



TECHNICAL REPORT 23-04

Solubility Limits for Bentonite Near Field
(Update of NTB 14-06)

August 2023

W. Hummel, D.A. Kulik & G.D. Miron

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

Hardstrasse 73 | 5430 Wettingen | Switzerland
T. +41 56 437 11 11 | info@nagra.ch | nagra.ch



TECHNICAL REPORT 23-04

Solubility Limits for Bentonite Near Field
(Update of NTB 14-06)

August 2023

W. Hummel, D.A. Kulik & G.D. Miron

Paul Scherrer Institut, Villigen PSI

ISSN 1015-2636

Copyright © 2023 by Nagra, Wettingen (Switzerland) / All rights reserved. All parts of this work are protected by copyright. Any utilisation outwith the remit of the copyright law is unlawful and liable to prosecution. This applies in particular to translations, storage and processing in electronic systems and programs, microfilms, reproductions, etc.

Abstract

Solubility limits for the 29 elements Ac, Ag, Am, C, Ca, Cf, Cl, Cm, Cs, Ho, I, Mo, Nb, Ni, Np, Pa, Pb, Pd, Po, Pu, Ra, Se, Sm, Sn, Sr, Tc, Th, U, Zr have been calculated in bentonite porewater using the PSI Chemical Thermodynamic Database 2020 (TDB 2020) (Hummel & Thoenen 2023) with the most recent version of GEM Software (GEMS, <https://gems.web.psi.ch/>).

The majority of these 29 elements exhibit maximum solubilities below the micromolar range. The solubilities of Ca, Sr and inorganic carbon are determined by the definition of the porewater itself and Cs, Cl and I are chemically “unlimited”.

The solubility limits calculated using TDB 2020 can be considered in the safety assessments “as they are” as great care has been taken in the development of TDB 2020 that any lack of data may lead to overestimations but never to grossly underestimated solubilities.

Zusammenfassung

Die Löslichkeitslimiten für die 29 Elemente Ac, Ag, Am, C, Ca, Cf, Cl, Cm, Cs, Ho, I, Mo, Nb, Ni, Np, Pa, Pb, Pd, Po, Pu, Ra, Se, Sm, Sn, Sr, Tc, Th, U, Zr wurden in Betonporenwasser, mit Hilfe der PSI Chemisch-thermodynamischen Datenbank 2020 (TDB 2020) (Hummel & Thoenen 2023) und der neuesten Version der GEM-Software (GEMS, <https://gems.web.psi.ch/>) berechnet.

Die meisten dieser 29 Elemente weisen maximale Löslichkeiten unterhalb des mikromolaren Bereichs auf. Die Löslichkeiten von Ca, Sr und anorganischen Kohlenstoffverbindungen werden durch die Definition des Porenwassers selbst bestimmt. Die Löslichkeiten von Cs, Cl und I werden als «unbegrenzt» angesehen.

Die mit der TDB 2020 berechneten Löslichkeitslimiten können in Sicherheitsanalysen «so wie sie sind» berücksichtigt werden, da bei der Entwicklung der TDB 2020 sorgfältig darauf geachtet wurde, dass fehlende Daten zwar zu überschätzten, aber niemals zu grob unterschätzten Löslichkeiten führen können.

Table of Contents

Abstract	I
Zusammenfassung	II
Table of Contents	III
List of Tables.....	V
List of Figures	VII
1 Introduction	1
2 Basic data, chemical conditions and methods	3
2.1 Database and code	3
2.2 Porewater compositions.....	3
2.3 Operational approach for deriving solubilities	4
3 Calculated element solubilities	7
3.1 Actinium	7
3.2 Americium	8
3.3 Caesium	9
3.4 Calcium.....	9
3.5 Californium.....	10
3.6 Inorganic Carbon	10
3.7 Chlorine	11
3.8 Curium	12
3.9 Holmium.....	12
3.10 Iodine.....	13
3.11 Lead	14
3.12 Molybdenum.....	14
3.13 Neptunium	15
3.14 Nickel.....	15
3.15 Niobium	16
3.16 Palladium.....	16
3.17 Plutonium.....	17
3.18 Polonium.....	18
3.19 Protactinium.....	18
3.20 Radium.....	19
3.21 Samarium.....	20
3.22 Selenium	21
3.23 Silver.....	21
3.24 Strontium	22
3.25 Technetium	23
3.26 Thorium	23
3.27 Tin.....	24

3.28	Uranium	25
3.29	Zirconium	25
3.30	Calculation of all solubilities in one system	26
4	Summary and conclusions	31
5	References.....	35
App. A	Solubility limits for a saline bentonite porewater	A-1

List of Tables

Tab. 2-1:	Geochemical conditions (solids, exchanged cations, porewater composition) for bentonite pore waters	3
Tab. 3-1:	Solubility parameters for actinium	7
Tab. 3-2:	Solubility parameters for americium	8
Tab. 3-3:	Solubility parameters for caesium	9
Tab. 3-4:	Solubility parameters for calcium.....	9
Tab. 3-5:	Solubility parameters for californium.....	10
Tab. 3-6:	Solubility parameters for inorganic carbon	11
Tab. 3-7:	Solubility parameters for chlorine	11
Tab. 3-8:	Solubility parameters for curium	12
Tab. 3-9:	Solubility parameters for holmium.....	13
Tab. 3-10:	Solubility parameters for iodine	13
Tab. 3-11:	Solubility parameters for lead.....	14
Tab. 3-12:	Solubility parameters for molybdenum	14
Tab. 3-13:	Solubility parameters for neptunium	15
Tab. 3-14:	Solubility parameters for nickel.....	15
Tab. 3-15:	Solubility parameters for niobium.....	16
Tab. 3-16:	Solubility parameters for palladium	17
Tab. 3-17:	Solubility parameters for plutonium.....	17
Tab. 3-18:	Solubility parameters for polonium.....	18
Tab. 3-19:	Solubility parameters for protactinium.....	19
Tab. 3-20:	Solubility parameters for radium.....	20
Tab. 3-21:	Solubility parameters for samarium.....	20
Tab. 3-22:	Solubility parameters for selenium.....	21
Tab. 3-23:	Solubility parameters for silver	22
Tab. 3-24:	Solubility parameters for strontium.....	22
Tab. 3-25:	Solubility parameters for technetium.....	23
Tab. 3-26:	Solubility parameters for thorium.....	24
Tab. 3-27:	Solubility parameters for tin	24
Tab. 3-28:	Solubility parameters for uranium.....	25
Tab. 3-29:	Solubility parameters for zirconium	26
Tab. 3-30:	Summary of solubilities computed for E3-BPW-Ref, E3-BPW-h[igh]pCO ₂ cases without- and with dose-relevant radionuclides (RN).....	27
Tab. 3-31:	GEM-Selektor recipes for all-in-one systems.....	28

Tab. 3-32: Properties of aqueous solution for the E3-BPW-Ref, E3-BPW-h[igh]pCO ₂ systems without- and with dose-relevant radionuclides (RN).....	29
Tab. 4-1: Summary of element solubilities including lower and upper limits	34
Tab. A-1: Geochemical conditions (solids, exchanged cations, porewater composition) for bentonite pore waters	A-1
Tab. A-2: Solubility parameters for actinium	A-2
Tab. A-3: Solubility parameters for americium	A-2
Tab. A-4: Solubility parameters for caesium	A-3
Tab. A-5: Solubility parameters for calcium.....	A-3
Tab. A-6: Solubility parameters for californium.....	A-3
Tab. A-7: Solubility parameters for inorganic carbon	A-4
Tab. A-8: Solubility parameters for chlorine	A-4
Tab. A-9: Solubility parameters for curium	A-4
Tab. A-10: Solubility parameters for holmium	A-5
Tab. A-11: Solubility parameters for iodine	A-5
Tab. A-12: Solubility parameters for lead.....	A-5
Tab. A-13: Solubility parameters for molybdenum	A-6
Tab. A-14: Solubility parameters for neptunium	A-6
Tab. A-15: Solubility parameters for nickel.....	A-6
Tab. A-16: Solubility parameters for niobium	A-7
Tab. A-17: Solubility parameters for palladium	A-7
Tab. A-18: Solubility parameters for plutonium.....	A-7
Tab. A-19: Solubility parameters for polonium.....	A-8
Tab. A-20: Solubility parameters for protactinium.....	A-8
Tab. A-21: Solubility parameters for radium	A-8
Tab. A-22: Solubility parameters for samarium.....	A-9
Tab. A-23: Solubility parameters for selenium.....	A-9
Tab. A-24: Solubility parameters for silver	A-9
Tab. A-25: Solubility parameters for strontium.....	A-10
Tab. A-26: Solubility parameters for technetium.....	A-10
Tab. A-27: Solubility parameters for thorium.....	A-10
Tab. A-28: Solubility parameters for tin	A-11
Tab. A-29: Solubility parameters for uranium.....	A-11
Tab. A-30: Solubility parameters for zirconium	A-11

List of Figures

Fig. 1-1:	Chemical elements considered for solubility calculations.....	1
Fig. 4-1:	Distribution of solubility limits in bentonite reference porewater.....	31
Fig. 4-2:	Comparison of present (red bars) solubility limits with those from Berner (2014) (blue bars).....	32

1 Introduction

Solubility limits of safety relevant chemical elements in the bentonite near-field are needed for the safety assessments related to the general license application (Rahmenbewilligungsgesuch – RBG) in the framework of the Sachplan Geologische Tiefenlager (Sectoral Plan for Deep Geological Repositories – SGT) (Bundesamt für Energie 2008) for the planned repository for spent fuel (SF) and high-level (HLW) radioactive waste in Switzerland. The solubility limits describe the maximum amounts of an element dissolving in the pore space solution of the considered chemical reference system (i.e. pore water chemistry).

Solubility calculations were performed with the most recent version of GEM-Selektor v.3.9.4 using the PSI Chemical Thermodynamic Database 2020 (Hummel and Thoenen, 2023) for the 29 elements Ac, Ag, Am, C, Ca, Cf, Cl, Cm, Cs, Ho, I, Mo, Nb, Ni, Np, Pa, Pb, Pd, Po, Pu, Ra, Se, Sm, Sn, Sr, Tc, Th, U, Zr. This list of elements comprises all considered dose-relevant nuclides which have been selected for SF and HLW (NTB 24-19, Appendix C). A graphical summary of all elements considered here is given in Fig. 1-1.

		Radiotoxic										Chemotoxic				Porewater															
		29										4				5															
H																										He					
Li	Be															B	C	N	O	F	Ne										
Na	Mg															Al	Si	P	S	Cl	Ar										
K	Ca															Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr															Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn	Nh	Fl	Mc	Lv	Ts	Og

Fig. 1-1: Chemical elements considered for solubility calculations.

Some elements shown in two colours are chemotoxic and have radioactive isotopes occurring in the list of dose-relevant nuclides for radioactive waste disposal. Likewise, elements can be constituents of ground- and porewaters and also occur in the list of dose-relevant radionuclides.

This study is an update of the solubility limits derived by Berner (2014). Calculation procedures and the structure of this report are based on Berner (2014).

2 Basic data, chemical conditions and methods

2.1 Database and code

The solubility calculations were performed with the most recent version of GEM-Selektor v.3.9.4 (GEMS, <https://gems.web.psi.ch/>) using the PSI Chemical Thermodynamic Database 2020 (TDB 2020, Hummel & Thoenen 2023) as imported by G.D. Miron into the GEMS format.

TDB 2020 contains thermodynamic data for all radionuclides considered in this solubility modelling study and thus, no additional thermodynamic data were needed from other sources.

2.2 Porewater compositions

The solubility limit calculations of the safety considered chemical elements were performed for two variants of bentonite pore waters as selected from the calculations performed by Curti (2023): a reference pore water (E3-BPW-Ref), which is a representative water for the selected siting region at Nördlich Lägern and a variant representing the high pCO₂ concentration (E3-BPW-highpCO₂). The high pCO₂ variant BPW is selected as a bounding case with the highest expected carbonate concentration, which tests the impact of carbonate complexes on the solubility limits in bentonite pore water. These reference pore waters are assumed to exist in equilibrium with the following mineral solids: barite BaSO₄, calcite CaCO₃, dolomite CaMg(CO₃)₂, celestine SrSO₄, kaolinite Al₂Si₂O₅(OH)₄, gypsum CaSO₄·2H₂O, quartz SiO₂, rhodochrosite MnCO₃, magnetite Fe^{II}Fe^{III}₂O₄ and pyrite Fe^{II}S₂. The last two minerals also represent a redox buffer determining the “anoxic” Eh of the pore water.

Tab. 2-1: Geochemical conditions (solids, exchanged cations, porewater composition) for bentonite pore waters

From Curti (2023)

	E3-BPW-Ref	E3-BPW-highpCO₂	
<i>Solutes</i>	<i>Concentration [mol/kg H₂O]</i>		<i>Speciation in solution</i>
Al	2.08 × 10 ⁻⁸	2.39 × 10 ⁻⁸	Al(OH) ₄ ⁻ , Al(OH) ₂ F(aq), Al(OH) ₃ (aq)
Ba	7.18 × 10 ⁻⁸	6.86 × 10 ⁻⁸	Ba ²⁺ , BaSO ₄ (aq)
Ca	1.77 × 10 ⁻²	1.69 × 10 ⁻²	Ca ²⁺ , CaSO ₄ (aq)
Carbonate (inorganic C)	2.94 × 10 ⁻³	4.99 × 10 ⁻³	HCO ₃ ⁻ , NaHCO ₃ (aq)
Chloride (total Cl)	0.239	0.240	Cl ⁻
F	1.74 × 10 ⁻⁴	1.74 × 10 ⁻⁴	F ⁻ , MgF ⁺ , NaF(aq)
Fe	2.09 × 10 ⁻⁵	4.65 × 10 ⁻⁵	Fe ²⁺ , FeSO ₄ (aq), FeCO ₃ (aq)
K	1.83 × 10 ⁻³	1.79 × 10 ⁻³	K ⁺ , KSO ₄ ⁻
Mg	1.02 × 10 ⁻²	9.78 × 10 ⁻³	Mg ²⁺ , MgSO ₄ (aq)
Mn	1.84 × 10 ⁻⁵	1.86 × 10 ⁻⁵	Mn ²⁺ , MnSO ₄ (aq)
Na	0.375	0.366	Na ⁺ , NaSO ₄ ⁻
Si	1.70 × 10 ⁻⁴	1.70 × 10 ⁻⁴	Si(OH) ₄ (aq)

Tab. 2-1: Cont.

	E3-BPW-Ref	E3-BPW-highpCO2	
Sr	1.72×10^{-4}	1.64×10^{-4}	Sr ²⁺ , SrSO ₄ (aq)
Sulphate (total S)	7.85×10^{-2}	8.30×10^{-2}	SO ₄ ²⁻ , Na(SO ₄) ⁻ , Ca(SO ₄)(aq), Mg(SO ₄)(aq)
<i>Exchange Cations</i>	<i>Mass fraction [mol/kg clay]</i>		
BaZ ₂	1.53×10^{-7}	1.52×10^{-7}	
CaZ ₂	3.62×10^{-2}	3.58×10^{-2}	
KZ	1.30×10^{-2}	1.30×10^{-2}	
MgZ ₂	1.91×10^{-2}	1.89×10^{-2}	
NaZ	0.668	0.669	
SrZ ₂	3.68×10^{-4}	3.64×10^{-4}	
<i>System characteristics</i>			
pH	7.24	7.05	
Eh [mV]	-173.0	-159.0	
log ₁₀ pO ₂ [bar]	-2.20	-1.80	
Ionic strength [mol/kg]	0.452	0.453	

2.3 Operational approach for deriving solubilities

During the simulations, the individual elements were “titrated”, i.e., elements are added to the reference system as chlorides, hydroxides, oxides, likewise also as acids or as alkali salts, in order not to disturb the basic chemical system, until a solid precipitated. This solid was taken as the solubility limiting solid for a given element.

Uncertainties of the calculated solubilities were estimated from the uncertainties (\pm values) given in TDB 2020 for the solubility product of the precipitating solid phase and the formation constant of the dominating aqueous species, using Gauss' law of error propagation:

$$(\pm \log_{10}\text{solubility}) = \sqrt{[(\pm \text{solubility product})^2 + (\pm \text{formation constant})^2]}$$

Final upper and lower limits of solubility were then selected (Tab. 4-1, values shown in bold face) such that they encompass both the uncertainties of the reference case and the high pCO₂ bounding case.

The calculations of solubility limits using the GEM-Selektor code have been performed in two steps, using the efficient “all-in-one” approach, verified in our previous report on solubility limits in cement pore waters (Hummel et al. 2022).

At the first stage (preliminary and trial calculations, results not shown), the system definitions for the normative bentonite pore water models (in the present report, E3-BPW-Ref, E3-BPW-h[igh]pCO₂ and (in Appendix) E3-BPW-sal¹) were extended with the full list of elements as defined in the introduction, their respective species and phases. The montmorillonite part of the model was retained without extensions, i.e., it only included main cations of OPA and bentonite pore waters on ion exchange and only protolysis on edge sites, as defined in Curti (2023).

In the model, the additions of dose-relevant elements were adjusted to be as small as possible to still produce stable solids in small amounts (about 10⁻⁶ mol), to minimize the effects on pH, Eh and ionic strength. The elements with conditionally unlimited solubilities were added in amounts up to 10⁻⁴ mol, but only in trial calculations. The pH and pCO₂ were adjusted by adding/subtracting CO₂ to/from the bulk composition recipe. Redox was fixed by adding 1 g of Fe₃O₄+FeS₂ buffer (defined as 1 mol of Fe₃O₄ and 1 mol of FeS₂) with minor addition of oxygen to produce about equal amounts of Fe₃O₄ and FeS₂ in equilibrium. 0.1 g SiO₂ was added to ensure the equilibrium with quartz as assumed in Opalinus clay and bentonite pore water models (Curti 2023).

Trial calculations have been performed to identify the solubility-limiting phases for each element, to check the presence of the main aqueous species, and confirm the absence of limiting solids in equilibrium for Br, Cl, F, Ac, Cf, Cs and I.

It was also found that some solubilities were limited by Ag₂Se(alpha) for Ag and Se, FeSe₂(cr) for Se, with the aqueous speciation for Ag and Se dominated by Ag₂Se(aq) complex. These phases and species were considered as not realistic for the given system and were suppressed in the subsequent calculations by setting upper-bound amount constraints to zero (see Sections 3.22 and 3.23)

At the second stage (and series of system definitions), the elements with “unlimited” solubility (Ac, Cf, Cs, I), i.e., elements without limiting solid phases in the database and which are not part of the porewater definition like Cl) were excluded, and the redox state was fine-tuned by adding O until approximately equal mole amounts of Fe₃O₄(cr) and FeS₂(s) phases were obtained; pCO₂ was fine-tuned by adding/removing CO₂. No adjustment of ionic strength and pH relative to the normative porewater models were necessary to obtain the exact match of pH, Eh, pCO₂ and *I* between the “solubility limits” systems and the normative porewater systems. The results are summarised in Section 3.30 for E3-BPW-Ref, E3-BPW-h[igh]pCO₂ based cases, and in Appendix for the E3-BPW-sal case. The dominating speciation is reported, ranges indicate the interval between reference and high-CO₂ pore water.

¹ The bentonite pore water entitled E3-BPW-sal is representing the highly saline pore OPA porewater measured at the Bülach-1-1 site in the scope of Nagra’s deep drilling campaign, equilibrated with bentonite. The salinity measured at the Bülach-1-1 site is the highest salinity measured across the siting regions (of all drill sites). However, Bülach-1-1 is far outside of the repository perimeter and analysis of the waters from the Stadel-2-1 and Stadel-3-1 sites have indicated that no such high salinities are to be expected in the repository perimeter. Therefore, this saline water for Bülach-1-1 is not considered for safety assessment calculations. However, for completeness and allowing to compare the impact of such elevated chlorine concentrations on the solubility limits of the considered dose relevant nuclides, solubility limits for this water are presented in the appendix.

3 Calculated element solubilities

3.1 Actinium

The only inorganic actinium solid phases discussed in TDB 2020 (Hummel & Thoenen 2023) are $\text{Ac}(\text{OH})_3(\text{fresh})$ and $\text{Ac}(\text{OH})_3(\text{aged})$. The terms “fresh” and “aged” refer to fresh and aged precipitates. The latter solid leads at $\text{pH} > 9$ to two orders of magnitude lower $\text{Ac}(\text{III})$ solubilities than $\text{Ac}(\text{OH})_3(\text{fresh})$. However, even $\text{Ac}(\text{OH})_3(\text{aged})$ completely dissolves at $\text{pH} < 8$, formally resulting in molar $\text{Ac}(\text{III})$ concentrations around $\text{pH} 7$ (Fig. 2.1 in (Hummel & Thoenen, 2023)).

Hence, the solubility of actinium in bentonite pore waters is formally unlimited, and its aqueous speciation consists of AcSO_4^+ (61.1%), Ac^{3+} (34.1%), AcCl^{2+} (3.0%) and AcF^{2+} (1.5%).

Tab. 3-1: Solubility parameters for actinium

	E3-BPW-Ref	E3-BPW-highpCO2
Calculated solubility [mol/kg H ₂ O]	Unlimited	Unlimited
Limiting solid phase	-	-
Uncertainty of solubility product		
Dominating aqueous species	AcSO_4^+	AcSO_4^+
Uncertainty of formation constant	± 0.2	± 0.2
Uncertainty of \log_{10} (solubility)		
Upper limit of solubility [mol/kg H ₂ O]	Unlimited	Unlimited
Lower limit of solubility [mol/kg H ₂ O]	Unlimited	Unlimited

However, comparing these modelling results for $\text{Ac}(\text{III})$ with the results obtained for other three-valent actinides (Am, Cm) and lanthanides (Ho, Sm) it can be seen that in all these systems the solubility limiting solid is a hydroxycarbonate phase and the dominating species are always carbonate complexes (Sections 3.2, 3.8, 3.9, 3.21).

Hummel & Thoenen (2023) did not find any published data concerning $\text{Ac}(\text{III})$ carbonate solid phases or aqueous carbonate complexes, indicating that this system has never been studied.

Thus, the above modelling result is an artefact due to missing crucial thermodynamic data concerning the $\text{Ac}(\text{III})$ carbonate system.

We recommend taking the $\text{Am}(\text{III})/\text{Cm}(\text{III})$ results (see Sections 3.2 and 3.8: E3-BPW-Ref: $1.23 \cdot 10^{-5}$; E3-BPW-highpCO2: $1.72 \cdot 10^{-5}$ [mol/kg H₂O]) as estimates for the solubility of actinium (Tab. 4.1) because of consistency reasons within the three-valent actinides series.

3.2 Americium

The limiting solid phase in the americium system is found to be crystalline Am hydroxycarbonate $\text{AmOHCO}_3 \cdot 0.5\text{H}_2\text{O}(\text{cr})$ ($7.8 \cdot 10^{-8}$ to $1.1 \cdot 10^{-7}$ [mol/kg H₂O]); the closest undersaturated solid is amorphous hydrated Am hydroxycarbonate $\text{AmOHCO}_3(\text{am, hyd})$ with $\log_{10}\text{SI} = -2.2$.

Here the same question arises concerning amorphous versus crystalline Am(III) solid phases as discussed by Hummel et al. (2022) for $\text{Am}(\text{OH})_3(\text{cr})$ vs. $\text{Am}(\text{OH})_3(\text{am})$ in cementitious systems.

Hummel et al. (2022) state that as discussed by Guillaumont et al. (2003), “the thermodynamic properties and hence the solubility of $\text{Am}(\text{OH})_3(\text{s})$ depends on the degree of crystallinity, which can vary with the time of aging. Another important factor is the particle size, which is also affected by aging processes and by self-irradiation from the α -activity of americium, particularly in studies with $^{241}\text{Am}(\text{OH})_3(\text{s})$. The solubility study of Silva (1982) is the only one performed with a crystalline Am(III) hydroxide characterised by X-ray diffraction. The damage by α -radiation was diminished by the use of ^{243}Am ”. Guillaumont et al. (2003) therefore derived a solubility product for $\text{Am}(\text{OH})_3(\text{cr})$ solely based on the study of Silva (1982), and a solubility product for $\text{Am}(\text{OH})_3(\text{am})$ based on concordant results of experimental studies also including measurements using $^{241}\text{Am}(\text{OH})_3(\text{am})$.

^{241}Am with a half-life of 432.8 ± 0.7 years is part of the $4n+1$ series of the actinide decay chains. ^{241}Am will dominate the activity of the $4n+1$ series for about 5'000 years and will disappear after about 100'000 years in the SF/HLW waste inventory.

Hence, we assumed that whatever $\text{AmOHCO}_3 \cdot 0.5\text{H}_2\text{O}(\text{cr})$ may precipitate in the bentonite environment will internally be destroyed by α -radiation of ^{241}Am and $\text{AmOHCO}_3(\text{am, hyd})$ is a realistic representation of the solubility limiting phase of Am.

The recommended solubility of Am is determined by $\text{AmOHCO}_3(\text{am,hyd})$, and the dominating complexes in solution are AmCO_3^+ (44.0% – 48.7%), $\text{AmSiO}(\text{OH})_3^{2+}$ (26.1% – 17.5%), AmSO_4^+ (10.3% – 11.4%), Am^{3+} (7.1% – 7.3%), $\text{Am}(\text{CO}_3)_2^-$ (5.1% – 6.0%) and $\text{Am}(\text{SO}_4)_2^-$ (3.4% – 4.1%) (indicating the range between reference and high-CO₂ pore water).

Tab. 3-2: Solubility parameters for americium

	E3-BPW-Ref	E3-BPW-highpCO2
Calculated solubility [mol/kg H ₂ O]	$1.23 \cdot 10^{-5}$	$1.72 \cdot 10^{-5}$
Limiting solid phase	$\text{AmOHCO}_3(\text{am, hyd})$	$\text{AmOHCO}_3(\text{am, hyd})$
Uncertainty of solubility product	± 1.0	± 1.0
Dominating aqueous species	AmCO_3^+	AmCO_3^+
Uncertainty of formation constant	± 0.4	± 0.4
Uncertainty of \log_{10} (solubility)	± 1.1	± 1.1
Upper limit of solubility [mol/kg H ₂ O]	$1.6 \cdot 10^{-4}$	$2.2 \cdot 10^{-4}$
Lower limit of solubility [mol/kg H ₂ O]	$9.8 \cdot 10^{-7}$	$1.4 \cdot 10^{-6}$

3.3 Caesium

Neither pure limiting solid phases nor aqueous complexes of Cs are known. Thus, the cation Cs^+ is the only species present in solution.

The concentration of Cs in the bentonite environment depends on the waste inventory, the availability of natural Cs, its diffusive fluxes and its sorption to solid phases.

Tab. 3-3: Solubility parameters for caesium

	E3-BPW-Ref	E3-BPW-highCO2
Calculated solubility [mol/kg H ₂ O]	Unlimited	Unlimited
Limiting solid phase	-	-
Uncertainty of solubility product		
Dominating aqueous species	Cs^+	Cs^+
Uncertainty of formation constant		
Uncertainty of log ₁₀ (solubility)		
Upper limit of solubility [mol/kg H ₂ O]	Unlimited	Unlimited
Lower limit of solubility [mol/kg H ₂ O]	Unlimited	Unlimited

3.4 Calcium

Calcium is a major element of the chemical system. Its solubility is controlled by calcite, $\text{CaCO}_3(\text{cr})$; dolomite, $\text{CaMg}(\text{CO}_3)_2$ and gypsum, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$.

The dominant species in solution is Ca^{2+} (ca.69% – 67%). The sulphate complex $\text{CaSO}_4(\text{aq})$ contributes to ca. 31% – 32% (indicating the range between reference and high- CO_2 pore water) and Ca – (bi)carbonate complexes are minor species (< 1%).

Tab. 3-4: Solubility parameters for calcium

	E3-BPW-Ref	E3-BPW-highCO2
Calculated solubility [mol/kg H ₂ O]	$1.77 \cdot 10^{-2}$	$1.69 \cdot 10^{-2}$
Limiting solid phase	Calcite, $\text{CaCO}_3(\text{cr})$	Calcite, $\text{CaCO}_3(\text{cr})$
Uncertainty of solubility product (calcite)	± 0.07	± 0.07
Dominating aqueous species	Ca^{2+}	Ca^{2+}
Uncertainty of formation constant	± 0.18	± 0.18
Uncertainty of log ₁₀ (solubility)	± 0.19	± 0.19
Upper limit of solubility [mol/kg H ₂ O]	$2.7 \cdot 10^{-2}$	$2.6 \cdot 10^{-2}$
Lower limit of solubility [mol/kg H ₂ O]	$1.1 \cdot 10^{-2}$	$1.1 \cdot 10^{-2}$

3.5 Californium

Thermodynamic data for Cf(III) are very scarce and no solid phase data at all are available in TDB 2020 (Hummel & Thoenen, 2023). Thus, californium was not included in the actual chemical system for GEMS calculations.

Hence, the solubility of californium is formally considered unlimited, and its aqueous speciation consists of CfSO_4^+ (65%), Cf^{3+} (32%) and CfF^{2+} (3%).

Tab. 3-5: Solubility parameters for californium

	E3-BPW-Ref	E3-BPW-highpCO2
Calculated solubility [mol/kg H ₂ O]	Unlimited	Unlimited
Limiting solid phase	-	-
Uncertainty of solubility product		
Dominating aqueous species	CfSO_4^+	CfSO_4^+
Uncertainty of formation constant	± 0.4	± 0.4
Uncertainty of \log_{10} (solubility)		
Upper limit of solubility [mol/kg H ₂ O]	Unlimited	Unlimited
Lower limit of solubility [mol/kg H ₂ O]	Unlimited	Unlimited

Hummel & Thoenen (2023) state that “thermodynamic data for californium have mainly been obtained in experimental studies comprising the transplutonium elements americium, curium, berkelium, californium and sometimes even einsteinium. Generally, the differences in the stability constants obtained for these transplutonium elements are small. Considering that Guillaumont et al. (2003) decided to evaluate experimental Am(III) and Cm(III) data together and to select common Am(III)/Cm(III) stability constants, and further considering the small to insignificant difference to the few available Cf(III) data, this review recommends to use modelling results obtained for Am(III)/Cm(III) as a proxy for Cf(III)”.

We agree with this recommendation and have taken the Am(III)/Cm(III) results (Sections 3.2 and 3.8) as estimates for the solubility of californium (Tab. 4.1; E3-BPW-Ref: $1.23 \cdot 10^{-5}$; E3-BPW-highpCO2: $1.72 \cdot 10^{-5}$ [mol/kg H₂O]).

3.6 Inorganic Carbon

Inorganic carbon is present mainly as carbonate, CO_3^{2-} , in the chemical system. Its concentration is determined by the interplay of calcite, dolomite and Mn-carbonate. Its solubility is controlled mainly by calcite, $\text{CaCO}_3(\text{cr})$.

The dominant species in solution are HCO_3^- (77% – 79%), $\text{CO}_2(\text{aq})$ (ca. 7% – 10.5%), CaHCO_3^+ (2.2% – 2.5%), $\text{NaHCO}_3(\text{aq})$ (8.0% – 8.4%), at pH around 7.2.

Tab. 3-6: Solubility parameters for inorganic carbon

	E3-BPW-Ref	E3-BPW-highpCO2
Calculated solubility [mol/kg H ₂ O]	$2.96 \cdot 10^{-3}$	$5.01 \cdot 10^{-3}$
Limiting solid phase	Calcite CaCO ₃ (cr)	Calcite CaCO ₃ (cr)
Uncertainty of solubility product	± 0.07	± 0.07
Dominating aqueous species	HCO ₃ ⁻	HCO ₃ ⁻
Uncertainty of formation constant	± 0.05	± 0.05
Uncertainty of log ₁₀ (solubility)	± 0.09	± 0.09
Upper limit of solubility [mol/kg H ₂ O]	$3.6 \cdot 10^{-3}$	$6.2 \cdot 10^{-3}$
Lower limit of solubility [mol/kg H ₂ O]	$2.4 \cdot 10^{-3}$	$4.1 \cdot 10^{-3}$

3.7 Chlorine

Chlorine is part of the porewater, existing almost exclusively as the chloride anion Cl⁻.

As Hummel (2017) states, chloride forms highly soluble salts with all major and minor components of pore and surface waters; all alkali and alkaline earth elements, iron, manganese, nickel, copper, aluminium. These salts are only important if rock salt is considered as host rock of a geological repository.

The only sparingly soluble phases, also known as naturally occurring minerals, are AgCl (chlorargyrite) and Hg₂Cl₂ (calomel).

However, 98.8 mole% of the ^{108m}Ag inventory is in the L/ILW fraction (Hummel 2017), and ¹⁹⁴Hg is found exclusively in L/ILW waste (Hummel et al. 2022).

Hence, chloride and silver or chloride and mercury will never “meet” in quantities to precipitate as AgCl or Hg₂Cl₂ and ³⁶Cl can be dissolved in “unlimited” quantities in the bentonite environment of SF waste.

Tab. 3-7: Solubility parameters for chlorine

	E3-BPW-Ref	E3-BPW-highpCO2
Calculated solubility [mol/kg H ₂ O]	0.2390*	0.2396*
Limiting solid phase	-	-
Uncertainty of solubility product		
Dominating aqueous species	Cl ⁻	Cl ⁻
Uncertainty of formation constant		
Uncertainty of log ₁₀ (solubility)		
Upper limit of solubility [mol/kg H ₂ O]	Unlimited	Unlimited
Lower limit of solubility [mol/kg H ₂ O]	Unlimited	Unlimited

* Cl⁻ concentration of the pore waters

3.8 Curium

The recommended solubility of Cm is determined by $\text{CmOHCO}_3(\text{am, hyd})$.

The dominant complexes in solution are CmCO_3^+ (44.0% – 48.7%), $\text{CmSiO}(\text{OH})_3^{2+}$ (26.1% – 17.5%), CmSO_4^+ (10.3% – 11.4%), Cm^{3+} (7.1% – 7.3%), $\text{Cm}(\text{CO}_3)_2^-$ (5.1% – 6.0%), and $\text{Cm}(\text{SO}_4)_2^-$ (3.4% – 4.1%). Bicarbonate, chloride, fluoride and hydroxide complexes are minor species under present conditions.

Note that that Guillaumont et al. (2003) decided to evaluate experimental Am(III) and Cm(III) data together and to select common Am(III)/Cm(III) stability constants. Hummel & Thoenen (2023) followed this practice and thus, the thermodynamic data for $\text{CmOHCO}_3(\text{am, hyd})$ and the aqueous Cm complexes are identical with the respective Am data.

Tab. 3-8: Solubility parameters for curium

	E3-BPW-Ref	E3-BPW-highpCO2
Calculated solubility [mol/kg H ₂ O]	$1.23 \cdot 10^{-5}$	$1.72 \cdot 10^{-5}$
Limiting solid phase	$\text{CmOHCO}_3(\text{am, hyd})$	$\text{CmOHCO}_3(\text{am, hyd})$
Uncertainty of solubility product	± 1.0	± 1.0
Dominating aqueous species	CmCO_3^+	CmCO_3^+
Uncertainty of formation constant	± 0.4	± 0.4
Uncertainty of $\log_{10}(\text{solubility})$	± 1.1	± 1.1
Upper limit of solubility [mol/kg H ₂ O]	$1.6 \cdot 10^{-4}$	$2.2 \cdot 10^{-4}$
Lower limit of solubility [mol/kg H ₂ O]	$9.8 \cdot 10^{-7}$	$1.4 \cdot 10^{-6}$

3.9 Holmium

The recommended solubility of Ho is determined by $\text{HoOHCO}_3(\text{cr})$.

The dominant complexes in solution are HoCO_3^+ (49.9% – 49.8%), HoSO_4^+ (26.9% – 26.8%), $\text{Ho}(\text{SO}_4)_2^-$ (12.7% – 13.7%) and Ho^{3+} (6.3% – 5.9%) at pH 7.1 – 7.23. Minor aqueous species are $\text{Ho}(\text{CO}_3)_2^-$, HoF^{2+} , HoOH^{2+} and $\text{Ho}(\text{OH})_2^+$.

Tab. 3-9: Solubility parameters for holmium

	E3-BPW-Ref	E3-BPW-highpCO2
Calculated solubility [mol/kg H ₂ O]	$4.22 \cdot 10^{-7}$	$6.49 \cdot 10^{-7}$
Limiting solid phase	HoOHCO ₃ (cr)	HoOHCO ₃ (cr)
Uncertainty of solubility product	± 2.0	± 2.0
Dominating aqueous species	HoCO ₃ ⁺	HoCO ₃ ⁺
Uncertainty of formation constant	± 0.2	± 0.2
Uncertainty of log ₁₀ (solubility)	± 2.0	± 2.0
Upper limit of solubility [mol/kg H ₂ O]	$4.2 \cdot 10^{-5}$	$6.5 \cdot 10^{-5}$
Lower limit of solubility [mol/kg H ₂ O]	$4.2 \cdot 10^{-9}$	$6.5 \cdot 10^{-9}$

3.10 Iodine

Iodine occurs in aqueous solutions of environmental concern mainly as iodide, I⁻.

As Hummel (2017) states, iodide forms highly soluble salts with all major and minor components of pore and surface waters; all alkali and alkaline earth elements, iron, manganese, nickel, aluminium. By contrast, iodide forms sparingly to slightly soluble solid phases with “soft” metal cations, e.g. Hg₂I₂ and AgI (iodargyrite).

However, 99.9 mole% of the ¹²⁹I inventory is in the SF/HLW fraction while 98.8 mole% of the ^{108m}Ag inventory is in the L/ILW fraction (Hummel 2017); and ¹⁹⁴Hg is found exclusively in L/ILW waste (Hummel et al. 2022).

Hence, iodide and silver or iodide and mercury will never “meet” in quantities to precipitate as AgI or Hg₂I₂ and ¹²⁹I can be dissolved in “unlimited” quantities in the bentonite environment of a SF/HLW repository.

Tab. 3-10: Solubility parameters for iodine

	E3-BPW-Ref	E3-BPW-highpCO2
Calculated solubility [mol/kg H ₂ O]	Unlimited	Unlimited
Limiting solid phase	-	-
Uncertainty of solubility product		
Dominating aqueous species	I ⁻	I ⁻
Uncertainty of formation constant		
Uncertainty of log ₁₀ (solubility)		
Upper limit of solubility [mol/kg H ₂ O]	Unlimited	Unlimited
Lower limit of solubility [mol/kg H ₂ O]	Unlimited	Unlimited

3.11 Lead

Under conditions of bentonite pore water, PbS(s) is the solubility limiting solid phase. Note that galena, PbS, is the most common lead mineral in nature.

The dominating aqueous speciation pattern of Pb is quite rich and includes PbCl^+ (25.3% – 23.8%), $\text{PbSO}_4(\text{aq})$ (16.7% – 16.8%), Pb^{2+} (15.0% – 14.1%), $\text{PbCO}_3(\text{aq})$ (12.2% – 12.3%), $\text{PbCl}_2(\text{aq})$ (11.8% – 11.1%), PbHCO_3^+ (7.1% – 11.0%) and several minor species.

Tab. 3-11: Solubility parameters for lead

	E3-BPW-Ref	E3-BPW-highpCO2
Calculated solubility [mol/kg H ₂ O]	$7.65 \cdot 10^{-9}$	$2.08 \cdot 10^{-8}$
Limiting liquid or solid phase	PbS(s)	PbS(s)
Uncertainty of solubility product	± 0.10	± 0.10
Dominating aqueous species	PbCl^+	PbCl^+
Uncertainty of formation constant	± 0.03	± 0.03
Uncertainty of log ₁₀ (solubility)	± 0.10	± 0.10
Upper limit of solubility [mol/kg H ₂ O]	$9.6 \cdot 10^{-9}$	$2.6 \cdot 10^{-8}$
Lower limit of solubility [mol/kg H ₂ O]	$6.1 \cdot 10^{-9}$	$1.7 \cdot 10^{-8}$

3.12 Molybdenum

The recommended solubility of Mo under bentonite pore water conditions is determined by tugarinovite, MoO₂(cr).

The dominant species in solution is MoO₄²⁻ (100%).

Note that the solubility limiting Mo solid phase is in redox state +IV, while the aqueous Mo species is in redox state +VI.

Tab. 3-12: Solubility parameters for molybdenum

	E3-BPW-Ref	E3-BPW-highpCO2
Calculated solubility [mol/kg H ₂ O]	$6.35 \cdot 10^{-7}$	$3.49 \cdot 10^{-7}$
Limiting liquid or solid phase	MoO ₂ (cr)	MoO ₂ (cr)
Uncertainty of solubility product	± 0.47	± 0.47
Dominating aqueous species	MoO ₄ ²⁻	MoO ₄ ²⁻
Uncertainty of formation constant	± 0.15	± 0.15
Uncertainty of log ₁₀ (solubility)	± 0.5	± 0.5
Upper limit of solubility [mol/kg H ₂ O]	$2.0 \cdot 10^{-6}$	$1.1 \cdot 10^{-6}$
Lower limit of solubility [mol/kg H ₂ O]	$2.0 \cdot 10^{-7}$	$1.1 \cdot 10^{-7}$

3.13 Neptunium

The recommended solubility of Np in bentonite pore water is determined by an amorphous, hydrated neptunium oxide $\text{NpO}_2(\text{am, hyd})$.

The significant complexes in solution are $\text{Np}(\text{OH})_2(\text{CO}_3)_2^{2-}$ (95.2% – 98.9%) and $\text{Np}(\text{OH})_4(\text{aq})$ (1.8% – 4.6%).

Note that both, the solubility limiting Np solid phase and the aqueous Np complexes are in redox state +IV.

Tab. 3-13: Solubility parameters for neptunium

	E3-BPW-Ref	E3-BPW-highpCO2
Calculated solubility [mol/kg H ₂ O]	$2.07 \cdot 10^{-8}$	$5.41 \cdot 10^{-8}$
Limiting solid phase	$\text{NpO}_2(\text{am, hyd})$	$\text{NpO}_2(\text{am, hyd})$
Uncertainty of solubility product	± 0.5	± 0.5
Dominating aqueous species	$\text{Np}(\text{OH})_2(\text{CO}_3)_2^{2-}$	$\text{Np}(\text{OH})_2(\text{CO}_3)_2^{2-}$
Uncertainty of formation constant	± 0.5	± 0.5
Uncertainty of \log_{10} (solubility)	± 0.7	± 0.7
Upper limit of solubility [mol/kg H ₂ O]	$1.0 \cdot 10^{-7}$	$2.7 \cdot 10^{-7}$
Lower limit of solubility [mol/kg H ₂ O]	$4.1 \cdot 10^{-9}$	$1.1 \cdot 10^{-8}$

3.14 Nickel

The recommended solubility of Ni is determined by $\text{NiCO}_3(\text{cr})$.

The dominant complexes in solution are Ni^{2+} (55.6% – 56.9%), $\text{NiSO}_4(\text{aq})$ (27.7% – 30.4%), $\text{NiSiO}(\text{OH})_3^+$ (13.2% – 8.8%) and NiCl^+ (2.8% – 2.9%). at pH 7.0 – 7.3. Other solute complexes are not significant.

Tab. 3-14: Solubility parameters for nickel

	E3-BPW-Ref	E3-BPW-highpCO2
Calculated solubility [mol/kg H ₂ O]	$6.07 \cdot 10^{-5}$	$5.52 \cdot 10^{-5}$
Limiting solid phase	$\text{NiCO}_3(\text{cr})$	$\text{NiCO}_3(\text{cr})$
Uncertainty of solubility product	± 0.18	± 0.18
Dominating aqueous species	Ni^{2+}	Ni^{2+}
Uncertainty of formation constant	± 0.77	± 0.77
Uncertainty of \log_{10} (solubility)	± 0.8	± 0.8
Upper limit of solubility [mol/kg H ₂ O]	$3.8 \cdot 10^{-4}$	$3.5 \cdot 10^{-4}$
Lower limit of solubility [mol/kg H ₂ O]	$9.6 \cdot 10^{-6}$	$8.8 \cdot 10^{-6}$

3.15 Niobium

The solubility of Nb is determined by Nb₂O₅(pr).

The dominant complexes in solution are Nb(OH)₆⁻ (97.5% – 97.6%) and Nb(OH)₇²⁻ (1.5% – 1.4%).

Note that the thermodynamic data for Nb₂O₅(pr) and Nb(OH)₆⁻ were derived from experimental solubility data using a Nb(V) precipitate (Hummel & Thoenen 2023).

Tab. 3-15: Solubility parameters for niobium

	E3-BPW-Ref	E3-BPW-highpCO2
Calculated solubility [mol/kg H ₂ O]	1.08 · 10 ⁻⁶	7.29 · 10 ⁻⁷
Limiting solid phase	Nb ₂ O ₅ (pr)	Nb ₂ O ₅ (pr)
Uncertainty of solubility product	± 0.5	± 0.5
Dominating aqueous species	Nb(OH) ₆ ⁻	Nb(OH) ₆ ⁻
Uncertainty of formation constant	± 0.14	± 0.14
Uncertainty of log ₁₀ (solubility)	± 0.5	± 0.5
Upper limit of solubility [mol/kg H ₂ O]	3.4 · 10 ⁻⁶	2.3 · 10 ⁻⁶
Lower limit of solubility [mol/kg H ₂ O]	3.4 · 10 ⁻⁷	2.3 · 10 ⁻⁷

3.16 Palladium

Elemental palladium Pd(cr) has a large Eh – pH stability field. Hence, the solubility of Pd under bentonite porewater conditions is determined by Pd(cr) and the dominant species in solution is dissolved palladium in redox state zero, Pd(aq).

Pd(cr) is the reference state of palladium, and no uncertainty can be given. The formation constant of Pd(aq) is an estimate with an assumed uncertainty of ± 0.5 log₁₀-units for the equilibrium Pd(cr) ⇌ Pd(aq), as given in TDB 2020 (Hummel & Thoenen 2023).

Tab. 3-16: Solubility parameters for palladium

	E3-BPW-Ref	E3-BPW-highpCO2
Calculated solubility [mol/kg H ₂ O]	$3.12 \cdot 10^{-10}$	$3.12 \cdot 10^{-10}$
Limiting solid phase	Pd(cr)	Pd(cr)
Uncertainty of solubility product	-	-
Dominating aqueous species	Pd(aq)	Pd(aq)
Uncertainty of formation constant	± 0.5	± 0.5
Uncertainty of log ₁₀ (solubility)	± 0.5	± 0.5
Upper limit of solubility [mol/kg H ₂ O]	$9.9 \cdot 10^{-10}$	$9.9 \cdot 10^{-10}$
Lower limit of solubility [mol/kg H ₂ O]	$9.9 \cdot 10^{-11}$	$9.9 \cdot 10^{-11}$

3.17 Plutonium

The recommended solubility of Pu under bentonite porewater conditions is determined by an amorphous, hydrated plutonium oxide PuO₂(am, hyd).

The significant complexes in solution are PuCO₃⁺ (31.0% – 34.7%), PuSO₄⁺ (18.7% – 20.9%), Pu(SO₄)₂⁻ (12.4% – 14.8%), PuSiO(OH)₃²⁺ (21.8% – 14.8%), Pu³⁺ (5.1% – 5.3%), Pu(CO₃)₂⁻ (3.6% – 4.2%) and PuCO₃(OH)₃⁻ (3.8% – 2.1%); other complexes e.g. chloride-, hydroxo-, are minor.

As the stability constant for PuCO₃⁺ is an estimate without an uncertainty given by Hummel & Thoenen (2023), the uncertainty value for PuSO₄⁺ has been used as an estimate for PuCO₃⁺.

Note that the solubility limiting Pu solid phase is in redox state +IV, while all most significant aqueous Pu complexes are in redox state +III.

Tab. 3-17: Solubility parameters for plutonium

	E3-BPW-Ref	E3-BPW-highpCO2
Calculated solubility [mol/kg H ₂ O]	$1.39 \cdot 10^{-8}$	$4.23 \cdot 10^{-8}$
Limiting solid phase	PuO ₂ (am, hyd)	PuO ₂ (am, hyd)
Uncertainty of solubility product	± 0.52	± 0.52
Dominating aqueous species	PuCO ₃ ⁺	PuCO ₃ ⁺
Uncertainty of formation constant	± 0.6	± 0.6
Uncertainty of log ₁₀ (solubility)	± 0.8	± 0.8
Upper limit of solubility [mol/kg H ₂ O]	$8.8 \cdot 10^{-8}$	$2.7 \cdot 10^{-7}$
Lower limit of solubility [mol/kg H ₂ O]	$2.2 \cdot 10^{-9}$	$6.7 \cdot 10^{-9}$

3.18 Polonium

Elemental polonium Po(s) has a large Eh – pH stability field. Hence, the solubility of Po under bentonite porewater conditions is determined by Po(s) and the dominant species in solution is dissolved polonium in redox state zero, Po(aq).

Po(s) is the reference state of polonium, and no uncertainty can be given. The formation constant of Po(aq) is a rough guess, and no uncertainty is provided for this guess in TDB 2020 (Hummel & Thoenen 2023). We assume ± 1.0 log₁₀-units for the formation constant of Po(aq).

Tab. 3-18: Solubility parameters for polonium

	E3-BPW-Ref	E3-BPW-highpCO2
Calculated solubility [mol/kg H ₂ O]	$9.9 \cdot 10^{-8}$	$9.9 \cdot 10^{-8}$
Limiting liquid or solid phase	Po(s)	Po(s)
Uncertainty of solubility product	-	-
Dominating aqueous species	Po(aq)	Po (aq)
Uncertainty of formation constant	± 1.0	± 1.0
Uncertainty of log ₁₀ (solubility)	± 1.0	± 1.0
Upper limit of solubility [mol/kg H ₂ O]	$9.9 \cdot 10^{-7}$	$9.9 \cdot 10^{-7}$
Lower limit of solubility [mol/kg H ₂ O]	$9.9 \cdot 10^{-9}$	$9.9 \cdot 10^{-9}$

3.19 Protactinium

The solubility of Pa is given by an estimate of the upper limit of an active solid phase Pa₂O₅(act), whose solubility product has never been measured (Hummel & Thoenen 2023).

The dominant complexes in solution are PaO(OH)₃(aq) (98%) and PaO(OH)₄⁻ (1%) at pH 7.0 – 7.3.

The calculated solubility represents the upper limit of the Pa solubility at pH 7.0 – 7.3. No data are available for an estimate of the lower limit.

Protactinium generally has an oxidation state of +V.

There are scarce experimental data at pH < 3 concerning the hydrolysis of Pa(IV), and a vague assumption about the solubility product of PaO₂(s) (Hummel & Thoenen 2023).

Hummel & Thoenen (2023) discuss whether this assumption could “at least serve as a rough estimate for calculating the solubility and hydrolysis behaviour of Pa(IV) in environmental systems”. Given no experimental data concerning the solubility of PaO₂(s) and no experimental data at pH > 3 are available, it is difficult to determine an assumption about the stability of the species Pa(OH)₄(aq), which would accompany the above estimate of the solubility product of PaO₂(s).

Consequently, since any assumptions of solubility products of PaO₂(s) in speciation calculations for strongly reducing conditions and pH > 3 would lead to false output and potential underestimation of the solubility of Pa(IV) by orders of magnitude, no estimate for PaO₂(s) is included in TDB 2020 (Hummel & Thoenen 2023).

Tab. 3-19: Solubility parameters for protactinium

	E3-BPW-Ref	E3-BPW-highpCO2
Calculated solubility [mol/kg H ₂ O]	$9.0 \cdot 10^{-8}$	$9.0 \cdot 10^{-8}$
Limiting solid phase	Pa ₂ O ₅ (act)	Pa ₂ O ₅ (act)
Uncertainty of solubility product	-	-
Dominating aqueous species	PaO(OH) ₃ (aq)	PaO(OH) ₃ (aq)
Uncertainty of formation constant	± 0.35	± 0.35
Uncertainty of log ₁₀ (solubility)	-	-
Upper limit of solubility [mol/kg H ₂ O]	$9.0 \cdot 10^{-8}$	$9.0 \cdot 10^{-8}$
Lower limit of solubility [mol/kg H ₂ O]		

3.20 Radium

In clay rock such as OPA or COX, i.e., at near-neutral pH, the solubility of the minor cation Ra depends on the stability of the ternary non-ideal (Sr,Ba,Ra)SO₄ solid solution; the minimum is achieved at temperatures < 20 °C and at ca. 7 – 10% mole fraction of Sr and 90% of Ba (Vinograd et al. 2018a, 2018b).

The reduction of Ra solubility depends on its mole fraction in the solid solution, set by the available inventories of Ba and Ra in the system. As discussed by Curti (2023), the inventory of Ba is up to $5.0 \cdot 10^{-4}$ mol per 1 kg of bentonite containing ca. 0.1175 kg of porewater (or ca. $4.255 \cdot 10^{-3}$ mol Ba per 1 kg of bentonite porewater). So, assuming 1 micromole inventory of Ra per 1 kg of bentonite, and that all Ba reacts to BaSO₄ taking up all that Ra into solid solution, the mole fraction of Ra will be $x_{\text{Ra}} = 1\text{e-}6/(1\text{e-}6+4.255\text{e-}4) = 0.235\%$ or $\log_{10}x_{\text{Ra}} = -2.63$. Taking into account mild non-ideality (in a regular (Ba,Sr)SO₄ solid solution with $W_{\text{Ba-Ra}} = 2.47$, the activity coefficient of RaSO₄ at low concentration tends to $\gamma_{\text{Ra}} = 2.7$ or $\log_{10}\gamma_{\text{Ra}} = 0.43$), the activity of Ra end member in this case will be $\log_{10}a_{\text{Ra}} = -2.63 + 0.43 = -2.2$ or $a_{\text{Ra}} = 0.0063$.

This means that the dilution of Ra in solid solution with BaSO₄ at given inventories of Ba and Ra will decrease the solubility of Ra in bentonite porewater about 160 times relative to the solubility of pure RaSO₄.

The calculated solubility of pure RaSO₄, along with the Ra solubility in equilibrium with the above-considered solid solution, are given in Tab. 3-20.

The recommended solubility is low even in case of pure RaSO₄ in equilibrium (because of relatively high dissolved sulphate molality about 0.08 *m*), and very low if determined by the (Ba,Ra)SO₄ solid solution formation.

The dominant species in bentonite porewater are Ra²⁺ (71.2% – 69.6%) and RaSO₄(aq) (28.4% – 29.7%). The minor species is RaHCO₃⁺ (0.4% – 0.7%).

Tab. 3-20: Solubility parameters for radium

	E3-BPW-Ref	E3-BPW-highpCO2
Calculated solubility of pure RaSO ₄ [mol/kg H ₂ O]	$3.64 \cdot 10^{-8}$	$3.48 \cdot 10^{-8}$
Solubility of Ra in equilibrium with (Ba,Ra)SO ₄ solid solution at $1 \cdot 10^{-6}$ mol Ra added per 1 kg of bentonite (0.1175 kg of bentonite porewater)	$2.3 \cdot 10^{-10}$	$2.2 \cdot 10^{-10}$
Limiting solid phase	RaSO ₄ (cr)	RaSO ₄ (cr)
Uncertainty of solubility product	± 0.3	± 0.3
Dominating aqueous species	Ra ²⁺	Ra ²⁺
Uncertainty of formation constant	± 0.5	± 0.5
Uncertainty of log ₁₀ (solubility)	± 0.6	± 0.6
Upper limit of solubility [mol/kg H ₂ O]	$1.5 \cdot 10^{-7}$	$1.4 \cdot 10^{-7}$
Lower limit of solubility [mol/kg H ₂ O]	$9.1 \cdot 10^{-9}$	$8.7 \cdot 10^{-9}$

3.21 Samarium

The recommended solubility of Sm is determined by SmOHCO₃(cr).

The dominant complexes in solution are SmCO₃⁺ (50.3% – 50.1%), SmSO₄⁺ (27.0% – 26.9%), Sm(SO₄)₂⁻ (12.8% – 13.7%), Sm³⁺ (6.5% – 6.0%), minor species are Sm(CO₃)₂⁻, SmF²⁺, SmOH²⁺.

Tab. 3-21: Solubility parameters for samarium

	E3-BPW-Ref	E3-BPW-highpCO2
Calculated solubility [mol/kg H ₂ O]	$4.19 \cdot 10^{-7}$	$6.46 \cdot 10^{-7}$
Limiting liquid or solid phase	SmOHCO ₃ (cr)	SmOHCO ₃ (cr)
Uncertainty of solubility product	± 1.0	± 1.0
Dominating aqueous species	SmCO ₃ ⁺	SmCO ₃ ⁺
Uncertainty of formation constant	± 0.3	± 0.3
Uncertainty of log ₁₀ (solubility)	± 1.0	± 1.0
Upper limit of solubility [mol/kg H ₂ O]	$4.2 \cdot 10^{-5}$	$6.5 \cdot 10^{-5}$
Lower limit of solubility [mol/kg H ₂ O]	$4.2 \cdot 10^{-9}$	$6.5 \cdot 10^{-9}$

3.22 Selenium

Elemental selenium Se(cr) has a large Eh – pH stability field. Hence, the solubility of selenium under bentonite porewater conditions is determined by Se(cr).

The dominant species in solution is dissolved selenium in redox state zero, Se(aq) (98% – 99%).

Se(cr) is the reference state of selenium, and no uncertainty can be given. The formation constant of Se(aq) is an estimate with an assumed uncertainty of $\pm 1.0 \log_{10}$ -units for the equilibrium $\text{Se(cr)} \rightleftharpoons \text{Se(aq)}$, as given in TDB 2020 (Hummel & Thoenen 2023).

Ferroselite, FeSe₂(cr), has the potential to limit the dissolved selenium concentrations to lower values than currently estimated via $\text{Se(cr)} \rightleftharpoons \text{Se(aq)}$. TDB 2020 contains thermodynamic data for FeSe₂(cr), derived from calorimetric data for the solid, but with a warning not to use this solid in solubility calculations as no data for aqueous Fe(II) selenide complexes are available (Hummel & Thoenen 2023). This lack of aqueous Fe(II) selenide complexes in the model can lead to unrealistically low calculated solubilities, and there is no way to estimate this effect. Hence, FeSe₂(cr) has not been considered in the final stage of the current solubility calculations.

Tab. 3-22: Solubility parameters for selenium

	E3-BPW-Ref	E3-BPW-highpCO2
Calculated solubility [mol/kg H ₂ O]	$1.0 \cdot 10^{-6}$	$1.0 \cdot 10^{-6}$
Limiting liquid or solid phase	Se(cr)	Se(cr)
Uncertainty of solubility product	-	-
Dominating aqueous species	Se(aq)	Se(aq)
Uncertainty of formation constant	± 1.0	± 1.0
Uncertainty of \log_{10} (solubility)	± 1.0	± 1.0
Upper limit of solubility [mol/kg H ₂ O]	$1.0 \cdot 10^{-5}$	$1.0 \cdot 10^{-5}$
Lower limit of solubility [mol/kg H ₂ O]	$1.0 \cdot 10^{-7}$	$1.0 \cdot 10^{-7}$

3.23 Silver

Elemental silver Ag(cr) has a large Eh – pH stability field. Nevertheless, the solubility of silver in bentonite porewater is determined by Ag₂S(cr). However, Ag(cr) is only slightly undersaturated ($\log \text{SI} = -0.13$ to -0.16) (SI means Saturation Index).

The dominant species in solution is dissolved silver in redox state zero, Ag(aq) (100%).

Ag(cr) is the reference state of silver, and no uncertainty can be given. The uncertainty for the formation constant of Ag(aq) is $\pm 0.5 \log_{10}$ -units.

During the first stage of our “all-in-one” calculations Ag₂Se(cr) appeared as the solubility limiting solid for silver (and selenium), with Ag₂Se(aq) as the dominating aqueous species. The thermodynamic data for Ag₂Se(cr) and Ag₂Se(aq) in TDB 2020 were derived from a solubility study (Hummel & Thoenen 2023) and are “in itself” considered reliable.

However, 98.8 mole% of the ^{108m}Ag inventory is in the L/ILW fraction (Hummel 2017), and thus both, Ag and Se will occur as trace elements in bentonite porewater at such low concentration levels that they will, if at all, only occasionally “meet” in space and time in amounts high enough to establish the equilibrium $\text{Ag}_2\text{Se}(\text{cr}) \rightleftharpoons \text{Ag}_2\text{Se}(\text{aq})$. Hence, $\text{Ag}_2\text{Se}(\text{cr})$ and $\text{Ag}_2\text{Se}(\text{aq})$ have not been considered in the final stage of the present solubility calculations.

Tab. 3-23: Solubility parameters for silver

	E3-BPW-Ref	E3-BPW-highpCO2
Calculated solubility [mol/kg H ₂ O]	$2.94 \cdot 10^{-7}$	$2.71 \cdot 10^{-7}$
Limiting liquid or solid phase	$\text{Ag}_2\text{S}(\text{cr})$	$\text{Ag}_2\text{S}(\text{cr})$
Uncertainty of solubility product	± 0.2	± 0.2
Dominating aqueous species	$\text{Ag}(\text{aq})$	$\text{Ag}(\text{aq})$
Uncertainty of formation constant	± 0.5	± 0.5
Uncertainty of \log_{10} (solubility)	± 0.5	± 0.5
Upper limit of solubility [mol/kg H ₂ O]	$9.3 \cdot 10^{-7}$	$8.6 \cdot 10^{-7}$
Lower limit of solubility [mol/kg H ₂ O]	$9.3 \cdot 10^{-8}$	$8.6 \cdot 10^{-8}$

3.24 Strontium

Strontium is a minor element of the clay rock porewater and bentonite chemical system. Its solubility is controlled by celestite $\text{SrSO}_4(\text{cr})$ or $(\text{Ba},\text{Sr})\text{SO}_4$ solid solutions (Vinograd et al. 2018a, 2018b, and references therein).

The dominant species in solution are Sr^{2+} (69.9% – 68.3%) and $\text{SrSO}_4(\text{aq})$ (29.5% – 30.9%); SrHCO_3^+ is minor species (< 1%).

Tab. 3-24: Solubility parameters for strontium

	E3-BPW-Ref	E3-BPW-highpCO2
Calculated solubility [mol/kg H ₂ O]	$1.71 \cdot 10^{-4}$	$1.64 \cdot 10^{-4}$
Limiting solid phase	Celestite, $\text{SrSO}_4(\text{cr})$	Celestite, $\text{SrSO}_4(\text{cr})$
Uncertainty of solubility product	± 0.10	± 0.10
Dominating aqueous species	Sr^{2+}	Sr^{2+}
Uncertainty of formation constant	± 0.14	± 0.14
Uncertainty of \log_{10} (solubility)	± 0.17	± 0.17
Upper limit of solubility [mol/kg H ₂ O]	$2.5 \cdot 10^{-4}$	$2.4 \cdot 10^{-4}$
Lower limit of solubility [mol/kg H ₂ O]	$1.2 \cdot 10^{-4}$	$1.1 \cdot 10^{-4}$

3.25 Technetium

The recommended solubility of Tc is determined by an amorphous, hydrated and aged technetium oxide precipitate, $\text{TcO}_2(\text{am, hyd, aged})$.

The dominant complexes in solution are $\text{TcO}(\text{OH})_2(\text{aq})$ (90.9% – 80.5%), $\text{TcCO}_3(\text{OH})_2(\text{aq})$ (8.0% – 17.9%), minor $\text{TcCO}_3(\text{OH})_3^-$ (1.1% – 1.5%).

As $\text{TcO}(\text{OH})_2(\text{aq})$ is the Tc(IV) “master species” where all other Tc(IV) aqueous complexes are related to, no uncertainty for $\text{TcO}(\text{OH})_2(\text{aq})$ is given in TDB 2020 (Hummel & Thoenen 2023). Instead, the uncertainty value of $\text{TcCO}_3(\text{OH})_2(\text{aq})$ has been used here as an estimate for $\text{TcO}(\text{OH})_2(\text{aq})$.

Note that both, the solubility limiting Tc solid phase and the aqueous Tc complexes are in redox state +IV.

Tab. 3-25: Solubility parameters for technetium

	E3-BPW-Ref	E3-BPW-highpCO2
Calculated solubility [mol/kg H ₂ O]	$2.04 \cdot 10^{-9}$	$2.31 \cdot 10^{-9}$
Limiting solid phase	$\text{TcO}_2(\text{am, hyd, aged})$	$\text{TcO}_2(\text{am, hyd, aged})$
Uncertainty of solubility product	± 0.4	± 0.4
Dominating aqueous species	$\text{TcO}(\text{OH})_2(\text{aq})$	$\text{TcO}(\text{OH})_2(\text{aq})$
Uncertainty of formation constant	± 0.3	± 0.3
Uncertainty of \log_{10} (solubility)	± 0.5	± 0.5
Upper limit of solubility [mol/kg H ₂ O]	$6.5 \cdot 10^{-9}$	$7.3 \cdot 10^{-9}$
Lower limit of solubility [mol/kg H ₂ O]	$6.5 \cdot 10^{-10}$	$7.3 \cdot 10^{-10}$

3.26 Thorium

The recommended solubility of Th is determined by an amorphous, hydrated and aged thorium hydroxide precipitate, $\text{Th}(\text{OH})_4(\text{am, hyd, aged})$.

The dominant complexes in solution are $\text{Th}(\text{OH})_3\text{CO}_3^-$ (48.7% – 52.6%), $\text{Th}(\text{OH})_2(\text{CO}_3)_2^{2-}$ (39.8% – 39.2%), $\text{Th}(\text{OH})_4(\text{aq})$ (8.3% – 4.1%) and $\text{Th}(\text{OH})_2\text{CO}_3(\text{aq})$ (3.0% – 3.6%).

Tab. 3-26: Solubility parameters for thorium

	E3-BPW-Ref	E3-BPW-highpCO2
Calculated solubility [mol/kg H ₂ O]	$1.47 \cdot 10^{-8}$	$2.99 \cdot 10^{-8}$
Limiting solid phase	ThO ₂ (am, hyd, aged)	ThO ₂ (am, hyd, aged)
Uncertainty of solubility product	± 0.9	± 0.9
Dominating aqueous species	Th(OH) ₃ CO ₃ ⁻ , Th(OH) ₂ (CO ₃) ₂ ²⁻	Th(OH) ₂ (CO ₃) ₂ ²⁻ , Th(OH) ₃ CO ₃ ⁻
Uncertainty of formation constant	± 0.7	± 0.7
Uncertainty of log ₁₀ (solubility)	± 1.1	± 1.1
Upper limit of solubility [mol/kg H ₂ O]	$1.9 \cdot 10^{-7}$	$3.8 \cdot 10^{-7}$
Lower limit of solubility [mol/kg H ₂ O]	$1.2 \cdot 10^{-9}$	$2.4 \cdot 10^{-9}$

3.27 Tin

The recommended solubility of Sn is determined by solid SnO₂(cr) (cassiterite). SnO₂(am) has log₁₀SI = -0.84, i.e. it is moderately undersaturated.

The dominant complexes in solution are Sn(OH)₄(aq) (93.8% – 95.9%) and Sn(OH)₅⁻ (6.2% – 4.1%) at pH 7.0 – 7.3.

Tin has an oxidation state of +IV under oxidising conditions but, as discussed by Berner (Berner 2014), the known redox potential of the Sn⁴⁺/Sn²⁺ couple should favour at least aqueous Sn(II) complexes under reducing conditions. However, the complex formation of Sn(IV) with OH⁻ is extremely strong at near-neutral pH and favours Sn(IV) even under reducing conditions.

Tab. 3-27: Solubility parameters for tin

	E3-BPW-Ref	E3-BPW-highpCO2
Calculated solubility [mol/kg H ₂ O]	$8.94 \cdot 10^{-9}$	$8.75 \cdot 10^{-9}$
Limiting solid phase	SnO ₂ (cr)	SnO ₂ (cr)
Uncertainty of solubility product	± 0.11	± 0.11
Dominating aqueous species	Sn(OH) ₄ (aq)	Sn(OH) ₄ (aq)
Uncertainty of formation constant	± 0.69	± 0.69
Uncertainty of log ₁₀ (solubility)	± 0.7	± 0.7
Upper limit of solubility [mol/kg H ₂ O]	$4.5 \cdot 10^{-8}$	$4.4 \cdot 10^{-8}$
Lower limit of solubility [mol/kg H ₂ O]	$1.8 \cdot 10^{-9}$	$1.8 \cdot 10^{-9}$

3.28 Uranium

The recommended equilibrium solubility of U in reference porewater at excess SiO₂(cr) is determined by USiO₄(cr) (coffinite).

The dominating complexes in bentonite pore water are Ca₂UO₂(CO₃)₃(aq) (70.1% – 68.6%), CaUO₂(CO₃)₃²⁻ (21.2% – 22.2%), UO₂(CO₃)₃⁴⁻ (5.6% – 6.3%), MgUO₂(CO₃)₃²⁻ (2.1% – 2.2%) with minor (< 1%) UO₂(CO₃)₂²⁻ and UCO₃(OH)₃⁻.

Grenthe et al. (2020) state that coffinite, USiO₄, is found in nature in igneous and metamorphic rocks and uranium sedimentary deposits. This mineral is expected to be an important alteration product of spent nuclear fuel in contact with silica-bearing aqueous solutions under reducing conditions. In nature coffinite forms fine-grained crystals almost always associated with other minerals, often uraninite, UO₂(cr), quartz and organic matter. Hence, the determination of experimental data from natural samples is questionable. The synthesis of coffinite, either by reaction oxides at high temperatures or by precipitating from aqueous solutions, is faced with several difficulties, presumably because this phase is thermodynamically metastable with respect to quartz and uraninite.

Grenthe et al. (2020) discuss experimental values which have recently been published and come to the conclusion that the problem of precise determination of thermodynamic properties of coffinite is not yet resolved. Grenthe et al. (2020) provide thermodynamic values but state that “these values are given for information only”. These data have been included in TDB 2020 and an uncertainty of one log-unit is assigned to the solubility product.

Note that the solubility limiting U solid phase is in redox state +IV, while all significant aqueous U complexes are in redox state +VI.

Tab. 3-28: Solubility parameters for uranium

	E3-BPW-Ref	E3-BPW-highpCO2
Calculated solubility [mol/kg H ₂ O]	3.09 · 10 ⁻⁸	1.02 · 10 ⁻⁷
Limiting solid phases	USiO ₄ (cr)	USiO ₄ (cr)
Uncertainty of solubility product	± 1.0	± 1.0
Dominating aqueous species	Ca ₂ UO ₂ (CO ₃) ₃ (aq)	Ca ₂ UO ₂ (CO ₃) ₃ (aq)
Uncertainty of formation constant	± 0.4	± 0.4
Uncertainty of log ₁₀ (solubility)	± 1.1	± 1.1
Upper limit of solubility [mol/kg H ₂ O]	3.9 · 10 ⁻⁷	1.3 · 10 ⁻⁶
Lower limit of solubility [mol/kg H ₂ O]	2.5 · 10 ⁻⁹	8.1 · 10 ⁻⁹

3.29 Zirconium

The recommended solubility of Zr is determined by ZrO₂(cr) (baddeleyite).

The dominant complex in solution is Zr(OH)₄(aq) (100%).

Available uncertainties are rather large: ± 1.6 log₁₀-units for the solubility product of the solid phase and ± 1.7 log₁₀-units for the formation constant of the dominating complex.

At near-neutral pH, the solubility of Zr is neither sensitive to $p\text{CO}_2$ nor to complexation with calcium, carbonate or silicate.

Tab. 3-29: Solubility parameters for zirconium

	E3-BPW-Ref	E3-BPW-highCO2
Calculated solubility [mol/kg H ₂ O]	$6.22 \cdot 10^{-10}$	$6.22 \cdot 10^{-10}$
Limiting solid phase	ZrO ₂ (cr)	ZrO ₂ (cr)
Uncertainty of solubility product	± 1.6	± 1.6
Dominating aqueous species	Zr(OH) ₄ (aq)	Zr(OH) ₄ (aq)
Uncertainty of formation constant	± 1.7	± 1.7
Uncertainty of log ₁₀ (solubility)	± 2.3	± 2.3
Upper limit of solubility [mol/kg H ₂ O]	$1.2 \cdot 10^{-7}$	$1.2 \cdot 10^{-7}$
Lower limit of solubility [mol/kg H ₂ O]	$3.1 \cdot 10^{-12}$	$3.1 \cdot 10^{-12}$

3.30 Calculation of all solubilities in one system

The results reported in Sections 3.1 to 3.29 are based on simultaneous calculations in “all-in-one” systems, as described in Section 2. This is possible because most Radionuclide and Fission products solubility limits are quite low ($< 1 \cdot 10^{-6} m$, many even $< 1 \cdot 10^{-9} m$), so it is very unlikely that they would influence each other or the chemical state of bentonite porewater according to Henry’s law (perfectly buffered by clay and accessory minerals) even if all at once added to the same chemical system. So, we were able to obtain the solubility limits for all elements of interest just in three GEM-Selektor calculations for systems E3-BPW-Ref, E3-BPW-h[igh]pCO₂ (and E3-BPW-sal, see Appendix). The results are summarised below in Tables 3-30 to 3-32. In Tables 3-30 and 3-32, “E3-BPW-Ref” key is for the system of the reference bentonite porewater (without dose-relevant radionuclides), and “E3BPWRefRN” key is for the same reference bentonite porewater system, but with minor/trace amounts of dose-relevant radionuclides (RN) added (see Recipe “OPW_E3_SL:G:E3BPWrefRN:1:0:1:25:1:” in Table 3-31). The “E3-BPW-hpCO₂” key is for the system of the high- $p\text{CO}_2$ bentonite porewater model (without dose-relevant radionuclides), and “E3BPWhpCRN” key is for the same high- $p\text{CO}_2$ bentonite porewater system, but with minor/trace amounts of dose-relevant radionuclides added (see Recipe OPW_E3_SL:G:E3BPWhpCRN:1:0:1:25:1: in Table 3-31).

Tab. 3-30: Summary of solubilities computed for E3-BPW-Ref, E3-BPW-h[igh]pCO₂ cases without- and with dose-relevant radionuclides (RN)

Element symbol	E3-BPW-Ref, molal	E3BPWrefRN, molal	E3-BPW-hpCO ₂ , molal	E3BPWhpCRN, molal
Ac		Unlimited		Unlimited
Ag		2.94E-07		2.71E-07
Al	2.08E-08	2.08E-08	2.39E-08	2.39E-08
Am		1.229E-05		1.724E-05
Ba	7.18E-08	7.19E-08	6.86E-08	6.86E-08
Br	9.96E-10	9.96E-10	9.96E-10	9.96E-10
C	2.9446E-03	2.956E-03	4.9911E-03	5.0069E-03
Ca	1.7695E-02	1.7683E-02	1.6930E-02	1.6915E-02
Cf		Unlimited		Unlimited
Cl	2.3901E-01	2.3901E-01	2.3958E-01	2.3958E-01
Cm		1.229E-05		1.724E-05
Cs		Unlimited		Unlimited
F	1.736E-04	1.736E-04	1.735E-04	1.735E-04
Fe	2.087E-05	2.087E-05	4.6525E-05	4.6492E-05
Ho		4.22E-07		6.49E-07
I		Unlimited		Unlimited
K	1.833E-03	1.833E-03	1.789E-3	1.788E-01
Mg	1.0241E-02	1.0232E-02	9.7822E-03	9.7725E-03
Mn	1.84E-05	6.381E-05 *	1.86E-05	6.104E-05 ^A
Mo		6.35E-07		3.49E-07
Na	3.75091E-01	3.74972E-01	3.66469E-01	3.66335E-01
Nb		1.08E-06		7.29E-07
Ni		6.065E-05		5.524E-05
Np		2.07E-08		5.41E-08
Pa		9.01E-08		9.03E-08
Pb		7.65E-09		2.08E-08
Pd		3.12E-10		3.12E-10
Po		9.88E-08		9.88E-08
Pu		1.39E-08		4.23E-08
Ra		3.64E-08		3.48E-08
S	7.8547E-02	7.8577E-02	8.3006E-02	8.3011E-02
Se		1.01E-06		9.98E-07
Si	1.697E-04	1.8097E-04	1.696E-04	1.7748E-04
Sm		4.19E-07		6.46E-07

Tab. 3-30: Cont.

Element symbol	E3-BPW-Ref, molal	E3BPWrefRN, molal	E3-BPW-hpCO ₂ , molal	E3BPWhpCRN, molal
Sn		8.94E-09		8.75E-09
Sr	1.716E-04	1.714E-04	1.642E-04	1.639E-04
Tc		2.04E-09		2.31E-09
Th		1.47E-08		2.99E-08
U		3.09E-08		1.02E-07
Zr		6.22E-10		6.22E-10

* Assuming that redox state is controlled by minerals Fe₃O₄(cr), FeS₂(cr), and MnCO₃(cr).

Tab. 3-31: GEM-Selektor recipes for all-in-one systems

Small amounts of BaSO₄ and SrSO₄ were added to ensure dissolved Ba and Sr in equilibrium with barite and strontianite, respectively.

Recipe: OPW_E3_SL:G:E3BPWrefRN:1:0:1:25:1:				Recipe: OPW_E3_SL:G:E3BPWhpCRN:1:0:1:25:1:			
Property	Compos Name	Quantity	Units	Property	Compos Name	Quantity	Units
xa_	BaSO ₄	1.00E-07	M	xa_	BaSO ₄	1.00E-07	M
xa_	CO ₂	2.00E-05	M	xa_	CO ₂	2.00E-05	M
xa_	E3-BPW-Ref	1	M	xa_	E3-BPW-hpCO ₂	1	M
xa_	RedoxMtPy	1	g	xa_	RedoxMtPy	1	g
xa_	SiO ₂	0.1	g	xa_	SiO ₂	0.1	g
xa_	SrSO ₄	1.00E-06	M	xa_	SrSO ₄	1.00E-06	M
xa_	UO ₂	2.00E-05	M	xa_	UO ₂	2.00E-05	M
bi_	Ag	3.00E-07	M	bi_	Ag	3.00E-07	M
bi_	Al	2.00E-08	M	bi_	Al	2.00E-08	M
bi_	Am	2.00E-08	M	bi_	Am	2.00E-06	M
bi_	Cm	2.00E-06	M	bi_	Cm	2.00E-06	M
bi_	Ho	1.00E-07	M	bi_	Ho	1.00E-07	M
bi_	Mn	1.00E-05	M	bi_	Mn	1.00E-05	M
bi_	Mo	2.00E-07	M	bi_	Mo	2.00E-07	M
bi_	N_atm	-5.00E-06	M	bi_	N_atm	-5.00E-06	M
bi_	Nb	1.00E-06	M	bi_	Nb	1.00E-06	M
bi_	Ni	1.00E-05	M	bi_	Ni	1.00E-05	M
bi_	Np	3.00E-08	M	bi_	Np	3.00E-08	M
bi_	O	3.00E-05	M	bi_	O	3.00E-05	M
bi_	Pa	1.00E-07	M	bi_	Pa	1.00E-07	M
bi_	Pb	1.00E-08	M	bi_	Pb	1.00E-08	M
bi_	Pd	1.00E-09	M	bi_	Pd	1.00E-09	M

Tab. 3-31: Cont.

Recipe: OPW_E3_SL:G:E3BPWrefRN:1:0:1:25:1:				Recipe: OPW_E3_SL:G:E3BPWhpCRN:1:0:1:25:1:			
Property	Compos Name	Quantity	Units	Property	Compos Name	Quantity	Units
bi_	Po	1.00E-07	M	bi_	Po	1.00E-07	M
bi_	Pu	1.00E-08	M	bi_	Pu	1.00E-08	M
bi_	Ra	2.00E-08	M	bi_	Ra	2.00E-08	M
bi_	Se	1.00E-06	M	bi_	Se	1.00E-06	M
bi_	Sm	1.00E-07	M	bi_	Sm	1.00E-07	M
bi_	Sn	1.00E-08	M	bi_	Sn	1.00E-08	M
bi_	Tc	1.00E-09	M	bi_	Tc	1.00E-09	M
bi_	Th	1.00E-08	M	bi_	Th	1.00E-08	M
bi_	Zr	1.00E-09	M	bi_	Zr	1.00E-09	M
dul_	Ag2Se(aq)	0	M	dul_	Ag2Se(aq)	0	M
dul_	Ag2Se(alpha)	0	M	dul_	Ag2Se(alpha)	0	M
dul_	Am(OH)3(cr)	0	M	dul_	Am(OH)3(cr)	0	M
dul_	FeSe2(cr)	0	M	dul_	FeSe2(cr)	0	M
dul_	Smectite_MX80	0	M	dul_	Smectite_MX80	0	M
				xa_ : Compos object quantity to add			
				bi_ : IComp object quantity to add			
				dul_ : Upper bound on amount of DComp			

Tab. 3-32: Properties of aqueous solution for the E3-BPW-Ref, E3-BPW-h[igh]pCO2 systems without- and with dose-relevant radionuclides (RN)

Property	E3-BPW-Ref	E3BPWrefRN	E3-BPW-hpCO2	E3BPWhpCRN
pH	7.235	7.235	7.050	7.050
Eh,mV	-173	-173	-159	-159
IS,molal	0.452	0.452	0.453	0.453
log ₁₀ (pCO ₂)	-2.202	-2.202	-1.800	-1.800

As seen in Tab. 3-32, the overall conditions in all-in-one calculations with dose-relevant radionuclides (RN) were obtained the same as in the respective reference bentonite porewater models without RN. In Tab. 3-31, the loadings for all RN elements were set just slightly more than sufficient to reach precipitation of small amounts of respective condensed phases.

4 Summary and conclusions

Solubility limits for the 29 chemical elements Ac, Ag, Am, C, Ca, Cf, Cl, Cm, Cs, Ho, I, Mo, Nb, Ni, Np, Pa, Pb, Pd, Po, Pu, Ra, Se, Sm, Sn, Sr, Tc, Th, U, Zr have been calculated in bentonite porewater using the PSI Chemical Thermodynamic Database 2020 (TDB 2020) (Hummel & Thoenen 2023).

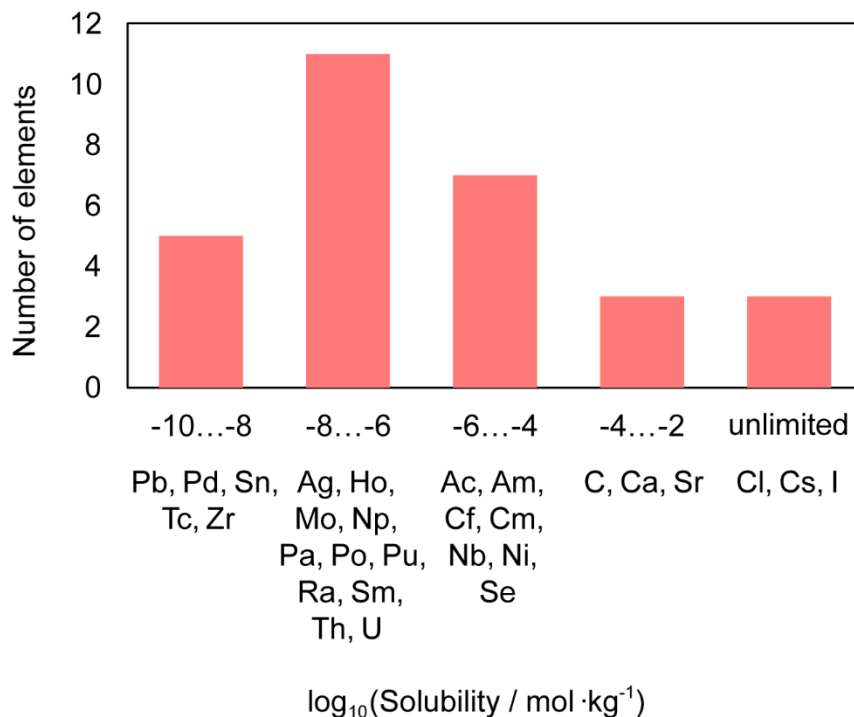


Fig. 4-1: Distribution of solubility limits in bentonite reference porewater

Fig. 4-1 summarises the results obtained for the reference bentonite pore water E3-BPW-Ref (Tab. 4-1, leftmost column).

Generally, the calculated solubilities are very low, 16 out of the 29 elements exhibit maximum solubilities below the micromolar range, i.e., $< 10^{-6}$ mol/kg H₂O.

Nb and Se are close to micromolar solubility, while Am (and the chemical analogues Ac, Cm and Cf) dissolves in ten micromolar amounts and Ni reaches 60 micromolar solubility.

The solubilities of Ca, Sr and inorganic carbon are determined by the definition of the porewater itself.

Cs, Cl and I are chemically “unlimited”, i.e., their concentration in the porewater is only limited by radioisotope inventory in the waste and the availability of stable isotopes in the bentonite environment (Hummel 2017).

The results obtained in this modelling study are compared with those obtained by Berner (Berner 2014). Generally, good agreements between the data provided by Berner (Berner 2014) and the new results are observed (Fig. 4-2). However, a few elements where deviations are observed are worthwhile to mention.

The large ambiguity in the thermodynamic data of Ag and Pd, discussed by Berner (2014) and shown in Fig. 4-2 as bars extending over many orders of magnitude, has now been resolved by an extensive review of Ag and Pd data for TDB 2020 (Hummel & Thoenen 2023).

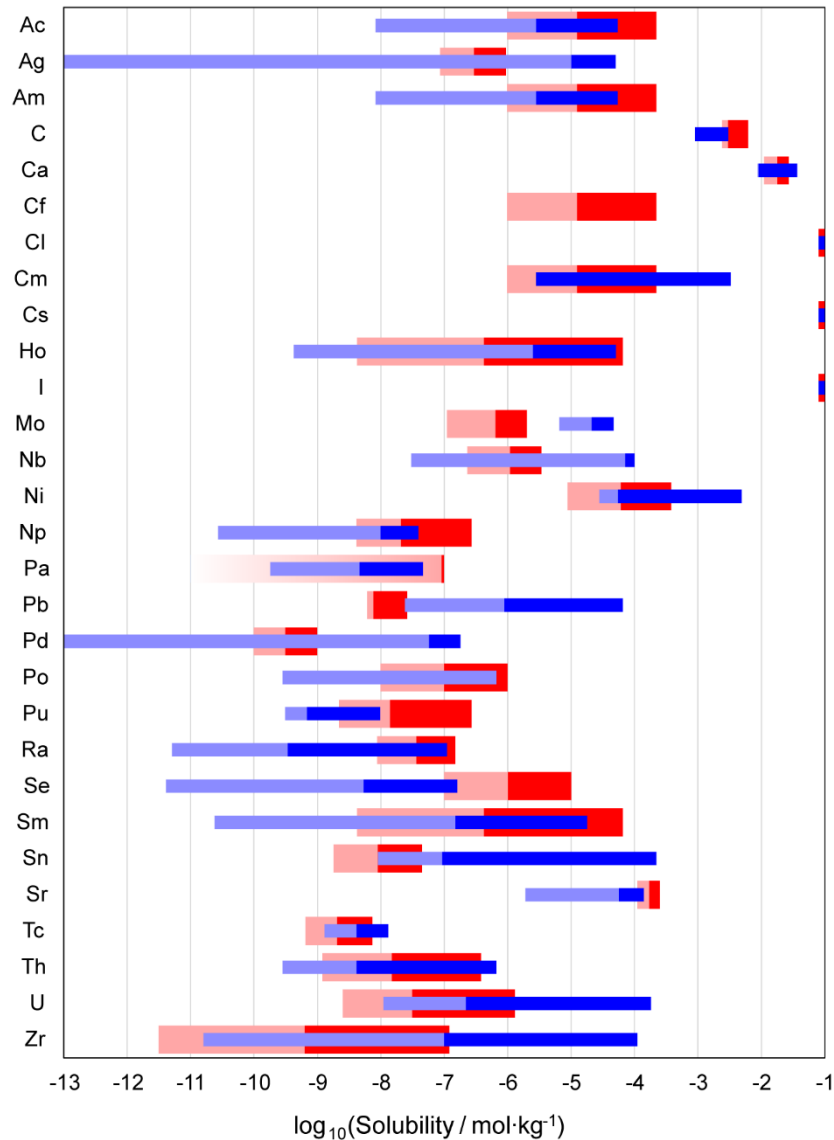


Fig. 4-2: Comparison of present (red bars) solubility limits with those from Berner (2014) (blue bars)

The results of the present modelling study are shown as red bars and those of Berner (2014) as blue bars. The length of the bar represents the range between lower and upper limiting values. The “interface” between the light and strong colour indicates the calculated or recommended value. “Unlimited” solubilities are arbitrarily shown as small bars at $\log_{10}(\text{Solubility}) = -1$. For details see text.

Likewise, extensive data reviews of Mo, Nb, Pb, Po and Se data for TDB 2020 have led to reduced uncertainties and sometimes different recommended values.

No progress has been made concerning Pa. Just an upper limit can be given for its solubility and the lack of data is symbolised in Fig. 4-2 by a fading bar towards lower values.

A summary of the 29 chemical element solubilities for E3-BPW-Ref and E3-BPW-h[igh]pCO₂ including lower and upper limits is given in Tab. 4-1.

Tab. 4-1: Summary of element solubilities including lower and upper limits

The lowest and highest values for lower and upper limits, respectively, are shown in boldface.

	E3-BPW-Ref			E3-BPW-h[igh]pCO2		
	Calculated [mol/kg H ₂ O]	Lower limit [mol/kg H ₂ O]	Upper limit [mol/kg H ₂ O]	Calculated [mol/kg H ₂ O]	Lower limit [mol/kg H ₂ O]	Upper limit [mol/kg H ₂ O]
Ac	1.23 · 10 ⁻⁵	9.8 · 10⁻⁷	1.6 · 10 ⁻⁴	1.72 · 10 ⁻⁵	1.4 · 10 ⁻⁶	2.2 · 10⁻⁴
Ag	2.94 · 10 ⁻⁷	9.3 · 10 ⁻⁸	9.3 · 10⁻⁷	2.71 · 10 ⁻⁷	8.6 · 10⁻⁸	8.6 · 10 ⁻⁷
Am	1.23 · 10 ⁻⁵	9.8 · 10⁻⁷	1.6 · 10 ⁻⁴	1.72 · 10 ⁻⁵	1.4 · 10 ⁻⁶	2.2 · 10⁻⁴
C_{inorg}	2.96 · 10 ⁻³	2.4 · 10⁻³	3.6 · 10 ⁻³	5.01 · 10 ⁻³	4.1 · 10 ⁻³	6.2 · 10⁻³
Ca	1.77 · 10 ⁻²	1.1 · 10⁻²	2.7 · 10⁻²	1.69 · 10 ⁻²	1.1 · 10 ⁻²	2.6 · 10 ⁻²
Cf*	1.23 · 10 ⁻⁵	9.8 · 10⁻⁷	1.6 · 10⁻⁴	1.72 · 10⁻⁵	1.4 · 10⁻⁶	2.2 · 10⁻⁴
Cl	0.2390	Unlimited	Unlimited	0.2396	Unlimited	Unlimited
Cm	1.23 · 10 ⁻⁵	9.8 · 10⁻⁷	1.6 · 10 ⁻⁴	1.72 · 10 ⁻⁵	1.4 · 10 ⁻⁶	2.2 · 10⁻⁴
Cs	Unlimited	Unlimited	Unlimited	Unlimited	Unlimited	Unlimited
Ho	4.22 · 10 ⁻⁷	4.2 · 10⁻⁹	4.2 · 10 ⁻⁵	6.49 · 10 ⁻⁷	6.5 · 10 ⁻⁹	6.5 · 10⁻⁵
I	Unlimited	Unlimited	Unlimited	Unlimited	Unlimited	Unlimited
Mo	6.35 · 10 ⁻⁷	2.0 · 10 ⁻⁷	2.0 · 10⁻⁶	3.49 · 10 ⁻⁷	1.1 · 10⁻⁷	1.1 · 10 ⁻⁶
Nb	1.08 · 10 ⁻⁶	3.4 · 10 ⁻⁷	3.4 · 10⁻⁶	7.29 · 10 ⁻⁷	2.3 · 10⁻⁷	2.3 · 10 ⁻⁶
Ni	6.07 · 10 ⁻⁵	9.6 · 10 ⁻⁶	3.8 · 10⁻⁴	5.52 · 10 ⁻⁵	8.8 · 10⁻⁶	3.5 · 10 ⁻⁴
Np	2.07 · 10 ⁻⁸	4.1 · 10⁻⁹	1.0 · 10 ⁻⁷	5.41 · 10 ⁻⁸	1.1 · 10 ⁻⁸	2.7 · 10⁻⁷
Pa	9.0 · 10 ⁻⁸		9.0 · 10⁻⁸	9.0 · 10 ⁻⁸		9.0 · 10 ⁻⁸
Pb	7.65 · 10 ⁻⁹	6.1 · 10⁻⁹	9.6 · 10 ⁻⁹	2.08 · 10 ⁻⁸	1.7 · 10 ⁻⁸	2.6 · 10⁻⁸
Pd	3.12 · 10 ⁻¹⁰	9.9 · 10⁻¹¹	9.9 · 10⁻¹⁰	3.12 · 10 ⁻¹⁰	9.9 · 10 ⁻¹¹	9.9 · 10 ⁻¹⁰
Po	9.9 · 10 ⁻⁸	9.9 · 10⁻⁹	9.9 · 10⁻⁷	9.9 · 10 ⁻⁸	9.9 · 10 ⁻⁹	9.9 · 10 ⁻⁷
Pu	1.39 · 10 ⁻⁸	2.2 · 10⁻⁹	8.8 · 10 ⁻⁸	4.23 · 10 ⁻⁸	6.7 · 10 ⁻⁹	2.7 · 10⁻⁷
Ra	3.64 · 10 ⁻⁸	9.1 · 10 ⁻⁹	1.5 · 10⁻⁷	3.48 · 10 ⁻⁸	8.7 · 10⁻⁹	1.4 · 10 ⁻⁷
Se	1.0 · 10 ⁻⁶	1.0 · 10⁻⁷	1.0 · 10⁻⁵	1.0 · 10 ⁻⁶	1.0 · 10 ⁻⁷	1.0 · 10 ⁻⁵
Sm	4.19 · 10 ⁻⁷	4.2 · 10⁻⁹	4.2 · 10 ⁻⁵	6.46 · 10 ⁻⁷	6.5 · 10 ⁻⁹	6.5 · 10⁻⁵
Sn	8.94 · 10 ⁻⁹	1.8 · 10⁻⁹	4.5 · 10⁻⁸	8.75 · 10 ⁻⁹	1.8 · 10 ⁻⁹	4.4 · 10 ⁻⁸
Sr	1.71 · 10 ⁻⁴	1.2 · 10 ⁻⁴	2.5 · 10⁻⁴	1.64 · 10 ⁻⁴	1.1 · 10⁻⁴	2.4 · 10 ⁻⁴
Tc	2.04 · 10 ⁻⁹	6.5 · 10⁻¹⁰	6.5 · 10 ⁻⁹	2.31 · 10 ⁻⁹	7.3 · 10 ⁻¹⁰	7.3 · 10⁻⁹
Th	1.47 · 10 ⁻⁸	1.2 · 10⁻⁹	1.9 · 10 ⁻⁷	2.99 · 10 ⁻⁸	2.4 · 10 ⁻⁹	3.8 · 10⁻⁷
U	3.09 · 10 ⁻⁸	2.5 · 10⁻⁹	3.9 · 10 ⁻⁷	1.02 · 10 ⁻⁷	8.1 · 10 ⁻⁹	1.3 · 10⁻⁶
Zr	6.22 · 10 ⁻¹⁰	3.1 · 10⁻¹²	1.2 · 10⁻⁷	6.22 · 10 ⁻¹⁰	3.1 · 10 ⁻¹²	1.2 · 10 ⁻⁷

* Solubility limits for Cf are assumed by analogy with trivalent actinides Am and Cm.

5 References

- Berner, U. (2014): Solubility of Radionuclides in a Bentonite Environment for Provisional Safety Analyses for SGT-E2. Nagra Technical Report NTB 14-06.
- Bundesamt für Energie (2008): Sachplan Geologische Tiefenlager: Konzeptteil. BFE 2. April 2008 (Revision vom 30. November 2011). Departement für Umwelt, Verkehr, Energie und Kommunikation UVEK, Bern.
- Curti, E. (2023): Bentonite pore waters (BPW) for the Sectoral Plan, phase SGT-3: Model development, testing and final calculations. Nagra Work Report NAB 22-43, Wettingen, Switzerland.
- Grenthe, I., Gaona, X., Plyasunov, A.V., Rao, L., Runde, W.H., Grambow, B., Konings, R.J.M., Smith, A.L. & Moore, E.E. (2020): Second Update on the Chemical Thermodynamics of Uranium, Neptunium, Plutonium, Americium and Technetium. Chemical Thermodynamics, Vol. 14. OECD Publications, Paris, France, 1503 pp.
- Guillaumont, R., Fanghänel, T., Fuger, J., Grenthe, I., Neck, V., Palmer, D.A. & Rand, M.H. (2003): Update on the Chemical Thermodynamics of Uranium, Neptunium, Plutonium, Americium and Technetium. Chemical Thermodynamics, Vol. 5. Elsevier, Amsterdam, 919 pp.
- Hummel, W. (2017): Chemistry of selected dose-relevant radionuclides. Nagra Technical Report NTB 17-05.
- Hummel, W., Kulik, D.A. & Miron, G.D. (2022): Solubility of radionuclides and influence of EDTA for use in the development of the cement sorption database (SDB 2022). Nagra Arbeitsbericht NAB 22-38.
- Hummel, W. & Thoenen, T. (2023): The PSI Chemical Thermodynamic Database 2020. Nagra Technical Report NTB 21-03.
- Silva, R.J. (1982): The solubilities of crystalline neodymium and americium trihydroxides. Lawrence Berkeley Laboratory, Report LBL-15055, 57 pp.
- Vinograd, V.L., Kulik, D.A., Brandt, F., Klinkenberg, M., Weber, J., Winkler, B. & Bosbach, D. (2018a): Thermodynamics of the solid solution – aqueous solution system (Ba,Sr,Ra)SO₄ + H₂O: I. The effect of strontium content on radium uptake by barite. Applied Geochemistry 89, 59-74
- Vinograd, V.L., Kulik, D.A., Brandt, F., Klinkenberg, M., Weber, J., Winkler, B. & Bosbach, D. (2018b): Thermodynamics of the solid solution – aqueous solution system (Ba,Sr,Ra)SO₄ + H₂O: II. Radium retention in barite-type minerals at elevated temperatures. Applied Geochemistry 93, 190-208

App. A Solubility limits for a saline bentonite porewater

A bentonite pore water entitled “E3-BPW-sal” is representing the highly saline OPA porewater measured at the Bülach-1-1 site in the scope of Nagra’s deep drilling campaign, equilibrated with bentonite. The salinity measured at the Bülach-1-1 site is the highest salinity measured across the siting regions (of in all drill sites). However, Bülach-1-1 is far outside of the repository perimeter and analysis of the waters from the Stadel-2-1 and 3-1 sites have indicated that no such high salinities are to be expected in the repository perimeter. Therefore, this saline water for Bülach-1-1 is not considered for safety assessment calculations. However, for the sake of completeness and allowing to compare the impact of such elevated chlorine concentrations on the solubility limits of the considered dose relevant nuclides, solubility limits for this water are presented here (Tables A-2 to A-30), together with the results for the reference bentonite pore water “E3-BPW-Ref” for comparison.

Tab. A-1: Geochemical conditions (solids, exchanged cations, porewater composition) for bentonite pore waters

	E3-BPW-Ref	E3-BPW-sal	
<i>Solutes</i>	<i>Concentration [mol/kg H₂O]</i>		<i>Speciation in solution</i>
Al	2.08×10^{-8}	2.21×10^{-8}	Al(OH) ₄ ⁻ , Al(OH) ₂ F(aq), Al(OH) ₃ (aq)
Ba	7.18×10^{-8}	1.13×10^{-7}	Ba ²⁺ , BaSO ₄ (aq)
Ca	1.77×10^{-2}	2.70×10^{-2}	Ca ²⁺ , CaSO ₄ (aq)
Carbonate (inorganic C)	2.94×10^{-3}	1.20×10^{-3}	HCO ₃ ⁻ , NaHCO ₃ (aq)
Chloride (total Cl)	0.239	0.405	Cl ⁻
F	1.74×10^{-4}	1.70×10^{-4}	F ⁻ , MgF ⁺ , NaF(aq)
Fe	2.09×10^{-5}	8.55×10^{-6}	Fe ²⁺ , FeSO ₄ (aq), FeCO ₃ (aq)
K	1.83×10^{-3}	2.41×10^{-3}	K ⁺ , KSO ₄ ⁻
Mg	1.02×10^{-2}	1.56×10^{-2}	Mg ²⁺ , MgSO ₄ (aq)
Mn	1.84×10^{-5}	1.83×10^{-5}	Mn ²⁺ , MnSO ₄ (aq)
Na	0.375	0.496	Na ⁺ , NaSO ₄ ⁻
Si	1.70×10^{-4}	1.66×10^{-4}	Si(OH) ₄ (aq)
Sr	1.72×10^{-4}	2.63×10^{-4}	Sr ²⁺ , SrSO ₄ (aq)
Sulphate (total S)	7.85×10^{-2}	5.91×10^{-2}	SO ₄ ²⁻ , Na(SO ₄) ⁻ , Ca(SO ₄) ₂ (aq), Mg(SO ₄) ₂ (aq)
<i>Exchange Cations</i>	<i>Mass fraction [mol/kg clay]</i>		
BaZ ₂	1.53×10^{-7}	1.47×10^{-7}	
CaC ₂	3.62×10^{-2}	3.50×10^{-2}	
KZ	1.30×10^{-2}	1.30×10^{-2}	
MgZ ₂	1.91×10^{-2}	1.85×10^{-2}	

Tab. A-1: Cont.

	E3-BPW-Ref	E3-BPW-sal	
NaZ	0.668	0.671	
SrZ ₂	3.68×10^{-4}	3.52×10^{-4}	
System characteristics			
pH	7.24	7.42	
Eh [mV]	-173.0	-189.0	
log ₁₀ pO ₂ [bar]	-2.20	-2.80	
Ionic strength [mol/kg]	0.452	0.592	

Tab. A-2: Solubility parameters for actinium

	E3-BPW-Ref	E3-BPW-sal
Calculated solubility [mol/kg H ₂ O]	Unlimited	Unlimited
Limiting solid phase	-	-
Uncertainty of solubility product		
Dominating aqueous species	AcSO ₄ ⁺	AcSO ₄ ⁺
Uncertainty of formation constant	± 0.2	± 0.2
Uncertainty of log ₁₀ (solubility)		
Upper limit of solubility [mol/kg H ₂ O]	Unlimited	Unlimited
Lower limit of solubility [mol/kg H ₂ O]	Unlimited	Unlimited

Tab. A-3: Solubility parameters for americium

	E3-BPW-Ref	E3-BPW-sal
Calculated solubility [mol/kg H ₂ O]	$1.23 \cdot 10^{-5}$	$1.16 \cdot 10^{-5}$
Limiting solid phase	AmOHCO ₃ (am,hyd)	AmOHCO ₃ (am,hyd)
Uncertainty of solubility product	± 1.0	± 1.0
Dominating aqueous species	AmCO ₃ ⁺	AmSiO(OH) ₃ ²⁺
Uncertainty of formation constant	± 0.4	± 0.5
Uncertainty of log ₁₀ (solubility)	± 1.1	± 1.1
Upper limit of solubility [mol/kg H ₂ O]	$1.6 \cdot 10^{-4}$	$1.5 \cdot 10^{-4}$
Lower limit of solubility [mol/kg H ₂ O]	$9.8 \cdot 10^{-7}$	$9.2 \cdot 10^{-7}$

Tab. A-4: Solubility parameters for caesium

	E3-BPW-Ref	E3-BPW-sal
Calculated solubility [mol/kg H ₂ O]	Unlimited	Unlimited
Limiting solid phase	-	-
Uncertainty of solubility product		
Dominating aqueous species	Cs ⁺	Cs ⁺
Uncertainty of formation constant		
Uncertainty of log ₁₀ (solubility)		
Upper limit of solubility [mol/kg H ₂ O]	Unlimited	Unlimited
Lower limit of solubility [mol/kg H ₂ O]	Unlimited	Unlimited

Tab. A-5: Solubility parameters for calcium

	E3-BPW-Ref	E3-BPW-sal
Calculated solubility [mol/kg H ₂ O]	$1.77 \cdot 10^{-2}$	$2.70 \cdot 10^{-2}$
Limiting solid phase	Calcite, CaCO ₃ (cr)	Calcite, CaCO ₃ (cr)
Uncertainty of solubility product	± 0.07	± 0.07
Dominating aqueous species	Ca ²⁺	Ca ²⁺
Uncertainty of formation constant	± 0.18	± 0.18
Uncertainty of log ₁₀ (solubility)	± 0.19	± 0.19
Upper limit of solubility [mol/kg H ₂ O]	$2.7 \cdot 10^{-2}$	$4.2 \cdot 10^{-2}$
Lower limit of solubility [mol/kg H ₂ O]	$1.1 \cdot 10^{-2}$	$1.7 \cdot 10^{-2}$

Tab. A-6: Solubility parameters for californium

	E3-BPW-Ref	E3-BPW-sal
Calculated solubility [mol/kg H ₂ O]	Unlimited	Unlimited
Limiting solid phase	-	-
Uncertainty of solubility product		
Dominating aqueous species	CfSO ₄ ⁺	CfSO ₄ ⁺
Uncertainty of formation constant	± 0.4	± 0.4
Uncertainty of log ₁₀ (solubility)		
Upper limit of solubility [mol/kg H ₂ O]	Unlimited	Unlimited
Lower limit of solubility [mol/kg H ₂ O]	Unlimited	Unlimited

Tab. A-7: Solubility parameters for inorganic carbon

	E3-BPW-Ref	E3-BPW-sal
Calculated solubility [mol/kg H ₂ O]	$2.96 \cdot 10^{-3}$	$1.21 \cdot 10^{-3}$
Limiting solid phase	Calcite CaCO ₃ (cr)	Calcite CaCO ₃ (cr)
Uncertainty of solubility product	± 0.07	± 0.07
Dominating aqueous species	HCO ₃ ⁻	HCO ₃ ⁻
Uncertainty of formation constant	± 0.05	± 0.05
Uncertainty of log ₁₀ (solubility)	± 0.09	± 0.09
Upper limit of solubility [mol/kg H ₂ O]	$3.6 \cdot 10^{-3}$	$1.5 \cdot 10^{-3}$
Lower limit of solubility [mol/kg H ₂ O]	$2.4 \cdot 10^{-3}$	$9.8 \cdot 10^{-4}$

Tab. A-8: Solubility parameters for chlorine

	E3-BPW-Ref	E3-BPW-sal
Calculated solubility [mol/kg H ₂ O]	0.239	0.405
Limiting solid phase	-	-
Uncertainty of solubility product		
Dominating aqueous species	Cl ⁻	Cl ⁻
Uncertainty of formation constant		
Uncertainty of log ₁₀ (solubility)		
Upper limit of solubility [mol/kg H ₂ O]	Unlimited	Unlimited
Lower limit of solubility [mol/kg H ₂ O]	Unlimited	Unlimited

Tab. A-9: Solubility parameters for curium

	E3-BPW-Ref	E3-BPW-sal
Calculated solubility [mol/kg H ₂ O]	$1.23 \cdot 10^{-5}$	$1.16 \cdot 10^{-5}$
Limiting solid phase	CmOHCO ₃ (am,hyd)	CmOHCO ₃ (am,hyd)
Uncertainty of solubility product	± 1.0	± 1.0
Dominating aqueous species	CmCO ₃ ⁺	CmSiO(OH) ₃ ²⁺
Uncertainty of formation constant	± 0.4	± 0.5
Uncertainty of log ₁₀ (solubility)	± 1.1	± 1.1
Upper limit of solubility [mol/kg H ₂ O]	$1.5 \cdot 10^{-4}$	$1.5 \cdot 10^{-4}$
Lower limit of solubility [mol/kg H ₂ O]	$9.8 \cdot 10^{-7}$	$9.2 \cdot 10^{-7}$

Tab. A-10: Solubility parameters for holmium

	E3-BPW-Ref	E3-BPW-sal
Calculated solubility [mol/kg H ₂ O]	$4.22 \cdot 10^{-7}$	$2.84 \cdot 10^{-7}$
Limiting solid phase	HoOHCO ₃ (cr)	HoOHCO ₃ (cr)
Uncertainty of solubility product	± 2.0	± 2.0
Dominating aqueous species	HoCO ₃ ⁺	HoCO ₃ ⁺
Uncertainty of formation constant	± 0.2	± 0.2
Uncertainty of log ₁₀ (solubility)	± 2.0	± 2.0
Upper limit of solubility [mol/kg H ₂ O]	$4.2 \cdot 10^{-5}$	$2.8 \cdot 10^{-5}$
Lower limit of solubility [mol/kg H ₂ O]	$4.2 \cdot 10^{-9}$	$2.8 \cdot 10^{-9}$

Tab. A-11: Solubility parameters for iodine

	E3-BPW-Ref	E3-BPW-sal
Calculated solubility [mol/kg H ₂ O]	Unlimited	Unlimited
Limiting solid phase	-	-
Uncertainty of solubility product		
Dominating aqueous species	I ⁻	I ⁻
Uncertainty of formation constant		
Uncertainty of log ₁₀ (solubility)		
Upper limit of solubility [mol/kg H ₂ O]	Unlimited	Unlimited
Lower limit of solubility [mol/kg H ₂ O]	Unlimited	Unlimited

Tab. A-12: Solubility parameters for lead

	E3-BPW-Ref	E3-BPW-sal
Calculated solubility [mol/kg H ₂ O]	$7.65 \cdot 10^{-9}$	$3.9 \cdot 10^{-9}$
Limiting liquid or solid phase	PbS(s)	PbS(s)
Uncertainty of solubility product	± 0.10	± 0.10
Dominating aqueous species	PbCl ⁺	PbCl ⁺
Uncertainty of formation constant	± 0.03	± 0.03
Uncertainty of log ₁₀ (solubility)	± 0.10	± 0.10
Upper limit of solubility [mol/kg H ₂ O]	$9.6 \cdot 10^{-9}$	$4.9 \cdot 10^{-9}$
Lower limit of solubility [mol/kg H ₂ O]	$6.1 \cdot 10^{-9}$	$3.1 \cdot 10^{-9}$

Tab. A-13: Solubility parameters for molybdenum

	E3-BPW-Ref	E3-BPW-sal
Calculated solubility [mol/kg H ₂ O]	$6.35 \cdot 10^{-7}$	$1.13 \cdot 10^{-6}$
Limiting liquid or solid phase	MoO ₂ (cr)	MoO ₂ (cr)
Uncertainty of solubility product	± 0.47	± 0.47
Dominating aqueous species	MoO ₄ ²⁻	MoO ₄ ²⁻
Uncertainty of formation constant	± 0.15	± 0.15
Uncertainty of log ₁₀ (solubility)	± 0.5	± 0.5
Upper limit of solubility [mol/kg H ₂ O]	$2.0 \cdot 10^{-6}$	$3.6 \cdot 10^{-6}$
Lower limit of solubility [mol/kg H ₂ O]	$2.0 \cdot 10^{-7}$	$3.6 \cdot 10^{-7}$

Tab. A-14: Solubility parameters for neptunium

	E3-BPW-Ref	E3-BPW-sal
Calculated solubility [mol/kg H ₂ O]	$2.07 \cdot 10^{-8}$	$4.5 \cdot 10^{-9}$
Limiting solid phase	NpO ₂ (am, hyd)	NpO ₂ (am, hyd)
Uncertainty of solubility product	± 0.5	± 0.5
Dominating aqueous species	Np(OH) ₂ (CO ₃) ₂ ²⁻	Np(OH) ₂ (CO ₃) ₂ ²⁻
Uncertainty of formation constant	± 0.5	± 0.5
Uncertainty of log ₁₀ (solubility)	± 0.7	± 0.7
Upper limit of solubility [mol/kg H ₂ O]	$1.0 \cdot 10^{-7}$	$2.3 \cdot 10^{-8}$
Lower limit of solubility [mol/kg H ₂ O]	$4.1 \cdot 10^{-9}$	$8.9 \cdot 10^{-10}$

Tab. A-15: Solubility parameters for nickel

	E3-BPW-Ref	E3-BPW-sal
Calculated solubility [mol/kg H ₂ O]	$6.07 \cdot 10^{-5}$	$9.77 \cdot 10^{-5}$
Limiting solid phase	NiCO ₃ (cr)	NiCO ₃ (cr)
Uncertainty of solubility product	± 0.18	± 0.18
Dominating aqueous species	Ni ²⁺	Ni ²⁺
Uncertainty of formation constant	± 0.77	± 0.77
Uncertainty of log ₁₀ (solubility)	± 0.8	± 0.8
Upper limit of solubility [mol/kg H ₂ O]	$3.8 \cdot 10^{-4}$	$6.2 \cdot 10^{-4}$
Lower limit of solubility [mol/kg H ₂ O]	$9.6 \cdot 10^{-6}$	$1.6 \cdot 10^{-5}$

Tab. A-16: Solubility parameters for niobium

	E3-BPW-Ref	E3-BPW-sal
Calculated solubility [mol/kg H ₂ O]	$1.08 \cdot 10^{-6}$	$1.08 \cdot 10^{-6}$
Limiting solid phase	Nb ₂ O ₅ (pr)	Nb ₂ O ₅ (pr)
Uncertainty of solubility product	± 0.5	± 0.5
Dominating aqueous species	Nb(OH) ₆ ⁻	Nb(OH) ₆ ⁻
Uncertainty of formation constant	± 0.14	± 0.14
Uncertainty of log ₁₀ (solubility)	± 0.5	± 0.5
Upper limit of solubility [mol/kg H ₂ O]	$3.4 \cdot 10^{-6}$	$3.4 \cdot 10^{-6}$
Lower limit of solubility [mol/kg H ₂ O]	$3.4 \cdot 10^{-7}$	$3.4 \cdot 10^{-7}$

Tab. A-17: Solubility parameters for palladium

	E3-BPW-Ref	E3-BPW-sal
Calculated solubility [mol/kg H ₂ O]	$3.12 \cdot 10^{-10}$	$3.12 \cdot 10^{-10}$
Limiting solid phase	Pd(cr)	Pd(cr)
Uncertainty of solubility product	-	-
Dominating aqueous species	Pd(aq)	Pd(aq)
Uncertainty of formation constant	± 0.5	± 0.5
Uncertainty of log ₁₀ (solubility)	± 0.5	± 0.5
Upper limit of solubility [mol/kg H ₂ O]	$9.9 \cdot 10^{-10}$	$9.9 \cdot 10^{-10}$
Lower limit of solubility [mol/kg H ₂ O]	$9.9 \cdot 10^{-11}$	$9.9 \cdot 10^{-11}$

Tab. A-18: Solubility parameters for plutonium

	E3-BPW-Ref	E3-BPW-sal
Calculated solubility [mol/kg H ₂ O]	$1.39 \cdot 10^{-8}$	$4.0 \cdot 10^{-9}$
Limiting solid phase	PuO ₂ (am, hyd)	PuO ₂ (am, hyd)
Uncertainty of solubility product	± 0.52	± 0.52
Dominating aqueous species	PuCO ₃ ⁺	PuSiO(OH) ₃ ²⁺
Uncertainty of formation constant	± 0.6	± 0.5
Uncertainty of log ₁₀ (solubility)	± 0.8	± 0.7
Upper limit of solubility [mol/kg H ₂ O]	$8.8 \cdot 10^{-8}$	$2.0 \cdot 10^{-8}$
Lower limit of solubility [mol/kg H ₂ O]	$2.2 \cdot 10^{-9}$	$8.0 \cdot 10^{-10}$

Tab. A-19: Solubility parameters for polonium

	E3-BPW-Ref	E3-BPW-sal
Calculated solubility [mol/kg H ₂ O]	$9.9 \cdot 10^{-8}$	$9.9 \cdot 10^{-8}$
Limiting liquid or solid phase	Po(s)	Po(s)
Uncertainty of solubility product	-	-
Dominating aqueous species	Po(aq)	Po (aq)
Uncertainty of formation constant	± 1.0	± 1.0
Uncertainty of log ₁₀ (solubility)	± 1.0	± 1.0
Upper limit of solubility [mol/kg H ₂ O]	$9.9 \cdot 10^{-7}$	$9.9 \cdot 10^{-7}$
Lower limit of solubility [mol/kg H ₂ O]	$9.9 \cdot 10^{-9}$	$9.9 \cdot 10^{-9}$

Tab. A-20: Solubility parameters for protactinium

	E3-BPW-Ref	E3-BPW-sal
Calculated solubility [mol/kg H ₂ O]	$9.0 \cdot 10^{-8}$	$8.9 \cdot 10^{-8}$
Limiting solid phase	Pa ₂ O ₅ (act)	Pa ₂ O ₅ (act)
Uncertainty of solubility product	-	-
Dominating aqueous species	PaO(OH) ₃ (aq)	PaO(OH) ₃ (aq)
Uncertainty of formation constant	± 0.35	± 0.35
Uncertainty of log ₁₀ (solubility)	-	-
Upper limit of solubility [mol/kg H ₂ O]	$9.0 \cdot 10^{-8}$	$8.9 \cdot 10^{-8}$
Lower limit of solubility [mol/kg H ₂ O]		

Tab. A-21: Solubility parameters for radium

	E3-BPW-Ref	E3-BPW-sal
Calculated solubility of pure RaSO ₄ [mol/kg H ₂ O]	$3.64 \cdot 10^{-8}$	$5.72 \cdot 10^{-8}$
Solubility of Ra in equilibrium with (Ba,Ra)SO ₄ solid solution at $1 \cdot 10^{-6}$ mol Ra added per kg of bentonite (0.1175 kg of bentonite porewater)	$2.3 \cdot 10^{-10}$	$3.6 \cdot 10^{-10}$
Limiting solid phase	RaSO ₄ (cr)	RaSO ₄ (cr)
Uncertainty of solubility product	± 0.3	± 0.3
Dominating aqueous species	Ra ²⁺	Ra ²⁺
Uncertainty of formation constant	± 0.5	± 0.5
Uncertainty of log ₁₀ (solubility)	± 0.6	± 0.6
Upper limit of solubility [mol/kg H ₂ O]	$1.5 \cdot 10^{-7}$	$2.3 \cdot 10^{-7}$
Lower limit of solubility [mol/kg H ₂ O]	$9.1 \cdot 10^{-9}$	$1.4 \cdot 10^{-8}$

Tab. A-22: Solubility parameters for samarium

	E3-BPW-Ref	E3-BPW-sal
Calculated solubility [mol/kg H ₂ O]	$4.19 \cdot 10^{-7}$	$2.80 \cdot 10^{-7}$
Limiting liquid or solid phase	SmOHCO ₃ (cr)	SmOHCO ₃ (cr)
Uncertainty of solubility product	± 2.0	± 2.0
Dominating aqueous species	SmCO ₃ ⁺	SmCO ₃ ⁺
Uncertainty of formation constant	± 0.2	± 0.2
Uncertainty of log ₁₀ (solubility)	± 2.0	± 2.0
Upper limit of solubility [mol/kg H ₂ O]	$4.2 \cdot 10^{-5}$	$2.8 \cdot 10^{-5}$
Lower limit of solubility [mol/kg H ₂ O]	$4.2 \cdot 10^{-9}$	$2.8 \cdot 10^{-9}$

Tab. A-23: Solubility parameters for selenium

	E3-BPW-Ref	E3-BPW-sal
Calculated solubility [mol/kg H ₂ O]	$1.0 \cdot 10^{-6}$	$1.0 \cdot 10^{-6}$
Limiting liquid or solid phase	Se(cr)	Se(cr)
Uncertainty of solubility product	-	-
Dominating aqueous species	Se(aq)	Se(aq)
Uncertainty of formation constant	± 1.0	± 1.0
Uncertainty of log ₁₀ (solubility)	± 1.0	± 1.0
Upper limit of solubility [mol/kg H ₂ O]	$1.0 \cdot 10^{-5}$	$1.0 \cdot 10^{-5}$
Lower limit of solubility [mol/kg H ₂ O]	$1.0 \cdot 10^{-7}$	$1.0 \cdot 10^{-7}$

Tab. A-24: Solubility parameters for silver

	E3-BPW-Ref	E3-BPW-sal
Calculated solubility [mol/kg H ₂ O]	$2.94 \cdot 10^{-7}$	$3.3 \cdot 10^{-7}$
Limiting liquid or solid phase	Ag ₂ S(cr)	Ag ₂ S(cr)
Uncertainty of solubility product	± 0.2	± 0.2
Dominating aqueous species	Ag(aq)	Ag(aq)
Uncertainty of formation constant	± 0.5	± 0.5
Uncertainty of log ₁₀ (solubility)	± 0.5	± 0.5
Upper limit of solubility [mol/kg H ₂ O]	$9.3 \cdot 10^{-7}$	$1.0 \cdot 10^{-6}$
Lower limit of solubility [mol/kg H ₂ O]	$9.3 \cdot 10^{-8}$	$1.0 \cdot 10^{-7}$

Tab. A-25: Solubility parameters for strontium

	E3-BPW-Ref	E3-BPW-sal
Calculated solubility [mol/kg H ₂ O]	$1.71 \cdot 10^{-4}$	$2.63 \cdot 10^{-4}$
Limiting solid phase	Celestite, SrSO ₄ (cr)	Celestite, SrSO ₄ (cr)
Uncertainty of solubility product	± 0.10	± 0.10
Dominating aqueous species	Sr ²⁺	Sr ²⁺
Uncertainty of formation constant	± 0.14	± 0.14
Uncertainty of log ₁₀ (solubility)	± 0.17	± 0.17
Upper limit of solubility [mol/kg H ₂ O]	$2.5 \cdot 10^{-4}$	$3.9 \cdot 10^{-4}$
Lower limit of solubility [mol/kg H ₂ O]	$1.2 \cdot 10^{-4}$	$1.8 \cdot 10^{-4}$

Tab. A-26: Solubility parameters for technetium

	E3-BPW-Ref	E3-BPW-sal
Calculated solubility [mol/kg H ₂ O]	$2.04 \cdot 10^{-9}$	$1.9 \cdot 10^{-9}$
Limiting solid phase	TcO ₂ (am, hyd, aged)	TcO ₂ (am, hyd, aged)
Uncertainty of solubility product	± 0.4	± 0.4
Dominating aqueous species	TcO(OH) ₂ (aq)	TcO(OH) ₂ (aq)
Uncertainty of formation constant	± 0.3	± 0.3
Uncertainty of log ₁₀ (solubility)	± 0.5	± 0.5
Upper limit of solubility [mol/kg H ₂ O]	$6.5 \cdot 10^{-9}$	$6.0 \cdot 10^{-9}$
Lower limit of solubility [mol/kg H ₂ O]	$6.5 \cdot 10^{-10}$	$6.0 \cdot 10^{-10}$

Tab. A-27: Solubility parameters for thorium

	E3-BPW-Ref	E3-BPW-sal
Calculated solubility [mol/kg H ₂ O]	$1.47 \cdot 10^{-8}$	$5.1 \cdot 10^{-9}$
Limiting solid phase	Th(OH) ₄ (am, hyd, aged)	Th(OH) ₄ (am, hyd, aged)
Uncertainty of solubility product	± 0.9	± 0.9
Dominating aqueous species	Th(OH) ₃ CO ₃ ⁻	Th(OH) ₃ CO ₃ ⁻
Uncertainty of formation constant	± 0.7	± 0.7
Uncertainty of log ₁₀ (solubility)	± 1.1	± 1.1
Upper limit of solubility [mol/kg H ₂ O]	$1.9 \cdot 10^{-7}$	$6.4 \cdot 10^{-8}$
Lower limit of solubility [mol/kg H ₂ O]	$1.2 \cdot 10^{-9}$	$4.1 \cdot 10^{-10}$

Tab. A-28: Solubility parameters for tin

	E3-BPW-Ref	E3-BPW-sal
Calculated solubility [mol/kg H ₂ O]	$8.94 \cdot 10^{-9}$	$9.1 \cdot 10^{-9}$
Limiting solid phase	SnO ₂ (cr)	SnO ₂ (cr)
Uncertainty of solubility product	± 0.11	± 0.11
Dominating aqueous species	Sn(OH) ₄ (aq)	Sn(OH) ₄ (aq)
Uncertainty of formation constant	± 0.69	± 0.69
Uncertainty of log ₁₀ (solubility)	± 0.7	± 0.7
Upper limit of solubility [mol/kg H ₂ O]	$4.5 \cdot 10^{-8}$	$4.6 \cdot 10^{-8}$
Lower limit of solubility [mol/kg H ₂ O]	$1.8 \cdot 10^{-9}$	$1.8 \cdot 10^{-9}$

Tab. A-29: Solubility parameters for uranium

	E3-BPW-Ref	E3-BPW-sal
Calculated solubility [mol/kg H ₂ O]	$3.09 \cdot 10^{-8}$	$4.9 \cdot 10^{-9}$
Limiting solid phase	USiO ₄ (cr)	USiO ₄ (cr)
Uncertainty of solubility product	± 1.0	± 1.0
Dominating aqueous species	Ca ₂ UO ₂ (CO ₃) ₃ (aq)	Ca ₂ UO ₂ (CO ₃) ₃ (aq)
Uncertainty of formation constant	± 0.4	± 0.4
Uncertainty of log ₁₀ (solubility)	± 1.1	± 1.1
Upper limit of solubility [mol/kg H ₂ O]	$3.9 \cdot 10^{-7}$	$6.2 \cdot 10^{-8}$
Lower limit of solubility [mol/kg H ₂ O]	$2.5 \cdot 10^{-9}$	$3.9 \cdot 10^{-10}$

Tab. A-30: Solubility parameters for zirconium

	E3-BPW-Ref	E3-BPW-sal
Calculated solubility [mol/kg H ₂ O]	$6.22 \cdot 10^{-10}$	$6.1 \cdot 10^{-10}$
Limiting solid phase	ZrO ₂ (cr)	ZrO ₂ (cr)
Uncertainty of solubility product	± 1.6	± 1.6
Dominating aqueous species	Zr(OH) ₄ (aq)	Zr(OH) ₄ (aq)
Uncertainty of formation constant	± 1.7	± 1.7
Uncertainty of log ₁₀ (solubility)	± 2.3	± 2.3
Upper limit of solubility [mol/kg H ₂ O]	$1.2 \cdot 10^{-7}$	$1.2 \cdot 10^{-7}$
Lower limit of solubility [mol/kg H ₂ O]	$3.1 \cdot 10^{-12}$	$3.1 \cdot 10^{-12}$