

Final report on radionuclide sorption in Boom Clay

OPERA-PU-NRG6123

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-Produktiemaatschappij 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 <u>www.covra.nl</u>.

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Summary

The migration of radionuclides through the host rock plays an important role in the long-term safety of disposal facilities in clay. Due to the slow transport of radionuclides in the host rock, most radionuclides will have decayed before they can enter the surrounding aquifers. For the generic OPERA disposal concept in Boom Clay, the delayed transport of radionuclides through the host rock can be assumed as the most important safety function on the long-term. It is therefore important to understand the basic processes behind the migration of radionuclides in the host rock sufficiently well to be able to make a credible quantitative assessment of the long-term effects of deep disposal of radioactive waste in Boom Clay.

In a preceding report, 'Report on model representation of radionuclide sorption in Boom Clay' (OPERA-PU-NRG6121), processes are discussed that determine which part of the radionuclides will be present in solution, and which will be bound by adsorption to the solid matter and can therefore be considered as immobile. Based on the information summarized there, in the present report the 'OPERA reference sorption model' is described and applied for determination of so-called ' K_{d} -values' that are a measure for the distribution of radionuclides over the solid and solution phase. K_{d} -values for all radionuclides considered in OPERA are determined, for the geochemical conditions expected in the Netherlands. The outcome is presented in a way that it can be used in the deterministic calculations of the OPERA performance assessment calculations, to be performed as part of OPERA WP7.

Samenvatting

De migratie van radionucliden door het gastgesteente speelt een belangrijke rol voor de langtermijn veiligheid van eindbergingsconcepten in klei. Vanwege de zeer trage diffusie van stoffen in het gastgesteente zullen de meeste radionucliden vervallen zijn voordat deze de klei kunnen verlaten. Het zeer trage transport van radionucliden speelt een essentiële rol voor de veiligheid van het generieke OPERA bergingsconcept in Boomse Klei. Om tot een betrouwbare uitspraak over de langetermijn veiligheid te kunnen komen, is het daarom belangrijk om de processen achter dit transportgedrag goed te begrijpen en in kaart te brengen.

In een voorgaand rapport 'Report on model representation of radionuclide sorption in Boom Clay' (OPERA-PU-NRG6121) zijn de processen besproken die bepalen of een radionuclide in de Boomse Klei zich in oplossing bevindt, of door adsorptie aan de matrix van de klei gebonden is en daardoor als immobiel beschouwd mag worden. Op basis van de informatie in dat rapport wordt in het huidige rapport het 'OPERA referentie sorptiemodel' beschreven en toegepast om zogenaamde K_d -waarden te bepalen, die een maat zijn voor de verdeling van radionucliden over de vaste en opgeloste fase. Voor alle radionucliden die binnen OPERA beschouwd worden zijn K_d -waarden bepaald voor de verschillende geochemische omstandigheden die in Nederland verwacht worden. De resultaten zijn zodanig gedocumenteerd, dat deze als input kunnen dienen voor de veiligheidsanalyses die in OPERA WP7 uitgevoerd moeten 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 [2]. This report (M6.1.2.3) presents results of the OPERA research project *RANMIG* (Radionuclide migration), as part of OPERA Task 6.1.2, *Modelling approach for sorption processes*.

In the OPERA research programme, all safety relevant aspects of a given generic reference disposal concept for radioactive waste [1] are evaluated and assessed in order to evaluate the long-term safety of such a facility [2]. The programme follows in general terms the methodology known as 'Safety Case' [3, 4, 5]. 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.

1.2.Objectives

Radionuclide adsorption is a key process in defining the mobility (or migration) of radionuclides in Boom Clay. The objective of the present report is to derive model parameter values that adequately address radionuclide sorption in Boom Clay. Because of the generic state of the OPERA disposal concept (no specific location given, therefore properties of the host rock not exactly known), the influence of factors that may affect the sorption properties of the host rock are evaluated. The final outcome of this report is a list of K_d -values for all radionuclides considered in OPERA.

1.3.Realization

This report represents revision 1 of the public report M6.1.2.3, Final report on radionuclide sorption in Boom Clay, and is prepared by NRG. The present report is a follow-up of M6.1.2.1 [6], Report on model representation of radionuclide sorption in Boom Clay, where an approach is discussed to model radionuclide sorption processes in Boom Clay in the Netherlands, and key concepts and modelling approaches for sorption were evaluated. In the present report, a step-wise procedure is followed leading to the 'OPERA reference sorption model' that describes sorption of radionuclides to the various phases in Boom Clay. The variability of the calculated K_d 's, due to the uncertainty on several input parameters, is evaluated and the resulting K_d ranges compared to Belgian data. Eventually, using that model, for the various radionuclides considered in [7] conservative K_d -values and their distribution is determined for use in the deterministic calculations of the normal evolution scenario. The calculations are part of the OPERA Central Assessment Case ([8], Section 4.2) and will be performed as part of OPERA WP 7.

The interaction between the OPERA Tasks 6.1.2, 6.1.3, 6.1.4 and WP7 is given in Figure 1-1.



Figure 1-1: Schematic overview of relationship between OPERA WP6.1 tasks and WP7

A revision of the report was prepared in order to clarify some information and to account for new information provided in May - July 2017.

1.4. Explanation contents

Chapter 2 gives a condensed outline of the overall approach followed in this report. Chapter 3 describes the set-up and testing of the 'OPERA reference sorption model' that will be used to determine K_d -values for the performance assessment in OPERA WP7. In Chapter 4, ranges of K_d -values for conditions relevant in the Netherlands are calculated and discussed. Chapter 5 gives an overview on the K_d -values recommended for the OPERA performance assessments. Finally, in Chapter 6 a brief conclusion and outlook is given. In Appendix A, all species used in the OPERA reference sorption model are documented.

2. Outline of the approach followed to derive sorption parameters

For the derivation of sorption parameter values for the OPERA performance assessment, a two-phase approach was described and argued in [6], briefly summarized here:

- In the first phase, a reference multi-surface sorption model representation is developed ('*OPERA reference sorption model*') and compared with experimental results from the Belgian research programme. The outcome of the first phase is summarized in Chapter 3.
- In the second phase, this reference sorption model is used to calculate resulting K_d ranges due to application of that model in the OPERA safety assessment, with input parameter ranges representative for Dutch Boom Clay properties. These K_d ranges are derived by uncertainty analyses with the reference sorption model, in order to investigate the influence of the varying geochemical conditions in the Netherlands on the sorption behaviour. The outcome of the second phase is summarized in Chapter 4.



Figure 2-1: Two-phase approach to derive K_d -values for the OPERA safety assessment

3. Set-up of reference model

The 'OPERA reference sorption model' is developed in three steps:

- Step 1: Set-up of reference model: Based on existing models and databases, a geochemical model representation is developed and implemented in the geochemical workbench ORCHESTRA [9]. The principal processes covered by the model are discussed in [6; Section 4.3.1]. The model will be parameterized by geochemical data measured in Boom Clay samples from Mol and requires no fitting of parameters.
- Step 2: Calculation of apparent K_d -values: The fully parameterized model will calculate the sorption behaviour of all radionuclides of interest. The overall sorption behaviour will be translated into K_d -values for each considered radionuclide. The K_d -values are apparent, conditional values only valid for the specific conditions of the system under consideration.
- Step 3: Comparison of outcomes: The outcome of the modelling will be compared with experimentally supported sorption data from SCK·CEN.



Figure 3-1: Steps and elements of the first phase

3.1.Set-up of the OPERA reference sorption model for Boom Clay

Based on existing models and databases as discussed in [6; Chapter 3] and the considerations discussed in [6; Chapter 4.1], a geochemical model representation was developed, further denoted as 'OPERA reference sorption model'.

3.1.1. Selection of submodels and databases

As described above, the purpose of the reference model is to calculate the sorption behaviour of radionuclides for a large range of Boom Clay properties expected in the Netherlands. To allow addressing the variability of the Boom Clay, the distribution of radionuclides over different chemical forms, including dissolved, colloidal, and immobile adsorbed species is calculated by the reference model.

Description of the overall mechanistic modelling approach

A mechanistic multi-surface model description for Boom Clay was set up in the geochemical modelling workbench *ORCHESTRA* [9], following a comparable approach as the generic sorption model for inorganic contaminants in Dutch soils described and evaluated by Dijkstra et al. [10]. The multi-surface model approach distinguishes several reactive surfaces present in Boom Clay ('additivity assumption').

The rationale behind the selection of the sorption models is the following: for the mobility of cations, the solid-solution partitioning of reactive surfaces is often dominating the overall distribution (see [6] and the literature cited therein). Organic matter is known to be the far most relevant reactive surface with respect to its solid-solution partitioning, and its effect on contaminant transport is well known and described in literature as 'facilitated transport'. In this study, the dissolved fraction of the organic matter ranges from 0.02 to 1.25 % (Table 4-1), resulting in up to 1.25% of strongly adsorbing radionuclides present in solution. A proper modelling of ion interaction with reactive organic matter is therefore essential, and is implemented by means of the *consistent NICA-Donnan model* (see below).

At first instance, the influence of colloidal iron is assumed to be of less relevance: based on the expected concentrations of soluble iron and crystalline iron in Boom Clay (Table 3-2 and Table 4-1), less than 0.01% of crystalline iron is expected to be present in solution. However, the chemistry of iron is complex, and soluble amounts are often not in accordance with equilibrium modelling. To evaluate for which elements sorption on iron(hydr)oxides is of principal interest, adsorption to iron(hydr)oxides is modelled by a well-established surface complexation model (*Generalized two layer model*, see below).

No other colloidal reactive surfaces of relevance to be included in the model have been identified (see also M6.1.4, [11]). However, due to its large exchange capacity and well known role in ion exchange and adsorption, sorption to clay is also added to the reference sorption model. A rather straightforward approach is followed by only addressing (nonspecific) exchange in the *electrostatic double layer*. The applied ion exchange model requires no assumption on individual elemental binding affinities. Although sufficient information is available in the literature to model also specific surface interactions of the radionuclides of interest (see [6] and the literature cited therein), these interactions are not integrated in the reference model. The main reason is that translation of results from sorption experiments on pure materials to a complex natural medium as the Boom Clay is not trivial: the additivity assumption, as discussed in [6], can lead to overestimation of the overall sorption due to neglection of interactions between different reactive surfaces (e.g. [12, 13, 14]). Suitable mechanistic model descriptions for the interactions between reactive surfaces are currently not available. It is expected that this conservative simplification avoids an underestimation of radionuclide mobility, while it is also likely that this approach can lead to an overestimation of the mobility of some radionuclides.

The chosen mechanistic approach (Figure 3-2) is based on selected thermodynamic data and enables independent predictions of speciation and sorption behaviour of radionuclides, i.e. without fitting. This allows studying the effects of different expected chemical conditions on the sorption behaviour. By comparing such independent calculations with available experimental data on sorption from the Belgian research programme, it is possible to estimate the accuracy of the mechanistic model representation.



Figure 3-2: Overview of application of model to estimate K_d -values

Selection of submodels and applied databases

The multi-surface model consists of the following six sub-models representing interactions in the aqueous phase and with the solid and colloidal phase [10]:

- Aqueous complexation model (interaction between aqueous ions),
- Ion activity correction model (effect of ionic strength of solution on activity),
- Precipitation of mineral phases,
- Adsorption of ions by clay particles,
- Adsorption of ions by solid and dissolved organic matter, and
- Adsorption of ions by oxide particles.

The applied model components related to the calculation of the aqueous chemistry of the pore water solution can be summarized as follows:

Modelling of aqueous complexation reactions

The first sub-model takes into account aqueous complexation reactions for the main components *H*, *O*, *Ca*, *Na*, *Cl*, *S*, inorganic carbon, and *Fe*, and the radionuclides *Am*, *Cd*, *Cm*, *Cs*, *Eu*, *K*, *I*, *Ni*, *Np*, *Pb*, *Pu*, *Se*, *Sn*, *Sr*, *Ra*, *Tc*, *Th*, and *U*. Furthermore, redox reactions can be accounted for by introducing the electron as component (*e*). The equilibrium constants are taken from the NEA database [15]. Additional data on missing chloride and carbonate complexes are added from [16, 17, 18, 19]. Species with concentrations below 10^{-35} mol/l for all samples are neglected in order to increase the numerical efficiency of the calculations. The complete set of dissolved species used in the model and their stoichiometric composition is summarized in Appendix A. Table 3-1 summarizes how the different component values are entered into the model.

Table 3-1: Modelling input entities

| entity | input as |
|--------------------------|--------------------------|
| Ca, Fe, S, radionuclides | total amount |
| Na, Cl | soluble concentrations |
| рН | <i>log</i> activity |
| pe | <i>log</i> activity |
| inorganic carbon | CO ₂ pressure |

Activity correction

Activity corrections are necessary to link concentrations and reactivity of charged aqueous ions in solution. The correction is performed according to the *Davies equation*, an extension of the *Debye-Hückel equation* [19], with the activity coefficient γ_i computed according to:

$$\log \gamma_i = -0.509 \cdot Z_i^2 \left(\frac{\sqrt{\mu}}{1 + \sqrt{\mu}} - 0.3\mu \right)$$
 Eq. 3-1

with Z_i the valence of the ion *i* and μ the ionic strength of the solution.

Modelling of precipitation reactions

Precipitation reactions are addressed by selecting the relevant minerals. The minerals considered by the reference model are calcite, gypsum, pyrite, siderite, and microcrystalline $Fe(OH)_{3,}$ and corresponds to the pH and pe ranges used and the minerals abundant in Boom Clay. Data on the mineral solubility are taken from the NEA database [15].

Modelling of sorption to clay particles

For clay, non-specific adsorption to the permanently charged clay surfaces is addressed by a *Donnan volume* with a fixed charge. This model takes into account the effects of charge on ion sorption and exchange and does not require ion or surface specific exchange parameters. Specific effects of ion size or specific binding are not accounted for. The input parameters necessary for this model are the *amount of clay*, the *charge density* and the *Donnan volume*. The charge of the clay, q, is balanced by counter ions in the Donnan volume V_d to electrical neutrality, with the electrical charge balance expressed as

$$q/V_D = -\sum Z_i \ (c_{D,i} - c_{i,})$$
 Eq. 3-2

with Z_i the charge of the ion *i*, and c_i and $c_{D,i}$ the concentration in the bulk solution and Donnan phase, respectively. The latter two are related to each other by a Boltzmann factor:

$$c_{D,i} = c_i e^{-z_i F \Psi_D / RT}$$
 Eq. 3-3

with ψ_D the Donnan potential and RT the Boltzmann-factor and temperature. A charge density of 25 meq/g of clay is used, which is an average value for illitic clay minerals [20]. The Donnan volume varies with the square root of the ionic strength [21], according to

 $V_D = B\sqrt{\mu}$ Eq. 3-4

with the empirical factor B = 0.05 resulting in a maximum Donnan volume V_d of about 1 L/kg for the considered conditions [10]. The charge density is within the range of values measured in Boom Clay in Mol (Table 3-4). The simplified approach followed here differs from the approach followed by SCK·CEN that includes more detailed sorption models on

clay (i.e. the 2 SPNE SC/CE model [22, 23, 24, 25, 26, 27, 28] and the general 3-site ion exchange model (3-IEX) developed by Bradbury and Baeyens [29, 30], see also [6], Chapter 3.3). The consequences of this modelling choice will be discussed later in this report.

Modelling of sorption to iron (hydr)oxides

In reduced Boom Clay, the amount of oxides will most likely be small as iron oxides will be reduced or dissolved. Under oxidized conditions available iron will precipitate as iron (hydr)oxide. Sorption to iron (hydr)oxides is expected to have only a minor contribution to overall sorption behaviour of the clay. However, iron(hydr)oxides may be present as soluble colloids and facilitate the migration of radionuclides [31], and it is therefore important to get some understanding on the relevance of such a migration route. Although no quantitative information on the presence of such colloids in Boom Clay is available, it is decided to model sorption to solid phase iron(hydr)oxides in order to gain some insight in the potential relevance of that surface for the overall distribution of radionuclides, and to identify the elements for which iron(hydr)oxides are of relevance. The widely used *Generalized two layer model* for sorption on hydrous ferric oxide (HFO) [32] is applied to describe sorption on iron (hydr)oxides. In the *Generalized two layer model*, the surface charge σ in the double layer plane d is calculated by

$$\sigma_d = -\frac{Sa}{F} \sqrt{8\varepsilon_0 \mu DRT} \cdot \sinh\left(F \Psi_d / 2RT\right)$$
 Eq. 3-5

where *S* is the surface area, *a* the suspension density, *F* the Faraday constant, ε_o the permittivity, *D* the dielectric constant of water, and μ the ionic strength. The intrinsic conditional equilibrium constants for protonation-dissociation are defined as

$$K_{+}(int) = \frac{[X \cdot OH_{2}^{+}]}{[X \cdot OH][H^{+}]} e^{F\psi_{0}/RT}$$
Eq. 3-6

and

$$K_{(int)} = \frac{[X \cdot O^{-}][H^{+}]}{[X \cdot OH]} e^{F\psi_{0}/RT}$$
Eq. 3-7

with ψ_o , the surface potential, equal to ψ_d . The intrinsic conditional equilibrium constants for surface complexation reactions of metals and ligands of the valence m and l are defined as

$$K_{M}^{1}(int) = \frac{[X \cdot OM^{m-1}][H^{+}]}{[X \cdot OH][M^{m+}]} e^{(m-1)F\psi_{0}/RT}$$
Eq. 3-8

and

$$K_{L}^{1}(int) = \frac{[X \cdot L^{l-1}][H^{+}]}{[X \cdot OH][L^{l-}][H^{+}]} e^{-(l-1)F\psi_{0}/RT}$$
Eq. 3-9

The model is supported by a large database with empirically determined binding constants that are applied in the model. A specific surface area of 600 m²/gram of iron (hydr)oxide is used [10]. Sorption parameter values for *Ca*, *Cd*, *Cl*, *Ni*, *Pb*, *S*, *Se*, *Sn*, and *Sr* are based on [33], sorption parameter values for *Cs*, *Eu*, *Np*, *Pu*, *Am*, *Cm*, *Th*, and *Tc* are based on [39].

Modelling of sorption to organic matter

For adsorption of ions to organic matter (both dissolved and particulate) the *consistent NICA-Donnan* model [34] is used. This model takes into account ion competition and the heterogeneity of organic matter binding sites, and the enclosing charged double layer. The *NICA-Donnan* model represents binding of ions to organic matter surface by a continuous distribution of the binding constant [35]. That approach differs from other model descriptions (e.g. [36, 37]) that approximate this heterogeneity by using a finite number of discrete binding sites with various binding constants. In the *NICA-Donnan* model, the reactive organic matter fraction is considered to behave as a gel phase with the net charge of the humic material balanced by counter ions to electrical neutrality, equivalent to Eq. 3-2 and Eq. 3-3. The volume of the Donnan-layer is calculated dependent on the ionic strength, according to

$$\log V_d = b(1 - \log I) - 1$$
 Eq. 3-10

with b = 0.49 [38, Table 6.4]. The amount of protons bound, Q_{H} , is expressed in the bimodal consistent NICA model as

$$Q_{H} = Q_{\max,H1} \frac{\left(\tilde{K}_{H1}[H_{s}]\right)^{m_{1}}}{1 + \left(\tilde{K}_{H1}[H_{s}]\right)^{m_{1}}} + Q_{\max,H2} \frac{\left(\tilde{K}_{H2}[H_{s}]\right)^{m_{2}}}{1 + \left(\tilde{K}_{H2}[H_{s}]\right)^{m_{2}}}$$
Eq. 3-11

with $Q_{max,H}$ the maximum site density, \tilde{K}_{H1} is the median of the affinity distribution with width m, and [H_s] the surface concentration of protons. The fractional site occupancy of an ion i, θ_i , is related to the amount of component bound, Q_i , by

$$Q_{i} = \theta_{i} \left(\frac{n_{i}}{n_{H}}\right) \cdot \left(Q_{\max,H1} + Q_{\max,H2}\right)$$
Eq. 3-12

with n_i/n_H the ratio of the Freundlich-exponents of the ion *i* and the proton. The amount of cations bound to the two surface sites can be calculated by

$$Q_{\max,H1} = \frac{\left(\tilde{K}_{i1}[c_i]\right)^{n_{i1}}}{1 + \sum_i \left(\tilde{K}_{i1}[c_i]\right)^{n_{i1}}} \cdot \frac{\left[\sum_i \left(\tilde{K}_{i1}[c_i]\right)^{n_{i1}}\right]^{p_1}}{1 + \left[\sum_i \left(\tilde{K}_{i1}[c_i]\right)^{n_{i1}}\right]^{p_1}}$$
Eq. 3-13

and

$$Q_{\max,H2} = \frac{\left(\widetilde{K}_{i2}[c_i]\right)^{n_{i2}}}{1 + \sum_i \left(\widetilde{K}_{i2}[c_i]\right)^{n_{i2}}} \cdot \frac{\left[\sum_i \left(\widetilde{K}_{i2}[c_i]\right)^{n_{i2}}\right]^{p_2}}{1 + \left[\sum_i \left(\widetilde{K}_{i2}[c_i]\right)^{n_{i2}}\right]^{p_2}}$$
Eq. 3-14

where \tilde{K}_i is the median of the affinity distribution with width *n*, and $[c_i]$ the surface concentration of the ion *i*.

The *NICA-Donnan* model is well tested on multi-component natural and waste systems. The model comes with a standard set of generic binding parameter values [34, 38], and distinguishes between two fractions of organic matter: fulvic and humic acids. However, since the fulvic and humic acid's sorption behaviour is quite similar in comparison to existing uncertainties [34, 38], and no data on the SOC and DOC composition in Dutch Boom Clay is available, only sorption to humic acid is modelled, assuming to be representative for all reactive organic matter fractions [45].

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For a number of radionuclides for which no experimental data were available (*Cs*, *Eu*, *Np*, *Pu*, *Sn*, and *Tc*), binding constants on organic matter where derived by the use of linear free energy relationships (LFERs) [39,40]. The binding constants of *Ra* were set equal to the constants of *Ca*, due to its chemical similarity and the lack of better data. The anions *Se* and *I* were not taken into account.

3.1.2. Boom Clay properties in Mol

Table 3-2 to Table 3-4 below provide overviews concerning the pore water composition, the mineralogical composition and physical properties of Boom Clay samples from Mol as used for the evaluation.

| Parameter | Reference pore water composition | References |
|----------------------------------|----------------------------------|------------|
| CI ⁻ [mg/l] | 26 | [41] |
| SO 4 ⁻² [mg/l] | 2.2 | [41] |
| Na [mg/l] | 359 | [41] |
| K [mg/l] | 7.2 | [41] |
| Ca [mg/l] | 2.0 | [41] |
| Mg [mg/l] | 1.6 | [41] |
| Fe [mg/l] | 0.2 | [41] |
| Si [mg/l] | 3.4 | [41] |
| AI [μg/l] | 0.6 | [41] |
| Ionic strength [mol/l] | 0.016 | [41] |
| HCO₃ ⁻ [mg/l] | 879 | [41] |
| DOC [mg C/I] | 120-200 [*] | [41] |
| рН [-] | 8.5 | [41] |
| E _h [mV] | -274 | [41] |

Table 3-2: Reference pore water composition in Boom Clay in Mol

* note that the synthetic *reference pore water* does not contain DOC

| Table 3-3: Minera | concentrations i | n Boom | Clay in | Mol [| [42] |
|-------------------|------------------|--------|---------|-------|------|
|-------------------|------------------|--------|---------|-------|------|

| Mineral | % dry weight (min-max) |
|----------|------------------------|
| Siderite | 0.0 - 1.5 |
| Calcite | 0.0 - 4.6 |
| Dolomite | 0.0 - 1.0 |
| Pyrite | 0.3 - 5.0 |

Table 3-4: Other properties of Boom Clay in Mol

| Parameter | min - max | References |
|---------------------------------------|---------------|------------|
| Bulk wet density [kg/m ³] | 1.900 - 2.100 | [43] |
| Porosity [wt. %] | 36 - 40 | [43] |
| Clay fraction [wt. %] | 35 - 75 | [43] |
| CEC clay [meq/100g] | 19.5 - 25.9 | [44] |
| SOC [wt. %] | 1.0 -4.0 | [45] |
| Proton exchange capacity SHA [meq/g] | 2 | [45] |
| DOC [mg/L] | 50 - 200 | [45] |
| Proton exchange capacity DHA [meq/g] | 4 | [45] |
| Inorganic carbon [wt. %] | 0.3 - 0.5 | [43] |

3.2. Calculation of apparent K_d-values

The elements *I*, *Cd*, *Cs*, *K*, *Ni*, *Th*, *Se*, *Np*, *U*, *Pu*, *Tc*, *Am*, *Cm*, *Sn*, *Ra*, *Pb*, *Sr* and *Eu* were implemented in the reference sorption model and tested within the present analysis. Calculations were carried out with the object-oriented modelling workbench ORCHESTRA [9], the databases described in Section 3.1.1 and the ranges of Boom Clay properties summarized in Section 3.1.2. The reactive behaviour was analysed and summarized as ranges of K_d -values (in L/kg) according to

$$\mathbf{K}_{d,i} = \frac{\mathbf{X}_i}{C_i}$$
 Eq. 3-15

with X_i the amount of a radionuclide *i* sorbed to the solid matrix, and C_i the concentration in solution. The resulting K_d -values are conditional values that are valid for the specified conditions only ("apparent K_d ").

3.3. Comparison of outcomes

In [6], expert ranges of K_d -values representative for Boom Clay in Mol are provided by SCK-CEN. The K_d -ranges related to strongly DOC-bound radionuclides (*Th*, *Np*, *U*, *Pu*, *Am*, *Cm*, *Ni*, *Tc*, *Eu*) are not directly applicable, because they refer to a solution without DOC. In the presence of DOC, however, the mobility of these radionuclides can be higher, mainly depending on the migration behaviour of DOC ('facilitated transport').

In order to allow a sensible comparison of the outcomes of the model calculation with the data ranges provided in [6], it was necessary to convert the given ranges into K_{d} -values valid for the expected range of DOC concentrations in Mol (96 - 146 mg/l, best estimate 115 mg/l; [46], p. 62). This is done by using the relation in Eq. 3-16 (see also Eq. 3-13 in [46]):

$$\frac{C_{RN-DOC}}{C_{sol}}[-] = C_{DOC} \cdot K_{RN-DOM}$$
Eq. 3-16

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 proton exchange capacity of 2 meq/kg DOC is assumed [45].

Figure 3-3 provides a graphical overview on the sorption data of strongly DOC-binding radionuclides compiled by SCK-CEN as function of the DOC concentration, and the expert ranges as documented in [6, 46]. In the same figure, for the assumed DOC concentrations (vertical lines) the derived equivalent K_{d} -values (horizontal lines) are shown for three cases: the best estimate (black), the lower limit (blue), and the upper limit (red).



Figure 3-3: Equivalent K_d -values of strongly DOC-binding radionuclides for DOC concentrations ranging from 96 to 146 mg/l (best estimate = 115 mg/l) and related log K_{RN-DOM} values ranging from 5.0 - 5.6 (best estimate = 5.3). Adapted from [46].

Table 3-5 summarizes, based on the assumptions and analyses described above, the best estimate and range of the 'equivalent' K_d -values for strongly DOC-bound radionuclides for the expected DOC concentrations in Boom Clay, as present in Mol.

| Table 3-5: | DOC | concentratio | n and estimat | ed proton e | xchange | capac | ities in B | oom Clay i | n Mol, |
|------------|-------|---------------|---------------|-------------------------|----------|--------|------------|-------------|--------|
| | and | calculated | 'equivalent | K _d -values' | valid | for s | strongly | DOC-comp | olexed |
| | radio | nuclides at t | he given DOC | amounts. Bl | E = best | estima | te, $LL =$ | lower limit | , UL = |
| | uppe | r limit. | | | | | | | |

| | BE | LL | UL |
|---------------------------------------|----------|----------|----------|
| DOC [mg/l]: | 115 | 96 | 146 |
| Proton exchange capacity DOC [eq/kg]: | 2 | 2 | 2 |
| Proton exchange capacity DOC [eq/l]: | 2.30E-04 | 1.92E-04 | 2.92E-04 |
| log К _{RN-DOM} [-]: | 5.3 | 5.6 | 5.0 |
| Equivalent K _d [L/kg]: | 128 | 39 | 993 |

In Table 3-6, the resulting K_{d} -values are compared with the values calculated by the OPERA reference sorption model for Boom Clay in Mol.

Table 3-6: Overview of K_d -values for Boom Clay in Mol calculated with the OPERA reference sorption model, and equivalent K_d -values recalculated on basis of K_d -values provided by SCK·CEN [6] - Table 3.5. Recalculation of equivalent K_d -values was performed for strongly DOC-bound elements only and are rendered in italics.

| | | K _d ranges for Bo | | | |
|---------|--------------|------------------------------|------------------------------|--------------|---|
| Element | Calculated | by OPERA | Equivalent K _d -v | alues, based | Support by experiments in Boom |
| | reference so | rption model | expert ranges | of SCK·CEN | Clay in Mol |
| | range | median | range | median | |
| К | 1 - 2 | 1 | - | - | |
| Ca | 40 - 132 | 78 | 180 - 800 | 340 | diffusion experiments |
| Ni | 40 - 253 | 100 | 40 - 1000 | 128 | |
| Sr | 40 - 236 | 97 | 180 - 800 | 340 | sorption & diffusion experiments |
| Тс | 40 - 253 | 100 | 40 - 1000 | 128 | sorption, diffusion & complexation experiments |
| Sn | 40 - 253 | 100 | - | - | |
| Cd | 40 - 253 | 100 | - | - | |
| Cs | 183 - 1038 | 605 | 600 - 18'600 | 9600 | sorption & diffusion experiments |
| Eu | 44 - 282 | 109 | 40 - 1000 | 128 | sorption, diffusion & complexation experiments |
| Pb | 53 - 309 | 123 | - | - | |
| Ra | 40 - 237 | 97 | 1800 - 8000 | 3400 | diffusion experiments |
| Th | 40 - 253 | 100 | 40 - 1000 | 128 | sorption experiments |
| Np | 40 - 253 | 100 | 40 - 1000 | 128 | diffusion & complexation experiments |
| U | 27 - 243 | 93 | 40 - 1000 | 128 | diffusion & complexation experiments |
| Pu | 40 - 253 | 100 | 40 - 1000 | 128 | diffusion & complexation experiments |
| Am | 52 - 414 | 134 | 40 - 1000 | 128 | sorption, diffusion & complexation experiments |
| Cm | 40 - 253 | 100 | 40 - 1000 | 128 | diffusion experiments |

The calculated <u>median</u> K_d -values of all elements except Ca, Sr, and Ra fall in the ranges recalculated from the SCK·CEN expert ranges. The calculated <u>ranges</u> of K_d -values fall generally within the expert ranges as well, except of Ca and Ra which are below the given ranges, and Cs, Sr, and U that show only partial overlap. None of the calculated ranges underestimated the mobility of the radionuclides.

The lower K_d -value for Cs is attributed to the known strong specific binding to clay minerals, which is not accounted for in the current model. This leads to a underestimation of the solid-solution partitioning. Furthermore, some limitations of the quality of the data fit of Am and Eu organic matter sorption parameter were noted in [38], but as will be shown in the next chapter, these are hardly significant for the studied system.

3.4. Conclusions

The reference sorption model shows - without any parameter fitting - sufficient resemblance with the estimates provided by SCK-CEN for the purpose of this study. The chosen set-up was expected to lead to a conservative (under)estimation of the solid-solution partitioning. Part of the higher solubility estimates made here might be attributed to the (estimated) sorption parameter values for organic matter, but are more

likely related to the chosen simplified modelling approach for sorption on clay, where only non-specific binding was accounted for. This modeller's choice results in organic matter to be the dominant sorbent for almost all elements. The ratio of dissolved and solid organic matter is one of the key parameter for the understanding the sorption behaviour of radionuclides in Boom Clay, as will be elaborated in more detail in the next chapter.

However, there is no principal constraint to add a more specific binding by clay into the reference sorption model in a later stage, e.g. in case the outcomes of the OPERA safety assessment calculations show that for some scenarios uncertainties on the long term safety might be relevantly reduced by refining the model for some radionuclides. In M6.1.2.1 [6] a variety of references on experimental data is given that allow a more detailed modelling of radionuclide sorption on clay within the current OPERA reference sorption model. Such an effort could also be considered in support of future experimental research on Boom Clay.

The most important conclusion is that in no case the solid-solution partitioning was overestimated by the reference sorption model, making it a convenient, conservative tool for evaluating radionuclide sorption in the context of performance assessment calculations. The relevance of organic matter sorption vs. clay sorption, and its effects on the derived K_d -values will be discussed in more detail in the next chapter.

4. Derivation of K_d -values

The derivation of K_d -values that will be used in the OPERA safety assessment calculations is performed in four steps:

- Step 1: Generation of distributed parameter samples: Based on the parameter ranges on Boom Clay properties in the Netherlands [6; Section 4.3.3], parameter distributions for the model calculations are defined and samples are generated. The samples are used as input for the OPERA reference sorption model for Boom Clay discussed in the previous chapter.
- Step 2: Calculation of apparent K_d-values: The OPERA reference sorption model is used to compute K_d-values for all parameter samples.
- Step 3: Analysis of calculated range of K_d -values: Uncertainty analyses are performed for all sample results computed in the previous step, and central K_d -values and their distribution are derived for each radionuclide considered.
- Step 4: Comparison of outcomes: The outcomes are compared with the K_{d} -values used by the Belgian research programme, and a recommended set of reference values to be used in the deterministic calculations of the OPERA Central Assessment Case [8] is derived and discussed. The resulting set of K_{d} -values is summarized in Chapter 5.



Figure 4-1: Steps and elements of the second phase

4.1. Generation of distributed parameter samples

Based on the parameter ranges on Boom Clay properties in the Netherlands [6; Section 4.3.3], parameter distributions for the model calculations are defined and 9000 samples are generated. The samples are used as input for the *OPERA reference sorption model* for Boom Clay discussed in the previous chapter.

Handling of uncertainties and heterogeneous data ranges

In [6], three regions with different properties could be identified. However, given the limited amount of data available on key parameters for sorption, it is decided to cumulate the data of all regions rather than defining specific K_d -values for each of these three regions. The resulting ranges of input parameter values represent various types of uncertainty: next to the variability of parameters that can always be found in nature, the ranges used in this study also reflect site-specific features. Variability of parameters leads usually to a distribution around a mean value and can be treated by standard statistical tools. In contrast, the data ranges that reflect different site properties (e.g. clay and organic matter content) vary to a much larger extent than the expected variations on a specific location. Beside, due to the lack of data on some key parameters (e.g. DOC, bicarbonate concentration, pH), the ranges reflect expected values based on geochemical expert judgement, but no distribution or 'most likely value' can be defined. As a consequence, any basis for the application of weighted parameter distributions (e.g. Gaussian distribution) is lacking. Therefore uniform ranges were defined for most parameters (log uniform distributions for Na and Cl, uniform distributions for the others). Since the available samples do not cover all areas of interest, these uniform ranges are extended beyond the measured range of values. In most cases the lowest and highest average value found in any region ±2·sd was applied, except for SOC, Ca, Cl, Na, inorganic carbon and S, where the lowest measured values are taken as lower boundary. However, it must be emphasized that this approach gives more weight to extreme values than e.g. a Gaussian distribution.

Derivation of parameter ranges

Only minor variations of the redox potential have been reported for Boom Clay in Mol. In soil systems, redox potentials are negatively correlated to the pH via equilibria of redox active elements (mainly iron) with mineral phases. The redox status of a soil system is therefore often expressed by a pH + pe value (e.g. [19]), and it was decided to vary the redox state in correlation with pe rather than to fix it by equilibrium with a mineral phase (e.g. pyrite, calcite and/or siderite). This leads to a larger variability of these influential parameters used for the performed calculations than actually measured in Mol.

The CEC of clay particles in Boom Clay is determined by assuming 36-50 meq per 100 g of the <2 µm-fraction ([6], Table 4-3), rather than making use of the limited number of samples summarized in ([6], Table 4-6). The amount of iron (hydr)oxide is based on the amounts of crystalline iron derived in [47], assuming a specific surface area of $600 \text{ m}^2/\text{gram}$ of iron (hydr)oxide [10]. DOC concentrations measured in the Netherlands in sub-surface layers *above* the Boom Clay ([6], Table 4-9) are much lower than values from samples in Mol. Because of the relevance of DOC for radionuclide migration ([6], Section 2.2.3), for the upper limit of DOC concentrations the conservative high values from Mol are used. Maximum proton exchange capacities (Q_{max}) of 2 and 4 meq per gram of solid humic acids (SHA) and dissolved humic acids (DHA) were measured in Boom Clay from Mol [45, Table 3.6]. These values are roughly one and two-thirds of the values used for sorption modelling on SHA and DHA by the *NICA-Donnan* model [34, 38]. To cover uncertainties on the DOC and SOC composition generally found in literature and the lack of data on Boom Clay in the Netherlands, Q_{max} is varied by a factor of 2 (SOC) and 3 (DOC).

For inorganic carbon, a constant partial pressure of 10^{-2.65} atm is applied. The gas pressure is not varied independently, but together with other factors as the pH, soluble bicarbonate concentrations vary within a range comparable to what is measured in Mol (see Table 3-2). Porosity and wet bulk density distributions were directly adopted from the RANMIG report on diffusion [48].

| property | min - max | Source |
|---|---------------|-----------------------------|
| Bulk wet density [kg/m ³] | 1.900 – 2.150 | [48] |
| Porosity [%] | 29 – 43 | [48] |
| CEC Boom Clay [meq/100g Boom Clay] | 2.0 - 42 | [6, Table 4-6], see text |
| SOC [wt. %] | 0.35 – 2.0 | [43] |
| Proton exchange capacity SHA [meq/g] | 1 – 2 | [45] |
| DOC [mg/L] | 20 - 200 | [43], see text |
| Proton exchange capacity DHA [meq/g] | 2 – 6 | [45] |
| HFO [g/kg] | 0.4 - 3.3 | [6, Table 4-11] |
| Inorganic carbon [wt. %] | 0.0 – 2.5 | [6, Table 4-6] |
| Total amount Ca [wt. %] | 0.2 – 7.3 | [6, Table 4-7] |
| Total amount Fe [wt. %] | 2.2 - 5.4 | [6, Table 4-6] |
| Total amount S [wt. %] | 0.35 – 2.6 | [6, Table 4-6] |
| Soluble concentration CI [mg/L] | 4 – 20'000 | [6, Table 4-12, Table 4-13] |
| Soluble concentration Na [mg/L] | 4 – 11'000 | [6, Table 4-12, Table 4-13] |
| pH [-] | 7.7 – 9.2 | [43] |
| pe + pH [-] | 3.8 – 5.8 | [43], see text |

Table 4-1: Expected properties of Boom Clay in the Netherlands

On basis of the distribution in Table 4-1, 9000 samples were generated as input for the model calculations. Table 4-2 shows the translation of the values given in Table 4-1 into actual input values for the OPERA reference sorption model.

| Property | Implementation | Remarks |
|--|--|---|
| Bulk wet density [kg/m ³] | <i>density</i> : 2.600 – 2.800 kg/m ³ | |
| Porosity [%] | porosity: 29 – 43 % | |
| CEC [meq/100g Boom Clay] | <i>Clay_kgkg:</i> 0.04 – 0.84 kg/kg | surface charge fixed at 50 meq/100g |
| SOC [wt. %] | <i>SHA_kgkg:</i> 7.0 – 40 g/kg | HA consist of about 50 wt % of carbon |
| Proton exchange capacity SHA [meq/g] | Reactivity_SOC: 0.17 - 0.33 | this factor allows to vary the (fixed) proton exchange capacity of the model |
| | DHA_kgl: | |
| | <i>base case:</i> 200 mg/l | HA consist of about 50 wt % of carbon; |
| DOC [IIIg/L] | <i>low DOC case:</i> 40 mg/l | for case definition see text |
| | <i>high DOC case:</i> 400 mg/l | |
| Proton exchange capacity DHA | Pagetivity DOC: 0.22, 1 | this factor allows to vary the (fixed) |
| [meq/g] | <i>Neuclivity_DOC.</i> 0.55 - 1 | proton exchange capacity of the model |
| HFO [g/kg] | <i>HFO_kgkg:</i> 0.4 – 3.3 g/kg | HFO surface area is fixed at 600 m ² /g |
| Inorganic carbon [wt. %] | CO2[g].logact: -2.65 | see text |
| Total amount Ca [wt. %] | <i>Ca+2.kg:</i> 2 – 73 g/kg | |
| Total amount Fe [wt. %] | <i>Fe+3.kg:</i> 22 – 54 g/kg | |
| Total amount S [wt. %] | <i>SO4-2.kg:</i> 3.5 – 26 g/kg | |
| Soluble concentration CI [mg/L] | <i>Cldiss:</i> 4 – 20'000 mg/l | |
| Soluble concentration Na [mg/L] | Na+.diss: 4 – 11'000 mg/l | |
| pH [-] | <i>pH:</i> 7.7 – 9.2 | |
| pe + pH [-] | pe = 4.9 - pH ±2.2 | pe & pH are correlated (see text) |

A large group of radionuclides was found to be strongly bound to organic matter, as will be discussed in more detail below. Their solid-solution distribution is dominated by the ratio DOC/SOC. However, because no relevant data on DOC concentrations in Boom Clay of the Netherlands is available, a conservative, large range of DOC concentrations was established (Table 4-1), covering low concentrations as measured in the Netherlands *above* the Boom Clay [6] and in Boom Clay in Dessel, Essen and Herenhout [49, 50, 51] - expected under saline conditions - and the higher concentrations as found in Mol. Because of the relevance of DOC for the partitioning, this results in very broad K_d ranges, while it is evident that these large DOC (and SOC) ranges reflect differences between sites or regions rather than variability expected on a particular location. Therefore three typical cases are defined. This results in smaller K_d ranges, while the overall set of cases covers a large range of DOC concentrations. The three cases are defined as follows:

- a *base case* with a DOC concentration of 100 mg/l,
- a low DOC case with a DOC concentration of 20 mg/l, and
- a *high DOC case* with a DOC concentration of 200 mg/l.

Correspondingly, three sets of calculations were carried out and for each of these cases ranges of K_d -values were computed. The DOC concentration of the *base case* is between the median value of the range of Table 4-1, and the average value found in Mol (see Table 3-2). The *high DOC case* corresponds to the upper range of DOC concentrations as found in Mol. The *low DOC case* reflects typical DOC concentrations as found in the subsurface, and might occur in more saline Boom Clays. However, given the lack of proper data, from current point of knowledge actually *any* DOC concentration is equally likely, and it is recommended to analyse and compare these three cases in the OPERA performance assessments in WP7.

4.2. Calculation of apparent K_d-values

The OPERA reference model is used to compute K_d -values for all parameter samples according to Eq. 3-1. The principal list of radionuclides to be covered by the safety assessment is based on the inventory reported in [7] and [52] and contains all radionuclides present in the waste and with half-lifes >10 years. More precisely, the list contains 69 radionuclides, distributed over 42 elements (Table 4-3).

| 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 |

Table 4-3: Overview of all radionuclides considered in OPERA

Not all of the above given radionuclides are equally relevant for the OPERA risk assessment and are analysed in depth in the RANMIG project. The relevance of a radionuclide depends on several factors such as its total amount, radiotoxicity, half-life, and the considered scenario. By evaluating the radiotoxicity inventory, half-life and expected travel time, a first, conservative screening was made to exclude radionuclides for which no relevant contribution is expected, even in case of no adsorption. Furthermore, for a number of elements, sorption is judged to be of little relevance due to their chemical properties. For these radionuclides, a generic K_d -value of zero is recommended for PA. Table 4-4 summarizes these 15 elements.

Table 4-4: Elements with a recommended K_d -value of zero due to their small inventory and/or their chemical behaviour

| Element | Reason |
|---------|--|
| н | chemical behaviour / total radiotoxicity ~10 ⁻³ Sv after 250 years |
| С | chemical behaviour |
| Si | no inventory given in [52] / chemical behaviour |
| Cl | chemical behaviour (anion) |
| Ar | no inventory given in [52] |
| Ti | no inventory given in [52] |
| K. | no inventory given in [52] / total radiotoxicity < 10 ⁻⁴ Sv after 250 years / |
| | chemical behaviour (gaseous compound) |
| Мо | chemical behaviour (anion) |
| Nb | chemical behaviour (anion) |
| Ra | no inventory given in [52] / total radiotoxicity < 10 ⁻⁴ Sv after 250 years / |
| Da | chemical behaviour (gaseous compound) |
| Pm | total radiotoxicity < 10 ⁻⁴ Sv after 100 years |
| Но | no inventory given in [52] |
| Re | no inventory given in [52] |
| Bi | total radiotoxicity $\sim 3 \cdot 10^{-4}$ Sv after 250 years |
| Ро | no inventory given in [52] |

The following 19 elements were analysed by calculations with the OPERA reference sorption model:

Table 4-5: Elements covered by the OPERA reference sorption model

| Elements | | | | | |
|----------|----|--|--|--|--|
| К | Eu | | | | |
| Ca | Pb | | | | |
| Ni | Ra | | | | |
| Se | Th | | | | |
| Sr | Np | | | | |
| Тс | U | | | | |
| Sn | Pu | | | | |
| Cd | Am | | | | |
| I | Cm | | | | |
| Cs | | | | | |

For the remaining elements, *Be*, *Zr*, *Pd*, *Ag*, *Sm*, *Ac*, *Pa*, and *Cf*, little information is available and therefore no quantitative model analyses are performed. For these 8 elements, the recommended K_d range for the purpose of the OPERA PA calculation is described in Chapter 5.

For the 19 elements of Table 4-5, Se, I, C, K, U, Th, Np, Pu, Am, Cm, Tc, Sn, Cd, Eu, Ni, Cs, Sr, Ra, and Pb, the distribution over different chemical forms is calculated using the generated values for the parameters as described in Table 4-2 as input. Calculated results include the distribution of each element over dissolved, solid, and colloidal forms. This information is subsequently used to calculate the apparent K_d -values.

4.3. Analysis of calculated range of K_d-values

Uncertainty analyses were performed for all samples generated in the previous step. Central K_d -values and their distribution over dissolved fractions were derived for each of the considered radionuclides. In this section, only results of the *base case* are presented and discussed, but - unless noted otherwise - the general findings apply also to the other two cases defined in the previous section.

Consistency of the model

The selected range of input parameters results in calculated values for macro chemical parameters of the Boom Clay as given in Table 4-3. The averages are largely in agreement with the values measured in Mol (Table 3-2), and the resulting ranges provided a reasonable bandwidth of concentrations found in subsurface systems (see [6]).

| Table 4-3: Calculated concentrations of bicarbonates, | Ca, and Fe, | ionic strength | and total |
|---|-------------|----------------|-----------|
| amount of inorganic carbon | | | |

| | Bicarbonates [mg/l] | ТІС [%] | Ca [mg/l] | Fe [mg/l] | Ionic strength [M] |
|---------|------------------------|------------|--------------|--------------|-----------------------|
| minimum | 143 | 0.01 | 1.3E-05 | 1.2E-05 | 0.003 |
| average | 1039 | 0.82 | 5.1 | 0.1 | 0.16 |
| maximum | 6172 | 3.64 | 202 | 1.1 | 0.58 |

Calculated ranges of K_d-values

The calculated ranges of K_{d} -values have been aggregated and are presented as percentiles, maximum, and minimum values. However, as discussed in Section 3.1, the percentiles shown in this section should <u>not</u> be interpreted as representing expected values within a distribution. Because of lacking data, uniform uncorrelated distributions of the Boom Clay property ranges have been assumed, and the percentiles are merely descriptive. The most influential parameters are, as will be shown below, the SOC/DOC content, the bicarbonate concentration and the ionic strength. These parameters are expected to be highly location specific, and it is likely that the variability of these parameters on a given location is much smaller than the range that is used to represent all potential conditions expected in the Netherlands. Again, because no relevant data on DOC and bicarbonate concentration in Boom Clay in the Netherlands is currently available, no statement can be made on which value is the most likely one.

The results for the elements with weak sorption behaviour, the anions *I* and *Se*, and the monovalent cation *K* are shown in Table 4-6. The anions show - as expected - little interaction with any of the present surfaces, and thus remain almost exclusively in the dissolved fraction, resulting in very low K_d -values. Potassium was added for illustration purposes and as representative of non-reactive monovalent cations that only interact electrostatically with negatively charged surfaces.

| <i>K_d</i> [l/kg] | Se | I | К |
|-----------------------------|-----|-----|-----|
| maximum | 0.0 | 0.0 | 763 |
| 1% percentile | 0.0 | 0.0 | 435 |
| 5% percentile | 0.0 | 0.0 | 254 |
| 10% percentile | 0.0 | 0.0 | 153 |
| 25% percentile | 0.0 | 0.0 | 40 |
| 50% percentile | 0.0 | 0.0 | 6.7 |
| 75% percentile | 0.0 | 0.0 | 1.5 |
| 90% percentile | 0.0 | 0.0 | 0.7 |
| 95% percentile | 0.0 | 0.0 | 0.4 |
| 99% percentile | 0.0 | 0.0 | 0.2 |
| minimum | 0.0 | 0.0 | 0.1 |

Table 4-6: Calculated minimum, maximum and percentiles for the K_d -value of Se, I, and K in Boom Clay of the Netherlands for the 'base case' (100 mg/l DOC)

Table 4-7 and Table 4-8 below provide the calculated K_d -values for the elements U, Th, Np, Pu, Am, Cm, Tc, Sn, Cd, Eu, Ni, Cs, Sr, Ra, Ca and Pb. The elements U, Th, Np, Pu, Cm, Tc, Sn, Cd and Ni appear to behave very similarly, and their K_d -values vary by a factor of 20. In the upper part of range, U has comparable K_d -values, but in the lower part of the range, K_d -values of U decrease quickly, eventually with a minimum value close to zero. In the higher K_d ranges, Am, Pb, Eu, and Cs show higher values than the elements dominated by organic matter interactions.

| Table 4-7: Calculated minimum, | maximum and percentiles for | the K_d of the actinides U, Th, Np, |
|--------------------------------|-------------------------------|---------------------------------------|
| Pu, Am, and Cm in Boom Clay of | the Netherlands for the 'base | e case' (100 mg/l DOC) |

| <i>K_d</i> [l/kg] | U | Th | Np | Pu | Am | Cm |
|-----------------------------|-----|-----|-----|-----|------|-----|
| maximum | 165 | 165 | 165 | 165 | 5409 | 165 |
| 1% percentile | 115 | 118 | 118 | 118 | 843 | 118 |
| 5% percentile | 92 | 95 | 95 | 95 | 366 | 95 |
| 10% percentile | 80 | 83 | 83 | 83 | 227 | 83 |
| 25% percentile | 61 | 65 | 65 | 65 | 117 | 65 |
| 50% percentile | 42 | 46 | 46 | 46 | 71 | 46 |
| 75% percentile | 24 | 30 | 30 | 30 | 47 | 30 |
| 90% percentile | 13 | 20 | 20 | 20 | 31 | 20 |
| 95% percentile | 5.6 | 16 | 16 | 16 | 24 | 16 |
| 99% percentile | 0.5 | 12 | 12 | 12 | 17 | 12 |
| minimum | 0.1 | 8 | 8 | 8 | 9 | 8 |

| Table 4-8: Calculated minimum, maximum and percentiles for the K_d of the elements Pb, Eu, Tc, |
|--|
| Sn, Cd, Ni, Cs, Sr, Ra, and Ca in Boom Clay of the Netherlands for the 'base case' (100 mg/l |
| DOC) |

| K _d [l/kg] | Pb | Eu | Тс | Sn | Cd | Ni | Cs | Sr | Ra | Ca |
|-----------------------|------|------|-----|-----|-----|-----|-------|-----|-----|------|
| maximum | 2677 | 1076 | 165 | 165 | 165 | 184 | 19314 | 776 | 689 | 3786 |
| 1% percentile | 504 | 301 | 118 | 118 | 118 | 120 | 9310 | 390 | 384 | 2283 |
| 5% percentile | 235 | 146 | 95 | 95 | 95 | 96 | 5968 | 271 | 268 | 1755 |
| 10% percentile | 163 | 109 | 83 | 83 | 83 | 84 | 4319 | 217 | 216 | 1430 |
| 25% percentile | 103 | 79 | 65 | 65 | 65 | 65 | 2486 | 141 | 141 | 893 |
| 50% percentile | 69 | 56 | 46 | 46 | 46 | 47 | 1184 | 81 | 77 | 301 |
| 75% percentile | 47 | 37 | 30 | 30 | 30 | 31 | 497 | 46 | 40 | 58 |
| 90% percentile | 32 | 25 | 20 | 20 | 20 | 21 | 189 | 26 | 20 | 15 |
| 95% percentile | 25 | 20 | 16 | 16 | 16 | 17 | 102 | 19 | 13 | 9 |
| 99% percentile | 17 | 14 | 12 | 12 | 12 | 13 | 35 | 10 | 7 | 4 |
| minimum | 9 | 9 | 8 | 8 | 8 | 8 | 7 | 4 | 2 | 1 |

Distribution of radionuclides over different phases

Figure 4-2 gives an overview of the distribution of the elements over the different soluble and solid phases of the reference sorption model. The elements *U*, *Cm*, *Th*, *Np*, *Pu*, *Tc*, *Sn*, *Cd* and *Ni* are dominantly bound to organic matter. The largest fractions of *Am*, *Eu*, *Ni*, *Pb*, *Sr*, and *Ra* are bound to SOC. The monovalent *Cs* is mainly bound to iron(hydr)oxide, while *Ca* is mainly bound to clay.

Figure 4-3 depicts the largest fractions found in any of the 9000 samples analysed. Here, a more diverse picture can be seen for some elements: For some conditions, for Cm, Am, Eu, Ni, Pb, and Ca, iron(hydr)oxide can be an important reactive surface as well , and considerable fractions of U can be present in the dissolved phase due to the formation of dissolved carbonate complexes.



Figure 4-2: Calculated average distribution of radionuclides over several phases implemented in the reference model for the '*base case*' (100 mg/l DOC). SOC: soil organic carbon; *HFO*: hydrous ferric oxide; *DOC*: dissolved organic carbon.



Figure 4-3: Calculated maximum contribution of several phases to the distribution of radionuclides for the '*base case*' (100 mg/l DOC). SOC: soil organic carbon; *HFO*: hydrous ferric oxide; *DOC*: dissolved organic carbon.

Key parameter for the solid-solution distribution of radionuclides

The key parameters for the solid-solution distribution of most radionuclides are the amount of reactive dissolved and solid organic matter. Figure 4-4 depict the calculated K_d -values of Tc, Th, Np, Pu, Cm, Ni, Sn, and Cd as function of the ratio of proton bindings sites (Q_{max}) in the solid and in the solution phase. Due to the strong binding of these elements to organic matter, this ratio almost fully explains the found variations.



Figure 4-4: Calculated K_d -values for the 'base case' (100 mg/l DOC) as function of the ratios of the total number of available proton binding sites (Q_{max}) of SOC and DOC for Tc, Th, Np, Pu, Cm, Ni, Sn, and Cd.

Am, Eu and Pb show a similar behaviour (Figure 4-5), however, many samples have higher K_d -values because of their high affinity for HFO (see also Figure 4-3).



Figure 4-5: Calculated K_d -values for the 'base case' (100 mg/l DOC) for Am, Eu, and Pb as function of the ratios of the total number of available proton binding sites (Q_{max}) of SOC and DOC.

A different behaviour is found for U (Figure 4-6): although most of the samples are strongly correlated with the Q_{max} -ratio, a small fraction of the results show relevantly lower K_{d} -values. These lower K_{d} -values are related to the presence of soluble U-carbonate complexes (Figure 4-7, see also Figure 4-3). The amount of bicarbonates in solution is related to the overall amount of inorganic carbon present in the clay, and the pH of the solution (data not shown).



Figure 4-6: Calculated K_a -values for the 'base case' (100 mg/l DOC) for U as a function of the ratios of the total number of available proton binding sites (Q_{max}) of SOC and DOC.



Figure 4-7: Calculated K_d -values for the 'base case' (100 mg/l DOC) of U, normalized for the ratios of the total number of available proton binding sites (Q_{max}) of SOC and DOC, and the concentration of bicarbonates in solution.

The monovalent *Cs* shows a different behaviour than the aforementioned elements, because it is only weakly bound to organic matter (see Figure 4-2 and Figure 4-3). Although *Cs* is bound to HFO (Figure 4-8), the calculated K_d as a function of the amount of HFO varies by about one order of magnitude, and the correlation with the clay content is even weaker (data not shown). Figure 4-9 shows a strong invers relation of *Cs* partitioning and the concentration of dissolved *Ca*, pointing to a strong competition of these two cations.



Figure 4-8: Calculated K_d -values for Cs for the 'base case' (100 mg/l DOC) as a function of the fraction HFO (Hydrous Ferric Oxides).



Figure 4-9: Calculated K_a -values for Cs for the 'base case' (100 mg/l DOC) as a function of the Ca concentration.

Although large fractions of Sr, Ra, and Ca are bound to organic matter (Figure 4-2), their K_d -value correlates only weakly with the ratio of the proton exchange capacities of solid

and dissolved organic matter. Figure 4-10 show as example the relation for Sr. Strontium can be outcompeted by other divalent cations, comparable to Cs. Figure 4-11 shows the invers relation between the normalized K_d -values of Sr and the concentration of dissolved Ca. Ra and Ca shows a similar behaviour as Sr (data not shown).



Figure 4-10: Calculated K_d -values for Sr for the 'base case' (100 mg/l DOC) as a function of the ratios of the total number of available proton binding sites (Q_{max}) of SOC and DOC.



Figure 4-11: Calculated K_d -values of Sr for the 'base case' (100 mg/l DOC), normalized for the ratios of the total number of available proton binding sites (Q_{max}) of SOC and DOC, and the concentration of bicarbonates in solution.

Distribution of radionuclides in the solution

Figure 4-12 shows for the modelled cations the average and minimum fractions of the solution bound to colloidal DOC. For *Tc*, *Th*, *Np*, *Pu*, *Am*, *Sn*, *Cd*, *Eu*, *Ni*, *Cm* and *Pb* the average (and minimum) fraction bound to DOC close to 100%. For *U*, the average fraction is about 95%, while under conditions with high bicarbonate concentrations uranyl carbonates dominate the solution, leading to a minimum fraction close to zero. The DOC-bound fractions of *Cs*, *Sr*, *Ra*, and *Ca* are much lower than of the aforementioned elements, consistent with the distribution presented in the previous section (see Figure 4-2 and Figure 4-3).



Figure 4-12: Calculated average and minimum fraction of radionuclides in the solution phase bound to dissolved organic carbon (DOC) for the 'base case' (100 mg/l DOC).

 K_d -values are usually defined as the ratio of solid bound and soluble species (Section 3.2). For the purpose of transport calculations, K_d -values can be converted by correction for the density ρ and the porosity η into a dimensionless retardation factor R_f :

$$R_f = \frac{\rho}{\eta} K_d + 1$$
 Eq. 4-1

This is a common procedure for advection-dominated systems, in which aqueous ions and colloidal particles are assumed to have equal mobility. For diffusion-dominated systems, however, this is not appropriate, as colloidal particles could be expected to diffuse slower than aqueous ions [48]. To be able to account in performance assessment calculations for the varying mobility of these two fractions, it is necessary to differentiate between DOC-bound and dissolved radionuclides. As Figure 4-12 showed, the DOC-bound fraction is not constant for all K_d -values, but can vary for some elements.

To facilitate a proper implementation in a diffusion-dominated system, two fractional K_d -values are defined, K_{d_diss} and K_{d_DOC} :

$$R_f = \frac{\rho}{\eta} K_d + 1$$
 Eq. 4-2

They represent the ratio between the amount of a radionuclide *i* bound to the solid matrix and the dissolved respectively DOC-bound concentrations of radionuclide *i* according to

$$K_{d_{diss,i}} = \frac{X_i}{C_{diss,i}}$$
 Eq. 4-3

and

$$K_{d_{DOC,i}} = \frac{X_i}{C_{DOC,i}}$$
 Eq. 4-4

Likewise, dimensionless retardation factors for both fractions can be computed according to

$$R_{f_{diss,i}} = \frac{\rho}{\eta} K_{d_{diss,i}} + 1$$
 Eq. 4-5

and

$$R_{f_{DOC,i}} = \frac{\rho}{\eta} K_{d_{DOC,i}} + 1$$
 Eq. 4-6

Table 4-9 and Table 4-10 on the next page summarize for the 'base case' (100 mg/l DOC) the resulting ranges of K_d -values and retardation factors, respectively. Table B-1 to B-3 in the Appendix B summarizes the calculated K_d -values and retardation factors for all three cases.

Table 4-9: Ranges of calculated K_{d_diss} - and K_{d_DOC} -values in Boom Clay of the Netherlands for the *'base case'* (100 mg/l DOC). Lower, central, and upper values correspond to 5-, 50- and 95-percentiles of the calculated K_d -values, respectively.

| | | K _{d_diss} [l/kg] | | | K _{d_DOC} [l/kg] | |
|---------|---------|----------------------------|---------|-------|---------------------------|---------|
| Element | lower | central | upper | lower | central | upper |
| | value | value | value | value | value | value |
| Se | 0 | 0 | 0 | 51 | 129 | 247 |
| Ca | 9 | 1114 | >10'000 | 133 | 603 | 1831 |
| К | 0 | 7 | 387 | 113 | 485 | 1068 |
| Ni | >10'000 | >10'000 | >10'000 | 17 | 47 | 96 |
| Sr | 33 | 2762 | >10'000 | 35 | 95 | 273 |
| Тс | >10'000 | >10'000 | >10'000 | 16 | 46 | 95 |
| Sn | >10'000 | >10'000 | >10'000 | 16 | 46 | 95 |
| Cd | >10'000 | >10'000 | >10'000 | 16 | 46 | 95 |
| Cs | 103 | 1329 | 7596 | 3413 | >10'000 | >10'000 |
| Eu | >10'000 | >10'000 | >10'000 | 20 | 56 | 146 |
| Pb | >10'000 | >10'000 | >10'000 | 25 | 69 | 237 |
| Ra | 18 | 1554 | >10'000 | 34 | 95 | 275 |
| Th | >10'000 | >10'000 | >10'000 | 16 | 46 | 95 |
| Np | >10'000 | >10'000 | >10'000 | 16 | 46 | 95 |
| U | 7 | >10'000 | >10'000 | 16 | 46 | 95 |
| Pu | >10'000 | >10'000 | >10'000 | 16 | 46 | 95 |
| Am | >10'000 | >10'000 | >10'000 | 24 | 71 | 366 |
| Cm | >10'000 | >10'000 | >10'000 | 16 | 46 | 95 |

Table 4-10: Ranges of calculated R_{f_diss} - and R_{f_DOC} -values in Boom Clay of the Netherlands for the 'base case' (100 mg/l DOC). Lower, central, and upper values correspond to 5-, 50- and 95-percentiles of the calculated R_{f} -values, respectively.

| | | R _{f_diss} [-] | | | R _{f_DOC} [-] | |
|---------|---------|--------------------------------|---------|-------|------------------------|---------|
| Element | lower | central | upper | lower | central | upper |
| | value | value | value | value | value | value |
| Se | 1 | 1 | 1 | 236 | 621 | 1263 |
| Ca | 46 | 5409 | >50'000 | 611 | 2881 | 9584 |
| К | 3 | 34 | 1997 | 525 | 2300 | 5694 |
| Ni | >50'000 | >50'000 | >50'000 | 81 | 227 | 494 |
| Sr | 160 | 13329 | >50'000 | 161 | 461 | 1375 |
| Тс | >50'000 | >50'000 | >50'000 | 77 | 221 | 489 |
| Sn | >50'000 | >50'000 | >50'000 | 77 | 221 | 489 |
| Cd | >50'000 | >50'000 | >50'000 | 78 | 222 | 490 |
| Cs | 476 | 6454 | 38699 | 16611 | >50'000 | >50'000 |
| Eu | >50'000 | >50'000 | >50'000 | 95 | 267 | 706 |
| Pb | >50'000 | >50'000 | >50'000 | 120 | 338 | 1145 |
| Ra | 87 | 7320 | >50'000 | 161 | 458 | 1364 |
| Th | >50'000 | >50'000 | >50'000 | 77 | 221 | 489 |
| Np | >50'000 | >50'000 | >50'000 | 77 | 221 | 489 |
| U | 33 | >50'000 | >50'000 | 77 | 221 | 489 |
| Pu | >50'000 | >50'000 | >50'000 | 77 | 221 | 489 |
| Am | >50'000 | >50'000 | >50'000 | 116 | 349 | 1676 |
| Cm | >50'000 | >50'000 | >50'000 | 78 | 222 | 489 |

4.4. Comparison of outcomes

 K_d -values and their distribution were derived for 19 elements of interest: for the expected ranges of Boom Clay properties in the Netherlands, 9000 samples were generated and three cases were analysed:

- a *base case*, with DOC concentration of 100 mg/l,
- a *low DOC case*, with a DOC concentration of 20 mg/l, and
- a high DOC case, with a DOC concentration of 200 mg/l.

In Table 4-11 on the next page, the results of the calculations for each of the three cases are shown and compared with the ranges provided by the SCK·CEN for the Belgian conditions (see [6] for more detail).

Table 4-11: Ranges of calculated K_d -values in Boom Clay of the Netherlands for the 'low DOC case', the 'base case', and the 'high DOC case'. Lower, central, and upper values correspond to 5-, 50- and 95-percentiles of the calculated K_d -values, respectively. "Equivalent K_d -values" for Mol are recalculated values as discussed in Section 3.3.

| | | | <i>K_d-values</i> | for Boom | Clay of the | Netherla | nds [l/kg] | | | Equivalent |
|-----|-------|------------|-----------------------------|----------|-------------|----------|------------|------------|-------|-------------------------|
| ent | L | ow DOC cas | se | | Base case | | н | igh DOC ca | se | K_{d} -values in Boom |
| em | lower | central | upper | lower | central | upper | lower | central | upper | Clay at Mol |
| Ξ. | value | value | value | value | value | value | value | value | value | [l/kg] |
| I | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | |
| Se | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | |
| К | 0 | 7 | 350 | 0 | 7 | 254 | 0 | 7 | 190 | |
| Са | 9 | 716 | 8281 | 9 | 301 | 1755 | 9 | 182 | 892 | 180 - 800 |
| Ni | 85 | 236 | 479 | 17 | 47 | 96 | 9 | 24 | 48 | 40 - 1000 |
| Sr | 30 | 337 | 1323 | 19 | 81 | 271 | 13 | 43 | 136 | 180 - 800 |
| Тс | 81 | 231 | 473 | 16 | 46 | 95 | 8 | 23 | 47 | 40 - 1000 |
| Sn | 81 | 231 | 473 | 16 | 46 | 95 | 8 | 23 | 47 | |
| Cd | 82 | 232 | 474 | 16 | 46 | 95 | 8 | 23 | 47 | |
| Cs | 103 | 1293 | 7159 | 102 | 1184 | 5968 | 101 | 1067 | 5135 | 600 - 18'600 |
| Eu | 100 | 278 | 732 | 20 | 56 | 146 | 10 | 28 | 73 | 40 - 1000 |
| Pb | 125 | 347 | 1150 | 25 | 69 | 235 | 12 | 35 | 118 | |
| Ra | 17 | 303 | 1304 | 13 | 77 | 268 | 10 | 41 | 135 | 1800 - 8000 |
| Th | 81 | 231 | 473 | 16 | 46 | 95 | 8 | 23 | 47 | 40 - 1000 |
| Np | 81 | 231 | 473 | 16 | 46 | 95 | 8 | 23 | 47 | 40 - 1000 |
| U | 7 | 191 | 453 | 6 | 42 | 92 | 5 | 21 | 46 | 40 - 1000 |
| Pu | 81 | 231 | 473 | 16 | 46 | 95 | 8 | 23 | 47 | 40 - 1000 |
| Am | 119 | 357 | 1829 | 24 | 71 | 366 | 12 | 36 | 183 | 40 - 1000 |
| Cm | 82 | 231 | 473 | 16 | 46 | 95 | 8 | 23 | 47 | 40 - 1000 |

The K_d -values computed for elements strongly bound to organic matter (e.g. *Tc*, *Sn*, and *Cd*), are strongly related to the assumed DOC concentrations (Table 4-11). In contrast, the K_d range calculated for Cs does not differ much between the three cases.

In general, the K_d -values for the Dutch situation are about half of what was calculated for the conditions in Mol (Section 3.3). One important explanation for this effect is the higher amount of organic matter assumed for the Belgian case (about twice as much). At the same time, for the Netherlands the assumed range of clay amounts is about 4 times higher, resulting in higher K_d -values for Cs, Ca, and Ra. The lower limit of the K_d range of U is higher under the Belgian condition, mainly because of the assumed constraint pH-value (pH 8.5), for which uranyl carbonates are less abundant.

Compared with the K_d -values provided by SCK·CEN, the K_d -values derived in this study are generally smaller. The calculated central K_d -values for the base case are within the ranges provided by SCK·CEN.

5. Proposed set of K_d -values for the OPERA safety assessment

Based on the results of the previous chapters, a set of K_d -values for the purpose of OPERA safety assessment calculations is derived and summarized in Table 5-1. Four groups of radionuclides are distinguished:

- the first group of radionuclides consists of radionuclides that are set conservatively to zero because of their limited abundance, and/or their chemical behaviour,
- the second group is based on model calculations, but no support by experimental data from Boom Clay in Mol is available,
- the third group is based on model calculations and has support by experimental data from Boom Clay in Mol, and
- the fourth group is extrapolated on basis of chemical similarities: 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 [6, Table 3-1], and Be is set equal to the values of Ca.

Members of the first and fourth group are not expected to contribute relevantly to the risk under the conditions of the normal evolution scenario. However, if it appears that these radionuclides are of importance, e.g. for a specific scenario, than it is recommended to critically review the given values.

In Table 5-1, central values and ranges for the K_d are provided, recommended for the deterministic analysis of the normal evolution scenario. The K_d -values distinguish between radionuclides in the dissolved phase, and radionuclides bound to DOC. In several cases, either one of the fraction can be neglected, or - if more convenient for the technical implementation of the performance assessment model - set to a conservative value of 10'000.

With respect to the application of the central value and accompanying range it needs to be understood that the applied K_d -values strongly depend on a number of key parameters. These key parameters include the SOC content, the DOC concentration, the bicarbonate concentration and related *pH*-value, and the salinity (or ionic strength). All of these parameters are location specific. The central values given in Table 5-1 represent neither the 'most likely' geochemical composition of Boom Clay in the Netherlands, nor the 'average composition' of Boom Clay. It just marks the median value that results from the applied range of expected properties in Table 4-1. Table 5-1: Recommended lower, central, and upper K_d -values of dissolved and DOC-bound fractions of the radionuclides considered in OPERA for the base case (100 mg/l DOC). '-':no model representation necessary, because the contribution can be neglected in comparison to the other K_d

| | | | K _{d_diss} [l/kg] | | | K _{d_DOC} [l/kg] | |
|--------------------------------|---------|-------|----------------------------|---------|-------|---------------------------|---------|
| Group | Element | Lower | Central | Upper | Lower | Central | Upper |
| | | value | value | value | value | value | value |
| | н | | | | | | |
| | С | | | | | | |
| | Si | | | | | | |
| | Cl | | | | | | |
| | Ar | | | | | | |
| | Ti | | | | | | |
| consorvatively set to | Kr | | | | | | |
| | Мо | | 0 | | | >10'000 | |
| 2010 | Nb | | | | | | |
| | Ва | | | | | | |
| | Pm | | | | | | |
| | Но | | | | | | |
| | Re | | | | | | |
| | Bi | | | | | | |
| | Ро | | | | | | |
| | к | 0 | 7 | 387 | 113 | 485 | 1068 |
| based on model | Ni | | >10'000 | | 17 | 47 | 96 |
| based on model calculations | Sn | | >10'000 | | 16 | 46 | 95 |
| calculations | Cd | | >10'000 | | 16 | 46 | 95 |
| | Pb | | >10'000 | | 25 | 69 | 237 |
| | I | | 0 | | | >10'000 | |
| | Se | | 0 | | | >10'000 | |
| | Ca | 9 | 1114 | >10'000 | 133 | 603 | 1831 |
| | Sr | 33 | 2762 | >10'000 | 35 | 95 | 273 |
| | Тс | | - | | 16 | 46 | 95 |
| based on model | Cs | 103 | 1329 | 7596 | 3413 | >10'000 | >10'000 |
| calculations, | Eu | | >10'000 | | 20 | 56 | 146 |
| experimental support | Np | | >10'000 | | 16 | 46 | 95 |
| trom Boom Clay (Mol) | Pu | | >10'000 | | 16 | 46 | 95 |
| | Am | | >10'000 | | 24 | 71 | 366 |
| | Cm | | >10'000 | | 16 | 46 | 95 |
| | Ra | 18 | 1554 | >10'000 | 34 | 95 | 275 |
| | Th | | >10'000 | | 16 | 46 | 95 |
| | U | 7 | >10'000 | >10'000 | 16 | 46 | 95 |
| | Be | 9 | 1114 | >10'000 | 133 | 603 | 1831 |
| | Zr | | >10'000 | | 16 | 46 | 95 |
| | Pd | | >10'000 | | 16 | 46 | 95 |
| extrapolated on basis of | Ag | | >10'000 | | 16 | 46 | 95 |
| chemical similarities | Sm | | >10'000 | | 16 | 46 | 95 |
| | Ac | | >10'000 | | 16 | 46 | 95 |
| | Ра | 7 | >10'000 | >10'000 | 16 | 46 | 95 |
| | Cf | 7 | >10'000 | >10'000 | 16 | 46 | 95 |

6. Conclusions and outlook

For the purpose of this study, a model representation of Boom Clay was developed, the 'OPERA reference sorption model'. The chosen mechanistic approach (Figure 3-2) is based on selected thermodynamic data and enables independent predictions of speciation and sorption behaviour of radionuclides, i.e. without fitting. This allowed studying the effect of varying chemical conditions as expected in the Netherlands. The complete sorption model together with the generated ranges of input values represents a transparent reproducible mechanism for estimating K_{d} -values and can easily be updated in case newer insights would require this. This includes also the analysis of specific scenarios, e.g. the effect of an alkaline plume or high bicarbonate concentrations.

The multi-surface model approach applied here distinguishes several reactive surfaces present in Boom Clay and focusses on the proper modelling of ion interaction with reactive organic matter. At the same time, a rather straightforward approach is followed for modelling interactions with clay: here only (non-specific) exchange in the electrostatic double layer is addressed. This conservative simplification expectedly leads to an overestimation of the mobility of some radionuclides, but prevents on the other hand an underestimation of risks. There is no principal constraint to add specific binding by clay to the reference sorption model in a following stage, e.g. in case the outcomes of the OPERA safety assessment calculations show that for some scenarios uncertainties concerning the long term safety might be relevantly reduced by refining the model for some radionuclides. The object-oriented structure of the ORCHESTRA workbench allows implementing a variety of models or other extensions to the current OPERA reference sorption model in a time-efficient manner. Sufficient experimental data exists to implement current or future state-of-the-art models on clay sorption for a variety of radionuclides. Such an effort could also be useful in support of future experimental research on Boom Clay.

The reference sorption model shows sufficient resemblance with the estimates provided by SCK-CEN, without any parameter fitting/optimisation. It also gives a realistic representation of relevant macrochemical parameters that influence sorption (pH, pe, dissolved Ca, Fe, bicarbonates, sulphates). A large group of radionuclides is found to bind strongly to organic matter: the ratio between dissolved (mobile) and solid (immobile) organic matter is a key parameter for the mobility of relevant radionuclides. Of some concern is the strongly increasing mobility of U due to the formation of soluble carbonate complexes under certain condition (high pH, high amount of inorganic carbon). Of lesser relevance - although clearly present - is the effect of increasing salinity. It is expected that this effect can be more than compensated by the lower DOC concentrations that might be present in Boom Clay at high salinities. This correlation is currently not considered in the model due to lack of data.

With little data support for the expected DOC and bicarbonate concentrations, some uncertainties remain, resulting in large ranges of K_d -values. Three cases are analysed, but if necessary, additional cases can be evaluated by the reference sorption model. The applied K_d -values depend strongly on a small number of key parameters, including the SOC content, the DOC concentration, the bicarbonate concentration/pH, and the ionic strength. These parameters are location specific, causing the central value not necessarily to represent the 'most likely' value. However, the approach followed here allows for adaptation of the reference sorption model and narrow down the resulting bandwidth of K_d -values when more data comes available in future.

The most important conclusion is that in no case the solid-solution partitioning was overestimated by the reference sorption model, making it a convenient, conservative tool for evaluating best estimates and ranges for radionuclide sorption in the context of performance assessment calculations, and giving confidence in the K_d -values established in this study. However, the relevance of remaining uncertainties for the long term safety has to be established by performance assessment calculations as will be performed in OPERA WP7.

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Appendix A: Species of the OPERA reference sorption model

| species | reference | log K | stoichiometri | c composition | ı | | |
|---|-----------|--------|-----------------------|---------------------------------|----------------------|--------------------|-------------------|
| Am ⁺² | 1 | -38.88 | 1 Am ⁺³ | 1 e ⁻ | | | |
| Am ⁺⁴ | 1 | -44.21 | 1 Am ⁺³ | -1 e | | | |
| AmCO ₃ ⁺ | 1 | -10.15 | 1 Am ⁺³ | 1 CO ₂ [g] | -2 H ⁺ | 1 H ₂ O | |
| AmCI ⁺² | 1 | 0.24 | 1 Am ⁺³ | 1 Cl | | - | |
| AmCl ₂ ⁺ | 1 | -0.74 | 1 Am ⁺³ | 2 Cl ⁻ | | | |
| AmHCO ₃ ⁺² | 1 | -4.73 | 1 Am ⁺³ | 1 CO ₂ [g] | -1 H ⁺ | 1 H ₂ O | |
| AmO ₂ ⁺ | 1 | -58.37 | 1 Am ⁺³ | -4 H ⁺ | 2 H ₂ O | -2 e | |
| AmO_2^{+2} | 1 | -85.35 | 1 Am ⁺³ | -4 H ⁺ | 2 H ₂ O | -3 e ⁻ | |
| AmO ₂ OH | 1 | -71.00 | 1 Am ⁺³ | -5 H ⁺ | 3 H ₂ O | -2 e ⁻ | |
| AmO ₂ [OH] ₂ ⁻ | 1 | -83.30 | 1 Am ⁺³ | -6 H ⁺ | 4 H ₂ O | -2 e ⁻ | |
| AmOH ⁺² | 1 | -7.20 | 1 Am ⁺³ | -1 H ⁺ | 1 H ₂ O | | |
| AmSO4 ⁺ | 1 | 3.30 | 1 Am ⁺³ | 1 SO ₄ ⁻² | | | |
| $Am[CO_3]_2^{-1}$ | 1 | -23.40 | 1 Am ⁺³ | $2 CO_2[g]$ | -4 H ⁺ | 2 H ₂ O | |
| $Am[CO_3]_3^{-3}$ | 1 | -39.46 | 1 Am ⁺³ | $3 CO_2[g]$ | -6 H ⁺ | 3 H ₂ O | |
| Am[OH] ₂ ⁺ | 1 | -15.10 | 1 Am ⁺³ | -2 H ⁺ | 2 H ₂ O | - | |
| Am[OH] ₃ | 1 | -26.20 | 1 Am ⁺³ | -3 H ⁺ | 3 H ₂ O | | |
| $Am[SO_4]_2$ | 1 | 3.70 | 1 Am ⁺³ | 2 SO4 ⁻² | - | | |
| CO ₂ | 1 | -1.47 | $1 CO_{2}[g]$ | - | | | |
| CO_{3}^{-2} | 1 | -18.15 | $1 CO_{2}[g]$ | -2 H ⁺ | 1 H ₂ O | | |
| CSe ₂ | 1 | 158.03 | $1 CO_{2}[g]$ | 20 H ⁺ | -10 H ₂ O | 2 SeO4-2 | 16 e ⁻ |
| CaCO ₃ | 1 | -14.92 | $1 CO_{2}[g]$ | 1 Ca ⁺² | -2 H ⁺ | 1 H ₂ O | |
| CaCm[OH]3 ⁺² | 1 | -26.30 | 1 Ca ⁺² | 1 Cm ⁺³ | -3 H⁺ | 3 H ₂ O | |
| | 1 | -6.71 | $1 CO_{2}[g]$ | 1 Ca ⁺² | -1 H ⁺ | 1 H ₂ O | |
| CaOH ⁺ | 1 | -12.78 | 1 Ca ⁺² | -1 H ⁺ | 1 H ₂ O | 2 - | |
| CaSO ₄ | 1 | 2.30 | 1 Ca ⁺² | 1 SO4 ⁻² | - | | |
| CaSeO₄ | 1 | 2.00 | 1 Ca ⁺² | 1 Se O_4^{-2} | | | |
| $CaUO_2[CO_3]_3^{-2}$ | 1 | -27.27 | 3 CO ₂ [g] | 1 Ca ⁺² | -6 H ⁺ | 3 H ₂ O | $1 UO_2^{+2}$ |
| CdCO ₃ | 2 | -14.06 | $1 CO_{2}[g]$ | 1 Cd ⁺² | -2 H ⁺ | 1 H ₂ O | 2 |
| CdCl⁺ | 2 | 1.98 | 1 Cd ⁺² | 1 Cl ⁻ | | - | |
| | 2 | 2.60 | 1 Cd ⁺² | 2 Cl ⁻ | | | |
| CdCl ₃ | 2 | 2.40 | 1 Cd ⁺² | 3 Cl ⁻ | | | |
| CdHCO ₃ | 2 | -5.73 | $1 CO_{2}[g]$ | 1 Cd ⁺² | -1 H ⁺ | 1 H ₂ O | |
| CdOH⁺ | 2 | -11.10 | 1 Cd ⁺² | -1 H ⁺ | 1 H ₂ O | - | |
| Cd[OH] ₂ | 2 | -20.30 | 1 Cd ⁺² | -2 H ⁺ | 2 H ₂ O | | |
| CmCO ₃ ⁺ | 1 | -10.15 | $1 CO_{2}[g]$ | 1 Cm ⁺³ | -2 H ⁺ | 1 H ₂ O | |
| CmCl ⁺² | 1 | 0.24 | 1 Cl | 1 Cm ⁺³ | | - | |
| CmCl_2^+ | 1 | -0.74 | 2 Cl ⁻ | 1 Cm ⁺³ | | | |
| CmHCO ₃ ⁺² | 1 | -4.72 | $1 CO_{2}[g]$ | 1 Cm ⁺³ | -1 H ⁺ | 1 H ₂ O | |
| CmOH ⁺² | 1 | -7.20 | 1 Cm ⁺³ | -1 H ⁺ | 1 H ₂ O | - | |
| CmSO ₄ ⁺ | 1 | 3.30 | 1 Cm ⁺³ | 1 SO4 ⁻² | - | | |
| $Cm[CO_3]_2$ | 1 | -23.40 | 2 $CO_{2}[g]$ | 1 Cm ⁺³ | -4 H ⁺ | 2 H ₂ O | |
| $Cm[CO_3]_3^{-3}$ | 1 | -39.45 | $3 CO_2[g]$ | 1 Cm ⁺³ | -6 H ⁺ | 3 H ₂ O | |
| Cm[OH] ₂ ⁺ | 1 | -15.10 | 1 Cm ⁺³ | -2 H ⁺ | 2 H ₂ O | - | |
| Cm[OH] ₃ | 1 | -26.20 | 1 Cm ⁺³ | -3 H ⁺ | 3 H ₂ O | | |
| Cm[SO ₄] ₂ | 1 | 3.70 | 1 Cm ⁺³ | $2 SO_4^{-2}$ | - | | |
| EuCO ₃ ⁺ | 1 | -10.05 | $1 CO_{2}[g]$ | 1 Eu ⁺³ | -2 H ⁺ | 1 H ₂ O | |
| EuCl ⁺² | 1 | 1.10 | 1 Cl | 1 Eu ⁺³ | | - | |
| EuCl ₂ ⁺ | 1 | 1.50 | 2 Cl ⁻ | 1 Eu ⁺³ | | | |
| EuOH ⁺² | 1 | -7.64 | 1 Eu ⁺³ | -1 H ⁺ | 1 H ₂ O | | |
| EuSO4 ⁺ | 1 | 3.95 | 1 Eu ⁺³ | 1 SO4 ⁻² | - | | |
| $Eu[CO_3]_2$ | 1 | -24.20 | 2 CO ₂ [g] | 1 Eu ⁺³ | -4 H ⁺ | 2 H ₂ O | |
| Eu[OH] ₂ ⁺ | 1 | -15.10 | 1 Eu ⁺³ | -2 H ⁺ | 2 H ₂ O | 2 | |
| Eu[OH] ₃ | 1 | -23.70 | 1 Eu ⁺³ | -3 H⁺ | 3 H ₂ O | | |
| Eu[OH] ₄ | 1 | -36.20 | 1 Eu ⁺³ | -4 H ⁺ | 4 H ₂ O | | |

Table A-1: Listing of all used species, their stoichiometric composition, log K value, and source of the data. 1 = [15], 2 = [19], 3 = [16], 4 = [17], 5 = [18]

| | reference | log K | Stol | chiomet | ric co | mposition | | | | |
|---|-----------------------|--|------------------------|---|---------------------------|--|-------------------|---|--|------------------|
| Lu[304]2 | 1 | 5.70 | 1 | Eu ⁺³ | 2 | SO4 ⁻² | | | | |
| Fe ⁺² | 1 | 13.02 | 1 | Fe ⁺³ | 1 | e | | | | |
| Fe ₂ [OH] ₂ ⁺⁴ | 1 | -2.95 | 2 | Fe ⁺³ | -2 | H⁺ | 2 | H ₂ O | | |
| FeCO ₃ | 1 | -0.75 | 1 | CO ₂ [g] | 1 | Fe ⁺³ | -2 | Η [∓] | 1 H ₂ O | 1 e ⁻ |
| FeCl | 1 | 13.16 | 1 | Cl | 1 | Fe ⁺³ | 1 | e | - | |
| FeCl ⁺² | 1 | 1.48 | 1 | CI | 1 | Fe ⁺³ | | | | |
| FeCl ₂ ⁺ | 1 | 2.13 | 2 | Cl | 1 | Fe ⁺³ | | | | |
| FeCl | - | 1 13 | - २ | | - 1 | Γ0 ⁺³ | | | | |
| FeHCO ⁺ | 1 | 7 20 | 1 | | 1 | Fe ⁺³ | -1 | н⁺ | 1 H ₂ O | 1 e ⁻ |
| FeHSO. ⁺ | 1 | 16.09 | 1 | ΕΟ2[6] Ερ ⁺³ | 1 | н ⁺ | 1 | SO. ⁻² | 1 m ₂ 0 | пс |
| | 1 | 10.05 | 1 | ге Бо ⁺³ | 1 | и+ | 1 | 504 50 ⁻² | те | |
| | 1 | 4.47 | 1 | Fe +3 | 1 | п п ₊ | 1 | | 1 0 | |
| | 1 | 5.5Z | 1 | ге Бо ⁺³ | -1 | п u ⁺ | 1 | | те | |
| | 1 | 15 27 | 1 | ге го ⁺³ | -1 | п со ⁻² | 1 | п ₂ 0 | | |
| $FeSO_4$ | 1 | 15.27 | T | ге г.+3 | T | 50_4 | T | e | | |
| | 1 | 4.04 | 1 | Fe +3 | 1 | SO ₄ | | | 1 c c ⁻² | a - |
| FeSeO ₃ | 1 | 39.20 | 1 | Fe - | 2 | H + | -1 | H ₂ O | 1 SeO ₄ | 2 e |
| Fe[OH] ₂ | 1 | -5.67 | 1 | Fe - +3 | -2 | H [†] | 2 | H ₂ O | | |
| Fe[OH] ₃ | 1 | -12.56 | 1 | Fe ⁻ | -3 | H + | 3 | H ₂ O | | |
| Fe[OH] ₄ | 1 | -21.60 | 1 | Fe | -4 | H' | 4 | H ₂ O | | |
| Fe[SO ₄] ₂ | 1 | 5.38 | 1 | Fe | 2 | SO ₄ ² | | | | |
| H ₂ | 1 | -3.15 | 2 | Η | 2 | e | | 2 | | |
| H ₂ S | 1 | 40.68 | 10 | H⁺ | -4 | H ₂ O | 1 | SO ₄ ⁻² | 8 e ⁻ | |
| H ₂ SO ₃ | 1 | 5.66 | 4 | H⁺ | -1 | H ₂ O | 1 | SO ₄ ⁻² | 2 e ⁻ | |
| H ₂ Se | 1 | 85.42 | 10 | H^+ | -4 | H ₂ O | 1 | SeO ₄ ⁻² | 8 e ⁻ | |
| H ₂ SeO ₃ | 1 | 39.05 | 4 | H⁺ | -1 | H ₂ O | 1 | SeO ₄ ⁻² | 2 e ⁻ | |
| HCO3 ⁻ | 1 | -7.83 | 1 | CO ₂ [g] | -1 | H^{+} | 1 | H ₂ O | | |
| HIO ₃ | 1 | -110.78 | -5 | H^{+} | 3 | H₂O | 1 | Ľ | -6 e ⁻ | |
| HS | 1 | 33.69 | 9 | H⁺ | -4 | H ₂ O | 1 | SO4 -2 | 8 e ⁻ | |
| HS ₂ O ₃ ⁻ | 1 | 39.60 | 11 | H⁺ | -5 | H ₂ O | 2 | SO ₄ ⁻² | 8 e ⁻ | |
| HSO | 1 | 3.82 | 3 | H⁺ | -1 | H ₂ O | 1 | SO₄ ⁻² | 2 e ⁻ | |
| HSO ₄ | 1 | 1.98 | 1 | H⁺ | 1 | SO_4^{-2} | | 4 | - | |
| HSe | 1 | 81.57 | 9 | H⁺ | -4 | H ₂ O | 1 | SeO ₄ ⁻² | 8 e ⁻ | |
| HSeO | 1 | 36.40 | 3 | H⁺ | -1 | μ ₂ ο | 1 | SeQ ⁴⁻² | 2 e | |
| HSeQ | - | 1 75 | 1 | Н ⁺ | - 1 | SeQ. ⁻² | - | 0004 | | |
| | - | -111 56 | -6 | Н ⁺ | - 3 | H ₂ O | 1 | r | -6 e ⁻ | |
| KOH | 1 | -14 46 | -1 | Н ⁺ | 1 | H ₂ O | 1 | κ ⁺ | 0 0 | |
| KSO. | 1 | 0.85 | 1 | κ+ | 1 | SO. ⁻² | - | IX . | | |
| NaCO. | 1 | -16.88 | 1 | | _2 | 50 ₄ н ⁺ | 1 | H.O | 1 No ⁺ | |
| | 1 | -10.00 9.07 | 1 | | -2 | и+ | 1 | | 1 No ⁺ | |
| | 1 | -0.07 | 1 | | -1 | | 1 | No ⁺ | 1 Na | |
| | 1 | -14.18 | -1 | П No ⁺ | 1 | Π ₂ U | Т | Nd | | |
| NdSU ₄ | 1 | 0.70 | 1 | Nd Ni: ⁺² | 1 | 50 ₄ | | | | |
| NI OU ⁺³ | 1 | -10.48 | 1 | INI 11 ⁺ | 2 | e | 2 | NI:+2 | | |
| | 1 | -10.60 | -1 | | 1 | п ₂ 0 | 2 | | 4 NI ⁺² | |
| NICO ₃ | 1 | -13.95 | 1 | | -2 | H | 1 | H ₂ O | 1 NI | |
| | 1 | 0.08 | 1 | | 1 | NI + | | | 4 • • • + 2 | |
| NIHCO ₃ | 1 | -6.82 | 1 | CO ₂ [g] | -1 | Н | 1 | H_2O | 1 NI | |
| NIHS | 1 | 38.87 | 9 | H | -4 | H ₂ O | 1 | NI - | $1 SO_4^{-1}$ | 8 e |
| NIOH | 1 | -9.54 | -1 | H' | 1 | H ₂ O | 1 | Ni | | |
| NiSO ₄ | 1 | 2.35 | 1 | Ni | 1 | SO ₄ ² | | | | |
| NiSeO ₄ | 1 | 2.67 | 1 | Ni | 1 | SeO ₄ ² | | | 12 | |
| $Ni[CO_3]_2^{2}$ | 1 | -30.30 | 2 | CO ₂ [g] | -4 | ΗŤ | 2 | H ₂ O | 1 Ni ⁺² | |
| | 1 | 78.48 | 18 | H | -8 | H ₂ O | 1 | Ni ⁺² | $2 SO_4^{-2}$ | 16 e |
| NI[HS] ₂ | 1 | -18.00 | -2 | H⁺ | 2 | H ₂ O | 1 | Ni ⁺² | | |
| Ni[HS] ₂ Ni[OH] ₂ | | | 2 | H | 3 | H ₂ O | 1 | Ni ⁺² | | |
| NI[HS] ₂ NI[OH] ₂ NI[OH] ₃ | 1 | -29.20 | -5 | | | | | | | |
| NI[HS] ₂ NI[OH] ₂ NI[OH] ₃ Np ⁺³ | 1 1 | -29.20 12.00 | -3 4 | H⁺ | -4 | H ₂ O | 1 | Np[OH] ₄ | 1 e ⁻ | |
| NI[H5] ₂ NI[OH] ₂ NI[OH] ₃ Np ⁺³ Np ⁺⁴ | 1 1 1 | -29.20 12.00 8.31 | -3 4 4 | H ⁺ H ⁺ | -4 -4 | H ₂ O H ₂ O | 1 1 | Np[OH] ₄ Np[OH] ₄ | 1 e ⁻ | |
| NI[HS] ₂ NI[OH] ₂ NI[OH] ₃ Np ⁺³ Np ⁺⁴ NpCO ₃ ⁺ | 1 1 1 | -29.20 12.00 8.31 1.85 | -3 4 4 1 | H^{\dagger} H^{\dagger} $CO_2[g]$ | -4 -4 2 | H₂O H₂O H [⁺] | 1 1 -3 | Np[OH] ₄ Np[OH] ₄ H ₂ O | 1 e ⁻ 1 Np[OH] ₄ | 1 e ⁻ |
| NI[H5] ₂ NI[OH] ₂ NI[OH] ₃ Np ⁺³ Np ⁺⁴ NpCO ₃ ⁺ NpCO ₃ ⁻ | 1 1 1 1 | -29.20 12.00 8.31 1.85 -7.85 | -3 4 4 1 1 | H^{+} H^{+} $CO_2[g]$ $CO_2[g]$ | -4 -4 2 -1 | H ₂ O H ₂ O H [⁺] H [⁺] | 1 1 -3 1 | Np[OH] ₄ Np[OH] ₄ H ₂ O Np[OH] ₄ | 1 e ⁻ 1 Np[OH] ₄ | 1 e ⁻ |
| NI[HS] ₂ NI[OH] ₂ NI[OH] ₃ Np ⁺³ Np ⁺⁴ NpCO ₃ ⁺ NpCO ₃ ⁻ NpCO ₃ [OH] ₃ Npl ⁺³ | 1 1 1 1 1 | -29.20 12.00 8.31 1.85 -7.85 9.81 | -3 4 1 1 4 | H^+ H^+ $CO_2[g]$ $CO_2[g]$ H^+ | -4 -4 2 -1 -4 | H_2O H_2O H^+ H^+ H_2O | 1 -3 1 | $Np[OH]_4$ $Np[OH]_4$ H_2O $Np[OH]_4$ I^{-} | 1 e ⁻ 1 Np[OH] ₄ 1 Np[OH] ₄ | 1 e ⁻ |

| species | reference | log K | stoichiometr | ic composition | | | |
|--|-----------|----------------|-----------------------------|---|----------------------------------|-----------------------------------|-------------------|
| NpO2 ⁺² | 1 | -21.50 | -2 H₂O | 1 Np[OH] | -2 e ⁻ | | |
| NpO ₂ CO ₂ | 1 | -15.10 | 1 CO ₂ [g] | $-2 H^{+}$ | -1 H ₂ O | 1 Np[OH]₄ | -1 e ⁻ |
| NnO ₂ IO ₂ | - | -112 97 | -6 H ⁺ | - ·· 1 Η ₂ Ο | 1 1 | 1 Np[OH]₄ | -7 e ⁻ |
| NnO ₂ IO ₂ ⁺ | - | -131.86 | -6 H ⁺ | 1 H ₂ O | 1 I | 1 Np[OH]₄ | -8 e ⁻ |
| | 1 | -13 21 | -1 H ⁺ | -1 H ₂ O | 1 Nn[OH]. | -1 e ⁻ | 0 0 |
| | 1 | -26.60 | -1 H ⁺ | -1 H ₂ O | 1 Np[OH]_4 | -2 e ⁻ | |
| NpO ₂ On NpO ₂ SO | 1 | -18 22 | -2 H-O | 1 Np[OH]. | $1 \text{ sp}[0, 1]_4$ | -2 e ⁻ | |
| | 1 | 1 47 | 2 1120 | 1 Np[OH]4 | $1 SO_4$ | 1 0 | |
| NpO $[CO 1^{-3}]$ | 1 | -1.47 | $-2 \Pi_2 O$ | т пр[Оп] ₄ л ц ⁺ | | -1 e | |
| | 1 | 12 21 | 2 CO _{2[8]} | -4 II 1 L O | 1 Np[OII] ₄ | -1 e | |
| | 1 | -15.21 | -1 H | -1 H ₂ U | 1 NP[OH]4 | -1 e | |
| | 1 | -25.51 | -2 Π | 1 NP[OH]4 | -1 e | 2 - | |
| $NpO_2[OH]_3$ | 1 | -41.50 | -3 Π | | 1 Np[OH] | -2 e | |
| NpO ₂ [OH] ₄ | 1 | -53.50 | -4 H | 2 H ₂ U | 1 NP[UH]_4 | -2 e | |
| NpO ₂ [SO ₄] ₂ | 1 | -16.80 | -2 H ₂ O | 1 Np[OH] ₄ | $2 SO_4$ | -2 e | |
| NPOH | 1 | 5.20 | 3 H | -3 H ₂ O | 1 Np[OH] ₄ | 1 e | |
| NpOH [*] | 1 | 8.86 | 3 H | -3 H ₂ O | 1 Np[OH] ₄ | • • • • [−] ² | |
| NpSO ₄ | 1 | 15.30 | 4 H | -4 H ₂ O | 1 Np[OH] ₄ | $1 SO_4^{-1}$ | 1 e |
| NpSO ₄ | 1 | 15.16 | 4 H | -4 H ₂ O | 1 Np[OH] ₄ | 1 SO ₄ | |
| Np[CO ₃] ₄ | 1 | -27.62 | 4 CO ₂ [g] | -4 H | 1 Np[OH] ₄ | _ | |
| Np[OH] ₂ | 1 | -2.70 | 2 H | -2 H ₂ O | 1 Np[OH] ₄ | 1 e | |
| Np[OH] ₂ ⁺² | 1 | 8.66 | 2 H [*] | -2 H ₂ O | 1 Np[OH] ₄ | | |
| Np[OH] ₃ | 1 | -13.80 | 1 H [*] | -1 H ₂ O | 1 Np[OH] ₄ | 1 e | |
| Np[OH] ₃ ⁺ | 1 | 5.50 | 1 H ⁺ | -1 H ₂ O | 1 Np[OH] ₄ | | |
| Np[SO ₄] ₂ | 1 | 19.36 | 4 H ⁺ | -4 H ₂ O | 1 Np[OH] ₄ | 2 SO_4^{-2} | |
| Np[SO ₄] ₂ | 1 | 15.70 | $4 H^+$ | -4 H ₂ O | 1 Np[OH] ₄ | 2 SO_4^{-2} | 1 e ⁻ |
| O ₂ | 1 | -86.08 | -4 H ⁺ | 2 H ₂ O | -4 e | | |
| OH | 1 | -14.00 | -1 H ⁺ | 1 H ₂ O | | | |
| Pu ⁺³ | 1 | 17.69 | 1 Pu ⁺⁴ | 1 e ⁻ | | | |
| PuCO ₃ ⁺ | 1 | 7.54 | 1 CO ₂ [g] | -2 H⁺ | 1 H ₂ O | 1 Pu ⁺⁴ | 1 e ⁻ |
| PuCO ₃ [OH] ₃ ⁻ | 1 | -12.15 | 1 CO ₂ [g] | -5 H⁺ | 4 H ₂ O | 1 Pu ⁺⁴ | |
| Pul ⁺² | 1 | 18.79 | 1 I ⁻ | 1 Pu ⁺⁴ | 1 e ⁻ | | |
| PuO ₂ ⁺ | 1 | -17.45 | -4 H ⁺ | 2 H ₂ O | 1 Pu ⁺⁴ | -1 e ⁻ | |
| PuO_2^{+2} | 1 | -33.27 | -4 H ⁺ | 2 H ₂ O | 1 Pu ⁺⁴ | -2 e ⁻ | |
| PuO ₂ OH | 1 | -27.18 | -5 H ⁺ | 3 H ₂ O | 1 Pu ⁺⁴ | -1 e | |
| PuO₂OH⁺ | 1 | -38.77 | -5 H ⁺ | 3 H ₂ O | 1 Pu ⁺⁴ | -2 e ⁻ | |
| PuO ₂ SO ₄ | 1 | -29.89 | -4 H ⁺ | 2 H ₂ O | 1 Pu ⁺⁴ | 1 SO4 ⁻² | -2 e ⁻ |
| PuO ₂ [OH] ₂ | 1 | -46.47 | -6 H ⁺ | 4 H ₂ O | 1 Pu ⁺⁴ | -2 e ⁻ | |
| $PuO_2[SO_4]_2^{-2}$ | 1 | -28.87 | -4 H ⁺ | 2 H ₂ O | 1 Pu ⁺⁴ | 2 SO_4^{-2} | -2 e ⁻ |
| PuOH ⁺² | 1 | 10.79 | -1 H ⁺ | 1 H ₂ O | 1 Pu ⁺⁴ | 1 e ⁻ | |
| PuOH ⁺³ | 1 | 0.60 | -1 H ⁺ | 1 H ₂ O | 1 Pu ⁺⁴ | - | |
| PuSO4 ⁺ | 1 | 21.61 | 1 Pu ⁺⁴ | $1 SO_4^{-2}$ | 1 e ⁻ | | |
| $PuSO_4^{+2}$ | 1 | 6.89 | 1 Pu ⁺⁴ | $1 SO_4^{-2}$ | | | |
| Pu[CO ₂] | 1 | -5.71 | 2 CO ₂ [g] | -4 H ⁺ | 2 H ₂ O | 1 Pu ⁺⁴ | 1 e ⁻ |
| $Pu[CO_{2}]_{2}^{-3}$ | - | -21 76 | 3 CO ₂ [g] | -6 H ⁺ | 3 H ₂ O | 1 Pu ⁺⁴ | 1 e ⁻ |
| | 1 | 2 89 | -2 H ⁺ | 2 H ₂ O | 1 Pu ⁺⁴ | 1 e ⁻ | 10 |
| | 1 | 0.60 | -2 H ⁺ | 2 H ₂ O | 1 Pu ⁺⁴ | 10 | |
| | 1 | -8.21 | -2 H ⁺ | 3 4.0 | 1 Pu ⁺⁴ | 1 o ⁻ | |
| | 1 | -2.30 | -3 Н ⁺ | 3 H.O | 1 Du ⁺⁴ | IC | |
| | 1 | -8 50 | -1 H ⁺ | 1 H O | 1 Du ⁺⁴ | | |
| | 1 | -0.50 | -4 11 1 Du ⁺⁴ | 2 SO -2 | I FU | | |
| $Pu[SO_{4}]_{2}$ | 1 | 22.40 | 1 Pu ⁺⁴ | $2 30_4$ | 1 0 | | |
| $Pu[3O_4]_2$ | 1 | 25.40 1E CE | | 2 304 2 u ⁺ | | 1 Ro ⁺² | |
| | 1 | -15.05 | $1 CO_2[g]$ | -2 H | I H ₂ U | I Nd | |
| | 1 | -0.10 | 1 U | | 1 Da ⁺² | | |
| RaUH | 1 | -13.50 | -1 H | $1 H_2 O$ | тка | | |
| $raso_4$ | 1 | 2.75 | т ка | 1 504 | 4 60 -2 | 0 | |
| S | 1 | 14.69 | 8 H | -4 H ₂ O | $1 SO_4^{-2}$ | х е | |
| S_2O_3 | 1 | 38.01 | 10 H | -5 H ₂ O | $2 SO_4^{-2}$ | 8 e | |
| SO ₃ - | 1 | -3.40 | 2 H | -1 H ₂ O | $1 SO_4^{-2}$ | 2 e | |
| Se ² | 1 | 66.66 | 8 H | -4 H ₂ O | 1 SeO_4^2 | 8 e | |
| Se ₂ ⁻² | 1 | 158.63 | 16 H [*] | -8 H ₂ O | 2 SeO ₄ ⁻² | 14 e | |

| species | reference | log K | stoichiomet | ric composition | | | |
|---|-----------|----------------|---------------------------------------|---|---------------------------|---------------------------|--------------------|
| Se_3^{-2} | 1 | 249.93 | 24 H ⁺ | -12 H ₂ O | 3 SeO4 ⁻² | 20 e ⁻ | |
| Se ⁻² | 1 | 339.65 | 32 H ⁺ | -16 H ₂ O | 4 SeO $^{-2}$ | 26 e ⁻ | |
| SeH ₂ O ₂ | 1 | 39.04 | 4 H ⁺ | -1 H ₂ O | 1 SeQ $^{-2}$ | 2 e | |
| SeO_2^{-2} | 1 | 28.04 | 2 H ⁺ | -1 H ₂ O | 1 SeO₄ ⁻² | 2 e | |
| SrCO ₂ | 1 | -15 34 | 1 CO ₂ [g] | -2 H ⁺ | 1 H₂O | 1 Sr ⁺² | |
| SrHCO ⁺ | 1 | -6 64 | 1 CO ₂ [g] | -1 H ⁺ | 1 H ₂ O | 1 Sr ⁺² | |
| Sr∩H ⁺ | 1 | _13 29 | -1 H ⁺ | 1 H-O | 1 Sr^{+2} | 1 51 | |
| SrSO | 1 | 2 20 | 1 so ⁻² | 1 Gr^{+2} | 1 51 | | |
| | 1 | 2.23 | $1 50_4$ | т эі л ц ⁺ | 1 4 0 | 1 TcO - | 2 0 |
| | 1 | 50.55 22 22 | $1 CO_{2}[g]$ | 4 ⊓ 2 ⊔ ⁺ | $-1 H_2 O^{-1}$ | $1 100_4$ | 5 6 |
| | 1 | 22.25 | | 5 П | $1 T_{c}O_{4}$ | 5 e | |
| TCU | 1 | 33.43 | 6 H | -3 H ₂ U | 1 TCO ₄ | 3 e | |
| | 1 | -10.80 | | 1 e | 4 - 0 ⁻ | a - | |
| | 1 | 31.93 | 5 H | -2 H ₂ O | 1 TcO_4 | 3 e | |
| | 1 | 29.43 | 4 H | -1 H ₂ O | 1 ICO_4 | 3 e | |
| TcO[OH] ₃ | 1 | 18.53 | 3 H | 1 TcO ₄ | 3 e | | |
| Th ₂ [OH] ₃ ¹⁹ | 1 | -6.80 | -3 H | 3 H ₂ O | 2 Th ¹¹ | | |
| ThCl ¹³ | 1 | 1.70 | 1 Cl | 1 Th'⁺ | | +1 | |
| ThIO3 | 1 | -107.43 | -6 H | 3 H ₂ O | 1 | 1 Th [™] | -6 e |
| ThOH ^{+°} | 1 | -2.50 | -1 H ⁺ | 1 H ₂ O | 1 Th ⁺⁴ | . 4 | |
| ThOH[CO ₃] ₄ ⁻⁵ | 1 | -50.99 | 4 CO ₂ [g] | -9 H [*] . | 5 H ₂ O | 1 Th ⁺⁴ | |
| ThSO4 ⁺² | 1 | 6.17 | $1 SO_4^{-2}$ | 1 Th $^{+4}$ | | | |
| Th[CO ₃] ₅ - ⁶ | 1 | -59.74 | 5 CO ₂ [g] | -10 H ⁺ | 5 H ₂ O | 1 Th^{+4} | |
| Th[IO3]2 ⁺² | 1 | -216.16 | -12 H ⁺ | 6 H ₂ O | 2 I ⁻ | 1 Th^{+4} | -12 e ⁻ |
| Th[IO3]₃ ⁺ | 1 | -324.83 | -18 H ⁺ | 9 H₂O | 3 I ⁻ | 1 Th^{+4} | -18 e ⁻ |
| Th[OH] ₂ ⁺² | 1 | -6.20 | -2 H ⁺ | 2 H ₂ O | 1 Th ⁺⁴ | | |
| Th[OH] ₂ CO ₃ | 1 | -15.65 | $1 CO_2[g]$ | -4 H ⁺ | 3 H ₂ O | 1 Th ⁺⁴ | |
| Th[OH] ₂ [CO ₃] ₂ ⁻² | 1 | -27.50 | $2 CO_{2}[g]$ | -6 H⁺ | 4 H ₂ O | 1 Th^{+4} | |
| Th[OH] ₂ CO ₂ | 1 | -21.85 | 1 CO ₂ [g] | -5 H ⁺ | 4 H ₂ O | 1 Th ⁺⁴ | |
| Th[OH] | 1 | -17.40 | $-4 H^{+}$ | 4 H ₂ O | 1 Th ⁺⁴ | | |
| | - | -33 75 | 1 CO ₂ [g] | -6 H ⁺ | 5 H ₂ O | 1 Th ⁺⁴ | |
| | 1 | 9 69 | 2 so^{-2} | 1 Th ⁺⁴ | 5 1120 | 1 | |
| Th[SO]. ⁻² | 1 | 10 75 | $2 50_4$ | 1 Th ⁺⁴ | | | |
| 11 ⁺³ | 1 | -0.32 | 3 50 ₄ л н ⁺ | -2 H.O | 1 110.+2 | 3 0 | |
| U ⁺⁴ | 1 | 0.52 | 4 11 1 LI ⁺ | -2 H ₂ O | $1 UO_2^{+2}$ | 3 e ⁻ | |
| | 1 | 5.04 | | -2 H ₂ O 1 ⊔ ⁺ | 2 4 0 | 2 E 1 UO ⁺² | 2 0- |
| | 1 | 10.76 | | -т II л Ц ⁺ | 2 H ₂ O | $1 UO_2^{+2}$ | 2 0 |
| UU ⁺³ | 1 | 10.70 | 1 Ci | 4 11 | -2 H ₂ O | $1 00_2$ | 2 6 |
| | 1 | 10.29 | 4 Π 1 μ0 ⁺² | -2 H ₂ U | 11 | 1 002 | ze |
| | 1 | 1.48 | $1 00_2$ | 1 e 2 u ⁺ | 4.11.0 | 4 UO ⁺² | |
| UU_2CU_3 | 1 | -8.21 | | -2 H | 1 H ₂ O | 1 002 | |
| | 1 | 0.17 | | $1 00_2$ | | | |
| | 1 | -1.10 | 2 CI | 1 002 | | +2 | a - |
| | 1 | -109.56 | -6 H | 3 H ₂ O | 11 | 1 002 | -6 e |
| UO ₂ OH | 1 | -5.25 | -1 H | 1 H ₂ O | $1 UO_2^{-1}$ | | |
| $UO_2S_2O_3$ | 1 | 40.81 | 10 H | -5 H ₂ O | $2 SO_4^2$ | $1 UO_2^{+2}$ | 8 e |
| UO_2SO_3 | 1 | 3.20 | 2 H ⁻ | -1 H ₂ O | 1 SO ₄ - | $1 UO_2^{12}$ | 2 e |
| UO ₂ SO ₄ | 1 | 3.15 | 1 SO4 | 1 UO ₂ '2 | | | |
| UO ₂ SeO ₄ | 1 | 2.74 | 1 SeO ₄ -2 | 1 UO2 ⁺² | | .2 | |
| $UO_2[CO_3]_2^{-2}$ | 1 | -19.69 | 2 CO ₂ [g] | -4 H ⁺ | 2 H ₂ O | 1 UO2 ⁺² | |
| $UO_2[CO_3]_3^{-4}$ | 1 | -32.62 | 3 CO ₂ [g] | -6 H ⁺ | 3 H ₂ O | $1 UO_2^{+2}$ | |
| $UO_2[CO_3]_3^{-5}$ | 1 | -46.02 | 3 CO ₂ [g] | -6 H ⁺ | 3 H ₂ O | 1 UO2 ⁺² | 1 e |
| $UO_2[IO3]_2$ | 1 | -219.54 | -12 H ⁺ | 6 H ₂ O | 2 I ⁻ | 1 UO2 ⁺² | -12 e ⁻ |
| $UO_2[OH]_2$ | 1 | -12.15 | -2 H⁺ | 2 H ₂ O | 1 UO2 ⁺² | | |
| UO ₂ [OH] ₃ | 1 | -20.25 | -3 H⁺ | 3 H ₂ O | 1 UO2 ⁺² | | |
| $UO_2[OH]_4^{-2}$ | 1 | -33.40 | -4 H ⁺ | 4 H ₂ O | $1 UO_2^{+2}$ | | |
| $UO_{2}[SO_{4}]_{2}^{-2}$ | 1 | 4.14 | $2 SO_4^{-2}$ | $1 UO_{2}^{+2}$ | - | | |
| $UO_{2}[SO_{4}]_{3}^{-4}$ | 1 | 3.02 | $3 SO_4^{-2}$ | $1 UO_2^{+2}$ | | | |
| UOH ⁺³ | 1 | 8.50 | 3 H ⁺ | -1 H ₂ O | 1 UO2 ⁺² | 2 e | |
| USO_4^{+2} | 1 | 15.62 | 4 H ⁺ | -2 H ₂ O | $1 SO_{2}^{-2}$ | $1 U \Omega_{2}^{+2}$ | 2 e |
| $U[CO_{2}]_{4}^{-4}$ | 1 | -28.45 | 4 CO ₂ [σ] | -4 H ⁺ | 2 H ₂ O | $1 U \Omega_2^{+2}$ | 2 e |
| $U[CO_{2}]_{2}^{-6}$ | 1 | -47.72 | $5 CO_{2}[g]$ | -6 H ⁺ | 3 H ₂ O | $1 U \Omega_2^{+2}$ | 2 e ⁻ |
| | - | | 0 002181 | • • • • | 5 | | |

| species | reference | log K | stoichiometr | ic composition | | | |
|---|-----------|--------|---------------------------------|---------------------|-----------------------|----------------------|------------------|
| U[OH]₃ ⁺ | 1 | 4.34 | 1 H ⁺ | 1 H ₂ O | 1 UO2 ⁺² | 2 e ⁻ | |
| U[OH] ₄ | 1 | -0.97 | 2 H ₂ O | 1 UO2 ⁺² | 2 e ⁻ | | |
| $U[SO_4]_2$ | 1 | 19.55 | $4 H^+$ | -2 H ₂ O | 2 SO_4^{-2} | 1 UO2 ⁺² | 2 e ⁻ |
| [NpO ₂] ₂ [OH] ₂ ⁺² | 1 | -49.27 | -2 H ⁺ | -2 H ₂ O | 2 Np[OH] ₄ | -4 e | |
| [NpO ₂] ₃ [OH] ₅ ⁺ | 1 | -81.61 | -5 H ⁺ | -1 H ₂ O | 3 Np[OH] ₄ | -6 e | |
| [PuO ₂] ₂ [OH] ₂ ⁺² | 1 | -74.04 | -10 H ⁺ | 6 H ₂ O | 2 Pu ⁺⁴ | -4 e | |
| $[UO_2]_2CO_3[OH]_3$ | 1 | -19.01 | 1 CO ₂ [g] | -5 H ⁺ | 4 H ₂ O | 2 UO2 ⁺²² | |
| [UO ₂] ₂ OH ⁺³ | 1 | -2.70 | -1 H ⁺ | 1 H ₂ O | $2 UO_2^{+2}$ | | |
| [UO ₂] ₂ [OH] ₂ ⁺² | 1 | -5.62 | -2 H ⁺ | 2 H ₂ O | 2 UO2 ⁺² | | |
| $[UO_2]_3O[OH]_2HCO_3^+$ | 1 | -17.49 | 1 CO ₂ [g] | -5 H ⁺ | 4 H ₂ O | 3 UO2 ⁺² | |
| $[UO_2]_3O[OH]_2[HCO_3]^+$ | 1 | -17.50 | 1 CO ₂ [g] | -5 H ⁺ | 4 H ₂ O | 3 UO2 ⁺² | |
| [UO ₂] ₃ [CO ₃] ₆ ⁻⁶ | 1 | -54.91 | 6 CO ₂ [g] | -12 H ⁺ | 6 H₂O | 3 UO2 ⁺² | |
| [UO ₂] ₃ [OH] ₄ ⁺² | 1 | -11.90 | -4 H ⁺ | 4 H ₂ O | 3 UO2 ⁺² | | |
| [UO ₂] ₃ [OH] ₅ ⁺ | 1 | -15.55 | -5 H⁺ | 5 H ₂ O | 3 UO2 ⁺² | | |
| [UO ₂] ₃ [OH] ₇ | 1 | -32.20 | -7 H ⁺ | 7 H₂O | 3 UO2 ⁺² | | |
| [UO ₂] ₄ [OH] ₇ ⁺ | 1 | -21.90 | -7 H ⁺ | 7 H ₂ O | 4 UO2 ⁺² | | |
| CaCl⁺ | 3 | -0.70 | 1 Cl ⁻ | 1 Ca ⁺² | | | |
| CaCl ₂ | 3 | -0.64 | 2 Cl ⁻ | 1 Ca ⁺² | | | |
| CsCl | 3 | -0.14 | 1 Cl ⁻ | 1 Cs ⁺ | | | |
| KCI | 3 | -1.49 | 1 Cl ⁻ | 1 K ⁺ | | | |
| SnCl3 | 3 | 1.69 | 3 Cl ⁻ | 1 Sn ⁺² | | | |
| SrCl ⁺ | 3 | -0.25 | 1 Cl ⁻ | 1 Sr ⁺² | | | |
| NaCl | 3 | -0.78 | 1 Cl ⁻ | 1 Na $^+$ | | | |
| PbCl⁺ | 4 | 1.60 | 1 Cl ⁻ | 1 Pb ⁺² | | | |
| PbCl ₂ | 4 | 1.80 | 2 Cl ⁻ | 1 Pb ⁺² | | | |
| PbCl3 | 4 | 1.70 | 3 Cl | 1 Pb ⁺² | | | |
| PbCO ₃ | 4 | 7.24 | 1 CO ₃ ⁻² | 1 Pb ⁺² | | | |
| $Pb[CO_{3}]_{2}^{-2}$ | 4 | 10.64 | 2 CO ₃ ⁻² | 1 Pb ⁺² | | | |
| PbHCO ₃ ⁺ | 4 | 2.90 | 1 HCO3 | 1 Pb ⁺² | | | |
| SnCl ⁺ | 5 | 1.52 | 1 Cl ⁻ | 1 Sn ⁺² | | | |
| SnCl ₂ | 5 | 2.17 | 2 Cl ⁻ | 1 Sn ⁺² | | | |

| Element | _ | K _{d-diss} | - | | K _{d-DOC} | - | | R _{dis} | - | | R _{DOC} | - |
|---------|---------|---------------------|---------|-------|--------------------|---------|---------|-------------------------|---------|-------|-------------------------|---------|
| | lower | central | upper | lower | central | upper | lower | central | upper | lower | central | upper |
| Se | 0 | 0 | 0 | 51 | 129 | 247 | 1 | 1 | 1 | 236 | 621 | 1263 |
| U | 7 | >10'000 | >10'000 | 16 | 46 | 95 | 33 | >50'000 | >50'000 | 77 | 221 | 489 |
| Тс | >10'000 | >10'000 | >10'000 | 16 | 46 | 95 | >50'000 | >50'000 | >50'000 | 77 | 221 | 489 |
| Th | >10'000 | >10'000 | >10'000 | 16 | 46 | 95 | >50'000 | >50'000 | >50'000 | 77 | 221 | 489 |
| Np | >10'000 | >10'000 | >10'000 | 16 | 46 | 95 | >50'000 | >50'000 | >50'000 | 77 | 221 | 489 |
| К | 0 | 7 | 387 | 113 | 485 | 1068 | 3 | 34 | 1997 | 525 | 2300 | 5694 |
| Са | 9 | 1114 | >10'000 | 133 | 603 | 1831 | 46 | 5409 | >50'000 | 611 | 2881 | 9584 |
| Pu | >10'000 | >10'000 | >10'000 | 16 | 46 | 95 | >50'000 | >50'000 | >50'000 | 77 | 221 | 489 |
| Am | >10'000 | >10'000 | >10'000 | 24 | 71 | 366 | >50'000 | >50'000 | >50'000 | 116 | 349 | 1676 |
| Sn | >10'000 | >10'000 | >10'000 | 16 | 46 | 95 | >50'000 | >50'000 | >50'000 | 77 | 221 | 489 |
| Eu | >10'000 | >10'000 | >10'000 | 20 | 56 | 146 | >50'000 | >50'000 | >50'000 | 95 | 267 | 706 |
| Ni | >10'000 | >10'000 | >10'000 | 17 | 47 | 96 | >50'000 | >50'000 | >50'000 | 81 | 227 | 494 |
| Cs | 103 | 1329 | 7596 | 3413 | >10'000 | >10'000 | 476 | 6454 | 38'699 | 16611 | >50'000 | >50'000 |
| Cm | >10'000 | >10'000 | >10'000 | 16 | 46 | 95 | >50'000 | >50'000 | >50'000 | 78 | 222 | 489 |
| Sr | 33 | 2762 | >10'000 | 35 | 95 | 273 | 160 | 13'329 | >50'000 | 161 | 461 | 1375 |
| Ra | 18 | 1554 | >10'000 | 34 | 95 | 275 | 87 | 7320 | >50'000 | 161 | 458 | 1364 |
| Pb | >10'000 | >10'000 | >10'000 | 25 | 69 | 237 | >50'000 | >50'000 | >50'000 | 120 | 338 | 1145 |

Table B-1: Ranges of calculated K_{d} - and R-values in Boom Clay of the Netherlands for the *base case* (100 mg/l DOC). Lower, central, and upper values correspond to 5-, 50- and 95-percentiles of the calculated values, respectively.

Table B-2: Ranges of calculated K_d - and R-values in Boom Clay of the Netherlands for the *low* DOC case (20 mg/l DOC). Lower, central, and upper values correspond to 5-, 50- and 95-percentiles of the calculated values, respectively.

| Element | | K _{d-diss} | = | | K _{d-DOC} | = | | R _{dis} | - | | R _{DOC} | = |
|---------|---------|---------------------|---------|---------|--------------------|---------|---------|-------------------------|---------|---------|-------------------------|---------|
| Liement | lower | central | upper | lower | central | upper | lower | central | upper | lower | central | upper |
| Se | 0 | 0 | 0 | 257 | 646 | 1235 | 1 | 1 | 1 | 1178 | 3100 | 6311 |
| U | 7 | >10'000 | >10'000 | 81 | 231 | 473 | 33 | >50'000 | >50'000 | 382 | 1103 | 2442 |
| Тс | >10'000 | >10'000 | >10'000 | 81 | 231 | 473 | >50'000 | >50'000 | >50'000 | 382 | 1103 | 2442 |
| Th | >10'000 | >10'000 | >10'000 | 81 | 231 | 473 | >50'000 | >50'000 | >50'000 | 382 | 1103 | 2442 |
| Np | >10'000 | >10'000 | >10'000 | 81 | 231 | 473 | >50'000 | >50'000 | >50'000 | 382 | 1103 | 2442 |
| К | 0 | 7 | 387 | 567 | 2423 | 5339 | 3 | 34 | 1996 | 2619 | 11496 | 28464 |
| Са | 9 | 1114 | >10'000 | 663 | 3016 | 9153 | 46 | 5400 | >50'000 | 3051 | 14'398 | 47'917 |
| Pu | >10'000 | >10'000 | >10'000 | 81 | 231 | 473 | >50'000 | >50'000 | >50'000 | 382 | 1103 | 2442 |
| Am | >10'000 | >10'000 | >10'000 | 119 | 357 | 1829 | >50'000 | >50'000 | >50'000 | 578 | 1741 | 8379 |
| Sn | >10'000 | >10'000 | >10'000 | 81 | 231 | 473 | >50'000 | >50'000 | >50'000 | 382 | 1103 | 2442 |
| Eu | >10'000 | >10'000 | >10'000 | 100 | 278 | 732 | >50'000 | >50'000 | >50'000 | 473 | 1332 | 3527 |
| Ni | >10'000 | >10'000 | >10'000 | 86 | 236 | 481 | >50'000 | >50'000 | >50'000 | 402 | 1130 | 2468 |
| Cs | 103 | 1328 | 7594 | >10'000 | >10'000 | >10'000 | 476 | 6453 | 38'699 | >50'000 | >50'000 | >50'000 |
| Cm | >10'000 | >10'000 | >10'000 | 82 | 231 | 473 | >50'000 | >50'000 | >50'000 | 384 | 1105 | 2442 |
| Sr | 33 | 2761 | >10'000 | 173 | 474 | 1365 | 160 | 13'289 | >50'000 | 802 | 2303 | 6873 |
| Ra | 18 | 1550 | >10'000 | 173 | 475 | 1373 | 87 | 7315 | >50'000 | 799 | 2287 | 6816 |
| Pb | >10'000 | >10'000 | >10'000 | 125 | 347 | 1184 | >50'000 | >50'000 | >50'000 | 595 | 1685 | 5722 |

Table B-3: Ranges of calculated K_{d} - and R-values in Boom Clay of the Netherlands for the high DOC case (200 mg/l DOC). Lower, central, and upper values correspond to 5-, 50- and 95-percentiles of the calculated values, respectively.

| Element | | K _{d-diss} | | | K _{d-DOC} | | | R _{dis} | | | R _{DOC} | |
|---------|---------|---------------------|---------|-------|--------------------|---------|---------|-------------------------|---------|-------|------------------|---------|
| | lower | central | upper | lower | central | upper | lower | central | upper | lower | central | upper |
| Se | 0 | 0 | 0 | 26 | 65 | 123 | 1 | 1 | 1 | 119 | 311 | 632 |
| U | 7 | >10'000 | >10'000 | 8 | 23 | 47 | 33 | >50'000 | >50'000 | 39 | 111 | 245 |
| Тс | >10'000 | >10'000 | >10'000 | 8 | 23 | 47 | >50'000 | >50'000 | >50'000 | 39 | 111 | 245 |
| Th | >10'000 | >10'000 | >10'000 | 8 | 23 | 47 | >50'000 | >50'000 | >50'000 | 39 | 111 | 245 |
| Np | >10'000 | >10'000 | >10'000 | 8 | 23 | 47 | >50'000 | >50'000 | >50'000 | 39 | 111 | 245 |
| К | 0 | 7 | 387 | 57 | 242 | 534 | 3 | 34 | 1999 | 263 | 1151 | 2847 |
| Ca | 9 | 1114 | >10'000 | 66 | 302 | 915 | 46 | 5427 | >50'000 | 306 | 1441 | 4793 |
| Pu | >10'000 | >10'000 | >10'000 | 8 | 23 | 47 | >50'000 | >50'000 | >50'000 | 39 | 111 | 245 |
| Am | >10'000 | >10'000 | >10'000 | 12 | 36 | 183 | >50'000 | >50'000 | >50'000 | 58 | 175 | 838 |
| Sn | >10'000 | >10'000 | >10'000 | 8 | 23 | 47 | >50'000 | >50'000 | >50'000 | 39 | 111 | 245 |
| Eu | >10'000 | >10'000 | >10'000 | 10 | 28 | 73 | >50'000 | >50'000 | >50'000 | 48 | 134 | 353 |
| Ni | >10'000 | >10'000 | >10'000 | 9 | 24 | 48 | >50'000 | >50'000 | >50'000 | 41 | 114 | 248 |
| Cs | 103 | 1329 | 7597 | 1706 | >10'000 | >10'000 | 476 | 6457 | 38'699 | 8302 | >50'000 | >50'000 |
| Cm | >10'000 | >10'000 | >10'000 | 8 | 23 | 47 | >50'000 | >50'000 | >50'000 | 39 | 111 | 245 |
| Sr | 34 | 2764 | >10'000 | 17 | 47 | 136 | 160 | 13'382 | >50'000 | 81 | 231 | 688 |
| Ra | 18 | 1557 | >10'000 | 17 | 47 | 137 | 87 | 7330 | >50'000 | 81 | 230 | 682 |
| Pb | >10'000 | >10'000 | >10'000 | 12 | 35 | 118 | >50'000 | >50'000 | >50'000 | 60 | 169 | 573 |

Disclaimer

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OPERA

Meer informatie:

Postadres Postbus 202 4380 AE Vlissingen

T 0113-616 666 F 0113-616 650 E info@covra.nl

www.covra.nl