.7×10^{-5} [mol/kg H_2O] the calculated solubility of $NiO_{(cr)}$ is twenty times higher than that of $Ni(OH)_{2(cr)}$ (3.0×10^{-6} [mol/kg H_2O]). Such behaviour is unexpected and raises a question as to the consistent evaluation of thermodynamic data for the two solids. Obviously, $NiO_{(cr)}$ is not a stable phase in the presence of water. Hence, it is disregarded as a Limiting phase. Lower- and upper guideline values were calculated considering the given uncertainties simultaneously and at the extremes of their bandwidth.

Note that at the lower guideline concentration the neutral hydroxide $Ni(OH)_{2(aq)}$ instead of the anionic $Ni(OH)_3^-$ dominates the speciation ($Ni(OH)_{2(aq)}$ 64.2 %, $Ni(OH)_3^-$ 35.8 %).

Ni-speciation at specified solubility:

Limiting phase	Calculated solubility [mol/kg H_2O]	Distribution of solute components
$Ni(OH)_2(cr,beta)$	3.0×10^{-6}	$Ni(OH)_3^-$ (96.5 %) $Ni(OH)_{2(aq)}$ (3.5 %)

Ni-speciation at upper guideline value:

Limiting phase	Calculated solubility [mol/kg H_2O]	Distribution of solute components
$Ni(OH)_2(cr,beta)$; uncertainties of solid formation constant and dominant complex formation constant at extreme values	2.3×10^{-4}	$Ni(OH)_3^-$ (99.9 %) $Ni(OH)_{2(aq)}$ (0.1 %)

For comparison: Wieland et al. (2006) determined a mean value of $(2.9 \pm 0.5) \times 10^{-7}$ [mol/kg H_2O] of dissolved Ni in artificial cement pore water at pH 13.3.

Impact of Isosaccharinic acid on solubility of Nickel

Isosaccharinic acid	Calculated solubility [mol/kg H_2O]	Distribution of solute components for Ni	Distribution of solute components for ISA
ISA^-_{tot} 5×10^{-3} [mol/kg H_2O] $Ni(OH)_{2(cr,beta)}$	3.5×10^{-6}	$Ni(OH)_3^-$ (84.9 %) $Ni_2(ISA)(OH)_4^-$ (6.1 %) $Ni(OH)_{2(aq)}$ (3.0 %)	ISA^- (55.5 %) $Ca(OH)ISA_{(aq)}$ (30.6 %) $CaISA^+$ (13.9 %)
$Ca(ISA)_2$ saturated ISA^-_{tot} 2.0×10^{-2} [mol/kg H_2O] $Ni(OH)_{2(cr,beta)}$	4.7×10^{-6}	$Ni(OH)_3^-$ (61.5 %) $Ni_2(ISA)(OH)_4^-$ (18.2 %) $Ni(OH)_{2(aq)}$ (2.1 %)	ISA^- (54.1 %) $Ca(OH)ISA_{(aq)}$ (31.0 %) $CaISA^+$ (14.9 %)

The isosaccharinic acid system is not significantly influenced by nickel.

Selenium

Preliminary comment: Because of its predominant occurrence as anionic species selenium may be strongly related to the chemistry and to the available inventory of other elements. Examples are ($Ag_2Se_{(aq)}$, $Ag_2Se_{(cr)}$, $CoSe_{2(s)}$, $Co_{0.84}Se_{(s)}$ and M^+,M^{2+}(selenides, selenites, selenates)). Consequently, the relation extends to other elements, which themselves are related to the mentioned elements (e.g., iodine ($AgI_{(s)}$) sulfur ($Ag_2S_{(s)}$) and many others). Such interdependencies were not worked out in detail in the present work but are mentioned where appropriate.

Since the former study on the same subject (Berner 2002b), thermodynamic data of improved quality were made available for selenium (Olin et al. 2005) and were taken up in the updated data base 12/07 (Thoenen 2012a). Data on polymeric species of the type Se_x^{2-} (x = 1, 2, 3, 4) are of particular interest in high pH environments. The former study revealed $Se_{(cr)}$ as the limiting solid phase. The improved thermodynamic data show that the polymeric species Se_x^{2-} become essential at pH 12.5 /Eh -498 [mV] when total dissolved Se increases above the range 2×10^{-6} to 2×10^{-5} [mol/kg H_2O]. According to Olin et al. (2005) the polymeric species were investigated by several independent authors at KOH concentrations ranging from 0.5 to 2 M and were produced by adding elemental Se to solutions of varying HSe^-/Se^{2-} concentrations. In conclusion, the polymeric species seem to be prominent at high pH, but the impact of extrapolating to lower hydroxide concentrations was not further evaluated. It may well be that their impact at lower pH is less than anticipated from present calculations. There are indications based on the chemical analogy to the sulfur system that potentially important solution species (i.e., $Se_{x(aq)}$ in analogy to $S_{x(aq)}$) are missing. Boulegue (1978) reported the solubility of elemental sulfur to be $(1.9 \pm 0.6) \times 10^{-8}$ [mol/kg H_2O] of $S_{8(aq)}$ in water at 298 K (this result was later on confirmed by Kamyshny 2009). Based on the chemical similarities between Se an S one would expect a similar concentration range of dissolved $Se_{x(aq)}$-species in the presence of $Se_{(cr)}$, but such issues are not discussed in Olin et al. (2005) and are therefore not (yet) included in the database (Thoenen 2012a). As a consequence, the present work does not regard $Se_{(cr)}$ as being a limiting solid under present chemical conditions.

The presently available selection of thermodynamic data lists potential limiting selenide/ diselenide solids for Ag, Co (Thoenen 2012b) and Mn (Thoenen 2012a). Data on Co were taken over as a whole set from Colàs et al. (2007). More than thirty other solid Se(-II)/Se(-I)-phases including selected and most likely reliable values of $\Delta_f G^0_m / \Delta_f H^0_m$ are provided Olin et al. (2005). However, thermodynamic data on solid phases alone are not sufficient to appraise their solubility in aqueous environments. At least an observation/measurement in solution is an indispensable requirement to assess potential complex formation processes and consequently solubility. Olin et al. (2005) report only three studies (on Mn, Ag, Hg; Mehra & Gubeli 1970a, Mehra & Gubeli 1970b, Mehra & Gubeli 1970c) dealing with selenide complexes in solution, all of them tracing back to one single Ph. D. Thesis (Mehra 1968). For $Ag_2Se_{(s)}$ and $HgSe_{(s)}$ solubilities around 3×10^{-8} [mol/kg H_2O] are reported, for $MnSe_{(s)}$ Olin et al. report an intrinsic solubility of 4×10^{-7} [mol/kg H_2O] in the pH range from 6 to 13.6.

The present work uses the thermodynamic data of $CoSe_{2(cr)}$ as taken from (Colàs et al. 2007) as a placeholder for a potential limiting solid of the form $(M(I)/M(II))_x(Se(-I)/Se(-II))_y$. This decision is based on the idea to use "consistent" thermodynamic data, at least throughout the present work (note that the solubility of Co was also evaluated using the data from Colàs et al. 2007).

The formation constant of $CoSe_{2(cr)}$ is associated with an uncertainty of ± 2.6 $\log_{10}$-units. $CoSe_{2(cr)}$, taken as an individual phase produces a calculated solubility of 7.2×10^{-11} [mol/kg H_2O]. This concentration was taken for the lower guideline value. Note that the thermodynamic

data of Colàs et al. (2007) do not include Co-selenide complexes. If the more soluble border of the given uncertainty range is considered ($CoSe_{2(cr)}$ 2.6 log_{10}-units less stable), dissolved selenium concentrations increase to 2.1×10^{-6} [mol/kg H_2O] and lead to a situation where Co becomes limited by $Co_2SiO_{4(cr)}$. In this case we are faced with silicate as a third player entering the "game", which adds an addional dimension to this highly complex system. The phase combination "$CoSe_{2(cr)}$ 2.6 log_{10}-units less stable/$Co_2SiO_{4(cr)}$" serves as the recommended solubility of Se. However, as in the case of $Co_2SiO_{4(cr)}$ the potential precipitation of $CoSe_{2(cr)}$ from solution needs to be verified. In this selected "recommended" system dissolved Co has a concentration of 3.8×10^{-11} [mol/kg H_2O]. Note that the recommended concentration of Co earlier in this report was based on the solubility of $Co(OH)_{2(s,rose)}$ (5.4×10^{-7} [mol/kg H_2O]), which in turn would justify dissolved Se concentrations below 2.1×10^{-6} [mol/kg H_2O].

If Se solubility is calculated using $MnSe_{(s)}$, independently of any other phase, it would limit dissolved Se (in the form of "$MnSe_{(aq)}$") at 1.9×10^{-6} [mol/kg H_2O]. Note that Olin et al. (2005) do not provide a formation constant for the complex $MnSe_{(aq)}$. On the other hand, pyrochroite ($Mn(OH)_{2(s)}$) limits dissolved Mn at only 1.5×10^{-8} [mol/kg H_2O] (at pH 12.5). Such limitation of dissolved Mn would in turn lead to higher dissolved Se concentrations, provided that a well-defined solute equilibrium $Mn^{2+} + Se^{2-} \Leftrightarrow MnSe_{(aq)}$ is operative.

The fact that Se(-II)/Se(-I) is shared by many relevant cations including a considerable variety of potential limiting phases constitutes a presently unmanageable system of interdependencies. Investigating this complex system would require to have a closer look at the involved inventories.

There seems to be little doubt that $(M(I)/M(II))_x(Se(-I)/Se(-II))_y$ type solids will exhibit low concentrations in the range from 10^{-8} to 10^{-6} [mol/kg H_2O] under high pH/reducing conditions. Evidence is based on general chemical knowledge, on analogy with the sulfur system which consists of low solubility M(II)-sulfides and phases like pyrite ($FeS_{2(s)}$), and on three indications from solubility studies.

In order to acknowledge this weak evidence, the upper guideline value was selected to be high. This should also reflect the difficulty to establish the true nature of the limiting solid.

Se-speciation at specified solubility:

Limiting phase	Calculated solubility [mol/kg H_2O]	Distribution of solute components
$CoSe_2(cr)$ / $Co_2SiO_4(s)$	2.1×10^{-6}	HSe^- (94.5 %) Se_2^{2-} (1.5 %) Se_3^{2-} (0.6 %) Se^{2-} (0.8 %)

Se-speciation at upper limit:

Limiting phase	Assumed solubility	Distribution of solute components
	Not limited	Se_4^{2-} (50 %) Se_3^{2-} (50 %)

Strontium

Sr is an element that is controlled by the basic solution composition. Strontianite ($SrCO_{3(cr)}$) is the limiting solid. Upper- and lower guideline values are not given since uncertainties are not available for the stability of the solid. The recommended value corresponds to the concentration reported in Tab. 1.

Sr-speciation at specified solubility:

Limiting phase	Concentration [mol/kg H_2O]	Distribution of solute components
$SrCO_3$(cr) strontianite	2.4×10^{-3}	Sr^{2+} (92.1 %) $Sr(OH)^+$ (7.8 %) $SrSO_{4(aq)}$ (0.1 %)

Zirconium

From the database no other solid phases than ZrO_2 (cr & amorphous) are available. The uncertainty of the solubility product of the crystalline phase (baddeleyite) is ±1.7 log_{10}-units, that of the amorphous phase is only ± 0.1 log_{10}-units, which is not consistent with the much larger uncertainty associated with baddeleyite. A essential uncertainty originates from the existence of the polymeric hydroxide complex $Zr_4(OH)_{16(aq)}$, which has been selected by the NEA reviewers (Brown et al. 2005) based on solubility and hydrolysis data from a series of research studies. Unfortunately these determinations have been performed at low pH values. Scoping calculations revealed that the polymeric species may become dominant when the 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 $Zr_4(OH)_{16(aq)}$. Hence, specifying a recommended value based on "calculated" values, including uncertainty bands, is very speculative. 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. Based on recent experimental studies at elevated pH the NEA review (Brown et al. 2005) selected a new class of solute complexes ($Ca_x(Zr(OH)_6^{(2x-2)+})$) which become dominant at high pH and common Ca concentrations. Note that the former report on the same subject (Berner 2002b) did not yet have access to this new solution species and relied on $Zr(OH)_5^-$ as the only and thus dominating solute.

The solubility of ZrO_2 evaluated in the former study (Berner 2002b) had been criticised with the argument that an experimental confirmation of the solubility of ZrO_2 was missing (Wanner 2004). Fortunately, there exists a new study covering the solubility of "$Zr(OH)_{4(s)}$" (an amorphous solid) in perchlorate solution over the whole pH range (Ekberg et al. 2004), presented on Page 427 of Brown et al. (2005). These measurements agree well with the presently used hydrolysis model and help disabling the mentioned criticism.

The recommended value is based on the calculated solubility of $ZrO_{2(cr)}$, the lower guideline value simultaneously reflects the uncertainty of the formation constants of $ZrO_{2(cr)}$ and of the solute complex $Ca_2Zr(OH)_6^{2+}$ at the "low end" border. The upper guideline value is based on the solubility of amorphous $ZrO_{2(am)}$. Note that solubility of the non-specified "$Zr(OH)_{4(s)}$" measured by Ekberg et al. (2004) is ~5×10^{-8} [mol/kg H_2O] over the pH range from 3 to 13.

Zr-speciation at specified solubility:

Limiting phase	Solubility [mol/kg H$_2$O]	Distribution of solute components
ZrO$_2$(cr) baddeleyite	4.5×10^{-9}	Ca$_2$Zr(OH)$_6^{2+}$ (49.1 %) CaZr(OH)$_{6(aq)}$ (34.8 %) Zr(OH)$_{4(aq)}$ (14.2 %) Ca$_3$Zr(OH)$_6^{4+}$ (1.3 %) Zr(OH)$_6^{2-}$ (0.7 %)

Zr-speciation at upper guideline value:

Limiting phase	Solubility [mol/kg H$_2$O]	Distribution of solute components
Zr(OH)$_4$(s, fresh)	1.3×10^{-4}	Zr$_4$(OH)$_{16(aq)}$ (20.1 %)* Ca$_2$Zr(OH)$_6^{2+}$ (9.6 %) CaZr(OH)$_{6(aq)}$ (6.8 %) Zr(OH)$_{4(aq)}$ (2.8 %) Ca$_3$Zr(OH)$_6^{4+}$ (0.2 %) Zr(OH)$_6^{2-}$ (0.1 %)

*   Note that the tetrameric complex includes 80.4 % of dissolved Zr.

Impact of Isosaccharinic acid on solubility of Zirconium

Data on Zr complexation with ISA are not available. Assuming that a hypothetical complex Zr(OH)$_4$ISA$^-$ has a similar formation constant as has the thorium complex (Th(OH)$_4$ISA$^-$) leads to a value of 4.9×10^{-7} [mol/kg H$_2$O] of dissolved Zr. ([Zr(OH)$_{4(aq)}$] = 6.96×10^{-10} [mol/kg H$_2$O] times $10^{5.4}$ times [ISA$^-$]= 2.78×10^{-3} [mol/kg H$_2$O]).

Niobium

The data base on Nb is meagre, including only data on NbO$_{2(s)}$, Nb$_2$O$_{5(s)}$, and three solute species. In an experimental study, Lothenbach et al. (1999) identified Nb solubilities around 10^{-8} [mol/kg H$_2$O], but under near neutral pH conditions. The nature of the limiting solid is unclear. However, at elevated pH the anionic complex Nb(OH)$_6^-$ is stabilised and produces high concentrations of dissolved Nb.

Nb-speciation at specified solubility:

Potential limiting phases at low pH	Estimated solubility [mol/kg H$_2$O]	Distribution of solute components
(NbO$_2$(s), Nb$_2$O$_5$(cr))	high	Nb(OH)$_6^-$ (100 %)

Talerico et al. (2004) investigated the solubility of Nb(V) under cementitious conditions and generally found Nb(V)-concentrations in the range 2×10^{-5} to 2×10^{-9} [mol/kg H$_2$O] in the pH range 9.5 to 13.2. The authors ascribed decreasing Nb concentrations with increasing Ca concentrations to a poorly crystalline Ca-Nb-oxide phase (CaNb$_4$O$_{11}$.8H$_2$O) and developed an empirical relation for Nb-solubility as a function of [Ca] and pH:

$$[Nb]_{predicted} = 1.4643 \times e^{-1.3402 \times pH} \times [Ca]^{-0.8922}/474.9.$$

At pH = 12.54, [Ca] = 18.06×10^{-3} [mol/kg H$_2$O] this relation would lead to [Nb] $\sim 6 \times 10^{-9}$ [mol/kg H$_2$O]. Hence, the selected recommendation based on a very small database is potentially too pessimistic.

Molybdenum

The data situation on molybdenum has only slightly changed since the last study on this subject (Berner 2002b). 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 ± 0.3 log$_{10}$-units (powellite) and ± 0.5 log$_{10}$-units (solute complex), respectively. The calculated solubility was 7.2×10^{-6} [mol/kg H$_2$O], which serves as the recommended value. Upper- and lower guideline values were based on simultaneously considering the uncertainties of powellite and the solute complex CaMoO$_{4(aq)}$. Further available solids (Mo(s), Mo(IV)O$_{2(s)}$ (tugarinovite), Mo(VI)O$_{3(s)}$, BeMoO$_{4(s)}$, Ag$_2$MoO$_{4(s)}$), taken over from Hummel et al. (2002) and Thoenen (2012a) have solubility constants of not well known quality.

Mo-speciation at specified solubility:

Limiting phase	Calculated solubility [mol/kg H$_2$O]	Distribution of solute components
CaMoO$_4$(s) powellite	7.2×10^{-6}	Mo(VI)O$_4^{2-}$ (82.9 %) CaMoO$_{4(aq)}$ (17.1 %)

Mo-speciation at upper guideline value (i.e. considering the given uncertainties for the solid and the solute complex CaMoO$_{4(aq)}$):

Limiting phase	Calculated solubility [mol/kg H$_2$O]	Distribution of solute components
CaMoO$_4$(s) powellite	2.0×10^{-5}	Mo(VI)O$_4^{2-}$ (60.5 %) CaMoO$_{4(aq)}$ (39.5 %)

Technetium

TcO$_2$.1.6H$_2$O$_{(s)}$ is the only solid phase available from the database and TcO(OH)$_3^-$ is the dominant complex in solution at pH 12.5. Available uncertainties are ± 0.5 log$_{10}$-units for the formation constant of the solid and ± 0.4 log$_{10}$-units for the formation constant of the dominant complex. Carbonate complexes are not significant under given chemical conditions.

Tc(VII) (i.e. TcO_4^-) is not stable at -498 mV, but emanating from $TcO(OH)_{2(aq)}$, the formation of TcO_4^- strongly depends on Eh and pH. Under given pH-conditions the very soluble pertechnetate TcO_4^- would become stable and dominant at ~ -370 mV. Above this threshold Eh value the solubility of $TcO_2.1.6H_2O_{(s)}$ will increase with about one order of magnitude per 20 mV. Vice versa, keeping Eh constant at -498 mV would require a pH of about 14.6 to stabilise pertechnetate. No data were selected by Rard et al. (1999) for potential Tc(V) and Tc(VI) complexes because these redox states quickly disproportionate to Tc(IV) and Tc(VII) (a similar situation is observed in the chemically similar Mn system where the penta- and hexa-valent oxide complexes are known to form in concentrated hydroxide solutions only).

The solid phase $TcO_2.1.6H_2O_{(s)}$ leads to a calculated solubility of 2.3×10^{-7} [mol/kg H_2O] of technetium. Applying the available uncertainties as given above leads to a lower guideline value of 2.9×10^{-8} [mol/kg H_2O] and to an upper guideline value of 1.8×10^{-6} [mol/kg H_2O]. Bearing a pronounced sensitivity to Eh/pH conditions in mind, it is proposed to take the upper guideline value for the recommended value.

Tc-speciation at specified solubility:

Limiting phase	Calculated solubility [mol/kg H_2O]	Distribution of solute components
$TcO_2.1.6H_2O$	1.8×10^{-6}	$TcO(OH)_3^-$ (99.3 %) $TcO(OH)_{2(aq)}$ (0.7 %)

Note that the speciation at 2.3×10^{-7} [mol/kg H_2O] of dissolved Tc is very similar.

Palladium

At -498 mV elemental Pd is identified as the limiting solid. It produces an absolutely insignificant concentration of $< 10^{-25}$ [mol/kg H_2O] of dissolved Pd (note that the formation constant of $Pd_{(s)}$ has an uncertainty of ~ ± 0.8 log_{10}-units).

Hummel (2013) recently reported on the possibility that noble metals like Pd, Ag, Pt, Au (and Hg) show tendencies to dissolve in the zero-valent state. Hummel claims that "*The calculated "solubility abyss" for heavy metals under reducing conditions (i.e. $< 10^{-25}$ [mol/kg H_2O]) does not exist*". Most likely, expectations of 10^{-9} to 10^{-7} [mol/kg H_2O] for dissolved zero-valent metals are much more reliable. Clear indications for such behaviour are available for sulfur (Boulegue 1978, Kamischny 2009) and for selenium (Tits, pers. comm.). Future work on this topic will have to show the validity of such speculations.

A fair amount of solubility data for $Pd(OH)_{2(s)}$ were published by Van Middlesworth & Wood (1999) and Wood (1991) (see Figure 2 in Berner 2014) and allowed for establishing a solubility constant for this hydroxide (Hummel et al. 2000). Uncertainties were estimated to be ± 0.5 log_{10}-units for the formation constant of the solid phase and ± 1 log_{10}-units for the dominant complex $Pd(OH)_3^-$. These experimental data form the basis for the recommended value and, considering the estimated uncertainty bandwidths, for the upper guideline value. The lower guideline value reflects the insolubility of $Pd_{(cr)}$.

Pd-speciation at specified solubility:

Limiting phase	Calculated solubility [mol/kg H_2O]	Distribution of solute components
$Pd(OH)_2(s)$	8.5×10^{-7}	$Pd(OH)_3^-$ (93.3 %) $Pd(OH)_{2(aq)}$ (6.7 %)

The speciation of Pd at the upper guideline value is similar.

Silver

Potential limiting solids are $Ag_{(cr)}$ $Ag_2S_{(s)}$ (acanthite), $Ag_2Se_{(\alpha)}$, $AgCl$, AgI, $Ag(OH)_{(s)}$, the sequence approximately reflecting the (increasing) calculated solubility. The speciation in solution is determined by the chloride and hydroxide complexes (including very minor contributions from sulfides). Elemental silver $Ag_{(cr)}$ produces an absolutely insignificant calculated solubility $< 10^{-20}$ [mol/kg H_2O] (see also comments on the solubility of elemental $Pd_{(s)}$ in the paragraph above). The formation constant of $Ag_2S_{(s)}$ (acanthite), taken from Colàs et al. (2007), leads to 2.9×10^{-14} [mol/kg H_2O] of dissolved Ag, which is taken for the lower guideline value. $AgCl_{(s)}$ fixes total dissolved silver at 1.8×10^{-6} [mol/kg H_2O] under the condition that total dissolved chloride has a concentration of 3.75×10^{-2} [mol/kg H_2O]. $AgCl_{(s)}$ is probably among the best investigated solid phases of silver. Its solubility for is taken for the recommended value. Finally, the solubility of $AgOH_{(s)}$ (1.7×10^{-4} [mol/kg H_2O]) serves as the upper guideline value.

Note that for other types of host rocks (and consequently also for the cementitious environment) the concentration of chloride could be as high as 0.66 [mol/kg H_2O] (Mäder 2009). In this case the solubility of $AgCl_{(s)}$ would lead to 1.4×10^{-4} [mol/kg H_2O] of dissolved silver (with strong dominance of complex $AgCl_4^{3-}$ in solution).

For both, $Ag_2Se_{(\alpha)}$ and $AgI_{(s)}$ a specific discussion seems necessary since the two solids include elements for which the present work also provides solubility limits. Olin et al. (2005) provide a selected formation constant for $Ag_2Se_{(\alpha)}$, leading to extremely low Ag solubilities when used without considering corresponding solute complexes. Unfortunately, Olin et al. (2005) do not select a formation constant for $Ag_2Se_{(aq)}$ because the nature of solute complexes is unclear and the presence of colloidal $Ag_2Se_{(s)}$-particles cannot be excluded. Hence, we are faced with the fact that the solid-solute couple $Ag_2Se_{(\alpha)}/Ag_2Se_{(aq)}$ produces silver concentrations around 4.4×10^{-8} [mol/kg H_2O] and Se-concentrations around 2.2×10^{-8} [mol/kg H_2O] (in 1 M $NaClO_4$). Since the recommended value for the Se-solubility is 3×10^{-6} [mol/kg H_2O], we could expect dissolved Ag of $\sim 4 \times 10^{-9}$ [mol/kg H_2O] under the assumption of full thermodynamic equilibrium (see also comment on $MnSe_{(aq)}$ under the heading "selenium").

$AgI(s)$ may co-exist with $AgCl(s)$. In this case, the ratio of the formation constants ($10^{+6.29}$) essentially determines the ratio of Cl^-/I^- activities in solution. In the present solution composition dissolved iodine would accordingly be at a concentration of 1.8×10^{-8} [mol/kg H_2O] (see also comments under the heading "iodine").

Ag-speciation at specified solubility:

Limiting phase	Calculated solubility [mol/kg H_2O]	Distribution of solute components
AgCl(s)	1.8×10^{-6}	$AgCl_2^-$ (69.4 %) $AgCl_{(aq)}$ (18.5 %) $Ag(OH)_2^-$ (5.2 %) $AgCl_3^{2-}$ (4.5 %) $Ag(OH)_{(aq)}$ (1.2 %) $AgCl_4^{3-}$ (0.7 %) Ag^+ (0.4 %) AgS^- (0.1 %)

Ag-speciation at upper guideline value:

Limiting phase	Calculated solubility [mol/kg H_2O]	Distribution of solute components
Ag(OH)(s)	1.7×10^{-4}	$AgCl_2^-$ (69.3 %) $AgCl_{(aq)}$ (18.6 %) $Ag(OH)_2^-$ (5.3 %) $AgCl_3^{2-}$ (4.4 %) $Ag(OH)_{(aq)}$ (1.2 %) $AgCl_4^{3-}$ (0.7 %) Ag^+ (0.4 %) AgS^- (0.1 %)

Tin

Limiting solid is $CaSn(OH)_{6(s)}$, reported by Lothenbach et al. (2000). The uncertainty of the reported formation constant is ±0.3 $\log_{10}$-units. Dominant complex at pH 12.5 is $Sn(OH)_6^{2-}$. Amaya et al. (1997) reported on the solubility of poorly crystalline $SnO_{2(s)}$ under near neutral pH conditions ($\sim 2 \times 10^{-7}$ [mol/kg H_2O]). In the absence of Ca^{2+} in solution its solubility increases to near molal solutions at high pH. A similar behaviour is found for crystalline $SnO_{2(cr)}$ (cassiterite), which has a solubility of $\sim 1 \times 10^{-8}$ [mol/kg H_2O] under near neutral conditions. The speciation in solution is dominated by Sn(IV)-species. Species of Sn(II) are not found to be relevant using present data.

The recommended value of 1.0×10^{-7} [mol/kg H_2O] is based on the calculated solubility of the stannate solid $CaSn(OH)_{6(precip.)}$ reported by Lothenbach et al. (2000). Lower and upper guideline values reflect the uncertainty of its formation constant. Note that the limited solubility of tin at elevated pH solely depends on the presence of calcium. Solute complexes with Ca (as expected to form at high pH, in analogy to Zr, Sm, Mo, Th, Pu, Am) are not (yet) known and are also not addressed in the recent OECD NEA thermodynamic series on tin by Gamsjäger et al. (2012). Such complexes could potentially increase dissolved tin. At -0.5 V one would expect the formation of Sn(II) species considering a recent report from Gajda et al. (2009) who found the redox potential of the Sn^{4+}/Sn^{2+} couple to be at $\sim$+0.4 V. This redox potential in principle should favour Sn(II) under reducing conditions. However, the complex formation of Sn(IV) with OH^- (and Cl^-) is extremely strong at high pH and favours Sn(IV) even under reducing conditions.

Sn-speciation at specified solubility:

Limiting phase	Calculated solubility [mol/kg H$_2$O]	Distribution of solute components
CaSn(OH)$_{6(precip.)}$	1.0×10^{-7}	Sn(OH)$_6^{2-}$ (99.7 %) Sn(OH)$_5^-$ (0.3 %)

The speciation of Sn does not change at the upper guideline value of 2.0×10^{-7} [mol/kg H$_2$O].

Note: The NEA review of thermodynamic tin data (Gamsjäger et al. 2012) has been issued after the "freezing" of thermodynamic data for the present work. Hence, the data are not included in the present thermodynamic database (Thoenen 2012a), (Thoenen 2012b). However, a superficial comparison reveals that the relevant values provided in Gamsjäger et al. (2012) do not very significantly deviate from those given in the former Nagra/PSI Thermodynamic Database 01/01 (Hummel et al. 2000). There is, however, a notable exception to this. Gamsjäger et al. (2012) mention the work of Lothenbach et al. (2000) on the solubility of Ca-stannate (CaSn(OH)$_{6(s)}$) with a few lines, but neither criticise the given solubility constant nor use it anywhere in their review. The present work relies on the report of Lothenbach et al.

Impact of isosaccharinic acid: Thermodynamic data are absent. A potential analogy with the tetravalent Th, i.e. the formation of a hypothetical complex Sn(OH)$_4$ISA$^-$ exhibiting the same formation constant as the Th-complex would lead to insignificant concentrations and would not increase tin solubility.

Iodine

Preliminary comments: Iodine data present in the current database had been taken over from a former database without additional re-evaluation, but it was recognised that errors had occurred in transforming from the former to the current database. 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 1.8×10^{-7} [mol/kg H$_2$O]. I$^-$ is the dominant complex in solution. This calculated solubility is used for the recommended value and for the upper guideline value. Uncertainties are not available for the solubility constant.

Since the recommended value for silver is based on the solubility of AgCl$_{(s)}$ we investigated a situation where both solids, AgCl$_{(s)}$ and AgI$_{(s)}$ are saturated. Under such conditions total dissolved iodine is calculated to be 1.8×10^{-8} [mol/kg H$_2$O] and it is suggested to use this concentration for the lower guideline value.

I-speciation at recommended solubility (and upper guideline value):

Limiting phase	Calculated solubility [mol/kg H_2O]	Distribution of solute components
AgI(s)	1.8×10^{-7}	I^- (99.8 %) $AgI_{(aq)}$ (0.2 %) AgI_2^- (0.01 %)

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 at elevated pH 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 measured in alike chemical systems may serve to justify reduced Cs concentrations in solution. This work qualifies Cs as not solubility limited in terms of distinct solid phases. Restricted inventories may potentially limit concentrations in solution.

Cs-speciation: Cs^+ (100.0 %)

Samarium

Preliminary notes concerning lanthanide hydrolysis: From a chemical point of view one would expect more or less similar hydrolysis constants among the fourteen lanthanide elements. This is, however, not fully reflected in the data for Sm, Eu and Ho dealt with in this work. Data for Eu were taken from Hummel et al. (2000), data for Sm and Ho from Thoenen (2012b) (on the basis of Colàs et al. (2007)). The two datasets differ primarily in the constants of the third and fourth hydrolysis complex, which are the dominant complexes at high pH. Note that an earlier set of constants on Sm and Ho from Duro et al. (2006) (notably the same group of authors as for Colàs et al. (2007)) are more alike those from Hummel et al. (2002). The obvious ambiguity on hydrolysis species at high pH is currently under scientific debate. It will need substantial effort on thermodynamic database evaluation work to resolve the presently open questions. Hence, the present work accepts a certain inconsistency in the speciation (and consequently in the solubility) among Sm, Eu and Ho.

Thermodynamic data on samarium were taken as provided by Thoenen (2012b) (ThermoChimie v.7.b database, see also Colàs et al. 2007). Potential limiting solids are $Sm(OH)_{3(cr)}$, $Sm(OH)_{3(am)}$ and $SmPO_{4(s)}$. Dominating complex in solution will be $Sm(OH)_{3(aq)}$, carbonate complexes will not be relevant. Available uncertainties for the hydroxide solids and for the dominating complex are ± 1.0 $\log_{10}$-units. $Sm(OH)_{3(cr)}$ produces a calculated solubility of 8.9×10^{-11} [mol/kg H_2O] and $Sm(OH)_{3(am)}$ a solubility of 4.8×10^{-9} [mol/kg H_2O].

The solubility of $Sm(OH)_{3(cr)}$ serves for the lower guideline value. The solubility of $Sm(OH)_{3(am)}$, simultaneously including maximum uncertainties for the solid phase and the dominating complex is calculated to be 4.6×10^{-7} [mol/kg H_2O] which serves for the upper guideline value. This upper guideline value, within a factor of 4 compatible with other Me^{3+} solubilities, is selected for the recommended concentration and accounts for the presently not resolvable inconsistency with Eu-data.

$SmPO_{4(cr)}.H_2O$, taken as an independent single phase, would limit dissolved Sm (and consequently dissolved phosphate) at 1.2×10^{-7} [mol/kg H_2O]. For the formation constant Duro et al. (2006) provide an unrealistic low uncertainty of only ± 0.03 $\log_{10}$-units which is not further commented here. The basic system does not include phosphate. However, considering the low solubilities of phosphate solids indicates that future studies should probably pay more attention to this less well investigated, but potentially important anion.

Sm-speciation at specified solubility:

Limiting phase	Calculated solubility [mol/kg H_2O]	Distribution of solute components
$Sm(OH)_{3(am)}$ maximum uncertainties applied for solid/dominant complex.	4.6×10^{-7}	$Sm(OH)_{3(aq)}$ (98.3 %) $Sm(OH)_4^-$ (1.7 %) $Sm(OH)_2^+$ (0.1 %) $Ca(Sm(OH)_3)^{2+}$ (0.1 %) $Ca_2(Sm(OH)_4)^{3+}$ (0.1 %)

Impact of Isosaccharinic acid on solubility of Samarium

Data for samarium-ISA-complexes are not available. Exclusively based on chemical analogy with Eu it is assumed that Sm forms the same ISA-complexes exhibiting identical formation constants ($Sm(OH)_{3(aq)} + ISA^- <=> Sm(OH)_3ISA^-$, $\log_{10}K = 5.4$). Under these conditions the present work estimates a $Sm(OH)_3ISA^-$ concentration of 2.9×10^{-4} [mol/kg H_2O].

Isosaccharinic acid	Estimated solubility [mol/kg H_2O]	Estimated distribution of solute components for Sm
ISA^-_{tot} 5×10^{-3} [mol/kg H_2O] $Sm(OH)_{3(am)}$	2.9×10^{-4}	$Sm(OH)_3ISA^-$ (~100 %)

Europium

Limiting solid at pH 12.5 is a hydroxide phase (either $Eu(OH)_{3(cr)}$ or $Eu(OH)_{(am)}$). Dominating complexes in solution are $Eu(OH)_4^-$ and $Eu(OH)_{3(aq)}$. The silicate complex $EuHSiO_3^{2+}$, relevant at pH 8 is not stable against the hydroxide complexes. Available uncertainties are ± 0.3, ± 0.8 and ± 0.5, $\log_{10}$-units for $Eu(OH)_{3(cr)}$, $Eu(OH)_{3(am)}$ and $Eu(OH)_4^-$, respectively. The solubility of $Eu(OH)_{3(cr)}$ serves for the lower guideline value (including ± 0.3 $\log_{10}$-units of uncertainty), the solubility of $Eu(OH)_{3(am)}$ for the recommended value. The upper guideline value was calculated considering maximum uncertainties in the formation constants of $Eu(OH)_{3(am)}$ and $Eu(OH)_4^-$. This upper guideline value is about two orders of magnitude above those for Sm and Ho, confirming the preliminary notes made under the heading "Samarium".

Eu-speciation at specified solubility:

Limiting phase	Calculated solubility [mol/kg H_2O]	Distribution of solute components
$Eu(OH)_{3(am)}$	1.9×10^{-6}	$Eu(OH)_4^-$ (58.3 %) $Eu(OH)_{3(aq)}$ (41.7 %) $Eu(OH)_2^+$ (0.01 %)

Eu-speciation at the upper guideline value, considering uncertainties in the formation constants of $Eu(OH)_{3(am)}$ and $Eu(OH)_4^-$:

Limiting phase	Calculated solubility [mol/kg H_2O]	Distribution of solute components
$Eu(OH)_{3(am)}$	2.7×10^{-5}	$Eu(OH)_4^-$ (81.5 %) $Eu(OH)_{3(aq)}$ (18.5 %)

Impact of Isosaccharinic acid on solubility of Europium

Isosaccharinic acid	Calculated solubility [mol/kg H_2O]	Distribution of solute components for Eu	Distribution of solute components for ISA
ISA^-_{tot} 5×10^{-3} [mol/kg H_2O] $Eu(OH)_{3(cr)}$	1.1×10^{-6}	$Eu(OH)_3ISA^-$ (99.7 %) $Eu(OH)_4^-$ (0.2 %) $Eu(OH)_{3(aq)}$ (0.1 %)	ISA^- (55.5 %) $Ca(OH)ISA_{(aq)}$ (30.6 %) $CaISA^+$ (13.9 %)
ISA^-_{tot} 5×10^{-3} [mol/kg H_2O] $Eu(OH)_{3(am)}$	5.0×10^{-4}	$Eu(OH)_3ISA^-$ (99.6 %) $Eu(OH)_4^-$ (0.23 %) $Eu(OH)_{3(aq)}$ (0.16 %)	ISA^- (49.9 %) $Ca(OH)ISA_{(aq)}$ (27.6 %) $CaISA^+$ (12.6 %) $Eu(OH)_3ISA^-$ (10.0 %)
$Ca(ISA)_2$ saturated ISA^-_{tot} 2.24×10^{-2} [mol/kg H_2O] $Eu(OH)_{3(am)}$	2.2×10^{-3}	$Eu(OH)_3ISA^-$ (99.9 %) $Eu(OH)_4^-$ (0.05 %) $Eu(OH)_{3(aq)}$ (0.04 %)	ISA^- (48.4 %) $Ca(OH)ISA_{(aq)}$ (28.2 %) $CaISA^+$ (13.7 %) $Eu(OH)_3ISA^-$ (9.7 %)

The isosaccharinic acid system is significantly influenced by europium at $[Eu]_{tot} > 5 \times 10^{-5}$ [mol/kg H_2O] (and additionally by other tri-valent elements).

Holmium

Consistent with its position in the periodic table of the elements a solubility behaviour dominated by either $Ho(OH)_{3(cr)}$ or $Ho(OH)_{3(am)}$, similar to that of Eu and Sm is expected. Thermodynamic data were taken from Thoenen (2012b). Uncertainties are not provided for the formation constants of the hydroxide solids and complexes, but may be estimated from data provided in Duro et al. (2006).

From the uncertainty of the formation constant of the dominant solute $Ho(OH)_{3(aq)}$ (± 0.1 $\log_{10}$-units) provided in Duro et al. (2006) the missing uncertainties for the reactions $Ho(OH)_{3(s,am)} \Leftrightarrow Ho(OH)_{3(aq)}$ could in principle be estimated to be of the same size, but this is not consistent with the uncertainties for the Sm-system provided in the same tables (Table 12-3, 12-4) in Duro et al. (2006), giving ± 1.0 $\log_{10}$-units. Solid $Ho(OH)_{3(s)}$ would produce 1.8×10^{-11} [mol/kg H_2O] of dissolved Ho. This concentration is taken to represent the lower guideline value. The solubility of $Ho(OH)_{3(am)}$, including the much higher uncertainties for the homologue Sm (± 1.0 $\log_{10}$-units for $Sm(OH)_{3(s)}$ and for $Sm(OH)_{3(aq)}$) are taken to represent the upper guideline value. Note that holmium speciation disagrees with that of Eu as outlined under the section "Samarium". Crystalline $HoPO_{4(cr)}$ would produce 4.7×10^{-7} [mol/kg H_2O] of dissolved Ho and PO_4^{3-}, but a control by $HoPO_{4(cr)}$ is not to be expected.

Ho-speciation at specified solubility:

Limiting phase	Calculated solubility [mol/kg H$_2$O]	Distribution of solute components
Ho(OH)$_{3(am)}$ maximum uncertainties included (see text)	1.9×10^{-7}	Ho(OH)$_{3(aq)}$ (98.5 %) Ho(OH)$_4^-$ (1.4 %) Ho(OH)$_2^+$ (0.1 %)

Impact of Isosaccharinic acid on solubility of Holmium

Data for holmium-ISA-complexes are not available. Exclusively based on chemical analogy with Eu it is assumed that Ho forms the same ISA-complexes exhibiting identical formation constants (Ho(OH)$_{3(aq)}$ + ISA$^-$ <=> Ho(OH)$_3$ISA$^-$, log$_{10}$K = 5.4). Under these conditions the present work estimates a Ho(OH)$_3$ISA$^-$ concentration of 1.2×10^{-4} [mol/kg H$_2$O].

Isosaccharinic acid	Estimated solubility [mol/kg H$_2$O]	Estimated distribution of solute components for Ho
ISA$^-_{tot}$ 5×10^{-3} [mol/kg H$_2$O] Ho(OH)$_{3(am)}$	1.2×10^{-4}	Ho(OH)$_3$ISA$^-$ (~100 %)

Lead

Powell et al. (2009) published a new and careful evaluation on lead using the SIT approach. The evaluated complex and solid formation constants have uncertainties below ±0.1 log$_{10}$-units. This dataset, complemented with solubilities from Lothenbach et al. (1999) (hydro-cerrusite (Pb$_3$(CO$_3$)$_2$(OH)$_{2(cr)}$), Pb(OH)$_{2(pr)}$, PbS$_{(s)}$, no uncertainties provided) was used for calculating solubilities and speciation. Under given chemical conditions Pb(OH)$_3^-$ is the dominant complex in solution.

Limiting solids at elevated pH are PbO$_{(red)}$ and Pb(OH)$_{2(pr)}$, exhibiting solubilities between 10^{-3} and 10^{-2} [mol/kg H$_2$O]. PbO$_{(red)}$ (1.7×10^{-3} [mol/kg H$_2$O]) serves for the lower guideline value, the solubility of Pb(OH)$_{2(pr)}$ (4.6×10^{-3} [mol/kg H$_2$O]) for the upper guideline value and also for the recommended value. Pb$_3$(PO$_4$)$_{2(s)}$ would produce a lead solubility of 2.5×10^{-3} [mol/kg H$_2$O] (and an unlikely high phosphate concentration of 1.7×10^{-3} [mol/kg H$_2$O]). Including the phosphate as a limiting solid would significantly impact on ionic strength (from 0.100 to 0.111 [mol/kg H$_2$O]) and less significantly on pH (from 12.54 to 12.51). Note that phosphate complexes in solution (PbHPO$_{4(aq)}$) remain insignificant.

Pb-speciation at specified solubility:

Limiting phase	Calculated solubility [mol/kg H$_2$O]	Distribution of solute components
Pb(OH)$_{2(pr)}$	4.6×10^{-3}	Pb(OH)$_3^-$ (97.2 %) Pb(OH)$_{2(aq)}$ (2.8 %)

Polonium

Data on Polonium are rare, solubility data are absent and very few 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 (Hummel 2013, based on Treiman & Treiman 1953). It is supposed that probably Th(IV) could act as surrogate to make an estimate on the behaviour of polonium. Consequently, the present work used the rather conservative upper guideline value of Th (6.4×10^{-8} [mol/kg H_2O], solubility of $ThO_{2(am,hyd,fresh)}$, including an uncertainty of 0.9 $\log_{10}$-units) as a recommendation and as an upper guideline value. Consistently, the lower guideline value is also taken from Th. Even more speculative is to address the impact of ISA. However, taking the analogy with Th and applying the same enhancement factor (731) one could obtain an estimate of 4.7×10^{-5} [mol/kg H_2O] of dissolved Po ($Po(OH)_4ISA^- + PoCa(OH)_4(ISA)_{2(aq)}$). This very speculative estimate is not placed into Tab. 3.

Note that former reports on sorption issues (Bradbury & Baeyens 2003) used Se(IV) as an analogue for Po. In the meantime, the report (Treiman & Treiman 1953) has been declassified. This report suggests a behaviour of Po similar to tetravalent cations like Th(IV) rather than to Se(IV), which prefers forming the anionic oxide $Se(IV)O_3^{2-}$.

Radium

The database includes $RaSO_{4(s)}$ and $RaCO_{3(s)}$ as potential limiting solids. The solubility of $RaSO_{4(s)}$, considering an uncertainty of $\pm$ 0.2 $\log_{10}$-units in the solubility constant serves as an upper guideline value (1.7×10^{-5} [mol/kg H_2O]). Dominant complexes/species in solution are Ra^{2+} (94 %) and $RaOH^+$ (5 %). $RaSO_{4(aq)}$ (0.2 %) is of minor importance.

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. Note that a corresponding solid solution formation was historically used to isolate radium. Kulik et al. (2004) have modelled the partitioning of Ra using the solid solution functionality of the GEMS-code applied to (Ra,Ba)SO_4 solid solutions. In geothermal energy production the neo-formation of barite in the equipment concentrates dissolved Ra and leads to scale formation (crusts of precipitated minerals in tubes). Handling operations of such scales require radiological control. Grandia et al. (2008) summarised the potential impact of (Ra,Ba)SO_4 solid solution formation on the solubility of Ra in the near field of radioactive waste repository. Curti et al. (2010) have experimentally shown that radium forms (non-ideal) solid solutions with barite at fast kinetic rates and in complete thermodynamic equilibrium with the aqueous solutions. Hence, control of Ra by solid solutions formation with $BaSO_4$ in geochemical environments is a fact. As Grandia et al. (2008) pointed out, several parameters control the formation of solid solution precipitation. Among them, the involved masses of precipitated solids are of particular interest and we thus need to establish a concept to define corresponding inventories.

Tab. 1 defines the basic chemical system and one sees that the selected $BaSO_4$-inventory is 2.5×10^{-4} [mol/kg of solution] (most of it located in solid $BaSO_{4(s)}$). This corresponds to an operational minimum inventory, ensuring the presence of solid $BaSO_4$ in the system. From traces included in unhydrated cement ($\sim 6 \times 10^{-4}$ [mol Ba/kg of unhydrated cement]) and from waste-born Ba a $BaSO_4$-inventory well above 10^{-3} [mol/kg of solution] is estimated.

Due to decay and ingrowth processes the $RaSO_4$-inventory is time dependent. An estimate for high level wastes (spent fuel canister) results in a maximum $RaSO_4$-inventory of $\sim 4 \times 10^{-5}$ [mol/kg of solution] after 200'000 years (Berner 2014). The calculated solubility of pure

$RaSO_{4(s)}$ (not considering uncertainties) is 1.4×10^{-5} [mol/kg H_2O]. For the subsequent evaluation we therefore assume that the relevant $RaSO_4$-inventory is 1.4×10^{-5} [mol/kg of solution], very close to the maximum inventory after 200'000 years.

Why are inventories so important when dealing with solid solutions? If a (ideal) solid solution forms with equivalent (0.5 : 0.5) mol fractions of Ba & Ra both elements approximately show the solubility of their phase pure end members (i.e. $RaSO_{4(s)}$, $BaSO_{4(s)}$), multiplied by their mol fraction of 0.5. If the solid solution forms with strongly dissimilar mol fractions (for example $(Ra_{0.001},Ba_{0.999})SO_{4(ss)}$), the Ba concentration approximately corresponds to the solubility of $BaSO_{4(s)}$ times 0.999, but the Ra concentration now approximately corresponds to the solubility of $RaSO_{4(s)}$ times 0.001. This common (here: simplified) rule immediately connects the impact of solid solution formation to available and actually involved inventories.

Impact of (Ra,Ba)SO₄ solid solution formation: Considering the formation of an ideal $(Ra,Ba)SO_4(ss)$ based on the $BaSO_4$-inventory of 2.5×10^{-4} [mol/kg of solution] and the $RaSO_4$-inventory of 1.4×10^{-5} [mol/kg of solution] roughly decreases dissolved Ra by a factor of two (6×10^{-6} [mol/kg H_2O]) because half of the available $RaSO_4$ will be trapped by the $(Ra,Ba)SO_4$ solid solution. Increasing the available inventory of $BaSO_4$ inversely decreases the concentration of dissolved Ra, in accordance with the common rules of solid solution formation indicated above. The key question is now the size of the available inventory of $BaSO_4$ in the system or "how much is well above 10^{-3} [mol/kg of solution]"? A very precautious answer to this question could be 2×10^{-3} [mol/kg of solution], leading to a calculated Ra concentration of 9.7×10^{-7} [mol/kg H_2O]. This concentration is selected for the recommended value. To establish a lower guideline value the inventory of $BaSO_4$ was increased by a factor of 5 to 1×10^{-2} [mol/kg of solution], a value still consistent with "well above 10^{-3} [mol/kg of solution]". A Ra concentration of 2.1×10^{-7} [mol/kg H_2O] is calculated for this increased inventory of $BaSO_4$.

Justification: It was tried to select a maximum $RaSO_4$-inventory, a $BaSO_4$-inventory close to the known minimum provided by the concrete matrix, but not considering waste born Ba. Hence, the determining inventory-ratio $BaSO_{4(s)}/RaSO_{4(s)}$ and consequently its impact on the decrease of dissolved Ra is also minimum. Actions in both directions, i.e. increasing the (minimum) $BaSO_4$-inventory and decreasing the (maximum) $RaSO_4$-inventory would lead to lower Ra concentrations.

Ternary solid solution: The formation of a ternary ideal $(Ca,Ra,Ba)SO_4$ solid solution seems less likely because $CaSO_4$ does not form mixed phases with Ba or Ra that include significant portions of the latter elements. Nonetheless, a test calculation using a ternary solid solution was performed and indeed produced a solid solution with an insignificant mol fraction of $CaSO_{4(s)}$.

Note: Formation constants for the pure end members ($RaSO_{4(s)}$, $BaSO_{4(s)}$) and for the formation of corresponding solid solutions are very well established. To evaluate a solubility limit for Ra opens thus a new dimension of essential basic parameters. It is inevitable to evaluate the inventories of $RaSO_4$ and $BaSO_4$ that may contribute to the formation of the solid solution phase.

The present evaluation tried to stay on a conservative side. If the evaluated limit should lead to unacceptable doses in the performance assessment or if more detailed analyses of inventories would produce unfavourable limits, the principle of solid solution formation offers an elegant technical way to circumvent such problems. Critical wastes including/producing unacceptable amounts of radium could be placed in barite concrete providing the necessary amount of $BaSO_4$. Such type of concrete is well investigated and commonly used in nuclear building (x-ray shielding).

Ra-speciation at specified solubility:

Limiting phase	Calculated solubility [MOL/KG H$_2$O]	Distribution of solute components
Ra/BaSO$_{4(ss)}$ inventory per kg of solution Ra(SO$_4$) 1.4×10^{-5} Ba(SO$_4$) 1.0×10^{-2}	9.7×10^{-7}	Ra^{2+} (93.8 %) RaOH$^+$ (4.9 %) RaCl$^+$ (1.0 %) RaSO$_{4(aq)}$ (0.2 %)

Ra-speciation at upper guideline value:

Limiting phase	Calculated solubility [mol/kg H$_2$O]	Distribution of solute components
RaSO$_{4(s)}$	1.7×10^{-5}	Ra^{2+} (93.8 %) RaOH$^+$ (4.9 %) RaCl$^+$ (1.0 %) RaSO$_{4(aq)}$ (0.2 %)

Actinium

Since the last assessment of solubility limits (Berner 2002b) no new data or findings have been elaborated for actinium. Following the same principles as in Berner (2014), 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 1.9×10^{-6}, 5.4×10^{-10}, and 1.1×10^{-9} [mol/kg H$_2$O], respectively.

In order to stay on a safe side, 1.9×10^{-6} [mol/kg H$_2$O] as evaluated for Eu is also recommended for Ac. Upper and lower guidelines values are also taken from Eu. The numerical values in Tab. 3 are put in parentheses to indicate the speculative character of the recommendation.

Impact of ISA: Extending the analogy with Eu to the impact of ISA would produce 5.0×10^{-4} [mol/kg H$_2$O] of Ac(OH)$_3$ISA$^-$.

Thorium

The relevant solid phase determining the solubility will be an amorphous, hydrated ThO$_2$. Two modifications (fresh, aged) are include in the database. The uncertainty in the formation constants is estimated to be $\pm$ 0.9 log$_{10}$-units. Dominant complex in solution is Th(OH)$_{4(aq)}$, exhibiting an uncertainty of $\pm$ 0.7 log$_{10}$-units, but the two uncertainties are not independent. The solubility of the "aged" modification (ThO$_{2(am,hyd,aged)}$) is taken for the recommended value and the same solubility including the uncertainty represents the lower guideline value. The upper guideline value (6.4×10^{-8} [mol/kg H$_2$O]) is based on the solubility of the ThO$_{2(am,hyd,fresh)}$ modification, including 0.9 log$_{10}$-units of uncertainty.

Th-speciation at specified solubility:

Limiting phase	Calculated solubility [mol/kg H₂O]	Distribution of solute components
$ThO_{2(am,hyd,aged)}$	1.3×10^{-9}	$Th(OH)_{4(aq)}$ (99.4 %) $Ca_4Th(OH)_8^{4+}$ (0.6 %) $Th(OH)_4CO_3^{2-}$ (0.01 %)

Th-speciation at upper guideline value (including 0.9 $\log_{10}$-units of uncertainty):

Limiting phase	Calculated solubility [mol/kg H₂O]	Distribution of solute components
$ThO_{2(am,hyd,fresh)}$	6.4×10^{-8}	$Th(OH)_{4(aq)}$ (99.4 %) $Ca_4Th(OH)_8^{4+}$ (0.6 %) $Th(OH)_4CO_3^{2-}$ (0.01 %)

Impact of Isosaccharinic acid on solubility of Thorium

Isosaccharinic acid	Calculated solubility [mol/kg H₂O]	Distribution of solute components for Th	Distribution of solute components for ISA
ISA^-_{tot} 5×10^{-3} [mol/kg H₂O] $ThO_{2(am,hyd,aged)}$	9.5×10^{-7}	$Th(OH)_4ISA^-$ (92.1 %) $ThCa(OH)_4(ISA)_{2(aq)}$ (7.8 %) $Th(OH)_{4(aq)}$ (0.1 %)	ISA^- (55.5 %) $Ca(OH)ISA_{(aq)}$ (30.6 %) $CaISA^+$ (13.9 %)
ISA^-_{tot} 5×10^{-3} [mol/kg H₂O] $ThO_{2(am,hyd,fresh)}$	6.0×10^{-6}	$Th(OH)_4ISA^-$ (92.1 %) $ThCa(OH)_4(ISA)_{2(aq)}$ (7.8 %) $Th(OH)_{4(aq)}$ (0.1 %)	ISA^- (55.5 %) $Ca(OH)ISA_{(aq)}$ (30.6 %) $CaISA^+$ (13.9 %)
$Ca(ISA)_2$ saturated ISA^-_{tot} 2.04×10^{-2} [mol/kg H₂O] $ThO_{2(am,hyd,fresh)}$	3.0×10^{-5}	$Th(OH)_4ISA^-$ (73.4 %) $ThCa(OH)_4(ISA)_{2(aq)}$ (26.6 %) $Th(OH)_{4(aq)}$ (0.03 %)	ISA^- (54.1 %) $Ca(OH)ISA_{(aq)}$ (31.1 %) $CaISA^+$ (14.8 %)

The isosaccharinic acid system is not influenced by thorium.

Protactinium

Thermodynamic data on protactinium are still scarce. Based on its position (between Th and U) in the periodic table of the elements and based on the reducing environment one could potentially expect a tetra-valent redox state, but this is not the case. The present work uses a collection of data given by Duro et al. (2006). Compared to an earlier study (Berner 2002b) this recent data collection also includes sulfate complexes, but they do not become important under given solution conditions. Formation constants for potential carbonate complexes have been estimated in analogy to Np(V) (Berner 2014), but carbonate complexes never become significant under given chemical conditions.

The only relevant solid is $Pa(V)_2O_{5(s)}$, leading to a calculated solubility of 1.8×10^{-6} [mol/kg H_2O] of dissolved Pa, constituting the recommended value. The dominant complex in solution is $PaO_2(OH)_2^-$. Estimates for uncertainties are available for the dominant complex (± 0.2 log_{10}-units (Duro et al. 2006)) but this value seems rather optimistic. The present study adopts a value of ± 0.5 log_{10}-units, in analogy to other dominant actinides complexes. No uncertainty is available for the limiting solid but Duro et al. (2006) proposes ± 1 log_{10}-unit for $Pa(IV)O_{2(s)}$, which is also adopted for $Pa(V)_2O_{5(s)}$. This uncertainty leads to the definition of upper and lower guideline values.

Pa-speciation at specified solubility:

Limiting phase	Calculated solubility [mol/kg H_2O]	Distribution of solute components
$Pa_2O_{5(s)}$	1.8×10^{-6}	$PaO_2(OH)_2^-$ (99.9 %) $PaO_2(OH)_{aq}$ (0.1 %)

At the upper guideline value Pa speciation is identical

Impact of Isosaccharinic acid on solubility of Protactinium

Since no thermodynamic data are available to appraise a potential impact of isosaccharinic acid, the following estimate was carried out: The complex formation constants of $Eu(OH)_3ISA^-$, $Th(OH)_4ISA^-$, $U(OH)_4ISA^-$, $Np(OH)_4ISA^-$ and $Am(OH)_3ISA^-$ are $log_{10}K$ = 5.4, 5.4, 4, 2.8 and 4.8, respectively, when considering equilibria of the form $M(OH)_{x(aq)} + ISA^- \Leftrightarrow M(OH)_xISA^-$ (Tab. 2). The formation constant for the reaction $Pa(OH)_{5(aq)} + OH^- \Leftrightarrow Pa(OH)_5OH^-$ is $log_{10}K$ ~ 4.6. If it is assumed (based on chemical analogy and on the sequence of formation constants above) that $log_{10}K$ ~ 5.4 for the equilibrium $Pa(OH)_{5(aq)} + ISA^- \Leftrightarrow Pa(OH)_5ISA^-$, total dissolved Pa increases by about 30 % (to 2.3×10^{-6} [mol/kg H_2O]) at $ISA^-_{tot} = 5 \times 10^{-3}$ [mol/kg H_2O]. We conclude that the impact of isosaccharinic acid on the solubility of protactinium is well below one order of magnitude under given chemical conditions.

Uranium

Dissolved uranium usually appears in the hexa-valent redox state (+VI), but under reducing conditions also U(IV) forms are to be expected. U(V) is not very stable and disproportionates to U(IV) and U(VI). The distribution of redox states depends on the relative stabilities of the formed solute complexes. Under given chemical conditions the limiting solid has the redox state +IV, but dominant complexes in solution have the redox state +VI. $UO_{2(am,hyd)}$ is the stable solid phase exhibiting a total uranium solubility of 7.0×10^{-7} [mol/kg H_2O] and an uncertainty of ± 1.0 log_{10}-units in the formation constant. Dominant solutes are $UO_2(OH)_4^{2-}$ and $UO_2(OH)_3^-$ with uncertainties of ± 0.7 and ± 0.4 log_{10}-units, respectively. Other potential limiting solids are compreignacite ($K_2(UO_2)_6O_4(OH)_6.8H_2O$) and becquerelite ($Ca(UO_2)_6O_4(OH)_6.8H_2O$) or the uranium-silicates uranophane ($Ca(UO_2)_2(SiO_3OH)_2.5H_2O$) and Na-boltwoodite ($NaUO_2(SiO_3OH).1.5H_2O$). The recommended value is based on $UO_{2(am,hyd)}$. The lower guideline value is also based on $UO_{2(am,hyd)}$, but additionally taking into account uncertainties of solid and solutes. The solids compreignacite, becquerelite, uranophane and Na-boltwoodite would limit dissolved uranium in the range 1.7×10^{-5} to 1.4×10^{-4} [mol/kg H_2O]. The solubility of becquerelite was selected to represent the upper guideline value.

U-speciation at specified solubility:

Limiting phase	Calculated solubility [mol/kg H_2O]	Distribution of solute components
$UO_{2(am, hyd)}$	7.0×10^{-7}	$UO_2(OH)_4^{2-}$ (83.4 %) $UO_2(OH)_3^-$ (16.2 %) $U(OH)_{4aq}$ (0.4 %)

At the upper guideline value (1.4×10^{-4} [mol/kg H_2O]) the speciation is identical.

Impact of Isosaccharinic Acid on Solubility of Uranium

Isosaccharinic acid	Calculated solubility [mol/kg H_2O]	Distribution of solute components for U	Distribution of solute components for ISA
ISA^-_{tot} 5×10^{-3} [mol/kg H_2O] $UO_{2(am,hyd)}$	8.4×10^{-7}	$UO_2(OH)_4^{2-}$ (75.1 %), $UO_2(OH)_3^-$ (14.1 %), $U(OH)_4ISA^-$ (10.4 %) $U(OH)_{4aq}$ (0.4 %)	ISA^- (55.5 %) $Ca(OH)ISA_{(aq)}$ (30.6 %) $CaISA^+$ (13.9 %)
$Ca(ISA)_2$ saturated ISA^-_{tot} 2.03×10^{-2} [mol/kg H_2O] $UO_{2(am,hyd)}$	1.1×10^{-6}	$UO_2(OH)_4^{2-}$ (56.1 %) $U(OH)_4ISA^-$ (32.7 %) $UO_2(OH)_3^-$ (10.9 %) $U(OH)_{4aq}$ (0.3 %)	ISA^- (54.1 %) $Ca(OH)ISA_{(aq)}$ (31.1 %) $CaISA^+$ (14.8 %)

The impact of isosaccharinic acid on the solubility of uranium is not dramatic from an absolute point of view, but it should be recognised that the ratio U(IV)/U(VI) in solution is significantly increased in the presence of ISA. This is due to the formation of the U(IV)-ISA complex $U(OH)_4ISA^-$. The isosaccharinic acid system itself is not influenced by uranium.

Neptunium

Neptunium appears in the redox states +IV in reducing environments and in the redox state +V in non-reducing environments but also the redox states +III and +VI are possible. In the present chemical environment a dominance of the +IV redox state is expected. The only sensible limiting solid under present conditions is $NpO_{2(am,hyd)}$ with a $\pm$ 0.5 log_{10}-units uncertainty in the solubility constant. The exclusive solute is $Np(OH)_{4(aq)}$, whose formation constant has an uncertainty of $\pm$ 1.1 log_{10}-units. The calculated solubility is 1.0×10^{-9} [mol/kg H_2O], which is used for the recommended value. The lower- and upper guideline values were calculated by simultaneously applying the mentioned uncertainties. The resulting border values (2.5×10^{-11} [mol/kg H_2O] and 4.0×10^{-8} [mol/kg H_2O]) seem too far off, most likely a consequence of the fact that the two available uncertainties have hardly been evaluated independently.

Note that the solubility of Np will increase with increasing Eh. Above ~-100 [mV] it is expected that Np(V), exhibiting the solute species $Np(V)O_2(OH)_2^-$, $Np(V)O_2(HSiO_3)_{(aq)}$ and $Np(V)O_2(OH)_{(aq)}$ will become significant.

Np-speciation at specified solubility:

Limiting phase	Selected solubility [mol/kg H_2O]	Distribution of solute components
$NpO_{2(am, hyd)}$	1.0×10^{-9}	$Np(OH)_{4(aq)}$ (100 %)

Impact of Isosaccharinic acid on solubility of Neptunium

Isosaccharinic acid	Calculated solubility [mol/kg H_2O]	Distribution of solute components for Np	Distribution of solute components for ISA
ISA^-_{tot} 5×10^{-3} [mol/kg H_2O] $NpO_{2(am,hyd)}$	3.5×10^{-9}	$Np(OH)_4ISA^-$ (54.0 %) $Np(OH)_{4(aq)}$ (28.1 %) $Np(OH)_4(ISA)_2^{2-}$ (17.9 %)	ISA^- (55.5 %) $Ca(OH)ISA_{(aq)}$ (30.6 %) $CaISA^+$ (13.9 %)
$Ca(ISA)_2$ saturated ISA^-_{tot} 2.03×10^{-2} [mol/kg H_2O] $NpO_{2(am,hyd)}$	1.9×10^{-8}	$Np(OH)_4(ISA)_2^{2-}$ (53.9 %) $Np(OH)_4ISA^-$ (40.7 %) $Np(OH)_{4(aq)}$ (5.4 %)	ISA^- (54.1 %) $Ca(OH)ISA_{(aq)}$ (31.1 %) $CaISA^+$ (14.8 %)

The isosaccharinic acid system is not influenced by neptunium.

Plutonium

Under reducing conditions plutonium is expected to appear in the tetra valent redox state but the formation of Pu(III) is possible, depending on the stability of corresponding solute complexes (i.e. Pu(III)-silicates (Berner 2014)). Under oxidising conditions Pu may also appear in the redox states +V and +VI. In the present chemical environment $PuO_{2(am,hyd)}$ is the limiting solid (uncertainty of the formation constant $\pm$ 0.52 log_{10}-units), producing a solubility of 2.3×10^{-12} [mol/kg H_2O]. Dominant solute is $Pu(IV)(OH)_{4(aq)}$ (99.8 %, uncertainty of the formation constant $\pm$ 0.5 log_{10}-units), but traces of $Pu(III)(OH)_{3(aq)}$ may be present. The calculated solubility is taken for the recommended value. The lower guideline value simultaneously considers both mentioned uncertainties (leading to 2.3×10^{-13} [mol/kg H_2O]). When the solubility is modelled with $Pu(OH)_{3(cr)}$ being the limiting phase, the calculated solubility increases to 8.2×10^{-8} [mol/kg H_2O], but the speciation is still dominated by $Pu(IV)(OH)_{4(aq)}$. The solubility of $Pu(OH)_{3(cr)}$ serves for defining the upper guideline value.

Neck et al. (2007) reported on rather constant concentrations of colloidal $Pu(IV)_{(coll,hyd)}$ in the presence of $PuO_{2(am,hyd)}$ in the pH range 6 to 13. They measured amounts of colloidal Pu in solution ranging from 5×10^{-10} to 5×10^{-8} [mol/kg H_2O] ($log_{10}K(PuO_{2(am,hd)} \leftrightarrows Pu(IV)_{(coll,hyd)}$ = -(8.3 $\pm$ 1.0)) and claimed that the colloidal species are in equilibrium with the solid and with other Pu-solutes. However, a thermodynamic relation between these colloidal/polymeric species and the "classical" monomeric species in solution is not (yet) available. Present data and calculations do not reproduce the observations made by Neck et al. (2007) but the selected upper guideline value comprises the observed elevated concentrations of colloidal/polymeric species.

Pu-speciation at specified solubility:

Limiting phase	Calculated solubility [mol/kg H$_2$O]	Distribution of solute components
PuO$_{2(am, hyd)}$	2.3×10^{-12}	Pu(IV)(OH)$_{4(aq)}$ (99.8 %) Pu(III)(OH)$_{3(aq)}$ (0.1 %)

The calculated Pu-speciation at the upper guideline value is identical. However, if the model of Neck et al. is implemented the speciation is at the upper guideline value is Pu(IV)$_{(coll,hyd)}$.

Impact of Isosaccharinic acid on solubility of Plutonium

Since no thermodynamic data are available to appraise a potential impact of isosaccharinic acid, the following estimate was carried out: Available thermodynamic data indicate that both, Pu and Np exhibit similar limiting solids and similar dominant complexes in solution and for both elements the tetra-valent redox state is dominant. It is therefore assumed that a potential impact of the isosaccharinate ion is also similar for both elements. On the basis of an identical enhancement factor (see Tab. 4) it is estimated that total dissolved Pu increases to 8.1×10^{-12} [mol/kg H$_2$O] in the presence of 5×10^{-3} [mol/kg H$_2$O] of ISA$^-$ and to 4.4×10^{-11} [mol/kg H$_2$O] when solid Ca(ISA)$_2$ is additionally present. Numerical values in Tab. 3 were put in parentheses to indicate their speculative character.

Americium

Americium generally has an oxidation state of +III, but the penta- and hexavalent dioxo aqua ions Am(V)O$_2^+$ and Am(VI)O$_2^{2+}$ may be formed under strongly oxidising conditions (Am^{4+} was never found in solution) (Silva et al. 1995). Limiting solid in the americium system will be either crystalline (2.7×10^{-11} [mol/kg H$_2$O]) or amorphous (5.4×10^{-10} [mol/kg H$_2$O]) hydroxide Am(OH)$_{3(cr\ or\ am)}$. Corresponding uncertainties of the formation constants are ±0.6 and ±0.8 log$_{10}$-units for the crystalline and the amorphous solid, respectively. Dominant complexes in solution are Am(OH)$_{3(aq)}$ (uncertainty of formation constant ±0.5 log$_{10}$-units) and Am(OH)$_2^+$ (uncertainty of formation constant ±0.7 log$_{10}$-units). Different from the trivalent Eu, the database does not include the anionic tetra-hydroxide complex Am(OH)$_4^-$. Carbonate and mixed hydroxide/carbonate complexes and solids are not significant under given high pH/ low carbonate conditions. Based on a recent study on Cm(III) hydroxides (Rabung et al. 2008), a series of novel complexes of the form Ca$_x$An(III)(OH)$_y^{(3+2x-y)+}$ was entered into the thermodynamic database. Under present conditions the contribution of these new complexes to total solubility is below 5 %.

The recommended value of 5.4×10^{-10} [mol/kg H$_2$O] is based on the solubility of the amorphous hydroxide Am(OH)$_{3(am)}$. The upper guideline value (1.1×10^{-8} [mol/kg H$_2$O]) is based on the same solid, including the corresponding uncertainties. The lower guideline value (2.2×10^{-12} [mol/kg H$_2$O]) was taken from the solubility of the crystalline solid Am(OH)$_{3(cr)}$, considering given uncertainties.

Note on a potential inconsistency: In a similar report on element solubilities in bentonite environments (Berner 2014) (pH 7.8), the definition of an upper guideline value based on amorphous Am(OH)$_{3(am)}$ in combination with the strong silicate complex AmSiO$_3^{2+}$ was considered to be not realistic, based on missing experimental evidence. In the present cement environment silicate complexation is never relevant if compared to the complexation with

hydroxide. Therefore, selecting $Am(OH)_{3(am)}$ (including an uncertainty of 0.8 $\log_{10}$-units) as the limiting solid for the upper guideline value seems appropriate in this specific high-pH environment. Both, the former comment on further exploring the potential silicate complexation of di- and trivalent cations (Berner 2014) as well as the note on lanthanide hydrolysis under the heading "Samarium" above, are valid for americium.

Am-speciation at specified solubility:

Limiting phase	Calculated solubility [mol/kg H_2O]	Distribution of solute components
$Am(OH)_{3(am)}$	5.4×10^{-10}	$Am(OH)_{3(aq)}$ (93.6 %) $Am(OH)_2^+$ (4.4 %) $CaAm(OH)_3^{2+}$ (1.1 %) $Ca_2Am(OH)_4^{3+}$ (0.8 %) $Ca_3Am(OH)_6^{3+}$ (0.2 %)

At the upper guideline value of 1.1×10^{-8} [mol/kg H_2O] a small shift in the distribution of complexes is observed:

Limiting phase	Calculated solubility [mol/kg H_2O]	Distribution of solute components
$Am(OH)_{3(am)}$	1.1×10^{-8}	$Am(OH)_{3(aq)}$ (92.5 %) $Am(OH)_2^+$ (6.8 %) $CaAm(OH)_3^{2+}$ (0.3 %) $Ca_2Am(OH)_4^{3+}$ (0.3 %) $Ca_3Am(OH)_6^{3+}$ (0.1 %)

Impact of Isosaccharinic acid on solubility of Americium

Isosaccharinic acid	Calculated solubility [mol/kg H_2O]	Distribution of solute components for Am	Distribution of solute components for ISA
ISA^-_{tot} 5×10^{-3} [mol/kg H_2O] $Am(OH)_{3(am)}$	8.9×10^{-8}	$Am(OH)_3ISA^-$ (99.6 %) $Am(OH)_{3(aq)}$ (0.4 %) $Am(OH)_2^+$ (0.03 %) $CaAm(OH)_3^{2+}$ (0.01 %)	ISA^- (55.5 %) $Ca(OH)ISA_{(aq)}$ (30.6 %) $CaISA^+$ (13.9 %)
ISA^-_{tot} 5×10^{-3} [mol/kg H_2O] $Am(OH)_{3(cr)}$	4.4×10^{-9}		
$Ca(ISA)_2$ saturated ISA^-_{tot} 2.03×10^{-2} [mol/kg H_2O] $Am(OH)_{3(am)}$	3.5×10^{-7}	$Am(OH)_3ISA^-$ (99.8 %) $Am(OH)_{3(aq)}$ (0.2 %)	ISA^- (54.1 %) $Ca(OH)ISA_{(aq)}$ (31.1 %) $CaISA^+$ (14.8 %)

The isosaccharinic acid system is not influenced by americium.

Curium

Curium has an oxidation state of +III (in analogy to Am, the penta and hexavalent dioxo aqua ions may exist). 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). However, for Cm there is only one solid phase listed in the database ($Cm(OH)_{3(am,coll)}$). The formation constant ($\log_{10}K_{s,0}^0 = 17.2 \pm 0.4$) is very similar to the formation constant of the corresponding amorphous americium solid ($Am(OH)_{3(am)}$, $\log_{10}K_{s,0}^0 = 16.9 \pm 0.8$), except for the subscript "coll". Hence, it seems that the curium solid has colloidal properties. The dominant complex in solution is $Cm(OH)_{3(aq)}$, exhibiting an uncertainty of ± 0.5 $\log_{10}$-units in its formation constant. The recommended value of 1.1×10^{-9} [mol/kg H_2O] reflects the solubility of $Cm(OH)_{3(am,coll)}$, upper- and lower guideline values (8.6×10^{-9} [mol/kg H_2O], 1.5×10^{-10} [mol/kg H_2O]) were calculated by applying the mentioned uncertainties. As in the case of Am the novel complexes $Ca_xAn(III)(OH)_y^{(3+2x-y)+}$ contribute below 5 % to totally dissolved Cm.

Cm-speciation at specified solubility:

Limiting phase	Selected solubility [mol/kg H_2O]	Distribution of solute components
$Cm(OH)_{3(am,coll)}$	1.1×10^{-9}	$Cm(OH)_{3(aq)}$ (93.6 %) $Cm(OH)_2^+$ (4.4 %) $CaCm(OH)_3^{2+}$ (1.1 %) $Ca_2Cm(OH)_4^{3+}$ (0.8 %) $Ca_3Cm(OH)_6^{3+}$ (0.2 %)

Like in the case of the very similar Am, a small shift in the distribution of Cm complexes is observed at the upper guideline value of 8.6×10^{-9} [mol/kg H_2O]:

Limiting phase	Selected solubility [mol/kg H_2O]	Distribution of solute components
$Cm(OH)_{3(am,coll)}$	8.6×10^{-9}	$Cm(OH)_{3(aq)}$ (92.5 %) $Cm(OH)_2^+$ (6.8 %) $CaCm(OH)_3^{2+}$ (0.3 %) $Ca_2Cm(OH)_4^{3+}$ (0.3 %) $Ca_3Cm(OH)_6^{3+}$ (0.1 %)

Impact of Isosaccharinic acid on solubility of Curium

No thermodynamic data are available to appraise a potential impact of isosaccharinic acid. Therefore, the nearly identical behaviour of Cm and Am was used to estimate this impact. Am solubility is increased by a factor of ~165 in the presence of 5×10^{-3} [mol/kg H_2O] of ISA⁻, and by a factor of ~650 in the presence of 5×10^{-3} [mol/kg H_2O] of ISA⁻ and of solid $Ca(ISA)_{2(s)}$. Applying the same factors to the solubility of Cm produces estimates of 1.8×10^{-7} [mol/kg H_2O] of dissolved Cm ($Cm(OH)_3ISA^-$) in the presence of 5×10^{-3} [mol/kg H_2O] of ISA⁻, and of 7.1×10^{-7} [mol/kg H_2O] of dissolved Cm in the case when solid $Ca(ISA)_{2(s)}$ is additionally present. Numerical values in Tab. 3 were put in parentheses to indicate their speculative character. The isosaccharinic acid system is not influenced by curium.

6   Summary of Impact of Isosaccharinic Acid

The potential impact of isosaccharinic acid is summarised in Tab. 4. With 5×10^{-3} [mol/kg H_2O] of ISA^- a high total ISA^- concentration near the maximum concentration of 20×10^{-3} [mol/kg H_2O] was selected. Note that the maximum concentration is assumed to be defined by the solubility of solid $Ca(ISA)_2$. A solubility enhancement factor was introduced (Column 4 in Tab. 4) which is defined by the ratio of the element concentration in presence of 5×10^{-3} [mol/kg H_2O] of ISA^-, divided by the recommended concentration in the absence of ISA^-. The enhancement factor indicates that isosaccharinic acid may be critical for the tri-valent elements Eu (Sm, Ho, Ac), Am and Cm, and for Th (Po, Zr). The impact on Ca, Ni, Pa, U, Np and Pu is less significant. Thorium forms an exception if compared to the other tetravalent actinides. It is evident that further work on evaluating complex formation constants with isosaccharinic acid is necessary. There is no doubt that the isosaccharinate anion is one of the strongest complexing agent under given chemical conditions. Other organic molecules that potentially may form during the degradation of organic material at high pH will have less impact. Since a rather high ISA^- concentration has been selected to perform the impact analysis, it is concluded that a potential impact of degrading organic materials on the solubility of safety relevant elements is not significant or at most restricted to tri-valent elements.

The impact of ISA- on the solubility near the upper guideline value was not evaluated. If necessary, such impact can approximately be estimated by applying the appropriate solubility enhancement factor from Table 4 to the solubility of the element at the upper guideline value, provided that the resulting final element solubility is below 5×10^{-4} [mol/kg H_2O] (about one tenth of the ISA^- concentration). Otherwise, the solubility enhancement factor decreases and a full speciation/solubility calculation needs to be performed.

7   Concluding Remarks

The presented approach is a well-established, world-wide accepted and state-of-the-art approach to estimate maximum concentrations. The values evaluated by different organisations have been converging over the past decades. The approach is based on the most recent collection of thermodynamic data and on a careful and rather conservative (if possible) selection of limiting solid phases. The results reveal that in 29 cases the evaluated maximum concentration is lower or similar than in a former study, indicating a substantial improvement in evaluating solubility limits. In only three cases (Ni, Ag, Pa) improved thermodynamic data or revised considerations 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 systems[2]. Elements in question may form solid solutions (e.g. Ra/Ba) or may mutually interact (e.g. Ag, Se, I, Cl), leading tentatively to lower recommended concentrations. Presently, the improved performance of the chemical solver is not yet fully exploited. It is assumed that applying 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.

The impact of substantial amounts of organic complexing agents (isosaccharinic acid) on the solubility of 15 elements has been investigated. In high pH environments the isosaccharinate anion is amongst the most efficient complexing agents for many relevant cations and is taken as a representative for dissolved organic material in the reference solution. Thermodynamic data were taken from recent publications or were estimated from chemical analogies. It is concluded that significant impacts of isosaccharinic acid should be expected for trivalent elements and for Th, Zr and Po, but much less significant impacts can be expected for Ca, Ni, Pa, U, Np and Pu.

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[2]   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.

Tab. 4: Impact of 5×10^{-3} [mol/kg H_2O] of ISA^- on the solubility of selected elements.

The solubility enhancement factor (Column 4) is obtained by simply dividing the solubility in the presence of ISA^- by the solubility in the absence of ISA^-.

Element	Solubility without ISA^- [mol/kg H_2O]	Solubility in the presence of 5×10^{-3} [mol/kg H_2O] of ISA^- [mol/kg H_2O]	Solubility enhancement factor	Dominant complexes in solution Comments
Ca	1.8×10^{-2}	2.0×10^{-2}	1.1	Ca^{2+}; Ca-ISA complexes only 11.4 %
Ni	3.0×10^{-6}	3.5×10^{-6}	1.2	$Ni(OH)_3^-$; $Ni_2(ISA)(OH)_4^-$ only 6 %.
Zr	4.5×10^{-9}	(4.9×10^{-7})	109	$Zr(OH)_4ISA^-$; exclusively based on analogy with Th.
Sm	4.6×10^{-7}	2.9×10^{-4}	630*	$Sm(OH)_3ISA^-$ exclusively based on analogy with Eu.
Eu	1.9×10^{-6}	5.0×10^{-4}	263	$Eu(OH)_3ISA^-$
Ho	1.9×10^{-7}	1.2×10^{-4}	632*	$Ho(OH)_3ISA^-$ exclusively based on analogy with Eu.
Po	6.4×10^{-8}	(4.7×10^{-5})	(731)	$(Po(OH)_4ISA^-$ exclusively based on analogy with Th.
Ac	(1.9×10^{-6})	(5.0×10^{-4})	(263)	$Ac(OH)_3ISA^-$ exclusively based on analogy with Eu.
Th	1.3×10^{-9}	9.5×10^{-7}	731	$Th(OH)_4ISA^-$; $ThCa(OH)_4(ISA)_{2(aq)}$
Pa	1.8×10^{-6}	(2.3×10^{-6})	(1.3)	No thermodynamic data; Analogy with Eu, Th, U, Np.
U	7.0×10^{-7}	8.4×10^{-7}	1.2	$UO_2(OH)_4^{2-}$; $U(OH)_4ISA^-$ only 10 %; ratio U(IV)/UVI) increases from 0.004 to 0.11.
Np	1.0×10^{-9}	3.5×10^{-9}	3.5	$Np(OH)_4ISA^-$ and $Np(OH)_4(ISA)_2^{2-}$ (72 %)
Pu	2.3×10^{-12}	(8.1×10^{-12})	(3.5)	No thermodynamic data; Analogy (enhancement factor) with Np assumed
Am	5.4×10^{-10}	8.9×10^{-8}	165	$Am(OH)_3ISA^-$
Cm	1.1×10^{-9}	(1.8×10^{-7})	(165)	No thermodynamic data; Analogy with Am assumed

* The difference in impact factors between Eu and Sm & Ho has its origin in differing formation constants for the $Ln(OH)_4^-$ -complexes (see also the note in section "samarium").

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 hetero-geneously 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 recurrent 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 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

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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 cementitious near field of an ILW repository. This appendix presents the values that were 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. 3) and are in single cases adapted to the needs of the safety analysis. Requirements of the regulator (ENSI 2010) were considered.

Data sets are given for waste group 1 and waste group 2. For waste group 1 no increased solubility of the radionuclides by compounds contained in the waste is expected. For waste group 2 solubility limits for some radionuclides are increased due to the influence of Isosaccarinic acid (ISA) originating from the degradation of cellulose (Glaus & Van Loon 2004, Van Loon & Glaus 1998) contained in the waste.

A.2   Solubility Limits for Waste Group 1 (ILW 1)

Shared Solubilities

For the elements C_{inorg}, Co, Ni and Sr, "shared solubility" between the radionuclides and the stable isotopes is used for the dose calculations. The solubility of the above mentioned elements is controlled by a solid present in the cement paste. The radionuclides are exchanged with their stable isotopes in the solid and incorporated into the outer layer of the solid (extent of incorporation is defined by the accessibility factor f in Tabel A-1). As a result the radionuclides are partially depleted in the near-field porewater. Shared solubility leads to isotope dilution.

Shared solubility is used for the reference and the upper bound value for C_{inorg}, Ni and Co. The solubility values as given in this report are used for the dose calculations. In addition, as upper guideline value for C_{inorg} the carbonate concentration of cement degradation stage I is taken (Tab A4.1 in Kosakowski et al., 2014) to be compatible with the derivation of the corresponding operational K_d in Wieland (2014).

In contrast to Co, Ni and C_{inorg}, shared solubility is not used to characterize the sorption behavior of Sr. For Sr shared solubility is only used for the reference value, but not for the upper bound value, because uncertainties for the stability of strontianite are not available. As upper guideline value for Sr the reference value was taken.

Tab. A-1 lists the solid content c_{cem} in the cement paste, and, therefrom derived by an accessibility factor f, the content available for isotope exchange. The inventory for Sr was derived from the strontianite content of cement paste (Tab. 1 in the present report); the accessibility factor for Sr was adopted from C_{inorg} (carbonates).

Tab. A-1: Inventories of solids in the cement paste and availability for isotope exchange (Wieland 2014).

		Ni	**Co**	**C$_{inorg}$**	**Sr**
C$_{cem}$	mol/kg	3.20×10^{-4}	5.60×10^{-5}	0.11	0.012
f		0.1	0.1	0.01	0.01
c$_{cem}$ (available)	mol/kg	3.20×10^{-5}	5.60×10^{-6}	1.10×10^{-3}	1×10^{-4}

C$_{cem}$: content of stable element in cement paste
f: accessibility factor
c$_{cem}$ (available): amount of solid available for isotope exchange (C$_{cem} \times$ f)

Note that for Co, Ni and C$_{inorg}$, the K$_d$ values in ILW 1 and ILW 2 are set to zero, as they are derived from shared solubility, which is taken into account in the solubility limit.

Adjusted Solubility Values

Cl and K

As reference value for Cl and K, this report suggested to use the concentration in the cement pore water after 10'000 years of exchange with OPA. For safety assessment Cl and K are assumed to be "not limited" in the dose calculations.

I

In this report, Berner takes AgI as solubility limiting solid. However, waste sorts with high inventory of I-129 do not contain Ag. The solubility of I is therefore set to "not limited" for the dose calculations.

Po

In this report Th(IV) is used as an analogue for Po. As reference value the upper guideline value for Th(IV) is taken. Since the analogy is speculative (values in Tab. 3 were put in parentheses) we use "not limited" as an upper guideline value.

Reference Values and Upper Bound Values

A few elements have an upper bound value that is identical to the reference value. In case of Sm, the upper value was also set as the reference value to account for the inconsistency with Eu data.

The reference and upper bound values for Pb are also identical, owing to a lack of uncertainty data for the stability data and the unlikely high phosphate concentration.

Also for Sr both values are identical, although the reference value uses shared solubility and the upper bound value does not assume isotope exchange with strontianite due to the lack of uncertainty values for the stability of strontianite.

A.3   Solubility Limits for Waste Group 2 (ILW2)

The solubility limits of those elements that are influenced by the complexation with ISA were adapted. For the elements not influenced by ISA the reference value from ILW 1 was adopted. The reference values for elements influenced by ISA were taken from the values proposed in this report. However, the upper bound values were adapted, following a recommendation of the report reviewer (M. Ochs).

The upper bound value for ILW 2 was calculated by multiplying the upper bound value for ILW 1 with the solubility enhancement factor listed in Tab. 4 in this report. The method over-estimates the influence of ISA if the resulting value is $> 5 \times 10^{-4}$ mol/kg H_2O. Therefore, the upper bound values ILW 2 for Zr, Eu and Ac are too high but this is conservative. For the elements not influenced by ISA the upper bound value for ILW 1 was adopted.

A.4   Solubility Summary Tables for ILW 1 and ILW 2

The solubility limits for a cementitious near field to be used for dose calculations for the near field of the ILW repository within the provisional safety assessments are listed in Tab. A-2. Two sets of reference and upper bound values are given; one data set for ILW 1 and one set for ILW 2. The values are rounded to one significant digit. For conservative reasons the reference solubility of Zr was rounded to the next higher integer.

Tab. A-2:   Solubility limits for the ILW near field (cement).

Element	ILW 1		ILW 2 (influence of ISA)	
	Reference value [mol/kg H_2O]	**Upper bound value** [mol/kg H_2O]	**Reference value** [mol/kg H_2O]	**Upper bound value** [mol/kg H_2O]
Be	2×10^{-4}	5×10^{-4}	2×10^{-4}	5×10^{-4}
C_{inorg}*	8×10^{-6}	4×10^{-5}	8×10^{-6}	4×10^{-5}
Cl	Not limited	Not limited	Not limited	Not limited
K	Not limited	Not limited	Not limited	Not limited
Co*	5×10^{-7}	2×10^{-5}	5×10^{-7}	2×10^{-5}
Ni*	3×10^{-6}	2×10^{-4}	4×10^{-6}	3×10^{-4}
Se	2×10^{-6}	Not limited	2×10^{-6}	Not limited
Sr*	2×10^{-3}	2×10^{-3}	2×10^{-3}	2×10^{-3}
Zr	5×10^{-9}	1×10^{-4}	5×10^{-7}	1×10^{-2}
Nb	Not limited	Not limited	Not limited	Not limited
Mo	7×10^{-6}	2×10^{-5}	7×10^{-6}	2×10^{-5}
Tc	2×10^{-6}	2×10^{-6}	2×10^{-6}	2×10^{-6}
Ag	2×10^{-6}	2×10^{-4}	2×10^{-6}	2×10^{-4}
Sn	1×10^{-7}	2×10^{-7}	1×10^{-7}	2×10^{-7}
I	Not limited	Not limited	Not limited	Not limited
Cs	Not limited	Not limited	Not limited	Not limited
Sm	5×10^{-7}	5×10^{-7}	3×10^{-4}	3×10^{-4}
Eu	2×10^{-6}	3×10^{-5}	5×10^{-4}	7×10^{-3}
Pb	5×10^{-3}	5×10^{-3}	5×10^{-3}	5×10^{-3}
Po	6×10^{-8}	Not limited	5×10^{-5}	Not limited
Ra	1×10^{-6}	2×10^{-5}	1×10^{-6}	2×10^{-5}
Ac	2×10^{-6}	3×10^{-5}	5×10^{-4}	7×10^{-3}
Th	1×10^{-9}	6×10^{-8}	1×10^{-6}	5×10^{-5}
Pa	2×10^{-6}	2×10^{-5}	2×10^{-6}	2×10^{-5}
U	7×10^{-7}	1×10^{-4}	8×10^{-7}	2×10^{-4}
Np	1×10^{-9}	4×10^{-8}	4×10^{-9}	1×10^{-7}
Pu	2×10^{-12}	8×10^{-8}	8×10^{-12}	3×10^{-7}
Am	5×10^{-10}	1×10^{-8}	9×10^{-8}	2×10^{-6}
Cm	1×10^{-9}	9×10^{-9}	2×10^{-7}	1×10^{-6}

*   Use shared solubilities for C_{inorg}, Co, Ni for the reference and the upper bound scenarios, for Sr only for the reference scenario but not for the upper bound scenario. The inventories and accessibility for the stable elements are given in Tab.A-1.

A.5 References

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