

Methodology Development and Determination of Solubility-limiting Solid Phases for a Performance Assessment of Geological Disposal of High-level Radioactive and TRU Wastes

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高レベル放射性廃棄物および地層処分相当の TRU 廃棄物の地層処分システムの性能を評価するためには、地下水や緩衝材間隙水中における放射性核種の溶解度評価が必要である。その溶解度評価のためには、溶解度を制限する固相（溶解度制限固相）を選定する必要がある。本報告では、透明性の高い選定過程が示せるように、熱力学データベースを用いて溶解度制限固相の候補となる固相の飽和指数を算出することで溶解度制限固相を判断する選定手法を構築した。本手法では、飽和指数が大きい固相ほど溶解度制限固相の候補になることを基本とするものの、当該固相の生成や溶解度制限が現実的であるかどうかについて、文献調査により判断することとした。併せて、わが国における最新の安全評価報告書で定義された緩衝材およびセメント間隙水組成に対し、種々の組成を類型化した上で性能評価対象元素の溶解度制限固相を選定した。

Keywords: 高レベル放射性廃棄物, TRU 廃棄物, 地層処分, 溶解度, 溶解度制限固相, 熱力学データベース

Evaluation and estimation of solubility values are required for a performance assessment of geological disposal of high-level radioactive and TRU wastes. Selection of solubility-limiting solid phases (SSPs) that control the solubility of radionuclides is necessary for the evaluation and estimation of solubility values. The authors have developed a methodology for selection of the SSP through a calculation of saturation indices (SIs) using thermodynamic database to show a transparent procedure for the selection. Literature survey has been performed to confirm decision of the SSP from candidate SSPs which generally have larger SIs from realistic point of view for precipitation and solubility control. The authors have selected the SSPs for the elements of interest for the latest Japanese performance assessment in bentonite and cement porewaters after grouping various water compositions.

Keywords: high-level radioactive waste, TRU waste, geological disposal, solubility, solubility-limiting solid phase, thermodynamic database

1 Introduction

1.1 Background

Significant amount of various radionuclides are contained in high-level radioactive waste (HLW) and TRU waste packages, and some of them have long-lived toxicity (e.g. with half-lives more than 10^4 years), which requires isolating it from the biosphere for many hundreds of thousands of years. An international consensus has emerged that such isolation can best be provided by disposal of the waste in geologic repositories (e.g. [1]), a strategy that today is pursued by most countries in possession of nuclear waste. Latest projects for performance (and/or safety) assessments (PAs) of geological disposal of HLW in European and North American countries as well as Japan are summarized in **Table 1**, with showing brief content of bentonite porewater compositions in reference (main or basic) cases for prediction of radionuclide solubility and thermodynamic databases (TDBs) used for the PA for HLW (HLW-PA). In contrast, only Swiss and Japanese projects have predicted the radionuclide solubility for PA for TRU waste (TRU-PA) (or an intermediate-level waste (ILW-PA) for some countries) (e.g. [2]) as shown in **Table 2**, while all elements of interest have been

pessimistically assumed to be soluble for the other projects than the Swiss and Japanese projects shown in **Table 1**.

All of the projects have been using a TDB for prediction of radionuclide solubility (aqueous concentration limit) as shown in **Table 1**. It is necessary to select a solubility-limiting solid phase (SSP) for the prediction of radionuclide solubility when using the TDB. Selection of the SSP, however, is usually performed by an expert judgement (e.g. [3]) and is not always traceable.

Therefore the authors have developed a methodology for selection of SSP for the HLW-PA and the TRU-PA using a TDB.

1.2 Brief Review of Thermodynamic Databases

Thermodynamic database is a set of collected numerical values related to thermodynamic properties for substances, e.g., Gibbs free energy, enthalpy, entropy, heat capacity, equilibrium constant after checking their internal consistency. There are some TDBs specialized for PA of radioactive waste management.

The Nuclear Energy Agency (NEA) within Organisation for Economic Co-Operation and Development (OECD) initiated an international collaborative project on development of TDB (NEA-TDB) for radioactive waste management in 1984 [4]. Chemical thermodynamic series (so-called "Blue Books") have been published and updated for iron (Fe) [5, 6], nickel (Ni) [7], selenium (Se) [8] zirconium (Zr) [9], technetium (Tc) [10], tin (Sn) [11], thorium (Th) [12], uranium (U) [10], neptunium (Np) [10], plutonium (Pu) [10] and americium (Am) [10], and those of selected organic ligands [13]. All selected thermodynamic data (Gibbs free energies, enthalpies, entropies, heat capacities and equilibrium constants) have been based on those obtained from experimental studies, critically reviewed, sometimes integrated and referred to a standard state (at 298.15 K, zero ionic strength,

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Table 1 Brief content of reference (mainly bentonite) porewater compositions for interest of solubility prediction and thermodynamic databases used for a reference case in HLW-PA

Country	Project Name	Publ. Year	pH	redox potential (E _h ; mV vs. SHE)	TIC * ¹ (mol dm ⁻³)	TDB	ref.
Sweden	SR-Site (Forsmark)	2011	7.1	-130	0.153	Nagra/PSI-TDB 01/01 [14] + NEA-TDB of Ni [7], Zr [9], Th [12], U [10] + Newly developed Pb [15]	[3, 15]
Finland	TURVA-2012 (saline)	2012	7.94	-232	5.2 × 10 ⁻⁴	ThermoChimie [16] v.7b	[17]
	TURVA-2012 (blackish)		7.33	-163	1.05 × 10 ⁻³		
Switzerland	EN 2002	2002	7.25	-193	2.83 × 10 ⁻³	Nagra/PSI-TDB 01/01 [14]	[18, 19]
	SGT-E2	2014	7.79	-204	8.994 × 10 ⁻⁴	Nagra/PSI-TDB 12/07 [20]	[21]
France	Dossier 2005	2005	6.9 – 7.6	-180 – -150	7.5 × 10 ⁻⁴ – 3.4 × 10 ⁻³	ThermoChimie [16] v5.	[22]
Spain	ThermoChimie	2015	7.2	-179	2.95 × 10 ⁻³	ThermoChimie [16] v9.	[16]
USA	YMP-SAR	2008	7.41 ± 0.44	oxidizing (f _{o2} = 0.2 bar)	(2.1 ± 0.1) × 10 ⁻³	data0.ymp.R2 and data0.ymp.R4 data0.yc3.R1	[23]
Canada	the Fourth Case Study	2012	7.0	-200	1.1 × 10 ⁻³	ThermoChimie [16] v.7b	[24]
Japan	SF-1	2015	8.4	-280	1.7 × 10 ⁻²	JAEA-TDB (in 2014) [25]	[26]

*¹Concentration of total inorganic carbon

Table 2 Brief content of cement porewater compositions for interest of solubility prediction and thermodynamic databases used for a reference case in ILW-PA and TRU-PA

Country	Project Name	Publ. Year	pH	E _h (mV vs. SHE)	TIC (mol dm ⁻³)	TDB	ref.
Region (Stage) I							
Switzerland	EN 2002	2002	13.44	-430	2.04 × 10 ⁻⁴	Nagra/PSI-TDB 01/01 [14]	[27]
Japan	Cement PRJ.	2015	13.2	-258	7.3 × 10 ⁻⁵	JAEA-TDB (in 2014) [25]	[28]
Region (Stage) II							
Switzerland	EN 2002	2002	12.55	-230	9.74 × 10 ⁻⁶	Nagra/PSI-TDB 01/01 [14]	[27]
Switzerland	SGT-E2	2014	12.54	-498	8.064 × 10 ⁻⁶	Nagra/PSI-TDB 12/07 [20]	[29]
Japan	Cement PRJ.	2015	12.5	-240	1.2 × 10 ⁻⁶	JAEA-TDB (in 2014) [25]	[28]
Region (Stage) III							
Japan	Cement PRJ.	2015	11.4	-208	2.3 × 10 ⁻⁵	JAEA-TDB (in 2014) [25]	[28]

0.1 MPa). Thermodynamic data have been critically reviewed and selected on the basis of the NEA's guidelines [4], and some thermodynamic values on chemical species of importance for PA have not been selected due to low reliability of the value even though the data are important for PA of the geological disposal.

The Paul Scherrer Institut (PSI) in Switzerland and National Agency for Radioactive Waste Management (ANDRA) in France have developed, published and updated their own TDBs for PA of radioactive waste management (Nagra/PSI-TDB [14, 20] and ThermoChimie [16], respectively). Both TDBs have been developed with using the data selected by the NEA [5-13] and additional thermodynamic data due to insufficiency for prediction of solubility and speciation of radionuclides using selected data by the NEA [5-13] only. Most of thermodynamic data selected in these TDBs are equilibrium constants, and some enthalpies for reaction have also been selected. Detail of procedure for selection of thermodynamic data for the Nagra/PSI-TDB has been well

documented [14, 20], while only the selected data and their references for the ThermoChimie has been published [16]. Similar TDB has also been developed in the United States [23]. Most of the PA reports by European and North American countries have adopted to use either Nagra/PSI-TDB [14, 20] or ThermoChimie [16] as shown in **Tables 1 and 2**.

Another TDB for PA of radioactive waste management has been developed by Japan Atomic Energy Agency (JAEA) [25, 30, 31]. This (JAEA-)TDB has been appeared as JNC-TDB in 1999 [32], and updated after reviewing and selecting new data. Similar to Nagra/PSI-TDB [14, 20] and ThermoChimie [16], additional thermodynamic data have been selected. Features of JAEA-TDB are (1) a guideline for review and selection of thermodynamic data has been established [30], and (2) re-review of selected data by the NEA [7-13], especially for tetravalent metal ions (Zr [9], Tc(IV) [10] and actinides(IV) [10, 12]). Selection of thermodynamic data other than equilibrium constants should be a

future task.

Use of reliable TDB is important for reliable PA of radioactive waste management. The authors have adopted to use the latest update (at that time) of JAEA-TDB published in 2014 [25] because of inclusion of the latest review and selection of thermodynamic data and comprehensiveness of thermodynamic data on solid phases (i.e. potential SSP). The same candidate SSPs have been selected in the latest update of JAEA-TDB published in 2019 [31].

2 Procedure for Selection of Solubility-limiting Solid Phase

2.1 Summary of Fundamental Information

Before trying solubility estimation, fundamental information, e.g., water composition, elements of interest, applicability of thermodynamics to a system for radioactive waste management should be established. Furthermore, application of chemical analogues, coprecipitation and formation of solid-solution, high temperature conditions, correction of activities, effect of pressures, etc., should also be discussed and concluded before performing thermodynamic calculations.

Various compositions of bentonite and cement porewaters have been proposed in the latest safety assessment report for Japanese geological disposal of HLW and TRU waste [33] as follows:

- Two types of bentonite porewater. Before and after contacting corrosion products of overpacks,
- Three rock types: Plutonic, Neogene sedimentary and Pre-

Neogene sedimentary,

- Two types of chloride concentration in groundwater: Low and high,
- Two types of cement porewater: Regions I and II, and
- Four groups of TRU waste packages: Groups 1, 2, 4H and 4L.

In the present study, various water compositions of interest have been categorized to 7 groups by pH range by the authors as shown in **Table 3**. The composition of “bentonite porewater” is defined as that of the bentonite porewater at glass/overpack interface (i.e. after contacting corrosion products of overpacks) hereafter in the present study. The categorization of pH range is based on the previous observation that four indices (pH, E_h , TIC and total sulfur concentration) are mainly affecting solubility of radionuclides in a water composition [34]. Furthermore, the composition of bentonite porewater in high pH range shown in **Table 3** has been divided into 3 groups using lower and upper limits of pH and E_h values, because the range of these values is still wide for evaluation of SSPs. The combination of pH and E_h values of divided bentonite porewater in high pH range is defined as (1) maximum pH and minimum E_h , (2) minimum pH and maximum E_h , and (3) maximum pH and maximum E_h . The authors did not consider another combination of (4) minimum pH and minimum E_h since the combination of minimum pH (= 7.1) and minimum E_h (= -4.1×10^2 mV) is unlikely due to very strong reducing conditions to produce hydrogen gas.

Selection of elements of interest are selected on the basis of (1) RNs with half-lives longer than 1 y and (2) their radioactivity

Table 3 Bentonite and cement porewater compositions for selection of SSP for PA for HLW in the NUMO-SC [33] categorized by pH range by the authors

Waste type	HLW		TRU waste				
Water type	Bentonite porewater at glass/overpack interface		Cement porewater				
			Region I		Region II		
pH range	Lower	Higher	Lower	Higher	Lower	Middle	Higher
pH	6.2 ~ 6.6	7.1 ~ 9.8	12.6 ~ 12.7	13.2 ~ 13.3	11.7 ~ 11.8	12.3 ~ 12.4	12.8 ~ 12.9
E_h (mV)	$-(1.7\sim1.3)\times 10^2$	$-(4.1\sim0.89)\times 10^2$	$-(6.2\sim5.7)\times 10^2$	$-(6.2\sim5.4)\times 10^2$	$-(6.0\sim5.4)\times 10^2$	$-(5.9\sim5.4)\times 10^2$	$-(5.7\sim5.3)\times 10^2$
ionic strength	$(2.4\sim4.0)\times 10^{-1}$	$3.6\times 10^{-3}\sim2.5\times 10^{-1}$	$(3.7\sim7.0)\times 10^{-1}$	$(3.6\sim6.9)\times 10^{-1}$	$(0.45\sim2.7)\times 10^{-1}$	$(0.51\sim3.5)\times 10^{-1}$	$(1.6\sim3.5)\times 10^{-1}$
Na (mol kg ⁻¹)	$(2.2\sim3.4)\times 10^{-1}$	$2.8\times 10^{-3}\sim2.0\times 10^{-1}$	$(1.4\sim4.8)\times 10^{-1}$	$(1.4\sim4.9)\times 10^{-1}$	$2.5\times 10^{-3}\sim2.2\times 10^{-1}$	$2.8\times 10^{-3}\sim3.4\times 10^{-1}$	$(1.6\sim3.5)\times 10^{-1}$
Ca (mol kg ⁻¹)	$(0.35\sim1.5)\times 10^{-2}$	$1.4\times 10^{-5}\sim1.6\times 10^{-2}$	$(1.1\sim3.3)\times 10^{-3}$	$(0.75\sim1.2)\times 10^{-3}$	$(0.25\sim3.2)\times 10^{-2}$	$(0.25\sim3.2)\times 10^{-2}$	$(1.9\sim2.4)\times 10^{-2}$
K (mol kg ⁻¹)	$(1.9\sim3.2)\times 10^{-3}$	$1.6\times 10^{-5}\sim4.3\times 10^{-3}$	2.2×10^{-1}	2.2×10^{-1}	$1.6\times 10^{-5}\sim3.2\times 10^{-3}$	$3.0\times 10^{-5}\sim3.2\times 10^{-3}$	$(0.84\sim3.2)\times 10^{-3}$
Mg (mol kg ⁻¹)	$(1.4\sim4.9)\times 10^{-3}$	$4.0\times 10^{-7}\sim5.3\times 10^{-4}$	$(3.8\sim5.1)\times 10^{-7}$	$(2.1\sim3.0)\times 10^{-7}$	$(0.73\sim4.5)\times 10^{-6}$	$(0.52\sim4.5)\times 10^{-6}$	$(2.1\sim2.3)\times 10^{-6}$
Fe (mol kg ⁻¹)	$(4.1\sim8.9)\times 10^{-4}$	$1.3\times 10^{-9}\sim4.2\times 10^{-6}$	$(1.2\sim7.5)\times 10^{-6}$	$(0.12\sim2.6)\times 10^{-5}$	$(0.35\sim1.2)\times 10^{-6}$	$(0.75\sim3.5)\times 10^{-6}$	$(1.1\sim8.4)\times 10^{-6}$
Al (mol kg ⁻¹)	$(1.3\sim2.4)\times 10^{-9}$	$(0.22\sim7.9)\times 10^{-7}$	$(4.4\sim6.0)\times 10^{-5}$	$(3.4\sim4.8)\times 10^{-5}$	$(4.5\sim7.1)\times 10^{-6}$	$(0.37\sim2.5)\times 10^{-5}$	$(1.4\sim1.6)\times 10^{-5}$
Si (mol kg ⁻¹)	$(3.1\sim4.6)\times 10^{-4}$	$(0.33\sim1.4)\times 10^{-3}$	$(0.50\sim1.1)\times 10^{-4}$	$(0.65\sim1.5)\times 10^{-4}$	$(1.0\sim1.6)\times 10^{-5}$	$(1.0\sim3.9)\times 10^{-5}$	$(3.2\sim3.9)\times 10^{-5}$
S (mol kg ⁻¹)	$4.1\times 10^{-6}\sim7.7\times 10^{-2}$	$7.2\times 10^{-6}\sim7.8\times 10^{-2}$	$(3.8\sim8.7)\times 10^{-2}$	$(1.2\sim2.9)\times 10^{-2}$	$(2.8\sim9.1)\times 10^{-4}$	$7.2\times 10^{-5}\sim8.6\times 10^{-3}$	$(1.7\sim1.9)\times 10^{-3}$
TIC ^{*1} (mol kg ⁻¹)	$(3.1\sim4.7)\times 10^{-2}$	$(0.12\sim9.1)\times 10^{-3}$	$(1.3\sim3.4)\times 10^{-4}$	$(1.9\sim5.1)\times 10^{-4}$	$(0.83\sim1.1)\times 10^{-5}$	$(0.82\sim4.9)\times 10^{-5}$	$(4.6\sim4.9)\times 10^{-5}$
Cl (mol kg ⁻¹)	2.1×10^{-1}	$(0.11\sim5.1)\times 10^{-2}$	$1.1\times 10^{-3}\sim2.1\times 10^{-1}$	$1.1\times 10^{-3}\sim2.1\times 10^{-1}$	$1.1\times 10^{-3}\sim2.1\times 10^{-1}$	$1.0\times 10^{-3}\sim2.1\times 10^{-1}$	$3.3\times 10^{-3}\sim2.1\times 10^{-1}$
F (mol kg ⁻¹)	6.5×10^{-6}	$(1.3\sim5.7)\times 10^{-4}$	$6.5\times 10^{-6}\sim5.7\times 10^{-4}$	$6.5\times 10^{-6}\sim1.9\times 10^{-4}$	$6.5\times 10^{-6}\sim5.7\times 10^{-4}$	$6.5\times 10^{-6}\sim5.7\times 10^{-4}$	$6.6\times 10^{-6}\sim1.9\times 10^{-4}$
B (mol kg ⁻¹)	1.0×10^{-2}	$4.6\times 10^{-6}\sim2.7\times 10^{-4}$	$4.6\times 10^{-6}\sim1.0\times 10^{-2}$	$4.6\times 10^{-6}\sim1.0\times 10^{-2}$	$4.6\times 10^{-6}\sim1.0\times 10^{-2}$	$4.6\times 10^{-6}\sim1.0\times 10^{-2}$	$4.7\times 10^{-6}\sim1.0\times 10^{-2}$
P (mol kg ⁻¹)	5.9×10^{-6}	$(0.65\sim5.6)\times 10^{-6}$	$(0.64\sim5.9)\times 10^{-6}$	$(5.6\sim6.0)\times 10^{-6}$	$(0.65\sim5.9)\times 10^{-6}$	$(0.65\sim6.0)\times 10^{-6}$	$(0.57\sim6.0)\times 10^{-6}$
N (mol kg ⁻¹)	1.0×10^{-2}	$(0.25\sim2.8)\times 10^{-5}$	$2.5\times 10^{-6}\sim1.0\times 10^{-2}$	$2.5\times 10^{-6}\sim1.0\times 10^{-2}$	$2.5\times 10^{-6}\sim1.0\times 10^{-2}$	$2.5\times 10^{-6}\sim1.0\times 10^{-2}$	$2.6\times 10^{-6}\sim1.0\times 10^{-2}$
Br (mol kg ⁻¹)	8.0×10^{-4}	$(0.43\sim3.9)\times 10^{-5}$	$4.3\times 10^{-6}\sim8.0\times 10^{-4}$	$4.4\times 10^{-6}\sim8.1\times 10^{-4}$	$4.3\times 10^{-6}\sim8.0\times 10^{-4}$	$4.4\times 10^{-6}\sim8.1\times 10^{-4}$	$4.5\times 10^{-6}\sim8.1\times 10^{-4}$
I (mol kg ⁻¹)	1.8×10^{-4}	$(3.9\sim7.9)\times 10^{-6}$	$3.9\times 10^{-6}\sim1.8\times 10^{-4}$	$3.9\times 10^{-6}\sim1.8\times 10^{-4}$	$3.9\times 10^{-6}\sim1.8\times 10^{-4}$	$3.9\times 10^{-6}\sim1.8\times 10^{-4}$	$4.0\times 10^{-6}\sim1.9\times 10^{-4}$

more than one thousandth of maximum radioactivity of a certain RN, which are inorganic carbon (IC), organic carbon (OC), chlorine (Cl), cobalt (Co), nickel (Ni), selenium (Se), strontium (Sr), zirconium (Zr), niobium (Nb), molybdenum (Mo), technetium (Tc), palladium (Pd), tin (Sn), iodine (I), cesium (Cs), lead (Pb), radium (Ra), actinium (Ac), thorium (Th), protactinium (Pa), uranium (U), neptunium (Np), plutonium (Pu), americium (Am) and curium (Cm) [33].

2.2 Search of Potential Solubility-limiting Solid Phase

There are many potential solid phases to predict solubility of RNs. Various types of solid phase, e.g., crystalline (abbreviation “cr”), amorphous (“am”) and colloidal phases are proposed even for same chemical forms, e.g., $\text{UO}_2(\text{cr})$ and $\text{UO}_2(\text{am})$. Furthermore, some solid phases could be defined neither crystalline nor amorphous; the authors show these solid phases with another abbreviation “s”, e.g., $\text{Pa}_2\text{O}_5(\text{s})$. As mentioned above, the JAEA-TDB [25] includes comprehensive thermodynamic data (equilibrium constants in aqueous solutions) on solid phases.

It is easy to compare stability of solid phases to select potential SSPs. A saturation index (SI) is defined as logarithm of ratio between ion activation product (IAP) and solubility product (K_{sp}) as follows:

$$\text{SI} = \log_{10} \left(\frac{\text{IAP}}{K_{\text{sp}}} \right) = \log_{10} \left(\frac{\{A\}_{\text{actual}}^a \{B\}_{\text{actual}}^b}{\{A\}_{\text{equilibrium}}^a \{B\}_{\text{equilibrium}}^b} \right) \quad (1)$$

for the reaction of $A_a B_b(\text{s}) \rightleftharpoons a A(\text{aq}) + b B(\text{aq})$
(abbreviation “aq” shows aqueous species).

The SI is a useful quantity to determine whether the water is saturated, undersaturated or oversaturated with respect to the given mineral:

SI = 0 (IAP = K_{sp}): saturated (in equilibrium),
SI < 0 (IAP < K_{sp}): undersaturated,
SI > 0 (IAP > K_{sp}): oversaturated.

The authors have decided to calculate SIs using the PHEEQC [35], which is the powerful geochemical calculation programs, since JAEA-TDB [25] has a text file for use of the PHREEQC. Initial concentration of the elements of interest was tentatively set to $1 \times 10^{-8} \text{ mol kg}^{-1}$ for the calculation of SIs.

Preliminary thermodynamic calculations have been performed to obtain the SIs for categorized bentonite and cement porewater compositions listed in **Table 3**. The maximum values in each category have been chosen for the calculations because use of maximum values makes effects of redox and complexations clear. Effect of isosaccarinic acid (ISA) for determination of SIs could be ignored because of little contribution of the ISA at the maximum of expected concentration of $1 \times 10^{-5} \text{ mol kg}^{-1}$ [33]. Although effect of nitrate for some cement porewater compositions was considered by adding 0.5 mol kg^{-1} of sodium

nitrate (NaNO_3), no significant effects of SIs were found.

The authors have picked up a few candidate solid phases with high SIs since the solid phases with higher SIs are more stable. The authors have discussed about the most suitable solid phases as SSP among the candidate solid phases using available knowledge obtained from experimental and natural analogue studies, and considering bentonite and cement porewater compositions. Note that the obtained SIs are definitely tentative.

3 Results and Discussion

3.1 Carbon

Aqueous concentration of IC has already been controlled by calcite (CaCO_3) in simulated bentonite and cement porewaters based on thermodynamic calculations [33]; therefore, the authors have selected the calcite as a SSP of IC.

No candidate SSPs for OC have been found; therefore, OC is concluded to be soluble.

3.2 Chlorine

No candidate SSPs for Cl have been found; therefore, Cl is concluded to be soluble. Note that aqueous concentration of Cl may be decreased due to incorporation into cementitious materials after formation of Friedel’s salt [36].

3.3 Cobalt and Nickel

Part of the obtained SIs for Co and Ni of which chemical behavior in aqueous media are quite similar to each other, is shown in **Tables 4 and 5**, respectively. It is found that SIs of some sulfides such as $\beta\text{-CoS}$ and $\beta\text{-NiS}$ and carbonates ($\text{CoCO}_3(\text{cr})$ and $\text{NiCO}_3(\text{cr})$) are larger than others in bentonite porewater. However, no reliable equilibrium constants of these solid phases in aqueous media, even for millerite ($\beta\text{-NiS}$) which is a naturally occurred mineral [7, 37]. Therefore, selection of $\beta\text{-NiS}$ as a SSP for nickel may be severely underestimated. Furthermore, nickel carbonate ($\text{NiCO}_3(\text{cr})$) could be formed only under high partial pressure of carbon dioxide (CO_2) [38]; therefore, it is unlikely that $\text{NiCO}_3(\text{cr})$ forms in geological disposal conditions.

As a conclusion, selection of $\beta\text{-Ni(OH)}_2$ as a SSP for Ni is the most likely for all conditions listed in **Table 3**. Similar to Ni, the authors have selected $\beta\text{-Co(OH)}_2$ as a SSP for Co.

3.4 Selenium

Part of the obtained SIs for Se is shown in **Table 6**. Candidate SSP with the largest SI value is iron selenides such as $\text{FeSe}_2(\text{cr})$ at certain conditions and monomeric Se ($\text{Se}(\text{am}, \text{“cr, trigonal” and mono})$) at other conditions. Still there are an argument for selection of SSP for Se between $\text{FeSe}_2(\text{cr})$ and $\text{Se}(\text{cr, trigonal})$; only Nagra selects $\text{Se}(\text{cr})$ for estimation of Se solubility for HLW disposal [19, 21] while other implementations or research institutes select $\text{FeSe}_2(\text{cr})$. The authors have selected $\text{FeSe}_2(\text{cr})$ as the SSP at all conditions after reviewing the latest experimental studies such as Doi et al. [39]

Table 4 Saturation indices for candidate SSPs of cobalt

Water type	Bentonite porewater				Cement porewater				
					Region I		Region II		
pH range	Lower	Higher			Lower	Higher	Lower	Middle	Higher
		(1) Max. pH, min. E _h	(2) Min. pH, max. E _h	(3) Max. pH, max. E _h					
α-CoS	-4.98	-1.16	-14.33	-36.90	-1.34	-11.62	-1.16	-2.82	-9.88
β-Co(OH)₂	-8.16	-9.83	-7.09	-2.67	-2.99	-2.72	-5.66	-2.49	-2.56
β-CoS	-1.32	2.50	-10.67	-33.24	2.32	-7.96	2.50	0.84	-6.22
CoCO ₃ (cr)	-3.29	-9.10	-3.32	-1.94	-9.54	-10.32	-11.68	-9.18	-10.27
CoO(cr)	-8.13	-9.80	-7.06	-2.63	-2.95	-2.68	-5.63	-2.45	-2.53

Values with **bold** and *italic* faces denotes the selected SSP and solid phases with larger SIs than the selected SSP, respectively (ditto with later Tables).

Table 5 Saturation indices for candidate SSPs of nickel

Water type	Bentonite porewater				Cement porewater				
					Region I		Region II		
pH range	Lower	Higher			Lower	Higher	Lower	Middle	Higher
		(1) Max. pH, min. E _h	(2) Min. pH, max. E _h	(3) Max. pH, max. E _h					
α-NiS	-2.90	0.78	-12.30	-34.79	-0.43	-11.54	0.78	-2.07	-9.54
β-Ni(OH)₂	-6.75	-8.55	-5.73	-1.22	-2.74	-3.31	-4.39	-2.40	-2.89
β-NiS	-2.28	1.40	-11.68	-34.17	0.19	-10.92	1.40	-1.45	-8.92
Ni ₃ S ₂ (cr)	-12.11	-3.47	-32.29	-78.14	-0.47	-25.47	1.09	-3.82	-20.60
Ni ₉ S ₈ (cr)	-27.99	2.79	-104.56	-285.33	-1.52	-93.17	7.34	-14.67	-76.29
NiCO ₃ (cr)	-3.32	-9.26	-3.40	-1.93	-10.73	-12.34	-11.84	-10.53	-12.03
NiS ₂ (cr)	-2.34	3.77	-19.77	-63.85	-4.09	-23.53	-0.79	-7.28	-20.40

Table 6 Saturation indices for candidate SSPs of selenium

Water type	Bentonite porewater				Cement porewater				
					Region I		Region II		
pH range	Lower	Higher			Lower	Higher	Lower	Middle	Higher
		(1) Max. pH, min. E _h	(2) Min. pH, max. E _h	(3) Max. pH, max. E _h					
β-Fe _{1.04} Se	-2.83	-7.00	-6.30	-10.14	-4.21	-5.55	-3.06	-3.97	-5.00
FeSe₂(cr)	3.98	-5.56	1.04	-4.05	-5.53	-5.17	-4.27	-4.54	-4.66
Se(am)	-0.31	-5.64	0.07	-1.27	-8.20	-6.61	-8.04	-7.46	-6.63
Se(cr,trigonal)	0.73	-4.59	1.12	-0.23	-7.15	-5.57	-7.00	-6.41	-5.58
Se(mono)	0.51	-4.82	0.89	-0.45	-7.38	-5.79	-7.22	-6.64	-5.81
CaSeO ₃ ·H ₂ O(cr)	-25.86	-30.72	-19.68	-4.83	-27.66	-21.00	-29.57	-25.48	-21.19
CaSeO ₄ ·2H ₂ O(cr)	-48.83	-56.75	-40.26	-20.00	-53.31	-44.43	-56.00	-50.72	-45.08

3.5 Strontium and Radium

Both Sr and Ra belong to alkaline-earth metal group same as calcium. Part of the obtained SIs for Sr and Ra is shown in **Tables 7 and 8**, respectively. It is found that SrCO₃(strontianite) has the largest SSP for Sr while RaSO₄(cr) has the largest SSP for radium. Since calcium forms CaCO₃(calcite) which is one of the major mineral components, the most likely SSP for Ra can also be its carbonate (RaCO₃(cr)) based on the chemical analogies and possible formation of coprecipitates.

Note that aqueous concentration of Ra may be decreased due to incorporation of alkaline earth minerals such as calcite (CaCO₃) because of a tiny amount [40].

3.6 Zirconium

Part of the obtained SIs for Zr is shown in **Table 9**. It is found that many silicates and sulfides have larger SIs than hydroxides. Chemical behavior of these solid phases in aqueous media, however, is not clear because no experimental studies in aqueous media have been performed [9]. The equilibrium constants have not been selected by the NEA [9], although the equilibrium constants can be easily obtained from the Gibbs free energy of formation. Furthermore, estimated solubility values for Zr silicates and sulfides will be too low to detect with considering the huge SIs; therefore the estimated solubility values cannot be reliable. Since experimental studies on only hydroxides and/or hydrous oxides of Zr have been performed in aqueous media, the most suitable SSP is concluded to be Zr(OH)₄(am,fresh).

3.7 Niobium

Only Nb₂O₅(s) is the candidate SSP for Nb in the JAEA-TDB [25]; therefore, the authors have selected Nb₂O₅(s) as the SSP for Nb.

Although there is an experimental study on solubility of calcium niobate (CaNb₄O₁₁·8H₂O(hochelagaite)) under cementitious conditions, no equilibrium constants have been obtained but just an empirical model for predicting Nb solubility has been proposed [41]. Note that the obtained experimental values by Talerico et al. [41] are much smaller than the estimated

values using the JAEA-TDB; therefore, selection of Nb₂O₅(s) as the SSP is suitable from the pessimistic point of view.

3.8 Molybdenum

The obtained SIs for Mo are shown in **Table 10**. It is found that the SSP with the largest SI is MoO₂(cr) for reference cases in bentonite porewater and CaMoO₄(cr) for other cases. The equilibrium constant of MoO₂(cr) selected in the JAEA-TDB, however, has been just calculated from the Gibbs free energy of formation [42]; no reliable data on solubility of MoO₂(cr) in

Table 7 Saturation indices for candidate SSPs of strontium

Water type	Bentonite porewater				Cement porewater					
	pH range	Lower	Higher			Region I		Region II		
(1) Max. pH, min. E _h			(2) Min. pH, max. E _h	(3) Max. pH, max. E _h	Lower	Higher	Lower	Middle	Higher	
SrCO ₃ (strontianite)		-4.88	-2.48	-4.93	-2.58	-4.18	-4.09	-5.25	-4.78	-4.83
SrSO ₄ (celestite)		-4.11	-4.35	-3.93	-3.93	-4.26	-4.80	-6.12	-5.02	-5.69

Table 8 Saturation indices for candidate SSPs of radium

Water type	Bentonite porewater				Cement porewater					
	pH range	Lower	Higher			Region I		Region II		
(1) Max. pH, min. E _h			(2) Min. pH, max. E _h	(3) Max. pH, max. E _h	Lower	Higher	Lower	Middle	Higher	
RaCO ₃ (cr)		-5.86	-3.36	-6.00	-3.65	-5.09	-4.84	-5.96	-5.53	-5.53
RaSO ₄ (cr)		-0.94	-1.09	-0.85	-0.86	-1.03	-1.42	-2.69	-1.63	-2.26

Table 9 Saturation indices for candidate SSPs for zirconium

Water type	Bentonite porewater				Cement porewater					
	pH range	Lower	Higher			Region I		Region II		
(1) Max. pH, min. E _h			(2) Min. pH, max. E _h	(3) Max. pH, max. E _h	Lower	Higher	Lower	Middle	Higher	
Ca ₂ ZrSi ₃ O ₁₂ (cr)		91.74	99.27	100.21	120.61	97.43	100.08	95.80	98.80	100.43
Ca ₃ ZrSi ₂ O ₉ (cr)		-28.36	-8.19	-24.13	-8.73	-1.86	-2.14	-2.76	-0.73	-0.28
Na ₂ ZrSi ₂ O ₇ (cr)		-4.04	2.37	-2.29	2.30	0.58	-0.40	-1.17	-0.89	-1.79
Na ₂ ZrSi ₄ O ₁₁ (cr)		7.12	13.69	9.82	13.61	3.76	1.08	2.68	2.29	-0.01
Na ₂ ZrSiO ₅ (cr)		-10.42	-4.09	-9.15	-4.16	-1.81	-1.95	-3.89	-3.29	-3.49
Na ₄ Zr ₂ Si ₃ O ₁₂ (cr)		-13.04	-0.30	-10.02	-0.45	0.20	-0.93	-3.64	-2.77	-3.86
Zr(OH)₄(am,fresh)		-2.81	-2.57	-2.57	-2.57	-2.69	-3.25	-2.73	-3.36	-3.89
ZrO ₂ (mono)		0.96	1.19	1.19	1.19	1.09	0.53	1.03	0.41	-0.12
ZrSi _{1.5} (cr)		55.71	65.71	39.12	-4.08	54.86	37.38	59.49	51.02	39.34
ZrS ₂ (cr)		63.99	75.19	43.38	-10.62	61.02	39.37	66.70	56.40	41.91
ZrS ₃ (cr)		64.58	78.20	35.94	-39.66	57.38	27.41	65.15	51.22	31.07
ZrSiO ₄ (cr)		5.26	5.57	5.97	5.57	1.39	-0.01	1.67	0.71	-0.51

Table 10 Saturation indices for candidate SSPs for molybdenum

Water type	Bentonite porewater				Cement porewater					
	pH range	Lower	Higher			Region I		Region II		
(1) Max. pH, min. E _h			(2) Min. pH, max. E _h	(3) Max. pH, max. E _h	Lower	Higher	Lower	Middle	Higher	
CaMoO₄(cr)		-3.36	-3.06	-3.27	-3.27	-4.16	-4.80	-2.75	-2.88	-3.09
Mo(metal)		-28.99	-26.07	-37.07	-58.68	-33.20	-41.04	-28.93	-33.76	-38.78
MoO ₂ (cr)		-1.10	-4.32	-4.41	-15.21	-10.67	-14.09	-7.97	-10.41	-12.75

aqueous media under geological disposal conditions have been found. In contrast, solubility product of powellite ($\text{CaMoO}_4(\text{cr})$) has been determined by Felmy et al. [43] and Grambow et al. [44]. Furthermore, geochemical modelling for Mo leaching from a mine site showed that powellite is closest to mineral saturation and solubility control on aqueous Mo, with wulfenite (PbMoO_4) and other Mo minerals playing a much lesser role [45]. Therefore the authors have selected $\text{CaMoO}_4(\text{cr})$ as the SSP at all conditions.

3.9 Technetium

Part of the obtained SIs for Tc is shown in **Table 11**. It is found that the solid phase with the largest SI is $\text{TcO}_2(\text{cr})$. The equilibrium constants of $\text{Tc}(\text{cr})$ and $\text{TcO}_2(\text{cr})$, however, are not selected by the NEA [10] but just estimated from the Gibbs free energy of formation in JAEA-TDB [26]. Furthermore, the estimated solubility of $\text{Tc}(\text{cr})$ and $\text{TcO}_2(\text{cr})$ are too small to detect, and the experimental solubility measurements of hydrous $\text{Tc}(\text{IV})$ oxide fit to a thermodynamic calculation with SSP of $\text{TcO}_2 \cdot 1.6\text{H}_2\text{O}(\text{s})$ [46]. Therefore, the authors have selected $\text{TcO}_2 \cdot 1.6\text{H}_2\text{O}(\text{s})$ as the SSP at all conditions.

3.10 Palladium

The obtained SIs for Pd is shown in **Table 12**. Although monomeric $\text{Pd}(\text{cr})$ and $\text{Pd}(\text{s})$ are more stable than amorphous and colloidal Pd hydroxides ($\text{Pd}(\text{OH})_2(\text{am})$ and $\text{Pd}(\text{OH})_2(\text{colloidal})$),

respectively), the estimated solubility values are too small to detect. Experimental solubility values for Pd-OH-Cl system are well interpreted by assuming the SSP of $\text{Pd}(\text{OH})_2(\text{am})$ [47]. Therefore, the authors have selected $\text{Pd}(\text{OH})_2(\text{am})$ as the SSP.

3.11 Tin

The obtained SIs for Sn is shown in **Table 13**. Cassiterite (SnO_2) is the most stable solid phase and the solubility of $\text{SnO}_2(\text{cassiterite})$ is smaller than that of $\text{SnO}_2(\text{am})$ [48]. Solubility values from oversaturation direction, however, are well interpreted with assuming $\text{SnO}_2(\text{am})$ as SSP [11, 48]. Therefore the authors have selected $\text{SnO}_2(\text{am})$ as SSP.

3.12 Iodine

Part of the obtained SIs for I is shown in **Table 14**. Although $\text{KI}(\text{cr})$ is the most stable solid phase, calculation of solubility of I using the $\text{KI}(\text{cr})$ as SSP has not been well converged in the thermodynamic calculation due to changing pH and E_h of water composition drastically and very large concentration limit of I. Therefore the authors did not select any SSPs for I, and I is concluded to be soluble. Note that aqueous concentration of I may be decreased due to incorporation into cementitious materials after formation of ettringite, monosulfates, etc [49].

Table 11 Saturation indices for candidate SSPs for technetium

Water type	Bentonite porewater				Cement porewater				
	Lower	Higher			Region I		Region II		
		(1) Max. pH, min. E_h	(2) Min. pH, max. E_h	(3) Max. pH, max. E_h	Lower	Higher	Lower	Middle	Higher
Tc(cr)	-1.26	5.59	-5.42	-21.49	2.89	-2.13	5.35	2.37	-0.80
$\text{TcO}_2(\text{cr})$	3.65	4.36	4.26	-1.01	2.44	1.84	3.33	2.75	2.25
$\text{TcO}_2 \cdot 1.6\text{H}_2\text{O}(\text{s})$	-0.35	0.36	0.27	-5.00	-1.57	-2.17	-0.67	-1.25	-1.75

Table 12 Saturation indices for candidate SSPs for palladium

Water type	Bentonite porewater				Cement porewater				
	Lower	Higher			Region I		Region II		
		(1) Max. pH, min. E_h	(2) Min. pH, max. E_h	(3) Max. pH, max. E_h	Lower	Higher	Lower	Middle	Higher
Pd(cr)	15.20	22.60	17.16	11.75	18.60	17.53	17.72	17.68	17.33
$\text{Pd}(\text{OH})_2(\text{am})$	-5.29	-0.95	-0.93	-0.95	-4.57	-3.43	-6.23	-5.07	-4.09
$\text{Pd}(\text{OH})_2(\text{colloidal})$	-6.46	-2.12	-2.10	-2.12	-5.74	-4.60	-7.40	-6.24	-5.26
Pd(s)	11.91	19.31	13.87	8.46	15.31	14.24	14.43	14.39	14.04

Table 13 Saturation indices for candidate SSPs for tin

Water type	Bentonite porewater				Cement porewater				
	Lower	Higher			Region I		Region II		
		(1) Max. pH, min. E_h	(2) Min. pH, max. E_h	(3) Max. pH, max. E_h	Lower	Higher	Lower	Middle	Higher
$\text{SnO}(\text{cr})$	-12.93	-11.29	-15.34	-22.16	-16.70	-20.11	-14.03	-16.44	-18.78
$\text{SnO}_2(\text{am})$	-1.58	-3.01	-1.60	-3.02	-8.03	-9.23	-6.15	-7.36	-8.36
$\text{SnO}_2(\text{cassiterite})$	1.01	-0.42	0.99	-0.43	-5.44	-6.64	-3.56	-4.77	-5.77

Table 14 Saturation indices for candidate SSPs for iodine

Water type	Bentonite porewater				Cement porewater				
					Region I		Region II		
pH range	Lower	Higher			Lower	Higher	Lower	Middle	Higher
		(4) Max. pH, min. E _h	(5) Min. pH, max. E _h	(6) Max. pH, max. E _h					
CaI ₂ (cr)	-41.23	-41.01	-41.20	-41.20	-41.97	-42.52	-40.67	-40.76	-40.97
I ₂ (cr)	-38.80	-48.24	-37.40	-37.40	-53.68	-52.67	-52.65	-52.65	-52.32
KI(cr)	-12.48	-12.91	-12.96	-12.96	-10.64	-10.41	-12.42	-12.43	-12.42

3.13 Cesium

No candidate SSPs for Cs have been found; therefore, Cs is concluded to be soluble.

3.14 Lead

Part of the obtained SIs for Pb is shown in **Table 15**. Galena (PbS) is the most stable solid phase in most cases. The solubility of PbS(galena), however, is below detection limit ($< 10^{-7}$ mol dm⁻³) at pH = 8.6 [50]. No solubility data at room temperature on other lead compounds of which the SI is larger than PbCO₃(cerrusite) and Pb(OH)₂(am) listed in **Table 15**. Cerrusite is a naturally occurred mineral and its solubility and stability have been investigated [51]. Therefore, the authors have selected PbCO₃(cerrusite) or Pb(OH)₂(am) as the SSP of Pb.

3.15 Actinium, Americium and Curium

Actinium (Ac), Am and Cm are trivalent and chemically similar to each other in geological disposal conditions. Kitamura et al. [52] applied the selected thermodynamic data for Am to those for samarium (Sm), Ac and Cm after confirming an applicability of chemical analogy among these elements.

Part of the obtained SIs is shown in **Table 16** for Am and Cm, and in **Table 17** for Ac of which crystalline solid phases cannot be formed because of instability of solid phase of Ac due to its own α -radioactivity. Although the most stable solid phase is phosphate (MPO₄(am,hydr), M: Ac, Am and Cm), the expected solubility values are too small to detect [53]. Therefore, the authors have eliminated MPO₄(am,hydr) from candidate SSPs and have selected crystalline and amorphous hydroxides (M(OH)₃(cr) (M: Am and Cm) and Ac(OH)₃(am), respectively), and amorphous and crystalline mixed carbonate-hydroxide compounds (MCO₃OH·0.5H₂O(cr) and AcCO₃OH(am), respectively).

Saturation index of these solid phases of Am as a function of pH is shown in **Fig.1** for plutonic rock-type bentonite porewater. It is interesting that the most appropriate SSP changes from AmCO₃OH·0.5H₂O(cr) to Am(OH)₃(cr) at pH around 10.9, and from the AmCO₃OH(am) to the Am(OH)₃(am) at pH around 10.4. The authors have concluded that change of SSP as a function of pH was reasonable; therefore the authors have selected MCO₃OH·0.5H₂O(cr) and AcCO₃OH(am) as the SSP in bentonite porewaters, while that is M(OH)₃(cr) and Ac(OH)₃(am) as the SSP in cement porewaters.

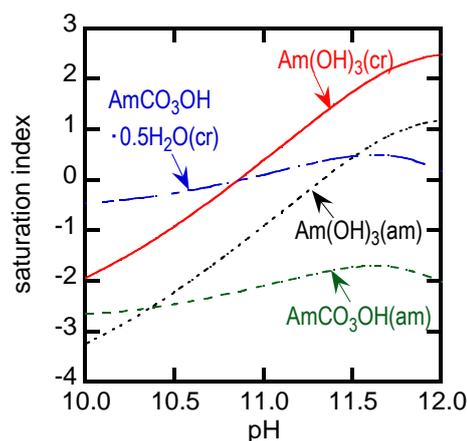


Fig.1 Saturation index of candidate SSPs of americium for plutonic rock-type bentonite porewater as a function of pH

3.16 Thorium

Part of the obtained SIs for Th is shown in **Table 18**. Although ThO₂(cr) is the most stable solid phases, there are no reliable solubility data on ThO₂(cr) at room temperature; therefore, the NEA has not been selected the equilibrium constant for solubility of ThO₂(cr) [12]. Furthermore, the preparation of water-free crystalline actinide(IV) dioxide (AnO₂(cr)) requires heating above 700 °C [54], and radiolytic amorphization and hydration on AnO₂(cr) surface cannot be ruled out [55]. Therefore the authors accepted the discussion by the NEA [12] and selected ThO₂(am, aged) as the SSP due to requirement for assessing long-term behavior of Th migration.

3.17 Protactinium

The obtained SIs for Pa is shown in **Table 19**. The authors have selected the pentavalent Pa oxide (Pa₂O₅(s)) as the SSP under all conditions.

3.18 Uranium

Part of the obtained SIs for U is shown in **Table 20**. Although there are many candidate SSPs for U, most of them may not be appropriate to select as the SSP, because some of them are not formed in aqueous media from oversaturation directions (e.g., CaU₆O₁₉·11H₂O(cr) and K₂U₆O₁₉·11H₂O(cr)), and the estimated solubility values are too small to detect even if the possible

Table 15 Saturation indices for candidate SSPs for lead

Water type	Bentonite porewater				Cement porewater				
	Lower	Higher			Region I		Region II		
		(1) Max. pH, min. E _h	(2) Min. pH, max. E _h	(3) Max. pH, max. E _h	Lower	Higher	Lower	Middle	Higher
Pb(cr)	-9.87	-8.21	-11.16	-13.92	-5.75	-9.13	-3.40	-5.55	-7.82
Pb(OH)₂(am)	-9.87	-11.28	-8.77	-6.14	-8.44	-9.61	-6.87	-7.82	-8.75
Pb ₅ (PO ₄) ₃ Cl(chloro_pyromorphite)	-3.02	-34.59	-0.82	-8.46	-45.83	-56.13	-32.72	-43.23	-52.26
PbCl ₂ (s)	-6.87	-15.86	-7.97	-10.74	-17.66	-20.03	-14.24	-16.41	-18.34
PbCO₃(cerussite)	-2.18	-7.73	-2.18	-2.59	-12.17	-14.38	-10.06	-11.69	-13.63
PbHOCl(cr)	-4.87	-10.07	-4.87	-4.94	-9.55	-11.32	-7.05	-8.62	-10.05
PbHPO ₄ (s)	-5.01	-13.33	-4.64	-8.04	-18.20	-20.65	-15.18	-17.85	-20.07
PbO(red,litharge)	-9.50	-10.90	-8.40	-5.77	-8.06	-9.23	-6.49	-7.45	-8.38
PbO(yellow,massicot)	-9.78	-11.18	-8.68	-6.05	-8.34	-9.51	-6.77	-7.73	-8.66
PbS(galena)	-1.34	2.74	-10.66	-35.02	-1.44	-13.16	2.99	-2.80	-10.72
PbSO ₄ (anglesite)	-4.19	-12.38	-3.96	-6.73	-15.03	-17.89	-13.73	-14.72	-17.29

Table 16 Saturation indices for candidate SSPs for americium and curium

Water type	Bentonite porewater				Cement porewater				
	Lower	Higher			Region I		Region II		
		(1) Max. pH, min. E _h	(2) Min. pH, max. E _h	(3) Max. pH, max. E _h	Lower	Higher	Lower	Middle	Higher
M(OH) ₃ (am) *	-8.19	-2.67	-6.93	-2.71	1.28	1.30	1.18	1.27	1.29
M(OH)₃(cr)	-6.89	-1.37	-5.63	-1.41	2.58	2.60	2.48	2.57	2.59
MCO ₃ OH(am)	-3.67	-2.31	-3.52	-2.34	-5.63	-6.66	-5.20	-5.78	-6.77
MCO₃OH·0.5H₂O(cr)	-1.47	-0.11	-1.32	-0.15	-3.44	-4.47	-3.00	-3.58	-4.57
MPO ₄ (am,hydr)	1.55	0.14	2.06	0.25	-3.62	-4.88	-2.27	-3.89	-5.16
NaM(CO ₃) ₂ ·5H ₂ O(cr)	-1.55	-1.30	-2.20	-1.38	-8.71	-10.16	-8.90	-9.38	-10.87

*M: Am or Cm

Table 17 Saturation indices for candidate SSPs for actinium

Water type	Bentonite porewater				Cement porewater				
	Lower	Higher			Region I		Region II		
		(1) Max. pH, min. E _h	(2) Min. pH, max. E _h	(3) Max. pH, max. E _h	Lower	Higher	Lower	Middle	Higher
Ac(OH)₃(am)	-8.18	-2.64	-6.93	-2.67	1.28	1.30	1.18	1.27	1.29
AcCO₃OH(am)	-3.66	-2.27	-3.52	-2.31	-5.63	-6.66	-5.20	-5.78	-6.77
AcPO ₄ (am,hydr)	1.55	0.17	2.07	0.29	-3.62	-4.88	-2.27	-3.89	-5.16

Table 18 Saturation indices for candidate SSPs for thorium

Water type	Bentonite porewater				Cement porewater				
	Lower	Higher			Region I		Region II		
		(1) Max. pH, min. E _h	(2) Min. pH, max. E _h	(3) Max. pH, max. E _h	Lower	Higher	Lower	Middle	Higher
ThO₂(am,aged)	-2.07	-0.26	-0.83	-0.34	0.91	0.91	0.90	0.90	0.82
ThO ₂ (am,fresh)	-2.87	-1.06	-1.63	-1.14	0.11	0.11	0.10	0.10	0.02
ThO ₂ (cr)	4.67	6.48	5.91	6.40	7.65	7.65	7.64	7.64	7.56
ThOF ₂ (cr)	-2.77	-3.40	1.42	-3.49	-8.06	-10.21	-6.28	-7.49	-9.50

formation in aqueous media (e.g., β-UO_{2+x}, UO_{2+x}(cr) and USiO₄(cr). Therefore the authors have selected UO₂(am) as the SSP for U.

3.19 Neptunium

Part of the obtained SIs for Np is shown in **Table 21**. Although NpO₂(cr) is the most stable solid phases, the authors did not select the NpO₂(cr) as the SSP, similar to ThO₂(cr). Therefore the authors have selected NpO₂(am) as the SSP for Np.

3.20 Plutonium

Part of the obtained SIs for Pu is shown in **Table 22**. Potential redox states of Pu under geological repository conditions are 3 and 4. Although $\text{PuO}_2(\text{cr})$, and $\text{Pu}(\text{III})$ phosphates ($\text{PuPO}_4(\text{am,hydr})$ and $\text{PuPO}_4(\text{s,hyd})$) are candidate SSPs for Pu, the authors did not select these solid phases as the SSP as discussed in section 3.16 and 3.15, respectively. Therefore the authors have selected $\text{PuO}_2(\text{am})$ as the SSP for Pu.

3.21 Comparison of Selected Solubility-limiting Solid Phases with Those Selected by Other Safety Assessments

The selected SSPs in the present study have been listed and compared with those selected in other PA reports for HLW disposal in European and North American countries in **Table 23**. The authors have not taken any information about SSPs from the Dossier 2005 [22] and the safety analysis report for Yucca

Table 19 Saturation indices for candidate SSPs for protactinium

Water type	Bentonite porewater				Cement porewater				
	Lower	Higher			Region I		Region II		
		(1) Max. pH, min. E_h	(2) Min. pH, max. E_h	(3) Max. pH, max. E_h	Lower	Higher	Lower	Middle	Higher
$\text{Pa}_2\text{O}_5(\text{s})$	0.68	2.07	1.38	2.07	2.10	2.10	2.08	2.08	2.09
$\text{PaO}_2(\text{cr})$	-7.28	-5.05	-8.12	-10.48	-5.23	-6.33	-4.85	-5.45	-6.11

Table 20 Saturation indices for candidate SSPs for uranium

Water type	Bentonite porewater				Cement porewater				
	Lower	Higher			Region I		Region II		
		(1) Max. pH, min. E_h	(2) Min. pH, max. E_h	(3) Max. pH, max. E_h	Lower	Higher	Lower	Middle	Higher
$\beta\text{-UO}_2$	0.26	2.64	0.08	-5.62	3.68	0.86	5.07	4.00	2.06
$\beta\text{-UO}_2$	-0.63	1.50	-0.61	-5.86	2.57	-0.07	3.89	2.92	1.09
$\text{CaU}_6\text{O}_{19} \cdot 11\text{H}_2\text{O}(\text{cr})$	31.98	39.10	42.73	38.19	51.89	45.53	56.24	56.29	51.46
$\text{K}_2\text{U}_6\text{O}_{19} \cdot 11\text{H}_2\text{O}(\text{cr})$	25.82	31.84	35.56	31.03	50.14	44.39	49.63	49.76	45.15
$\text{NaUO}_3(\text{cr})$	-8.49	-3.87	-7.79	-9.45	0.50	-1.14	0.51	0.52	-0.57
$\text{UO}_2(\text{am})$	-5.24	-2.09	-6.01	-13.06	-1.14	-4.52	0.44	-0.93	-3.20
$\text{UO}_2(\text{cr})$	1.92	5.07	1.15	-5.91	6.02	2.64	7.60	6.23	3.95
$\text{UO}_{2.25}(\text{cr})$	0.27	2.65	0.09	-5.61	3.69	0.87	5.08	4.01	2.07
$\text{UO}_{2.6667}(\text{cr})$	-3.91	-2.81	-3.09	-6.55	-1.61	-3.51	-0.54	-1.12	-2.50
$\text{UO}_2\text{CO}_3(\text{cr})$	-7.00	-11.06	-6.48	-11.19	-17.02	-19.23	-15.67	-16.52	-18.47
$\text{USiO}_4(\text{cr})$	1.80	5.03	1.51	-5.95	1.90	-2.32	3.82	2.12	-0.85

Table 21 Saturation indices for candidate SSPs for neptunium

Water type	Bentonite porewater				Cement porewater				
	Lower	Higher			Region I		Region II		
		(1) Max. pH, min. E_h	(2) Min. pH, max. E_h	(3) Max. pH, max. E_h	Lower	Higher	Lower	Middle	Higher
$\text{NaNpO}_2\text{CO}_3 \cdot 3.5\text{H}_2\text{O}(\text{cr})$	-8.63	-9.30	-6.92	-4.01	-12.41	-11.72	-13.43	-12.73	-12.56
$\text{NpO}_2(\text{am})$	-1.75	0.24	-0.42	0.14	1.01	1.01	1.00	1.01	1.01
$\text{NpO}_2(\text{cr})$	8.61	10.59	9.94	10.49	11.37	11.37	11.36	11.36	11.36

Table 22 Saturation indices for candidate SSPs for plutonium

Water type	Bentonite porewater				Cement porewater				
	Lower	Higher			Region I		Region II		
		(1) Max. pH, min. E_h	(2) Min. pH, max. E_h	(3) Max. pH, max. E_h	Lower	Higher	Lower	Middle	Higher
$\text{PuCO}_3\text{OH} \cdot 0.5\text{H}_2\text{O}(\text{cr})$	-1.54	-1.40	-1.91	-6.84	-6.48	-8.63	-5.55	-6.82	-8.50
$\text{PuO}_2(\text{am})$	-2.32	0.43	-0.39	0.43	2.84	2.84	2.83	2.83	2.84
$\text{PuO}_2(\text{cr})$	3.39	6.14	5.32	6.14	8.55	8.55	8.54	8.54	8.54
$\text{PuPO}_4(\text{am,hydr})$	1.47	-1.15	1.48	-6.44	-6.66	-9.05	-4.82	-7.13	-9.09
$\text{PuPO}_4(\text{s,hyd})$	1.28	-1.34	1.29	-6.63	-6.85	-9.24	-5.01	-7.32	-9.28

Mountain repository (YMP-SAR) [57]. Also the authors have compared the selected SSPs in the Swiss PA reports for TRU waste disposal as shown in **Table 24**. It is interesting that the selected SSPs are similar to each other for most elements, but there are discrepancies for selection of SSP in some elements such as Co, Ni, Se, Sr, Mo, Sn, Ra, Am and Cm. It is difficult to discuss the discrepancies because there is lack of information for selection of SSPs in other PA reports. The authors believe our selected SSPs are the most suitable for PA of the Japanese geological disposal system of HLW and TRU waste through determining SIs and discussion through experimental and natural analogue studies.

4 Conclusions

Selection of solubility-limiting solid phases (SSPs) that control the solubility of radionuclides has been performed for the elements of interest for the performance assessment (PA) in modeled bentonite and cement porewaters. It was found that determination of saturation indices of candidate SSPs using a

thermodynamic database was useful for showing a more transparent procedure for the selection than expert judgements. The selected SSPs were similar to those selected in PA reports in European and North American countries for most elements, but there are discrepancies for selection of SSP in some elements. The authors believe our selected SSPs are the most suitable for performance assessment of the Japanese geological disposal system of HLW and TRU waste through determining SIs and discussion through experimental and natural analogue studies.

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Table 23 Selected SSPs for HLW disposal in PA reports

Country	Sweden	Finland	Switzerland	Switzerland	Spain	Canada	Japan
Project Name	SR-Site (Forsmark)	TURVA-2012 (saline/blackish)	EN 2002	SGT-E2	Thermo Chimie	the Fourth Case Study	SF-1, present
Ref.	[3, 15]	[17]	[19]	[21]	[16]	[56]	[26], present
IC	CaCO ₃ (calcite)	CaCO ₃ (calcite)	CaCO ₃ (s)	CaCO ₃ (calcite), FeCO ₃ (siderite)	—	CaCO ₃ (calcite)	CaCO ₃ (calcite)
OC	—	(no SSPs)	—	—	—	—	(no SSPs)
Cl	—	(no SSPs)	(no SSPs)	(no SSPs)	—	—	(no SSPs)
Co	—	—	CoCO ₃ (s)	CoCO ₃ (spherocobaltite)	—	—	β -Co(OH) ₂
Ni	β -Ni(OH) ₂	Ni(OH) ₂ (s)	NiCO ₃ (cr)	NiCO ₃ (cr)	—	—	β -Ni(OH) ₂
Se	FeSe ₂ (s)	FeSe ₂ (s)	Se(cr)	Se(cr)	—	FeSe ₂ (s)	FeSe ₂ (cr)
Sr	SrSO ₄ (celestite)	(no SSPs) <saline> SrSO ₄ (celestite) <blackish>	sorption onto bentonite	ion exchange equilibria on montmorillonite	—	—	SrCO ₃ (strontianite)
Zr	Zr(OH) ₄ (am,aged)	Zr(OH) ₄ (am,aged)	ZrO ₂ (s)	Zr(OH) ₄ (s)	—	Zr(OH) ₄ (am, aged)	Zr(OH) ₄ (am,fresh)
Nb	Nb ₂ O ₅	Nb ₂ O ₅ (s)	Nb ₂ O ₅ (s)	Nb ₂ O ₅ (s)	Nb ₂ O ₅ (s)	Nb ₂ O ₅ (s)	Nb ₂ O ₅ (s)
Mo	—	MoO ₂ (tugarinovite)	MoO ₂ (s)	CaMoO ₄ (powellite)	MoO ₂ (s)	MoO ₂	CaMoO ₄ (cr)
Tc	TcO ₂ ·1.6H ₂ O	TcO ₂ ·1.63H ₂ O(s)	TcO ₂ ·1.6H ₂ O(s)	TcO ₂ ·1.6H ₂ O(s)	—	TcO ₂ ·1.6H ₂ O	TcO ₂ ·1.6H ₂ O(s)
Pd	Pd(OH) ₂ (s)	Pd(OH) ₂ (s)	Pd(OH) ₂ (precip.)	Pd(OH) ₂ (s)	—	Pd(OH) ₂ (s)	Pd(OH) ₂ (am)
Sn	SnO ₂ (am)	SnO ₂ (am)	SnO ₂ (cassiterite)	SnO ₂ (am)	—	SnO ₂ (am)	SnO ₂ (am)
I	—	(no SSPs)	(no SSPs)	AgI(s)	—	—	(no SSPs)
Cs	—	(no SSPs)	(no SSPs)	(no SSPs)	—	—	(no SSPs)
Sm (Eu)	SmOHCO ₃ (s)	SmCO ₃ OH ·0.5H ₂ O(cr)	EuCO ₃ OH(s)	SmCO ₃ OH ·0.5H ₂ O(cr)	—	—	SmCO ₃ OH ·0.5H ₂ O(cr)
Pb	PbCO ₃ (s)	—	2PbCO ₃ ·Pb(OH) ₂ (s)	PbCO ₃ (s)	PbCO ₃ (s)	PbCO ₃ (s)	PbCO ₃ (cerrusite)
Ra	RaSO ₄ (cr)	(Ra _x ,Ba _{1-x})SO ₄	(Ba,Ra)SO ₄ (ss)	(Ba,Ca,Ra)SO ₄ (ss)	—	RaSO ₄ (s)	(Ra _x ,Ba _{1-x})CO ₃ <SF-1> RaCO ₃ (s)<present>
Ac	—	—	analogous to Am	analogous to Am	—	—	AcCO ₃ OH(am)
Th	ThO ₂ (am,aged)	ThO ₂ ·2H ₂ O(am)	ThO ₂ (s)	ThO ₂ (am,hyd,aged)	ThO ₂ (aged)	ThO ₂ (aged)	ThO ₂ (am,aged)
Pa	Pa ₂ O ₅ (s)	Pa ₂ O ₅ (s)	Pa ₂ O ₅ (s)	Pa ₂ O ₅ (s)	—	Pa ₂ O ₅ (s)	Pa ₂ O ₅ (s)
U	UO ₂ (am,aged)	UO ₂ ·H ₂ O(am)	UO ₂ (s)	UO ₂ (am)	UO ₂ ·2H ₂ O(am)	UO ₂ (am)	UO ₂ (am)
Np	NpO ₂ ·2H ₂ O	NpO ₂ ·2H ₂ O(am)	NpO ₂ (hyd,am)	NpO ₂ (am,hyd)	NpO ₂ ·2H ₂ O(am)	NpO ₂ (am)	NpO ₂ (am)
Pu	Pu(OH) ₄ (am)	PuO ₂ ·2H ₂ O(am)	PuO ₂ (hyd,aged)	PuO ₂ (am,hyd)	—	PuPO ₄	PuO ₂ (am)
Am	NaAm(CO ₃) ₂ ·5H ₂ O(s)	NaAm(CO ₃) ₂ ·5H ₂ O(s)	AmCO ₃ OH(cr)	NaAm(CO ₃) ₂ ·5H ₂ O(s)	AmCO ₃ OH (am)	AmPO ₄ ·xH ₂ O (am)	AmCO ₃ OH ·0.5H ₂ O(cr)
Cm	Cm ₂ (CO ₃) ₃ (s)	analogous to Am	analogous to Am	analogous to Am	—	—	CmCO ₃ OH ·0.5H ₂ O(cr)

Table 24 Selected SSPs in PA reports under cementitious conditions

Country	Switzerland	Switzerland	Japan
Project Name	EN 2002	SGT-E2	Cement PRJ, present
Ref.	[27]	[29]	[28], present
IC	CaCO ₃ (s)	calcite, strontianite, Al,Fe-moncarbonate solid solutions	CaCO ₃ (calcite)
OC	—	—	(no SSPs)
Cl	(no SSPs)	(no SSPs)	(no SSPs)
Ca	Ca(OH) ₂ (s) / CaCO ₃ (s) / CaF ₂ (s)	portlandite, CSH, calcite, calcium-aluminate-phases	CaCO ₃ (calcite)
Co	Co(OH) ₂ (s)	Co(OH) ₂ (s,rose)	β -Co(OH) ₂
Ni	Ni(OH) ₂ (cr)	Ni(OH) ₂ (theophrastite)	β -Ni(OH) ₂
Se	CaSeO ₃ (s)	CoSe ₂ (cr)	FeSe ₂ (cr)
Nb	(no SSPs)	(no SSPs)	Nb ₂ O ₅ (s)
Mo	CaMoO ₄ (cr)	powellite (CaMoO ₄ (s))	CaMoO ₄ (cr)
Tc	TcO ₂ ·1.6H ₂ O(s)	TcO ₂ ·1.6H ₂ O(s)	TcO ₂ ·1.6H ₂ O(s)
Pd	Pd(OH) ₂ (precip.)	Pd(OH) ₂ (s)	Pd(OH) ₂ (am)
Sn	CaSn(OH) ₆ (s)	CaSn(OH) ₆ (precip)	SnO ₂ (am)
I	(no SSPs)	AgI(s)	(no SSPs)
Cs	(no SSPs)	(no SSPs)	(no SSPs)
Sm (Eu)	Eu(OH) ₃ (am)	Sm(OH) ₃ (am,cr)	Sm(OH) ₃ (cr)
Pb	Pb(OH) ₂ (s)	Pb(OH) ₂ (pr)	Pb(OH) ₂ (am)
Ra	RaSO ₄ (s)	(Ra,Ba)SO ₄ (ss)	RaCO ₃ (cr)
Ac	analogous to Eu	analogous to Eu	Ac(OH) ₃ (am)
Am	Am(OH) ₃ (am)	Am(OH) ₃ (am)	Am(OH) ₃ (cr)
Cm	analogous to Am	Cm(OH) ₃ (am,coll.)	Cm(OH) ₃ (cr)
Np	NpO ₂ (am,hyd)	NpO ₂ (am,hyd)	NpO ₂ (am)
Pa	—	Pa ₂ O ₅ (s)	Pa ₂ O ₅ (s)
Pu	PuO ₂ (hyd,aged)	PuO ₂ (am,hyd)	PuO ₂ (am)
Sr	SrCO ₃ (s)	SrCO ₃ (strontianite)	SrCO ₃ (strontianite)
Tc	(no SSPs)	TcO ₂ ·1.6H ₂ O(s)	TcO ₂ ·1.6H ₂ O(s)
Th	ThO ₂ (s)	ThO ₂ (am,hyd,aged)	ThO ₂ (am,aged)
U	(no SSPs)	UO ₂ (am)	UO ₂ (am)
Zr	ZrO ₂ (s)	ZrO ₂ (baddeleyite)	Zr(OH) ₄ (am.fresh)

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