

OPERA

Solubility limits in the Waste-EBS and Host Rock

OPERA-PU-NRG742

Radioactive substances and ionizing radiation are used in medicine, industry, agriculture, research, education and electricity production. This generates radioactive waste. In the Netherlands, this waste is collected, treated and stored by COVRA (Centrale Organisatie Voor Radioactief Afval). After interim storage for a period of at least 100 years radioactive waste is intended for disposal. There is a world-wide scientific and technical consensus that geological disposal represents the safest long-term option for radioactive waste.

Geological disposal is emplacement of radioactive waste in deep underground formations. The goal of geological disposal is long-term isolation of radioactive waste from our living environment in order to avoid exposure of future generations to ionising radiation from the waste. OPERA (OnderzoeksProgramma Eindberging Radioactief Afval) is the Dutch research programme on geological disposal of radioactive waste.

Within OPERA, researchers of different organisations in different areas of expertise will cooperate on the initial, conditional Safety Cases for the host rocks Boom Clay and Zechstein rock salt. As the radioactive waste disposal process in the Netherlands is at an early, conceptual phase and the previous research programme has ended more than a decade ago, in OPERA a first preliminary or initial safety case will be developed to structure the research necessary for the eventual development of a repository in the Netherlands. The safety case is conditional since only the long-term safety of a generic repository will be assessed. OPERA is financed by the Dutch Ministry of Economic Affairs and the public limited liability company Electriciteits-Produktie maatschappij Zuid-Nederland (EPZ) and coordinated by COVRA. Further details on OPERA and its outcomes can be accessed at www.covra.nl.

This report concerns a study conducted in the framework of OPERA. The conclusions and viewpoints presented in the report are those of the author(s). COVRA may draw modified conclusions, based on additional literature sources and expert opinions. A .pdf version of this document can be downloaded from www.covra.nl.

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Summary

In this report, solubility limits for radionuclides in the *Waste-EBS* and *Host Rock* compartment are derived for the purpose of performance assessment calculations (PA). First, it is established for which elements a solubility limit is of relevance, subsequently for this set of elements solubility limits are derived, and finally the resulting values are compared with the limits as applied in the Belgian research programme.

Samenvatting

In dit rapport zijn oplosbaarheidslimieten voor radionucliden in de *Waste-EBS* en *Host Rock* compartimenten afgeleid, ten behoeve van het doorvoeren van een zogenaamde 'performance assessment' (PA). Hiervoor is als eerste uitgezocht, voor welke radionucliden een oplosbaarheidslimit van belang zou kunnen zijn. Voor deze radionucliden zijn vervolgens oplosbaarheidslimieten afgeleid. De berekende waarden zijn tenslotte vergeleken met de oplosbaarheidslimieten die in het Belgische onderzoeksprogramma toegepast worden.

1. Introduction

1.1. Background

The five-year research programme for the geological disposal of radioactive waste - OPERA- started on 7 July 2011 with an open invitation for research proposals. In these proposals, research was proposed for the tasks described in the OPERA Research Plan [1].

In the OPERA research programme, all safety relevant aspects of a given generic reference disposal concept for radioactive waste [2] are evaluated and assessed in order to evaluate the long-term safety of such a facility [1]. The programme follows in general terms the methodology known as 'Safety Case' [3, 4, 5]. The central part of the Safety Case is formed by safety assessment calculations that will be performed in order to investigate potential risks of a disposal concept. In case of the OPERA Safety Case for a disposal concept in Boom Clay, the slow migration of radionuclides is expected to play a relevant role in the long-term safety of such a disposal concept.

On April 21st, 2017 an OPERA OSCG-meeting was held, and the preliminary outcomes of the PA calculations of the NES case 'N1-DV' were presented by NRG. The outcomes and its implication for communicating the results in a public OSC-report were discussed by the OSCG, which resulted in a more detailed definition of the assessment strategy. Some adaptation of the applied PA-approach and further refinement of model components were suggested. A list of actions was agreed, from which this report addresses Task 2, "Solubility limits in the Waste-EBS and Host Rock".

1.2. Objectives

The solid-solution partitioning of elements can be influenced by precipitation or mineral formation. Within the assessment strategy as discussed at the OSCG meeting, considerations are to establish solubility limits for a wider range of radionuclides both for the Host Rock and for the *Waste-EBS* compartment, in order to define a best estimate of the barrier's performance. In the preliminary calculations discussed with the OSCG only one solubility limit in the PA-model was applied: for uranium in the *Waste-EBS* compartment.

The uncertainties related to the solubility of radionuclides in an anaerobic, complex natural medium as Boom Clay and in the degrading cementitious matrix of the EBS are large. This makes the use of solubility limits in a PA-model, although technical simple to implement, disputable. The objective of this action is therefore to provide solubility limits of radionuclides in the *Host Rock* and *Waste-EBS* compartments for the Normal evolution scenario (NES) in case these are assessed to be relevant, i.e. in case concentrations in the compartments are in the order of magnitude that solubility limits apply, and application of solubility limits will relevantly affect the overall safety of the disposal system. This avoids unnecessary work and allows focussing on (few) relevant radionuclides. Besides, it also helps to avoid unnecessary discussions about the selected parameter values that have no beneficial influence on safety.

1.3. Realization

The work is separated in two subtasks:

Subtask 1: Evaluate elements of relevance

In this subtask, it is evaluated for which radionuclides in the *Waste-EBS* and *Host Rock* compartments concentrations are of a magnitude that solubility limits might be reached. This result in a limited list of elements of principal relevance, from which only a few will influence the overall results of the PA-model. Only the latter elements will be analysed in the next step.

Subtask 2: Compilation of solubility limits

In this subtask, the solubility for the selected elements is analysed for conditions as expected in the *Host Rock* and *Waste-EBS* compartments of the OPERA reference concept. Solubility limits, including their uncertainty are discussed, and a range of solubility limits to be applied in the PA-model are provided.

1.4. Explanation contents

In Chapter 2, a brief outline of the concept of “solubility”, its determination and application in performance assessment (PA) is given. In Chapter 3, the radionuclides for which solubility limits are of relevance are derived. Chapter 4 discusses the solubility of the radionuclides considered in the compartments “*Waste-EBS*” and “*Host Rock*”. Chapter 5 finally presents a recommended set of solubility values and contains brief conclusions and an outlook.

2. General concepts

2.1. Mineral solubility

The term “solubility product” is related to the solubility of a mineral phase, often expressed for a binary¹ mineral as²:

$$K = \frac{[A][B]}{[AB]} \quad \text{Equation 1}$$

with $[AB]$ the molar concentration of the mineral AB , $[A]$ and $[B]$ the molar activity concentration of the two constituting species in solution, and K the solubility constant. With the molar concentration of a single compound in its own phase always equal to one by definition, the above equation can be simplified to:

$$K = [A][B] \quad \text{Equation 2}$$

Since the value of K can span some orders of magnitude, the mineral solubility is often expressed as $\log K$ value.

Equation 2 already hints at the first complication in applying a constant solubility limit in PA: the concentration of a compound of interest A in equilibrium with a mineral AB is not a constant *per se*, but also depends on the molar concentration of B . The molar concentration of B can be influenced by the pH, the redox potential, the ionic strength or the presence of ligands. Generally, the number of potential interactions in natural systems is high, and one needs to consider carefully which elements or ligands have to be accounted for to provide a realistic model for the radionuclides of interest. In the best case, the molar concentration of B is more or less constant.

However, even in case of a more or less constant concentration of B , the concentration of the element of interest can be higher than the concentration of species A in solution only. E.g. the mineral phase UO_2 can be in equilibrium with the soluble species UO_2^{2+} , defined by the constant value of K , but dependent on the solution composition, other uranium species can be of relevance as well (e.g. $UO_2(OH)_2$). Next to the presence of soluble species, also colloidal fractions (e.g. [6, 7, 8, 9, 10, 11, 12, 13, 14, 23]) or species bound to colloidal particles (e.g. [15, 16, 17, 18, 19, 20]) can be present, in the latter case these can even be predominant (e.g. by strong sorption to dissolved organic matter, see e.g. [21]).

Another assumption is relevant when translating mineral solubilities into a PA-model: the above equations assume thermodynamic equilibrium, while in case of mineral formation and dissolution, reaction kinetics can play an important role. In case of mineral precipitation, often the most soluble form precipitates first, while it could take some time until thermodynamically more stable mineral forms appear (*‘Ostwald phase rule’* [22, 23, 24]). Precipitation of minerals is a complex process depending on many factors (e.g. [25]), and in natural systems one can expect that precipitates will rarely be ‘pure’ minerals consisting of two or three elements that are covered by thermodynamic data, but will often be a mixture of several elements, which is much more difficult to model (e.g. [26, 27, 28, 29, 30, 31, 32, 33]). This can limit the applicability of chemical equilibrium modelling, and raises the need to support (or validate) the models by experiments under realistic conditions.

¹ A mineral can also consist of more than two components, the equation has to be adapted correspondingly.

² Note that in literature, K -values are also defined the other way around, i.e. as $K=[AB]/[A][B]$. However, by taking a critical look on the value of K , it is usually evident which definition is used by the author.

Altogether, the above limits the ability to model the solubility of a mineral by speciation calculation [34, 22, 35], even while much effort is taken in radioactive waste management and elsewhere to compile consistent, critical databases that address thousands of species interactions (e.g. [34, 36, 37]) for this type of calculations. For complex mixtures as present in a natural system, model predictions should be envisaged with care: in an *expert judgement* exercise as part of the PAMINA project [38], experts were asked to calculate the solubility of Ra, Sn, Se, U and Pu for a disposal situation. Despite the use of comparable databases and programmes, varying results were found, and for the 90%-confidence intervals, ranges from three up to seven (!) orders of magnitude were given.

The complexity of the processes described above makes also the measurement of mineral solubilities in a complex, natural media cumbersome and difficult to interpret: to take an undisturbed sample in the deep subsurface can be quite challenging with respect to the oxidation state and its high internal gas pressure. Only a few techniques exist that may allow to directly measure species concentrations or activities in a complex medium (e.g. [39, 40]), and for natural, unaltered samples, species concentrations might be too low to use such techniques. Additional complexity comes from the redox-sensitivity of the mineral speciation of a large number of elements of interest, as example here serves the extensive research on the complex reduction/oxidation behaviour of the otherwise poorly adsorbing ⁷⁹Se which is performed as part of the Belgian research programme (e.g. [41, 42, 43, 44]).

In conclusion, within the limited scope of this study it is impossible to critically evaluate the rich literature on mineral solubility and derive values for it. Geochemical modelling may provide some insights into the principal behaviour of an element, but is often not capable to evaluate elemental solubilities in complex media quantitatively. Any approach chosen might also contain some degree of subjectivity, therefore a more modest approach is followed here, aiming at elaborating solubility only for elements which relevantly affect the dose rate.

2.2. Elemental solubility

Based on the consideration in the previous section, we define here the term “solubility” or “solubility limit” in a more practical way, with an eye on the implementation of this value in a PA-model.

The *solubility* of a radionuclide defines its concentration in the soluble phase, i.e. the sum of all free soluble species and colloidal radionuclides, i.e. the amount sorbed to colloidal phases, e.g. dissolved organic matter, or present as e.g. Eigencolloid. The *solubility limit* then defines the highest assumed concentration in solution that may appear in case sufficient total amounts are present. With respect to the *solubility ranges* [45] or *concentration limits* [46] provided by SCK-CEN, it should be noted that these define solubility limits without colloidal fractions bound to dissolved organic carbon (DOC). This needs to be accounted for when comparing expert ranges for solubility (see Chapter 5).

In this document the solubility limit is denoted with the letter “*S*”, in order to avoid confusion with the solubility constant related to the solubility product of a mineral in the previous section, denoted by “*K*”. The solubility limit *S* is, like the solid-solution partitioning factor *K_d*, a conditional value, i.e. its validity is limited to the system for which it is derived. This is different to the solubility product *K*, which in principle is a constant related to a mineral solubility, which should be valid in any system where the given mineral is present.

The conditional nature of the solubility limit S makes it necessary to evaluate carefully if the solubility values obtained by SCK·CEN for Boom Clay in Mol are also applicable for the variety of conditions expected in the Dutch case. The next three chapters therefore discuss for a set of relevant radionuclides recommended solubility limits for Boom Clay in the Netherlands, based on the values used by SCK·CEN.

3. Selection of radionuclides of relevance

The principal list of radionuclides to be covered by the OPERA safety assessment is based on the inventory reported in [47] and [48] and contains all radionuclides present in the waste and with half-lives >10 years. More precisely, the list contains 69 radionuclides, distributed over 42 elements (Table 3-1).

Table 3-1: Overview of all radionuclides considered in OPERA

Nuclides		
H-3	Nb-93m, Nb-94	Re-187
Be-10	Zr-93	Pb-202, Pb-210
C-14	Tc-99	Bi-207
Si-32	Pd-107	Po-209
Cl-36	Ag-108m	Ra-226
Ar-39	Cd-113m	Ac-227
K-40	Sn-121m, Sn-126	Th-229, Th-230, Th-232
Ca-41	I-129	Pa-231
Ti-44	Ba-133	Np-237
Ni-59, Ni-63	Cs-135, Cs-137	U-232, U-233, U-234, U-235, U-236, U-238
Se-79	Pm-145	Pu-238, Pu-239, Pu-240, Pu-241, Pu-242, Pu-244
Kr-81, Kr-85	Sm-146, Sm-147, Sm-151	Am-241, Am-242m, Am-243
Sr-90	Eu-152	Cm-243, Cm-244, Cm-245, Cm-246, Cm-247, Cm-248
Mo-93	Ho-166m	Cf-249

Not all of the above given radionuclides relevantly contribute to the risk, and not all of the radionuclides will be present in concentrations that solubility limits may apply. The relevance of a radionuclide depends on several factors such as its total amount, radiotoxicity, half-life, and the considered scenario.

The uncertainties related to the solubility of radionuclides in an anaerobic, complex natural medium as Boom Clay and in the degrading cementitious matrix of the EBS are large. This makes the use of solubility limits in a PA-model, although technical simple to implement, disputable. Therefore in this chapter it is assessed for which of the radionuclides in Table 3-1 it is relevant to determine the solubility limit. A simple two-step screening is performed:

1. it is evaluated for each radionuclide if concentrations in the two compartments are in the order of magnitude that solubility limits may apply in the NES;
2. for the radionuclide, where solubility limits may apply, it is evaluated whether application of solubility limits will relevantly affect the overall safety of the disposal system in the NES.

This approach avoids unnecessary work and allows focussing on (few) relevant radionuclides within the limited scope of this study. Besides, it also helps to avoid unnecessary discussions about the selected parameter values that have no beneficial influence on safety in the end.

3.1. Evaluation of soluble radionuclide concentrations

By comparing calculation outcomes of the current version of the OPERA PA-model (Model 7.9, [49]) with solubility-values given in literature, a first, conservative screening was made to exclude radionuclides for which no relevant contribution is expected. To evaluate the concentrations in the compartments *Waste-EBS* and *Host Rock*, a screening calculation with the current PA model has been carried out based on:

- Conservative values for diffusion parameters (diffusion coefficient, porosity), container failure times, and release rates as documented in the current version of [51]. The values to be used are summarised in Table 3-2 and Table 3-3 below.
- Retardation coefficients values as reported in [50] and [51] representing the median of the calculated ranges (see Table 3-4).

Conservative values for container failure times and release rates will be used for both sets of calculations. The parameters values to be used are summarised in Table 3-2.

Table 3-2: Overview of conservative container failure times and conservative release rates in the five Waste-EBS disposal sections used in solubility limit calculations [51]

Disposal Section	Time of container failure $t_{failure}$ [a]	Release rate λ_{rel} [1/a]
Vitrified HLW	1'000	$3.5 \cdot 10^{-4}$
Spent Fuel	1'000	∞
Non-heat-generating HLW	1'000	∞
Depleted Uranium	150	∞
LILW	0	∞

For diffusion parameters (diffusion coefficient, and porosity) conservative values are used for both sets of calculations. The values are based on [51] and are summarised in Table 3-3 below.

Table 3-3: Diffusion properties (conservative values) for the elements to be considered in solubility limit calculations

Element	Diffusion accessible porosity η [-]	Pore diffusion coefficient D_{pore} [m^2s^{-1}]
H	0.14	$2.0 \cdot 10^{-10}$
Be	0.07	$2.0 \cdot 10^{-10}$
C	0.05	$1.5 \cdot 10^{-11}$
Cl	0.05	$1.0 \cdot 10^{-10}$
K	0.14	$1.4 \cdot 10^{-10}$
Ca	0.14	$1.9 \cdot 10^{-10}$
Se	0.05	$8.4 \cdot 10^{-11}$
Kr	0.14	$2.0 \cdot 10^{-10}$
Sr	0.14	$1.9 \cdot 10^{-10}$
Mo	0.05	$5.0 \cdot 10^{-11}$
Nb	0.05	$6.7 \cdot 10^{-11}$
I	0.05	$1.0 \cdot 10^{-10}$
Ba	0.14	$1.9 \cdot 10^{-10}$
Cs	0.14	$1.4 \cdot 10^{-10}$
Pm	0.07	$2.0 \cdot 10^{-10}$
Re	0.05	$5.7 \cdot 10^{-12}$
Bi	0.05	$5.7 \cdot 10^{-12}$
Ra	0.14	$1.8 \cdot 10^{-10}$
Pa	0.07	$2.0 \cdot 10^{-10}$
U	0.07	$2.0 \cdot 10^{-10}$
Cf	0.07	$2.0 \cdot 10^{-10}$
DOC	0.07	$5.7 \cdot 10^{-12}$
Ni, Zr, Tc, Pd, Ag, Cd, Sn, Sm, Eu, Pb, Ac, Th, Np, Pu, Am, Cm	0.07	$5.7 \cdot 10^{-12}$

Retardation coefficients as reported in [50] and [51], representing the median value of the calculated ranges, are used in the screening calculations and are summarized in Table 3-4.

Table 3-4: R -values for dissolved and DOC-bound fractions of the radionuclides considered in OPERA for the central assessment case N1 (base case, 100 mg/l DOC), 50 percentile ([50]; Table 4-10)

Element	Retardation factor R_{diss} [-]	Retardation factor R_{DOC} [-]
H	1	>50000
Be	5409	2881
C	1	>50000
Cl	1	>50000
K	34	2300
Ca	5409	2881
Ni	>50 000	227
Se	1	621
Kr	1	>50000
Sr	13329	461
Mo	1	>50000
Nb	1	>50000
Zr	>50 000	221
Tc	>50 000	221
Pd	>50 000	221
Ag	>50 000	221
Cd	>50 000	222
Sn	>50 000	221
I	1	>50000
Ba	1	>50000
Cs	6454	>50 000
Pm	1	>50000
Sm	>50 000	221
Eu	>50 000	267
Re	1	>50000
Pb	>50 000	338
Bi	1	>50000
Ra	7320	458
Ac	>50 000	221
Th	>50 000	221
Pa	>50 000	221
Np	>50 000	221
U	>50 000	221
Pu	>50 000	221
Am	>50 000	349
Cm	>50 000	222
Cf	>50 000	221

The central R -values in Table 3-4 are based on the results presented in [50] (p.33 and Table 5-1). Following assumptions have been made:

- The K_d -values for H, C, Si, Cl, Ar, Ti, Kr, Mo, Nb, Ba, Pm, Ho, Re, Bi, Po are conservatively set to zero.
- The K_d -values of Zr, Pd, Ag, Sm, Ac, Pa, and Cf are set equal to the lowest values of any member of the related phenomenological group as defined in [52], and Be is set equal to the values of Ca.

The calculation were performed over a period of 1 million years, which was judged to be sufficient to establish the maximum reached concentration in the Waste-EBS compartment and in the lower cell of the Host Rock compartment. The maximum concentration in each

disposal section of the *Waste-EBS* compartment and the first cell of the *Host Rock* model was determined for each element of Table 3-1. The calculation results are summarized in Appendix A, Table A-1 to A-6.

The calculated concentrations in the *Waste-EBS* were compared with the upper and lower bounds of the solubility ranges established by SCK-CEN in [53], see also Appendix A for a complete overview of calculation results and solubility limits. The concentrations limits in Boom Clay were adopted equal to the concentration limit reported in [54, Table 3-12], see also Appendix A. It should be noted that the latter solubility limits, reported for Boom Clay, are *exclusive DOC-bound radionuclides* ([46], see also Section 2.2). The solubility limits of free soluble species for the elements of relevance are summarized in Table 3-5 and Table 3-6.

Table 3-5: Solubilities limits for free soluble species to be used for the safety assessment of B&C waste disposal under relevant Supercontainer conditions during three stages of the near field evolution [53, p.38-39]. UL: upper limit; LL: lower limit

Element	Stage	Solubility limit Waste-EBS [mol/l]			
		UL	95% confidence limit for upper bound	LL	95% confidence limit for lower bound
U (VI)	I	3E-6	2.6E-7 ... 7E-6	2E-6	1E-6 ... 6E-6
	II	2E-06	1E-6 ... 6E-6	2E-6	1E-6 ... 6E-6
	III	3E-5		2E-6	1E-6 ... 6E-6
Th	I - IV	1.0E-08	1E-9 ... 1E-7	1.0E-08	1E-9 ... 1E-7
Ra	I	1.0E-06		7E-9	
	II	1.0E-06		1E-6	
	III	1.0E-06		1E-8	
Pa	I - III	1.0E-08		1.0E-08	
Ac		?		?	
Nb	I	1.1E-5	2E-6 ... 2E-5	7E-9	4E-9 ... 8E-9
	II	7E-9	4E-9 ... 8E-9	7E-9	4E-9 ... 8E-9
	III	8E-7	1.8E-7 ... 4.2E-7	7E-9	4E-9 ... 8E-9
Np (IV)	I - III	1.0E-08		1.0E-09	
Se	I	no limit		5E-4	
	II			2E-5	
	III			1E-11	

Table 3-6: Concentration limits for free soluble species in Boom Clay under conditions at Mol [54, Table 3-12]. UL: upper limit; BE: best estimate; LL: lower limit

Element	Concentration limit Boom Clay [mol/l]		
	LL	BE	UL
U	4.1E-07	1.0E-06	2.5E-06
Th	1.0E-11	2.6E-06	6.1E-05
Ra	3.8E-05	6.7E-05	1.2E-04
Pa	1.0E-10	9.8E-10	1.0E-08
Ac	2.6E-07	3.8E-06	5.7E-05
Nb	1.0E-08	2.4E-06	1.0E-03
Np	1.2E-10	2.0E-09	3.3E-08
Se (I)	6.6E-12	3.6E-09	1.9E-06
Se (II)	no limit	no limit	no limit

Table 3-7 below indicates for each element and compartment whether the calculated concentrations are in an order of magnitude where a solubility limit may apply.

Table 3-7: Elements potentially limited by solubility

Element	<i>Waste-EBS</i>					<i>Host Rock</i> (first cell)
	Vitrified HLW	Spent Fuel	Non-heat-generating HLW	Depleted Uranium	LILW	
H						
Be						+
C		(+)	+		+	
Cl						
K						
Ca						
Ni			+		+	
Se	+	+	+		+	+
Kr						
Sr	+	+	(+)			
Mo			(+)			(+)
Nb	+	+	+		+	+
Zr	+	+	+		+	+
Tc						+
Pd	+		(+)			+
Ag					(+)	
Cd						
Sn	+	+	+			+
I						
Ba						
Cs						
Pm						
Sm	(+)	(+)	(+)		(+)	
Eu						
Re					(+)	
Pb						
Bi					(+)	
Ra	+	+	+		+	
Ac	(+)	+		(+)	(+)	
Th	+	+	+	+	+	+
Pa	(+)	+		+	+	+
Np	+	+	+		+	+
U	+	+	+	+	+	+
Pu	+	+	+		+	+
Am	+	+	+		+	(+)
Cm	+		+		(+)	
Cf						

(+) potentially limited by solubility: either close to the LB solubility concentration, either no solubility limit is available to establish whether it is relevant or not.

3.2. Evaluation of relevance for the long-term safety

The contribution of radionuclides to the dose rate were established by the use of PA-model 7.9 [49], but with less conservative parameterization for the radionuclide migration [51] than for the derivation of the solubilities. The reason is that if the calculations were carried out with the median K_d -values for Boom Clay, the second peak will not be reached in the simulated period of 10 million years and it would be necessary to repeat the calculation for a much longer simulation period.

Figure 3-1 shows the dose rate calculated for the NES-case N1 (PA-model version 7.9) and the most relevant contributing radionuclides.

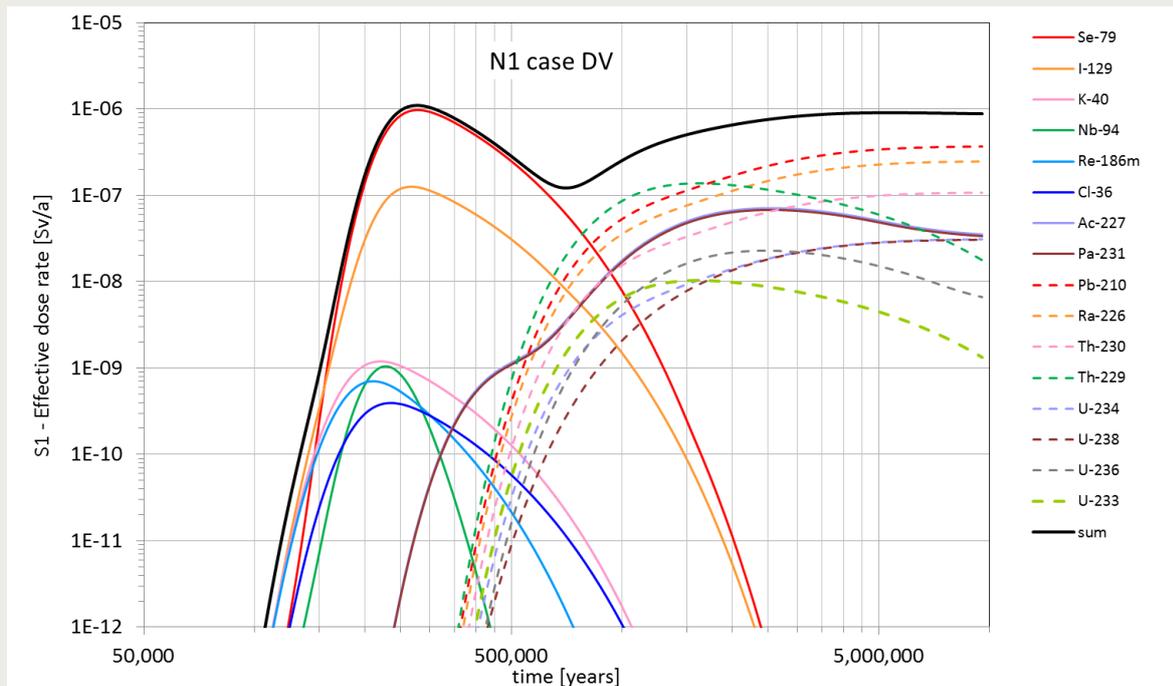


Figure 3-1: Dose rate in the biosphere. Calculations are performed with PA-model 7.9, with parameter values adapted as described in the text.

Figure 3-2 below shows the outcome of the same calculation, now expressed as relative contribution of a radionuclide to the overall dose rate. The element with relevant contribution to the dose rate and with maximum concentrations in *Waste-EBS* and the bottom cell of the Boom Clay which exceed their lower solubility limit are summarised in Table 3-8 below. The consideration of the solubility limits for these elements in the PA-model will lead to a less conservative estimation of contaminant transport.

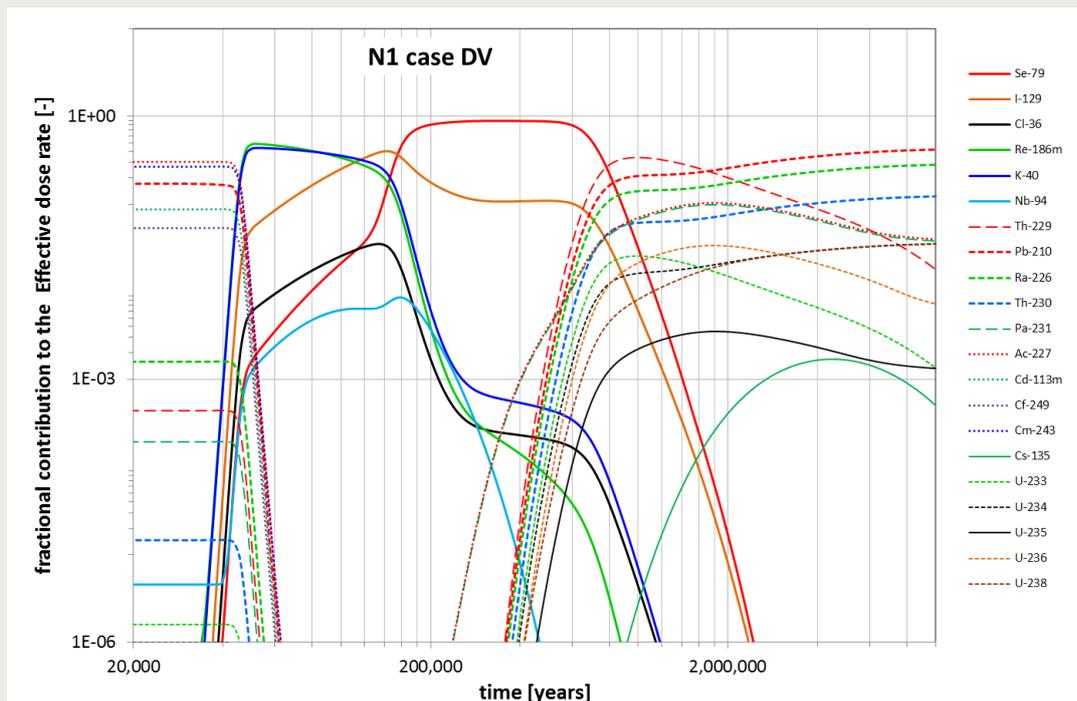


Figure 3-2: Contribution of radionuclides to the dose rate in the biosphere. Calculations are performed with PA-model 7.9, with parameter values adapted as described in the text.

The elements contributing relevantly to the resulting dose rate (Figure 3-2) are: *I*, *Se*, *K*, *Re*, *Pb*, *Ra*, *Th*, *Pa*, *Ac*, *Cl*, *Nb*, *U*, and *Cs*.

- For *U*, a solubility limit is evaluated in the next chapter for both compartments, the *Waste-EBS* and *Host Rock*.
- For *I*, *Cl*, and *Cs*, the solubility is high, and no solubility limit is given.
- For *Se*, [45, 46] defines a solubility limit for *Se(I)*, but not for *Se(II)*. Since in the current OPERA PA, no distinction between *Se(I)* and *Se(II)* is made, no solubility limit is applied.
- *Pb*, *Ra*, *Pa*, and *Ac* have a rather short half-life, and their impact on the dose rate is not related to the radionuclides in the inventory but to ingrowth from their mother nuclides in the *Overburden* and *Biosphere* compartment (see [51]).
- *Re*, *Nb*, and *Sn* only contribute relevantly to the dose rate at very early timesteps, however, their maximum dose rate is less than 0.1% of the overall peak dose rate.
- For *K*, although a solubility limit is not defined, it can be assumed that it will be much larger than the concentrations found in the LILW disposal section and the first Boom Clay cell ($<2 \cdot 10^{-5}$ mol/l, compare with e.g. [34]). Furthermore, *K* contributes only about 0.1% to the peak dose rate.
- The highest *Th* concentration calculated in the host rock (Table A-6, Appendix A) is only 50% higher than the solubility without DOC as provided in [46]. The concentration of soluble *Th* is dominated by ^{232}Th and ^{230}Th , from which only the latter relevantly contributes to the dose rate, related to ingrowth (half-life $\pm 75'000$ years). *Th* is assumed to be strongly bound to DOC ([50], see also [46]), and it can be assumed that the free soluble species concentration only is at least a factor of 100 lower than total soluble concentration. Therefore, for *Th* only in the *Waste-EBS* compartment a solubility limit is evaluated.
- Also *Np* is strongly DOC-bound, however, here the calculated maximum concentrations (Table A-6, Appendix) are more than 100 times larger than the best estimate concentration limit without DOC in [46]. Although impact of a solubility limit is unclear due to the complex role of ^{237}Np as intermediate in the $4N+1$ -decay

chain [51], a solubility limit is assessed in the next chapter for both compartments, the *Waste-EBS* and *Host Rock*.

Table 3-8 compares the outcome of the calculation with the solubility limits (Appendix A and Table 3-7) and summarizes the outcome of the screening.

Table 3-8: Screening of elements relevantly contributing to the long-term safety in relation to their solubility

Element	Consider solubility limit? (EBS-Waste/Host Rock)	Comment
Se	no	Se(I) is solubility limited, but in the OPERA PA no distinction between Se(I) and Se(II) is made
I	no	Solubility not limited
K	no	Solubility limit is not defined, contributes only about 0.1% to the dose rate
Re	no	Re only contributes relevantly to the total dose rate at early times when the dose rate is quite low. It contributes less than 0.1% to the peak dose rate.
Th Np	yes/no yes	Th-229 is a daughter of Np-237. The solubility limit of Np-237 needs therefore to be considered as well.
Pb	no	Pb is short-living ($t_{1/2} < 25$ years). Contribution to the dose rate is not related to the inventory, but to ingrowth.
Ra	no	Ra is relatively short-living ($t_{1/2} = 1600$ years). Contribution to the dose rate is not related to the inventory, but to ingrowth.
Pa	no	Pa has a $t_{1/2}$ of 32'700 years. Contribution to the dose rate at timesteps beyond 1 million years is not related to the inventory, but to ingrowth.
Ac	no	Ac is short-living ($t_{1/2} < 25$ years). Contribution to the dose rate is not related to the inventory, but to ingrowth.
Cl	no	Solubility not limited
Nb	no	Nb only contributes relevantly to the total dose rate at early timesteps. The maximum dose rate of Nb is less than 0.1% of the maximum total dose rate.
Sn		Sn only contributes relevantly to the total dose rate at early timesteps. The maximum dose rate of Sn is less than 0.001% of the maximum total dose rate.
U	yes	
Cs	no	Solubility not limited

4. Derivation of solubility limits

4.1. Solubility in the Waste-EBS compartment

4.1.1. Aim

The aim of this part of the work is to calculate the estimated maximum solubility S for Uranium in the projected EBS system, and in particular in a depleted uranium - cement mixture. The equilibrium calculations take into account expected local geochemical conditions with respect to DOC (dissolved organic carbon) concentrations, redox condition, pH, and CO_2 concentrations. It is assumed that DOC will over time diffuse into the EBS and pore water concentrations in the EBS will therefore eventually approach Boom Clay pore water concentrations. DOC concentrations in the EBS pore water were estimated to be 400 mg/l, which agrees with the highest range given for Belgian Boom Clay pore water conditions ([2]; p.59).

4.1.2. Procedure

The calculations were performed with a geochemical model system for cement that was set up in ORCHESTRA using the most recent thermodynamic database for cement chemical reactions [55]. This model was combined with Uranium reactions from the PSI and NEA thermodynamic databases and adsorption reactions to DOC according to the standard NICA DONNAN model [50].

The composition of cement (Table 4-1) was taken from [56], which lists this material basically as a cement type I concrete with CaCO_3 aggregates .

Table 4-1: Bulk composition of cement-depleted uranium mixture [56].

Component/ parameter	Type		
Cement	CEM I/42.5 N HS LA (LH)	365	kg m^{-3}
Water	-	175	kg m^{-3}
Plasticiser	TM OFT-II B84/39 CON. 35% (BT-SPL)	3.3	kg m^{-3}
Fine aggregate	U_3O_8 : 0-4 mm	2664	kg m^{-3}
Coarse aggregate	Limestone: 2-8 mm	911	kg m^{-3}
w/c	Property	0.48	

N Usual initial strength, HS High Sulphate resistance, LA Low Alkali content , (LH Low Hydration heat)

4.1.3. Results

Uranium

The results show that the calculated maximum total solubility of U in fresh cement (pH 13.26) under oxidized conditions (pe ca. 7) is ca $2.5 \cdot 10^{-4}$ mol/l (Figure 4-1). Under these conditions the predominant dissolved U form/species is $\text{UO}_2(\text{OH})_4^{2-}$. This agrees with calculated U speciation in [57]. Under high pH conditions the solubility is relatively high and is not further enhanced by DOC. From the figure can also be observed that the calculated concentrations are very sensitive for the pore water pH.

Over time, the pH of fresh cement/concrete will decrease as a result of different weathering processes and progress towards equilibration with the surrounding clay

material, which has a pH of ca. 8.2. The rate at which this is likely to occur depends on local conditions and physical dimensions, but is expected to be in the order of thousands of years. Probably the most important weathering processes are uptake of CO_2 and HCO_3^- from the surrounding environment (carbonation) and leaching out of alkaline ions (OH^-).

To evaluate the effects of weathering we simulate this by increasing the total amount of CO_2 in the system. As a result the pH decreases to a value of ca. 10 over time, resulting in a decreased U concentration of ca $1 \cdot 10^{-7}$ mol/l.

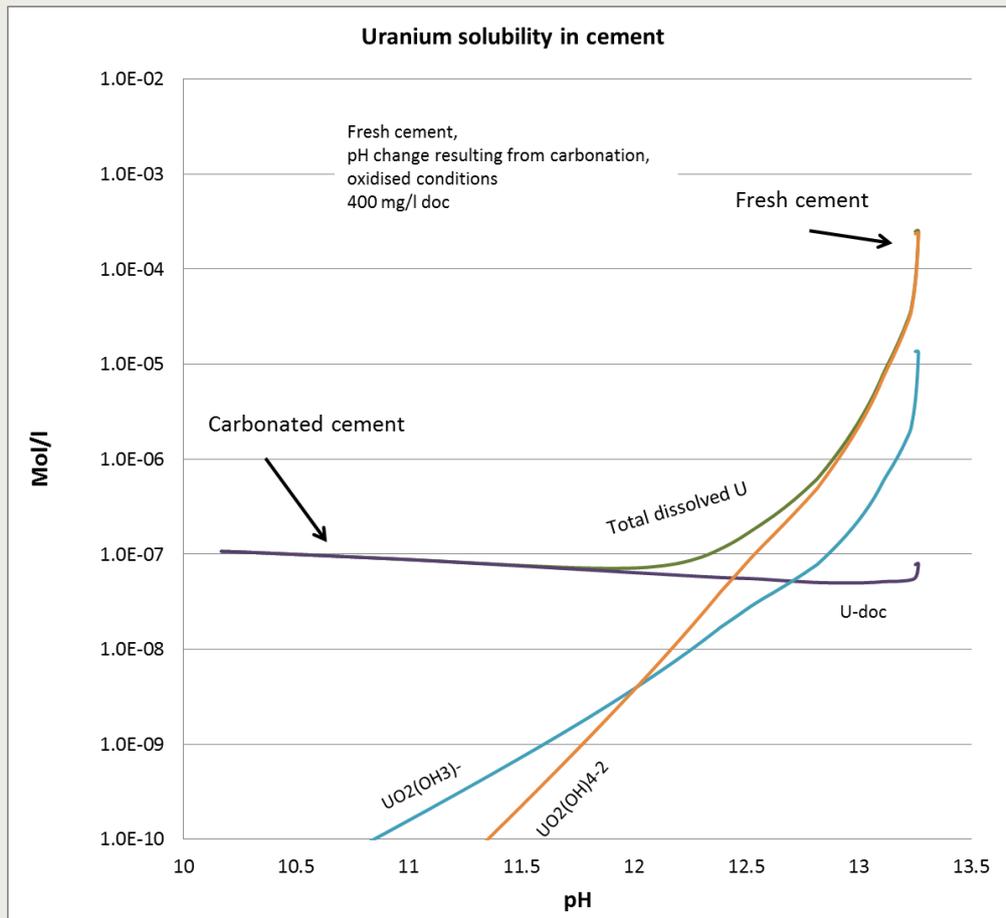


Figure 4-1: Calculated U concentrations in cement pore water under oxidising conditions, ranging from fresh cement (pH 13.25) to carbonated cement (pH 10).

Apart from the pH, the calculated U solubility is furthermore very sensitive to the estimated redox/pe levels. Simulations with lower oxygen levels show a drastically decreased U solubility as a result of conversion of U to lesser soluble $U(IV)$ forms (Figure 4-2). Although the exact redox conditions that will be prevalent in the EBS *in-situ* are not known, these conditions will most likely range from initially alkaline oxidised to slowly reaching equilibrium with reduced lower pH conditions of the surrounding Boom Clay.

The maximum dissolved uranium concentrations are those calculated under fresh oxidised cement conditions as shown in Figure 4-2.

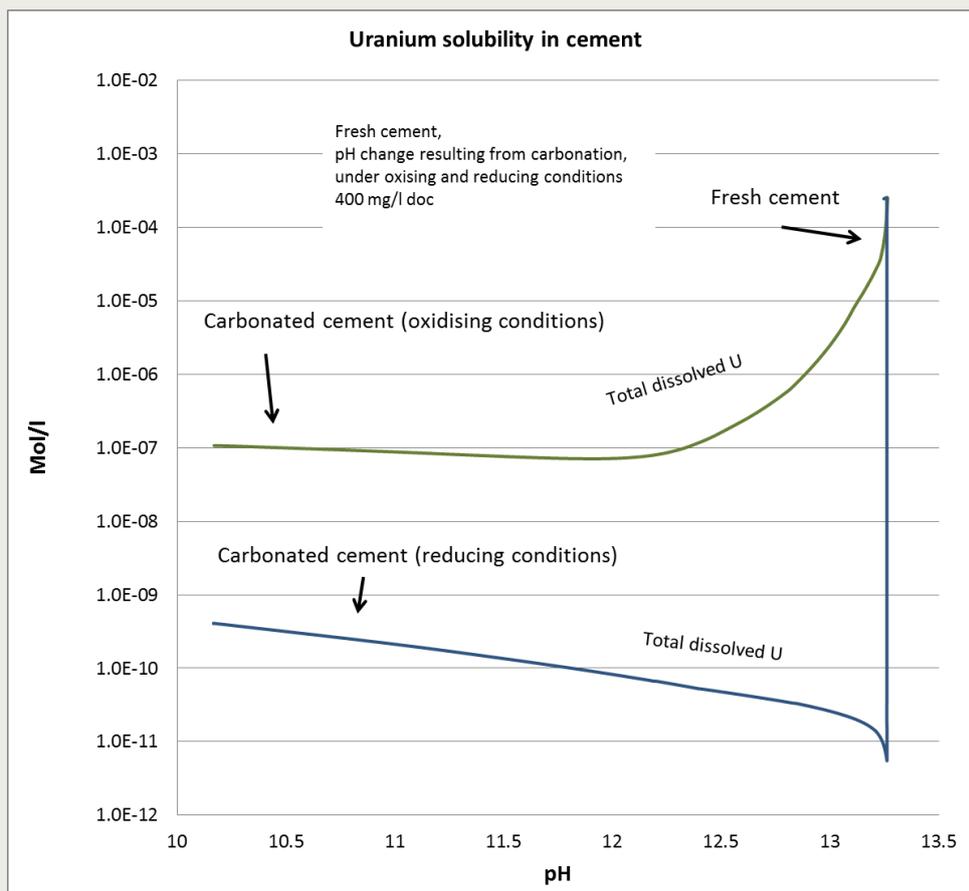


Figure 4-2: Calculated *U* concentrations in cement pore water under oxidising and reducing conditions, ranging from fresh cement (pH 13.25) to carbonated cement (pH 10).

Thorium

For Thorium a reverse pH - solubility relationship is observed (Figure 4-3). In this case the calculated solubility in fresh cement is low (ca $6 \cdot 10^{-7}$ mol/l), while this solubility increases to ca. $3 \cdot 10^{-5}$ mol/l upon carbonation. For *Th*, the concentration of dissolved organic carbon (DOC) is very important, as the concentrations of free *Th* ions (not attached to DOC) are minimal at all pH levels. Because carbonation starts at the EBS-Clay boundary, dissolved *Th* concentrations under the carbonated conditions here are relevant in determining diffusion rates from the EBS into the Boom Clay.

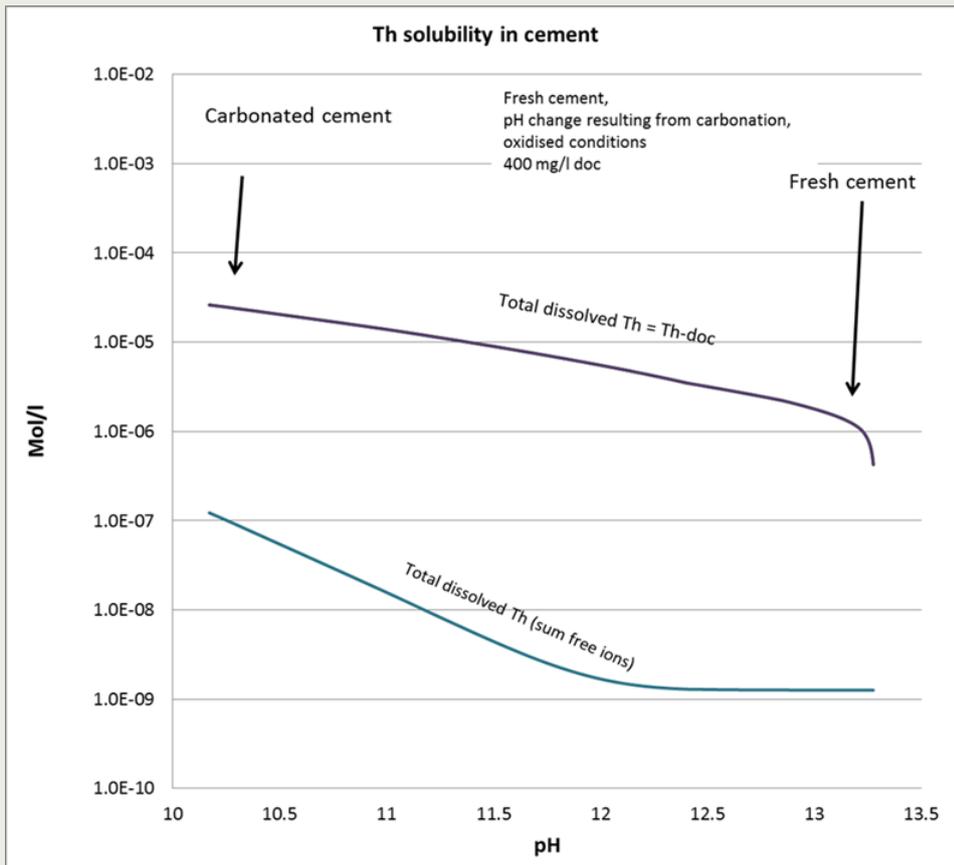


Figure 4-3: Calculated *Th* concentrations in cement pore water, ranging from fresh cement (pH 13.25) to carbonated cement (pH 10).

Neptunium

For Neptunium a significantly higher solubility is calculated under cementitious conditions than for *U* and *Th* (Figure 4-4). The lowest dissolved concentrations is calculated for fresh cement conditions (ca $3 \cdot 10^{-4}$ mol/l) while upon carbonations the concentration is predicted to decrease to ca $1 \cdot 10^{-3}$ mol/l. Only under the most alkaline conditions the binding of *Np* to DOC appears to be significant.

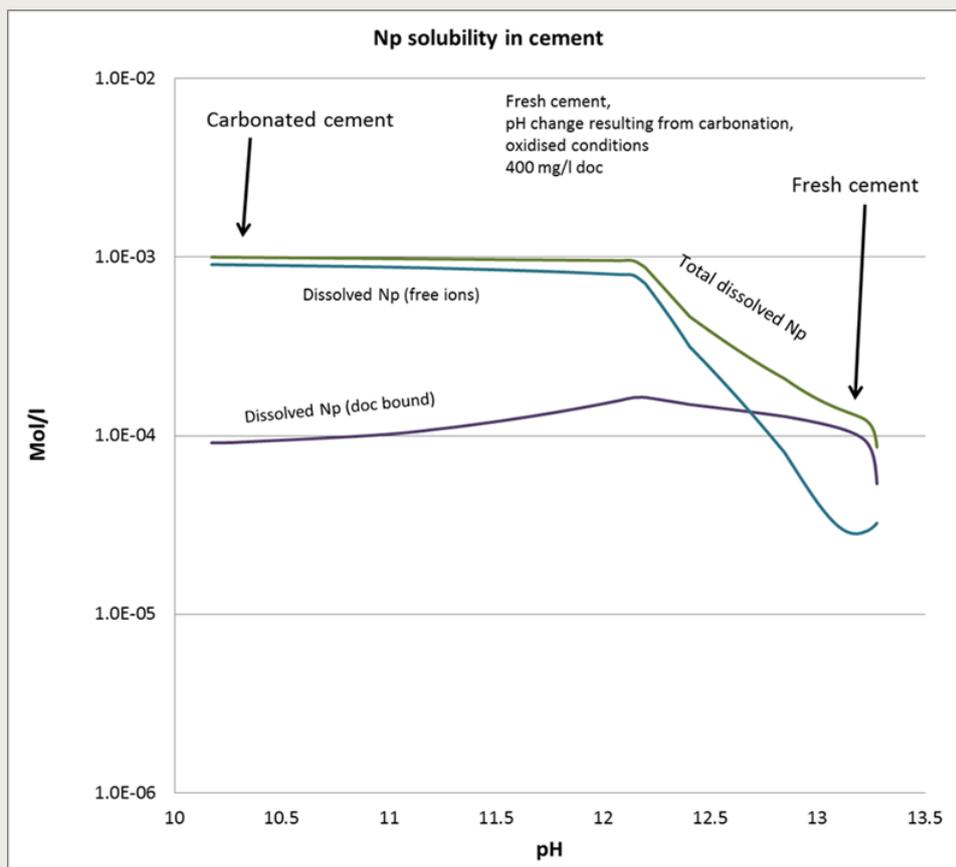


Figure 4-4: Calculated *Np* concentrations in cement pore water, ranging from fresh cement (pH 13.25) to carbonated cement (pH 10).

4.1.4. Conclusions

According to the calculations the maximum solubility of Uranium depends strongly on pH, p_e (redox condition), CO_2 and presence of DOC. Under fresh cement conditions, where pH and solubility of *U* is high, DOC does not further enhance solubility. For *U* initial high concentrations are calculated in fresh cement ($\pm 2 \cdot 10^{-4}$ mol/l). At first sight it seems logical to use these values as estimated maximum soluble concentrations in the cementitious waste sections. However, these conditions are unlikely to exist for longer times homogeneously throughout a cement/concrete system in contact with Boom Clay, as carbonation which will occur rapidly at the Boom Clay - cement boundary. Under conditions occurring at this boundary, the *U* solubility is expected to be significantly lower. It would therefore probably more realistic to use a lower value of $1 \cdot 10^{-5}$ mol/l. It could even be justified to use a lower value of $1 \cdot 10^{-6}$, but experimental evidence would be required to support this.

For *Th*, the reverse behaviour is visible: low concentrations in fresh cement, slightly higher concentrations in carbonated cement. Because the chemical conditions at the EBS-Clay boundary are expected to agree more with the carbonated conditions, it would be more realistic to use the higher concentration of $1 \cdot 10^{-5}$ mol/l.

For *Np* a relatively high solubility is calculated in carbonated cement. The calculation results show that $NpO_2SiO[OH]_3^+$ is the predominant dissolved *Np* species, and the stability of this species determines the total solubility of *Np*. Without this species, the calculated solubility would be 4-5 orders of magnitude lower. Possibly the large difference with the Belgian solubility estimations is caused by taking this species into account. The

concentration expected to be present at the EBS-Clay Boundary is likely to agree more with the carbonated cement conditions, therefore a the estimated Np solubility here would be $1 \cdot 10^{-3}$ Mol/l.

4.2. Solubility in the Host Rock compartment

In the screening in Chapter 3, two radionuclides were judged to relevantly affect the dose rate and to have soluble concentrations in Boom Clay comparable to the solubility limit for free soluble species as established in [54]: *U* and *Np*. These are discussed element-wise in the next two sections.

4.2.1. Uranium

In ([54], Table 3-12), for *U* concentration limits without DOC are given, ranging from $4.1 \cdot 10^{-7}$ to $2.5 \cdot 10^{-6}$ mol/l, with a best estimate of $1.0 \cdot 10^{-6}$ mol/l. It must be assumed that under Boom Clay conditions *U* is present as (more soluble) *U(VI)* [46]. Although in the given redox range, mixed valence uranium oxides (i.e. U_4O_8 and U_3O_8) might lower the solubility in geochemical model calculations, it is argued that these species should not be used since they lead to erroneous results underestimating the real solubility [58]. The soluble chemistry under the conditions in Mol is strongly influenced by carbonate species [45]. This is consistent with calculations performed in [50] for a variety of conditions expected in the Netherlands: the results show that the DOC-bound fractions can cover a large range, mainly dependent of the amounts of $UO_2(CO_3)_3^{4-}$ formed in solution. Figure 4-5 depicts the cumulative distribution of the ratio between DOC-bound *U* and free soluble *U*, as calculated with the model approach described in [50]. The median value is 625, and 10- and 90-percentiles are respectively 1.0 and $4 \cdot 10^{-5}$. The higher values should be used with care, here it is not unlikely that the model overestimate the affinity of *U* for binding to organic matter. Assuming safely that at most only 99% of the overall soluble *U* is bound to DOC, the best estimate given in [54] can be converted to a best estimate overall solubility *S* equivalent to $1.0 \cdot 10^{-4}$ mol/l. Applying the best estimate of the ratio between DOC-bound and free soluble *U* leads to larger central value of the overall solubility *S* of $6.3 \cdot 10^{-4}$ mol/l.

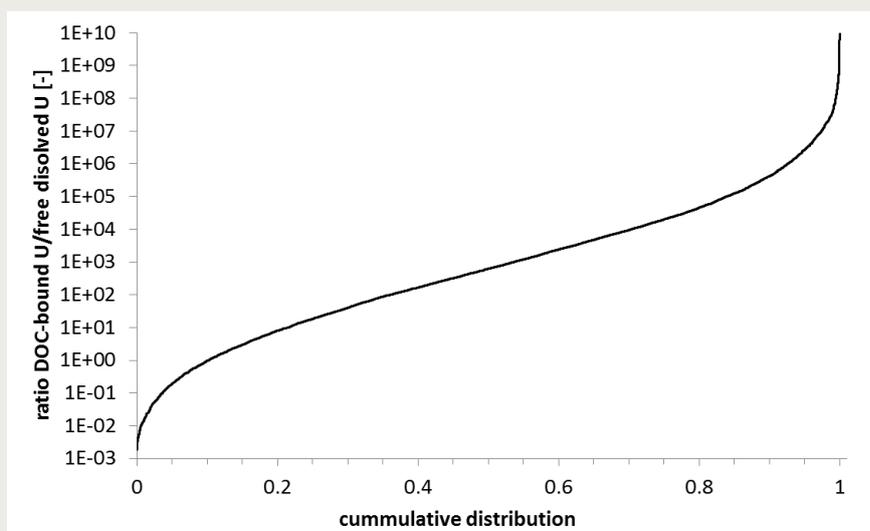


Figure 4-5: Cumulative distribution of the ratio DOC-bound Uranium / free soluble Uranium

The further geochemical analysis is not straightforward. The geochemical model described in [50] assumes equilibrium with amorphous UO_2 , equivalent to [45]. This results in comparable small concentrations of non-carbonated Uranium-species (median value: $9 \cdot 10^{-11}$ mol/l), with soluble concentrations varying due to the assumed variation of the redox potential by about 4 pe units. However, due to the high affinity of uranyl for carbonate, almost all carbonate will be complexed with Uranium, resulting in solubilities in the order of magnitude of the assumed bicarbonate concentration, and higher than the DOC-bound fractions. E.g. assuming a fixed bicarbonate concentration of 900 mg/l, results in a median overall solubility of $8 \cdot 10^{-4}$ mol/l (10- and 90-percentiles: $9 \cdot 10^{-5}$ and $2 \cdot 10^{-3}$ mol/l, respectively). Within the limited scope of this study, the relevance of this result is difficult to confirm, therefore a best estimate of the overall solubility of $1.0 \cdot 10^{-4}$ mol/l is suggested to be used in the OPERA PA, equivalent to the best estimate given in [54], and assuming 99% of the overall soluble U to be bound to DOC. However, large uncertainties with respect to this value need to be noted.

4.2.2. Neptunium

In ([54], Table 3-12), for Np concentration limits for free soluble species (i.e. without DOC) are given, ranging from $1.2 \cdot 10^{-10}$ to $3.3 \cdot 10^{-8}$ mol/l, with a best estimate of $2.0 \cdot 10^{-9}$ mol/l based on equilibrium with $NpO_{2(am,hd)}$ [45].

In [50] and [54], Np is assumed to be strongly bound to DOC. Figure 4-6 shows the calculated DOC-bound and free soluble species concentration of Np , by using the geochemical model described in [50] for the base case (100 mg/l DOC). Here, equilibrium with amorphous NpO_2 is assumed, equivalent to [45]. The calculated free soluble species concentration is very comparable to the values reported in [45]: at a pH of 8.5, as assumed to be present in Boom Clay in Mol, the soluble species concentration is close to $1 \cdot 10^{-9}$ mol/l, and within the pH-range considered in the Netherlands, this value increases to about $3.5 \cdot 10^{-9}$ mol/l. However, the DOC-bound concentration dominates the overall solubility, with $2.1 \cdot 10^{-5}$ mol/l as best estimate value, and a 10- to 90-percentile range of $1.5 \cdot 10^{-5}$ - $3.0 \cdot 10^{-5}$ mol/l. Thus, consequently, these three values are recommended respectively as best estimate, lower and upper limit for the overall solubility S for the base case, assuming 100 mg/l DOC. For other DOC cases [51], this values can be linearly scaled, i.e. 5 times lower for the *low DOC case* (20 mg/l DOC), and two times higher for *high DOC case* (200 mg/l DOC).

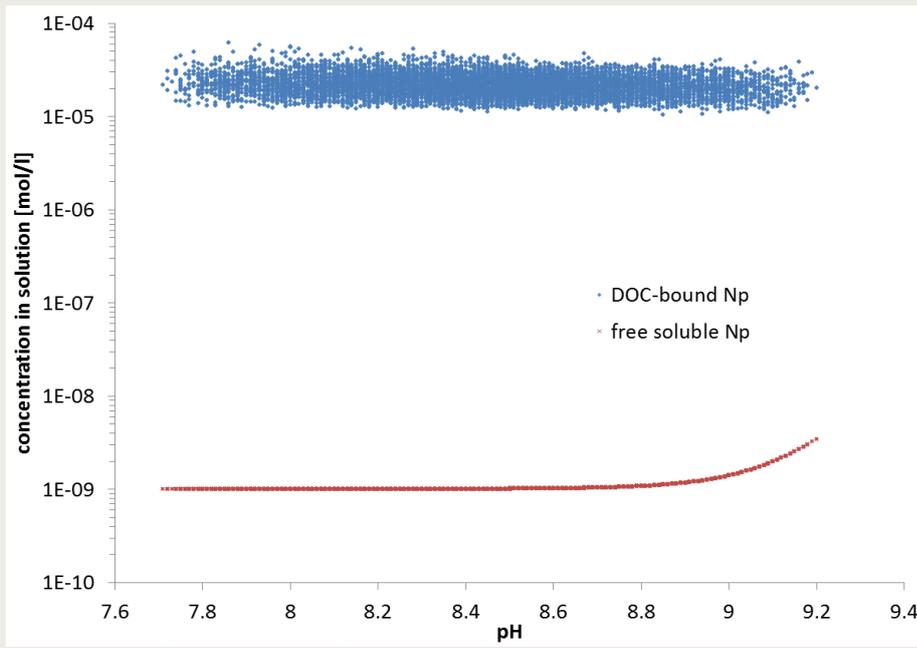


Figure 4-6: Calculated DOC-bound and free soluble concentration of *Np*

5. Proposed set of solubility limits for the OPERA PA

Based on the analyses in the previous sections, Table 5-1 summarizes the estimated set of 'best estimate' total solubility values for the *Waste-EBS* and the *Host Rock* compartments. Where necessary, different DOC-cases are distinguished (see also [51], Section 4.3.1). The results need to be interpreted with caution, since these are based on a limited evaluation of existing geochemical information and models, and are not supported by experimental data.

Table 5-1: Best estimate solubility values S for the OPERA PA.

Element	Case	Solubility limit S [mol/l]	
		Waste-EBS	Host Rock
U	all cases	$1.0 \cdot 10^{-5}$	$1.0 \cdot 10^{-4}$
Th		$1.0 \cdot 10^{-5}$	<i>n.d.</i>
Np	DOC base case (DV)	$1.0 \cdot 10^{-3}$	$2.1 \cdot 10^{-5}$
	low DOC case (LD)		$4.2 \cdot 10^{-6}$
	high DOC case (HD)		$4.2 \cdot 10^{-5}$

In order to compare these results with values derived by SCK-CEN for Boom Clay, a correction need to be applied, since the values provided in Table 3-6 do not consider the presence of DOC. Equivalent to [51], Section 3.3, the values for the three radionuclides of interest in Table 3-6 can be transformed to values representative for the expected DOC-concentrations by using the relation in Eq. 5-1 (see also Eq. 3-13 in [46]):

$$\frac{C_{RN-DOC}}{C_{sol}} [-] = C_{DOC} \cdot K_{RN-DOC} \quad \text{Eq. 5-1}$$

with C_{RN-DOC} / C_{sol} the ratio of DOC-bound and free soluble radionuclide concentrations, C_{DOC} the concentration of DOC in solution (in eq/l) and K_{RN-DOC} the equilibrium constant for the radionuclide-DOC association/dissociation reaction according to Table 3-2 in [46]. For C_{DOC} , a concentration of 0.23 meq/l DOC is assumed [50], and as best estimate for $\log K_{RN-DOC}$, a values of 5.3 is given, leading to a ratio of DOC-bound vs. free soluble radionuclides of 40:1. Table 5-2 summarized the resulting (equivalent) concentration limits.

Table 5-2: Solubilities limits relevant for Supercontainer conditions and recalculated 'equivalent' solubility limits for Boom Clay, assuming the presence of DOC as used in the Belgian research programme [53, 54]. BE: best estimate, UL: upper limit; LL: lower limit

Element	Stage	Concentration limit [mol/l]				
		Waste-EBS		Host Rock, equivalent values assuming 2 meq/kg DOC		
		UL	LL	LL	BE	UL
U (VI)	I	$3.0 \cdot 10^{-6}$	$2.0 \cdot 10^{-6}$	$1.6 \cdot 10^{-5}$	$4.0 \cdot 10^{-5}$	$1.0 \cdot 10^{-4}$
	II	$2.0 \cdot 10^{-6}$				
	III	$3.0 \cdot 10^{-5}$				
Th	I - IV	$1.0 \cdot 10^{-8}$	$1.0 \cdot 10^{-8}$	<i>n.d.</i>		
Np (IV)	I - III	$1.0 \cdot 10^{-8}$	$1.0 \cdot 10^{-9}$	$4.8 \cdot 10^{-9}$	$8.0 \cdot 10^{-8}$	$1.3 \cdot 10^{-6}$

- The proposed concentration limit for **Uranium** in **Waste-EBS** is about three times larger than the upper limit given for the Belgian case in stage III, accounting for the uncertainty with respect to the pH values that could be expected in depleted uranium.
- The proposed concentration limit for **Uranium** in the **Host Rock** is 2.5 times as large as the (recalculated) best estimate given for the Belgian case, and equivalent to the upper limit value. Here, the higher pH-range assumed for the Dutch case leads to more conservative values due to the formation of relevant amounts of uranyl carbonate. However, a rather high uncertainty is noted that cannot be resolved by geochemical modelling only.
- The proposed concentration limit for **Thorium** in **Waste-EBS** is about three orders of magnitude larger than the upper limit given for the Belgian case, accounting for the presence of DOC in the Waste-EBS compartment on the long term.
- The proposed concentration limit for **Neptunium** in **Waste-EBS** is about five orders of magnitude larger than the upper limit given for the Belgian case.
- The proposed concentration limit for **Neptunium** in the **Host Rock** for the base case is about three times larger than the (recalculated) best estimate given for the Belgian case. Based on the geochemical modelling as performed in RANMIG [21], a higher affinity to DOC binding is assumed, compared to the (generic) factor of 40 as applied by SCK·CEN. This lead to more conservative values.

With respect to the differences in solubility between the *Waste-EBS* and *Host Rock* compartment, it is obvious that the lowest solubility values will define the overall system behaviour, i.e. for *U* and *Th* the solubility in the Waste-EBS, and for *Np* the solubility in the host rock.

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Appendix A: Calculated solubility in *Waste-EBS* and *Host Rock*

Table A-1: Calculated total soluble concentrations of radionuclides in the Vitrified HLW section and solubility limits for free soluble species derived from [1]

Element	Concentration in Waste-EBS [mol/l]			Concentration limit in cementitious container near field [mol/kg]	
	Isotope	per isotope	per element	LL	UL
H	H-3	5.33E-25	5.33E-25		
Be	Be-10	5.33E-25	5.33E-25	1.0E-04	1.0E-04
C	C-14	5.33E-25	5.33E-25	8.0E-06	3.0E-04
Cl	Cl-36	5.33E-25	5.33E-25	not limited	not limited
K	K-40	5.33E-25	5.33E-25		
Ca	Ca-41	5.33E-25	5.33E-25	7.0E-04	1.5E-02
Ni	Ni-59	5.33E-25	1.1E-24	2.9E-07	2.9E-07
	Ni-63	5.33E-25			
Se	Se-79	1.46E-04	1.46E-04	1.0E-11	not limited
Kr	Kr-81	5.33E-25	1.07E-24		
	Kr-85	5.33E-25			
Sr	Sr-90	1.14E-04	1.14E-04	1.0E-04	2.5E-03
Mo	Mo-93	5.33E-25	5.33E-25	5.0E-6	9.0E-04
Nb	Nb-93m	3.29E-08	3.29E-08	7.0E-09	1.1E-05
	Nb-94	5.33E-25			
Zr	Zr-93	3.10E-03	3.10E-03	2.0E-08	3.0E-08
Tc	Tc-99	5.16E-03	5.16E-03	not limited	not limited
Pd	Pd-107	8.48E-04	8.48E-04	4.0E-06	1.0E-04
Ag	Ag-108m	5.33E-25	5.33E-25	very low	6E-05
Cd	Cd-113m	5.33E-25	5.33E-25		
Sn	Sn-121	5.33E-25	1.69E-04	1.0E-08	2.0E-06
	Sn-126	1.69E-04			
I	I-129	5.33E-25	5.33E-25	not limited	not limited
Ba	Ba-133	5.33E-25	5.33E-25		
Cs	Cs-135	1.33E-03	1.52E-03	not limited	not limited
	Cs-137	1.91E-04			
Pm	Pm-145	5.33E-25	5.33E-25	n.a.	n.a.
Sm	Sm-151	9.49E-05	9.49E-05	n.a.	n.a.
Eu	Eu-152	5.33E-25	5.33E-25	n.a.	n.a.
Re	Re-186m	5.33E-25	5.33E-25	n.a.	n.a.
Pb	Pb-210	1.69E-10	1.69E-10	not limited	not limited
Bi	Bi-207	5.33E-25	5.33E-25	n.a.	n.a.
Ra	Ra-226	1.22E-08	1.22E-08	7.0E-09	1.0E-06
Ac	Ac-227	1.34E-12	1.34E-12	n.a.	n.a.
Th	Th-229	2.28E-09	1.27E-06	1.0E-08	1.0E-08
	Th-230	5.76E-07			
	Th-232	6.96E-07			
Pa	Pa-231	2.02E-09	2.02E-09	1.0E-08	1.0E-08
Np	Np-237	2.69E-03	2.69E-03	1.0E-09	1.0E-08
U	U-232	3.97E-09	4.83E-03	2.0E-06	3.0E-05
	U-233	8.85E-07			
	U-234	3.06E-06			
	U-235	4.35E-05			
	U-236	2.39E-05			
Pu	U-238	4.76E-03	1.37E-04	1.0E-11	1.0E-08
	Pu-238	8.05E-07			
	Pu-239	9.81E-05			
	Pu-240	2.97E-05			
	Pu-241	2.03E-08			
Am	Pu-242	7.83E-06	1.25E-03	3.0E-10	3.0E-08
	Pu-244	7.57E-07			
	Am-241	8.85E-04			
Cm	Am-242m	4.24E-10	5.76E-06	3.0E-9	3.0E-9
	Am-243	3.65E-04			
	Cm-243	7.36E-08			
	Cm-244	7.68E-07			
	Cm-245	4.75E-07			
Cf	Cm-246	4.35E-06	5.33E-25		
	Cm-247	8.11E-08			
	Cf-249	5.33E-25	5.33E-25		

Red - relevant; Orange - potentially relevant, Black - not relevant

Table A-2: Calculated total soluble concentrations of radionuclides in the Spent Fuel section and solubility limits for free soluble species derived from [1]

Element	Concentration in Waste-EBS [mol/l]			Concentration limit in cementitious container near field [mol/kg]	
	Isotope	per isotope	per element	LL	UL
H	H-3	2.64E-24	2.64E-24		
Be	Be-10	2.64E-24	2.64E-24	1.0E-04	1.0E-04
C	C-14	1.12E-08	1.12E-08	8.0E-06	3.0E-04
Cl	Cl-36	2.64E-24	2.64E-24	NL (-)	NL (-)
K	K-40	2.64E-24	2.64E-24		
Ca	Ca-41	2.64E-24	2.64E-24	7.0E-04	1.5E-02
Ni	Ni-59	2.64E-24	2.12E-14	2.9E-07	2.9E-07
	Ni-63	2.12E-14			
Se	Se-79	1.52E-05	1.52E-05	1.0E-11	NL
Kr	Kr-81	2.64E-24	1.70E-08		
	Kr-85	1.70E-08			
Sr	Sr-90	4.32E-05	4.32E-05	1.0E-04	2.5E-03
Mo	Mo-93	2.64E-24	2.64E-24	5.0E-6	9.0E-04
Nb	Nb-93m	8.12E-09	8.92E-09	7.0E-09	1.1E-05
	Nb-94	8.01E-10			
Zr	Zr-93	7.64E-04	7.64E-04	2.0E-08	3.0E-08
Tc	Tc-99	7.09E-04	7.09E-04	NL	NL
Pd	Pd-107	2.52E-05	2.52E-05	4.0E-06	1.0E-04
Ag	Ag-108m	2.64E-24	2.64E-24	VL	6E-05
Cd	Cd-113m	2.64E-24	2.64E-24		
Sn	Sn-121	2.64E-24	1.05E-03	1.0E-08	2.0E-06
	Sn-126	1.05E-03			
I	I-129	1.27E-04	1.27E-04	NL	NL
Ba	Ba-133	2.64E-24	2.64E-24		
Cs	Cs-135	1.17E-03	1.23E-03	NL	NL
	Cs-137	5.48E-05			
Pm	Pm-145	2.64E-24	2.64E-24		
Sm	Sm-151	2.38E-05	2.38E-05		
Eu	Eu-152	2.64E-24	2.64E-24		
Re	Re-186m	2.64E-24	2.64E-24		
Pb	Pb-210	1.90E-10	1.90E-10	NL	NL
Bi	Bi-207	2.64E-24	2.64E-24		
Ra	Ra-226	1.37E-08	1.37E-08	7.0E-09	1.0E-06
Ac	Ac-227	7.86E-12	7.86E-12		
Th	Th-229	2.52E-10	2.91E-06	1.0E-08	1.0E-08
	Th-230	9.48E-07			
	Th-232	1.96E-06			
Pa	Pa-231	1.21E-08	1.21E-08	1.0E-08	1.0E-08
Np	Np-237	3.69E-04	3.69E-04	1.0E-09	1.0E-08
U	U-232	5.06E-08	1.16E-01	2.0E-06	3.0E-05
	U-233	1.15E-07			
	U-234	3.12E-04			
	U-235	1.10E-02			
	U-236	4.40E-03			
U-238	1.01E-01				
Pu	Pu-238	1.99E-05	1.22E-03	1.0E-11	1.0E-08
	Pu-239	9.12E-04			
	Pu-240	2.33E-04			
	Pu-241	3.29E-07			
	Pu-242	4.80E-05			
Pu-244	9.62E-06				
Am	Am-241	1.45E-04	1.52E-04	3.0E-10	3.0E-08
	Am-242m	2.64E-24			
	Am-243	6.32E-06			
Cm	Cm-243	9.33E-07	2.14E-06	3.0E-9	3.0E-9
	Cm-244	8.56E-09			
	Cm-245	3.08E-08			
	Cm-246	2.14E-09			
	Cm-247	1.03E-06			
Cm-247	1.35E-07				
Cf	Cf-249	2.64E-24	2.64E-24		

Red - relevant; Orange - potentially relevant, Black - not relevant

Table A-3: Calculated total soluble concentrations of radionuclides in the Non-heat-producing HLW section and solubility limits for free soluble species derived from [1]

Element	Concentration in Waste-EBS [mol/l]			Concentration limit in cementitious container near field [mol/kg]	
	Isotope	per isotope	per element	LL	UL
H	H-3	5.12E-09	5.12E-09		
Be	Be-10	3.65E-25	3.65E-25	1.0E-04	1.0E-04
C	C-14	1.32E-06	1.32E-06	8.0E-06	3.0E-04
Cl	Cl-36	3.65E-25	3.65E-25	NL (-)	NL (-)
K	K-40	3.65E-25	3.65E-25		
Ca	Ca-41	5.12E-09	5.12E-09	7.0E-04	1.5E-02
Ni	Ni-59	4.57E-04	4.86E-04	2.9E-07	2.9E-07
	Ni-63	2.94E-05			
Se	Se-79	5.30E-07	5.30E-07	1.0E-11	NL
Kr	Kr-81	3.65E-25	2.15E-10		
	Kr-85	2.15E-10			
Sr	Sr-90	1.50E-06	1.50E-06	1.0E-04	2.5E-03
Mo	Mo-93	3.87E-07	3.87E-07	5.0E-6	9.0E-04
Nb	Nb-93m	3.79E-09	1.86E-05	7.0E-09	1.1E-05
	Nb-94	1.86E-05			
Zr	Zr-93	2.29E-04	2.29E-04	2.0E-08	3.0E-08
Tc	Tc-99	1.32E-04	1.32E-04	NL	NL
Pd	Pd-107	8.40E-07	8.40E-07	4.0E-06	1.0E-04
Ag	Ag-108m	1.14E-14	1.14E-14	VL	6E-05
Cd	Cd-113m	3.65E-25	3.65E-25		
Sn	Sn-121	3.65E-25	4.35E-07	1.0E-08	2.0E-06
	Sn-126	4.35E-07			
I	I-129	1.47E-05	1.47E-05	NL	NL
Ba	Ba-133	3.65E-25	3.65E-25		
Cs	Cs-135	4.02E-05	4.19E-05	NL	NL
	Cs-137	1.71E-06			
Pm	Pm-145	3.65E-25	3.65E-25		
Sm	Sm-151	8.15E-07	8.15E-07		
Eu	Eu-152	8.81E-13	8.81E-13		
Re	Re-186m	3.65E-25	3.65E-25		
Pb	Pb-210	1.58E-10	1.58E-10	NL	NL
Bi	Bi-207	3.65E-25	3.65E-25		
Ra	Ra-226	1.14E-08	1.14E-08	7.0E-09	1.0E-06
Ac	Ac-227	2.26E-12	2.26E-12		
Th	Th-229	5.98E-10	1.25E-06	1.0E-08	1.0E-08
	Th-230	5.37E-07			
	Th-232	7.08E-07			
Pa	Pa-231	3.39E-09		1.0E-08	1.0E-08
Np	Np-237	1.61E-06	1.61E-06	1.0E-09	1.0E-08
U	U-232	3.48E-11	1.50E-03	2.0E-06	3.0E-05
	U-233	1.30E-08			
	U-234	2.98E-06			
	U-235	7.30E-05			
	U-236	2.43E-05			
	U-238	1.40E-03			
Pu	Pu-238	1.82E-06	1.41E-04	1.0E-11	1.0E-08
	Pu-239	8.59E-05			
	Pu-240	4.02E-05			
	Pu-241	3.37E-08			
	Pu-242	1.30E-05			
	Pu-244	6.65E-09			
Am	Am-241	3.96E-07	4.71E-07	3.0E-10	3.0E-08
	Am-242m	3.65E-10			
	Am-243	7.53E-08			
Cm	Cm-243	6.43E-10	7.51E-09	3.0E-9	3.0E-9
	Cm-244	4.13E-09			
	Cm-245	1.56E-09			
	Cm-246	3.76E-10			
	Cm-247	7.12E-10			
	Cm-247	9.35E-11			
Cf	Cf-249	1.90E-14	1.90E-14		

Red - relevant; Orange - potentially relevant, Black - not relevant

Table A-4: Calculated total soluble concentrations of radionuclides in the Depleted Uranium section and solubility limits for free soluble species derived from [1]

Element	Concentration in Waste-EBS [mol/l]			Concentration limit in cementitious container near field [mol/kg]	
	Isotope	per isotope	per element	LL	UL
H	H-3	3.68E-26	3.68E-26		
Be	Be-10	3.68E-26	3.68E-26	1.0E-04	1.0E-04
C	C-14	3.68E-26	3.68E-26	8.0E-06	3.0E-04
Cl	Cl-36	3.68E-26	3.68E-26	NL (-)	NL (-)
K	K-40	3.68E-26	3.68E-26		
Ca	Ca-41	3.68E-26	3.68E-26	7.0E-04	1.5E-02
Ni	Ni-59	3.68E-26	7.36E-26	2.9E-07	2.9E-07
	Ni-63	3.68E-26			
Se	Se-79	3.68E-26	3.68E-26	1.0E-11	NL
Kr	Kr-81	3.68E-26	7.36E-26		
	Kr-85	3.68E-26			
Sr	Sr-90	3.68E-26	3.68E-26	1.0E-04	2.5E-03
Mo	Mo-93	3.68E-26	3.68E-26	5.0E-6	9.0E-04
Nb	Nb-93m	3.68E-26	7.36E-26	7.0E-09	1.1E-05
	Nb-94	3.68E-26			
Zr	Zr-93	3.68E-26	3.68E-26	2.0E-08	3.0E-08
Tc	Tc-99	3.68E-26	3.68E-26	NL	NL
Pd	Pd-107	3.68E-26	3.68E-26	4.0E-06	1.0E-04
Ag	Ag-108m	3.68E-26	3.68E-26	VL	6E-05
Cd	Cd-113m	3.68E-26	3.68E-26		
Sn	Sn-121	3.68E-26	7.36E-26	1.0E-08	2.0E-06
	Sn-126	3.68E-26			
I	I-129	3.68E-26	3.68E-26	NL	NL
Ba	Ba-133	3.68E-26	3.68E-26		
Cs	Cs-135	3.68E-26	7.36E-26	NL	NL
	Cs-137	3.68E-26			
Pm	Pm-145	3.68E-26	3.68E-26		
Sm	Sm-151	3.68E-26	3.68E-26		
Eu	Eu-152	3.68E-26	3.68E-26		
Re	Re-186m	3.68E-26	3.68E-26		
Pb	Pb-210	2.48E-10	2.48E-10	NL	NL
Bi	Bi-207	3.68E-26	3.68E-26		
Ra	Ra-226	1.79E-08	1.79E-08	7.0E-09	1.0E-06
Ac	Ac-227	1.80E-11	1.80E-11		
Th	Th-229	3.68E-26	4.01E-06	1.0E-08	1.0E-08
	Th-230	1.39E-06			
	Th-232	2.61E-06			
Pa	Pa-231	2.77E-08	2.77E-08	1.0E-08	1.0E-08
Np	Np-237	1.80E-25	1.80E-25	1.0E-09	1.0E-08
U	U-232	8.25E-10	1.70E+01	2.0E-06	3.0E-05
	U-233	3.68E-26			
	U-234	1.07E-03			
	U-235	6.15E-02			
	U-236	2.45E-02			
U-238	1.69E+01				
Pu	Pu-238	3.68E-26	3.63E-25	1.0E-11	1.0E-08
	Pu-239	7.66E-26			
	Pu-240	7.25E-26			
	Pu-241	3.68E-26			
	Pu-242	7.57E-26			
Pu-244	6.45E-26				
Am	Am-241	6.62E-26	1.40E-25	3.0E-10	3.0E-08
	Am-242m	3.68E-26			
	Am-243	3.68E-26			
Cm	Cm-243	3.68E-26	2.86E-25	3.0E-9	3.0E-9
	Cm-244	3.68E-26			
	Cm-245	6.47E-26			
	Cm-246	3.68E-26			
	Cm-247	7.36E-26			
Cm-247	3.68E-26				
Cf	Cf-249	3.68E-26	3.68E-26		

Red - relevant; Orange - potentially relevant, Black - not relevant

Table A-5: Calculated total soluble concentrations of radionuclides in the LILW section and solubility limits for free soluble species derived from [1]

Element	Concentration in Waste-EBS [mol/l]			Concentration limit in cementitious container near field [mol/kg]	
	Isotope	per isotope	per element	LL	UL
H	H-3	3.05E-11	3.05E-11		
Be	Be-10	7.40E-09	7.40E-09	1.0E-04	1.0E-04
C	C-14	2.90E-07	2.90E-07	8.0E-06	3.0E-04
Cl	Cl-36	1.10E-08	1.10E-08	NL (-)	NL (-)
K	K-40	1.22E-05	1.22E-05		
Ca	Ca-41	1.35E-09	1.35E-09	7.0E-04	1.5E-02
Ni	Ni-59	2.19E-07	3.76E-07	2.9E-07	2.9E-07
	Ni-63	1.58E-07			
Se	Se-79	7.90E-09	7.90E-09	1.0E-11	NL
Kr	Kr-81	1.37E-12	1.40E-12		
	Kr-85	3.35E-14			
Sr	Sr-90	9.22E-09	9.22E-09	1.0E-04	2.5E-03
Mo	Mo-93	1.02E-11	1.02E-11	5.0E-6	9.0E-04
Nb	Nb-93m	1.94E-13	6.25E-09	7.0E-09	1.1E-05
	Nb-94	6.25E-09			
Zr	Zr-93	1.61E-08	1.61E-08	2.0E-08	3.0E-08
Tc	Tc-99	5.19E-08	5.19E-08	NL	NL
Pd	Pd-107	3.50E-09	3.50E-09	4.0E-06	1.0E-04
Ag	Ag-108m	8.91E-10	8.91E-10	VL	6E-05
Cd	Cd-113m	2.16E-26	2.16E-26		
Sn	Sn-121	7.18E-13	1.07E-08	1.0E-08	2.0E-06
	Sn-126	1.07E-08			
I	I-129	9.56E-08	9.56E-08	NL	NL
Ba	Ba-133	4.39E-17	4.39E-17		
Cs	Cs-135	3.07E-07	3.30E-07	NL	NL
	Cs-137	2.29E-08			
Pm	Pm-145	2.68E-21	2.68E-21		
Sm	Sm-151	3.18E-10	3.18E-10		
Eu	Eu-152	7.75E-16	7.75E-16		
Re	Re-186m	1.03E-09	1.03E-09		
Pb	Pb-210	1.43E-10	1.43E-10	NL	NL
Bi	Bi-207	2.49E-15	2.49E-15		
Ra	Ra-226	1.03E-08	1.03E-08	7.0E-09	1.0E-06
Ac	Ac-227	5.10E-12	5.10E-12		
Th	Th-229	2.44E-11	4.87E-07	1.0E-08	1.0E-08
	Th-230	4.86E-07			
	Th-232	1.42E-09			
Pa	Pa-231	7.65E-09	7.65E-09	1.0E-08	1.0E-08
Np	Np-237	8.75E-09	8.75E-09	1.0E-09	1.0E-08
U	U-232	2.70E-15	3.94E-02	2.0E-06	3.0E-05
	U-233	5.31E-10			
	U-234	1.63E-06			
	U-235	2.23E-04			
	U-236	5.19E-08			
	U-238	3.92E-02			
Pu	Pu-238	1.39E-09	2.45E-07	1.0E-11	1.0E-08
	Pu-239	7.18E-08			
	Pu-240	1.25E-09			
	Pu-241	1.54E-14			
	Pu-242	1.70E-07			
	Pu-244	1.21E-12			
Am	Am-241	1.49E-08	1.49E-08	3.0E-10	3.0E-08
	Am-242m	2.16E-26			
	Am-243	7.66E-11			
Cm	Cm-243	1.80E-11	4.14E-11	3.0E-9	3.0E-9
	Cm-244	2.23E-13			
	Cm-245	5.93E-13			
	Cm-246	4.13E-14			
	Cm-247	1.99E-11			
	Cm-247	2.75E-12			
Cf	Cf-249	1.06E-14	1.06E-14		

Red - relevant; Orange - potentially relevant, Black - not relevant

Table A-6: S Calculated total soluble concentrations of radionuclides in the lowest Host Rock cell and solubility limits for free soluble species derived from [2]

Element	Concentration in Boom Clay [mol/l]			Concentration limit in Boom Clay (Mol) [mol/l]		
	Isotope	per isotope	per element	BE	LL	UL
H	H-3	1.79E-13	1.79E-13	-	-	-
Be	Be-10	6.93E-12	6.93E-12	8.5E-15	8.5E-16	8.5E-14
C	C-14	2.10E-07	2.10E-07	-	-	-
Cl	Cl-36	5.01E-09	5.01E-09	-	-	-
K	K-40	4.88E-07	4.88E-07			
Ca	Ca-41	1.46E-12	1.46E-12	5.1E-05	3.2E-05	8.1E-05
Ni-59	Ni-59	2.10E-07	2.10E-07	2.6E-05	1.5E-05	4.4E-05
Ni-63	Ni-63	3.41E-11				
Se*	Se-79	7.87E-06	7.87E-06	3.6E-09	6.6E-12	1.9E-06
Kr	Kr-81	4.03E-13	4.03E-13			
	Kr-85	1.72E-16				
Sr	Sr-90	2.96E-13	2.96E-13	7.9E-06	4.7E-06	1.3E-05
Mo	Mo-93	2.69E-08	2.69E-08	1.7E-06	5.2E-07	5.2E-06
Nb	Nb-93m	2.78E-09	1.53E-06	2.4E-06	1.0E-08	1.0E-03
	Nb-94	1.53E-06				
Zr	Zr-93	1.17E-06	1.17E-06	1.8E-08	3.5E-10	9.3E-07
Tc	Tc-99	1.78E-06	1.78E-06	4.4E-09	1.4E-09	1.4E-08
Pd	Pd-107	2.80E-07	2.80E-07	4.0E-06	4.0E-07	4.0E-05
Ag	Ag-108m	7.42E-13	7.42E-13	2.5E-05	2.1E-05	3.0E-05
Cd	Cd-113m	1.32E-25	1.32E-25			
Sn	Sn-121	8.87E-17	1.24E-07	1.9E-07	1.1E-08	3.3E-06
	Sn-126	1.24E-07				
I	I-129	2.73E-06	2.73E-06	-	-	-
Ba	Ba-133	2.21E-19	2.21E-19			
Cs	Cs-135	2.06E-08	2.06E-08	-	-	-
	Cs-137	5.97E-14				
Pm	Pm-145	3.60E-23	3.60E-23			
Sm	Sm-151	5.52E-13	5.52E-13	8.9E-08	2.0E-08	4.1E-07
Eu	Eu-152	1.94E-20	1.94E-20			
Re	Re-186m	6.25E-10	6.25E-10			
Pb	Pb-210	2.44E-10	2.44E-10			
Bi	Bi-207	3.84E-17	3.84E-17			
Ra	Ra-226	1.37E-08	1.37E-08	6.7E-05	3.8E-05	1.2E-04
Ac	Ac-227	8.40E-12	8.40E-12	3.8E-06	2.6E-07	5.7E-05
Th	Th-229	2.28E-09	3.88E-06	2.6E-06	1.0E-11	6.1E-05
	Th-230	1.26E-06				
	Th-232	2.61E-06				
Pa	Pa-231	1.26E-08	1.26E-08	9.8E-10	1.0E-10	1.0E-08
Np	Np-237	9.63E-07	9.63E-07	2.0E-09	1.2E-10	3.3E-08
U	U-232	2.73E-14	8.01E-02	1.0E-06	4.1E-07	2.5E-06
	U-233	4.97E-08				
	U-234	5.06E-06				
	U-235	2.91E-04				
	U-236	1.16E-04				
	U-238	7.97E-02				
Pu	Pu-238	3.91E-13	2.05E-07	1.3E-08	1.3E-10	1.3E-06
	Pu-239	1.55E-07				
	Pu-240	3.53E-08				
	Pu-241	2.17E-13				
	Pu-242	1.39E-08				
	Pu-244	8.89E-10				
Am	Am-241	8.54E-09	6.87E-08	3.8E-06	2.6E-07	5.7E-05
	Am-242m	3.02E-16				
	Am-243	6.02E-08				
Cm	Cm-243	1.21E-15	1.23E-09	3.8E-06	2.6E-07	5.7E-05
	Cm-244	9.02E-18				
	Cm-245	1.28E-10				
	Cm-246	9.96E-10				
	Cm-247	9.48E-11				
	Cm-247	1.23E-11				
Cf	Cf-249	7.59E-18	7.59E-18			

Red - relevant; Orange - potentially relevant, Black - not relevant; * in OPERA calculations no distinction is made between Se (I) and Se(II)

References Appendix

- [1] Wang L, *Solubility of radionuclides in Supercontainer concrete*, External Report SCK•CEN ER-239 (2013) 1-43.
- [2] Bruggeman, C, N Maes, *Radionuclide migration and retention in Boom Clay*, SCK•CEN ER-0345, March 2017

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