Report on model representation of radionuclide sorption in Boom Clay

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.

Content

Summary

The migration of radionuclides through the host rock plays an important role for the long-term safety of disposal concepts in Boom Clay. Due to the slow transport of radionuclides in the host rock, most radionuclides will be decayed before they can enter the surrounding aquifers. For many scenarios that will be considered in OPERA, 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 effects of long-term underground disposal of radioactive waste.

This report focuses on the processes that determine the fraction of radionuclides that will be bound by adsorption to the solid matter of the Boom Clay and can therefore be considered as immobile. Adsorption of inorganic compounds on different surfaces has been studied for a long time, resulting in an extensive amount of available scientific literature on this topic, from which the most relevant approaches are discussed in this report.

Based on the available information, a modelling approach is presented on how to address adsorption in the OPERA safety assessment, and how to include existing uncertainties. The approach foresees a two-step procedure, during which for all radionuclides of interest so-called 'K_d-values' are derived, characteristic for radionuclide adsorption to Boom Clay as present in the Netherlands.

The approach will be applied in the next phase of the RANMIG project, and the outcomes will be documented and discussed in a subsequent report (*OPERA-PU-NRG6123*).

Samenvatting

De migratie van radionucliden door het gastgesteente speelt een belangrijke rol voor de langtermijn veiligheid van eindbergingsconcepten in Boomse Klei. Vanwege de zeer trage diffusie van stoffen in het gastgesteente zullen de meeste radionucliden vervallen zijn, voordat deze de klei kunnen verlaten. Het kan worden gesteld dat het zeer trage transport van radionucliden een essentiële rol speelt in 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.

Dit rapport is gericht op de processen die bepalen of een radionuclide in de Boomse Klei zich in oplossing zich bevindt, of door adsorptie aan de matrix van de klei gebonden is en hierdoor als immobiel beschouwd mag worden. Adsorptieprocessen van anorganische stoffen op verschillende oppervlakken worden al geruime tijd bestudeerd. Er is hierover een grote hoeveelheid wetenschappelijke literatuur beschikbaar, en de binnen de vraagstelling belangrijkste manieren om adsorptiegedrag te kwantificeren zullen in dit rapport besproken worden.

Op basis van bestaande informatie wordt in dit rapport een voorstel uitgewerkt, hoe adsorptieprocessen in de veiligheidsberekeningen voor de OPERA Safety Case het best benaderd kunnen worden, en hoe bestaande onzekerheden geadresseerd kunnen worden. Het voorstel bestaat uit een procedure om in twee stappen voor alle relevante radionucliden zogenaamde K_d-waarden uit te werken, die een maat zijn voor de adsorptie aan Boomse Klei, zoals deze in Nederland aanwezig is.

Volgens dit voorstel zullen vervolgens in een volgende fase van het project RANMIG K_d-waarden afgeleid worden. De resultaten daarvan zullen in een navolgend rapport besproken worden (*OPERA-PU-NRG6123*).

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 (M6.1.2.1) 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 are 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 disposals concept in Boom Clay, the slow migration of radionuclides is expected to have a relevant role in the long-term safety of such a disposal concept.

1.2. Objectives

Radionuclide adsorption is a key process that defines the mobility (or migration potential) of radionuclides in Boom Clay. The objective of this report is to define an approach to address radionuclide adsorption in performance assessment calculations, based on the current state-of-the-art of process understanding. Because of the generic state of the OPERA disposal concept (no specific location is given, therefore the properties of the host rock cannot exactly be known), it is important to evaluate the influence of factors that may affect the sorption properties of the host rock. In this report, an overview on the approach will be given. Further details and the outcome will be documented in a follow-up report, *Final report on radionuclide sorption in Boom Clay* (M6.1.2.3).

The interaction between the OPERA Tasks 6.1.2, 6.1.3, 6.1.4 and WP7 is shown in the figure below.
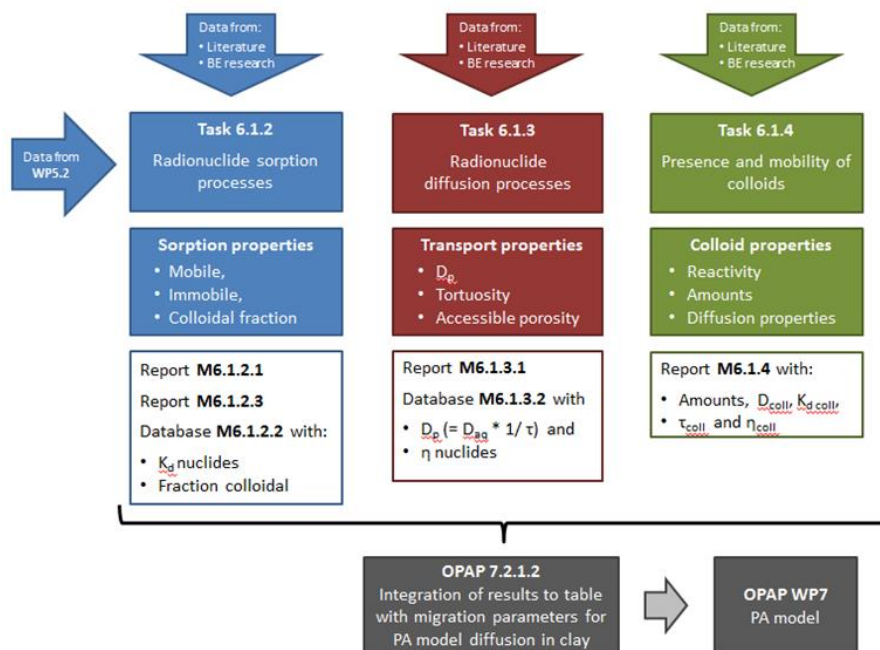
Figure 1-1 Schematic overview of relationship between OPERA WP6.1 tasks and WP7

1.3. Realization

This report represents the public report M6.1.2.1, *Report on model representation of radionuclide sorption in Boom Clay*, and is prepared by NRG and SCK·CEN. It provides an approach to model radionuclide sorption processes within the OPERA safety assessment calculations. To do so, key concepts and modelling approaches for sorption are evaluated.

This report will be followed up by M6.1.2.3, *Final report on radionuclide sorption in Boom Clay* [6], in which a compilation of so-called K_d-values for the radionuclides considered in [7] will be given. The K_d-values provide input to the OPERA Safety Case assessments performed in Work Package 7 [2]. The current report delivers the basis of M6.1.2.3, by providing general context, a general description of the approach followed and a compilation of data on Boom Clay properties in the Netherlands.

1.4. Explanation contents

Chapter 2 provides a condensed overview on key concepts in adsorption modelling, derives the main factors of relevance and clarifies what processes are regarded as "sorption" and are considered in this report. Chapter 3 reviews relevant modelling approaches for radionuclide modelling as applied in radioactive waste management and other fields of work, concluded by a description of the approach for Boom Clay used by the Belgian SCK·CEN. Chapter 4 proposes a modelling approach to address radionuclide sorption in Boom Clay for the purpose of the OPERA performance assessment calculations, based on an analysis of existing experimental data, and the expected variations of relevant parameters. In Chapter 5, a short conclusion and outlook is given on the follow-up report M6.1.2.3, *Final report on radionuclide sorption in Boom Clay*.

2. Current understanding on adsorption processes

2.1.Introduction

The migration of radionuclides through the host rock plays an important role for the long-term safety of disposal concepts in clay. Due to the slow transport of radionuclides through the vertical extent of the host rock, most radionuclides will have decayed before they can reach the boundaries of the host rock. For a generic disposal concept in Boom Clay [1], the delayed transport of radionuclides through the host rock can be assumed as the most important safety function on the long-term [2, 8, 9, 10, 11]. 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 effects of long-term underground disposal of radioactive waste in Boom Clay.

To assess the process of '*migration*' more closely, it can be decomposed into a physical, transport-related component, and a physico-chemical component, that describes the partitioning of the radionuclide over the solid and soluble phase. The most important transport process in Boom Clay is assumed to be diffusion, and will be discussed in OPERA Task 6.1.3 (*Modelling approach for diffusion processes*). Other potential transport processes are addressed in OPERA Task 6.1.5 (*Non-diffusion related transport processes of solutes in Boom Clay*) and 6.1.6 (*Gas migration in the EBS and in Boom Clay*) [2].

This report focuses on the processes that determine which part of the radionuclides will be present in solution and is mobile, and which part will be 'bound' in some way to the solid matter and can therefore be considered as immobile[1]. This is often expressed as '*solid-solution ratio*'. From the two relevant processes that determine the solid-solution ratio, *precipitation* and *adsorption*, this report evaluates the latter: the adsorption behaviour of radionuclides has a large effect on their ability to migrate through the host rock, and must be considered as a key process for the long-term safety.

The adsorption of inorganic compounds on various surfaces has been studied for a long time, resulting in an extensive amount of scientific literature available on this topic. In the beginning, simple interactions between single compounds and surfaces were studied under well-defined conditions. The adsorption behaviour of simple binary systems[2], with a single ion interacting with a homogeneous surface can be considered to be sufficiently well understood, and the adsorption behaviour in such systems can often be described sufficiently well with simple empirical or semi-mechanistic models, e.g. by the Freundlich- or Langmuir-model ([12], see also Section 3.2). However, the adsorption behaviour of radionuclides in natural systems is much more complex, although the principal processes are the same.

To evaluate adsorption behaviour for the purpose of assessing the long-term safety of a disposal facility in argillaceous host rocks, a number of factors need to be considered:
- The adsorption behaviour of a radionuclide also depends on its *speciation*[3], with different species of an element having different adsorption behaviour. The speciation of an element is determined by the solution composition, and thus related to general characteristics as *pH*, redox potential and ionic strength [13]. Often, one soluble species dominates the speciation, however, in some cases several species of relevance can be present.

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[1] Note that adsorption can also take place to small particles that can be part of the soluble phase, so-called '*colloids*'. The role of colloids will be discussed in OPERA Task 6.1.4 (*Mobility and presence of colloidal particles*). Particles can also move on a surface ('surface diffusion'), which is addressed in Task 6.1.3.
[2] A system with only two reactive compounds.
[3] The distribution of an element over various chemical forms.

- The *affinity* of a species *to a specific surface* can differ strongly, ranging from almost no adsorption in case of anions (e.g. I, Se) to strong interactions where more than 99.5% of the element is bound (e.g. Cs, Pu) [8].
- Natural systems consist of a variety of *reactive surfaces* that can have very different affinities for binding of various elements. Boom Clay is a complex mixture of kaolinite, illite, smectite and silica with pyrite, magnetite, organic matter and some calcium carbonate [14, 15, 16]. The basic characteristics of the various reactive surfaces differ considerably, resulting in a wide range of affinities of a species for different kinds of surfaces.
- The composition of the Boom Clay is *spatially variable*, in horizontal and vertical direction, as result of heterogeneity and/or spatial variability, and both in terms of the solid matrix as well as of the pore solution [8, 15, 16, 17]. Due to the early stage of the Dutch disposal programme, currently no location or region for the disposal facility has been selected. This means that the assessment to be performed in OPERA should address the resulting variability of host rock properties and its pore water composition.
- *Competition* of radionuclides with other ions is very relevant for understanding adsorption processes in natural systems. Ion adsorption processes are in most cases 'ion exchange' processes, i.e. the binding of a radionuclide to a surface results in the release of another ion into solution. Since the composition of the pore water has a strong influence on the adsorption behaviour, it is necessary to understand the sorption behaviour of other ions like e.g. Ca^{2+}, Fe^{2+} and Fe^{3+}, since their soluble concentrations can vary strongly with varying *pH*, redox potential and ionic strength [13].
- Argillaceous materials as Boom Clay have complex *electrostatic properties* that affect adsorption and strongly interact with the water in its pores [18]. The properties depend on the type of clay and its charge density, the lithostatic and hydrostatic pressure, and the salinity [19]. Any translation of *in-situ* experiments performed in the HADES URL in Mol (at 225 m) to the generic Dutch reference concept in Boom Clay with different geochemical compositions and at larger depth (500 m) needs to consider these properties and interactions.

In the last decades, sophisticated thermodynamics-based adsorption models have been developed that describe multi-component interactions of mixtures of compounds in a solution with (poly)crystalline or heterogeneous surfaces, e.g. for organic matter [20, 21, 22, 23], iron(hydr)oxides [24, 25, 26], manganese(hydr)oxides [27, 28, 29] and clay [30, 31]. These models can describe the interactions for a wide range of conditions, i.e. how adsorption is affected by pH, redox potential, or salinity, by explicitly taking into account the electrostatic properties of the surfaces (e.g. [32, 33, 34, 35, 20]). Model approaches exist that describe adsorption to poorly defined or heterogeneous materials, e.g. organic matter [22, 36, 37, 38]. Such models not only help to increase the fundamental understanding of complex systems but also have been successfully applied to natural systems for a wide range of pollutants (e.g. [39, 40, 41]).

Many studies have been performed to understand and quantify radionuclide adsorption in the context of radioactive waste disposal in geological formations (e.g. [42, 43, 44, 45, 46]). The necessity to understand geochemical interactions and behaviour of radionuclides on detailed level is internationally recognized (e.g. [47, 48, 49]). Boom Clay has been studied in Belgium for several decades (e.g. [8, 50, 51, 52, 53]). Studies on radionuclide adsorption in other types of argillaceous host rocks, e.g. Opalinus Clay, have been performed as well (e.g. [54, 55]).

In this section, a number of key processes with respect to the understanding of adsorption processes, and their modelling and experimental evaluation are shortly reviewed.

2.2.1. Speciation

The term *'speciation'* describes the distribution of an element over different chemical bindings or forms. E.g. uranium can – dependent on the chemical conditions - be present as mineral phase UO_2, as charged soluble ion UO_2^{2+}, as uncharged soluble $UO_2(OH)_2$, or, most likely, as a mixture of these (and other) species. The speciation determines which part is 'mobile' (i.e. present in solution) and which part is immobile (i.e. part of the solid matrix). Speciation also affects the charge and size of a mobile species and thus the diffusion and adsorption behaviour. Precipitations as mineral phases (e.g. UO_2) are mainly immobile, but under certain circumstances, small amounts may be present in the soluble phase as well (so-called '*colloids*', see below). It is thus important to know the speciation of a radionuclide in order to be able to understand its migration behaviour (e.g. the double charged UO_2^{2+} has a different migration behaviour then the uncharged $UO_2(OH)_2^{0}{}_{(aq)}$).

The speciation of a mixture is controlled by thermodynamic equilibrium reactions, although reaction kinetics may play an important role for some components (in particular precipitation/dissolution reactions). The speciation of a component is influenced by the pH, the redox potential and the presence of ligands. If the speciation is dominated by a single species, often simplifying assumptions can be made that make risk assessment more straightforward. However, the speciation of a number of actinides can be quite complex, (e.g. Pu and U) also due to the presence of different redox states, and in a natural system, i.e. with the presence of strong ligands as PO_4^{-3} and CO_3^{-2}, speciation might be difficult to predict. Generally, the number of potential interactions in natural systems is high, and one needs to consider carefully which elements or ligands have to be accounted for to provide a realistic model for the radionuclides of interest.

An important mathematical tool to evaluate the speciation is '*chemical equilibrium modelling*' or '*geochemical modelling*' [56, 12, 57], that assumes that all (selected) species are in thermodynamic equilibrium. The equilibrium assumption can then be used to compute which speciation distribution of a system has the lowest energy amount, i.e. can be assumed as 'thermodynamically' most stable. Several software packages are available to perform these calculations (e.g. [57, 58, 59, 60]). These codes use thermodynamic databases covering information on the Gibbs free energy or interactions of thousands of species (e.g. [56, 58, 61]). The quality of the database is important, which however is everything but trivial due to the size of the databases and the long period over which the experimental data behind the database is collected [62, 63]. The NEA *Thermochemical Database project* (TDB) [32] represents a relevant effort to provide a consistent database that covers the radionuclides of interest for assessing radioactive waste disposals. Currently, within the TDB project data on U, Am, Tc, Np, Pu, Ni, Se, Zr, Th, Sn, and Fe has been reviewed and published [64].

The principal assumption behind chemical equilibrium modelling - that all species are in equilibrium within the considered time intervals - is not necessarily true for all species or reactions. So-called 'labile elements' can show very slow reaction kinetics. In case of mass-transfer processes, equilibrium might only be reached after some time, and speciation calculations should use a different approach [65]. In case of mineral precipitation it is known that often first the most soluble form precipitates, while it could take some time until thermodynamic more stable mineral forms appear ('*Ostwald phase rule*' [12, 66, 67]). Precipitation of minerals is a complex process depending on many factors (e.g. [68]), and in natural systems one can expect that precipitations will rarely be

'pure' minerals consisting of two or three elements, but will often be a mixture of several elements, which is much more difficult to model (e.g. [69, 70, 71, 72, 73, 74, 75, 76]). This can limit the applicability of chemical equilibrium modelling, and raises some interest in other techniques as well underlines the need to support (or validate) the models by experiments under realistic conditions.

To be able to model speciation in a natural system, a deep insight on process level is essential, but even then model 'predictions' should be envisaged with care: in an *expert judgement* exercise as part of the *PAMINA* project [77], experts were asked to calculate the solubility of Ra, Sn, Se, U and Pu for a disposal situation. Despite the use of comparable databases and programmes, varying results were found, and for the 90%-confidence intervals, ranges from three up to seven (!) orders of magnitude were given. It is important to handle some momentum of subjectivity in the application of chemical equilibrium modelling by careful documentation of the used assumptions, the applied databases and the reactions considered.

Despite all discussed limitations, if used purposeful in the right context, chemical equilibrium modelling can be a valuable tool in analysing and understanding quantitative system performance, and to get insight which components of a natural system are relevant to understand its behaviour. The modelling allows to define problems more closely, and to identify knowledge gaps [78, 79, 40, 41].

2.2.2. Redox chemistry

The term '*redox chemistry*' describes the altering speciation of elements under variable oxygen concentrations. When investigating adsorption, understanding of the redox chemical behaviour of a disposal system is relevant because it can result in drastic changes of the solubility and speciation of the radionuclides of interest. These changes are not only the direct result of redox chemical reactions, but also due to altered *pH* values[4].

Usually, the amount of oxygen decreases with decreasing depth. However, the excavation of an underground disposal facility will lead to oxidation of the host rock due to the contact with ambient air during operation. Already a minor trace of oxygen that enters the host rock in case of building a disposal facility (or experiments performed in a URL) can influence the speciation and migration behaviour relevantly, complicating the performance and interpretation of experiments with host rock material in a laboratory environment as well as experiments performed *in-situ* in an URL. Also cores collected in deep boreholes may alter their redox state during sampling.

Essentially, redox processes can be investigated with the same tools as discussed in the previous section, although special care is needed because microbiological processes can play a dominant role in creating or maintaining a certain redox state, resulting in a thermodynamic non-equilibrium [80]. The redox behaviour of radionuclides and their influence on migration are investigated in more detail in the EU-FP7 project *RECOSY* [81] and OPERA Task 6.1.1. Of particular relevance is the extensive research on the complex reduction/oxidation behaviour of the otherwise poorly adsorbing [79]Se performed in Belgium [82, 83, 84, 85].

In this report, redox processes are not investigated in further detail[5], because for the undisturbed, 'bulk' Boom Clay that contribute to the safety function "delay of transport",

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[4] In buffered systems, the sum of *pe* + *pH* can be assumed to be rather constant
[5] For more information on redox processes see OPERA Task 6.1.1.

redox conditions are assumed to be constant, while the rather small 'disturbed' zone of oxidized Boom Clay in the near-field is of lower relevance for the long-term safety, i.e. can be addressed by assuming conservatively no sorption at all in the performance assessment calculations. Nevertheless, some understanding of redox processes is essential to analyse and interpret experimental results.

2.2.3. Colloids

'Colloids' are small particles (<0.5 µm[6] [66, 86]). For much smaller particles, in recent literature also terms as '*nanoparticle*' and '*nanocluster*' can be found [87, 88]. For colloids composed of pure phases (e.g. ThO_2), the term '*Eigencolloid*' or '*intrinsic colloid*' is established. Due to the small size, larger fractions of colloids can be present in solution, contributing to mass transport by diffusion (and advection, if applicable). E.g. in experiments 90% of Th in solution is found to be colloidal ThO_2 [89]. The rapid migration of Pu as found on the Nevada Test Site is explained by colloid formation [90, 91], providing evidence for the relevance of colloids for migration of radionuclides in natural systems. Next to the colloids of Pu [92, 93], colloid formation of U [94], Th [92], Tc [95], Cm [92] and Eu [96] is investigated.

Of particular interest for this study are colloids that have strong adsorption capabilities, e.g. amorphous iron(hydr)oxide or dissolved organic carbon (DOC). These colloids can affect the migration behaviour of radionuclides: while adsorption in general leads to immobilisation, adsorption to (mobile) colloids might increase the mobility of radionuclides, denoted in literature as '*facilitated transport*' (e.g. [97, 98, 99, 100, 101, 102]). The role of colloids is investigated in further detail in Task 6.1.4, but within the context of this report it is important to note that quantification of colloids in complex reactive solutions like Boom Clay pore water can be rather challenging [66, 103, 104, 105], and the solubility of colloids can be difficult to predict [106, 107]. Both aspects are of relevance in the experimental evaluation of adsorption behaviour, where the presence of colloids needs to be considered when interpreting results.

2.2.4. Adsorption reactions

In adsorption literature, usually two types of sorption processes are distinguished:
- sorption in the electrostatic double layer of a particle, often expressed as "ion exchange"
- specific interaction with surface groups of the sorbent, often expressed as "surface complexation"

Ion exchange
Around a charged surface or particle, the chemical composition (and speciation) is different from the remaining 'bulk' solution, because of the tendency of a solution to maintain electro-neutrality. This can result in perceptible gradients of species between a (charged) surface and the bulk solution, often expressed as 'electrostatic double layer' or 'diffuse double layer' (DDL). Due to this effect, mainly positively charged ions accumulate in the double layer. The generally low affinity of ions depends mainly on their charge/size ratio. Several macroscopic models exist to describe this behaviour (e.g. [20, 24]).

Understanding of the electrostatic properties of the host rock is relevant for two reasons:
1. The increased concentrations of ions in the DDL can relevantly contribute to the adsorption properties of an argillaceous host rock, with the extent and composition

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[6] In other sources, slightly other definitions are used (e.g. <1 µm, <0.45µm)

of the DDL (and thus the adsorption behaviour) depending on the ionic strength of the pore water.
2. Because adsorption to the surface of a charged particle can modify the surface charge distribution, it influences the extent and composition of the DDL.

Surface complexation
Next to the mainly charge-driven sorption, often correlated to the ratio charge/diameter of an ion, more specific ion adsorption may occur, resulting in high affinities of certain species for a surface, mainly based on the spatial configurations and charge distributions of the surface and the (hydrated) ion of interest. This specific sorption process occurs on all relevant surfaces, e.g. organic matter [20, 21, 22, 23], clay [30, 31], iron (hydr)oxides [24, 25, 34, 35], and manganese hydroxides [27, 28, 29]. The edge faces of phyllosilicate clay minerals have been identified to be of particular importance in the understanding of the electrostatic and chemical behaviour of clay [108, 109, 110].

An important group of adsorption models that covers electrostatic and complexation processes is denoted as '*Surface Complexation Models*' (SCM), where adsorption is seen as a specific interaction between a soluble ion and a reactive group on the surface of sorbent [111, 112, 113]. SCMs use a limited number of surface groups and thus allow to model competition with other ions. The properties of the DDL are variable, they reflect the composition of the soluble phase and the occupation of the surface sites. Several SCMs have been developed for a variety of surfaces and purposes (e.g. [114, 115, 116, 117, 118, 119]), and in some case several SCMs have been developed for the same surface (e.g. [112]). The challenge here is to develop a model that is thermodynamically consistent, can explain adsorption experiments reported in literature and is in accordance with mineralogical, crystallographic and spectroscopic observations (e.g. [163, 120, 121, 122]). More recently, modelling techniques have been developed to study these interactions and their effect on the migration behaviour on molecular scale ("molecular dynamics", e.g. [123, 124, 125, 126], see also [127]).

2.2.5. Other processes of interest

Two processes discussed in literature on radionuclide adsorption are related to a transition of *adsorption* to *mineral formation*: The concepts of '*surface precipitation*' and '*solid solutions*'.

The concept of '*surface precipitation*' describes a transition from adsorption to precipitation reaction on a surface, in order to explain experimentally perceived adsorption behaviour at high loads, where the adsorption capacity of a surface is exceeded. Models are proposed to describe this process [128] by making a distinction between adsorption (a surface complexation reaction between surface sites and metal sorbates) and surface precipitation (formation of a multilayer solid phase on the oxide surface).

The process of *surface precipitation* can be distinguished from co-precipitation or the formation of a '*solid solution*', which can influence the aqueous concentrations of radionuclides. The *solid solutions* concept addresses the presence of mixed compounds, where one compound is 'diluted' in the other. This results in lower solubility, with possible release or exchange of ions, which has some resemblance with adsorption processes. Also for that concept, mathematical models have been proposed, which make a link between sorption and the matrix formation, considering one end member as the solute and the other as the solvent. These processes can act simultaneously and distinguishing them is difficult and requires analytical methods with molecular-scale resolution [129].

2.3. Synthesis

This report aims to define an approach to address radionuclide adsorption in Boom Clay. 'Ads*orption*' or in short '*sorption*' includes all processes that affect the solid/solution distribution of an element due to interaction with reactive surfaces (or "sorbents") in Boom Clay, by electrostatic and/or chemical bonding. The definition does not include mineral precipitation/dissolution. Adsorption to colloids will be covered here only in a general way but will be addressed in more detail in OPERA Task 6.1.4.

As discussed above, the amount of literature on adsorption processes and their modelling is extensive, resulting in many useful but often diverging approaches. It can be concluded that for a sensible application of adsorption models a thorough understanding of speciation, redox processes, the complex mixture of surfaces present in Boom Clay, and its electrostatic properties is needed. Furthermore, for the evaluation of experimental evidence and its extrapolation for the purpose of safety assessments, the role of colloids needs to be understood.

In the next chapter, the most important modelling approaches will be discussed with respect to their applicability for the purpose of the OPERA safety assessments.

3. Modelling of adsorption processes in natural media

In this chapter, an evaluation is made of the type of models that can be used to calculate adsorption of radionuclides to Boom Clay for the purpose of the safety assessments performed for the OPERA Safety Case. In particular the question must be answered which model approach is the most sensible approach, given the present process understanding on the one hand, and the available experimental evidence in support of the Boom Clay properties as expected in the Netherlands on the other.

SCK·CEN has already collected substantial information on the adsorption behaviour of radionuclides in Boom Clay, performed many migration experiments (e.g. [130]), and has developed models with various degrees of complexity and mechanistic understanding that describes their data (Section 3.3). However, geophysical, mineralogical and geochemical properties of Boom Clay may vary between locations, not only between Belgium and the Netherland, but also between different locations or regions inside these countries (e.g. [131, 132, 133, 134, 135, 136, 137, 15, 16], see also Section 4.2.2). To be able to 'translate' results on Boom Clay provided by SCK·CEN or other parties to the (generic) Dutch situation, it must be understood how the factors as summarized in Section 2.1 affect the adsorption behaviour.

To be able to give an overview on the expected ranges of solid-solution partitioning for Boom Clay compositions expected in the Netherlands, a robust, credible chemical speciation model has to be set-up and sensitivity analyses have to be performed. Thus, a suitable general modelling approach has to be defined, and proper model descriptions for adsorption processes have to be selected. In support of this undertaking (see Chapter 4), in the remainder of this chapter a review of relevant adsorption modelling approaches is given, and its applicability for the OPERA Safety Case is considered. In the next section, mechanistic modelling approaches are discussed, that allows to understand and quantify adsorption on process scale. In Section 3.2, more 'applied' approaches used in PA are shortly reviewed, and in Section 3.3, the Belgian approach used by SCK·CEN is summarized. In the final section of this chapter, a short synthesis is given.

3.1. Mechanistic adsorption modelling approaches

As shortly touched in the previous chapter, there are numerous adsorption models that can be used to model the adsorption of radionuclides to reactive surfaces present in Boom Clay. Generally, approaches differ from very simple representations of adsorption phenomena that can be deployed by hand calculation, to extremely complex models that require numerical computation.

There is a difference in *descriptive modelling* (modelling observed phenomena) and *predictive modelling* (modelling outside the range of observations). For successful descriptive modelling of available data, any mathematical formula can in principle be used, and often simple statistical analyses lead to more precise descriptions than (non-fitted) geochemical models [41]. However, the first method does not allow extrapolation beyond the range of conditions under which the observations were made. This would in principle not pose a problem, as long as the available data represent the system under consideration, and when conditions are known and invariant. Usually, however, the available data consists mainly of laboratory experiments and form only a snapshot of the complexity in practice. Even data obtained from simple laboratory experiments can show certain features that require the modeller to develop the model according to a certain theory on how the adsorption process works. Examples could be non-linearity of adsorption, a finite sorption capacity, or competition of major elements

and radionuclides for adsorption sites. The observed complexity is the main reason to develop more complex models capable of describing/predicting these features. Models that are developed based on well characterized, fundamental processes usually perform better outside the range of conditions at which they were derived/calibrated [138] and allow to "translate" experimental results on adsorption behaviour to other environments with higher confidence. This is essential when assessing the safety of a disposal facility at an (yet) unknown location, as is the case for the OPERA generic reference concept in Boom Clay.

3.1.1. Thermodynamic Sorption Models (TSM)

In [13], the NEA provides a comprehensive guideline to address sorption in safety assessment, covering the modelling of experimental data. The expression '*Thermodynamic Sorption Models*' is introduced to denote models that integrate the main processes discussed in the previous chapter: chemical speciation, electrostatic properties of the surfaces and specific sorption. Several types of models for crystalline surfaces are distinguished, and a decision tree for model selection is provided (Figure 3-1). A list of generic recommendations, and recommendations on model development and application is discussed ([13], Table 5.1 and 5.3). Furthermore, recommendations are given to fill gaps in sorption databases when no experimental data exist for a radionuclide interaction with a specific surface, using e.g. the 'zero point of charge' [139] or so-called "linear free energy" relationships [114, 115, 140].

The long-term predictive value of TSM strongly depends on the way the model is parameterized, i.e. with respect to the applied thermodynamic parameters, estimates of sorbent-specific properties and related input parameters, such as the amount of reactive surfaces to which an element may adsorb. A preferred approach would therefore be to aim for consistency between the hypothesized processes, the chosen adsorption model to simulate those processes, necessary model input parameters, and the experimental methods to determine those parameters. Examples of how such an approach can be successfully used to predict the adsorption of metal and oxyanions to natural sorbents (in this case, natural and contaminated soils and sediments, waste materials and concrete construction products) are provided in [39, 40, 41, 141, 142, 143, 144].

When adsorption to a reactive surface is suspected to be an important process, mechanistic TSM can be selected, with a preference for models for which "generic" parameter sets have already been derived. "Generic" sets of parameters imply that both for major and trace elements, adsorption parameters have been derived in a consistent manner. Such a consistent set of parameters can be applied to natural systems in which major and trace elements are all subject to adsorption processes and mutually influence each other.

Although such generic parameter sets may not provide the best description of measurements for a particular system (see e.g. [40]), these parameter sets are internally consistent and are therefore of a more general validity. In addition, when the purpose is to model complex (natural) systems, there is a need for parameter sets that cover a broad range of major and trace elements in order to account for multi-component interactions. Examples of such interactions are competition between elements for the (limited) sorption "sites" on reactive surfaces, as well as the formation of precipitates and soluble complexes.
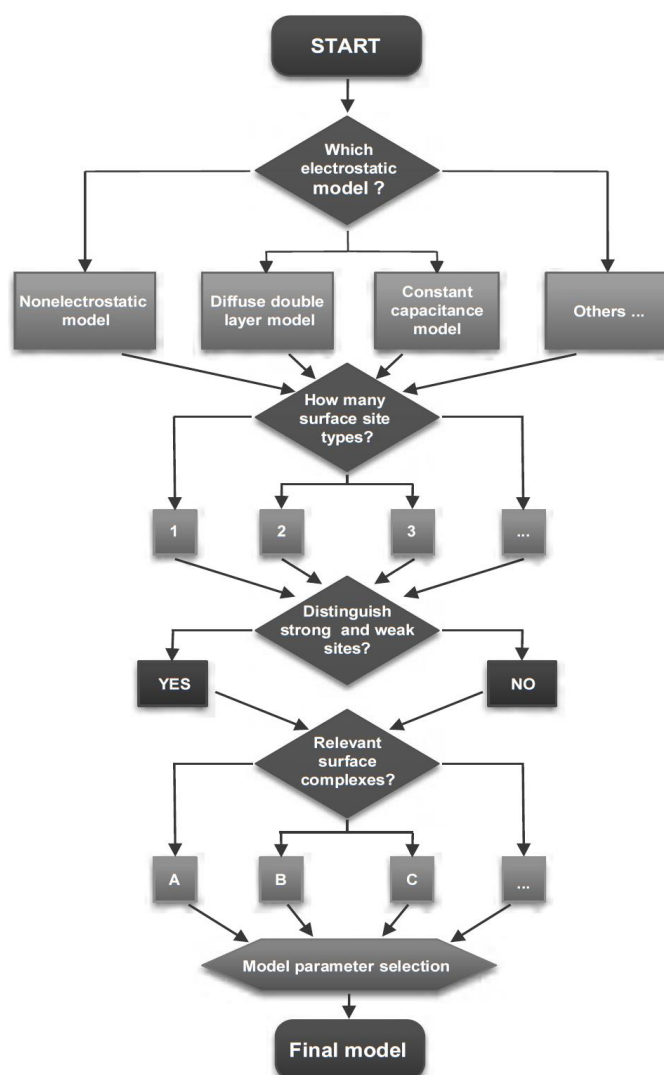
Figure 3-1: Generalised decision tree for TSM modelling choices ([13], Figure 2.6)

In order to achieve a general validity of the modelling approach, the selected models and associated parameter sets need to be applied without modification, and only published thermodynamic and binding parameters are used (i.e. without parameter fitting to individual sorbents or laboratory experiments). In this respect, it is important to note that not for all potentially important adsorption processes, mechanistic TSM and associated generic parameter sets are available. In those cases, it should be attempted to derive the necessary adsorption characteristics from those of similar reactive surfaces, for which this type of information is available.

Whenever adsorption models are taken into account for such reactive surfaces, information is needed concerning the amount of these surfaces present in the sample under study. To maintain consistency between the models and parameter sets, this information is collected using independent, carefully selected experimental procedures that aim to estimate the concentrations of the specific type of reactive surface of interest. Important reactive surfaces that have been used in this way to predict metal and (oxy)anion adsorption in soils include amorphous and crystalline iron- (e.g. [24, 25, 26, 33, 34, 35, 145]), and manganese (hydr)oxides (e.g.[27, 28, 29]), clays (e.g. [30, 31, 109, 110, 122, 125, 178, 179, 181, 182, 183, 189, 197]), and reactive fractions of dissolved and particulate organic matter (humic and fulvic acids, e.g. [20, 21, 22, 23, 32, 36, 37, 38, 190]).

3.1.2. Multi-surface approach

As discussed in the previous section, a range of mechanistic sorption models is available that describe interactions of relevant surfaces and which are parameterized in advance, often by evaluation of well-defined experiments in laboratory. The availability of such models and their underlying databases allows to take a step forwards in assessing the sorption behaviour of a complex, natural material: by combining chemical equilibrium calculation with a set of sorption models that addresses the interactions between surfaces and ions of interest, the overall distribution of elements can be calculated. Sorption to the overall systems is then described by the sum of interaction to the different types of surfaces ('multi-surface approach'). Examples of such an approach can be found in [39, 40, 41, 146, 144].

A practical advantage of the application of the "generic" multi-surface approach is that the solid-solution partitioning estimates can be obtained for individual soils for a variety of conditions, without much additional work such as laboratory titrations or parameter fitting, as required for e.g. the general composite approach by Davis et al. [167]. Although the latter approach may result in better model predictions in individual cases, a disadvantage is that the fitted model cannot be transferred to other soil compositions [144]. However, reactive surfaces can interact with each other (e.g. [147, 148, 149]), leading to a possible overestimation of the overall sorption. Although principal approaches exist to address this phenomenon (e.g. [149]), suitable model descriptions that allow building a mechanistic model representation of these interactions (i.e. without fitting), and experimental evidence from complex, natural systems are currently lacking.

3.2. Application of adsorption modelling in Performance Assessment

In performance assessment (PA), often simplified models are used, often with an eye for computational efficiency. One of the most applied approaches in the 'K_d-approach' that can also be integrated in analytical approaches for advective and/or diffusive mass transport (e.g. [127]).

3.2.1. Linear adsorption ('K_d-approach')

The most straightforward way to describe the effect of adsorption is to provide a measure on the distribution of an element over the solid phase and the dissolved phase, the so-called (solid-solution) distribution coefficient (K_d). The K_d is defined as the amount of element X sorbed per unit mass of substrate divided by the dissolved amount of element X [150]:

$$K_d = [S–X] / [X] \hspace{4cm} \text{Eq. 3-1}$$

where S represents the solid surface, and X the adsorbing element, $[X]$ is the total dissolved aqueous concentration (e.g. in mg/L) and $[S–X]$ the adsorbed concentration (e.g. in mg/kg). The resulting K_d is expressed in L/kg and represents the solid-solution distribution of element X at equilibrium conditions.

This approach is used very frequently to address adsorption and retardation processes of elements in porous media [8, 9, 10, 11, 12, 13]. In many PA calculations for radioactive waste disposals, the K_d is the concept in which all processes regarding adsorption and retardation are represented [13]. One advantage of the K_d-concept is that it can easily be integrated in numerical transport models but also in analytical transport equations (such as

the advection-dispersion equation (ADE); [12]). For instance, the K_d-approach is integrated with multi-dimensional hydrological transport models such as MODFLOW [151, 152].

Criticism on the K_d-approach is that it represents adsorption as a process in a too simple way (e.g. [13]). Strong arguments against the K_d-approach and in favour of more detailed mechanistic approaches are that K_d appears to be conditional, i.e. dependent on the conditions at which the K_d-value is derived. The K_d-approach is not a process model, e.g. sorption is rarely linear, and the amount of an element that can be adsorbed to the solid phase is limited (i.e. a limited availability of sorption "sites"). Hence, as discussed in Section 2.2, adsorption is sensitive to competition with other sorbing ions and varies with important chemical parameters such as *pH*, redox status and ionic strength (see e.g. [13] and references therein). As such, K_d-values selected for PA calculations are one of the most critical parameters, implying that confidence in the outcomes of the PA significantly depends on the confidence in the applied K_d-values. Using K_d in complex model calculations has significant advantages due to its simplicity and transparency, but from a mechanistic point of view, a well-motivated *range* of K_d-values should be used rather than a single "best estimate" K_d.

One step more complex than a linear distribution coefficient (K_d) is the Langmuir adsorption model, which is defined by addition of a limiting (maximum) sorption capacity s_m [150]:

$$[S-X] = s_m K_L [X] / (1 + K_L [X])$$
<div align="right">Eq. 3-2</div>

The sorption capacity can be determined experimentally via an adsorption isotherm. A main advantage of having a limited sorption capacity in the Langmuir model is that competitive sorption can be taken into account by extending Eq. 3-2 by a respective term (e.g. [20]).

Another often used simple approach is the Freundlich adsorption model (e.g., [150]):

$$[S-X] = K_F [X]^n$$
<div align="right">Eq. 3-3</div>

The Freundlich adsorption model is characterized by non-linear adsorption (i.e. an exponential variant of Eq. 3-1) and an unlimited sorption capacity. However, in practice the presence of a limited adsorption capacity is of minor relevance for the modelling of radionuclide adsorption as long as competition in general is taken into account sufficiently. This model is able to capture non-linear adsorption behaviour often observed for inorganic (metal) ions sorbing to natural surfaces, and addresses also heterogeneity in the affinity of surface sites [20, 153].

Both approaches are still strongly *conditional*, i.e. dependent on geochemical conditions at which the adsorption constants are determined, and therefore adsorption constants cannot be transferred from one to another sorbing medium. However, many combinations and cross-over forms exist that range from empirical to advanced (semi-) mechanistic (e.g. Langmuir-Freundlich, competitive Freundlich adsorption, *pH*-dependent Freundlich equations).

As adsorption of elements has been shown to vary strongly as a function of geochemical parameters, another frequently used approach is that of the "transfer functions" that relate the adsorption constant to a number of soil properties such as *pH*, organic matter content and other properties that correlate with observed adsorption through regression analysis [13]. To account for non-linearity at larger concentration intervals, also Freundlich type partition-relations have been derived. These Freundlich-based transfer functions,

once fitted to a data set, appear to be robust predictors for cation adsorption in soil and can be used for independent estimates, but due to its empirical nature its applicability remains within the environmental conditions of the data used for their derivation [13].

None of the above discussed (semi-) empirical adsorption models are directly related to the known thermodynamic speciation of elements. It can be argued that the model approaches that are based on fundamental thermodynamic processes have more general validity, i.e. should have validity to different environments without the necessity for experimental determination of adsorption parameters. The more mechanistically oriented TSMs generally account for chemical and physical parameters that influence the adsorption processes of interest, such as *pH*, specific properties of the minerals or mineral assemblages. Even though information on the variation of these parameters is often not available, a well-formulated and well-parameterized TSM can be much more realistic in terms of its representation of chemical processes than the simpler K_d-approach [151, 13]. The next section describes how TSMs can be used in order to provide conditional K_d-values that may satisfy the need of the OPERA PA.

3.2.2. Linking the K_d-approach with Thermodynamic Sorption Models

While the K_d-approach can be principally used for PA as long as the host rock properties stay sufficiently constant in time, a lack of justification of the K_d-values used in PA was marked as key problem [154, p.21]. NEA [13] summarizes the role of more complex, mechanistic TSMs in relation to the often used K_d-approach in performance assessment, namely mainly to identify, characterize and eventually parameterize the basic phenomena that are usually described by a K_d-value or range of K_d-values.

The analysis of measured adsorption data using TSMs ties K_d-values into functional and quantitative relationships between the adsorption behaviour of an element and relevant environmental parameters (such as *pH*, concentrations of the various components, binding site densities). In this way, TSMs may provide scientific support for the understanding of measured adsorption data, which in turn increases confidence in the applicability of K_d-values derived from such measurements. In the context of performance assessments that use a K_d-approach, the potential use of adsorption models can be summarized as follows [13]:

- Application to support specific K_d estimates in the frame of PA calculations, through:
  - direct estimation of distribution coefficients to provide approximations for parameter spaces that are difficult or time consuming to access experimentally (for example, to supplement limited site-specific data);
  - indirect support of experimentally measured K_d-values through explanation and justification of measured data, increasing confidence for K_d-values measured under complex site-specific conditions;
  - sensitivity and uncertainty analyses regarding the influence of variability and uncertainties in geochemical conditions on K_d;
  - interpolation or extrapolation from existing datasets to other conditions;
  - scoping calculations to estimate the possible effects of various scenarios on K_d-values.
- Guidance of experimental K_d acquisition programmes, for example through:
  - the selection of parameter spaces to be covered using sensitivity analyses;

- the optimisation of experimental design through screening calculations (for example, identifying the most critical conditions for experimental measurements);
- the interpretation and consistent combination of sets of laboratory data;
- the interpretation of adsorption data obtained from site-specific samples, using TSMs calibrated on the basis of laboratory data;
- the detection of gaps in the database for experimental study;
- the filling of data gaps with estimates based on TSMs, possibly complemented by the application of thermodynamic relationships and chemical reasoning.

- Building confidence with regard to the quantification of radionuclide adsorption under various conditions within the larger framework of safety case building.

The above applications of TSMs are based on the importance of K_d-values for safety analyses on the one hand, and in the highly conditional nature of K_d-values on the other. However, uncertainty and possible variability of relevant geochemical parameters, as well as the complexity of natural and engineered systems, may make it impossible to experimentally determine radionuclide adsorption behaviour systematically for every compartment and all sets of conditions. Therefore, experiments with site-specific conditions may be supplemented by an often much larger set of data for approximated, simplified, or generic systems. Because TSMs provide a consistent and quantitative framework for linking (geo)chemistry with adsorption, they represent an ideal tool for integrating all available types of adsorption information.

3.3. Overview of the adsorption modelling approach of SCK·CEN

In Belgium, since 1974 major studies have been conducted to assess the long-term safety of disposal of high-level waste and spent fuel in a clay formation. The Boom Clay is studied as a potential host formation for a disposal facility.

Clay sedimentary formations have to provide both a physical (limited or negligible water flow) and a chemical (retention) barrier for radionuclide transport. One of the key questions for a repository's safety assessment therefore concerns the predominant radionuclide-transport mechanism.

In order to describe diffusion-driven transport for solutes, performance assessment calculations in Belgium are based on the following parameters: *solute concentration* (C_{sol}, mol/l), *retardation factor* (R, dimensionless), *pore diffusion coefficient* (D_{pore}, m^2/s) and *diffusion accessible porosity* (η, dimensionless). Values for these parameters as well as a sound understanding of the underlying processes need to be provided for all radionuclides that are considered for the safety assessment. The collection of extensive data for all those radionuclides is however not an easy task, since the diffusion behaviour of radionuclides in porous media is a complex process affected by many parameters, such as the properties of the diffusing species, the properties of the medium itself (pore structure, degree of compaction, adsorption properties, dry density), the geochemistry of the system (pore water chemistry) and the temperature.

3.3.1. Strategy – Sorting the radionuclides in phenomenological groups

Ideally, a thermodynamic database should be constructed containing all intrinsic thermodynamic quantities related to the geochemical processes that occur. In reality, however, this is hard to achieve. Moreover, the objective when providing radionuclide transport parameters for PA is it necessary not only to deliver hard, quantitative data, but also to build confidence in these data. Confidence building relies upon the drafting of

scientifically defensible phenomenological models for each radionuclide under consideration. These models would describe all major processes and mechanisms which control the transport of each radionuclide under the far field conditions of interest for geological disposal in the Boom Clay. There are several reasons that can be cited why such a rigorous approach is unfeasible for all radionuclides at the present time:

1. The current scientific insight into the roles and importance of different phases (minerals, solid organic matter, humic colloids) and their interrelationships is limited.
2. Thermodynamic (sorption/interaction) models are available only for sufficiently pure solids and simple solid-fluid systems.
3. The setting up of an experimental programme for all radionuclides present in the waste would require a very time-consuming and costly research and development effort.
4. Uncertainties with respect to several processes limit the interpretation of data and not all processes are sufficiently understood (e.g. eigencolloid formation, functional group composition of humic substances etc.).
5. Thermodynamics alone is unsuitable for describing kinetic processes such as colloidal behaviour.

Because of these issues it was decided on a strategic approach that allows to deduce the aforementioned migration parameters from all available information and data sources (thermodynamic data, experiments on the Boom Clay, literature data) in a consistent way.

In brief, this strategic approach consists of:

1. subdividing all radionuclides considered into radionuclide groups exhibiting chemically analogous characteristics;
2. drafting phenomenological models that fit all radionuclides in a particular group;
3. assigning consistent parameter ranges for all radionuclides that belong to a particular group.

The cornerstone of this methodology involves the drafting of so-called "phenomenological models". Phenomenological models are geochemically consistent models that are able to describe, both in a qualitative and quantitative way, how radionuclides migrate under the specific far-field conditions of a disposal site.

These models are based on the combined insights gained from:

- experimental observations of the geochemical behaviour of the considered radionuclides; and
- general scientific insights/knowledge concerning their general chemical/thermodynamic characteristics.

Phenomenological models are also general enough to allow the variety of radionuclides to be considered by the PA, to be divided into groups. A group encompasses all radionuclides that have sufficient similarities with respect to the processes to which they are subjected during transport. Therefore, groups are selected based on similarities in speciation, sorption and migration behaviour. These characteristics are crucial to understand and predict retention/migration of all radionuclides within the group.

For each group, a phenomenological model is built, in which the shared characteristics play a dominant role. This model fulfils multiple purposes:

1. It allows to draw parallels between the retention/migration behaviours of all radionuclides within a specific group;

2. It is used to select parameter values that are then delivered as input to the safety assessment.
3. It is used to assess changes in these parameter values that are caused by physico-chemical perturbations or by the spatial heterogeneity of the Boom Clay formation.

By grouping radionuclides, SCK·CEN aims at providing scientifically justifiable retention/migration parameters for all individual radionuclides, even if not all data are available to be able to determine them specifically.

The grouping of chemical elements and the choices of distinctions between groups is based on various kinds of arguments:
1. thermodynamic considerations – similarities in inorganic speciation in Boom Clay pore water, calculated using the *MOLDATA* database [155];
2. experimental observations – similarities in sorption, solubility in the presence of organics, migration behaviour under conditions relevant for the Boom Clay; and
3. scientific literature – general similarities in environmental conditions (not limited to the Boom Clay).

As the next step, at least one "representative radionuclide" is selected for each group. Selection of that radionuclide is based on the amount of experimental and literature data available to support understanding, description and prediction of its retention/migration behaviour under Boom Clay conditions. For each representative radionuclide, a "Topical Report" (TR) is provided in which all these data are presented, and parameter values are delivered as input to the safety assessment, together with justifications for their selection. The main processes and mechanisms to which the radionuclide is subjected under Boom Clay conditions are highlighted. The main geochemical parameters that influence the behaviour of the radionuclide are discussed, preferably in a quantitative way. Possible uncertainties or knowledge gaps are pinpointed and their influence is assessed. As such, these TR's describe the scientific basis for the final parameter selection.

3.3.2. Choices and overview of groups and reference elements
The use of group-specific phenomenological models has several advantages:
- They aim at providing a thorough scientific basis (both qualitatively and quantitatively) for the migration parameter data sets that are delivered to PA. Additionally, they provide a realistic framework that enables assessment of parameter uncertainties and deviations of data ranges related to perturbations, spatial variability, etc.
- They make it possible to select realistic parameter ranges for radionuclides for which no or only limited batch and/or migration data are available. They allow different radionuclides to be compared to each other within the same conceptual framework: this will make different parameter value choices for different radionuclides more clear. Chemical consistency is maintained throughout parameter selection.
- They also allow pinpointing more precisely where more data is needed and for which an experimental programme should be set up as part of future scientific research studies.

The disadvantages are:
- Placing the radionuclides in a correct group/assign a correct phenomenological model to each nuclide is not always straightforward. For some nuclides no data are available and the choice relies on expert judgement.

- Phenomenological models must be sufficiently elaborate and scientifically sound to enable the selection of realistic migration parameter values. Model uncertainty is propagated to all radionuclides selected for that particular group.

For each phenomenological model at least one detailed TR has been prepared to explain in detail all the data and knowledge that culminates in the model. Up to now, the reference elements are tritium (as HTO) [156], iodine (I) [157], caesium (Cs) [158], strontium (Sr) [159], technetium (Tc) [160], americium (Am)/europium (Eu) [161], and uranium (U) [162]. Apart from these, a substantial report is also available on selenium (Se) [163], carbon (as HCO_3^-) [164] and the mobility of Dissolved Organic Matter (DOM), an important carrier for radionuclide migration [165]. It is argued that these elements sufficiently cover all the possible phenomena that potentially influence every safety-relevant radionuclide under the geochemical conditions of the Boom Clay.

The groups (and respective phenomenological models) that are considered as well as the assignment of the radionuclides to the various groups is outlined below (see also Table 3-1):

- The first group comprises the reference conservative tracer HTO. HTO is very frequently used both in lab-scale migration experiments and in meter-scale in situ experiments, to obtain reference transport parameters for the Boom Clay.

- A second group is made up by the anions, containing mostly non-metal elements from groups IVA to VIIA in Mendeleev's table (with the exception of Mo). The reference element for this group is iodine (as iodide, I^-). Se is also part of this group, both as the oxyanion selenate (SeO_4^{2-}) and as the biselenide anion (HSe^-). Other elements belonging to this group are carbon (C, as bicarbonate, HCO_3^-), molybdenum (as molybdate, MoO_4^{2-}) and chlorine (as chloride, Cl^-). The anion group is characterised by limited or no sorption/retardation and due to the anion-exclusion phenomenon, the diffusion accessible porosity is reduced compared to HTO.

- The third group consists of alkali and alkaline earth metals that are not hydrolysed under Boom Clay conditions (thus, excluding Be). These metals are predominantly adsorbed through ion exchange and their transport is influenced by surface diffusion processes. Two different subgroups are distinguished. The first subgroup contains monovalent cations with small hydrolysed radius that are preferably bound to illite ion exchange sites. These cations also do not have a solubility limit. The second subgroup contains divalent cations that may form aqueous complexes with CO_3^{2-} and that are solubility-limited due to the formation of carbonate phases. They preferably bind to the interlayer ion exchange sites of smectite minerals.

- The fourth and largest group consists of elements that exhibit transport behaviour determined mostly by their affinity for DOM colloids naturally present in the pore water of the Boom Clay. This affinity in practice means that a large part of the nuclide speciation in the Boom Clay pore water consists of humic-associated species (either as true complexes or as colloidal associations). Since these species are generally less well sorbed/retained, they will travel faster than their dissolved/inorganic counterparts. This large group is again subdivided. DOM itself is considered as a reference tracer and it is assumed that humic colloid-associated species have the same transport properties as DOM. Furthermore, the heavy metals, the trivalent lanthanides/actinides and the tetravalent lanthanides/actinides are distinguished (the latter group also contains the pentavalent Pa). The differences between these subgroups are not very significant, and other subdivisions are equally possible (e.g. a subgroup combining both the tetravalent lanthanides and actinides as well as the tetravalent heavy metals). The main difference between the trivalent lanthanides and actinides and the others is the importance of carbonate complexes

in their inorganic speciation. The main difference between tetravalent lanthanides and actinides and the others is their well-documented eigencolloid behaviour (although several heavy metals such as Tc, Zr, Sn may also form eigencolloids).

Table 3-1: Assignment of the radionuclides to different groups based on the considered phenomenological model describing their behaviour in Boom Clay

Group	Subgroup	Element	Eq. Species
Reference tracer		**HTO**	HTO
Anions		**I**	I^-
		Cl	Cl^-
		Se	HSe^-, SeO_4^{2-}
		Nb	$Nb(OH)_6^-$
		Mo	MoO_4^{2-}
		C	HCO_3^-
Alkali & Alkaline Earth Metals	Monovalent cations	**Cs**	Cs^+
		Rb	Rb^+
	Divalent cations	**Sr**	$Sr^{2+}/SrCO_3(aq)$
		Ca	$Ca^{2+}/CaCO_3(aq)$
		Ra	$Ra^{2+}/RaCO_3(aq)$
DOM associated Cations	Reference tracer	-	DOM
	Transition metals	**Tc**	$TcO(OH)_2(aq)$
		Ag	$AgHS(aq)$
		Be	BeO_2^{2-}
		Ni	$Ni(CO_3)_2^{2-}$
		Pd	$Pd(OH)_2(aq)$
		Zr	$Zr(OH)_4(aq)$
		Sn	$Sn(OH)_5^-$
	Trivalent Lanthanides & Actinides	**Am**	$Am(CO_3)_2^-$
		Ac	$Ac(CO_3)_2^-$
		Cm	$Cm(CO_3)_2^-$
		Sm	$Sm(CO_3)_2^-$
		Pu	$Pu(CO_3)_2^-$
	Tetravalent & pentavalent Lanthanides & Actinides	**U**	$U(OH)_4(aq)$
		Th	$Th(OH)_3(CO_3)^-$
		Np	$Np(OH)_4(aq)$
		Pa	$Pa(OH)_5(aq)$

3.3.3. Description of sorption behaviour in Boom Clay

The sorption of radionuclides by immobile phases in the Boom Clay is one of the most important processes influencing transport. As the Boom Clay is a complex mixture of several sorptive phases including clay minerals (illite, smectite, interstratified illite-smectite, chlorite, etc.), quartz, sulphides (pyrite) and carbonates (calcite, siderite), a fully comprehensive description of metal uptake on this geological substrate proves to be a scientifically extremely challenging, if not impossible, task. Therefore, SCK·CEN has opted to take on a more pragmatic approach that consists of formulating simplifying assumptions/hypotheses regarding the dominant adsorption processes and adsorptive phases for each element. This "simplification" in fact takes the form of a "component additivity" approach [166, 167, 168, 169], in which the sorption on the total substrate is explained by a straightforward addition of the contributions of all sorptive pure phases. This approach is currently preferred over a "generalised composite" view [167] in which a generic surface complexation model applies to the whole Boom Clay. SCK·CEN has chosen this additive approach because of the possibility to use well-acknowledged (quasi-) thermodynamic sorption models which have been developed for pure phases only [170].

Ideally, these models explain (and provide confidence in) experimentally measured solid-liquid distribution coefficients (K_d) obtained on the whole Boom Clay.

The most important phases considered to influence uptake of radionuclides are illitic and smectitic clays, as well as organic matter (both DOM and the solid organic matter fraction). The clay minerals (three-layer silicates) are characterised by permanent surface charges due to isomorphic substitutions. Due to this charge, the binding of cations is assumed to be caused by stoichiometric ion exchange of interlayer ions. These concepts hold well for alkaline and alkaline-earth cations; their adsorption and their ionic strength dependence can be characterised by distribution coefficients derived from ion exchange theory. On the other hand, the binding of transition metals and of lanthanides/actinides on clays cannot be fully accounted for by an ion exchange mechanism. Surface complex formation to the OH functional groups of the outer surface (the so-called "broken edges") has to be invoked as an additional process.

Presently, SCK·CEN does not take account of sorption on the solid organic matter fraction. This approach is taken partly because of the lack of a sufficiently adequate thermodynamic sorption model to simulate metal-organic complexation to that phase. Another reason is that more abundant clay minerals in the Boom Clay fabric tend to out-compete sorption to the solid organic matter fraction. A similar component additivity approach to explain the sorption behaviour of elements on the whole rock based mostly on the contributions of the clay mineral assembly, has also been invoked in the case of Opalinus Clay [171, 172, 173] and, for a more selected group of elements, also in the case of the Callovo-Oxfordian argillites [174].

Ion exchange on clay minerals
The ion exchange capacity of the Boom Clay stems mainly from the smectite, with a calculated/extrapolated value of 88 meq/100 g smectite at pH 8.3 [175]. Ion exchange on smectite occurs in the interlayer and on basal planes.

Next to the swelling clay minerals, also the non-swelling three-layer silicates, such as illite, contribute to ion-exchange but they usually cannot exchange their interlayer ions. In these clays, the outside surfaces and the weathered crystal edges ("frayed edges") participate in ion exchange reactions [176]. These sites have a high affinity towards monovalent cations with low hydration energies, such as Cs^+, K^+, Rb^+ and NH_4^+. Except at high concentrations H^+ and Na^+ are considerably less competitive and bivalent cations such as Mg^{2+}, Ca^{2+} and Sr^{2+} are generally non-competitive for steric reasons.

Double-layer theory predicts qualitatively that the affinity of the exchanger for bivalent ions is larger than that for monovalent ions and that this selectivity for ions of higher valence decreases with increasing ionic strength of the solution [176]. With the help of selectivity coefficients, a general order of affinity can be given. For most clays the *Hofmeister series* is observed: that is, the affinity increases with the (non-hydrated) radius of the ions [176]. In other words, the ion with the larger hydrated radius tends to be displaced by the ion of smaller hydrated radius:

$$Cs^+ > K^+ > Na^+ > Li^+$$
$$Ba^{2+} > Sr^{2+} > Ca^{2+} > Mg^{2+}$$
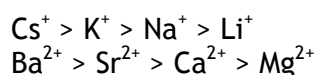
Radionuclide ion exchange with smectites is described by the generally accepted 2-site protolysis, non-electrostatic surface complexation/cation exchange (*2 SPNE SC/CE*) model, developed by Bradbury and Baeyens for montmorillonite and illite [177, 178, 179, 182, 183, 184].

The high specific affinity of Cs, K and Rb for illite ion exchange sites is well described by the general 3-site ion exchange model (3-IEX) developed by Bradbury and Baeyens [171, 180].

Surface complexation on clay minerals
At neutral to alkaline pH, adsorption of transition metals and lanthanides/actinides on clay minerals is dominated by surface complexation, with OH-containing surface sites (inorganic hydroxyl functional groups). Although several surface complexation models are available to describe pH-dependent metal uptake by clay minerals, SCK·CEN has opted to use the well-respected *2 SPNE SC/CE* model [177, 178, 179, 181, 182, 183, 184]. The model was successfully used to describe adsorption of Eu^{3+} [166], Am^{3+} [185], Th^{4+} (SCK·CEN, unpublished data) and Ni^{2+} (SCK·CEN, unpublished data) on Na-illite in synthetic Boom Clay water (without natural organic matter). For all these metals, sorption increases with increasing pH (from acid pH, where only ion exchange plays a role, to neutral pH, where surface complexation dominates) and with decreasing ionic strength. At very alkaline pH, sorption may decrease again, because of the formation of anionic hydrolysed aqueous species.

The application of the *2 SPNE SC/CE* model to describe sorption on clay (illite and montmorillonite) minerals in fact entails that the same basic sorption model parameters, i.e., amphoteric edge ($\equiv$SOH) site types, site capacities and protolysis constants, can be used to model sorption data of the transition metals and radionuclides (lanthanides/actinides) over an extensive range of pH, ionic strengths and metal concentrations. In fact, Bradbury and Baeyens [181] demonstrated that semi-empirical correlations exist between surface complexation constants on montmorillonite, derived via the *2 SPNE SC/CE* model, and related classes of reactions, i.e., linear free energy relationships, LFERs. Such LFERs are extremely useful since they allow surface complexation constants to be estimated for elements for which no data exist, enabling the prediction of their sorption properties [186, 187, 188].

Based on the LFERs, surface complexation constants on strong sites of montmorillonite [179] and Na-illite [183] are estimated in a consistent manner for a number of chemical elements such as Pd(II), Pb(II), Pu(III), Zr(IV), U(IV), Np(IV), Pu(IV) and Pa(V). This approach thus leads towards a thermodynamic sorption database (based on the *2 SPNE SC/CE* model) that can be used to calculate sorption in natural systems. This approach is applicable to all metal cations except for alkali and earth alkali metals, including transition metals, lanthanides and actinides. The wide applicability of the model makes it an extremely useful and reliable tool, capable of describing and predicting sorption under a wide range of geochemical conditions. It therefore allows not only simulation of sorption under (undisturbed) Boom Clay conditions, but also the predicting of changes in sorption affinity as a result of pH or ionic strength perturbations.

Under representative present-day conditions for the Boom Clay at Mol (pH ~ 8 and ionic strength ~ 0.01 M) typical solid-liquid distribution coefficients for the different elements are given in Table 3-2 for both illite and montmorillonite (assuming an inert background electrolyte, $NaClO_4$, and only hydrolysis reactions for cationic species). From Table 3-2 it appears that illite and montmorillonite have similar sorption (surface complexation) affinities for all metal valence states studied. The high logK_d-values also indicate that under these conditions, sorption by clay minerals is almost quantitative (i.e. clay mineral surface complexes will dominate the total speciation of the studied elements and, thus, clay minerals are an extremely important sink in natural media).

Table 3-2: Typical experimental ranges of solid-liquid distribution coefficients (as logK_d, l/kg) of metals, lanthanides and actinides with different valence state on conditioned Na-illite and Na-montmorillonite, at pH ~8 and ionic strength ~ 0.01 (NaClO$_4$ background electrolyte)

Element	logK_d illite	Ref	logK_d montmorillonite	Ref
Ni(II)	$4.0 - 4.5$	[182]	$4.0 - 4.5$	[177, 178]
Eu(III)	$5.5 - 6.0$	[182]	$5.5 - 6.0$	[189]
Sn(IV)	$5.0 - 6.0$	[182]	$5.5 - 6.0$	[181]
Th(IV)	$5.5 - 6.0$	[183]	$5.5 - 6.0$	[181]
U(VI)	$4.5 - 5.0$	[183]	$4.5 - 5.0$	[181]

Influence of organic matter on the uptake in Boom Clay suspensions
The previous section outlines how trace concentrations of multivalent radionuclides, with valence states from II to VI, are adsorbed in a similar way onto illite and montmorillonite clay minerals at slightly alkaline pH. This sorption occurs mainly by surface complexation on so-called strong sites present at the broken edges of the clays. Therefore, following the component additivity approach, it is expected that these elements are similarly retained on the solid Boom Clay phase. However, Boom Clay contains a considerable amount of DOM (humic and fulvic acids) which interact strongly with multivalent radionuclides. Hence this will influence the uptake behaviour in clay systems.

The effect of radionuclide-DOM interaction on the uptake behaviour in Boom Clay suspensions was however observed to be quite similar despite the different interaction mechanisms (complexation, colloid-colloid interaction). The overall picture is therefore one of competition for a metal between the solid Boom Clay phase and the DOM fraction.

The interaction of the radionuclide with DOM is taken up in SCK·CEN's component additivity approach. The applicability of this approach was tested thoroughly in the case of Eu^{3+} sorption in batch systems containing both pure Na-illite and Boom Clay DOM [166]. In this study, it was observed that Eu^{3+} uptake in the ternary system could be well described by a simple additivity rule combining the respective contributions to Eu^{3+} sorption by Na-illite (using the *2 SPNE SC/CE* model) and Eu^{3+} complexation by DOM (using the Humic Ion Binding Model VI, [190]). Also, the addition order of DOM did not play a role in the experimental K_d-values, indicating total reversibility of the complexation reaction.

SCK·CEN assumes that reversibility is always guaranteed, although slow kinetic processes might preclude species associated with selected phases (in casu, humic colloids) from being readily available for sorption on other phases and/or sinks. However, in the long term, equilibrium states reached from different starting positions should be the same.

Sorption of anionic species
The negatively charged surfaces present in the Boom Clay display mostly a high affinity only towards positively charged metal cations (and their hydrolysis products), repelling negatively charged species. However, sorption of anionic species cannot be completely ruled out. Slight retardation for some negative charged species (HCO$_3^-$ and SeO$_4^{2-}$, [164, 163]) has been observed in Boom Clay in transport experiments. The exact retention mechanisms of anionic species are unclear and less well-documented in scientific literature. No dedicated programme was put up to investigate sorption of anionic species so no conclusions can be drawn with respect to the underlying processes. Sorption parameters are therefore only based on observations and cannot be inferred from mechanistic modelling.

Conclusion with respect to sorption
Two major sorption groups can be discriminated based on their uptake behaviour in the Boom Clay.

Firstly, monovalent and divalent alkali and earth alkali metals (with the exception of Be) are mainly sorbed through cation exchange. For most of these metals, swelling clay minerals with accessible interlayers are the major sorption sink. Exceptions to this rule are K, Cs and Rb which are preferentially sorbed by illitic minerals, especially at very low concentrations. Sorption through ion exchange generally increases with increasing valence state and decreasing hydration radius. The influence of DOM and of surface complexation with hydroxyl-bearing surfaces on the sorption of these metals is negligible.

In contrast, transition metals and lanthanides/actinides with valence states between II and VI are mainly adsorbed through surface complexation reactions on both illite and montmorillonite-type minerals. Surface complexation constants increase with increasing hydrolysis stability constant and can be described using LFER. On the other hand, these elements are also prone to complexation by humic substance colloids. The combination of both sorption on clay minerals and complexation by DOM determines the solid-liquid distribution of these radionuclides in Boom Clay suspensions. Thus, humic colloids and solid phase sorptive surfaces compete with each other for aqueous metal species. Given that sorption at trace concentrations is generally linear and (assumed) reversible on the Boom Clay solid phase (K_d remains a constant), the solid-liquid distribution of trace metals in Boom Clay suspensions is mainly determined by the dissolved organic matter concentration.

3.3.4. Sorption parameters for Boom Clay at Mol

Based on the strategies outlined above, sorption parameter ranges are derived for the reference elements that apply for Boom Clay at Mol for current geochemical conditions. A short explanation will be given for the reference elements Cs(I), Sr(II), Am/Eu(III), Tc(IV), Th(IV) and NOM. This is then followed by an explanation on how this is used to derive sorption parameter ranges for the other elements that are within the groups of the respective reference elements.

Reference element Cs
Caesium K_d-values in Boom Clay suspensions may be sufficiently well predicted by assuming sorption only by the illite present. The amount of this mineral in a particular Boom Clay sample, together with the K^+ concentration in the pore water (the principle competing cation in pore water) essentially dictate the solid-liquid distribution in the Boom Clay suspension. Moreover, studies have found essentially no difference between K_d-values determined in diluted batch systems and on compacted samples [53, 158]. However, when transferring K_d-values to R-factors, some problems arise. These problems are predominantly due to the rather high D_{app}-value fitted from tracer profiles in migration experiments compared to the high R-factor when calculated from batch K_d data. If the relationship $D_{app} = D_{pore}/R$ is valid, and the values for D_{app} and R are correctly modelled/calculated, then the value for D_{pore} would exceed the diffusion coefficient in pure water. This paradox is observed by several research groups studying the migration of ion exchange cations in argillaceous media and is often referred to as "surface diffusion". The conceptual model which is currently being developed and which would explain these observations is called "double layer enhanced diffusion model" [191, 192]. This model subdivides the pore space in "free water", "double layer water" and "interlayer water". The free water is to be found in the region outside the influence of the double layer. The concentration of a species in these three types of water is different and governed by double layer phenomena. This implies that the overall transport is composed of transport

in the three different pore spaces each having a different concentration gradient. This has consequences for transport modelling as classical transport models only consider one concentration gradient. Within this concept however, the sorption model for ion exchange cations (and surface complexation) remains valid.

The double layer enhanced diffusion model is however not yet taken up in the PA models used by SCK·CEN. SCK·CEN therefore assumes that the R-factor ranges for Cs^+ can be inferred from K_d ranges based on the thermodynamic *3-IEX* sorption model. Using the classical relationship between K_d and R the range for R is set at the average value plus/minus two times the standard deviation of K_d (K_d ranges from 600 to 18600 l/kg): 2750 < R < 85000 (with porosity η = 0.37 and matrix density ρ = 1.7 kg/dm^3).

For a more detailed description see [158].

Reference element Sr
For Sr(II) the phenomenological model is about the same as for Cs(I), except: (1) Sr(II) is preferably adsorbed by smectite; and (2) additional solid phase sinks such as carbonate minerals are present in the Boom Clay. To simplify the calculations and the phenomenological model, this latter sink is conservatively neglected. The thermodynamic sorption model to describe Sr(II) ion exchange on smectite minerals is the *2 SPNE SC/CE* model. A good correlation between K_d-values in dispersed and compacted batch systems, and the thermodynamic sorption model was found. Because of its ion exchange uptake, double layer enhanced diffusion of Sr(II) in the electrical double layer would occur, making the transfer of sorption data from batch to migration R- and D_{app}-values difficult. Nevertheless, SCK·CEN assumes, similar to Cs(I), that all sorption sites are available under *in-situ* conditions and that the sorption model for ion exchange cations remains valid. Modelling of the influence of smectite content (hence CEC) from 10 to 30% resulted in K_d-values 180 to 570, which agreed well with the sorption experiments and the sorption parameters extracted from diffusion experiments. Indeed, for most migration experiments a good correlation between fitted R-values and calculated/measured K_d-values is obtained. The range that is eventually obtained, entails both sorption and migration data and amounts to: 800 < R < 3700 (180 < K_d < 800).

For a more detailed description see [159].

Reference elements Tc, Eu/Am, Th and DOM
In the case of the hydrolysing cations Am(III), Tc(IV) and Th(IV), sorption on the Boom Clay solid phase is assumed to be dominated by surface complexation reactions with the hydroxyl-bearing surfaces of clay minerals (both illite and smectite contribute to the overall sorption). The *2 SPNE SC/CE* model is suited to describe this behaviour. This model and its parameters were mostly derived in an (inert) $NaClO_4$ electrolyte. Recent findings suggest that additional (ternary) surface complexes need to be taken into account in electrolytes containing also HCO_3^-/CO_3^{2-} ions. In the cases of Am(III) and Eu(III) sorption on illite, the *2 SPNE SC/CE* model has also been validated for Synthetic Boom Clay Water (SBCW) (~0.014 mol/l $NaHCO_3$) background electrolyte. The average measured logK_d for trace Am concentration under these latter conditions is ~3.5. This value is lower than the solid-liquid distribution coefficient in $NaClO_4$ electrolyte (logK_d ~ 5-6 at pH 8-10 for both illite and (Na/Ca)-montmorillonite) mostly due to Am(III)-carbonate complexation. However, the value can be quantitatively compared to the range of logK_d-values measured in Boom Clay suspensions at very low dissolved humic substances concentration (or extrapolated to zero humic substances concentration as done in a Schubert approach) (3.5 < logK_d < 4.5). This latter range was also observed for Tc(IV) under the same experimental

conditions. Moreover, Th(IV) solid-liquid distribution coefficients in Boom Clay suspensions are quantitatively comparable to Am(III) K_d-values [193]. Cremers and Henrion [194] have found that K_d-values for Np, Tc, Pu, Am and Eu in Boom Clay suspensions at several solid-liquid ratios are equal within one order of magnitude. Moreover, SCK·CEN assumes that adsorption to the Boom Clay solid phase is reversible (as shown in the case of Tc(IV) and for Eu(III) in illite/Boom Clay humic substances mixtures, and almost linear at the trace concentrations representative for radionuclide transport. SCK·CEN also assumes that due to the high sorption capacity of sinks in the Boom Clay, no significant competition occurs between the nuclides. Therefore the relationship between K_d and R is valid, and the aforementioned K_d range ($3.5 < \log K_d < 4.5$) can be transformed into a range of R factors ($15'000 < R < 150'000$, for $\rho = 1.7$ kg/dm^3 and $\eta = 0.37$).

As mentioned in the phenomenological description for radionuclides that interact with NOM, two fractions need to be considered: the "inorganic fraction" and the "fraction linked to DOC". The behaviour of the latter fraction is linked to the sorption/migration behaviour of the DOM. The retardation factor for the larger size fraction of DOM, which is most relevant for long-term radionuclide transport, lies within the range 20-60. The smaller size fraction of DOM is less likely to interact with the Boom Clay solid phase and less prone to colloid filtration processes, and is therefore characterised by a range for R equal to 3 – 20.

For a more detailed description on Tc, Eu/Am, and DOM see [160, 161, 165].

Sorption parameters for other elements
In the cases of cations dominated by ion exchange uptake processes, SCK·CEN assumes that the available thermodynamic sorption models (*3-IEX* for ion exchange on illite and *2 SPNE SC/CE* for illite and montmorillonite) are applicable, similar to Cs(I) (*3-IEX* on illite) and Sr(II) (*2 SPNE SC/CE*). These models may therefore be used to delineate K_d-values which can be transformed into R factors following the classical K_d – R relationship. In the case of Rb(I), application of the *3-IEX* model to illite leads to a K_d-value of ~900 l/kg under Boom Clay conditions. This value is about 11 times lower than the value calculated for Cs ($K_d \sim$ 10500 l/kg). This ratio may thus be used to scale the R range for Rb, based on the R range for Cs given in the previous section. A similar reasoning is being employed for Ca(II) and Ra(II), which can be compared to Sr(II). Diffusion experiments with Ra resulted in a D_{app} value by a factor of 10 lower than the value of Sr and Ca. Considering that the difference in D_{app} is mainly due to the difference in the retardation factor, we can scale the R (and K_d) range of Sr for Ra ($1800 < K_d < 8000$). A higher sorption of Ra is also in line with the selectivity sequence.

For the hydrolysing cations, distinction is made between the tri- and tetravalent nuclides (lanthanides, actinides, metals, including Pa(V)) and the mono- and divalent transition metals). The tri- and tetravalent nuclides are all characterised by $\log K_d$-values on illite and montmorillonite clay minerals between $5 < \log K_d < 6$ in the 8-10 pH range (0.01 M NaClO$_4$ electrolyte). These values are comparable to Eu(III), Am(III) and Th(IV). It is also foreseen that in Boom Clay suspensions their solid-liquid distribution ratios are similar [194]. Therefore SCK·CEN may attribute the same R range as for Eu, Am, Tc and Th ($15'000 < R < 150'000$). On the other hand, mono- and divalent transition metals (Ag, Pd, Ni) are bound with less affinity to illite and montmorillonite ($3 < \log K_d < 5$ in the 8-10 pH range, 0.01 M NaClO$_4$ electrolyte). SCK·CEN assumes that simple scaling of the R range with respect to this $\log K_d$ range is a sufficient approximation to obtain a range for these nuclides ($150 < R < 15'000$).

3.3.5. Transferability

The bulk of information related to the transport (retention and migration) properties of radionuclides in the Boom Clay has been gathered by way of experiments and modelling under geochemical conditions which are relevant for the Boom Clay in the Mol area. However, the Boom Clay is not restricted to the Mol area and stretches west to east from East-Flanders to the Limburg province, and south to north from Flemish Brabant to the Netherlands. Given the relatively small area from which most of the data haven been gathered, relative to the vastness of the geological formation, an assessment is required regarding the possibility of using the data obtained on "Mol" samples for predicting/describing radionuclide transport at other locations within the Boom Clay (i.e., "Transferability" of data from Mol to other locations).

Many parameters influence the sorption of radionuclides. For the Boom Clay, the clay minerals are assumed to dominate the sorption (characteristics and magnitude) of (mostly cationic) radionuclides. The most important parameters accounting for sorption are then 1) the amount and type of clay minerals present; 2) the ionic strength of the pore water; 3) the pH of the pore water; 4) the presence of competing (aqueous) ligands. The sorption models that were selected to describe the sorption of radionuclides onto clay minerals are also presumed to remain valid under the geochemical conditions at other locations in the Belgian Campine area. These models are the *3-IEX* ion exchange model [171], which describes sorption of Cs and Rb on clay host rocks (dominated by ion exchange processes on illite), and the 2-site protolysis non-electrostatic surface complexation/ion exchange model (*2 SPNE SC/CE*), which describes sorption of a whole suite of metals and radionuclides to both illite and smectite clays [177, 178, 181, 182, 183].

In the following, the influence on sorption is described in more detail, discriminating between cation exchange and surface complexation processes.

Cation exchange processes
Cation exchange processes are mainly influenced by total cation exchange capacity (CEC) and amount of competing (major) cations.

The appraisal of cation exchange as a major retardation mechanism for cations is closely linked to the variations in mineralogy (clay mineral content, clay mineral type) and in pore water chemistry (amount of competing major cations). Both parameters show variability within the Belgian Campine area, indicating that cation exchange will also vary depending on the location.

Mainly the retention of alkaline and alkaline earth cations is driven by cation exchange processes. Other radionuclides (transition metals, lanthanides, actinides) are also participating in cation exchange mechanisms, but their solid phase uptake is mainly governed by surface complexation.

Influence of amount and type of clay minerals
The predominant clay mineral can shift from illite to smectite, and CEC increases with smectite content.

Both the grain size distribution and the mineralogy show variation within the Belgian Campine area. Generally speaking, the Boom Clay becomes a little sandier towards the west, while the clay mineral type predominance shifts from illite to smectite. Apart from this observation, the vertical variability over the stratigraphical column, which has already been evidenced in Mol, seems to be omnipresent in the Boom Clay. Thus, silty layers alternate with more clayey layers over the entire thickness, while also the different Members seem to stand out from each other (one being more silty, the other more clayey).

Although the Boom Clay is observed to become sandier towards the west, this is not reflected in a decrease of the cation exchange capacity (CEC). Indeed, measured values on (a few) selected samples from the Essen-1 core indicate that the CEC is situated in the same range as the values measured in Mol. Therefore, the total sorption capacity of the Boom Clay towards radionuclides is not assumed to vary considerably over the Belgian Campine area, although more data and measurements are needed to confirm this statement.

The shift from illite to smectite-dominated clay minerals would however indicate a decrease in sorption towards caesium and rubidium. Indeed, both radionuclides are known to exhibit a very high affinity towards illite (so-called frayed edge sites and type-II sites [180, 171] and SCK·CEN's phenomenological model uses a weight factor for the illite (& Montmorillonite) content in order to predict Cs and Rb solid-to-liquid ratio (Figure 3-2).
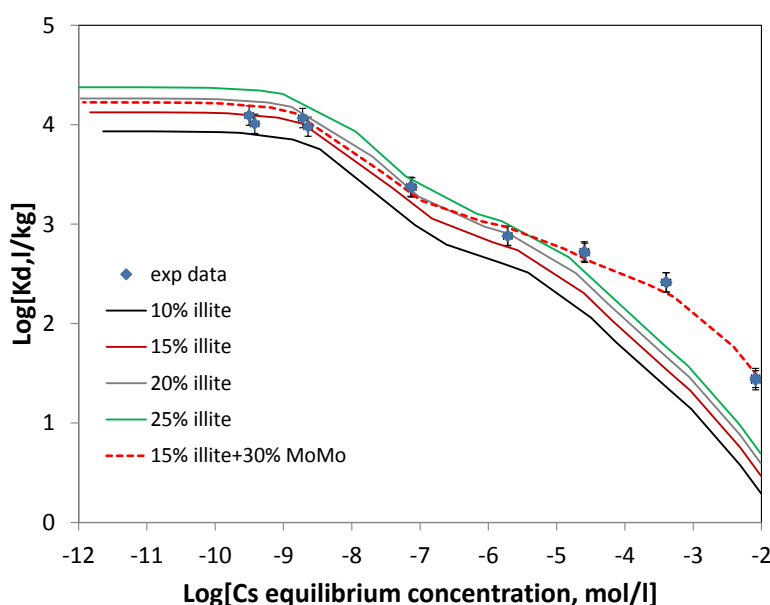

Figure 3-2: Modelled Cs sorption curves onto Boom Clay accounting for varying contents of illite (and Montmorillonite). Sorption model from Bradbury and Baeyens [171].

Influence of pore water composition

The amount of major cations in the pore water is a direct indication for the degree of competition for cation exchange sites. Since the salinity is increasing from the east towards the west (the pore water being dominated always by Na^+ as major cation), it is expected that competition for cation exchange sites will also increase. Therefore, the sorption of alkaline and alkaline earth cations will likely decrease (the CEC being approximately equal) compared to Mol conditions. The amount of decrease is dependent on the affinity (selectivity coefficient) for the radionuclide to the cation exchange sites and is most pronounced for radionuclides sorbing (mainly) on smectite clay minerals. Baeyens and Bradbury [195] measured a decrease of Ca sorption on montmorillonite by two orders of magnitude when increasing the ionic strength from 0.01 M $NaClO_4$ to 0.1 M $NaClO_4$ (Figure 3-3).

For radionuclides displaying a high affinity for illite, like caesium and rubidium, the competition is more dependent on the K^+ concentration than the Na^+ concentration. Poinssot *et al.* [180] determined Cs sorption at trace concentrations on conditioned Na-illite in 0.01 M $NaClO_4$ and 0.1 M $NaClO_4$ and found a decrease in logK_d of about 0.5-0.7 units at pH 8 with a 10-fold increase in ionic strength. Under the same conditions, but on a conditioned K-illite in 0.01 M, logK_d-values at pH 8 were about 3.5, which is more than 1.5 units lower compared to a Na-dominated electrolyte at the same ionic strength.
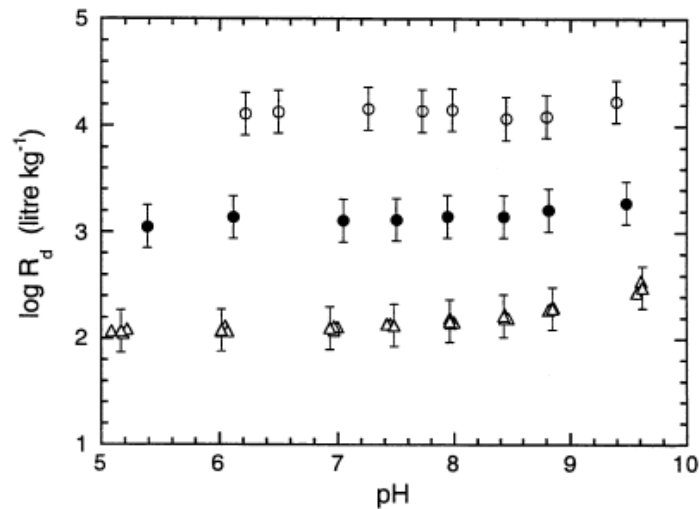
Figure 3-3: Ca sorption edge on conditioned Na-montmorillonite measured in 0.1 M (△), 0.03 M (●) and 0.01 M (○) NaClO$_4$ [195].

Maes et al. [158, 196] reported new Cs sorption data on Boom Clay using up-to-date knowledge on the pore water composition. When comparing the new data with the data of Baeyens [197] and further used by Bradbury and Baeyens [171] and De Preter et al. [198], the Cs sorption is systematically higher but this is due to the 5 times lower K concentration used compared to the study of Baeyens [197]. By roughly increasing the amount of Cs adsorbed and the K_d with a factor of 5 (consistent with a 5 times lower K concentration), the data from Baeyens [197] are more in line with the new determined data (Figure 3-4).
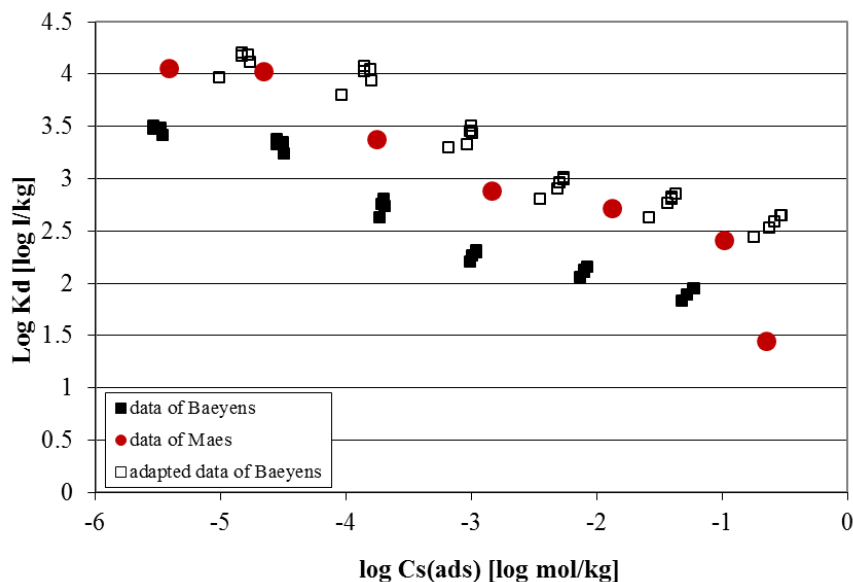
Figure 3-4: Comparison between the Cs sorption isotherm on Boom Clay determined by Baeyens [197] for pore water containing 5 times higher K concentration than the current used reference pore water resulting in the dataset of Maes et al. [159, 196]. The open squares are adapted data from Baeyens [197], the amount sorbed and K_d are multiplied by a factor of 5 to mimic the effect of a 5 times lower K concentration.

Scoping calculations, based on CEC and cation occupancy measurements on Boom Clay samples from various locations are needed to quantitatively assess the sorption of cations on ion exchange sites.

Surface complexation processes
Surface complexation processes are mainly influenced by total amount of clay minerals and presence of complexing ligands.

The retention of many radionuclides (belonging to the transition metal group, lanthanides and actinides) at neutral to alkaline pH is dominated by surface complexation mechanisms on the broken edge sites of clay minerals (illite and smectite) [177, 178, 189, 182, 183]. Surface complexation is mainly dependent on the amount and type of clay minerals present, the pH and the aqueous speciation of the radionuclides, and possibly the presence of competing cations.

Given the ubiquitous presence of illite/smectite clay minerals and pore water dominated by Na^+ with a pH in the neutral-to-alkaline range, the degree of surface complexation is not foreseen to vary considerably over the Belgian Campine area. The most influential factor for many radionuclides will likely be the amount of complexing ligands, aqueous carbonate species and the DOM.

Influence of amount and type of clay minerals
As discussed before, some general trends can be identified in the Belgian Campine area: from the east towards the west the Boom Clay tends to become sandier while the clay mineral predominance shifts from illite to smectite. With respect to surface complexation, illite and smectite behave more or less similar, both in amount of sorption (surface complexation) sites and in uptake behaviour towards radionuclides [177, 178, 189, 182, 183].

In the phenomenological models used, the amount of illite and/or smectite clay minerals in the mineral fabric is used as a weight factor to correct the solid-to-liquid distribution of a particular radionuclide. This rule can be maintained.

Influence of pore water composition
In the absence of DOM, less carbonate results in more sorption. A slightly more acidic pH or higher ionic strength has not much influence. In the presence of DOM, DOM dominates the speciation of many radionuclides: changing chemical conditions will have an influence on the concentration and size distribution of the DOM, but changes in sorption behaviour of radionuclides to DOM will probably be limited.

At the pH region of interest (neutral-to-alkaline pH), the sorption edges of most metals and radionuclides exhibits quite constant sorption. Therefore, the slight variation in pH that is expected for the pore waters over the whole Belgian Campine area is not assumed to influence the solid- liquid distribution a lot (see for example Figure 3-5). This is also the case for the increase in ionic strength: indeed, ionic strength mainly influences ion exchange processes (because of competition with major cations), but not surface complex formation. In fact, the sorption model adopted for surface complexation (*2 SPNE SC/CE*) is non-electrostatic in nature and therefore only the change in activity coefficient of the aqueous species as a result of ionic strength variation will influence the sorption equilibrium (Figure 3-5).
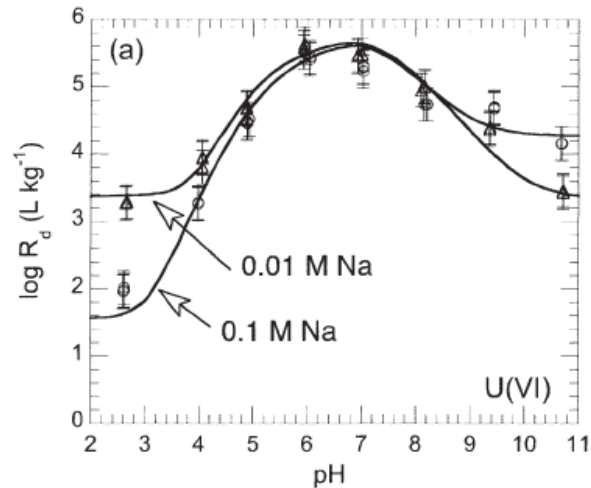
Figure 3-5: Sorption edges for U(VI) on Na-SWy-1. The continuous curves are best fits obtained using the *2 SPNE SC/CE* model [181].

Only in some selected cases, the combination of slightly more acidic pH combined with an increase in ionic strength might vary the sorption K_d considerably. An example is given below (Figure 3-6) for the sorption of Ni(II) on montmorillonite, where experimental log R_d-values decrease from above 4.0 to about 3.0 when changing the solution composition from 0.01 M NaClO$_4$ at pH 8 to 0.1 M NaClO$_4$ at pH 7 [181].
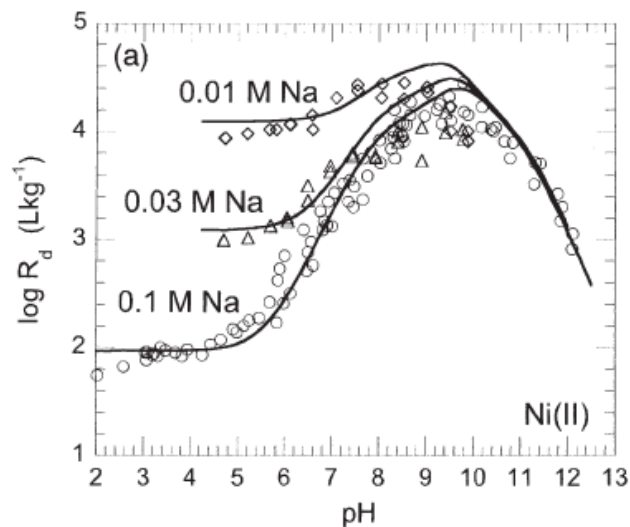
Figure 3-6: Sorption edges for Ni(II) on Na-SWy-1. The continuous curves are best fits obtained using the *2 SPNE SC/CE* model [181].

Another factor that might have an important influence on the sorption of some selected radionuclides, is the dissolved carbonate (or bicarbonate) concentration. Indeed, since carbonate is a strong ligand towards lanthanides and actinides [199, 200], the decrease in dissolved carbonate in other locations in the Belgian Campine area with respect to Mol conditions might increase the uptake of these radionuclides on clay minerals. This is visualised in Figure 3-7 and Figure 3-8 where experimental sorption data of Eu(III) and U(VI) on conditioned Na-montmorillonite under various regimes of pCO_2 are shown. The presence of dissolved carbonate clearly decreases the logK_d of both Eu and U by several units, depending on the solution composition and pH.
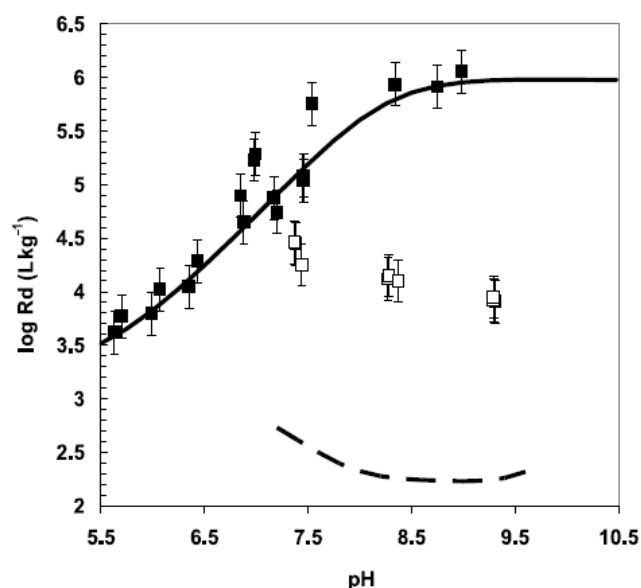
Figure 3-7: Eu sorption measurements onto Na-SWy-1. (■) sorption edge measurements in the absence of carbonate. (□) Eu sorption measurements at variable pCO_2. Black lines: modelled curves using the *2 SPNE SC/CE* model [201].
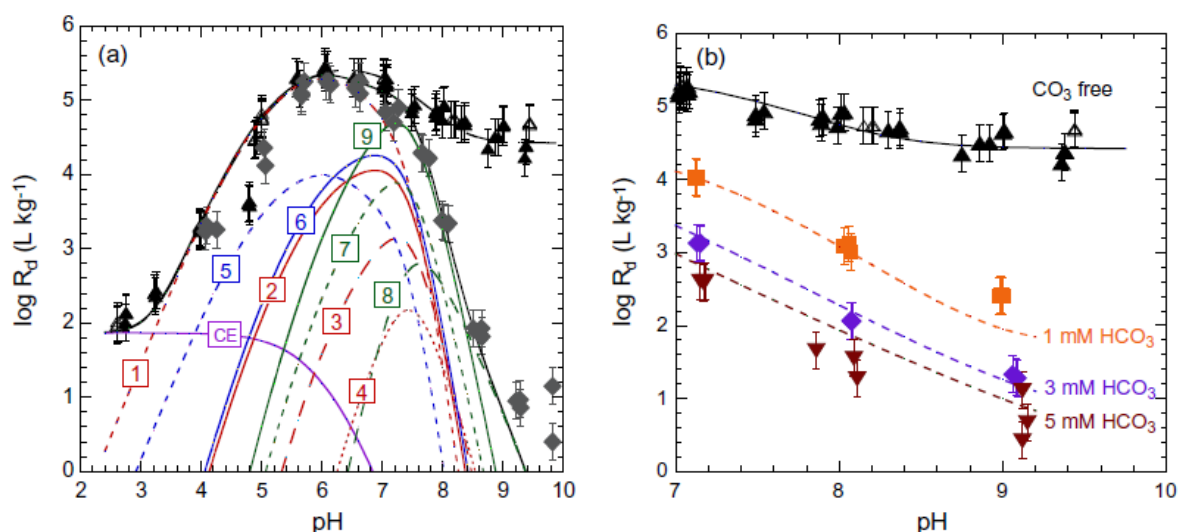
Figure 3-8: U(VI) sorption edge measurements on Na-SWy-1 in the absence of carbonate (▲,△) and (a) in equilibrium with atmospheric pCO_2 (grey diamonds); (b) in 1, 3 and 5 mM NaHCO₃. The modelled curves are obtained using the *2 SPNE SC/CE* model including ternary uranyl carbonate surface complexes [202].

The DOM present in the pore water controls the speciation of many radionuclides and is in competition mainly with carbonate species. The chemistry of the pore water (ionic strength/salinity) governs the concentration and the size of the DOC present in the pore water. At the current pCO_2 and pH however, even a few mg of DOM is sufficient to dominate the speciation of many radionuclides.

The overall picture is therefore one of competition for a metal between the solid Boom Clay phase and the DOM fraction. The *Humic Ion-Binding Model VI* [190], which was used to mimic trivalent radionuclide binding to dissolved organic matter in Mol conditions, is assumed to be adequate in assessing radionuclide binding to organic matter under other geochemical conditions. The changes in sorption of radionuclide-DOC species is considered limited. This aspect needs a more detailed study.

3.4. Synthesis

In this chapter, several principle approaches used to address radionuclide adsorption in radioactive waste management were reviewed, including a detailed description of the approach followed by the Belgian research programme. For the purpose of the OPERA PA, the use of conditional K_d-values is judged to be the most suitable approach. The conditional K_d-values need to be reported as ranges rather than single (best fit) values, in order to address the variable properties of Boom Clay present in the Netherlands (see Section 4.2.2). However, to translate existing experimental sorption data from the Belgian research programme to the variable Boom Clay properties of relevance for OPERA, detailed thermodynamic process modelling is necessary, both by modelling of basic processes and features summarized in Section 2.2 and by mechanistic sorption models as discussed in this chapter.

A specific approach for the purposes of OPERA will be described in the next chapter.

4. Towards a modelling approach for OPERA

In the previous chapters, we shortly summarized relevant processes behind radionuclide sorption, and discussed fundamental and more applied approached to address sorption. In [13, p.9], it is stated that

> "*Confidence in PA, and therefore in the predicted safety of a repository [...] will depend to a significant extent on the confidence in, and the justification of, the quantification of radionuclide sorption.*"

Five confidence-related needs were identified:

1. Awareness of the effects of modelling strategies and decision making during TSM development;
2. Transparent documentation by modellers regarding modelling decisions;
3. Identification of appropriate methods for determining the various TSM parameter values;
4. Development of a scientific foundation for applying TSMs to complex and intact materials (such as host rocks, engineered barriers and soils);
5. Justification of conceptual choices and quantification of uncertainty effects.

In line with these five needs, in this chapter a modelling approach is proposed, based on the specific boundary conditions and needs of the OPERA Safety Case, and the existing information that is available to support the approach. In the following section, important considerations behind the proposed modelling approach are discussed. In Section 4.2, the proposed approach is described. The last section of this chapter describes the experimental and scientific basis for the derivation of the applied parameter values.

4.1. General considerations

The purpose the RANMIG work package 6.1.2 is to provide a first full compilation of sorption data for all radionuclides to be assessed in OPERA. The objective of the modelling work performed is providing supported (ranges of) conditional K_d-values, applicable in the safety assessment calculations of the OPERA Safety Case [2].

Relevant experimental work in support of the modelling approach was out of the scope of this project, i.e. neither direct estimation of K_d-values or their indirect support was possible. While supportive experimental evidence for radionuclide sorption in Boom Clay is provided by the Belgian research programme, no relevant experiments on cores originating from the Netherlands have been performed that allow reflecting the large variations of Boom Clay properties expected for the Netherlands. Thus, analyses performed focus on sensitivity and uncertainty analyses regarding the influence of the expected variability on the adsorption behaviour of Boom Clay by a fully parameterized[7], mechanistic geochemical model.

The Boom Clay samples analysed as part of the OPERA programme [15] provide input on the expected horizontal and vertical variability of Boom Clay in the Netherlands and are discussed in Section 4.2.2.). The input is used to parameterize a detailed geochemical model representation of the Boom Clay in the Netherlands with explicitly addressing its spatial variability.

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[7] i.e., no fitting is involved

Experimentally derived sorption properties of Boom Clay samples from Belgium can be used as comprehensive calibration data set. This provides support for the geochemical model representation used to extrapolation the radionuclide sorption behaviour expected for the variety of Boom Clay properties in the Netherlands. The outcomes will be reported in the follow-up of this report *OPERA-PU-NRG6123* [6].

Because of the limited availability of experimental data in combination with the large set of radionuclides of interest [7], the extent in which quantitative evaluations can be performed within this project is limited. Focus was given to a selection of elements that are addressed in this project in more depths, while other elements are covered in a scoping, conservative manner only. The selection is mainly based on those radionuclides judged to be of relevance for the scenarios covered by the OPERA Safety Case [203], and availability of data, mainly provided by the Belgian research programme (see Section 3.3). Although some analyses on simplified systems have been performed before (e.g. [9, 10]), all selections had to be made *a priori* to the OPERA safety assessment[8].

The approach followed in the remainder of this chapter is based on several assumptions:

1. As highlighted in the previous section and in Section 3.1.1, it is relevant to provide a sound justification for the set of K_d-values that are used in the safety assessment. Such a justification should include a clear description on the used approach and its limitations.

2. Because OPERA assesses a generic disposal concept [1], no location is known and as consequence the exact local properties of the host rock are unknown. The variability of these properties and their effect on the conditional K_d-value needs to be addressed properly and a general understanding on how these properties affect adsorption is relevant.

3. A safety case is an iterative, stepwise process, with the OPERA Safety Case envisaged more as a starting point than the final answer [2, p.3]. Analyses of OPERA's PA outcomes [204] will allow identifying which radionuclides need further research or considerations.

4. The OPERA Safety Case focusses on the long-term safety [205, p.5], with the assessed scenarios defined in [203]. In later stages, additional scenarios might be assessed, which potentially leads to the need to evaluate the sorption properties of additional elements that are addressed here only conservatively (i.e. by assuming no sorption at all).

5. Previous assessments have learned that not all radionuclides relevantly contribute to the long-term safety (see e.g. [9, p.71*ff*]). Experimental evidence for the K_d-values proposed here might be needed in a later stage, but it is also expected that the number of radionuclides that relevantly contributes to the various kinds of risks is limited. Again, it is expected that the outcomes of OPERA will allow to identify which radionuclides need further research or considerations.

With respect to the last assumption, it can be demonstrated that for a number of radionuclides a K_d-value of zero (i.e. no adsorption at all) provides already sufficient evidence for safety, because the half-life of these radionuclides is either short, and/or the radiotoxicity inventory is small. By devoting no further efforts in evaluating the sorption behaviour of such radionuclides, more detailed evaluations can be performed regarding the nuclides that are expected to be of more relevance for the outcome of the safety

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[8] Later on in OPERA WP7, so-called "Safety and Performance indicators" as defined in [204] will be used to evaluate the soundness of the approach followed here.

assessments. For the selection of the relevant radionuclides the fourth assumption applies: i.e., it cannot be excluded that in later safety cases with different focus - e.g. on operational safety - other scenarios will be analysed and therefore sorption properties of additional, mainly short-lived radionuclides need to be elaborated. Likewise, as discussed in Section 2.2.3, the presence of mobile colloids might lead to the necessity to consider additional radionuclides. Task 6.1.4 will provide input to the impact of colloids on migration behaviour.

The approach that will be followed emphasises a proper justification and coverage of all radionuclides, based on mechanistic models that can be in principle verified by independent experiments at a later stage. It will form a suitable link between fundamental behaviour of radionuclides at surfaces of constituents of the Boom Clay on molecular level and the macroscopic sorption models discussed in the previous section (e.g. [108, 206]). It will also be of heuristic value, because analysing interactions of radionuclides with the complex matrix of Boom Clay on process level allows comparison with *in-situ* experiments in the HADES URL (the specific sorption modelling approaches of SCK·CEN were discussed in Section 3.3) and facilitates the set-up of future, additional experiments in support of the elaborated K_d-values.

4.2. Outline of the proposed approach

For the derivation of sorption parameters for the OPERA performance assessment, a two-phase approach is followed:

- In the first phase, a reference multi-surface sorption model representation is developed ('*OPERA reference model*') and compared with experimental results from the Belgian research programme. The model uses the geochemical framework ORCHESTRA [60] and is based on existing models and databases as discussed in Chapter 3. The model will be parameterized by geochemical data measured in Boom Clay samples from Mol and requires no parameter fits.

- In the second phase, the *reference model* is used to calculate recommended ranges of K_d-values for the OPERA safety assessment, representative for Dutch Boom Clay. K_d-values are derived by uncertainty calculations with the reference model, in order to investigate the influence of the varying geochemical conditions in the Netherlands on the sorption behaviour. Section 4.2.2 discusses parameter ranges on Boom Clay properties found in the Netherlands, and the resulting parameter distributions for the model calculations is summarized in Section 4.2.3.

Figure 4-1 gives an overview of two-phase approach to derive K_d-values for the OPERA safety assessment. Some general outlines and a discussion on the data used are given in the section below. A more detailed description of the model set-up and the calculation results will be documented in the follow-up report *OPERA-PU-NRG6123* [6].
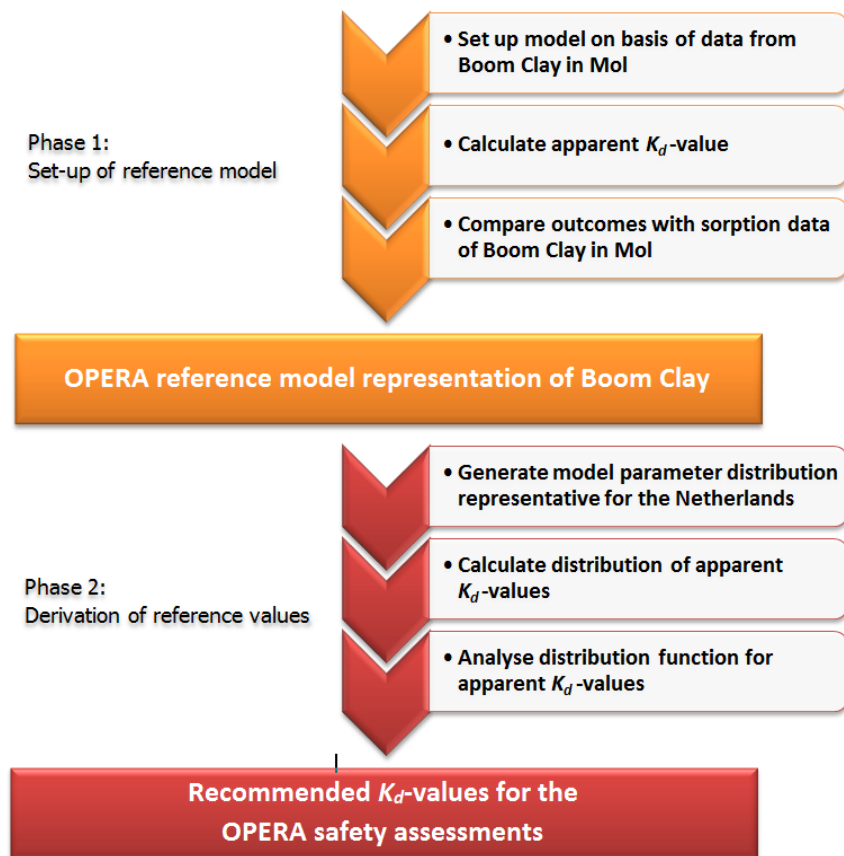
Figure 4-1: Two-phase approach to derive K_d-values for the OPERA safety assessment

4.2.1. Description of the overall mechanistic modelling approach

A mechanistic multi-surface model description for Boom Clay will be set up in the geochemical modelling framework *ORCHESTRA* [60], following a comparable approach as the generic sorption model for inorganic contaminants in Dutch soils described and evaluated by Dijkstra et al. [144]. The multi-surface model approach is based on the assumption that the overall sorption behaviour of the Boom Clay can be represented by addition of the interactions of all reactive surfaces with the radionuclide of interest ('*additivity assumption*'). Because the tendency of reactive surfaces to interact with each other, the additivity assumption is under discussion (e.g. [147, 148, 149]). However, suitable model descriptions and parameter sets that allow building a mechanistic model representation of these interactions are currently lacking.

The chosen mechanistic approach allows making independent predictions of speciation and sorption behaviour of radionuclides, i.e. without fitting, and is based on selected thermodynamic data. This allows studying the effects of different geochemical conditions on the sorption behaviour. In a next step (reported in [6]), by comparing the independent calculations with available experimental data on sorption from Belgian research programme, it will be possible to estimate the accuracy of the mechanistic model representation.
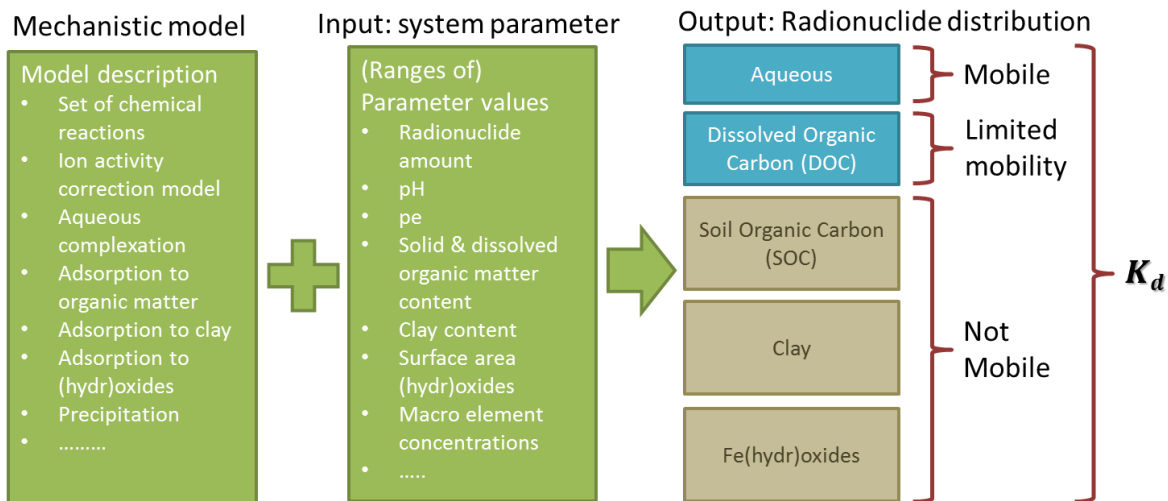
Figure: 4-2 Overview of application of model to estimate K_d-values

4.2.2. Compilation of Boom Clay properties in the Netherlands

Currently, no relevant experimental data on radionuclide sorption on Boom Clay samples from the Netherlands exist. Also no relevant data on pore water composition in Boom Clay from the Netherlands is available. However, in the remainder of this chapter, the existing geochemical data on Boom Clay - mainly provided by OPERA - is reviewed and analysed.

To start with, as part of OPERA samples of Boom Clay from depths between 21 and 739 m b.s.l. have been analysed and reported in [15]. The dataset is based on 152 samples from 17 cores from the Netherlands (Figure 4-3). These samples provide input to a) analyse the range of matrix compositions to be expected in the Netherlands and to b) compare these properties with Boom Clay samples from Belgium, in particular to samples that are used for sorption experiments or for which pore water data are available. Some caution is necessary in the processing of the data: due to the limited number of sample cores, the spatial distribution of the samples (Figure 4-3), and remaining uncertainties with respect to the classification of the samples as 'Boom Clay'[9] (see [207], Figures 2-2 to 2-4, and Figure 3-3), the statistical indicators provided below should not be overrated.

Overview of sample locations
Based on an analysis of grain size distribution (see next section), four regions are distinguished: north, middle, south and south-east. The grain size distribution as provided by [15], Table 14, is summarized in Figure 4-4.

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[9] or, stratigraphically correct, the Rupel Clay Member of the Rupel Formation according to the Dutch classification

Figure 4-3: Overview of sample locations (adapted from [15], Fig. 20)

Figure 4-4: Grain-size distribution of Boom Clay samples from The Netherlands as reported in [15] (Table 14)

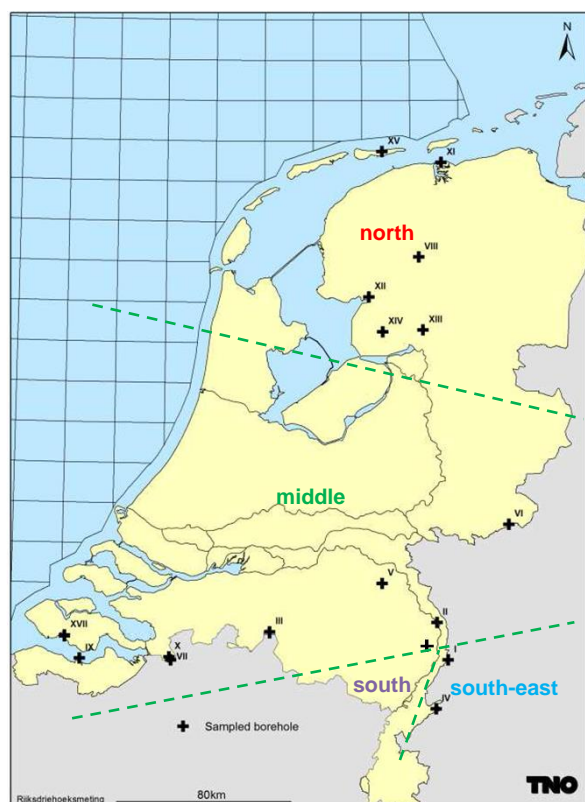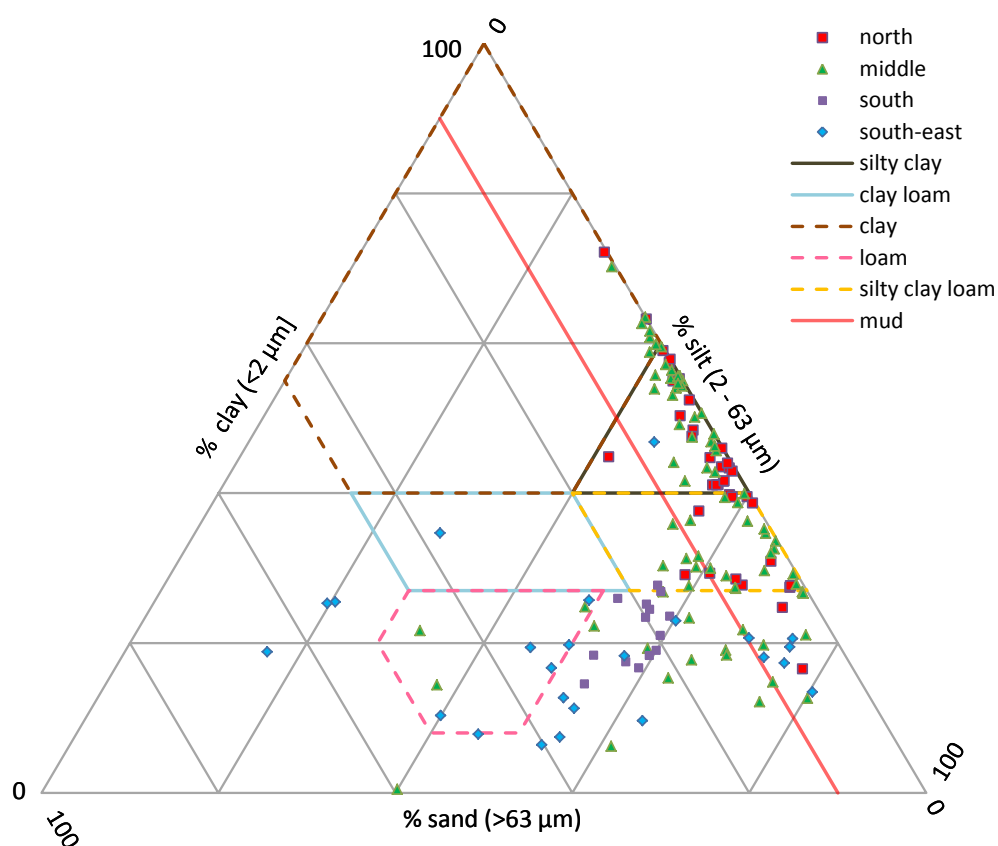In order to decide on how to accumulate and interpret these data, the spatial variability and heterogeneity in the analysed samples was briefly investigated, both between the individual samples of the same cores, and between different cores.

Horizontal variability
From the set of cores analysed, four different sets of cores are distinguished (Table 4-1 and Figure 4-3):

- In the north of the Netherlands, sample cores have lower sand fraction, with a relatively small variability;
- In the middle section, the core have on average less than 15% sand, with a higher variability;
- Two cores in the province of Limburg, close to the German border, marked as "south-east", are considerably sandier than samples from the other regions (around 30%); and
- one core in the south has about 20% sand, and a low variability over the whole core length.

Vertical variability
The compositions of the core samples vary with depth. Mostly variation in the cores is rather small, with incidentally single samples with higher sand content within the core. In a number of cases the samples at the lower and/or upper boundary of the sampled core show relevant higher sand contents. This should be interpreted as a feature of the Boom Clay (i.e. occurs due to the geomorphological boundary conditions for sedimentation) rather than an expression of the vertical variability.

Table 4-1: Average grain size distribution in Boom Clay samples of the Netherlands and their standard deviations based on [15], Table 14.

region	core	Average grain size distribution			Standard deviation		
		Clay [%]	Silt [%]	Sand [%]	Clay [%]	Silt [%]	Sand [%]
north	VIII	44.9	52.7	2.4	5.0	4.7	0.6
	XI	35.3	64.0	0.8	5.4	4.9	0.5
	XII	39.3	57.2	3.5	11.0	8.7	4.3
	XIII	50.5	47.4	2.2	13.7	11.0	3.3
	XIV	31.9	64.9	3.2	5.8	5.4	2.1
	XV	34.8	56.6	8.7	10.1	14.9	4.8
middle	II	38.4	46.9	14.6	20.7	11.6	19.5
	III	25.4	68.6	6.0	10.7	6.9	9.0
	V	33.5	58.7	7.8	13.8	12.1	12.9
	VI	44.9	49.5	5.6	12.7	8.9	4.1
	VII	40.7	52.5	6.8	17.7	10.2	8.6
	IX	46.9	50.1	3.1	12.3	9.0	4.7
	X	34.0	59.8	6.2	10.1	7.5	4.6
	XVII	33.0	54.0	13.0	11.0	6.6	10.5
south-east	I	20.2	52.7	27.0	10.8	11.2	13.1
	IV	16.9	51.5	31.6	5.2	23.2	21.2
south	XVI	21.6	56.8	21.6	4.1	2.4	4.2

In a straight forward approach, it was distinguished between the inner, more clayey and silty core, and eventually occurring sandier layers at the upper and lower boundary. Table 4-2 depicts the average fraction of *clay+silt* in each core. A 'correction' was applied by ignoring sandier samples at the top and bottom of the cores, if these exceeds 10% sand (right column). The resulting average fractions of *clay+silt* in the middle and northern

region is >85% for all samples, and >90% with sandy layers at the top and bottom of the core removed from the data. For the south-east samples, this fraction is <70%, and the average *clay+silt* fraction of the southern core is 78% (Table 4-2).

Table 4-2: Average fraction of clay and silt in Boom Clay samples of the Netherlands as reported in [15], Table 14. The right column shows the average content with more sandy samples (sand >10%) at the upper or lower boundary of the core removed.

region	core	average fraction of clay + silt [%]	
		all samples	inner samples*
north	VIII	97.6	97.6
	XI	99.2	99.2
	XII	96.5	96.5
	XIII	97.8	97.8
	XIV	96.8	96.8
	XV	91.3	96.2
middle	II	85.4	97.5
	III	94.0	96.7
	V	92.2	97.6
	VI	94.4	94.4
	VII	93.2	99.7
	IX	96.9	99.0
	X	93.8	93.8
	XVII	87.1	90.8
south-east	I	73.0	73.0
	IV	68.4	68.4
south	XVI	78.4	78.4

* see text

Figure 4-5 depicts the grain size distribution in the four regions with sandy upper and lower boundaries removes. Here, the principal differences in grain sizes distribution are more evident than in Figure 4-4.
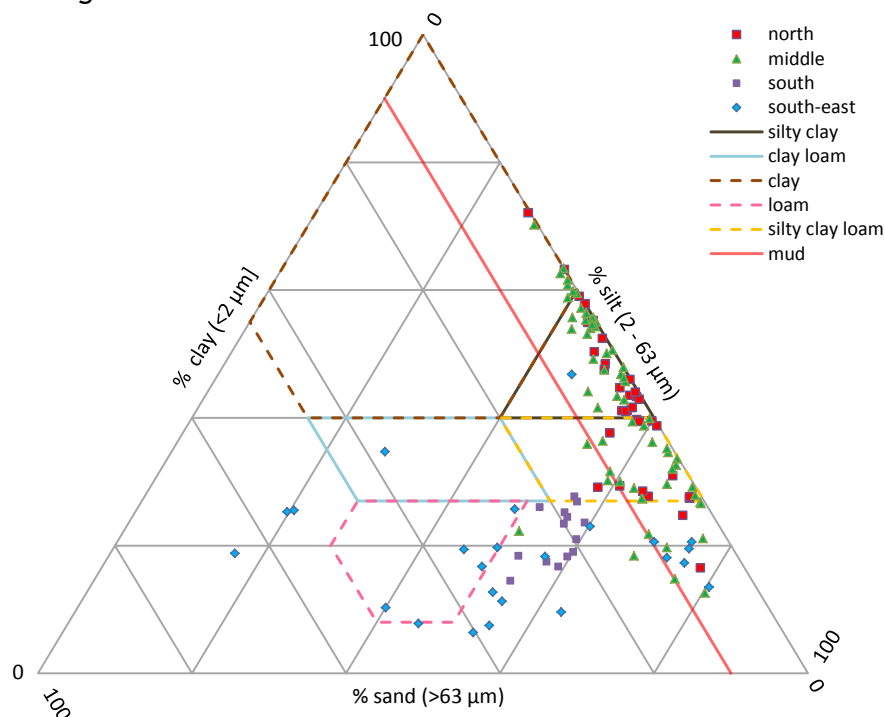

Figure 4-5: Grain-size distribution of Boom Clay samples from The Netherlands as reported in [15], Table 14, after removal of sandy samples at the upper and lower boundaries

Conclusions for further data processing

Data from the Netherlands presented in [15] show that sample cores from the southern and 'south-east' region differ relevantly from the other cores with respect to the sand content. Furthermore, next to incidentally increased sand fractions inside a number of cores, higher sand fractions are found at the upper and/or lower boundary of some cores. The increased fraction of sand is of relevance not only for the purpose of this study, but may also influence (uncertainty with respect to) the hydraulic conductivity (see e.g. [207], Figure 3-18a and b) and may affect the geomechanical behaviour and thus constructional aspects of the disposal design.

With respect to the presence of sandier layers in the top and bottom of the core, it is proposed to treat them in performance assessment as independent top- and/or bottom layer rather than averaging them over the core length. This is less relevant with respect to the sorption modelling as addressed in this report, but simplifies the transport modelling in the host rock by assuming diffusion only ([127], see also [207], Figure 3-18a and b). This can be conservatively done by decreasing the layer thickness of the model host rock (100 m according to the generic disposal concept). However, the average thickness of the sandier bottom and top can only be estimated roughly, because it is unclear if all 'Boom Clay' samples analysed in [15] mark a transition, or are already members of a subsequent layer[10]. Likewise, probably not all sandier upper and lower boundaries belonging to the Boom Clay layer have been analysed[11].

With respect to the two cores in the south-east, these are assumed not to represent a suitable host rock for the generic disposal facility to be assessed in OPERA[12]. From the analysis above and in [15] it also appears that these two samples consist a range of grain size distributions and hydraulic conductivities that goes beyond the range of properties covered by the Belgian research programme (e.g. [133]), i.e. will be more difficult to cover by experimental data. The single core from the south has to be treated as representative of Boom Clay with differing regional composition, probably marking a transition to the afore discussed samples from the south east region.

In summary, for the data treatment the following applies:
- Three regional representatives of "Boom Clay" are distinguished: north, middle, and south;
- The 'south-east' cores (location I and IV in [15]) are excluded from further analysis;
- The upper and/or lower core samples with >10% sand are not taken into account (16 samples of core II, III, V, VII, IX, XVII, and XV).

Mineralogical & chemical composition of the solid phase

Table 4-3 to Table 4-5 summarize relevant chemical and mineralogical properties of the Boom Clay samples analysed in [15], after sample processing as described in the previous section.

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[10] Although a meticulous analysis of mapping vs core data is beyond the scope of this research, it was noticed that the thickness of the Boom Clay layer of the cores I, III, VII, IX and XVII is marked as 'uncertain' (see [207], Figure 3.4), which implies that for some of the analysed samples it may not be sure if these belongs to the Boom Clay layer. By visual inspection of the mapped upper and lower boundaries of Boom Clay given in [10] it also seems that some samples analysed in [7] are not within these boundaries. E.g. the thickness of the Boom Clay layer at location II according to [207] is clearly less than 100 m (see Figure 3-1 and Figure 3-2 of that report), while the length of the analysed core was 140 m ([7], Table 7). In case of core IV and V, the core depth does not visually match with the mapping in ([207], Figure 3-1 and Figure 3-2).

[11] see the (updated) mapping of the Boom Clay in [207]

[12] which, however, does not mean that these locations are not suitable for the disposal of radioactive waste

Table 4-3: Average, standard deviation (*sd*) and relative standard deviation (*rsd*) of regional grain sizes and chemical composition of Boom Clay samples of the Netherlands as reported in [15] (Table 9, 10 & 14) without sandier samples (sand content >10%) at the upper or lower boundary of the core.

	region	<2 µm [%]	<63 µm [%]	C_{org} [%]	S_{tot} [%]	Fe_2O_3 [%]	MnO [%]	P_2O_5 [%]
	north	42.4	97.1	1.02	0.98	6.01	0.04	0.12
average	middle	42.3	96.2	1.04	0.92	5.21	0.02	0.08
	south	21.6	78.4	0.74	1.24	4.74	0.02	0.08
	north	11.6	3.4	0.39	0.38	0.84	0.02	0.05
sd	middle	14.1	5.4	0.50	0.41	1.07	0.01	0.03
	south	4.1	4.2	0.11	0.70	0.69	0.01	0.01
	north	27	3	38	38	14	62	41
rsd [%]	middle	33	6	48	45	20	36	33
	south	19	5	15	57	15	34	8

Table 4-4 summarizes the calcite content of Boom Clay as established by different analytical measurement techniques. Preference is given for the measurement of inorganic carbon, because these are based on the largest numbers of samples.

Table 4-4: Average, standard deviation (*sd*) and relative standard deviation (*rsd*) of calcite content of Boom Clay samples of the Netherlands as reported in [15] (Table 10, 13 & 14) derived by three methods, and with more sandy samples (sand content >10%) at the upper or lower boundary of the cores ignored.

	region	$CaCO_3$ from C_{inorg} [%]	$CaCO_3$ from XRD [%]	$CaCO_3$ from XRF [%]
	north	8.1	7.9	8.0
average	middle	2.1	2.8	2.9
	south	6.1	5.9	6.0
	north	6.1	5.2	5.3
sd	middle	4.1	3.9	3.9
	south	0.9	0.7	0.7
	north	76	67	66
rsd [%]	middle	194	138	138
	south	14	12	12

Table 4-5 summarizes the clay amount and mineralogical composition measured by XRD techniques. Although based on a smaller number of samples, the clay content by XRD is a more reliable measure than the <2µm fraction (Table 4-3).

Table 4-5: Regional average clay composition of Boom Clay samples of the Netherlands as reported in [15] (Table 13) with more sandy samples (sand content >10%) at the upper or lower boundary of the core ignored (K-S = Kaolinite/Smectite mixed layers, I-S = Illite/Smectite mixed layers, G-S = Glauconite/Smectite mixed layers).

region	Total clay [%]	Kaolinite [%]	K-S [%]	Chlorite [%]	Smectite [%]	I-S [%]	Illite [%]	G-S [%]
north	58.1	5.5	8.4	1.2	47.5	18.6	10.7	13.2
middle	41.9	7.2	7.4	1.3	37.6	25.3	15.2	13.3
south	28.4	4.8	3.4	1.6	36.8	36.2	17.2	0.0

Table 4-6 summarizes CEC measurements by three methods as performed in [208]. Although the estimates differ by up to a factor 4, they are generally in line with ([175], p.24), where the CEC is estimated as 13-27 meq/100 g of bulk material or 36-50 meq/100 g of the <2μm fraction. Likewise, assuming about 50-80 meq/100 g for a 'clean' mixture of illite/smectite/I-S, accounting for 75% of the clay fraction (Table 4-5) resulting in rather comparable values: about 17-30 meq/100 g for bulk material and 38-60 meq/100 g for clay. To avoid overweighting the rather small dataset in Table 4-6, originating from several cores sampled on only two locations, in this report a generic CEC is used: 36-50 meq/100 g of the <2μm fraction is assumed to estimate the CEC of the bulk material (Table 4-7).

Table 4-6: CEC of Boom Clay samples of the Netherlands determined by three methods as reported in [208] (Table A 1.3).

region	sample name	depth [m]	Cu content of solid [meq/100g]	decrease of Cu in solution [meq/100g]	cations released [meq/100g]
middle	101 t/m 104*	73-79	13.4	18.5	25.5
south	2	525	5.0	10.4	20.9
	9	570	8.1	10.6	22.9
	15	595	8.3	13.3	23.2
	19	620	6.7	11.7	20.5

* average value of 8 samples

Table 4-7: Regional average, standard deviation (sd) and relative standard deviation (rsd) of CEC of the clay fraction of Boom Clay samples estimated from <2μm fraction and [175].

	region	CEC_{clay} average / (min - max) [meq/100g bulk]
average	north	18.3 / (15.3 - 21.2)
	middle	18.1 / (13.6 - 22.6)
	south	9.8 / (6.7 - 13.0)
sd	north	5.6
	middle	7.6
	south	2.0
rsd [%]	north	30
	middle	42
	south	20

Table 4-8 provides estimations on the crystalline fractions of iron by sequential extraction of Boom Clay samples from two locations reported in [208]. The "min" value represents the iron concentrations in a sodium citrate/dithionate extract, the "max" value is derived from the sum of extractable iron in 0.1M sodium pyrophosphate and sodium citrate/dithionate.

Table 4-8: average, standard deviation (sd) and relative standard deviation (rsd) of crystalline iron in Boom Clay from two locations in the Netherlands estimated by sequential extraction, based on [208] (Table A 1.1).

	region	min [g/kg]	max [g/kg]
average	middle	1.34	1.65
	south	0.43	0.86
sd	middle	0.63	0.81
	south	0.04	0.04
rsd [%]	middle	47	49
	south	8	5

Pore water composition

Table 4-9 summarizes pore water properties as reported in [208]. The obvious oxidation of the samples affects relevant parameters as the pH, and the concentrations of Fe and SO_4. The measured sample values are assumed not to be representative for the anoxic condition of Boom Clay at much larger depth (>500 m).

Table 4-9: Composition of pore water of Boom Clay from a location in the middle region as reported in [208] (Table 4.1).

region	sample name	depth [m]	pH [-]	Ca [mg/l]	Na [mg/l]	Cl [mg/l]	Mg [mg/l]	K [mg/l]	Fe [mg/l]	SO_4 [mg/l]
middle	101	73	3.17	2,421	5,451	14,464	1,028	407	41,6	5,472
	103	79	6.70	2,794	3,061	13,967	1,419	145	182	374
	104	76	3.05	1,884	10,189	19,356	1,256	623	16,6	6,240

Figure 4-6 gives an impression of the variability of extractable chloride concentrations in five samples from several cores from the same location, covering a vertical transect of about 5 m. The measured concentrations vary, except for one extraction, by a factor of two.
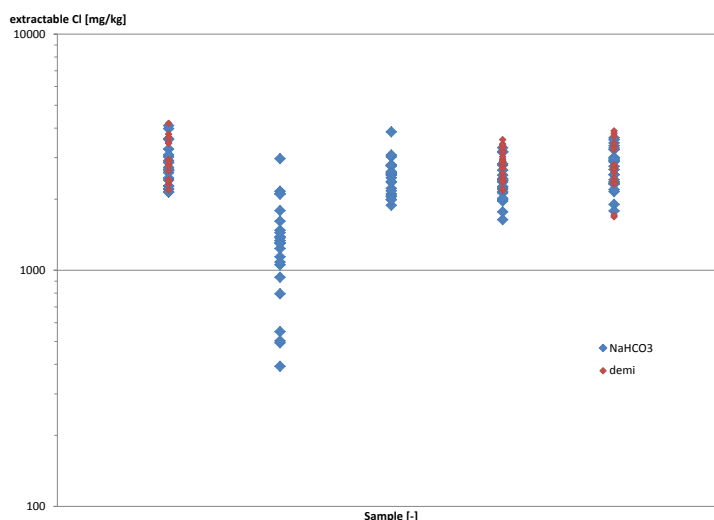

Figure 4-6: Variability of extractable Cl concentrations in five Boom Clay samples from Zeeland, close to location XVII, as reported in [208], Table A 1.4

Little information is available on the pore water composition in Boom Clay as expected at suitable locations in the Netherlands. However, Table 4-10 summarizes (arithmetic) average pore water concentration measured *above* the Boom Clay [209], to give at least some input on the expected variability of relevant pore water parameter. Although the variability of Na and Cl concentration is large (up to 4 orders of magnitude), regional differences are visible. The differences in pH and DOC concentrations found are smaller, but can be relevant with respect to radionuclide sorption behaviour.

Table 4-10: Regional average pore water composition above the Boom Clay as reported in [209] (Appendix 2)

	region	depth [m]	pH [-]	O_2 [mg/l]	DOC [mg/l]	Ca [mg/l]	Na [mg/l]	Cl [mg/l]	Mg [mg/l]	K [mg/l]	Fe [mg/l]	Mn [µg/l]	SO_4 [mg/l]
	north	254.2	7.4	0.2	5.7	44	109	104	7.5	8.9	2.2	97	3.6
average	middle	372.4	7.7	0.1	3.4	112	3324	5222	132	67	1.6	1678	157
	south	346.1	6.9	0.5	0.8	92	366	604	24	8.7	4.5	497	4.2
	north	46.9	0.5	0.1	6.3	30	97	81	3.4	8.3	2.7	71	7.7
sd	middle	80.2	0.3	0.1	0.5	113	2882	4652	115	28.4	1.2	1374	235
	south	72.1	0.4	0.4	0.4	47	1296	2218	44	20	2.4	462	2.1
	north	18	7.1	78	111	67	89	78	46	93	123	73	215
rsd	middle	22	4.2	72	16	100	87	89	87	43	75	82	150
	south	21	5.6	99	54	51	354	367	182	231	54	93	50

4.2.3. Generation of distributed parameter samples

Table 4-11 provides a compilation of modelling input parameters and their distribution, based on the previous chapter. The compilation is used as input for the calculations performed in the next phase of the RANMIG project. The outcomes of those calculations will be documented in *OPERA-PU-NRG6123* [6].

In the previous section, three regions with different properties could be identified. Given the limited amount of data available on key parameters for sorption, no distinction is made for the three regions. A weighted parameter distribution (e.g. a Gaussian distribution) is not applicable, therefore conservative, uniform ranges were defined for most parameter distributions. Since the available samples do not cover all areas of interest, these uniform ranges are extended beyond the measured range of values. This extrapolation uses in most cases the lowest and highest average value found in any region ±2·*sd*, except for SOC, Ca, Cl, Na, and S, where the lowest measured values are taken as lower boundary.

Only minor variations of the redox potential are 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 but also sulphur) with mineral phases. The redox status of a soil system is therefore often expressed by a *pH*+*pe* value (e.g. [56]), and it was decided to vary the redox state in correlation with the *pH*. The correlation and range of pH and pe values was chosen to be in the same range as reported for Boom Clay pore water in Mol and was consistent with calculated values in equilibrium with precipitated pyrite and calcite.

The CEC of clay particles in Boom Clay is determined by assuming 36-50 meq/100 g of the <2 µm-fraction (Table 4-3, see previous section), rather than making use of the limited

number of samples summarized in (Table 4-6). For the specific surface area of HFO, a conservative, large range is used.

Insufficient support by measurements exists for the range of expected DOC concentrations in Boom Clay in the Netherlands. DOC concentrations measured in the Netherlands *above* the Boom Clay (Table 4-9) are much lower than values from samples in Mol, as are DOC measurements performed in Boom Clay in Dessel, Essen and Herenhout [210, 211, 212]. Furthermore, it can generally be assumed that in solutions of higher salinity, DOC concentration tend to decrease (see e.g. [213], Fig. 2-13). Because of the relevance of DOC for radionuclide migration (Section 2.2.3), for the upper limit conservative high values from Mol are used. Maximum proton exchange capacities of 2 and 4 meq per gram of solid humic acids (SHA) and dissolved humic acids (DHA) were measured in Boom Clay from Mol [165, Table 3.6]. The values are roughly one and two-thirds of the values used for sorption modelling on SHA and DHA by the NICA-DONAN model [20, 21]. To cover uncertainties on the DOC and SOC composition generally found in literature and the lack of data on Boom Clay in the Netherlands, additional uncertainties are implemented.

Table 4-11: Expected properties of Boom Clay in the Netherlands

property	min - max	source
Bulk wet density [kg/m^3]	1.900 - 2.150	[127]
Porosity [%]	29 - 43	[127]
CEC Boom Clay [meq/100g Boom Clay]	2.0 - 42	Table 4-3, see text
SOC [wt. %]	0.35 - 2.0	[131]
proton exchange capacity SHA [meq/g]	1 - 2	[165], see text
DOC [mg/L]	20 - 200	[131], see text
proton exchange capacity DHA [meq/g]	2 - 6	[51, 165]
HFO [g/kg]	0.4 - 3.3	Table 4-8
HFO surface area [m^2/gram]	100-600	[144], see text
Inorganic carbon [wt. %]	0.0 - 2.5	Table 4-3
Total amount Ca [wt. %]	0.2 - 7.3	Table 4-4
Total amount Fe [wt. %]	2.2 - 5.4	Table 4-3
Total amount S [wt. %]	0.35 - 2.6	Table 4-3
Soluble concentration Cl [mg/L]	4 - 20'000	Table 4-9, Table 4-10
Soluble concentration Na [mg/L]	4 - 11'000	Table 4-9, Table 4-10
pH [-]	7.7 - 9.2	[131]
pe + pH [-]	3.8 -5.8	[131], see text

5. Conclusions and outlook

In this report, general aspects with respect to the modelling of radionuclide sorption in Boom Clay for the purpose of PA calculation as part of the OPERA Safety Case are summarized. While the basic processes are well understood and literature on sorption is very extensive (Chapter 2), experimental evidence of relevance for radionuclide sorption on Boom clay is mainly limited to the work performed by the Belgian research programme (their approach is summarized in Section 3.3). Several principle approaches used in radioactive waste management were reviewed in Chapter 3, and for the specific challenges of OPERA, an approach is chosen that allows translating existing experimental data on radionuclide sorption from Mol to the variable properties of Boom Clay present in the Netherlands (Section 4.2.2). A general outline of the approach developed is described in Section 4.2 and includes detailed modelling of the basic processes and features summarized in Section 2.2. The approach allows to derive the sorption data needed for the PA by presenting these as (ranges of) conditional K_d-values.

In order to provide these data, in the first step of the approach a fully parameterized *reference model* will be developed, shortly described in Section 4.2.1. The model will be compared with sorption data from the Belgian research programme and documented in a follow-up report, M6.1.2.3. In a second step, the reference model will be used to perform uncertainty analysed that address the variability of Boom Clay properties in the Netherlands. Also the second step and its outcome will be reported in M6.1.2.3, and summarized in the reference database of sorption properties of Boom Clay (M6.1.2.2).

Glossary

CEC   Cation exchange capacity
DHA   Dissolved humic acid
DOC   Dissolved organic carbon
DOM   Dissolved organic matter
Eh   redoxpotential (in [V])
G-S   Glauconite/Smectite mixed layers
HFO   Hydrous ferric oxide
K-S   Kaolinite/Smectite mixed layers
I-S   Illite/Smectite mixed layers
rsd   relative standard deviation
sd   standard deviation
SHA   Soil humic acid
SOC   Soil organic carbon
XRD   X-Ray diffraction
XRF   X-ray fluorescence

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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