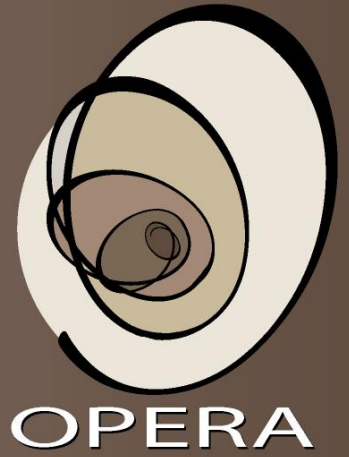




Presence and mobility of colloidal particles

OPERA-PU-SCK614

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

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

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

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

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Summary

Colloids are commonly defined as small particles with dimensions roughly between 1 nm and 1 μm . They represent important sorbents for environmental contaminants keeping them into suspension over long periods of time. Colloidal material is ubiquitous in nature, and includes biocolloids (viruses, bacteria, and protozoa), silicates, clays, oxides and dissolved organic carbon.

Within the context of geological disposal of radioactive waste in a clay sediment (Boom Clay), the presence of colloids would strongly impact the migration behaviour of radionuclides. It is therefore required to elucidate the role of colloids in the transport process to assess the suitability of Boom Clay to retain contaminants for time-frames in excess of thousands of years.

This report provides an overview on the current state of knowledge with respect to colloid facilitated transport under undisturbed Boom Clay conditions currently prevailing at the Mol site (Belgium) which is intensively studied in Belgium (SCK•CEN & ONDRAF/NIRAS) as a potential host formation for the geological disposal of radioactive waste.

An overview about different types of colloids, their generation, composition, and properties (e.g. stability) is given. In more detail, organic carrier colloids are discussed because of their predominance and special significance in Boom Clay. The transport of colloids, the governing mechanism and processes, and the role of colloid filtration are discussed. A careful extrapolation is made of the conclusions drawn for Boom Clay conditions at Mol site to the conditions prevailing in the Netherlands.

Samenvatting

Colloïden worden gedefinieerd als kleine deeltjes met een dimensie tussen 1 nm en 1 μm . Zij zijn belangrijke sorbenten voor contaminanten en houden ze voor lange periode in suspensie. Ze zijn veel voorkomend in de natuur en omvatten bio colloïden (virussen, bacteria, protozoa), silicaten, kleimineralen, oxides en opgeloste organische stof.

In de context van geologische berging van radioactief afval in kleisedimenten (Booms Klei), heeft de aanwezigheid van colloïden een belangrijke impact op het transportgedrag van radionucliden. Het is daarom nodig om de rol van colloïden in het transport proces te ontrafelen om zo de geschiktheid van Booms Klei om contaminanten vast te houden voor periodes van ettelijke duizenden jaren te kunnen evalueren.

Dit rapport geeft een overzicht van het huidige kennisniveau over de rol van colloïden in het transport gedrag van contaminanten voor Booms Klei onder de huidige onverstoorde condities relevant voor Mol (België) waar de Booms Klei zeer intensief wordt onderzocht (SCK•CEN & ONDRAF/NIRAS) in het kader van geologische berging van radioactief afval.

Een overzicht van verschillende types colloïden, hun ontstaan, samenstelling en eigenschappen (stabiliteit) wordt gegeven. In meer detail wordt er ingegaan op organische colloïden omdat zij veelvoorkomend zijn in de Booms Klei. Het mechanisme, de onderliggende processen en rol van filtratie bij colloïd transport wordt besproken. Er wordt ook een voorzichtige extrapolatie gedaan van de conclusies geldend voor Booms Klei condities te Mol naar de condities relevant voor Nederland.

1 Introduction

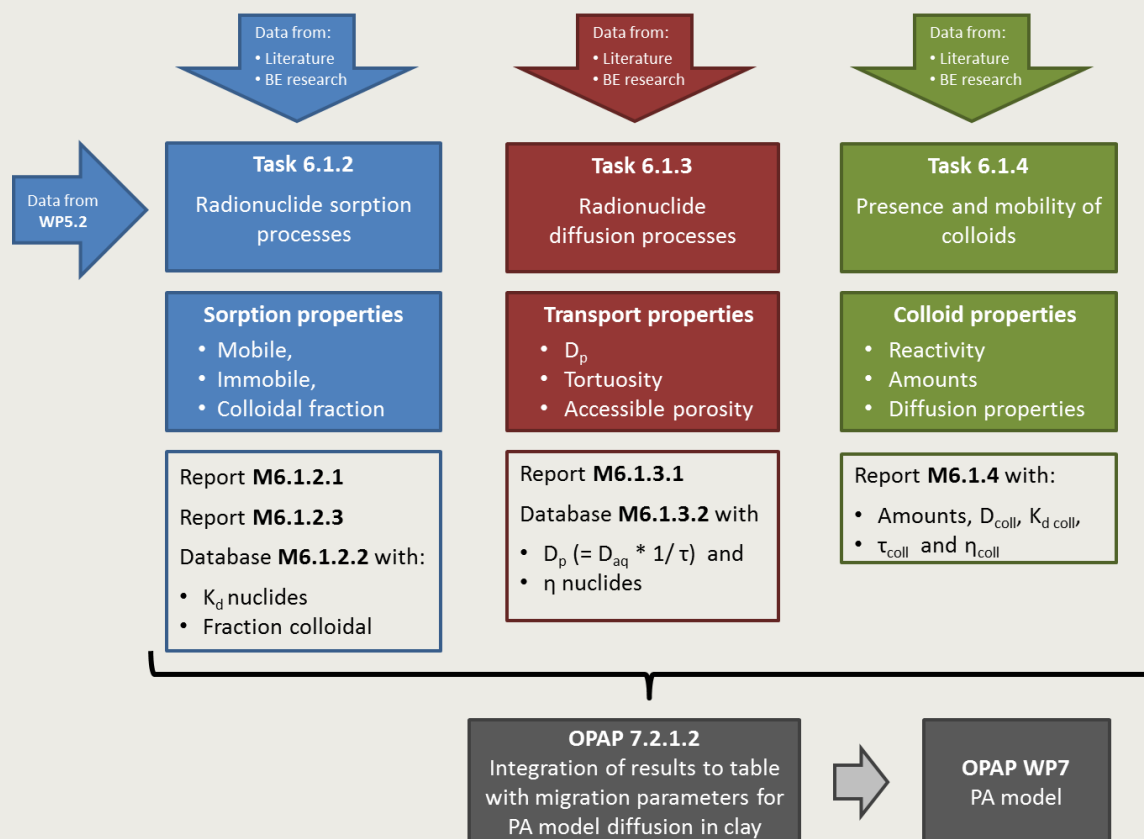
1.1 Background

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

1.2 Objectives

In this report, the relevance of colloids for the migration behaviour of radionuclides in Boom Clay is assessed, and the result, an estimation of the relevance of colloids for the migration of radionuclide, is presented as set out in the research proposed for Task 6.1.4 with the following title in the Research Plan: *Mobility and presence of colloidal particles*. This report is linked to Tasks 6.1.2 and 6.1.3 respectively "Radionuclide Sorption processes/transport processes as described in underlying scheme.

Relationship between OPERA Tasks 6.1.2, 6.1.3 and 6.1.4 and WP 7



1.3 Realization

The study presented in this report is performed by SCK•CEN in the OPERA-RanMig project, which is executed by a consortium consisting of NRG, TNO and SCK•CEN.

1.4 Explanation contents

The principal objective of any facility for the disposal of radioactive waste is to provide long-term safety by isolation and confinement. In Belgium, major studies have been under way (since 1974) to assess the long-term safety for high-level waste and spent fuel disposal in a clay formation. Following the release of the Waste Plan (ONDRAF/NIRAS, 2011), ONDRAF/NIRAS identified poorly indurated (plastic) clay formations as the preferable option for siting a repository in Belgium. The Boom Clay is studied as a potential host formation.

The Boom Clay is a sedimentary deposit, mainly composed of siliciclastic minerals, fossils and organic matter. The mineralogical composition of Boom Clay consists of clay minerals (up to 60 wt%), quartz (~20 wt%), feldspars (~10 wt%) and minor amounts of muscovite, biotite and some heavy minerals. The clay mineralogy is dominated by illite, smectite, illite/smectite interstratifications, and kaolinite. The authigenic mineral assemblage in the Boom Clay includes apatite, glauconite, authigenic quartz, carbonates (calcite and siderite, 1-5 wt%) and pyrite (1-5 wt%). The petrophysical and hydraulic parameters of the Boom Clay are summarised in Table 1-1 (taken from De Craen et al., 2004).

Parameter	Unity	Value
Bulk density (sat.)	[kg/dm ³]	1.9 - 2.1
Average grain density	[kg/dm ³]	2.65
Water content	[% dry wt]	19 - 24
Specific surface	[m ² /g]	44
<i>In situ</i> temperature	[°C]	16
Thermal conductivity	[W/m/K]	1.68
Specific Heat	[J/kg/K]	1400
Heat Capacity	[MJ/m ² /K]	2.8
Hydraulic conductivity	[m/s]	
• Lab experiments		Vert. $1.3\text{-}3.4\times 10^{-12}$, Hor. $3.5\text{-}7.9\times 10^{-12}$
• <i>In situ</i> field testing		Vert. 2.1×10^{-12} , Hor. 4.5×10^{-12}

Table 1-1: Petrophysical and hydraulic parameters of Boom Clay (De Craen et al., 2004)

At the site of Mol, where the underground research facility HADES is located, the porewater in contact (and presumed in equilibrium) with the clay is mainly a 0.015 M NaHCO₃ solution of pH ~ 8.5 (Table 1-2). The typified inorganic composition of this porewater is referred to as Synthetic Boom Clay Water (SBCW). If porewater is used directly from piezometer sampling, it is generally referred to as Real Boom Clay Water (RBCW)¹. The difference between SBCW and RBCW lies mainly in the presence of dissolved organic carbon in RBCW, whereas in SBCW it is totally absent.

¹ The most common type of Real Boom Clay Water used throughout the experiments is piezometer water derived from the Experimental Gallery/Bottom Shaft (EG/BS) piezometer. Its composition can be found in De Craen et al. (2004)

Species	[mg/l]
Al	0.6×10^{-3}
Si	3.4
Mg	1.6
Ca	2.0
Fe	0.2
K	7.2
Na	359
Cl ⁻	26
SO ₄ ²⁻	2.2
HCO ₃ ⁻	878.9
pCO ₂ (g) [atm]	$10^{-2.62}$
E _h [mV]	-274
pH [-]	8.5

Table 1-2: The Boom Clay reference water composition at 16 °C
Data taken from de Craen et al., (2004)

Clay sedimentary formations have to provide both, a physical (low hydraulic conductivity) 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. Transport through *advective* flow is defined as the transport of a solute with a moving fluid in which it is contained.

Since Boom Clay has a very low hydraulic conductivity ($K_v \sim 2 \times 10^{-12}$ m/s), the dominant solute-transport process within and out of a repository system would be molecular diffusion through the pore water, possibly retarded by, e.g., sorption onto clay mineral surfaces.

Consequently, by a combination of low hydraulic conductivity and sorption, slow migration of radionuclides through Boom Clay might be expected. Nevertheless some additive physical and geochemical processes might affect the transport of solutes in aquitard deposits. One important process that should not be neglected is colloid facilitated transport. The presence of organic or inorganic colloids within a repository by complexation/sorption of radionuclides would strongly impact their migration. It is therefore required to elucidate the role of colloid facilitated transport to assess the suitability of Boom Clay to contain contaminants for time-frames in excess of thousands of years (Hendry et al., 2003) and the subsequent chapters aim at evaluating the importance of this process in Boom Clay.

The current report is subdivided in 5 chapters and gives an overview on the current state of knowledge with respect to colloid facilitated transport under undisturbed Boom Clay conditions. These conditions refer to the Boom Clay formation, as it is nowadays present at the Mol site, with the in situ porewater composition and mineral assemblage.

Chapter 1 comprises the introduction. In chapter 2, an overview about different types of colloids, their generation, composition, and properties (e.g. stability) is given. The subchapter on organic carrier colloids was particularly elaborated due to their predominance and special significance in Boom Clay. Chapter 3 deals with the transport of colloids, the governing mechanism and processes, and the role of colloid filtration/straining. As example, some of the most relevant results obtained on organic

matter transport in Boom Clay are presented. Within the last subchapter, we tried to extrapolate conclusions drawn for BC conditions at Mol site to the conditions prevailing in the Netherlands. In the 4th chapter, different RN-DOM interaction mechanisms and some of the most commonly used modelling approaches are described. Afterwards, selected experiments (mainly migration type) that were performed at SCK•CEN over the last decades with representative waste-relevant radionuclides are presented, in order to illustrate the derivation of the current conceptual transport model for Boom Clay. The chapter is completed by the attempt to anticipate to what extent the model can be applied to the conditions encountered in the Netherlands.

It should be mentioned that different internal, as well as external SCK•CEN reports, journal articles and other references were taken into account when writing the current report.

2 Subsurface colloids

2.1 Nature and source of subsurface colloids

Colloids are commonly defined as small particles or other entities with dimensions roughly between 1 nm and 1 μm . These size limits to dissolved molecules on the one side and to larger suspended particles on the other side are gradual and to a certain extent arbitrary. Nevertheless, colloidal particles have some unique properties. First, they have very large specific surface areas ($> 10 \text{ m}^2/\text{g}$) and therefore represent important sorbents for environmental contaminants. Second, particle transport by diffusion can be faster than by sedimentation. Consequently, colloidal particles remain stable in suspension over long time periods unless they coagulate to form larger aggregates or deposit onto surfaces of larger grains (Kretzschmar *et al.*, 1999). Colloidal material is ubiquitous in nature, and includes biocolloids (viruses, bacteria, and protozoa), silicates, clays, Fe-, Mn-, and Al-oxides, mineral precipitates, and the macromolecular portion of dissolved organic carbon (DOC).

Based on their nature and composition, one can differentiate between three main classes of potentially hazardous colloidal particles: (i) intrinsic colloidal particles, (ii) carrier colloidal particles, and (iii) biocolloids (Grolimund *et al.*, 2007). For the intrinsic colloidal particles, the contaminant represents a structural component of the colloid. Precipitates or solid solutions of inorganic contaminants are typical examples of this class. The carrier colloidal particles bind the contaminants, which are present in the mobile fluid phase, to the surface of suspended organic or inorganic colloids. Viruses or bacteria are important examples of organisms in the colloidal size range representing the class of biocolloids (Figure 2-1).

Several potential sources of mobile colloidal particles in subsurface porous media have been identified. Such sources include *in situ* mobilisation of colloidal particles that are naturally present, formation of colloidal particles by precipitation from supersaturated solutions, mobilisation or introduction of "biocolloids" such as viruses or bacteria, and external sources, resulting from waste disposal practices.

Numerous studies have shown that dispersion and release of particles in most soils is favoured by high pH, high Na^+ saturation, and low ionic strength. Some field observations also suggested that *in situ* mobilisation of colloidal particles may also result from dissolution of cementing agents. The composition of *in situ* mobilised colloids is generally similar to that of the fine fractions naturally present in the porous medium, although the quantitative proportions of different mineral or organic phases can vary. Solid phases that can be mobilised as colloidal particles including aluminosilicate minerals (especially clay minerals), oxides and oxyhydroxides of Fe, Al, and Mn, silica, carbonates, and natural organic matter (Kretzschmar *et al.*, 1999).

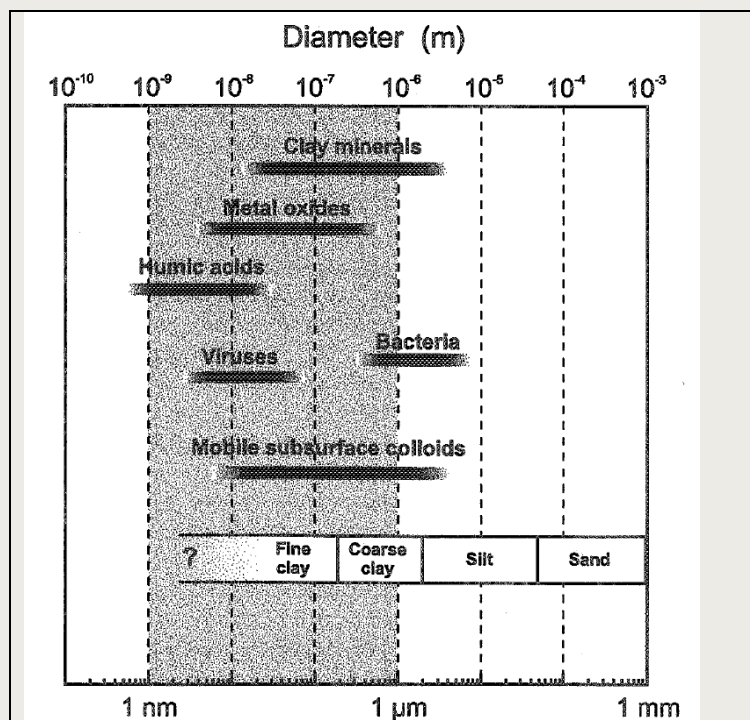


Figure 2-1: Size range of colloidal particles in subsurface environments. The classic size fractions commonly used in soil science are shown for comparison (Kretzschmar et al., 1999)

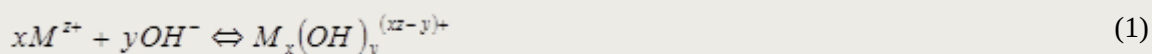
In natural environments, these components usually occur as mixtures or complex aggregates, which exhibit different behaviour than the corresponding pure components. A well-known example is organo-clay complexes, which show much higher colloidal stability than comparable reference clays without organic matter coatings.

2.2 Colloidal particles in Boom Clay

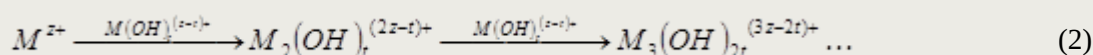
2.2.1 Intrinsic colloids

Intrinsic colloids (or eigencolloids) are oxidic nanoparticles that arise from aggregation of hydrolysed metal ions. Such colloids are important for radioactive waste disposal since several multivalent radionuclides like U(IV), Th(IV), Np(IV) and Pu(IV) easily form these ill-defined structures at neutral to alkaline pH (Bitea et al., 2003a; Bitea et al., 2003b; Cho et al., 2005; Fanghanel and Neck, 2002; Neck and Kim, 2001).

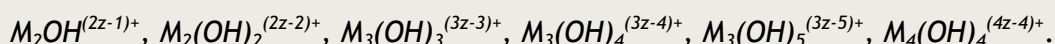
Hydrolysis reactions are common to most cations. This is not surprising since: 1) most metal atoms form strong bonds to oxygen; and (2) the OH⁻ ligand is always present in water at concentrations, which can be varied over a very wide range (>1 to <10⁻¹⁴ mol/kg) as a result of the small self-dissociation constant of water (Baes and Mesmer, 1976). The general simplified formation reaction for a soluble hydrolysis product can be written as:



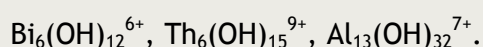
While the hydroxide complexes formed at very low concentrations are usually mononuclear, at higher concentrations polynuclear complexes are usually dominant. Historically, Sillén (1959) was led to propose a general mechanism of hydrolysis in which $M(OH)_t^{(z-t)+}$ groups are added stepwise to the cation:



However, it subsequently became clear that this stepwise polymerisation process rarely, if ever, occurs. Baes and Mesmer (1976), on the other hand, described how cations often formed a limited number, usually one to three, of polymer species, which predominate at usually encountered concentrations. All but a few such species are to be found among the following dimers, trimers, and tetramers:

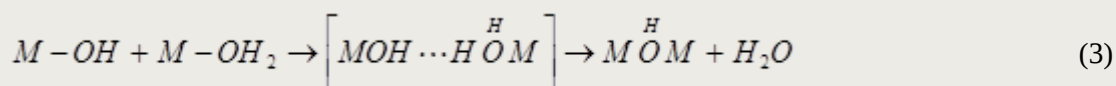


Occasionally, higher polymers occur such as

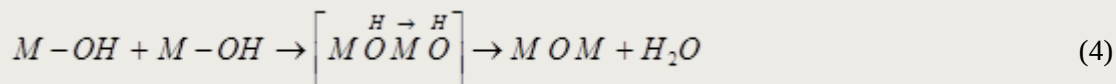


However, the identification of polynuclear species produced by the hydrolysis of a given cation remains a difficult task. Therefore, proposed species are best viewed with some scepticism, because most interpretations are not unique, and alternative interpretations could be made equally consistent with measured data (Baes and Mesmer, 1976).

Due to the ambiguity in the exact composition of these polymer species, we would rather assume the approach that formation of polynuclear species occurs through condensation of smaller hydrolysed species at concentrations above the thermodynamic solubility of the most stable (crystalline) pure phase (mostly an oxide). Condensation can occur according to two mechanisms, ololation and oxolation (Henry et al., 1992). Ololation reactions always concern hydroxylated aquo species, undergoing a nucleophilic attack from an OH group carrying a partial negative charge. In the transition state, an H₃O₂⁺ bridge is probably formed, from which an aquo ligand is lost resulting in the formation of an 'ol' bridge between two metal centres:



Oxolation reactions mainly concern oxyhydroxo hydrolysis species, without aquo ligands in their coordination sphere. Without a suitable leaving group, such a condensation can only proceed via a two-step associative mechanism leading to the formation of an 'oxo' bridge after removal of a water molecule formed by a proton transfer during the transition state:



Both reactions may lead to small solute condensed species (polyanions or polycations) or to the formation of an extensive network (colloids, gels, or precipitates) (Henry et al., 1992). The eventual end product is strongly dependent on the identity of the metal cation and the reaction conditions (pH, E_h , concentration, temperature) and is often ill-defined.

Intrinsic colloids have been shown to be important (especially) for tetravalent radionuclides forming sparsely soluble oxyhydroxide precipitates such as Tc(IV), U(IV), Zr(IV), Th(IV), Np(IV) and Pu(IV). Additionally, Be^{2+} is an example of a metal for which polynuclear species are known. Consequently, we will explicitly take intrinsic colloids into account in the assessment of the mobility of these elements. However, their ill-defined structure and size distribution make them difficult to handle. Moreover, considerable evidence is present that these intrinsic colloids readily associate with the dissolved humic substances in Boom Clay porewater (as will be shown later). **Therefore, we assume that their geochemical and colloidal transport behaviour is closely linked to and comparable with that of humic substances.**

2.2.2 Inorganic carrier colloids

2.2.2.1 Clay minerals (*illite, smectite, kaolinite, chlorite*) and feldspars

Phyllosilicates can form crystals of sub- μm size and bear a net negative surface charge under the Boom Clay conditions, as indicated² by their pH_{zpc} (Stumm, 1992). Therefore, they could potentially form stable colloids in the pore space of the Boom Clay. Clay colloid stability depends mostly on pH, the cation occupancy of the ion exchange sites and on the composition (ionic strength, cationic species) of the porewater.

When dealing with colloids, the term *stability* has an entirely different meaning to that in chemical thermodynamics. A system containing colloidal particles is said to be stable if, during the period of observation, it is slow in changing its state of dispersion (Stumm and Morgan, 1996). In a qualitative way, colloids are stable when they are electrically charged. In a physical model of colloid stability, particle repulsion due to electrostatic interaction is counteracted by Van der Waals attractive forces. The repulsion energy is affected by ionic strength and increasing ionic strength compresses the electric double layer, decreasing the colloid stability. Thus, colloids tend to be less stable in saline waters. But often more important than the effects of the electrolytes that influence the thickness of the electric double layer are the sorbing solutes that reduce or modify the surface charge.

² According to Stumm (1992), the pH_{zpc} of kaolinite is equal to 4.6, while that of montmorillonite is equal to 2.5

The coagulation behaviour of clay minerals has been extensively studied (Goldberg and Forster, 1990; Goldberg et al., 1991; Goldberg and Glaubig, 1987; Tombacz et al., 1999; Tombacz and Szekeres, 2004; Van Olphen, 1977). Important parameters in this context are the exchangeable sodium percentage (ESP = fraction of exchanger charge saturated with Na⁺) and the sodium adsorption ratio of the solution phase ($SAR = C_{Na} / (C_{Ca} + C_{Mg})^{1/2}$, where C_x is the concentration, in mol/L, of the subscripted element, x) (Sposito, 1989; Voegelin and Kretzschmar, 2002). Respective values for the Boom Clay are listed in Table 2-1. The data for the Mol-Dessel area were taken from De Craen et al. (2004). The calculated ESP is about 47% while the SAR equals about 47 (Table 2-1).

Mol	Cation occupancy [meq/100g]
Na	8.7
K	2.3
Mg	3.7
Ca	3.8
CEC	18.5
ESP (%)	47
	Solution phase composition [mol/m ³]
Na	15.6
Ca	0.05
Mg	0.06
SAR	47

Table 2-1: ESP and SAR values for the Boom Clay in Mol. Data taken from De Craen et al. (2004); cation occupancy data refer to Griffault et al. (1996)

Increasing pH, ESP and SAR indicate an increasing tendency of the clay minerals to disperse, and an increasing critical coagulation concentration (CCC) is required to keep the clay particles coagulated. The CCC or flocculation value is the minimum electrolyte concentration necessary to flocculate a given colloidal dispersion in a given time (Goldberg and Forster, 1990; Van Olphen, 1977). Thus, if the electrolyte concentration is less than the CCC, dispersion occurs.

Goldberg and Forster (1990) operationally determined the CCC as the salt concentration at which 80% of clay colloids were removed from solution after 3 h equilibration time. They evaluated the effect of ESP, SAR, electrolyte concentration and pH on the flocculation-dispersion behaviour of reference montmorillonite, kaolinite and illite. In their study, they report a CCC of 10-15 mmol/L for kaolinite, 20-25 mmol/L for montmorillonite, and 30-40 mmol/L for illite between pH 8 and 9 at SAR 40. For a 50/50 mixture of illite and montmorillonite at SAR 40, the CCC was about 25 mmol/L between pH 8 and 9 (Goldberg et al., 1991). However, CCC values for soil clay fractions (< 2 µm) were much higher than those of reference clays (Goldberg and Forster, 1990). This might be due to the presence of organic matter in the soil clay fractions, which has been shown to increase clay dispersion (Gupta et al., 1984; Tombacz et al., 1999).

Considering the values of ESP, SAR ionic strength, and pH of reference porewater (pH = 8.5), phyllosilicate colloids are likely to be stable in the Boom Clay.

Analysis of the Boom Clay porewater sampled from piezometers (De Craen et al., 2004) shows, that the aluminium concentration in unfiltered Boom Clay porewater is about one order of magnitude higher than expected at the measured Si concentration, assuming equilibrium with kaolinite. This may be explained either by the possible presence of Al-bearing colloids in water samples, or by the chosen thermodynamic data for kaolinite, i.e.

being inappropriate for the actual degree of kaolinite crystallinity (De Craen et al., 2004; Nordstrom and Munoz, 1994). Beaucaire et al. (2000) found that the measured Al concentration in the Boom Clay porewater was generally overestimated, if the water sample was not carefully filtered. They found that the ultrafiltration of a water sample at 10 nanometre resulted in a representative and truly dissolved Al concentration, which was in solubility equilibrium with kaolinite. Likely, the higher Al concentration measured without ultrafiltration is linked to Al complexation by dissolved organic matter, and not by the existence of clay colloids. Indeed, opposed to Al, the dissolved Si content in Boom Clay porewater does not exceed the solubility limit of known mineral phases. Thus, the potential influence of phyllosilicate colloids on radionuclide migration is very small compared to that of mobile dissolved organic matter colloids (DOM, see below). **Accordingly, we will not consider Al-bearing (phyllosilicate) colloids as important vectors in radionuclide transport.**

2.2.2.2 Quartz and amorphous silica

The abundance of quartz in the Boom Clay ranges up to about 60 wt%. According to the points of zero charge (p.z.c.) or isoelectric point (i.e.p.) listed in **Table 2-2**, quartz colloids are negatively charged at Boom Clay reference pH values.

The dissolved silica in Boom Clay porewater was previously believed to be controlled by the solubility of chalcedony, a form of silica with a slightly different chemical stability than quartz (De Craen et al., 2004). However, this assignment was purely due to issues related to the thermodynamic database used in geochemical modelling. Recent advances in thermodynamic data and current understandings of quartz solubility explain very well the observed concentration of dissolved silica in Boom Clay porewaters (Honty et al., in prep.).

Precipitate or Mineral	pH	
Amorphous $\text{Al}(\text{OH})_3$	7.1 - 9.5	i.e.p. ^(a)
Magnetite	6.5	p.z.c. ^(b)
Quartz	2.0	p.z.c.
Amorphous SiO_2	1.8	i.e.p.
Calcite	9.5	i.e.p.
Feldspars	2 - 2.4	p.z.c.
Kaolinite	4.6	p.z.c.
Montmorillonite	2.5	p.z.c.
Albite	2.0	p.z.c.
Pyrite	1.4	i.e.p.

^(a) i.e.p. = isoelectric point, pH at which electrophoretic mobility is zero

^(b) p.z.c. = point of zero charge, pH at which the net surface charge is zero

Table 2-2: Isoelectric points (i.e.p.) or points of zero charge (p.z.c.) of some mineral phases (Voegelin and Kretzschmar, 2002)

This solubility limitation implies that quartz or amorphous silica colloids do not contribute significantly to the quantity of silica in the water; were such colloids present at significant concentrations, then the total measured silica content of the aqueous phase would be higher. **Consequently we do not consider quartz or amorphous silica colloids as being important for the radionuclide transport in Boom Clay.**

2.2.2.3 Calcite

Little is known about the colloidal behaviour of calcite. From the pH_{zpc} of calcite (Table 2-2), it might be concluded that calcite bears a positive surface charge in the relevant pH range, which would lead to fast deposition on negatively charged rock surfaces. However, calcite surface charge depends also on the concentrations of Ca^{2+} , carbonate and the presence of organic coatings (Voegelin and Kretzschmar, 2002).

No indication of oversaturation of calcite was observed during analysis of the porewater chemistry of the Boom Clay in Mol (De Craen et al., 2004). It is also likely that calcite is in chemical equilibrium with the porewater (Nordstrom and Munoz, 1994). **For these reasons, calcite colloids are not considered either being relevant for the radionuclide transport.**

2.2.3 Biocolloids

Viruses and bacteria also fall into the colloidal size range. Transport of bacteria and viruses in porous media has been an active research area during the last few decades. In deep clay, bacteria are trapped in the extremely small pores. Consequently, their movements must be extremely restricted or even prevented and they must have adapted to a slow rate of cell division over time. It is only by diffusion that nutrients can be transported from outside the bacteria-containing rock volume. A result is that bacterial activity and numbers must be much reduced compared to environments in which pores are large compared to microbial cell sizes, and pore fluid transport is advection-dominated.

Boivin-Jahns et al. (1996) examined a 20-m-long horizontally drilled Boom Clay core for the presence of bacteria and studied the specific diversity of these organisms. Large numbers of heterotrophic bacteria (10^5 Colony-Forming Units (CFU)/ml) were observed in samples obtained within a few centimetres of the gallery wall. As the distance from the gallery wall increased, the microbial density decreased, and viable counts appeared to be limited to a few CFU/ml at distances greater than 80 cm (Figure 2-2). In all samples studied, the highest viable counts were recorded in aerobic conditions. Anaerobic bacteria were always either poorly represented or under the detection limit (~ 10 cells/ml). Bacterial respiration measurements equally showed a gradient decreasing with distance from the gallery wall.

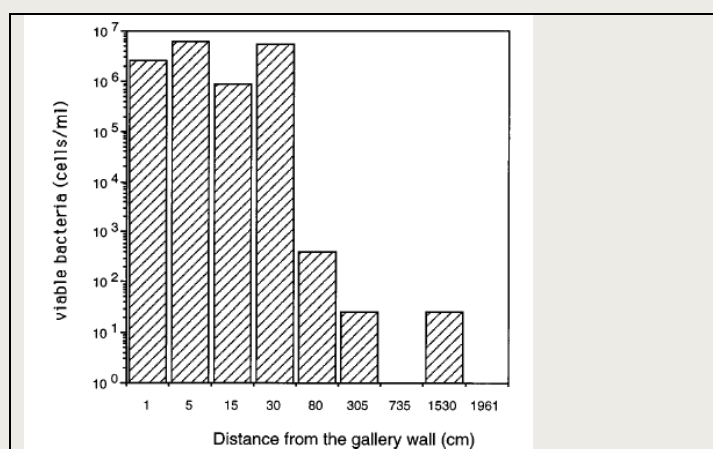


Figure 2-2: Viable bacteria in clay as a function of depth from the gallery wall. There was a sudden decrease in amounts of bacteria around 80 cm, with few or no bacteria at depths greater than 3 m (all colonies retrieved at these depths were identified as likely contaminants) (Boivin-Jahns *et al.*, 1996)

Most likely, many of the colonies obtained under culture conditions at distances of more than c. 80 cm from the gallery wall, were contaminants. Such contamination is very difficult to avoid when samples containing very few, slow-growing bacteria are collected using tools that are difficult to sterilise and under difficult working conditions, such as those in the URL gallery (Boivin-Jahns et al., 1996).

In order to discriminate between bacteria that were introduced by contamination and indigenous species, the surrounding environment (gallery, coring tools) was also sampled and comparisons with a database of known 16S rDNA sequences were made (Boivin-Jahns et al., 1996). Polymerase chain reaction (PCR) experiments showed the presence of bacteria in all samples studied. Among the bacteria that were found and were likely not contaminants are the taxons *Desulfotomaculum* (sulphate-reducing bacteria), *Acinetobacter*, *Pseudoalteromonas*, *Pseudomonas*, *Carnobacterium*, *Clostridium*, *Propionibacterium*, *Azoarcus* and *Rhodocylus*. These organisms were hypothesised to become trapped 35 million years ago during deposition of the Boom Clay. A vertical migration from the surface through the overlying Neogene sands (0 to 188 m deep) is not strictly impossible considering the time scale involved and the porosity of the sand (i.e., 200.000 years at 1 mm/year). However, starting at a depth of 188 m, the Boom Clay formation is characterised by an anisotropic porosity with connectivity that is mainly parallel to the bedding and with the majority of the pores not exceeding 100-250 nm (Desbois et al., 2010). Such a clay lattice structure makes it quite difficult for bacteria to migrate from a depth of 188 m to 224 m (the location of the URL).

In a more recent study, Wouters *et al.* (2012) sampled Boom Clay porewater from different Boom Clay layers using the Morpheus³ piezometer in order to determine a representative microbial community. Analysis was performed by a complementary set of microbiological and molecular techniques (including PCR on 16S rRNA genes in the DNA pool). The bacterial community was found to be quite diverse, with operational taxonomic units (OTUs) belonging to 8 different phyla (Proteobacteria, Actinobacteria, Firmicutes, Bacteroidetes, Chlorobi, Spirochetes, Chloroflexi and Deinococcus-Thermus). Due to the presence of anaerobic micro-organisms with specific properties like sulphate reduction and sporulation, it was speculated that at least part of the observed viable community was indigenous.

In summary, biocolloid presence cannot be ruled out in the Boom Clay, but the biota are probably dormant or have a very slow rate of metabolism, and are certainly not mobile within the confined pore structure.

2.2.4 Anthropogenic colloids

Colloids might also be generated in the near field by the corrosion of steel canisters and waste glass, by the alteration of the bentonite or cementitious backfill, or by direct precipitation of radionuclides. This type of colloids, i.e. anthropogenic colloids have not been studied yet by SCK•CEN, and are therefore not explicitly addressed in this report. However, if they were released into the far field, near field colloids would likely behave in analogy to natural colloids (Voegelin and Kretzschmar, 2002).

³ Morpheus vertical piezometer (cf Figure 2-7)

2.2.5 Organic carrier colloidal particles

Organic matter is an important component of soils and sediments and its distribution over the solid and the solution is known to control the fate of trace metals and contaminants in the environment. Solid or particulate organic matter immobilize the contaminants acting as a sorption phase while dissolved organic matter (DOM), mobile, was shown to transport metals (Kalmykova et al., 2010; Paradelo et al., 2012), hydrophobic organic compounds (Kögel-Knabner and Totsche, 1998; Sojitra et al., 1996) or radionuclides (Artinger et al., 1998a; Artinger et al., 2003; Artinger et al., 1999; Maes et al., 2011; Maes et al., 2006; Mibus et al., 2007; Schuessler et al., 2000; Trancom-II, 2004; Warwick et al., 2000). DOM can also influence inorganic colloid stability and participate in redox reactions (Kretzschmar et al., 1999; Stevenson, 1994; Stumm and Morgan, 1996). The presence of mobile DOM in the host rock may therefore strongly impact the transport of radionuclides otherwise highly retarded by sorption on the minerals composing the host rock.

In soils or sediments organic matter is divided in several pools that interact with each other in a dynamic way with regard to the environmental conditions. While it is believed that DOM and solid/particulate OM are linked, the high complexity of natural OM makes the identification of the relation between the different pools difficult. In soils, the concentration of DOM was shown to be mainly controlled by the combination of OM solubility and sorption/desorption equilibrium on mineral phases (Kaiser et al., 1996; Qualls, 2000; Vandenbruwane et al., 2007).

However, in low-permeability media, such as Boom Clay, the concentration of organic matter transported in pore water is also governed by physical constraints (e.g. colloidal filtration). These constraints partitioned the DOM into two fractions: a mobile and an immobile fraction. Accounting for these two fractions, the distribution of OM in low porous media might be sketched as presented in **Figure 2-3**. The mobile DOM is present in pore waters and can be retrieved by means of piezometers. The leachable OM pool accounts for potentially soluble and dissolved OM that is retained in the rock either by chemical (sorption, *i.e.* sorbed OM) or physical processes (filtration, *i.e.* immobile DOM). This fraction of OM can be leached from the powdered rock. The distribution of OM over the pools represented in **Figure 2-3** depends: 1/ on the nature and reactivity of the solid OM (SOM), 2/ on the chemical conditions that control the solubility of each pool, 3/ on the mineral assembly of the host rock that controls the sorption/desorption equilibrium, 4/ on the pore structure of the host rock that controls the role of colloidal filtration. Current environmental conditions in the Boom Clay at Mol site are very favourable for organic colloids to be stable, the porewaters having neutral to alkaline pH (pH ~8.5), relatively low ionic strength, and being Na-dominated with few multivalent cations (Ca and Mg together at 110 µmol/l). Moreover, the generation of organic colloids is favoured by the ubiquitous occurrence of NOM, which is mainly relatively immature kerogen.

In the next sections, we will give a picture of the partitioning of OM as it is in Boom Clay in the physico-chemical conditions found at the Mol Site with a focus on DOM. In a last section, we will discuss which parameters might influence the concentration and nature of mobile DOM giving heed to the role of ionic strength.

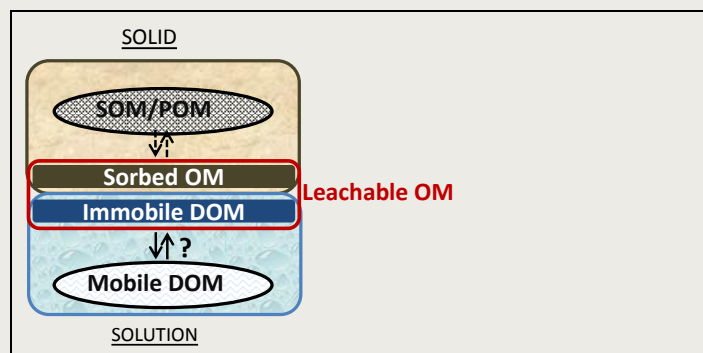


Figure 2-3. Schematic distribution of organic matter (OM) in low-porous media such as BC. SOM= solid OM, DOM=dissolved OM, POM= particulate OM

2.2.5.1 Solid Organic matter (SOM) in Boom Clay at Mol Site

In our representation of natural OM in Boom Clay (**Figure 2-3**), the SOM represents the pool of OM that is insoluble in aqueous solution, i.e the kerogen and bitumen fractions. Bitumen is the part of solid organic matter which can be dissolved in usual organic solvents, while kerogen is the remaining insoluble part (Vandenbroucke, 2003). As SOM is not soluble in pore waters, its role in colloidal transport is limited. In consequence, we will not give a complete description of the BC SOM in this report. More information can be retrieved from (Bruggeman and De Craen, 2012) and from the PhD pursued on the topic by Laenen (1997) and Deniau et al. (2001). Nevertheless, the reader should keep in mind that SOM is believed to participate in the release of DOM notably under perturbations (oxidation, heat...).

Organic matter in Boom Clay originates from different sources: allochthonous (terrestrial; angiospermal and gymnospermal + coal fragments) and autochthonous (marine + bacterial). Throughout the stratigraphy, all sources are always found, but in slightly different ratios. The organic-rich layers, for example, reflect a clearly higher continental input (Vandenbergh, 1978), but are the result of an increase of the material from all sources. Moreover, a better preservation and a lower sediment supply enhanced the organic carbon content within these layers (Laenen, 1997).

Laenen (1997), Van Geet (2002) and De Craen (2005) reported the results of Total Organic Carbon (TOC) measurements and rock-Eval data on selected samples cored in the Boom Clay layer. The **Figure 2-4** illustrates the TOC content and the kerogen type of the BC samples to their position of sampling. TOC values vary between 0.78 and 4.13 wt%. From the TOC and Rock-Eval analyses, two populations of organic matter can be discriminated. The first population has TOC values below 2% and is omnipresent throughout the stratigraphically sampled part. The second population has TOC values above 2% and is limited to the Putte member. From the analysis of the Rock-Eval data it is clear that the second population of data points consists of a mixture of Type II, III and IV kerogen, while population 1 only contains Type III and IV kerogen. Consequently, a mixture of organic matter derived from higher plants and reworked organic matter is found throughout the section of Boom Clay. However, in the Putte Member an additional input of autochthonous marine organic matter is found which may vary between 30 and 50 wt% of the non-dead carbon fraction (Van Geet, 2002). The results of Van Geet (2002) are comparable to those of Laenen (1997), who argued that type II kerogen was mainly found in sections with a high TOC content. However, as pointed out by both Laenen (1997) and Vandenbergh (1978), these sections also displayed a higher input of terrestrial organic matter. The data indicate a low and homogeneous maturity of the kerogen throughout the stratigraphical section.

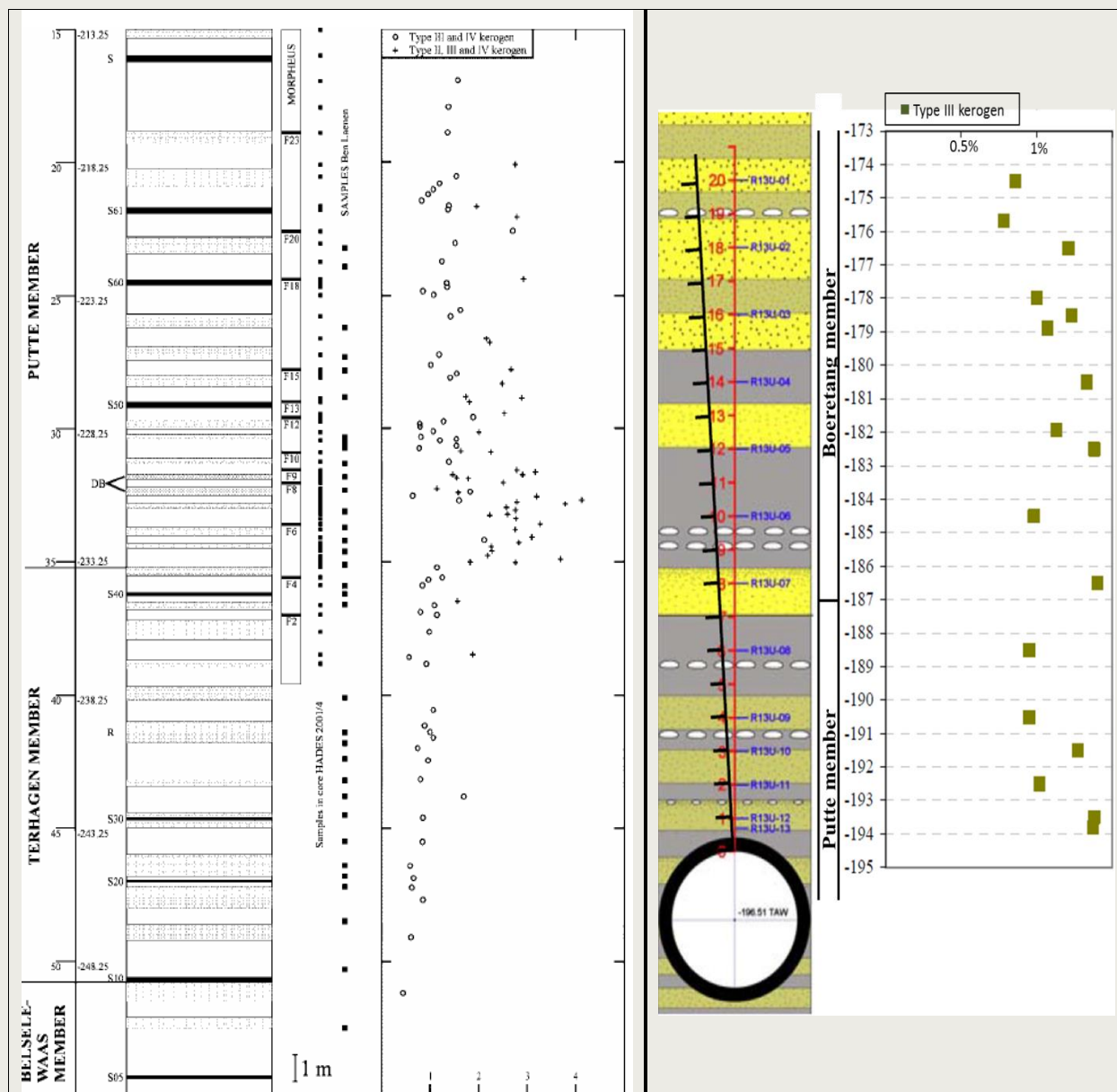


Figure 2-4: Stratigraphical distribution of kerogen types based on a cut-off value of the HI of 130 mg HC/g TOC, including data from Laenen (1997) and Van Geet (2002) on the left and De Craen (2005) on the right

2.2.5.2 Leachable organic Matter

In this report, we define leachable organic matter as the fraction of organic matter that can be soluble in Boom Clay pore water but is not retrieved by the means of piezometers either because it is sorbed on the BC solid or because it is trapped in the pores due to filtration. This fraction of OM can be leached from the powdered rock. The composition of the leaching solution can be variable to account for changes in the pore water chemistry. It should be acknowledged that in the physico-chemical conditions found at the Mol site this fraction of OM does not participate to the colloid-facilitated transport since it is immobile. However, changes in the conditions and/or perturbations could degrade the leachable OM species (oxidation, heat...) or impact their solubility (ionic strength, pH...) and by size reduction and/or modification of their chemical properties, turn them to mobile species.

In this section, we will expose the concentration and properties of the leachable OM pool as it is found in the BC at the Mol Site. A closer look at its possible evolution in other physico-chemical conditions will be given in the **section 2.2.5.4.2**.

The concentration, the size distribution and the reactivity of leachable OM in the BC was the subject of many researches spread over the years. To be representative of the conditions found at the Mol Site, the leachable OM pool was generally extracted in Synthetic Boom Clay Water (SBCW) that is a proxy of the *in situ* pore water. The composition of SBCW is detailed in **Table 2-3**. Leaching experiments were performed at various solid-liquid ratios and from several BC rock samples. The leaching experiments consist in mixing BC rock powder with SBCW and shake the suspension until equilibrium is reached. The suspension which contains the leachable OM is then centrifuged and the supernatant filtered (0.45 µm) and analysed.

Na	330
K	13
Ca	2 (saturated with calcite)
Mg	2.6
Fe	1.3
B	7.5
Cl	27.3
SO ₄ ²⁻	0.2
F	3.6

Table 2-3: Composition of the Synthetic Boom Clay Water
(concentrations given in mg/L)

2.2.5.2.1 Concentration of leachable OM in BC at Mol Site

The concentration of leachable OM in Boom Clay was measured either after one leaching event or by the means of sequential leaching. Sequential leaching experiments allow, to a certain extent, to estimate the total amount of leachable OM in BC. On the other hand, one leaching event allows to quickly access the variability along the BC layer and to better understand which parameters control the concentration of the leachable OM pool.

The sequential leaching experiments performed by Maes et al. (2003) at different solid-liquid ratios showed a characteristic dilution pattern (**Figure 2-5**). The latter was interpreted by the authors as showing the presence of an easily soluble organic matter pool, and an organic matter fraction for which the release is dictated by an adsorption/distribution mechanism. Durce et al. (2015) relied on sequential leaching to extrapolate the total amount of leachable OM using the model for the accumulation of a product of a first order (Qualls, 2000). On the two samples they investigated, they showed that the amount of leachable OM was correlated to the TOC content of the BC sample and that leachable OM represented about 12 % of the TOC.

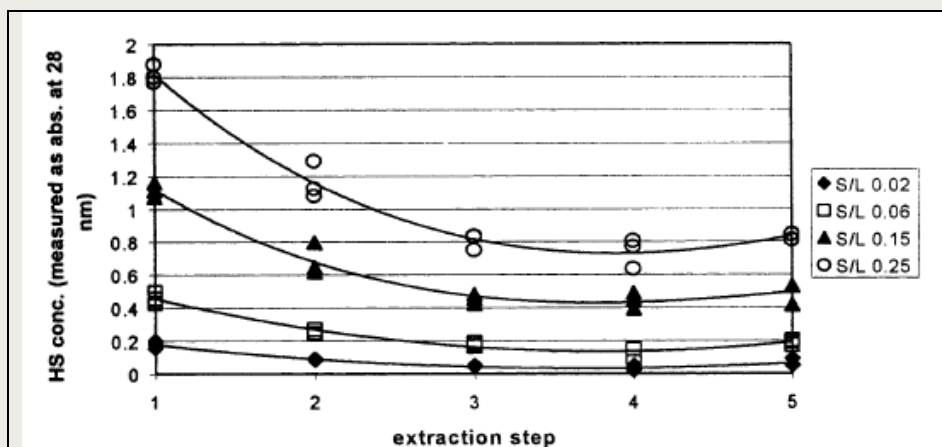


Figure 2-5: DOM (HS) concentration (measured as absorbance at 280 nm) per extraction step, per solid-liquid (S/L) ratio (expressed in kg/l) and corresponding regression lines (Maes et al., 2003)

The strong correlation between TOC content and concentration of leached OM was validated with one leaching event. The TOC of BC samples taken at various positions in the BC layer and the amount of dissolved organic carbon leached in SBCW was found to be highly correlated. In addition, Durce et al. (2015) evidenced that besides the TOC content, the concentration of leachable OM released in SBCW was also dependent on the hydrogen index (HI) of the kerogen, the bulk porosity and the mineralogical composition. The amount of leachable OM normalised over the TOC content of each BC sample and released after one or several leaching event in SBCW for a solid-liquid ratio of 0.15-0.22 kg/L is presented in **Figure 2-6**. It can be seen that the fraction of TOC released in SBCW is quite constant along the BC layer which shows that leachable OM is most likely released by SOM.

It should be brought to the reader's attention that the samples collected do not cover the complete Boom Clay layer. The latter is subdivided into four main stratigraphic units which are, from the basis to the top: the Belsele-Waas Member, the Terhagen Member, the Putte Member and the Boeretang Member (**Figure 2-4**). The Belsele-Waas Member was not covered by the leaching campaign.

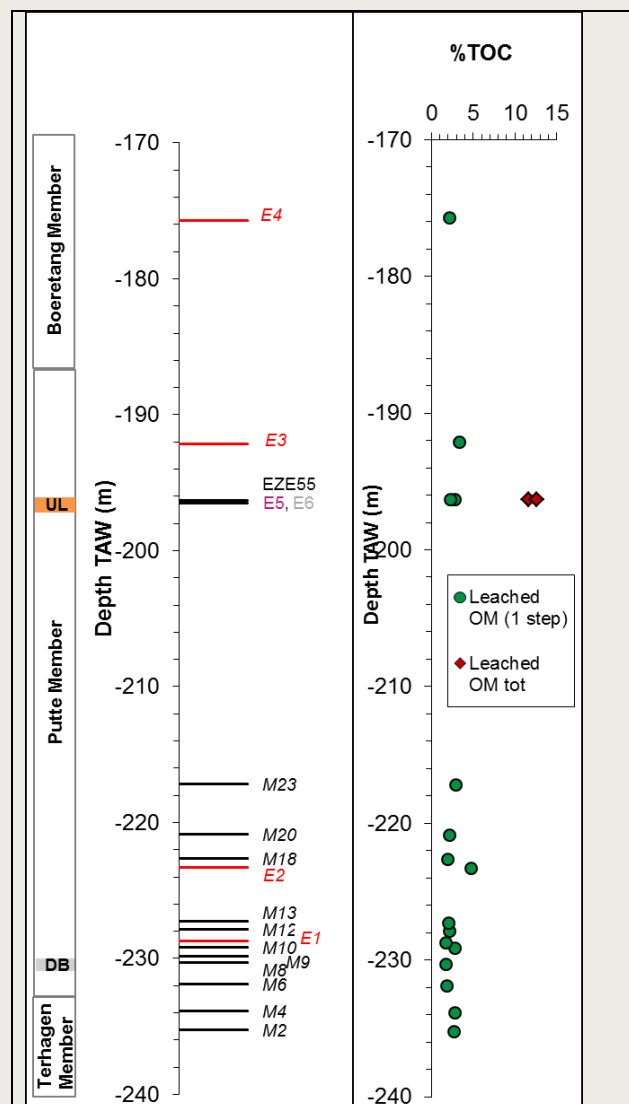


Figure 2-6: Depth profile of the amount of OM leached in SBCW normalized over the TOC content of the BC rock samples. Solid-liquid ratio= 0.15-0.22 kg/L. Data on BC rock samples M2 to M23 were extracted from De Craen et al., (2004). Samples E1 to E6 were collected and leached by Durce et al. (2015)

2.2.5.2.2 Size/Molecular Weight (MW) distribution of leachable OM

The size/MW distribution of leachable OM was measured by size exclusion chromatography by Durce et al. (2015). The authors showed that the size/MW distribution of the leachable OM pool was dominated by high MW organic species (> 50 kDa). Over the sequential leaching experiments they performed on two BC rock samples they measured the average size/MW distribution reported in **Table 2-4**. The results they obtained after one leaching event confirm the predominance of large organic structure over the BC layer but also reveal that the size/MW distribution of the leachable OM might depend on the mineralogical composition of BC. Due to the coupled sorption and filtration phenomenon, clay minerals preserve preferentially the OM species larger than 1 kDa while an increase of silt content favours the transport of a part of the large DOM species > 20 kDa. Hence, silty regions would have lower content of leachable OM > 20 kDa than clay-rich regions.

	MW < 1kDa R _H < 0.3nm	MW: 1-20 kDa R _H : 0.3-2.8 nm	MW: 20-50 kDa R _H : 2.8-5.3 nm	MW: 50 kDa- 0.45µm R _H : 5.3-450 nm
DOC%	9	7	6	78

Table 2-4: Size/MW distribution of leachable OM released in SBCW in 9-10 leaching events. S/L ratio=0.22 kg/L. Based on SEC-UV280 measurements and specific UV absorbance at 280 nm measurements (Durge et al., 2015)

2.2.5.2.3 Reactivity of leachable OM and humic acid fraction extracted from leachable OM

DOM is a heterogeneous mixture composed of small to large macromolecules that display various functional groups such as carboxyl (COOH), phenol (OH) or nitrogen-containing functional groups. It is common to divide DOM in two fractions: the humic and fulvic acids (HA and FA). These fractions are characterized by different solubility, the fulvic acids being soluble over all the range of pH while the humic acids precipitate at pH < 2. Many of the chemical properties of dissolved organic matter (DOM) in relation to cation binding and charge development depend on the type and quantity of functional groups born by the organic molecules (Kim et al., 1991a; Lumsdon and Fraser, 2005; Stevenson, 1994). Therefore, numerous attempts have been made to elucidate the amount of functional groups in leachable OM and in the humic acid (HA) fraction extracted from it.

Within the EC project TRANCOM-Clay (Trancom-Clay, 2000), potentiometric titrations were used to determine the functional group capacity under in situ pH conditions (pH 8.2 - 8.3) of leachable OM (referred to as 'Boom Clay Extract'). Dierckx *et al.* (1997) describe also the results of potentiometric titrations on the humic acid fractions of leachable OM extracted with five different leaching procedures. **Table 2-5** gives a brief overview of the procedures. All extracts were then subjected to a purification procedure in which the humic acid fraction was precipitated by addition of HCl and dialysed to salt-free conditions.

Leach test	Extraction step	Code
1	Extraction with 1.35×10^{-2} M NaHCO ₃	BC(1)
2a	Prior freeze drying	BC(2)
2b	Alkaline extraction of previous residue	BC(3)
2a+2b		
3a	Prior acidification (pH = 3) and redispersion at pH 8.6	BC(4)
3b	Alkaline extraction of previous residue	BC(5)
3a+3b		

Table 2-5: Comparison of the organic matter extraction yields for different leaching conditions (Dierckx et al., 1997)

The cobalthexammine capacity (Maes et al., 1992) of the humic acid fraction of leachable OM extracted with NaHCO₃ (-SBCW) was also determined as a function of pH.

For more information on the titration methodology and the cobalthexammine method, we refer the reader to Bruggeman and De Craen (2012).

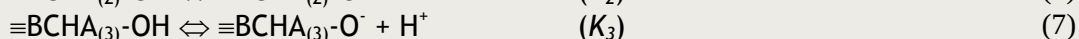
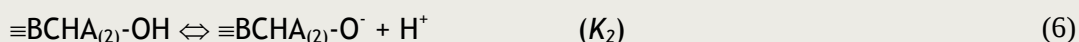
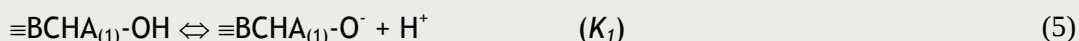
The functional group capacity estimated from the titrations and/or cobalthexammine method on leached OM and on the HA fraction of leached OM at pH 7-8 are reported in **Table 2-6**.

Sample	Capacity (eq/kg)	Method/reference
Leachable OM	1.80	Titration (Trancom-Clay, 2000)
HA fraction of leachable OM (BC1 to BC2)	1.80-2.30	Titration (Dierckx et al., 1997)
HA fraction of leachable OM	2.10	Cobalthexammine method (Maes et al., 1992)

Table 2-6: Functional group capacity at the inflection point in the pH range 7-8

All leachable OM and/or their HA fraction investigated show a constant functional group capacity of about 1.8 to 2.3 eq/kg. It is therefore concluded that the leachable OM is mostly composed of humic acids and that the humic acid fraction of leachable OM is fairly homogeneous. Compared to published values for soil organic matter, the functional group content of Boom Clay humic acids is rather low (Dierckx et al., 1997). This difference can be ascribed to the different nature (soil versus marine biomass) or to diagenetic processes.

The titration curves of the extracted humic acid fractions from leachable OM were modelled using the free ligand approach and surface complexation with electrostatic correction (Trancom-Clay, 2000). More information on these approaches is given in **section 4.2.1.1** and can also be found in Bruggeman and De Craen (2012) and in Trancom-Clay (2000). Three different functional groups were distinguished: two accounting for carboxylic groups and one for a phenolic group. The following deprotonation reactions were considered:



where “BCHA” represents Boom Clay Humic Acid.

Both, the different constants corresponding to reactions with groups $\equiv\text{BCHA}_{(1)}\text{-OH}$, $\equiv\text{BCHA}_{(2)}\text{-OH}$ and $\equiv\text{BCHA}_{(3)}\text{-OH}$, as well as the functional group concentrations, were fitted. The fitted parameters obtained with surface complexation and free ligand approaches are reported in **Table 2-7**. The two approaches give comparable results and a total functional group capacity (or proton exchange capacity) of 2 eq/kg.

	Leachable OM HA	
	Surface Compl.	Free ligand
Log(K_1)	-3.3	-4.1
Log(K_2)	-5.1	-6.2
Log(K_3)	-7.7	-9.0
Q_1 (eq/kg)	1.1	1.1
Q_2 (eq/kg)	0.5	0.5
Q_3 (eq/kg)	0.4	0.4
Q_T (eq/kg)	2.0	2.0

Table 2-7. Parameter configuration after data fitting of leachable OM humic acid (HA) acid-base titration. K_1 , K_2 and K_3 are the deprotonation constants, all determined within ± 0.05 log unit. Q_1 , Q_2 and Q_3 are the proton exchange capacities corresponding to group 1, 2 and 3 respectively. Q_T is the total proton exchange capacity.

The leachable OM fraction in BC at the Mol site conditions represents around 12% of the total organic content of the BC, is mainly composed (80%) of large macromolecules/assemblies (>50 kDa) which are essentially humic acids and display a low functional group capacity (~2 eq/kg).

2.2.5.3 Mobile DOM

Contrary to the leachable fraction, the mobile OM fraction, dissolved in the pore water, is expected to be mobile along the BC layer in the Mol site conditions. It is assumed that the pore waters collected by the piezometers installed directly in the BC layer contain mostly the mobile DOM. This assumption was validated by transport experiments (through-diffusion or percolation set-ups) in which mobile DOM was 'pushed out' by SBCW. The size distribution of the OM in the outlet of these experiments was indeed comparable to the size distribution of the DOM found in the piezometer pore waters.

In order to assess the role played by mobile DOM in the colloid facilitated transport of radionuclides, it is essential to first determine: 1/ the concentration of mobile DOM, 2/ its size distribution, 3/ its composition, 4/ its reactivity and 5/ its stability. In this section we will focus on the first four points, the stability of mobile DOM with respect to pore water chemistry will be discussed afterwards in **section 2.2.5.4.2**.

2.2.5.3.1 Concentration of mobile DOM

Several piezometers are installed in the HADES underground facility. They allow sampling pore water at different points of the BC layer. A schematic view of the most used piezometers is presented in **Figure 2-7**.

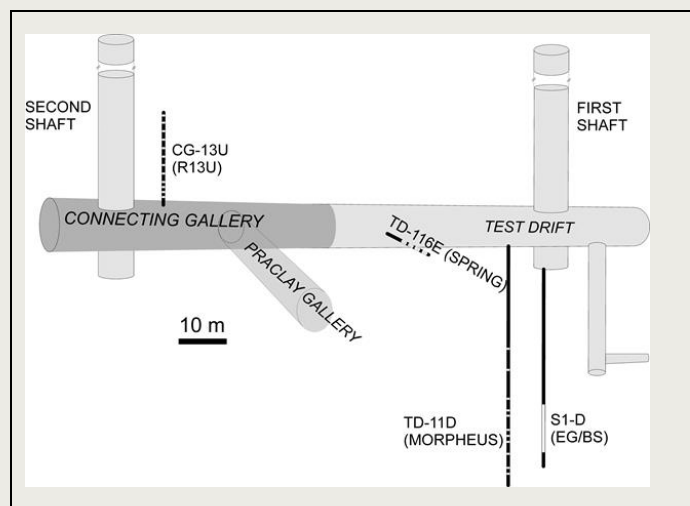


Figure 2-7: Schematic representation of the position of the piezometers in the HADES underground facility

The concentration of mobile DOM collected along the BC layer by these piezometers was reported by Durce et al. (2015) and is presented in **Figure 2-8**. The piezometers do not cover the Belsele-Waas Member and only partly the Terhagen Member.

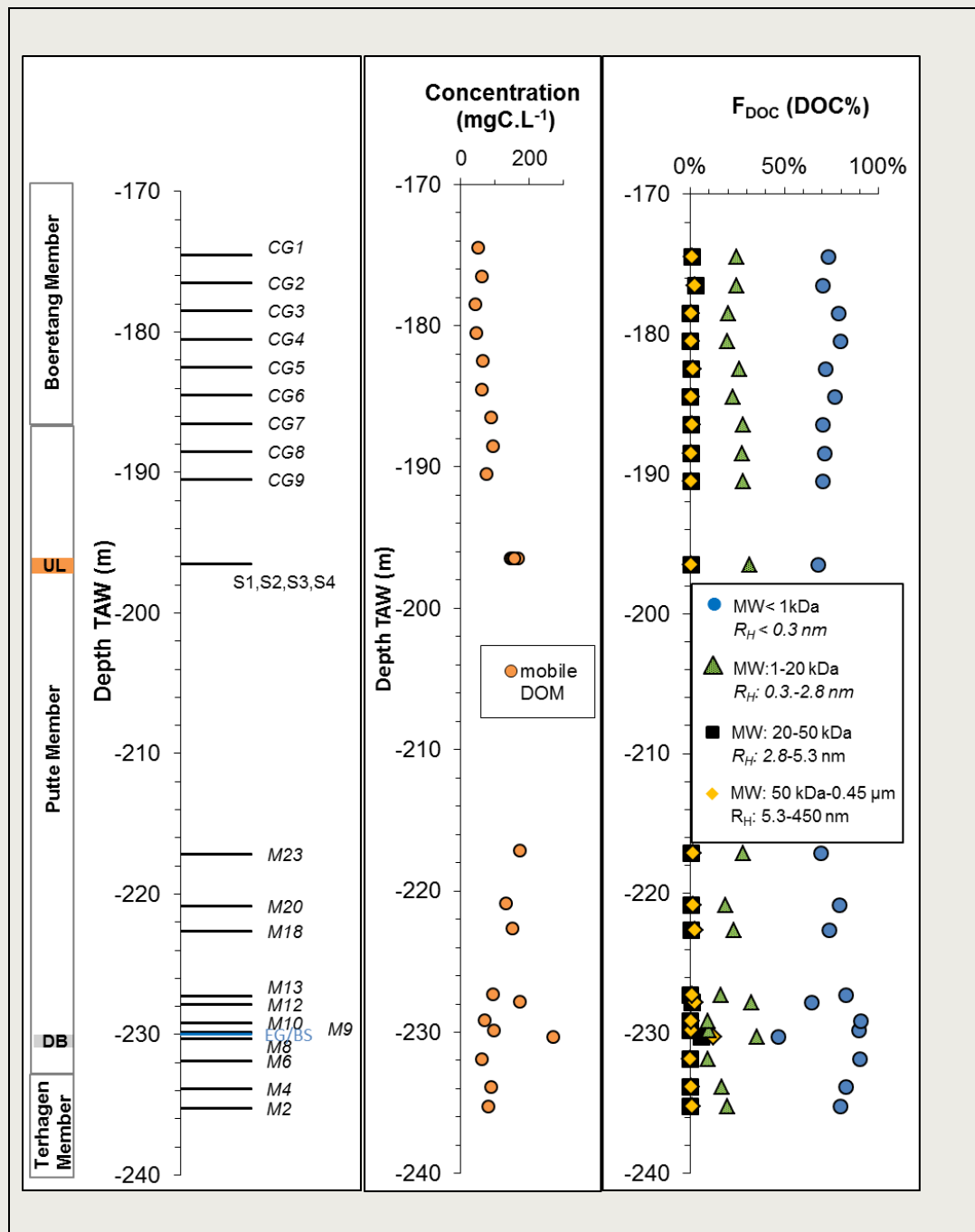


Figure 2-8: Depth Profile showing the vertical distribution of mobile DOM concentration measured by TOC analyser (in the middle) and Hydrodynamic Radius (R_H)/Molecular Weight (MW) distribution (on the right) measured by SEC in the MORPHEUS (M2-M23), SPRING (S1 to S4), CG13-U (CG1-CG9) and EG/BS (in blue) pore waters after filtration at 0.45 μ m. DB = double band. (Durge et al., 2015)

The mobile DOM concentration (Figure 2-8) measured in the pore waters is scattered over the Boom formation. At a same level, it remains quite constant with an average of 155 ± 10 mgC.L⁻¹ over the SPRING piezometer. But it varies widely along the BC layer from 43 to 270 mgC.L⁻¹. The lowest concentrations are measured in the Boeretang and Terhagen Members while the mobile DOM concentration seems to increase in the Putte Member. The highest value is measured in the so-called Double Band (sample M8). The Double Band corresponds to two thin, relatively sandy layers at the bottom of the Putte Member which display significantly higher hydraulic conductivity compared to the surrounding layers.

Considering the bulk porosity and the bulk density (values not reported), the mobile DOM represents in average only 0.15 ± 0.8 TOC%. Durce et al. (2015) showed that with a Pearson's coefficient of 0.34, the variability in mobile DOM content is not strongly correlated to the variability of TOC content in BC. Yet it is still partly related to the nature of the kerogen. A Pearson's coefficient between HI and mobile DOM content of 0.49 was determined.

This shows that mobile DOM is most likely generated, directly or indirectly, by the SOM pool but that its concentration depends on other parameters than only the TOC content.

2.2.5.3.2 Size/molecular weight distribution of mobile DOM

The size distribution of mobile DOM in EG/BS pore water was investigated by Bruggeman et al. (2010) by ultrafiltration and microfiltration technique. The authors showed a bimodal distribution in which molecules/assemblies bigger than 300 kDa were absent (**Figure 2-9**). This distribution was compared to the size distribution of leachable OM (rock+EG/BS and rock+SBCW) which contains molecule of significantly bigger size/MW. Based on the results, a colloid cut-off diameter imposed by the pore structure of the Boom Clay was determined as equivalent to an ultrafiltration at 300 kDa (Pall Microsep Omega, PES membranes) or ~ 35 nm.

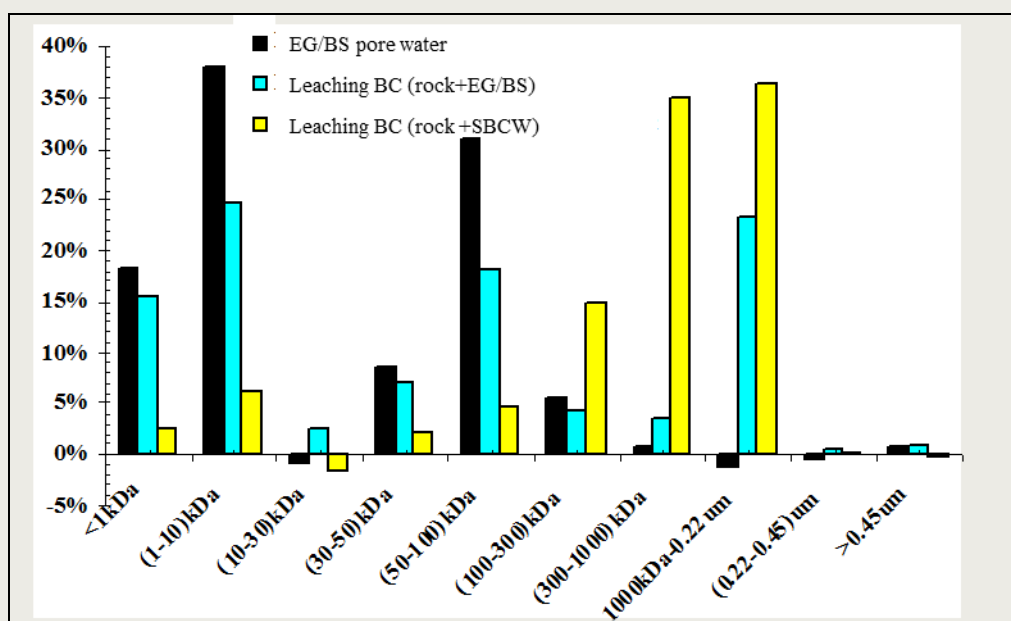


Figure 2-9: Size distribution of three DOM-containing solutions as determined by ultrafiltration (Pall Microsep Omega, PES membrane) and microfiltration (PVDF membrane) at various cut-offs (Bruggeman et al., 2010).

More recently, Durce et al. (2015) investigated the size/MW distribution of mobile DOM collected with the piezometers presented in **Figure 2-7** by the means of size exclusion chromatography (SEC) and UV280 detection. The size/MW distributions were calculated from the SEC/UV280 chromatograms using the calibration established beforehand with PSS standards, EDTA and arsenazo and the specific UV280 absorbance (SUVA₂₈₀) determined for different MW fractions of DOM such as:

$$SUVA_{280,i} = 100 \times \frac{UV280_i}{DOC_i} \quad (8)$$

$$F_{DOC,i} = \frac{A_{UV280,i}}{A_{UV280,tot} \times SUVA_{280,i}} \quad (9)$$

Where $SUVA_{280,i}$ is the specific UV280 absorbance of the mobile DOM fraction i , $UV280_i$ and DOC_i are the UV280 absorbance and the DOC content of the fraction i , respectively. $F_{DOC,i}$ corresponds to the relative concentration of the fraction i (DOC%) in the mobile DOM pool, $A_{UV280,i}$ corresponds to peak area of the SEC chromatogram of the fraction i and $A_{UV280,tot}$ corresponds to the total area of the SEC chromatogram.

The SEC results (**Figure 2-8**, on the right) point out that the composition of mobile DOM is dominated by organic species smaller than 20 kDa ($R_H = 2.8$ nm) which represent from 82 to 99 % of the total mobile DOM. The samples M8 and EG/BS, taken at the level of the Double Band, are notable exceptions in the BC formation and are composed in average of 49 DOC% of organic species < 1 kDa ($R_H = 0.3$ nm) and 17 DOC% of larger species (20 kDa -0.45µm, $R_H : 2.8-450$ nm). The coarser granulometry of this particular horizon compared to the rest of the BC portion investigated reduces both the filtration and the sorption by BC of DOM that is consequently more mobile in this special environment.

The polydispersity of DOM in EG/BS measured by SEC is consistent with the results obtained by ultrafiltration (**Figure 2-9**). However, with ultrafiltration the concentration of large organic species (>30 kDa) is higher than measured in SEC. This discrepancy shows the existence of membrane fouling or the accumulation/adsorption of DOM on the surface of the ultrafiltration membrane. Yet, both techniques reveal the strong variation in the size/MW distribution between mobile DOM and leachable OM highlighting the phenomenon of natural filtration and possible preferential sorption of large OM molecules/assemblies. These coupled processes lead to the immobilisation of large DOM species that are in consequence absent from the sampled pore waters.

Based on the data obtained along the BC layer, Durce et al. (2015) refined the colloidal filtration cut-off down to a MW around 20 kDa which would correspond to a hydrodynamic radius (R_H) around 2.8 nm. Over this cut-off species are assumed to be filtered by the rock and immobilised. This parameter characterises the transport at a global scale but one should keep in mind that some shifts may occur at a local level with mineralogical changes as it is observed in the region of the Double Band.

2.2.5.3.3 Composition and reactivity of mobile DOM

Mobile DOM is a strong actor in the facilitated-colloidal transport of radionuclides (RN) within the BC layer. To better understand and to characterise the complexation of radionuclides with mobile DOM, the composition and reactivity of the mobile DOM was investigated over the years by a combination of several analytical tools. We will present in the following the most relevant and conclusive results.

2.2.5.3.3.1 Elemental composition

Within the EC project MIRAGE-II, member laboratories of Complexation and Colloid Club (COCO-Club) launched a joint action to characterise selected humic and fulvic acids for their elemental compositions, inorganic impurities, spectroscopic properties, size distributions and proton exchange capacities (Kim et al., 1991a). Among these were humic and fulvic acids extracted and purified from EG/BS pore water. Humic acids were isolated by acid precipitation and centrifugation, while fulvic acids were obtained by solid phase extraction on a XAD-8 column. Both fractions were further purified by acid washing and NaF treatment. The humic acid was used in protonated form (Boom-Clay-HA (H⁺)) while the fulvic acid was kept in its Na-form (Boom-Clay-Fa (Na⁺)) due its small quantity. Elemental analyses were performed on both acids and the results are reported in **Table 2-8**. Based on the H/C and O/C ratio, BC mobile DOM appears to be mainly composed of aromatic and aliphatic structures while carbohydrate content is lower.

Element (%)	Boom-Clay-HA (H ⁺)	Boom-Clay-FA (Na ⁺)
C	62.4	56.8
H	6.1	5.5
N	2.9	1.8
O	27.0	34.7
S	1.7	1.2
H/C	1.16	1.16
O/C	0.32	0.46

Table 2-8: Elemental composition of humic and fulvic acids extracted from EG/BS pore water normalised to 100% and H/C and O/C ratio (KIM et al., 1991a)

2.2.5.3.3.2 Molecular characterisation

During her PhD, Blanchart (2011) sampled different piezometers in order to study the variability of DOM in the pore water surrounding the HADES underground research facility. Four different piezometers were studied: EG/BS, SPRING, N2TD and N2CG (for more information on the piezometers we refer to Blanchart (2011) and De Craen et al. (2004)) and analysed with a multi-technique approach, including 3D-Fluorescence, FTIR, size exclusion chromatography (HPLC-SEC) and pyrolysis-GC/MS. Some of the most important results will be discussed in this report, for more detailed information we refer the reader to Blanchart (2011).

The humic and fulvic acid fractions of EG/BS were determined by acid (pH < 2) precipitation. It appeared that about 58 % of the total DOC belonged to the fulvic acid fraction. This is higher than earlier reported values (70 % HA, 30 % FA) (Trancom-Clay, 2000) but confirms the presence of fulvic acids in the pore waters.

Analysis of the HPLC-SEC and 3D-Fluorescence signals has shown that the DOM signature of the four piezometers is very similar which reveals a relative homogeneity of the mobile DOM over the BC layer.

Molecular analysis of EG/BS piezometer water was performed (Blanchart et al., 2011) by flash pyrolysis - gas chromatography - mass spectrometry (Py-GC-MS). This technique allows analysing the molecules generated at 620 °C (vaporisation through cracking). Before analysis, the lyophilised EG/BS piezometer water sample was methylated (THM-GC-MS) to protect carboxylic and hydroxyl functional groups. The analysis of the pyrogram (**Figure 2-10**) shows that mobile DOM is composed of a ratio around 50:50 of linear and aromatic compounds. The linear compounds correspond to n-alkanes and alcanoic acids. The aromatic compounds are mostly monocyclic hydrocarbure and benzene-dicarboxylic acids. A part of the aromatic compounds is also derived from lignine (methoxybenzene). The observed functional groups are in agreement with the bands identified through FTIR that shows bands corresponding to aliphatic, aromatic and oxygenated organic compounds. The lignine derivates may indicate a terrestrial source for the DOM.

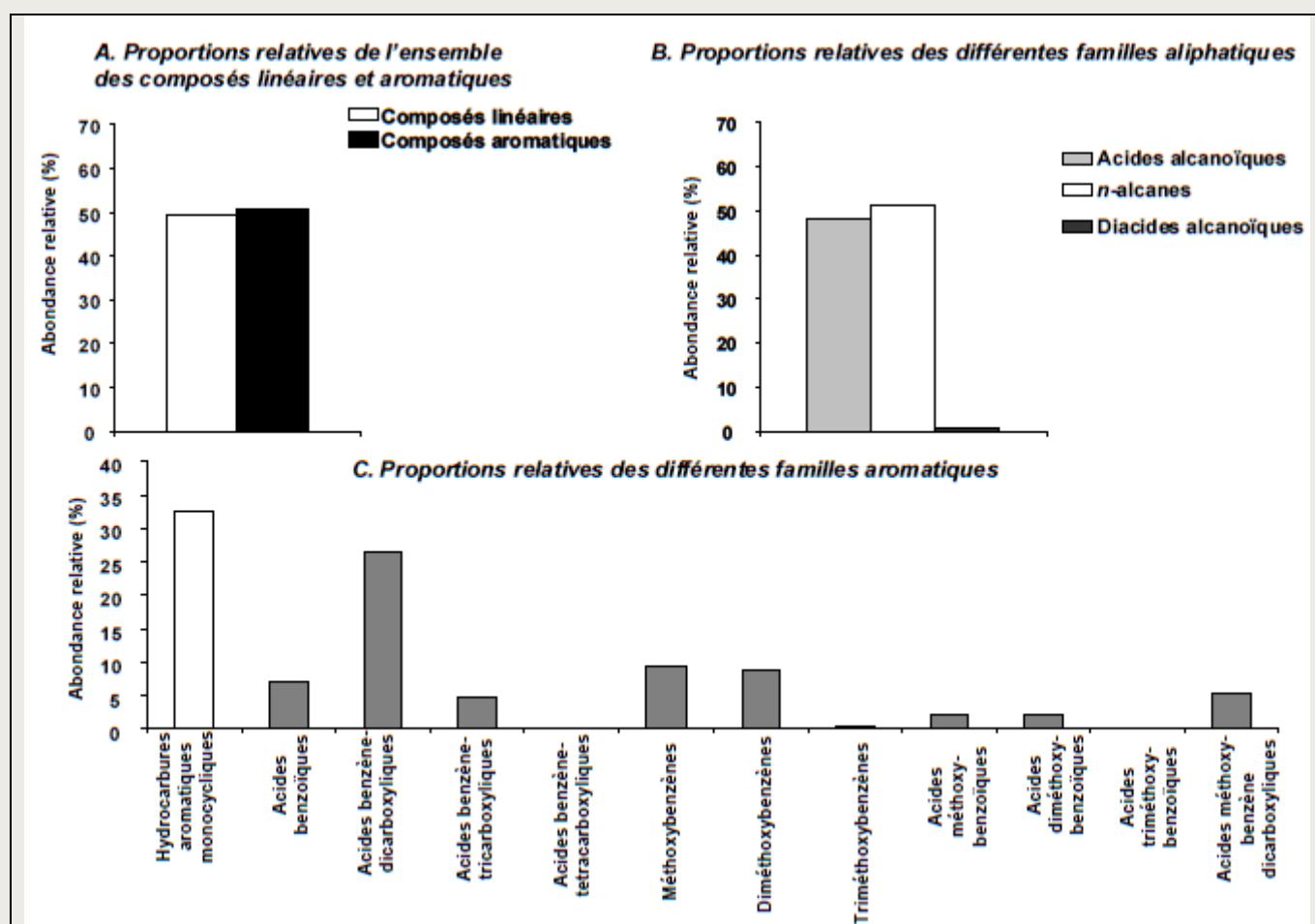


Figure 2-10: THM-GC-MS analysis results of EG/BS water. Relative abundances of A) linear and aromatic compounds, B) different aliphatic families and C) different aromatic families (Blanchart, 2011)

2.2.5.3.3.3 Functional group capacity

In addition to the potentiometric titration performed on leachable OM, numerous studies have been performed on mobile DOM in order to determine its functional group capacity and the protonation constants for the different functional groups (Equation (5) to (7)). More information on the titration methods and titration curves can be found in Trancom-Clay (2000).

The functional group capacity of the mobile DOM in EG/BS water reached values of about 5 to 6 eq/kg. These values are rather high and reflect the presence of fulvic acids in these waters which were mostly absent from leachable OM. Indeed, the titrations of leachable OM and its HA fraction lead to values for the functional group capacity of only 1.8 to 2.3 eq/kg (Table 2-6).

Following the same approach than for the extracted HA fraction of the leachable OM, the deprotonation constants and the concentration of the three functional groups were determined for the HA fraction from EG/BS (Equation (5) to (7)). The values are reported in Table 2-9.

	EG/BS HA		
	Surface compl.	Free ligand	FITEQL fit
$\text{Log}(K_1)$	-3.3	-4.45	-4.45
$\text{Log}(K_2)$	-6.4	-6.2	-6.23
$\text{Log}(K_3)$	-7.8	-9.8	-9.09
Q_1 (eq/kg)	2.8	1.9	2.0
Q_2 (eq/kg)	0.5	0.95	0.75
Q_3 (eq/kg)	0.7	1.15	0.7
Q_T (eq/kg)	4.0	4.0	3.45

Table 2-9: Parameter configuration after data fitting of Boom Clay extracted and porewater humic acid (HA) acid-base titration. K_1 , K_2 and K_3 are the deprotonation constants, all determined within ± 0.05 log unit. Q_1 , Q_2 and Q_3 are the proton exchange capacities corresponding to group 1, 2 and 3 respectively. Q_T is the total proton exchange capacity. The FITEQL fit was obtained with the fitting programme FITEQL, based on a free ligand approach without correction for ionic strength (Trancom-Clay, 2000)

The model confirms the experimental results and shows that with a functional group capacity (or proton exchange capacity) of 4 eq/kg, the mobile DOM is more reactive than the leachable OM and contains most likely more fulvic acids.

Mobile DOM in Mol site condition displays a concentration that varies from 43 to 270 mgC.L^{-1} along the BC layer but presents a relatively homogenous size/MW distribution except in the special feature of the double band. The size/MW of mobile DOM is smaller than 20 kDa (R_H 2.8 nm), value which is assimilated to a colloid filtration cut-off. In terms of reactivity, mobile DOM appears more reactive than leachable OM with a higher functional group capacity around 4 eq/kg. This result highlights the presence of a higher concentration of fulvic acids in mobile DOM than in leachable OM that is mainly composed of humic acids.

Because of its small size, its significant concentration and its relatively high functional group capacity, mobile DOM is expected to be a major actor in colloid facilitated transport in BC in the Mol Site conditions.

2.2.5.4 Role of compaction and ionic strength on the concentration and the size of mobile DOM

In the previous section, we gave a picture of the partitioning of OM as it is in Boom Clay under Mol site conditions. However, this partitioning is not static but dynamic with regards to environmental conditions and is subject to change under perturbations or for different physico-chemical conditions. To assess the role played by OM in colloid-facilitated transport of RN in other location of BC it is therefore necessary to understand which parameters control the concentration and the nature (size, composition) of mobile DOM. In this section, we will discuss two of these parameters: the role of the compaction and the effect of ionic strength. A strong focus will be given to ionic strength as it is expected to have a major influence on the stability of DOM. Nevertheless, it is evident that these parameters are not the only ones impacting the partitioning of OM but they are the most relevant for an extrapolation of the data acquired at Mol site to the conditions met in the Netherlands. For more information on other factors playing a role in the concentration of mobile DOM such as oxidation, heat or alkaline plume, we refer the reader to the report of Bruggeman and De Craen (2012).

2.2.5.4.1 The role of compaction and mineral assembly

As we previously reported, in Boom Clay DOM is divided into a mobile and an immobile pool by a combination of sorption and filtration processes. The filtration of DOM molecules/assembly is controlled by the pore structure of the rock, i.e by the pore size and the pore connectivity, parameters that fix the so-called colloid filtration cut-off. The pore structure of Boom Clay is partly drawn by the minerals present in the rock. Hemes et al. (2011) showed that the pore connectivity is almost exclusively linked to pores within the clay-matrix, i.e. the smaller size pores. The larger pores associated with non-clay grains such as quartz grains, appear to be hardly interconnected. As the pore connectivity controls the pore throat diameter, the clay content would also control the DOM filtration and so the concentration and size of mobile DOM.

We showed in the previous section that the concentration of the mobile DOM was poorly correlated to the TOC content of the BC. Hence, even though mobile DOM is most likely released by the SOM and/or leachable OM pools, its concentration is controlled by additive processes than dissolution/reaction of the SOM/leachable OM pools. Durce et al. (2015) showed that if the concentration of mobile DOM < 1 kDa ($R_H < 0.3$ nm) is partly related to the TOC content and to the hydrogen index (HI) of the kerogen, the concentrations of species > 1 kDa ($R_H > 0.3$ nm) in pore waters are rather governed by the mineralogy of the rock. The clay content and the concentration of all the R_H /MW fractions are negatively correlated. Clay minerals filter and sorb OM which reduces the concentration of mobile DOM in pore waters. These two processes have more influence on the concentration of species > 1 kDa ($R_H > 0.3$ nm) that are more sensitive to filtration and sorption on clay. Hence, the mineral assembly plays a major role in the concentration of mobile DOM and on the value of the colloid filtration cut-off by controlling the sorption/desorption equilibrium and delimiting the pore network of BC.

On the other hand, compaction is also influencing the pore network by reducing the pore size. Consequently, one might expect that higher compaction degree would lead to lower concentration and size of mobile DOM by reducing the colloid filtration cut-off. Such an effect was observed by squeezing experiments performed on BC rock samples (Van Geet, 2004). Pore waters retrieved by squeezing contained much lower concentration of DOM than piezometer pore water sampled at the same level in the Boom Clay layer (Table 2-10). The compared squeezing/piezometers values obtained on samples from the

MORPHEUS piezometer show that in average 50 % of mobile DOM is trapped in the pore network in the squeezing tests. Unfortunately, the size/MW distribution of the squeezed DOM was not measured.

	F2	F4	F6	F8	F9	F10	F12	F13	F15	F18	F20	F23
Squeezing (mgC/L)	43	50	43	82	70	79	105	73	41	74	54	89
MORPHEUS pore waters (mgC/L)	101	136	99	216	121	119	123	119	197	109	128	265

Table 2-10: TOC measurements of the pore water at 12 different levels within the Boom Clay at the corresponding depths of the MORPHEUS piezometer (**Figure 2-6**). DOC of the pore water is analysed by squeezing of a clay core or in situ sampling by the MORPHEUS piezometer (Van Geet, 2004).

2.2.5.4.2 The role of ionic strength

The pH and ionic strength strongly influence the stability and the structure of DOM. On the one hand, the ionic strength and the pH regulate the charges borne by the functional groups present on the DOM structure. On the other hand, the ionic strength controls the hydration of the DOM macromolecules/assemblies, and the pH controls the strength of the hydrophobic interactions and hydrogen bonds. Lowering the pH or increasing the ionic strength was observed to result either in a reduction of the DOM size most likely by compaction of the DOM macromolecules/ assemblies (Baalousha et al., 2006; Hosse and Wilkinson, 2001; Pédrot et al., 2010) or an aggregation (Baalousha et al., 2006; Kipton et al., 1992; Wang et al., 2013). The aggregation increases the apparent size of DOM which might then be converted into particulate OM, thus reducing the organic carbon content in solution. The aggregation mechanism is dependent on pH and IS but also on the nature of the counter-ion (Kipton et al., 1992; Wall and Choppin, 2003; Wang et al., 2013) and on the nature and concentration of the considered DOM species (Alberts et al., 2004; Ephraim et al., 1995; Palmer and von Wandruszka, 2001).

The effect of ionic strength and cationic composition on the mobile DOM and its released fraction from BC rock was recently investigated by (Durge et al., 2016).

On a first set of experiments, two mobile DOM solution, i.e EG/BS and SPRING pore water solutions, and one leachable OM solution were mixed with various concentrations of CaCl_2 and NaCl. The mixtures were agitated until equilibrium was reached. The suspensions were then centrifuged and the supernatants analysed by TOC analyser, SEC-UV280 and UV-Vis spectroscopy after filtration at 0.45 μm . The preparation, agitation of the suspensions and the collection of the supernatants were performed in a glovebox saturated with a mix 0.4% ppm CO_2/Ar .

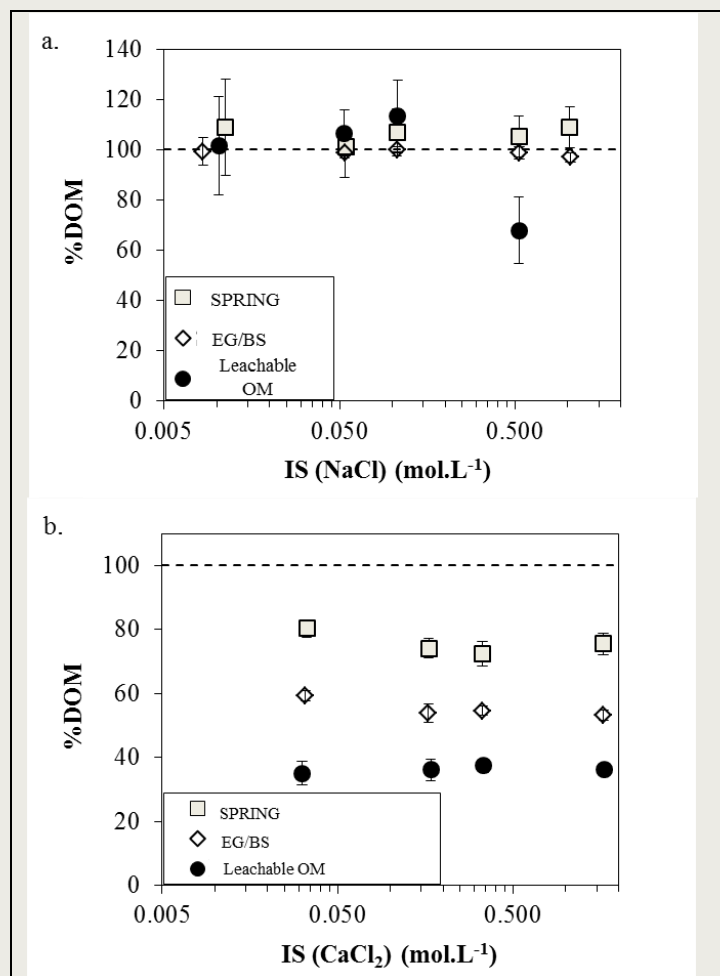


Figure 2-11: Evolution of DOM concentration in SPRING, EG/BS and leachable OM as a function of ionic strength in a. NaCl and b. CaCl₂. DOM content is given as percentage of the initial DOM content in each sample that is reported as 100 % with the dashed lines. The errors bars correspond to the standard deviations of DOC measurements (Durge et al., 2016)

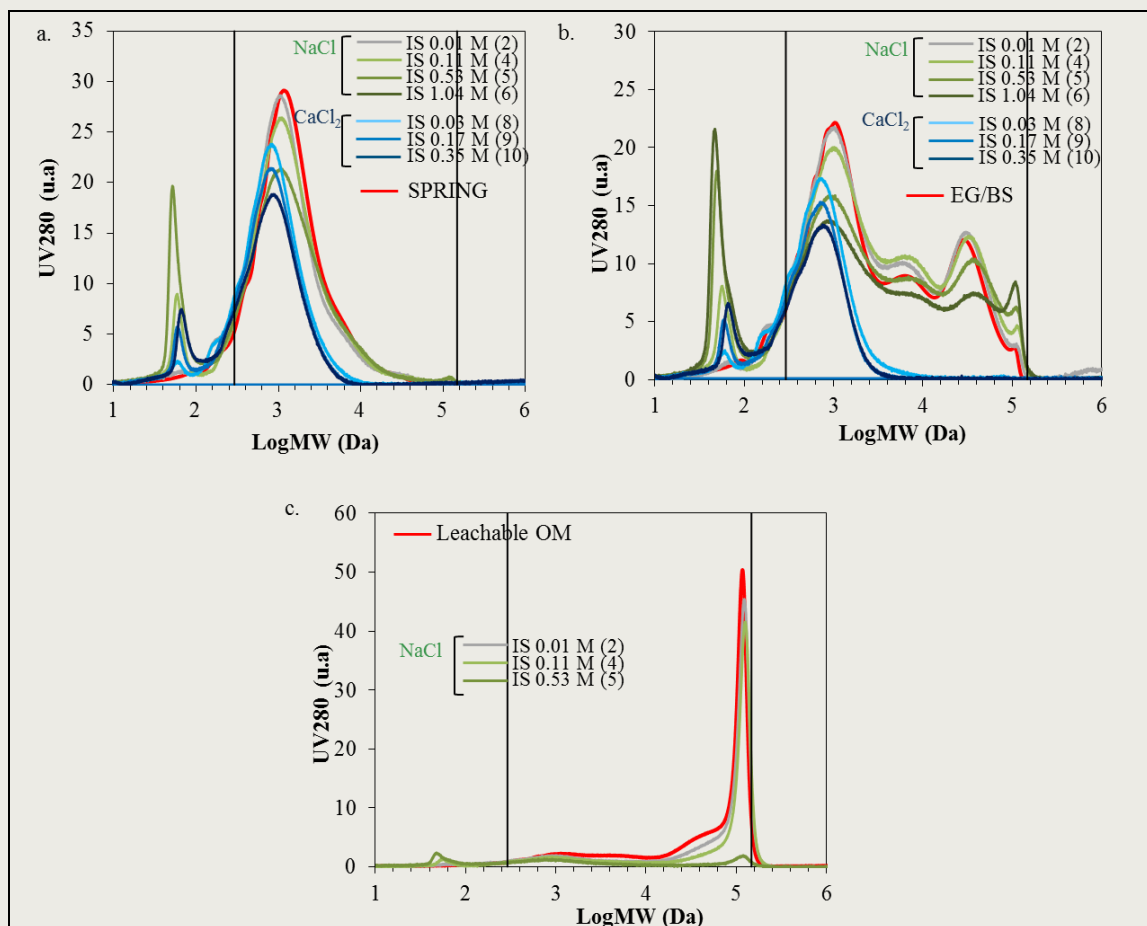


Figure 2-12: MW distribution as a function of ionic strength in NaCl and CaCl₂ measured by size exclusion chromatography with UV280 detection. MW are calculated based on calibration with polystyrene sulfonate standard, EDTA and arsenazo a) SPRING, b) EG/BS and c) leachable OM. The black lines delimit the calibration domain (Durge et al., 2016)

It is shown that in NaCl, an increase of ionic strength does not affect the concentration of mobile DOM neither in EG/BS nor in SPRING (Figure 2-11 a). However, 32 % of the leachable OM precipitates in NaCl 0.53 mol.L⁻¹. This difference between the three solutions is attributed to a molecular-weight (MW) dependent sensitivity of DOM to ionic strength. In other words, the high MW species present in leachable OM aggregate more easily which leads to their 'precipitation', i.e removal from the solution. This is evidenced in Figure 2-12 that shows the evolution of the MW distribution as a function of ionic strength for the three DOM solutions. As it can be observed in this figure, though mobile DOM precipitates neither in SPRING nor in EG/BS, its MW distribution is affected by an increase of NaCl concentration. In both samples, a peak appears at MW < 0.5 kDa from ionic strength of 0.11 mol.L⁻¹ (Figure 2-12 a,b) and its area increases with higher NaCl concentrations. On the contrary the concentration of species with MW comprised between 0.5 and 2 kDa decreases. They most likely compact or dissociate at higher ionic strength which shifts them to lower MW. On the other hand, larger MW species in EG/BS (20-80 kDa) see their size increasing with NaCl and by aggregation transfer to the > 80 kDa fraction. An increase of NaCl leads therefore to two phenomena: a compaction or dissociation of the low MW species and an aggregation and possibly precipitation of the high MW species.

In presence of Ca²⁺ the aggregation of DOM species is largely favoured in comparison to Na⁺. This aggregation leads to the precipitation of 20 %, 41 % and 65 % of DOM initially present in SPRING, EG/BS and leachable OM at ionic strength of 0.03 mol.L⁻¹ (Figure 2-11b). A slight decrease in DOM concentration is still observed from ionic strength of 0.03 mol.L⁻¹ to

0.17 mol.L⁻¹. Higher concentration of CaCl₂ does not remove more DOM from the solution and in the three samples at ionic strength ≥ 0.17 mol.L⁻¹ the total concentration of DOM remains constant. From this threshold, all the DOM species sensitive to aggregation are precipitated and only small species subjected mainly to compaction/dissociation remain in solution.

The strong aggregation totally removes species > 20 kDa and a large part of 0.5-20 kDa (Figure 2-12). In parallel, the peak around 50 Da visible on the chromatograms of both SPRING and EG/BS increases with ionic strength (Figure 2-12). Hence, once the aggregation is "completed", the compaction/dissociation of species between 0.5 and 20 kDa becomes predominant and reduces further the size of DOM down to 2 kDa in 0.1 mol.L⁻¹ CaCl₂ (ionic strength = 0.3 mol.L⁻¹).

In both NaCl and CaCl₂, the loss of DOM by aggregation/precipitation was observed to result in a loss of the SUVA₂₈₀ (Equation (8)) which is assumed to be representative of the degree of aromaticity of OM (Chin et al., 1994; Chin et al., 1998b; Pédrot et al., 2010). Hence, aggregation/precipitation leads to the loss of the large DOM molecules/assemblies that contain most of the aromaticity of DOM.

In pure solution, both compaction or dissociation and aggregation/precipitation of DOM were observed with an increase of ionic strength. A second set of experiment was performed to determine to which extent, these two processes impact the OM partitioning in Boom Clay. These experiments consist in leaching experiments in which a BC powder is suspended in various electrolytes (UP water, SBCW, NaCl and CaCl₂) and the amount, size distribution and the spectral parameters of the DOM released is followed.

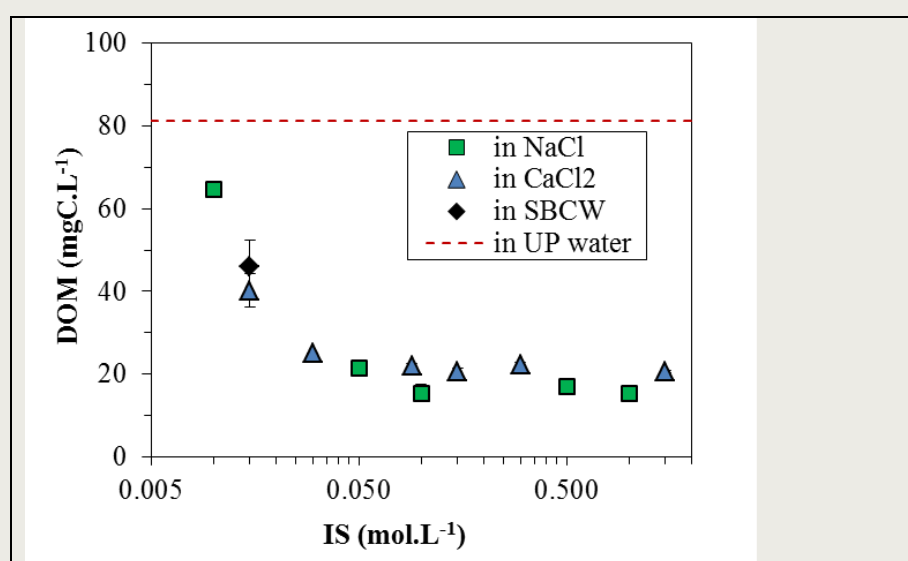


Figure 2-13: Evolution with the ionic strength and the nature of the electrolyte of the DOM content released in solution. UP water electrolyte is given as a reference (ionic strength=0)

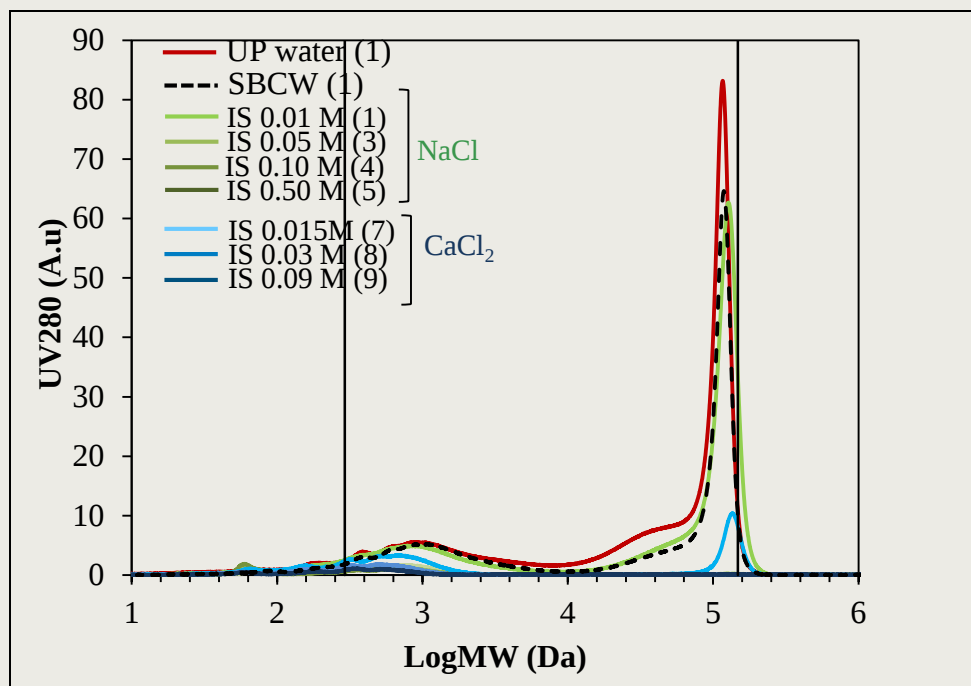


Figure 2-14: MW distribution of DOM released from BC in UP water, SBCW and in various IS of NaCl, and CaCl₂. Measured by size exclusion chromatography with UV280 detection. The black lines delimit the calibration domain

In ultrapure water and for a solid-liquid ratio of 0.25 L.kg⁻¹, the BC sample releases an average of 80 mgC.L⁻¹ (**Figure 2-13**). The amount of DOM released by the solid decreases exponentially in the three other electrolytes investigated, i.e. NaCl, SBCW and CaCl₂ up to an ionic strength of 0.03-0.05 mol.L⁻¹ where it stabilises at a concentration of 20 ± 3 mgC.L⁻¹ in NaCl and CaCl₂. At ionic strength < 0.03-0.05 mol.L⁻¹, the concentration of DOM released in solution, *i.e.* DOM solubility, is slightly higher in presence of Na⁺ than Ca²⁺. Indeed, at a same ionic strength of 0.015 mol.L⁻¹ more OM is soluble in SBCW that contains mostly NaHCO₃ than in CaCl₂. However at higher ionic strength, no difference is noticed between NaCl and CaCl₂ and the concentration of DOM released in solution remains constant. This is in agreement with the plateau observed in pure solution when DOM samples were mixed with Ca²⁺ (**Figure 2-11 b**). Hence, from 0.03-0.05 mol.L⁻¹, aggregation-sensitive species are not soluble anymore and are released in solution only species that do not aggregate. As it was observed in pure solution, the reduction of DOM concentration was observed to be concomitant with the reduction of the aromaticity of the DOM species.

The SEC chromatograms (**Figure 2-14**) show that both the nature of the electrolyte and its ionic strength impact the size distribution of the released species. At the same ionic strength of 0.015 mol.L⁻¹, 6 times more >80 kDa species is released in SBCW than in CaCl₂. However, at ionic strength >0.03-0.05 mol.L⁻¹ both in NaCl and CaCl₂, only species <2 kDa are soluble and are found in solution. The compaction (or dissociation) mechanism noticed in pure solution with an increase of ionic strength is not evident here with BC rock because the concentration of low MW species is too low.

The presence of Ca²⁺ and high ionic strength tends therefore to pull the DOM-solid OM (SOM) equilibrium towards SOM especially for the large organic species. This result is in agreement with the observations made in pure solution that showed a decrease of solubility of large DOM species with ionic strength and Ca²⁺ content due to aggregation/precipitation. However, in presence of BC, the solubility of large OM species appears even more sensitive to ionic strength than in pure solution. On the one hand, in presence of BC rock the equilibrium solution has a different composition than the initial

electrolyte and contains a broad range of multivalent cations released by ionic exchange that are susceptible to intensify the aggregation/precipitation. On the other hand, an increase in ionic strength is likely to enhance the sorption of organic species on the minerals composing BC and particularly on the clay phases. The compression of the electrical double layer magnifies the VDW interactions and the increase of cation concentration magnifies the sorption *via* cation bridging. The latter is strongly favoured in presence of divalent cations (Ca^{2+}) over monovalent (Na^+) (Feng et al., 2005; Majzik and Tombácz, 2007; Shen, 1999). In parallel, the compaction (or dissociation) of a fraction of DOM species could also increase sorption, independently of the sorbing phase, by reducing the steric barrier and increasing the amount of DOM molecule that can be sorbed (Shen, 1999).

The set of experiments performed on the effect of ionic strength on Boom Clay DOM in presence or absence of BC rock and in presence of mono or divalent cations leads to the same conclusions. An increase of ionic strength of BC pore water up to a composition in mono and divalent cations similar to seawater would tend to a reduction of the content of soluble organic species and to a reduction of the MW of the soluble species that are likely to be smaller than 2 kDa. These conclusions are however drawn based on the BC DOM found in Mol. One should keep in mind that some crucial differences may exist with the DOM present in other locations of BC which can affect the modifications brought by an increase of ionic strength.

2.3 Conclusion on colloids in Boom Clay

Due to the immaturity of Boom Clay organic matter, the pH and ionic strength of the Boom Clay porewater (in Mol) and the relative high porosity, DOM in the Boom Clay forms an important component of the porewater and may represent a significant migration vector for dissolved metals and radionuclides. The mobile DOM concentration at Mol site is between 47 and 270 mgC/l with an excess concentration in the double band. The concentration and the size of the mobile DOM pool is expected to vary both in time and in space with respect to physico-chemical conditions. Nevertheless, the impact of DOM on the speciation, retardation and migration of radionuclides (RN) must be sufficiently characterised in order to reliably assess RN transport in the Boom Clay.

Therefore, and in contrast with other safety assessments performed on argillaceous formations (the French Callovo-Oxfordian formation and the Swiss Opalinus Clay formation), the role of DOM as a transport vector in Boom Clay has to be taken explicitly into account in safety assessments of the Boom Clay.

3 Transport of colloids

Due to its determining role in natural environments, colloid transport in porous media has been the centre of numerous works over the last decades. From empirical to mechanistic models and from pore-scale to field scale, the behaviour of colloids has been dissected to produce more and more complete and precise models. Considering that large data sets were collected and numerous modelling approaches were developed and reported in the literature over the years, we do not pretend to be exhaustive in our following discussion. We will focus the next paragraphs on the main mechanisms/processes identified as controlling colloidal transport, on the theoretical approaches to describe them and on the macroscopic models used to interpret transport experiments. The transport of DOM in Boom Clay will be reported as a case study in which we will discuss both the experimental set-ups and the modelling approach.

3.1 Processes and mechanisms

3.1.1 Colloid deposition and colloid aggregation: the DLVO theory

Colloid particles transported in porous medium experience a large number of interactions with the medium which differentiate their transport behaviour from the solutes. Solutes might chemically interact with the minerals composing the solid phase, in a reversible or irreversible way. These interactions might be kinetically-controlled but in general, the reaction rates are such that in the time scale of in situ transport or laboratory experiments (diffusion, percolation or column experiments), local equilibrium can be assumed. The colloids undergo kinetic physico-chemical deposition on the surface. In addition, colloids are also subjected to colloid-colloid interaction more known as aggregation. The immobilization of a colloid via physical contact with a collector (surface or colloid) is commonly referred to as "attachment". This term refers to the DLVO theory (Derjaguin and Landau, 1941; Verwey and Overbeek, 1948) that describes the interactions colloid-surface or colloid-colloid in term of adhesive forces, *i.e* London-Van Der Waals (vdW), and repulsive forces, *i.e* electrical double layer (EDL). This theory describes the potential energy profile of the interaction colloid-surface or colloid-colloid as the sum of the contributions of each force as a function of distance as represented in **Figure 3-1**.

The determination of vdW and EDL forces depends on the geometry (sphere-sphere or sphere-plane) and the model considered (Stern Layer, Gouy-Chapman Model...). The vdW forces are almost always present while the double layer interactions are important for charged substrates, especially at lower salt level.

Typically, two energy profiles can be drawn: in case of favourable conditions and in case of unfavourable conditions. Favourable conditions are met when the collector displays an opposite charge than the colloids. In this situation, the repulsion forces are absent (curve 1, **Figure 3-1**) and attachment occurs easily in the energy primary minimum. On the other hand, when the colloid and the surface display the same charge a repulsive barrier exists that prevents attachment (no access to the energy primary minimum). However, experimental observations show that even in unfavourable conditions, the attachment is limited but not null. Beside the repulsive barrier exists a small region of attraction where colloids may accumulate in a secondary minimum at separation distances tens of nm from the collector surface (Molnar et al., 2015). In the theory, this accumulation does not lead to attachment that occurs only in the primary minimum. The colloid might be temporally retained in the secondary minimum but because not attached can be released in the bulk solution. On the other hand, when attachment occurs, the forces are strong and in the

classical DLVO theory the colloid is immobilised on the collector. Detachment can still occur in presence of short-range forces (Grolimund et al., 2007; Ruckenstein and Prieve, 1976) or if the physico-chemical conditions are modified. The DLVO can indeed predict the extent of attachment/detachment processes as a function of pH, ionic strength or cationic composition. Attachment is generally favoured for high ionic strength, low pH and high divalent/monovalent cation ratio (García-García et al., 2009; Kretzschmar, 2005; Kretzschmar and Sticher, 1998; Ryan and Elimelech, 1996). These conditions decrease the size of the EDL and the repulsive forces.

Even though not predicted by the theory, immobilisation was also observed in unfavourable conditions. Several strategies have been developed in order to 'defeat' the classical DLVO theory, which assumes homogenous surfaces, and mechanistically describe the experimental attachment under unfavourable conditions. These strategies use heterogeneity such as surface roughness, charge heterogeneity and variability in colloid characteristics (Bolster et al., 1999; Kretzschmar et al., 1997; Molnar et al., 2015) and references therein) as an explanation for the attachment under unfavourable conditions. By generalizing the theory to the bulk surface properties of colloids and collectors, the mean-field DLVO theory can be of great utility to interpret colloid transport in porous media. However, because of the deviation of the theory from the experiments in case of unfavourable conditions, that are mostly met in natural environments, the DLVO is hardly implemented in the transport models developed under these conditions.

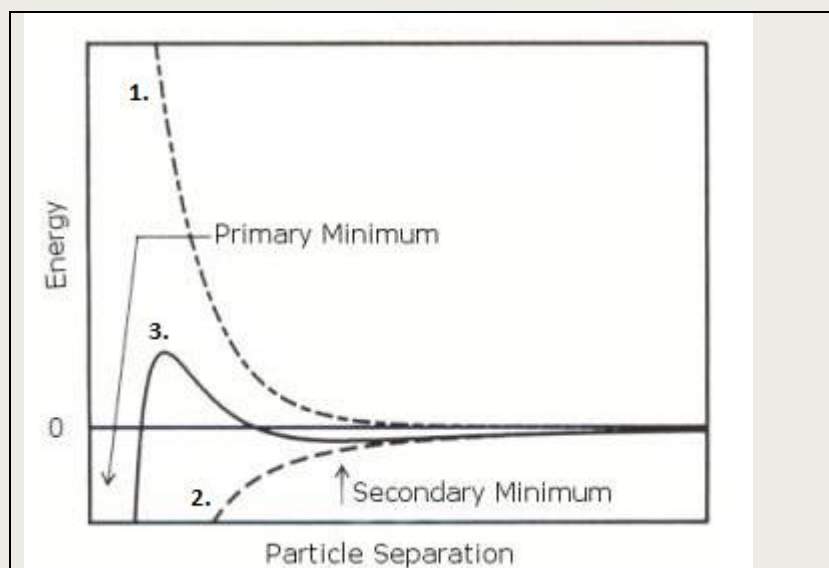


Figure 3-1: DLVO theory. 1. Electrical double layer, repulsion forces 2. Van der Waals forces, attractive forces 3. Net energy

3.1.2 Colloid Filtration Theory

The physico-chemical retention of colloids on the surface has led in the early 70's at the development of the Colloid Filtration Theory (CFT, (Yao et al., 1971)). The CFT theory is derived from mathematical descriptions of water flow and colloid filtration and describe the transports of a particle to a collector and the probability that the colloid-collector collision will succeed in attachment (Elimelech, 1994).

In the CFT developed by Yao et al. (1971) the main forces leading the transport of particles to a collector are the interception, diffusion and gravity. Diffusion represents the dominant process for small particle (<1 µm) whereas interception and sedimentation dominate for larger particles (Lin et al., 2008). Yao et al. (1971) describes each process as follows:

$$\eta_D = 0.9 \left(\frac{kT}{\mu d_p d_c v} \right)^{2/3} \quad (10)$$

$$\eta_I = \frac{3}{2} \left(\frac{d_p}{d_c} \right)^2 \quad (11)$$

$$\eta_G = \frac{3}{2} \left(\frac{(\rho_p - \rho_f) g d_p^2}{18 \mu v} \right) \quad (12)$$

Where η_D , η_I and η_G correspond to diffusion, interception and sedimentation (by gravity) processes. k is the Boltzmann constant, T the absolute temperature, μ the fluid dynamic viscosity, d_p the average particle diameter, d_c the average collector diameter, v the fluid approach velocity, ρ_p the particle density, ρ_f the fluid density and g the gravitational constant.

Diffusion allows colloids to move across streamlines and come into contact with the collector (Molnar et al., 2015). Interception is defined as occurring when a particle following a fluid streamline comes in contact with a collector. Sedimentation, occurs when a particle is transported out of its fluid streamline to a collector surface due to gravitational settling (Lin et al., 2008). The sum of these three processes serves as basis for the theoretical single collector efficiency, $\eta_{c,0}$, defined as the ratio of the rate at which particles strike a collector surface to the rate at which particles flow towards that collector, such as:

$$\eta_{c,0} = \eta_D + \eta_I + \eta_G \quad (13)$$

The model proposed by Yao et al. (1971) considered colloids approaching a single, isolated collector that was perfectly spherical and surrounded by an infinite fluid. This approach, as noted by the authors, produced velocity distributions that were likely poor representations of realistic porous media. The isolated-sphere approach was subsequently modified to employ a Happel sphere-in-cell geometry (Happel, 1958) that includes porosity, as well as constricted tube geometry (Molnar et al., 2015) and references therein: (Burganos et al., 1994; Burganos et al., 1992; Paraskeva et al.; Payatakes et al., 1974; Payatakes et al.). The Happel sphere-in-cell approach considers the collector, otherwise isolated from the influence of other collectors and perfectly spherical, to be surrounded by an envelope of fluid that is associated with the collector (Molnar et al., 2015). Based on this geometry several approaches were developed in the course of the years leading to various single-collector efficiency correlations. As an example, we provide in **Equation**

(14), the correlation used by Tufenkji and Elimelech (2004). For more examples, we refer the reader to the review provided by Molnar et al. (2015).

$$\eta_{c,0} = 2.4A_s^{1/3}N_R^{-0.081}N_{Pe}^{-0.715}N_{vdW}^{-0.052} + 0.55A_sN_R^{1.675}N_A^{0.125} + 0.22N_R^{-0.24}N_G^{1.11}N_{vdW}^{-0.053} \quad (14)$$

where A_s is the porosity-dependent parameter of Happel's model: $A_s = 2(1 - \gamma^5)/(2 - 3\gamma + 3\gamma^5 - 2\gamma^6)$ and $\gamma = (1 - \varepsilon)^{1/3}$, with ε the porosity of the media. $N_R = d_p/d_c$ is the aspect ratio, $N_{Pe} = 3\pi\eta\mu d_p d_c/kT$ is the Peclet number characterising the ratio of convective to diffusive transport, $N_{vdW} = A/kT$ is the van der Waals number characterising the ratio of van der Waals interaction energy to the particle's thermal energy; A is the Hamaker constant of the interacting media, $N_A = A(\frac{d_p}{2})^2/12\pi\mu$ is the attraction number characterizing the combined influence of van der Waals attraction forces and fluid velocity on particle deposition by interception, and $N_G = \eta_G$ is the gravity number, i.e. the ratio of Stokes particle settling velocity to approach velocity of fluid.

The correlation equations are valid for favourable attachment conditions. However in natural environments, physico-chemical conditions are often unfavourable to particle-collector attraction and η_c will be less than the theoretical value, $\eta_{c,0}$. An empirical collision efficiency factor (τ) is consequently needed to account for the effect of repulsion such as:

$$\eta_c = \tau\eta_{c,0} \quad (15)$$

The value of τ should range from 0 to unity. When $\tau = 0$, the conditions are highly unfavourable and no attachment will take place. On the contrary when $\tau = 1$, attachment of the colloid on the collector is guaranteed. τ can be obtained experimentally from either removal efficiencies of suspended particles through porous media and theoretical values of single-collector efficiency or flocculation rates of particles undergoing mixing in a batch reactor (Lin et al., 2008).

3.2 Continuum-scale models

The predictive tools developed to explore column and field-scale colloid transport phenomena are primarily continuum-based numerical models that solve the advection-dispersion equation (ADE, Equation (16)) for solute transport in porous media. Terms employing rate coefficients to drive colloid mass transfer to the solid phase and back are used to describe the macroscopically observed transport behaviour of colloids. Rate constants for colloid transfer to the solid phase may be independently determined using upscaled predictions from colloid filtration theory or alternatively optimized on the experimental breakthrough curves and concentration profiles of the colloids in the solid sample.

$$\frac{\partial C}{\partial t} = -v \frac{\partial C}{\partial x} + D \frac{\partial^2 C}{\partial x^2} - r_{att} \quad (16)$$

Where C is the concentration of the colloid; t is the time; x is the position; D is the dispersivity coefficient of the colloid; v is the apparent advection velocity; r_{att} is the colloid attachment.

The implementation of r_{att} into continuum-scale models is performed under the simple assumption that the control volume considered in the continuum model is represented by a collection of identical pore-scale collectors comprising the same volume and having the same porosity as the control volume ((Molnar et al., 2015) and references therein). Under this assumption, the equation expressing the attachment rate constant (k_{att}) for the Happel sphere-in-cell geometry in the conceptual model employed by Tufenkji and Elimelech (2004) is:

$$k_{att} = \frac{3(1 - \theta_w)}{2d_c} \eta_{c,0} \tau v \quad (17)$$

Where θ_w is the water porosity.

Attachment is integrated in the advection-dispersion-reaction equation such as:

$$r_{att} = \theta_w k_{att} C \quad (18)$$

The reader should keep in mind that the equation to determine k_{att} is function of the model employed for the determination of the single-collector efficiency correlations and varies from one model to another.

In favourable conditions, log linear experimental profiles of colloids show that k_{att} is constant with transport distance and the upscaled mechanistic predictions provide good prediction of colloid transport at the continuum scale for spheroidal colloids in uniform media (e.g., Elimelech, 1991).

On the other hand, in unfavourable conditions, the use of theoretical k_{att} often leads to discrepancies between model and experimental results. Experimental observations report an accumulation of colloids at the entrance of the porous media which suggests a variation of k_{att} with transport distance. In order to describe these experimental results a discretisation between high from low attachment zones is often made. Two kinetics of attachment are considered: a "fast" kinetic attachment coefficient that characterises the strong retention at the inlet and a "slow" kinetic attachment coefficient that describes the moderate-weak attachment at longer distance. Alternatively, k_{att} was allowed to vary by the use of dimensionless colloid attachment function, ψ_{att} (Bradford et al., 2003). These functions might for example account for a reduction in the attachment rate due to blocking (filling up) of attachment sites (Treumann et al., 2014):

$$\psi_{att} = \left(\frac{S_{max} - S}{S_{max}} \right) \text{ and consequently } r_{att} = \theta_w C k_{att} \psi_{att} \quad (19)$$

Where S_{max} , is the maximum solid phase concentration of attached colloids and S is the solid phase concentration of attached colloids.

The theory does not predict detachment from the surface but as we mentioned previously, even in favourable conditions some colloids might exit the energy primary minimum and return to the bulk solution. In unfavourable conditions, neither attachment nor detachment is predicted by the theory. Yet, in these conditions extended tailing may occur during the elution phase reflecting the slow release of retained colloids. We previously discussed the possibility of attachment in unfavourable conditions due to heterogeneity and so of detachment in a similar way than in favourable conditions. On the other hand

colloids might accumulate in the secondary minima and be slowly released from this position. In order to describe such behaviour a detachment kinetic coefficient (k_{det}) is often integrated in the continuum-scale models such as (Bradford et al., 2003):

$$r_{att} = \theta_w k_{att} C - \rho_b k_{det} S \quad (20)$$

Where ρ_b is the soil bulk density.

Because of strong deviations from the theory, k_{att} (and k_{det}) in unfavourable conditions, i.e in most of the environmental systems is often extrapolated from the experiments and not independently predicted by the theory.

3.3 Low-porous media and straining

There is a growing body of evidence suggesting that a variety of processes other than physicochemical filtration such as wedging (Li et al., 2006), hydrodynamic drag (Li et al., 2005), retention within relatively “immobile” regions (Torkzaban et al., 2008) and straining (Bradford et al., 2003; Porubcan and Xu, 2011; Xu et al., 2006) can affect the transport behaviour of colloid-sized particles in saturated porous media.

Straining is the trapping of colloid particles in down gradient pore throats that are too small to allow particle passage (Bradford et al., 2003). It plays an important role in the colloid transport in low-porous media such as Boom Clay. The Boom Formation is a clay-rich sedimentary rock and displays small and hardly connected pores (Hemes et al., 2013a; Hemes et al., 2013b). Hemes et al. (2013a) reported that if the pore sizes in the clay matrices are log-normally distributed around 60 nm, the connecting pore throats in BC are probably smaller than 10-50 nm. Straining occurs when colloids are retained in pores that are smaller than some critical size. This critical size is not only related to the size of the pores but also to the connectivity. We talk of pore throat which might be represented by what we called the 'colloid filtration cut-off'.

Classical attachment theory does not account for straining. Straining is a process that cannot be investigated at the single pore scale and instead requires investigation at the assemblage scale where pore throat size distribution can be determined and compared to colloid size distribution (Molnar et al., 2015). Developing mechanistic methods to predict colloid straining will require an understanding of the pore throat distributions and flow fields. Pore-scale visualization methods such as micromodels and X-ray computed tomography (XCT) are uniquely suited to this purpose (Molnar et al., 2015). However, because of its importance in colloid transport in porous media, several attempts were made to define straining and integrate it in continuum-scale models. Early criteria for colloid straining were based on the ratio of mean particle to the collector diameter (d_p/d_g) that should initially exceed 0.05 (Herzig et al., 1970). More recent studies have shown that straining might become a relevant process from d_p/d_g as low as 0.002 and that it is also dependent on the colloid shape and size non-uniformity, pore-scale hydrodynamics and porewater chemistry (Bradford et al., 2003; Li et al., 2006; Shen et al., 2008; Tufenkji et al., 2004; Xu et al., 2006). In a similar way than for attachment, straining is commonly incorporated in continuum-scale models as a first order kinetic reaction such as (Bradford et al., 2003; Porubcan and Xu, 2011; Xu et al., 2006):

$$r_s = \theta_w k_{str} C \quad (21)$$

Where k_{str} is the straining rate constant.

Moreover, likewise attachment, straining is experimentally found to vary within the porous-medium. These variations can be interpreted and described in different ways. Some authors impose an exponential decline of straining rate with the increase of strained colloids (**Equation (22)**) (Porubcan and Xu, 2011; Xu et al., 2006). Other incorporate a decline of straining rate with the distance (**Equation (23)**) (Bradford et al., 2003).

$$\psi_{str} = \left(\frac{d_{50} + z}{d_{50}} \right)^{-\beta} \quad (22)$$

$$\psi_{str} = C^{-S/\lambda} \quad (23)$$

$$\text{and } r_s = \theta_w k_{str} \psi_{str} C \quad (24)$$

Where ψ_{str} is the colloid staining function, z is the down gradient distance from the porous medium inlet or some soil texture discontinuity in the medium, d_{50} is used as a surrogate parameter for pore length and $\left(\frac{d_{50} + z}{d_{50}} \right)$ is related to the number of pore lengths, β and λ are fitting parameters.

3.4 Case study: DOM transport in Boom Clay

In **section 2.2.5.3** we have provided arguments for the existence of mobile organic colloids, *i.e* mobile DOM, in the Boom Clay. We also showed that the concentration and the size of these organic colloids are subject to change with changes in the chemistry of the pore water. In parallel to the mobile DOM, leaching experiments performed in SBCW evidenced the presence of larger organic colloids absent from the piezometer samples but still soluble in the pore water (**section 2.2.5.2**). We attributed the differences between the size/MW of piezometer DOM and of leached DOM to natural filtration occurring in the pore network of BC and preferential sorption of larger OM colloids. Based on these data, a "filtration cut-off" which demarcates the division into "mobile" and "immobile" colloids was set at ~20 kDa (or 2.8 nm).

Below this cut-off, transport of DOM can still be retarded by chemical reversible sorption and/or physico-chemical filtration in unfavourable conditions. Both DOM and BC surface are indeed negatively charged in the chemical conditions found in the Mol site (pH ≈ 8.3) which lead to unfavourable attachment conditions. On the other hand, a fraction of 'mobile' DOM can also be immobilised by straining. However, a distinction between the different types of colloid retention is difficult to make. Up till now, few experiments have been carried out, and consequently few data have been made available that allow the effect of different colloid retention mechanisms in the Boom Clay to be discerned. There are, however, sufficient indications that colloid filtration is a significant process in the Boom Clay. The experiments performed on DOM transport in BC encompass laboratory scale experiment (percolation and/or diffusion) as well as larger scale experiments performed *in situ* in the HADES underground facility. The objective of this report is not to list all of them, but to focus on the most relevant ones in the following sections.

3.4.1 Evidence of DOM filtration during laboratory scale transport experiments

In order to study the influence of the molecular size on the mobility of organic matter, fractions of different sizes were separated, labelled with ^{14}C and used in a column migration experiment through intact Boom Clay cores (Put et al., 1998; Trancom-Clay, 2000):

- Low size range (cut-off < 1000 Da Amicon Diaflo YM membrane).
- High size range (cut-off > 100 kDa Amicon Diaflo YM membrane).
- Full size range (all mobile DOM present).

The breakthrough curves of the labelled DOM fractions were monitored and used to calculate migration parameters. **Figure 3-2** shows examples of the ^{14}C concentration evolution at the outlet of the tests, for the low-, high- and full- size ranges. The figures show a tailing of the concentration of DOM at the outlet. The colloid retardation mechanisms that are most likely to explain the observed behaviour are attachment and straining, followed by a gradual detachment/liberation of the molecules.

This idea is supported by the evolution of the recovery curves given in **Figure 3-3**. For the large size fraction a recovery of less than 20% is observed. But even for the small size fraction recovery under the experimental conditions was incomplete. Thus, the behaviour of colloids in the Boom Clay shows a kinetic hindrance of a part of the mobile organic matter: the larger the molecules, the larger the 'storage'. For the experiments with the large size range, the size distribution in the percolate at the outlet has been examined by Gel Permeation Chromatography (GPC)-runs performed for different percolated volumes. From these results it was concluded that only small molecules are percolated, indicating that larger molecules are filtered by the clay.

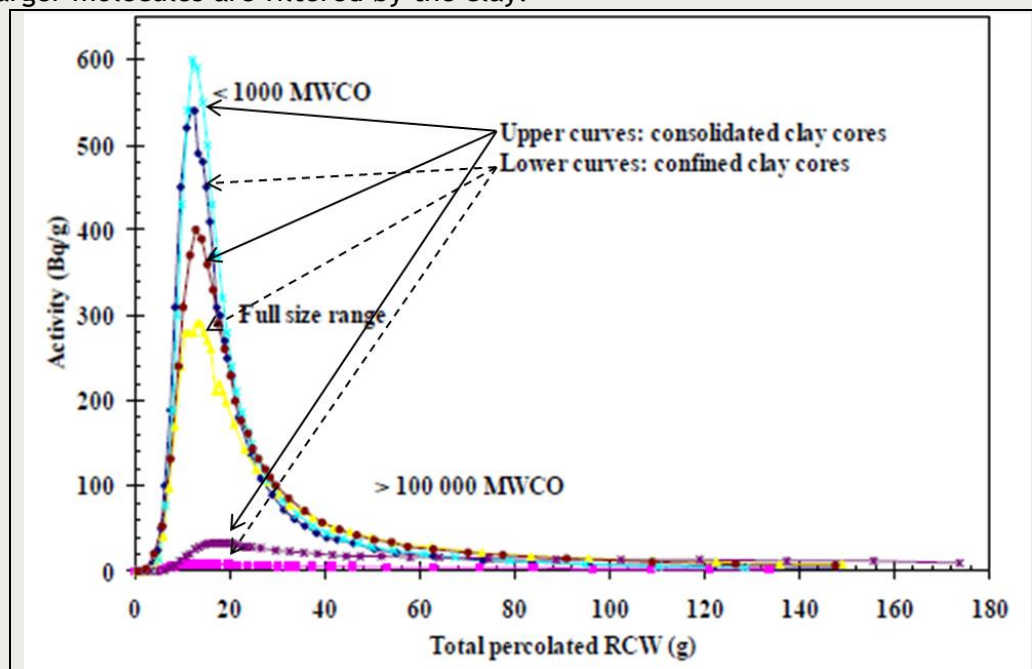


Figure 3-2: Concentration evolution profiles at the outlet of a clay core for impulse injection experiments with ^{14}C labelled mobile organic matter. Light and dark blue curves: < 1000 MWCO; brown and yellow curves: full size range; purple and pink curves: > 100000 MWCO. Dark blue, yellow and pink curves refer to experiments performed on confined clay cores, while light blue, brown and purple curves refer to experiments performed on consolidated clay cores (Trancom-Clay, 2000)

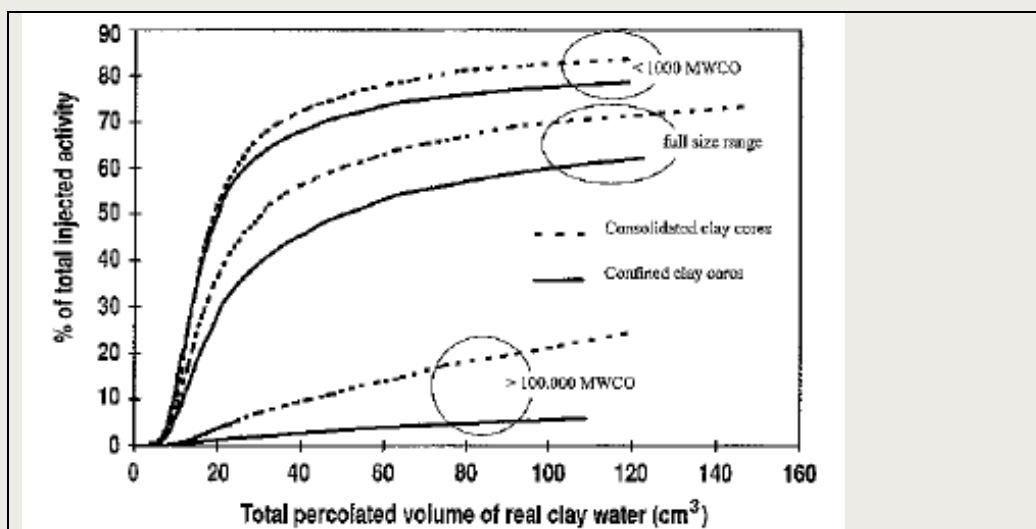


Figure 3-3: Cumulative recovery curves from the impulse injection experiments, showing the influence of the molecular size fractions of NOM and the influence of the effective stress in the clay press (Put et al., 1998)

Figure 3-3 also shows different behaviours between the tests in consolidation cells and those in confinement cells. The recovery for the consolidation cells (oedometers) is much higher than for the confinement cells. This is explained by the higher porosity, resulting from a lower effective stress, for the clay cores in the consolidation cells. **Figure 3-3** also supports the retardation due to straining (physical filtration) of the colloids, because the higher the porosity, the higher the recovery.

3.4.2 Transport of DOM in in-situ experiment

3.4.2.1 Experimental set-up and results

Large-scale (m), long-running (> 10 years) *in situ* migration experiment with ^{14}C -labelled DOM was initiated during the Trancom-Clay project (Trancom-Clay, 2000) and was followed up during Trancom-II (Trancom-II, 2004) and thereafter. The outline of the in-situ experiment is as follows. Diluted ^{14}C -NOM batches were pumped continuously over a filter placed in the Boom Clay to allow the labelled organic matter to diffuse out into the formation **Figure 3-4**. One horizontal piezometer (TDR41H, started June 9, 1997) and one vertical piezometer (TDR41V, started June 25, 1997) were used. At regular time intervals, the source filter and neighbouring filters are sampled for ^{14}C analysis and the time at which ^{14}C activity reached the detection limit in each neighbouring filter was determined (Trancom-Clay, 2000). The stability of the ^{14}C -labelled NOM source solution, was evaluated by comparing the size distribution of the OM (via UV absorbance) and of the ^{14}C (via LSC) using ultrafiltration separation. The size distributions based on UV absorbance and ^{14}C activity were similar which ruled out the potential release of smaller species such as $^{14}\text{CH}_3\text{NH}_3$ and showed that the source solution is stable (Martens et al., 2010) .

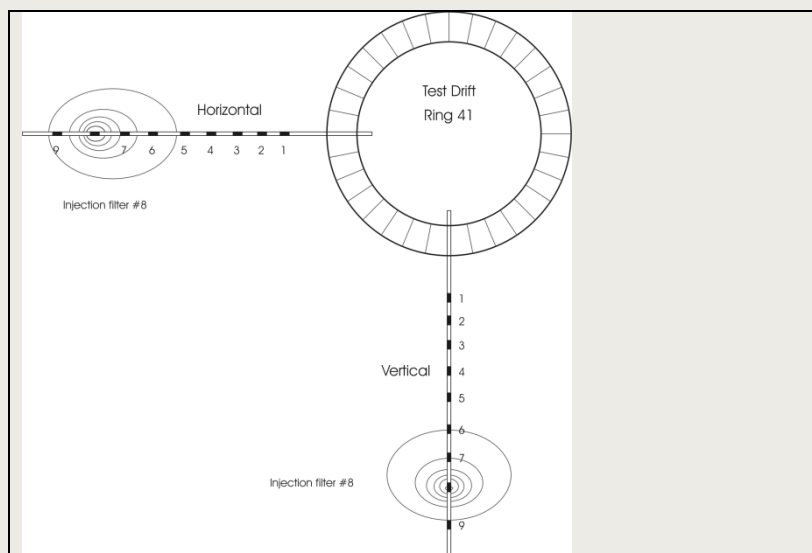


Figure 3-4: Schematic representation of the emplacement of the piezometers in the HADES URF (SCK•CEN, Mol, Belgium) for the migration experiment with ^{14}C -labelled Organic Matter

The experimental data from the in-situ migration test are shown in **Figure 3-5**. The *in-situ* experiments demonstrate on a larger scale the mobility of DOM.

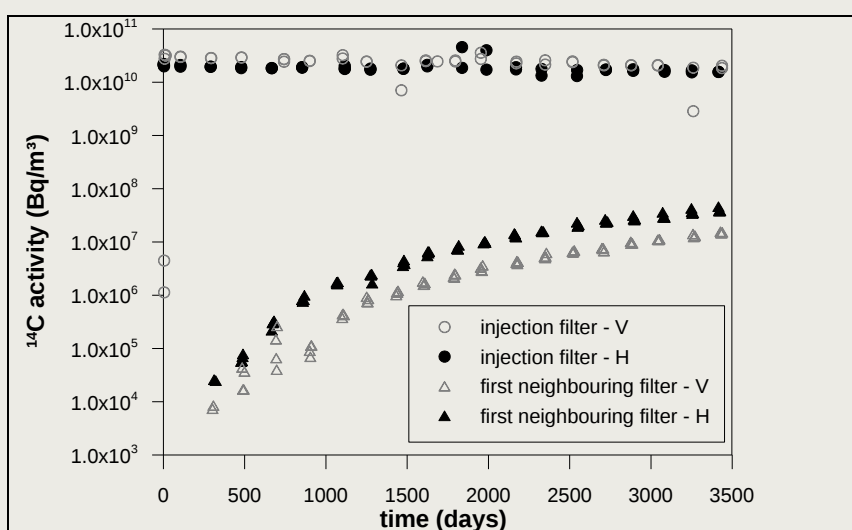


Figure 3-5: Measured ^{14}C -activity in the sampling filters nearest to the injection filters (filters 7) and in the injection filters (filters 8). Data for the horizontal and vertical piezometer are indicated with a "H" and "V" respectively (Martens et al., 2010)

3.4.2.2 Modelling approach

Martens *et al.* (2010) aimed to model the experimental data for the vertical piezometer, by gradually developing an axisymmetric model using the HYDRUS 2D/3D code (Šimůnek *et al.*, 2007).

In the HYDRUS transport code, colloidal transport is described by a combination of the convection-dispersion-retardation equation and colloid attachment theory :

$$\frac{\partial(\eta c)}{\partial t} + \rho_b \frac{\partial(s_e)}{\partial t} + \rho_b \frac{\partial(s_1)}{\partial t} + \rho_b \frac{\partial(s_2)}{\partial t} = \frac{\partial}{\partial x} \left(\eta D_{pore}^i \frac{\partial c}{\partial x} \right) - \frac{\partial(qc)}{\partial x} - \mu_w \eta_{HTO} c - \mu_s \rho_b (s_e + s_1 + s_2) \quad (25)$$

The parameters used in this model are summarised in **Table 3-1**.

Parameter	Units	Definition
c	N_c/l	Colloid concentration in the aqueous phase.
N_c	-	Number of colloids
ρ_b	kg/dm^3	Bulk dry density
$s_{e, 1 \text{ or } 2}$	N_c/kg	Colloid solid phase concentration, subscripts e , 1 and 2 represent equilibrium and two kinetic sorption sites, respectively
μ_w	s^{-1}	Represents inactivation and degradation processes (e.g., decay rates) in the liquid phase
μ_s	s^{-1}	Represents inactivation and degradation processes (e.g., decay rates) in the solid phase
D_{pore}^i	m^2/s	Pore dispersion coefficient; $D_{pore}^i = D_{pore} + \alpha V_{pore}$
D_{pore}	m^2/s	Pore diffusion coefficient
α	m	dispersivity
V_{pore}	m/s	Porewater velocity; $V_{pore} = q/\eta$
q	m/s	Darcy flux
η	-	Diffusion accessible porosity (or "effective porosity") for colloids
η_{HTO}	-	Diffusion accessible porosity (or "effective porosity") for HTO

Table 3-1: Parameters of the HYDRUS colloidal transport model

Sorption to equilibrium sites, s (m^3/kg), can generally be described by:

$$s_e = \frac{\kappa \cdot c^\beta}{1 + \chi \cdot c} \quad (26)$$

There κ (m^3/kg), β (-) and χ (m^3/kg) are empirical coefficients.

When $\beta = 1$, **Equation (26)** becomes the Langmuir Equation, when $\chi = 0$, **Equation (26)** becomes the Freundlich Equation (and when both $\beta = 1$ and $\chi = 0$, **Equation (26)** leads to a linear adsorption isotherm. In case of linear sorption, κ is usually referred to as K_d such as:

$$K_d = \frac{s_e}{c} \quad (27)$$

And a retardation factor, R , which describes the delay in the breakthrough of the species of interest can be defined as:

$$R = 1 + \frac{\rho_b K_d}{\eta} \quad (28)$$

Net kinetic accumulation of colloids on the solid phase from the aqueous phase can be described as the result of attachment or straining and detachment or liberation such as:

$$\rho_b \frac{\partial s_1}{\partial t} = \eta k_{att} \Psi_{att} c - k_{det} \rho_b s_1 \quad \text{or/and} \quad \rho_b \frac{\partial s_2}{\partial t} = \eta k_{str} \Psi_{str} c - k_{lib} \rho_b s_2 \quad (29)$$

where:

k_{att} , k_{str} are the first-order attachment and straining coefficients (s^{-1}), respectively;
 k_{det} , k_{lib} are the first-order detachment and liberation coefficients (s^{-1}), respectively
and Ψ_{att} , Ψ_{str} are the colloid attachment and liberation functions, respectively. Ψ_{att} is calculated with Equation (19) and Ψ_{str} with Equation (22).

Model complexity was increased step by step by introducing different colloid retention processes. Firstly, only diffusion and linear sorption ($\chi = 0$ and $\beta = 1$ in Equation (26)) were included. In a subsequent step advection was added and non-linear sorption (Freundlich, $\chi = 0$ in Equation (26)) was examined. Finally, the effect of adding a colloid transport model was evaluated. The initial parameter values were taken from small-scale lab experiments. The final model was then validated on the dataset from the horizontal piezometer. The anisotropy of the clay was accounted for through the hydraulic conductivity and the pore diffusion coefficient.

Figure 3-6 shows the results of the step-by-step model building for the vertical piezometer dataset. The most simple model, assuming only diffusion and linear equilibrium sorption ($R = 3.1$ while $\eta = 0.16$) shows a reasonably good fit (**Figure 3-6 a**) for a pore diffusion coefficient of $8.5 \times 10^{-11} \text{ m}^2/\text{s}$ (equals a $D_{app} = D_{pore}/R = 2.7 \times 10^{-11} \text{ m}^2/\text{s}$). However, if the curve is examined closely (**Figure 3-6 b**) it is also clear that variation of the diffusion coefficient does not reproduce exactly the same shape as the experimental curve, which indicates that other processes need to be included.

Therefore, in a subsequent simulation, advection was added to the model. The advective flow is due to the pressure difference between the gallery and the formation. During fitting, the pore diffusion coefficient was set at $8.5 \times 10^{-11} \text{ m}^2/\text{s}$. Predictions for the simulation with and without advection are compared in **Figure 3-6c**. The magnitude of the difference between the two curves indicates that advection is not a dominant transport process for this experiment, but neither can it be neglected. It is also clear that introduction of an advective term does not reproduce the experimental curve, which indicates that still other processes need to be included.

Therefore non-linear sorption was investigated to account for the specific shape of the diffusion curve. An excellent fit to the experimental values was obtained with the following (pseudo-) Freundlich parameters: $\beta = 1.325$ and $\kappa_F = 4.5 \cdot 10^{-7} \text{ m}^3/\text{kg}$ (**Figure 3-6d**). However, for a conventional Freundlich sorption mechanism, β should be < 1 (hence the name "pseudo-Freundlich"). A surface precipitation process can sometimes be described with a $\beta > 1$, but such a process has not been observed for DOM in the Boom Clay. Therefore, we only consider linear equilibrium sorption in the following steps.

The size distribution of the ^{14}C -DOM from the sampling filters was also analysed. It was observed that the size distribution shifted towards smaller molecules as the fraction < 1 kDalton increases while the fraction between 1-10 kDalton decreases compared to the distribution of the source solution. This indicates that a physical filtration process is influencing the NOM transport, as described previously for lab migration experiments.

Therefore a colloidal mechanism was introduced in the model besides linear equilibrium sorption. Kinetically controlled colloid attachment/detachment was included in its most simple form. The colloid retention function Ψ was set to 1 and the starting values for the attachment and detachment coefficients were taken from Ionescu *et al.* (2008) and then optimized. Ionescu *et al.* (2008) used HYDRUS 1D to model laboratory scale percolation experiments with ^{14}C -labelled DOM and in presence of ^{241}Am . The experimental set-up of these experiments is reported in **section 4.3.1** and in Maes *et al.* (2006). The fitted HYDRUS 1D parameters for these experiments can be found in Ionescu *et al.* (2008). These laboratory percolations experiments were also modelled using POPCORN model. More details on this modelling approach and on the results are reported in **section 4.3.3**. In Martens *et al.* (2010), the detachment rate has been considered to be one order of magnitude smaller than the attachment rate, referring to a situation where the process of a colloid entering a pore and interacting with the surface (attachment) occurs faster than the reverse process (detachment). The final parameter values are $k_{att} = 8.1 \times 10^{-9} \text{ s}^{-1}$ and $k_{det} = 8.1 \times 10^{-10} \text{ s}^{-1}$ and also the D_{pore} was slightly adjusted to $D_{pore} = 9.5 \times 10^{-11} \text{ m}^2/\text{s}$. The model results obtained with these parameters are shown in **Figure 3-6d**. Including colloid transport clearly improved the shape of the modelled curve but still the fit is not perfect. Probably, this can be improved by optimising the colloid model, for example by the introduction of blocking/straining mechanisms. However, this approach would increase the number of fitting parameters for which we do not have independent data.

To verify the approach of adding the different processes, test simulations were carried out to establish whether or not linear sorption could be neglected, with consideration being given only to a kinetic interaction with the solid phase. The results of this exercise (**Figure 3-6d**) with optimised k_{att} and k_{det} (respectively: 3.2×10^{-8} and $3.2 \times 10^{-9} \text{ s}^{-1}$), show that by neglecting the linear sorption, no reasonable reproduction of the experimental curve could be obtained.

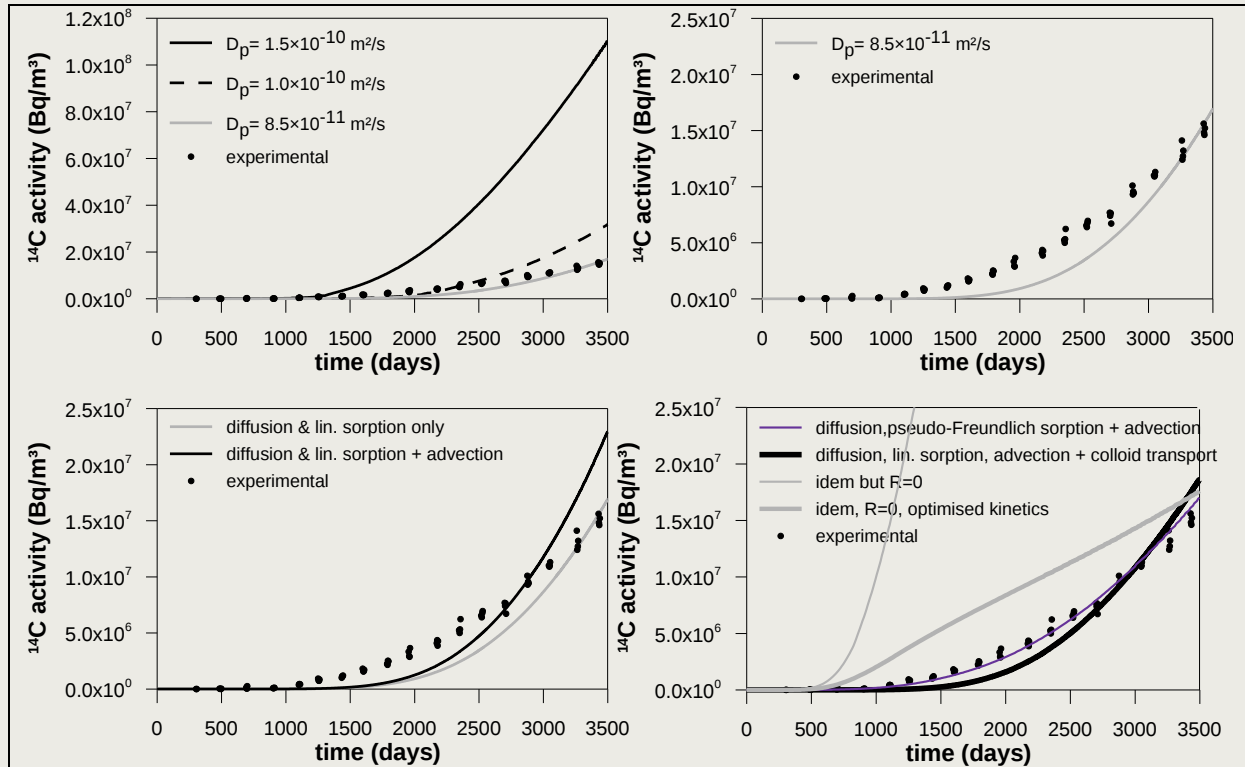


Figure 3-6: ^{14}C -activity in filter 7 (Bq/m³) as a function of time (days). Experimental values and modelled curves for the vertical piezometer. In the figure, D_p stands for D_{pore} . (a) Model considering only diffusion & linear sorption: sensitivity analysis on the pore diffusion coefficient. (b) Model considering only diffusion & linear sorption: best fit. (c) Model considering only diffusion & linear sorption versus a model including advection (both for $D_{\text{pore}} = 8.5 \times 10^{-11} \text{ m}^2/\text{s}$). (d) Comparison between simulation results for a model including diffusion & linear sorption vs. non-linear sorption (pseudo-Freundlich because fitted $B > 1$) & advection and a model also including kinetic colloid attachment/detachment kinetics with or without linear sorption taken into account (both with a $D_{\text{pore}} = 9.5 \times 10^{-11} \text{ m}^2/\text{s}$). (Martens et al., 2010)

The model including linear sorption, diffusion, advection and kinetically controlled colloid attachment/detachment was then tested for the horizontal dataset. Due to the anisotropy of the Boom Clay, the hydraulic conductivity and the pore diffusion coefficient are different for the horizontal and vertical directions. In this modelling exercise, a horizontal hydraulic conductivity of $4.1 \times 10^{-12} \text{ m/s}$ was used (within the range of typical measured values for the Boom Clay (Boisson, 2005)). This is 2.4 times higher than the vertical hydraulic conductivity. There should be no anisotropy for sorption and colloid attachment/detachment, so the same parameters as for the vertical dataset were used for these processes. The pore diffusion coefficient is thus the only fitting parameter, which means that a validation of the sorption and colloid processes is performed.

Results are shown in **Figure 3-7**. From this figure it is clear that the model, which was deduced based on the vertical dataset, is also applicable for the horizontal dataset. The best fit was obtained for $D_{\text{pore}} = 1.33 \times 10^{-10} \text{ m}^2/\text{s}$. This is 1.4 times higher than the best fit D_{pore} value for the vertical pore diffusion coefficient.

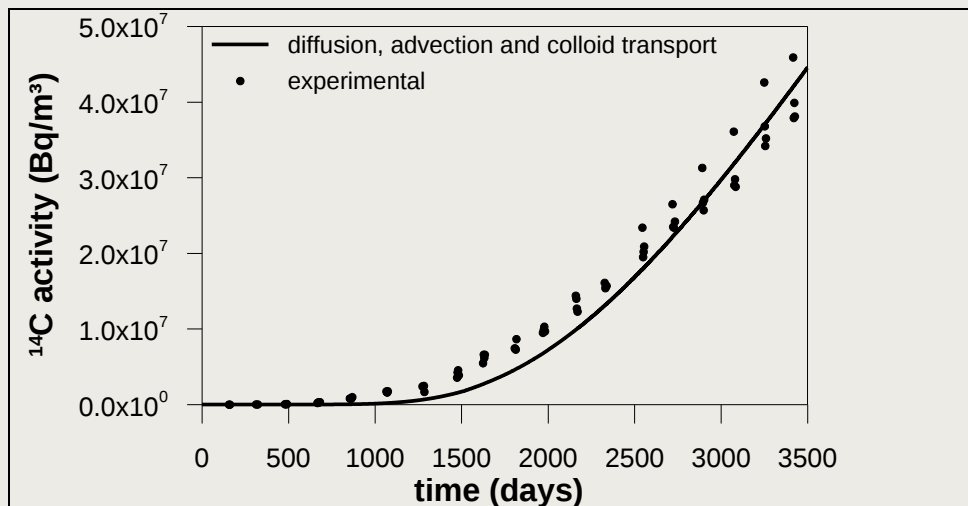


Figure 3-7: Activity in filter 7 (Bq/m^3) as a function of time (days). Experimental values and modelled curve for the horizontal piezometer (Martens et al., 2010)

It was concluded that more elaborate transport models (including a colloidal transport part) can indeed better describe the migration of the colloidal NOM in the Boom Clay, but this remains a parameter fitting exercise because there are no independent determinations of the attachment/detachment kinetics. Nevertheless, the modelling exercise revealed that the "lumped" parameters obtained from lab experiments can be transferred to larger scale experiments and that even a classic diffusion-advection description gives quite good results.

3.4.3 Conclusion and Transport model for Boom Clay DOM

3.4.3.1 Transport model

From the description of the different DOM migration experiments and of the different colloidal transport models that were used to simulate them (Ionescu et al., 2008; Martens et al., 2010), it is clear that there exists currently no unique set of colloidal transport equations that are able to reproduce the features observed in these experiments. Moreover, most colloidal transport equations take into account a wide range of processes and mechanisms (linear and non-linear equilibrium sorption-desorption, kinetic attachment-detachment, straining, etc.). All these processes are in their turn described by a number of parameters for which values need to be assessed. This assessment would require a huge number of experiments and data, which are currently not available.

According to Martens *et al.* (2010), the modelling of the in-situ ^{14}C -DOM diffusion experiment revealed that these "lumped" parameters can be transferred to larger scale experiments and that a classic diffusion-advection description gives quite good results for describing colloidal transport behaviour of DOM in the Boom Clay. We therefore chose to simplify the description of the colloidal transport process in the Boom Clay in such a way that it can be described by a simple diffusion-advection equation, which closely resembles the transport equation used for dissolved radionuclides.

$$\frac{\partial C_{DOM}}{\partial t} = \frac{D_{pore, OM}}{R_{OM}} \frac{\partial^2 C_{DOM}}{\partial x^2} \quad (30)$$

where:

C_{DOM} , is the concentration of DOM in solution (mol/m^3);

$D_{pore, OM}$ is the pore diffusion coefficient for organic matter (m^2/s); and

R_{OM} is the retardation factor for organic matter (-).

This equation entails that no irreversible or non-equilibrium processes take place. However, if only linear, reversible sorption would be considered as a factor in the retardation of organic matter-related colloids, we would neglect straining or filtration of colloids leading to over-conservatism. We will therefore consider R_{OM} as a "lumped" constant in which several colloid retention processes are represented, although we acknowledge that current understanding of these processes in Boom Clay is too limited to be able to discern and treat them separately. Nevertheless, it is likely that future model developments will take into account more explicitly different size fractions of dissolved Boom Clay organic matter, that are expected to play a different role in the colloid facilitated transport of radionuclides (Bruggeman and De Craen, 2012)

3.5 Extrapolation to the Netherlands

3.5.1 Influence of ionic strength

The effect of ionic strength on the diffusion accessible porosity of anions is studied in De Cannière *et al.* (1996), Moors (2005) and Aertsens *et al.* (2005). It was shown that the value of ηR for iodide (I^-) increased from an average of 0.17 using RBCW as background electrolyte to an average of 0.28 when percolating Boom Clay cores with $1 \text{ mol}\cdot\text{L}^{-1}$ NaCl. This effect can be explained by the decrease in anion exclusion due to a decrease of the double layer thickness with increasing ionic strength. A similar effect would be expected also for dissolved organic carbon.

In parallel, a change in ionic strength would also affect the dissolved organic carbon concentration and size. We indeed showed in **section 2.2.5.4.2** that an increase of ionic strength would, due to coagulation/precipitation, decrease the concentration, the size and the aromaticity of DOM. No batch experiments were performed to evaluate the reversibility of the coagulation process. However, the few transport experiments performed to investigate the effect of ionic strength tend to confirm/reveal that: 1/ an increase of ionic strength reduces the concentration of mobile DOM and 2/ the coagulation would be reversible with a lowering of ionic strength.

In Moors (2005), three Boom Clay cores were percolated with electrolytes of different ionic strength. The effect on the dissolved organic carbon concentration was monitored using the UV-absorbance at 280 nm. It is observed, in the three Boom Clay cores that the UV280 increases after the period of no percolation and/or a change of ionic strength (**Figure 3-8**). It is not clear yet why the stop event favours the release of organic matter but the increase of UV280 with a lowering of ionic strength suggests a 'solubilisation' of the coagulated organic material.

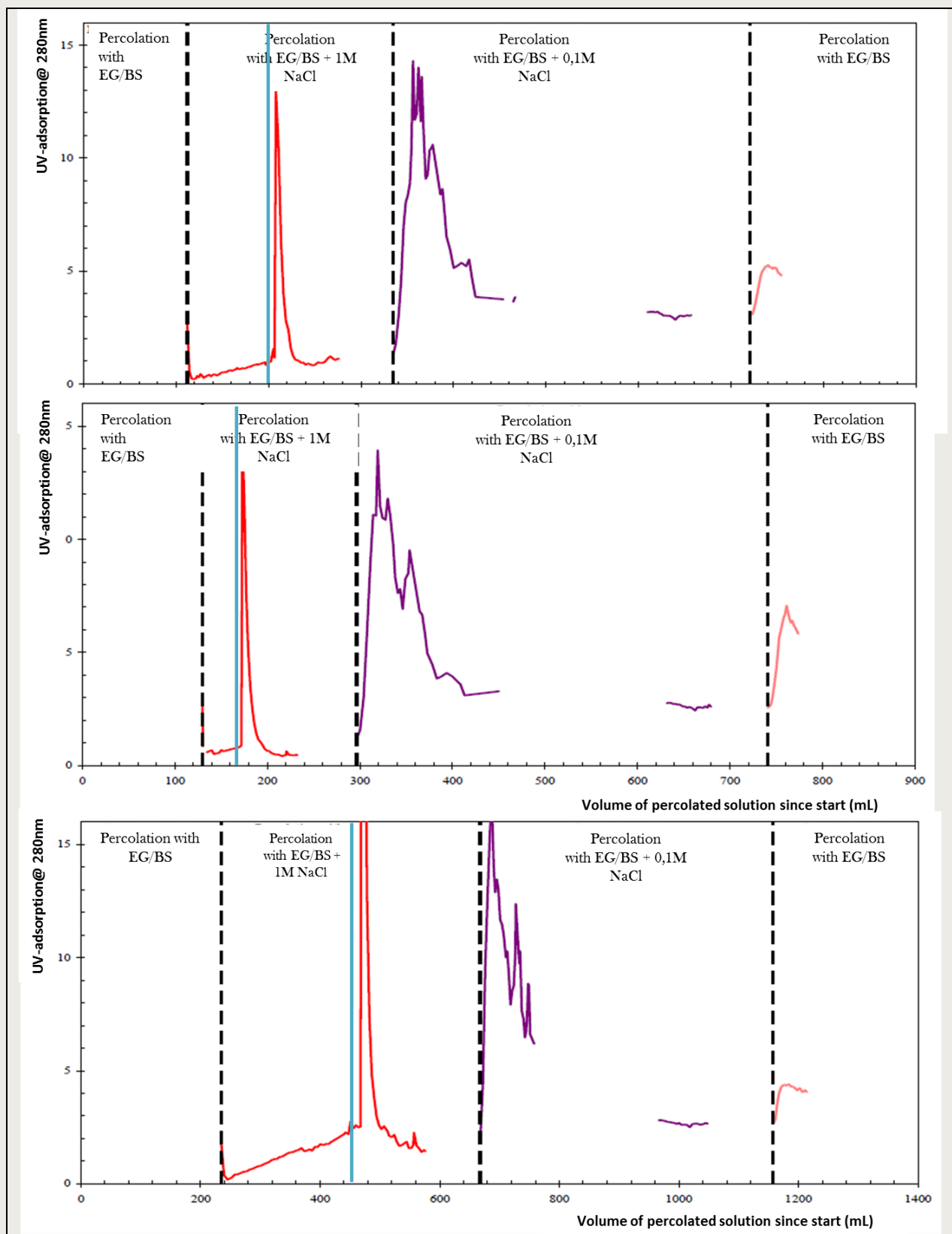


Figure 3-8: Evolution of UV-signal at 280 nm as function of volume of percolated solution. The blue line correspond of a period of no percolation of 770 days (Moors, 2005)

3.5.2 Influence of the degree of compaction

The degree of compaction has a profound influence on the diffusion accessible porosity and the pore diffusion coefficient because it will determine the constrictivity, the pore size distribution and pore throat diameters. It is furthermore expected that a decrease in HTO-accessible porosity due to increasing compaction will result in a relatively bigger decrease in anion-accessible porosity. This is due to the fact that anions, and especially negatively-charged colloidal species such as humic acids, will especially enter larger pores containing free water and will be excluded from smaller pores where double layers of soil minerals may overlap. An increase in compaction likely results in a relatively larger decrease of the number of larger pores, while the smaller pores will be almost unaffected.

Henrion *et al.* (1991) studied the influence of compaction on the diffusion of non-sorbed species and especially humic-like molecules in Boom Clay (consolidation pressure up to 6.86 MPa). HTO and I^- were used as reference molecules to estimate parameters such as tortuosity. Among the molecules used to simulate small humic molecules, labelled sucrose, lactose, triiodothyronine and phenylalanine were used.

As a general observation, the volume fraction accessible for diffusion (Table 3-2 and Figure 3-9) decreases as the consolidation pressure increases. Compared to HTO however, the porosity decrease for anions is much more significant and values for η as low as 0.03-0.04 were reached. Larger molecules (such as lactose and TIT) show also a consistently lower value for ηR compared to iodide.

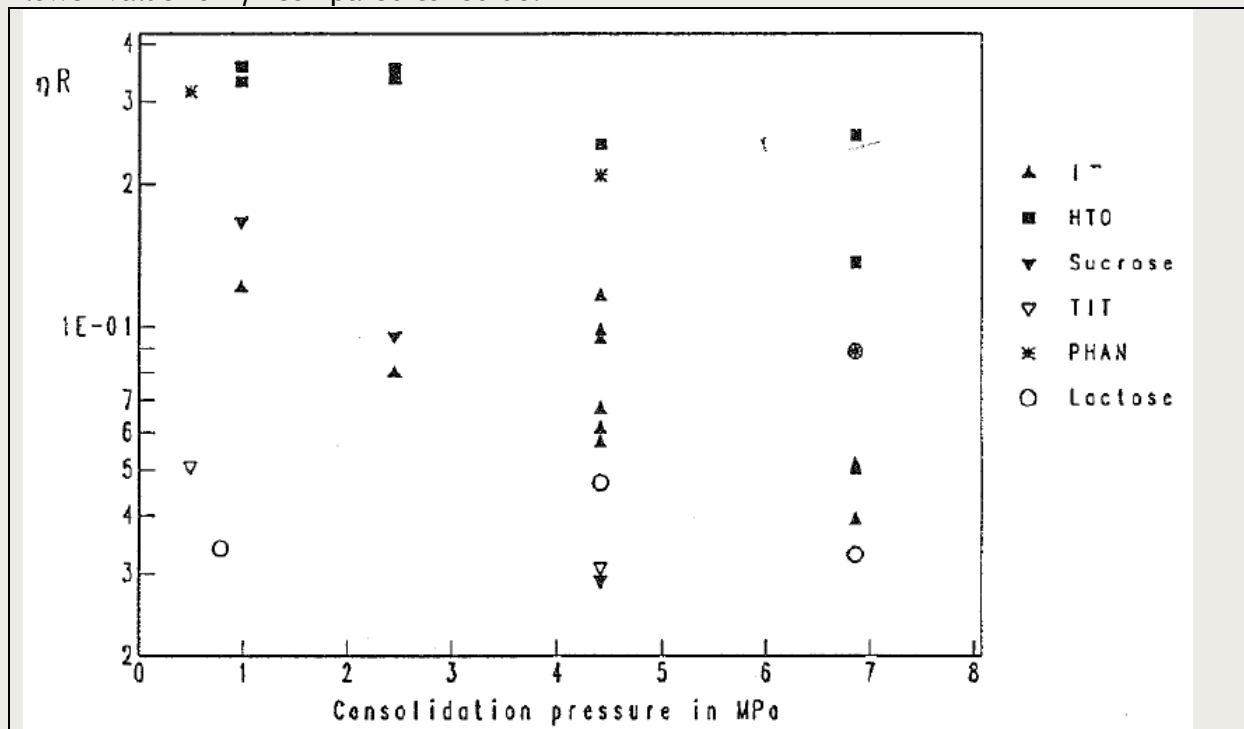


Figure 3-9: ηR as a function of consolidation pressure for different species on clay pastes consolidated to different pressures (Henrion *et al.*, 1991).

P_{consol} MPa	L cm	$\square R$	D cm ² /s	Species
0.98	4.10	0.121	2.90	Iodide
2.45	3.65	0.080	2.35	
4.41	3.60	0.061	2.11	
4.41	1.60	0.098	1.41	
4.41	3.20	0.067	2.83	
.41	3.60	0.057	2.24	
6.86	3.45	0.039	1.70	
6.86	1.60	0.051	1.77	
4.41	2.00	0.094	1.49	
6.86	1.60	0.050	1.57	
4.41	1.70	0.116	2.16	
0.98	4.10	0.356	4.38	HTO
2.45	3.50	0.353	4.39	
2.45	3.65	0.336	3.72	
4.41	3.60	0.243	3.15	
0.98	3.90	0.331	5.18	
6.86	0.45	0.254	2.46	
6.86	1.90	0.137	4.25	
0.98	4.10	0.167	1.02	Sucrose
2.45	3.65	0.096	0.88	
4.41	3.60	0.029	0.94	
0.49	1.90	0.051	2.29	TIT
4.41	1.65	0.031	1.23	
0.49	1.90	0.315	1.47	PHAL
4.41	1.65	0.209	0.44	
6.86	1.60	0.089	0.48	
0.785	3.15	0.034	2.88	Lactose
4.41	1.95	0.047	0.97	
6.86	1.80	0.089	0.72	
6.86	2.70	0.033	0.92	

Table 3-2: Data relative to type through-diffusion tests for different species on clay pastes consolidated to different pressures (Henrion et al., 1991)

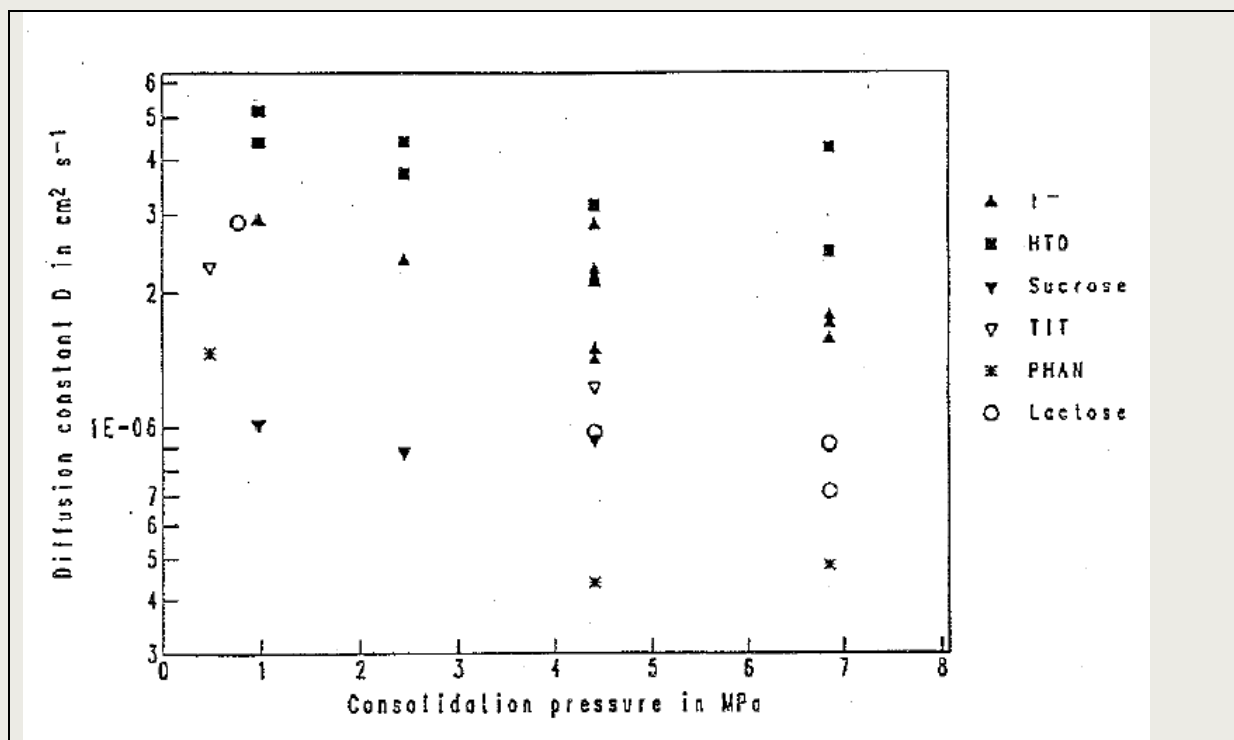


Figure 3-10: D_{app} (in $\text{cm}^2 \cdot \text{s}^{-1}$) as a function of consolidation pressure for different species on clay pastes consolidated to different pressures (Henrion et al., 1991).

Compared to the changes in diffusion accessible porosity, the decrease in apparent diffusion coefficient with increasing consolidation pressure is much less pronounced (Table 3-2 and Figure 3-10). Moreover, the same trend is noted for small organic molecules as for HTO. A decrease of factor 2 to maximum 3 is noted when increasing the consolidation pressure from 0.98 to 6.86 MPa.

In conclusion, for the physico-chemical conditions prevailing in the Netherlands, i.e. higher ionic strength and higher compaction degree than at Mol site, the role of colloid-facilitated transport can be expected to be much more limited than at Mol site. Higher ionic strength would decrease the solubility of OM in pore waters while compaction would limit their mobility. Nevertheless, the reader should keep in mind that this conclusion is based on an extrapolation of data acquired at Mol site and it should be supported by measurement performed on samples taken directly from the Boom Clay in the Netherlands.

4 Radionuclide facilitated colloidal transport

4.1 Introduction

Due to the complex and heterogeneous nature of humic substances the solution chemistry of natural organics is still not fully understood and a thermodynamically based description of their complexation behaviour is not straightforward. Although organic compounds have been extensively studied in the last decades, their composition and molecular structures are however not sufficiently determined yet, the nature and number of functional groups involved in metal binding are still largely unknown, and the stereochemistry of the complexes is poorly defined (Delecaut, 2004). Due to these shortcomings, modelling the complexation (and transport) behaviour of humics remains a challenge.

4.2 Radionuclide - DOM interaction mechanisms

Dissolved humic materials, i.e. humic and fulvic acids, are omnipresent compounds in the groundwaters (porewater) of the Boom Clay formation. These compounds exhibit polyelectrolytic properties as observed for hydrophilic and negatively charged colloids (Stumm and Morgan, 1996). In this report dissolved humic substances are considered as colloids (opposed to dissolved species). This consideration is based on measurements of humic substance size ranges in the Boom Clay pore waters and on observations related to its transport behaviour. Colloids are microscopic particles with sizes in the range of 1 μm to 1 nm. Due to their small size, they tend not to settle out of suspensions, being influenced by Brownian motion and minor currents in the bulk solutions. As mentioned previously, colloids may behave - due to their negative charge - as non- (or weakly-)sorbing carriers for contaminants, resulting in "colloid-facilitated transport" (McCarthy and Zachara, 1989).

Due to their complex and very heterogeneous nature, the exact nature of the mechanisms behind the binding of metals by humic substances is still poorly understood. Despite this fact, big progress has been made in the modelling of these interactions (Jones and Bryan, 1998).

A number of models exist, which describe the partition of metal between humic bound and other inorganic forms. In these models, the chemical heterogeneity of humic substances is represented either by a finite number of discrete binding sites (Charge Neutralisation Model, Tipping Model) or as a continuous distribution (NICA-Donnan). Kim and Czerwinski (1996) used the so-called "Charge Neutralisation Model (CNM)", which is based on the assumption of a metal M^{z+} neutralizing z negative functional charges of an organic molecule, to represent the complexation of a range of actinides. Tipping developed discrete site models (Model V, Model VI,...) (Tipping, 1993; Tipping, 1998; Tipping and Hurley, 1992) in which two types of binding sites are considered (carboxylic and phenolic) with different affinity and density (for more details see section 4.2.1.5). In parallel, continuous distribution-type models (like NICA-Donnan) have been developed to model the behaviour of transition metals (Benedetti et al., 1995; Kinniburgh et al., 1996; VanRiemsdijk et al., 1996). The Non-Ideal Competitive Adsorption model (NICA) also considers two binding sites but each site is characterized by a continuous distribution of affinities in which the heterogeneity is described by two parameters, one related to the intrinsic heterogeneity of organic matter and one related to the cation in question.

Although different modelling approaches exist all of them agree in predicting that humic substances will bind metal ions very strongly. However, they do not predict the effect that humic substances will have upon the migration of radionuclides through the geosphere. Indeed, because these models assume equilibrium conditions, they do not account for slow changes in speciation with time.

Several authors have reported the influence of kinetics in the interaction of metals with humic substances (Cacheris and Choppin, 1987; Choppin, 1988; Choppin and Nash, 1981; Clark and Choppin, 1990; Schussler et al., 2001). These authors have found that it is not possible to describe the desorption behaviour of metal-humate complexes in terms of a single fraction. Rather, at least two distinct fractions are required with decreasing rate constants. Indeed, it has been shown that the uptake of metal ions by humic substances during long term batch experiments can be modelled very well using a kinetic speciation model (Schussler et al., 2001).

Natural organic matter contains a variety of functional groups which are known to form complexes with transition metals and radionuclides such as actinides. Under environmental conditions, this complexation reaction will compete with other geochemical reactions and is considered to be very important. Although many studies have reported measurements of the stability constants of metal-humic substance complexes, few studies have given insight into the exact mechanisms of metal binding. Due to the inherent chemical heterogeneity and polydispersity, humic acids exhibit a manifold of possible interactions in the environment. This includes complexation of actinide ions (e.g., Am(III) ions) released by spent nuclear fuel dissolution, interaction with actinide 'eigencolloids' (e.g., Tc(IV) or Pu(IV) oxo/hydroxo colloids) or coating of inorganic colloids like clays. The generated (hetero-) aggregates can be stabilised or destabilised depending on the geochemical environment, thus strongly affecting their transport behaviour. *In situ* spectroscopy and microscopy allow the characterisation of these aquatic colloids in their hydrated state. However, typical humic substance characteristics like the varying complexation strength (described in terms of stability or complexation constants) or quasi-irreversible reaction kinetics observed for certain humic substance fractions (sometimes identified as binding by 'strong sites') are not well understood and mostly based on bulk characterisation techniques (Plaschke et al., 2009).

The following binding mechanisms are typically considered in metal humic acid complexation: (i) covalent bonding, in which each of the joined atoms supplies one of the binding electrons, (ii) coordinative bonding, a special case of covalent bonding in which the metal accepts an electron-pair from the ligand molecule, with the formation of complexes or more commonly chelates, and (iii) electrostatic bonding of cations due to the negative electrostatic field of the humic acid. It is however not uncommon to not discriminate between these types of bonding and instead the terminology "sorption" is used. The "sorption reaction" between a metal at trace concentration and a humic substance is defined as "any process that results in a close association, on the molecular level, between the metal and one or more functional groups in the humic material" (Sposito, 1986). As a result of this sorption reaction two major types of interaction can be distinguished: (i) a specific interaction corresponding to covalent and coordinative bonding and resulting in inner-sphere complexes, (ii) a non-specific interaction corresponding to the electrostatic bonding and to the accumulation of cations in the diffuse ion swarm adjacent to the negative charge on the humic substance, resulting in outer-sphere complexes.

Although relatively few information is available concerning the exact nature of binding mechanisms between trivalent radionuclides and (Boom Clay) humic substances, it is generally acknowledged that there is a certain degree of heterogeneity involved, both in terms of binding sites (carboxylic acids, phenolic acids) and of complexes formed

(monodentate, multidentate). These different degrees of heterogeneity are reflected in the geochemical models available to describe metal-HS complexation (**section 4.2.1**).

4.2.1 Determination of interaction constants

The understanding of the environmental behaviour of radionuclides necessitates the knowledge of their interaction with organic matter. The determination of interaction constants is a fundamental tool for the calculation of their speciation. It is recommended that these interaction constants should be obtained under conditions close to the *in situ* situation (Maes et al., 1988). Among other techniques, solvent extraction (Torres and Choppin, 1984), UV/Vis absorption spectroscopy (Buckau et al., 1992; Kim et al., 1991b), Schubert's method (Schubert, 1948) or modifications thereof (Dierckx, 1995; Dierckx et al., 1994; Maes et al., 1988; Trancom-Clay, 2000), solubility measurements (Liu et al., 2008), TRLFS (Buckau et al., 1992; Kim et al., 1993b), ultrafiltration (Kim et al., 1993b; Pourret et al., 2007; Pourret et al., 2005) and Donnan membrane technique (Marang et al., 2006; Marang et al., 2008) were successfully used to determine Europium humic acid interaction constants.

The main problem in the determination of stability constants of humic substances with metal ions or radionuclides, is the fact that humic substances are a structurally complex mixture of natural organic acids, i.e. humics, fulvics and humines (Maes et al., 1991). It has been theoretically argued (Perdue and Lytle, 1983) that in such complex systems, it is impossible to experimentally determine stability constants in the thermodynamic sense. Despite this objection, in recent years several geochemical models have been developed that better reflect the extreme complexity of the mixture of ligands in humic substances, among which discrete site (Tipping, 1994; Tipping, 1998; Tipping and Hurley, 1992; Tipping et al., 1994) and continuous ligand distribution (Benedetti et al., 1995; Dewit et al., 1990; Kinniburgh et al., 1996; Kinniburgh et al., 1999; Koopal et al., 2005; Koopal et al., 2001; Perdue and Lytle, 1983) models.

In the next paragraph (**section 4.2.1.1**) the different modelling approaches to describe the interaction between metals and humic substances, and the interaction parameters associated with them, will be discussed. We will focus primarily on the modelling approaches adopted at SCK•CEN or at other facilities to describe the interaction of radionuclides with Boom Clay humic substances. These approaches include 1- and 3-site free ligand or surface complexation models and Tipping's discrete site model.

Other approaches, such as the charge neutralisation model developed by Forschungszentrum Karlsruhe (Kim and Czerwinski, 1996; Kim et al., 1994) or continuous ligand distribution models (widely adopted but not yet applied on Boom Clay humic substances), will not be discussed here.

4.2.1.1 Modelling approaches

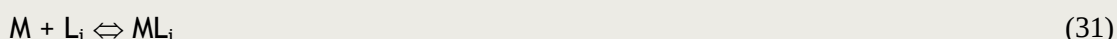
Over the course of years, several modelling approaches have been developed and used to quantitatively describe the interaction between radionuclides and Boom Clay natural organic matter. The development of these approaches was not only led by the changing views on organic matter composition, structure and behaviour, but also by the increasing calculation capacity of personal computers, making it possible to perform fast speciation calculations with complex geochemical models.

While the earlier models were quite successful in describing individual data sets, their scope in terms of pH range, competing metal ions, and ionic strength was often very limited and did not match the range of conditions found in natural waters. The metal binding “constants” were mostly conditional in the sense that they depended on pH, ionic strength, and the presence of other metal ions.

However, it became more and more clear that metal ion binding to humic substances depends on many factors, including the overall metal loading of the system, pH, salt level, and the concentrations of all ions that compete with the metal ions. Therefore, binding models were developed that attempted to address these issues. Nowadays, various physicochemical models have been developed that can account for the effects of chemical heterogeneity, electrostatic interactions, and competition. In these models the chemical heterogeneity is incorporated through a distribution of metal-ion humic binding or affinity constants.

4.2.1.2 The free ligand modelling approach

In this approach, natural organic matter molecules are being treated as simple organic ligands. The functional group heterogeneity of humic molecules is reflected in the existence of multiple ligands with different concentration and proton binding affinity. All ligands are assumed to behave independently from each other (*i.e.*, there are no interactions among sites). The general reaction between a metal ion M and a particular organic ligand L_i (corresponding to a particular site on a humic molecule) at constant pH can be represented by Equation (31)



The corresponding conditional stability constant is written as:

$$K_i = \frac{[ML_i]}{[M][L_i']} \quad (32)$$

where $[M]$ is the concentration of free metal, $[ML_i]$ is the concentration of metal bound to ligands (sites) of the i th class, and $[L_i']$ is the unbound-ligand concentration. The conditional constant K_i includes the effects of acid-base speciation of the ligand, specific interactions with major ions (e.g., Ca^{2+} and Mg^{2+}), and activity coefficients for unspecific interactions with electrolyte ions. It is therefore only valid under the precise conditions under which it is determined.

The polyfunctional nature of humic substances involves the presence of multiple complexing sites; the abundance and stability constant of each site group may be different,

resulting in an overall stability constant which can be represented as a summation over n different site groups:

$$K = \frac{\sum_i [ML_i]}{[M] \sum_i [L_i]} \quad (33)$$

In general, the discrete ligand (or free ligand) model only requires a few (2 to 4) ligands to fit experimental binding data. Given the complexity of humic materials, the small number of ligands needed to fit data is certainly less than the true number of site types; hence, these ligands do not represent actual site types. Because of their simple formalism, the free ligand model is easily incorporated into chemical equilibrium computer programs and is therefore quite popular.

A major problem in determining the interaction constants of metal ions with humic substances is the estimation of the free ligand concentration involved in the reaction (Maes et al., 1991). Several methods have been used:

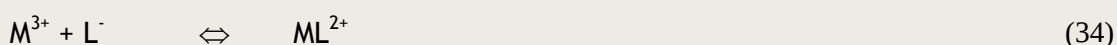
1. Determination of the molecular weight;
2. Determination of reactive groups by potentiometric titrations in either aqueous or in non-aqueous solutions. In this case H^+ is the index cation;
3. Estimation of total complexation capacities using transition metal cations or other index cations such as $Ag(thiourea)_n$ or Cobalthexamine.

The corresponding concentration scales are respectively (1) moles/L (or M) and (2) and (3) equivalents/L (or eq/L). Since humic substances are a mixture of different molecular weights only a mean molecular weight is used in the equations. The second and third methods render an overall ligand concentration which, according to the model used, is assigned to the different functional group entities involved. Equilibrium constants are sometimes calculated in which the ligand concentration is on a g/L basis. Despite the fact that the free ligand concentration is meant to be involved according to **Equation (33)**, frequent use is made of a total ligand concentration determined at a convenient equivalence point, usually around pH 7.

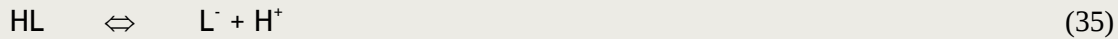
The discrete ligand model can successfully predict metal ion binding by humic material in the absence of competing ions (protons excluded) and within the range of the conditions of the calibrating titrations. The model should however not be used to extrapolate outside this range.

4.2.1.3 The Schubert ion exchange method

The Schubert ion exchange method relies on a free-ligand type reaction mechanism, but is built around the experimental approach to determine metal-humic substance interaction constants. This experimental approach is based on the competition between the dissolved humic substance and a solid ion exchanger for the free metal ions. Both the conventional Schubert ion exchange method (Schubert, 1948) and the modified Schubert method (Maes et al., 1988; Maes et al., 1992) were used for determining the Eu complexation constant with Boom Clay organic matter present in the solution phase. The complexation reaction of a trivalent metal, M^{3+} , with humic substances is represented by the following equilibrium reaction:



in which M^{3+} reacts with dissociated humic substance groups. The humic substance functional groups are represented as monomeric acids that dissociate according to the reaction:



The overall number of dissociated functional groups (L^-) is expressed in eq/L and is calculated from the functional group capacity (eq/kg) at the experimental pH and the organic matter content (kg/L). Since 1:1 complexes are assumed to be formed, the Schubert equation reads:

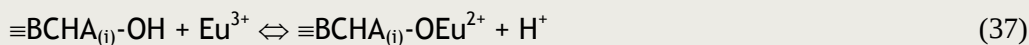
$$\log \left(\frac{K_d^0}{K_d} - 1 \right) = \log K_1 + \log L^- - \log A_s \quad (36)$$

K_d^0 and K_d are distribution coefficients respectively in the absence and presence of Boom Clay organic matter ligand L^- ; K_1 is the conditional complexation constant; A_s is the side reaction coefficient, which accounts for the complexation of M^{3+} with hydroxyl and carbonate ligands.

4.2.1.4 The surface complexation method

Dissociation of carboxylic and/or phenolic groups present in the three-dimensional humic substance structure leads to a potential around the humic particle or in the humic gel phase. Several models are available to take this potential into account and to ensure overall electroneutrality of the gel phase at all times by the penetration of salt ions. The surface complexation method (Trancom-Clay, 2000), normally reserved for inorganic surfaces with a high surface site density and a homogeneously distributed surface charge, involves an electrostatic correction factor but generally applies the same formalism as the free ligand model. A few binding sites are generally sufficient to describe humic material titration data and metal ion-binding reactions.

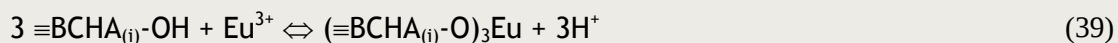
During the Trancom-Clay project, two surface complexation model types were tested to describe Eu^{3+} /OM binding. Each type started out from the assumption that the free Eu^{3+} cation reacted with Boom Clay organic matter. However, distinction was made in the reaction laws. In the first approach a 1:1 stoichiometric relationship was assumed:



with

$$[\equiv BCHA_{(i)}-OEu^{2+}] = K_i \times [\equiv BCHA_{(i)}-OH] \times [Eu^{3+}] / [H^+] \quad (38)$$

In the second approach, a charge neutralisation stoichiometry was assumed:



The mass-action law for this equation can be written as:

$$[(\equiv BCHA_{(i)}-O)_3Eu] = K_i \times [\equiv BCHA_{(i)}-OH]^3 \times [Eu^{3+}] / [H^+]^3 \quad (40)$$

This (conventional) approach was called the (common) surface complexation model, or SCM. In an alternative version, similar to the charge neutralisation approach (Kim and Czerwinski, 1996), the mass-action law was written as follows:

$$3 \times [\equiv\text{BCHA}_{(i)}\text{-OEu}^{2+}] = K_i \times [\equiv\text{BCHA}_{(i)}\text{-OH}] \times [\text{Eu}^{3+}] / [\text{H}^+]^3 \quad (41)$$

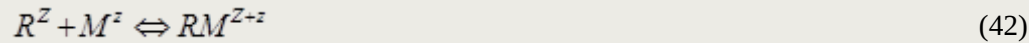
This approach was called the amended surface complexation model (ASCM).

4.2.1.5 Humic Ion Binding Model VI

Humic Ion Binding Model VI, and its immediate predecessor, Model V, have been described in detail in literature (Tipping, 1998; Tipping and Hurley, 1992; Tipping et al., 1994). The following is a brief description of Model VI.

Humic ion-binding model VI is a discrete site electrostatic model for proton and metal ion interactions with humic acids. Fulvic and humic acids are pictured as rigid spheres of uniform size, with ion-binding groups positioned on the surface. The discrete binding sites are represented by two types of sites (types A and B), and within each type of site four different sites are present in equal amounts. Type A sites are associated with carboxylic groups, and the amount is represented by n_A (mol/g), while type B sites are associated with phenolic type groups, with an amount equal to $n_B = n_A/2$ (mol/g). Furthermore, each type of site is described by an intrinsic proton binding constant (pK_A and pK_B) and a spread of this value over the four different sites within each type (ΔpK_A and ΔpK_B).

Metal binding occurs at single-proton binding sites or by bidentate/tridentate complexation between pairs/triplets of sites depending on geometric calculations. Monodentate binding takes place according to the general **Equation (42)**:



The intrinsic equilibrium constants for monodentate binding at the type A sites are given by:

$$\log K(i) = \log K_{MA} + \frac{(2i-5)}{6} \Delta LK_1 \quad (43)$$

and for the type B sites by:

$$\log K(i) = \log K_{MB} + \frac{(2i-13)}{6} \Delta LK_1 \quad (44)$$

where ΔLK_1 is a constant, the value of which is the same for all metals. The fractions of sites forming bidentate (f_{BD}) or tridentate (f_{TD}) sites are determined geometrically. For HA, $f_{BD} = 0.50$ and $f_{TD} = 0.065$, while for FA, $f_{BD} = 0.42$ and $f_{TD} = 0.03$. Their ranges of binding strength are increased for additional terms. Thus, for bidentate sites (i, j):

$$\log K(i, j) = \log K(i) + \log K(j) + x \Delta LK_2 \quad (45)$$

while for tridentate sites (i, j, k):

$$\log K(i, j, k) = \log K(i) + \log K(j) + \log K(k) + y \Delta LK_2 \quad (46)$$

The values of x and y are chosen so as to make possible a range of binding strengths and are characterised by a single parameter. For bidentate sites, the value of x is set to 0 for 90.1% of the sites, 1 for 9% and 2 for 0.9%. For a tridentate site, y is set to 0, 1.5 and 3, again for 90.1, 9.0 and 0.9% of the sites, respectively. The adjustable term ΔLK_2 , characteristic of each metal, is determined by data fitting, or estimated by correlation (Tipping, 1998). To avoid over-complication, a subset of the possible metal binding sites is used in the model, consisting of eight monodentate sites, 12 bidentate sites and 16 tridentate sites.

All the above reactions are described with intrinsic equilibrium constants, which apply to the (usually) hypothetical case where the reactants are uncharged. The effects of the variable charge, and ionic strength, on the humic/fulvic molecules are taken into account with terms that correct for (a) the electrostatic modification of binding at the specific sites, and (b) the accumulation of non-specifically attracted counterions.

The application of Model VI depends on the types and ranges of available data. Six parameters (site density, four parameters defining the proton dissociation constants, and the electrostatic parameter) can be determined from comprehensive proton binding data, and four parameters ($\log K_{MA}$, $\log K_{MB}$, ΔLK_1 , ΔLK_2) per metal given sufficient metal binding data. However, when proton binding by the humic material in question has not been studied, sparse metal binding data can be fitted with a single adjustable parameter, $\log K_{MA}$. This is achieved by (a) assuming that the average values of the six parameters obtained from proton binding data apply to all samples of humic/fulvic acids, (b) using a universal average value of 2.8 for ΔLK_1 , (c) estimating $\log K_{MB}$ by correlation with $\log K_{MA}$, and (d) estimating ΔLK_2 from a correlation with the equilibrium constant for complexation of the metal with NH_3 . The value of ΔLK_2 for Eu^{3+} was found to be 0.29 (Lead et al., 1998), which is a small value.

4.3 Experimental data and associated modelling

4.3.1 Example: transport of trivalent lanthanides/actinides in Boom Clay (Belgium)

During the TRANCOM-Clay project (Trancom-Clay, 2000), the migration behaviour of ^{241}Am through Boom Clay was studied by so-called "double labelled" (labelled DOM contacted with radionuclides) column migration experiments. In this type of experiments, ^{241}Am was complexed with ^{14}C labelled BC NOM of different ultrafiltered size fractions prior to injection.

Most of the experiments were pulse injection experiments in confined clay core holders. The intact clay cores are placed in a stainless steel clay holder (diameter = 38 mm; length = 30 mm), sandwiched between sintered stainless steel filters with a porosity of 40 %. The experiments are performed in a room at 25° C and the percolating solution, generally Real Boom Clay Water (RBCW= EG/BS pore water) is forced through the clay core at a hydraulic pressure difference of about 1 MPa. At equilibrium hydraulic conditions, a pulse of ^{241}Am - ^{14}C -OM solution is injected by means of a HPLC valve (Rheodyne).

During these experiments, sorption of Am on the stainless steel injection loop and filter occurred which made the interpretation of the obtained results difficult. Then, new migration experiments were started with ^{241}Am - ^{14}C -OM of the percolation type, making use of inert materials to prevent sorption of Am to stainless steel.

The aim of the TRANCOM-II project (Trancom-II, 2014) was to perform experiments using optimized experimental set-ups (percolation-type), and to study the role of kinetics in the transport of Am. The objective was to evaluate if the exchange kinetics of trivalent Am between the mobile and immobile phase could explain the fact that a constant aqueous Am concentrations percolates from the migration experiments, and that we have as well the occurrence of a fast - but small - breakthrough of Am accompanying the OM breakthrough. In order to investigate these effects, improved percolation-type experiments were done by using varying clay plug lengths and Darcy velocities (to vary interaction time of Am-NOM complexes with BC). BC OM extracted during the TRANCOM-clay project (batch TROM34) was radiolabelled with ^{14}C by Loughborough University. The ^{14}C -labelled TROM34 was in a second phase double-labelled with ^{241}Am . All the information (concentration, labelling procedure..) on the ^{14}C -labelled TROM34 and ^{241}Am - ^{14}C TROM34 solutions can be retrieved in Maes et al. (2006). The size distributions of the double-labelled ^{241}Am - ^{14}C TROM34 solution (Am-241 (Schindler) and C-14 (DL)) was determined by ultrafiltration using membranes of 0.2 μm , 100 kDa, 30 kDa, 10 kDa and 1 kDa and were compared to the one of the original ^{14}C -labelled TROM34 (C-14 original) (Figure 4-1).

Results revealed that the distribution of the ^{241}Am - ^{14}C TROM solution resembled the ones of the other two solutions, which indicated that upon mixing the ^{14}C -TROM34 with the ^{241}Am -spike, Am was complexed by OM and mostly followed its distribution, with the majority of the Am-DOM complexes having a size between 30 and 100 kDa.

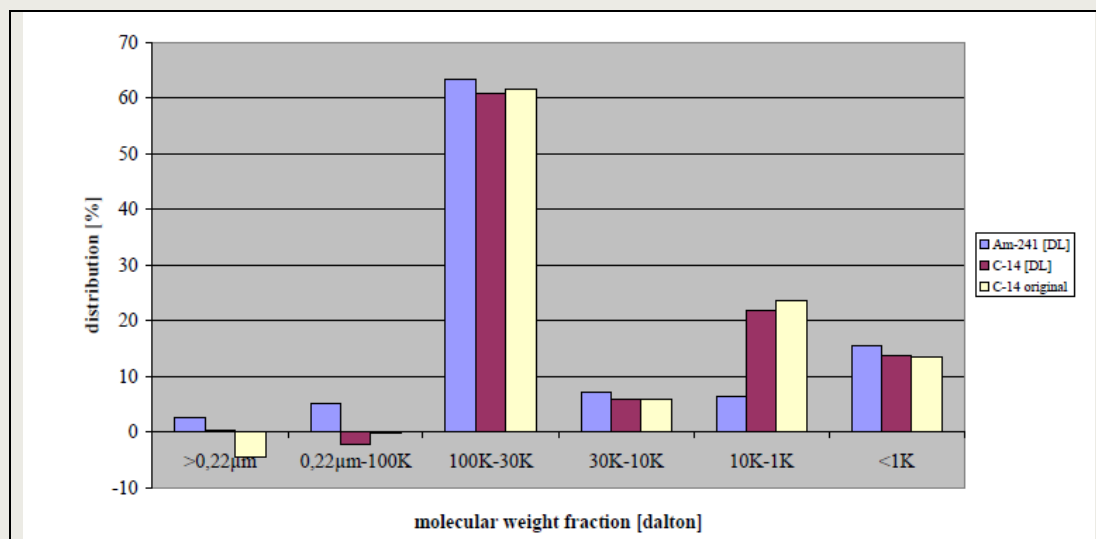


Figure 4-1: Size distribution of the ^{241}Am complexes with ^{14}C -labelled NOM (DL, double labelled solution compared to the ^{14}C -labelled NOM (original) solution

The observations of the different percolation experiments (different clay plug lengths and Darcy velocities) showed, that when the Am-NOM complexes were contacted with BC, the major part of the Am was immobilized (either by sorption on BC minerals or by complexation to the immobile NOM), which pointed to an almost instantaneous dissociation of the "easily" exchangeable Am-fraction. In general, a slightly retarded breakthrough (with respect to the bulk of the ^{14}C -NOM breakthrough) of a tiny Am-fraction (0.1% of the initial inventory) was observed, which was correlated with the NOM breakthrough. The small delay in the Am breakthrough was explained by the fact that larger NOM molecules form more stable complexes than smaller ones. This was already revealed before in column, as well as batch experiments. Combined with the fact, that the transport of bigger molecules is hindered by the dense clay matrix, this can lead to the delayed Am-breakthrough with respect to the bulk ^{14}C -NOM.

Besides this, it was observed that by increasing the travel time (by lowering the Darcy velocity, or by using a longer clay plug), the Am breakthrough peaks were more and more decreasing (**Figure 4-2** and **Figure 4-3**). This becomes more obvious when plotting the Am recoveries (%) to the ratio $\text{Plug length}/V_{\text{darcy}}$ (= "travel time"). Then, an exponential decrease is noticed (**Figure 4-4**) which can be fitted by a decay function (Maes et al., 2006; Trancom-II, 2004) indicating a further, much slower dissociation of the so-called "non-exchangeable" fraction. A kinetic constant of $8 \times 10^{-8} \text{ s}^{-1}$ was obtained.

Also the recovery of the ^{14}C -labelled NOM decreased as the travel time increased (**Figure 4-4**). This decrease was also fitted with a first order kinetics and a kind of filtration rate constant of $1.1 \times 10^{-8} \text{ s}^{-1}$. The decrease in Am recovery with travel time could be therefore the result of both dissociation of the 'non-exchangeable' Am-NOM complexes and filtration of the same complexes. Yet, the relative Am-recovery presented in **Figure 4-5** shows that dissociation is the dominant mechanism. Unfortunately, the acquired data did not give more insight into the nature of the interaction of Am with the matrix (BC): whether it is sorbed on the mineral phases or complexed to immobile NOM and whether these potential processes were kinetically controlled or not.

A more detailed description of the experiments can be found in Maes et al. (2006).

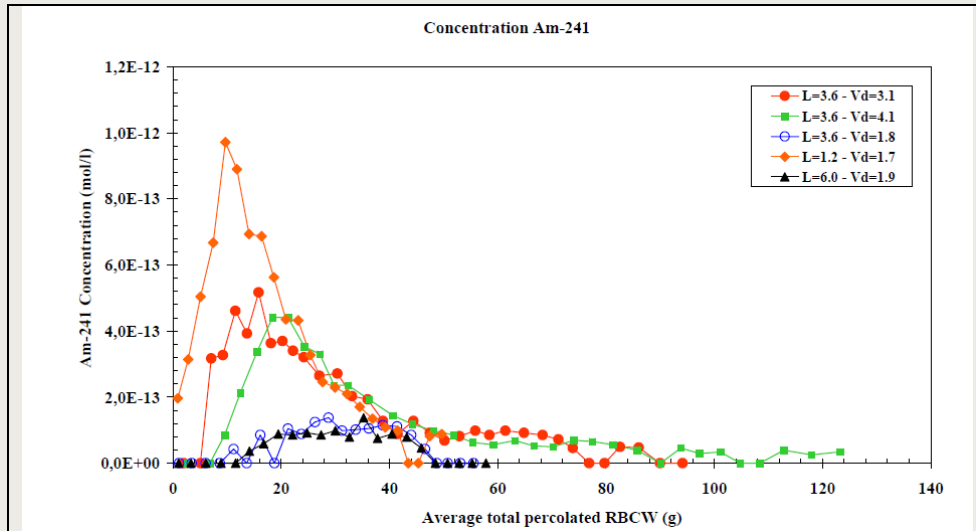


Figure 4-2: Details on the ^{241}Am breakthrough curves for the Am-DOM double label experiments at different V_d (10^{-9} m/s) and L_{plug} (10^{-2} m) (Trancom-II, 2004; Maes et al., 2006)

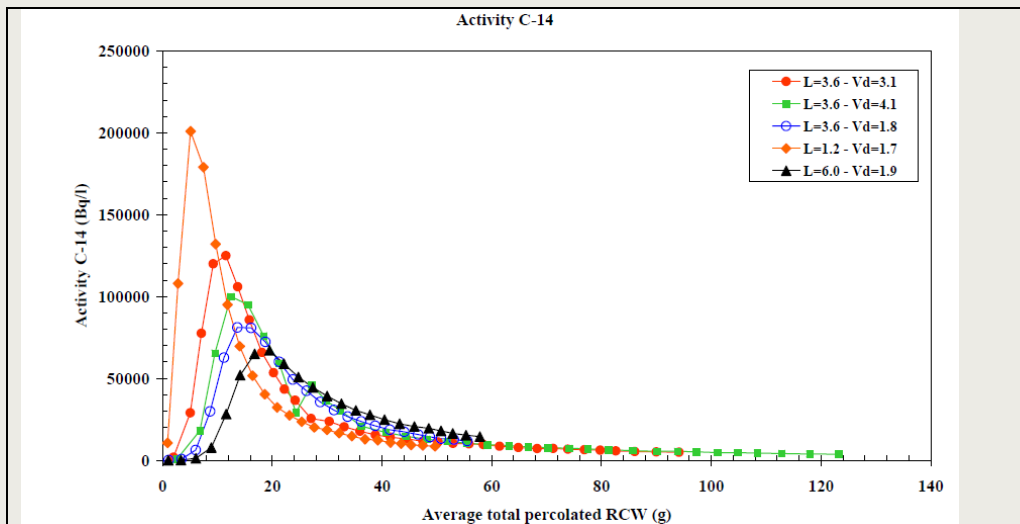


Figure 4-3: Details on the ^{14}C -DOM (right) breakthrough curves for the Am-DOM double label experiments at different V_d (10^{-9} m/s) and L_{plug} (10^{-2} m) (Trancom-II, 2004; Maes et al., 2006)

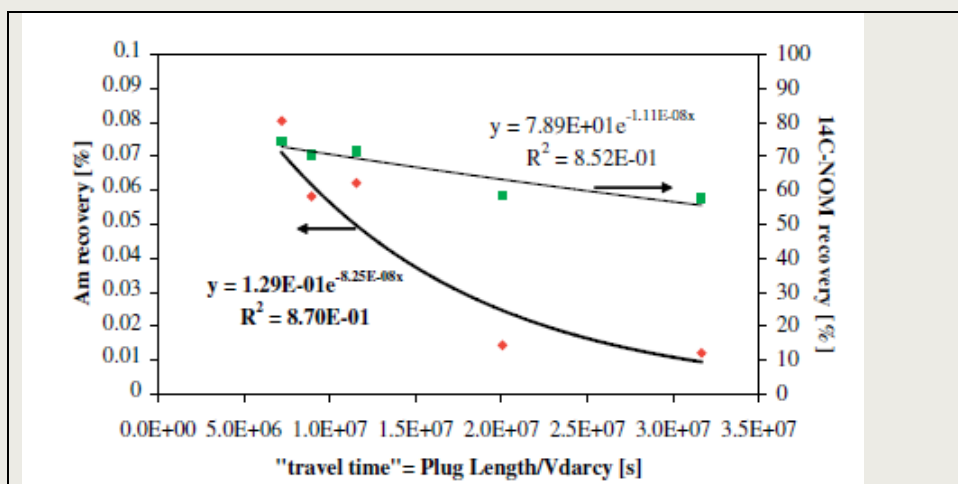


Figure 4-4: Influence of the "travel time" (plug length/Darcy velocity) on the recovery of americium and ¹⁴C-labelled NOM (Maes et al., 2006)

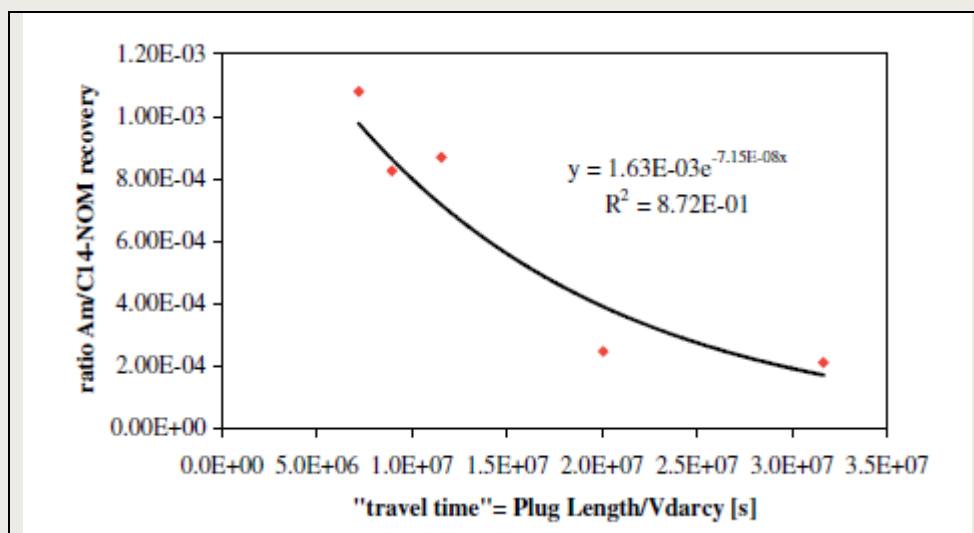


Figure 4-5: Influence of the "travel time" (plug length/Darcy velocity) on the relative Am recovery (Am/¹⁴C-NOM) (Maes et al., 2006)

4.3.2 Literature evidence for kinetic binding of trivalent Ac/Ln to natural organic matter

4.3.2.1 Introduction

Typically, studies of metal complexation with humic substances in natural water systems have been done using equilibrium models, and the assumptions of local equilibrium have been the dominant tool for explaining the metal speciation in aquatic environments. There is however growing evidence that kinetic approaches of complexation and decomplexation of metal ions with humic substances are required to determine the chemical speciation of metals more realistically.

In recent years, the view on dissolved humic substances has evolved considerably and it is now assumed that these macromolecules have fairly robust structures that are highly penetrated by solvent molecules and small ions (Benedetti et al., 1996). Furthermore, they can swell and contract. The hydrodynamic radius of humic substances increases significantly over the pH range 3 - 6 (Chin et al., 1998a). Also, pH titration curves indicate that humic charge density varies with ionic strength (Benedetti et al., 1996). Von Wandruszka *et al.* (Engelbreton and von Wandruszka, 1998; von Wandruszka et al., 1997) observed that although humics display hydrophilic properties in the absence of metals, on addition of polyvalent cations hydrophobic zones are formed. Slower structural changes, on the time scale of days, take place after the addition of metals, and are attributed to the movement of bound metals within the structure from weaker to stronger binding sites.

These two binding modes, "strong" actinide binding within the coiled humic acid structure and "weak" binding to peripheral sites showing either slow or fast dissociation kinetics (Geckeis et al., 2002; Rao et al., 1994), have indeed been invoked to explain different dissociation rates of colloid-borne actinides observed in various investigations. The strong binding sites are assumed to arise from folding of the humic acid molecule, thus stabilising the metal-humic acid-mineral particle interaction. The kinetics of complexation/decomplexation reactions of metals with humic substances can be studied by a number of experimental methods, including fluorescence techniques (TRLFS), isotopic exchange, ligand exchange, ion exchange and transport studies.

Several authors described kinetic effects, at different time scales and in different experiments, when studying interaction of trivalent radionuclides and dissolved organic matter; (Artinger et al., 1998b; Artinger et al., 2002a; Artinger et al., 2002b; Buckau et al., 2002; Cacheris and Choppin, 1987; Choppin, 1988; Choppin and Cacheris, 1986; Choppin and Clark, 1991; Clark and Choppin, 1990; Clark and Choppin, 1995; Geckeis et al., 2002; Kim, 2000; Kim et al., 1993a; Monsallier et al., 2003a; Monsallier et al., 2003b; Rao et al., 1994; Schuessler et al., 2000; Schussler et al., 2001).

4.3.3 Model description of Am-DOM kinetic interaction

4.3.3.1 The POPCORN model

Based on the experimental data presented above (**section 4.3.1**), the POPCORN model was developed by Galson Sciences (UK) within the framework of the Trancom-II project (Trancom-II, 2004; Hicks, 2008).

The POPCORN radionuclide transport model includes representation of the effects of dissolved organic matter on radionuclide migration in a porous medium, but focuses mainly on the radionuclide itself while DOM features only as an "accessory" transport vector. Dissolved radionuclides may be sorbed on the rock matrix or may be complexed with DOM. Mass transport occurs by advection and dispersion of the dissolved radionuclide and radionuclide-DOM complexes. The movement of radionuclide-DOM complexes may be affected by exchange between mobile and immobile phases by, for example, filtration and remobilisation in the rock matrix. The one-dimensional advection and dispersion equations for transport of dissolved radionuclides and radionuclides complexed to mobile DOM are⁴:

$$R \frac{\partial c_s}{\partial t} = D_s \frac{\partial^2 c_s}{\partial x^2} - u_s \frac{\partial c_s}{\partial x} - R \lambda c_s - \kappa_m (K_m c_s - c_m) - \kappa_f (K_f c_s - c_f) \quad (47)$$

$$R \frac{\partial c_s}{\partial t} = D_s \frac{\partial^2 c_s}{\partial x^2} - u_s \frac{\partial c_s}{\partial x} - R \lambda c_s - \kappa_m (K_m c_s - c_m) - \kappa_f (K_f c_s - c_f) \quad (48)$$

$$\frac{\partial c_m}{\partial t} = D_m \frac{\partial^2 c_m}{\partial x^2} - u_m \frac{\partial c_m}{\partial x} - \lambda c_m + \kappa_m (K_m c_s - c_m) - (s_m c_m - s_f c_f) \quad (49)$$

and the behaviour of immobile radionuclide-OM complexes is described by the following:

$$\frac{\partial c_f}{\partial t} = -\lambda c_f + \kappa_f (K_f c_s - c_f) + (s_m c_m - s_f c_f) \quad (50)$$

where c_s , c_m and c_f (Bq/m³) are the concentrations of radionuclides in solution, complexed to mobile DOM, and complexed to immobile OM, respectively. The parameters in **Equations (48) to (50)** are defined in **Table 4-1** and the modelled processes are illustrated in **Figure 4-6**.

⁴ Note: in this part of the report, we maintain the notations as in the original publications regarding the respective transport models

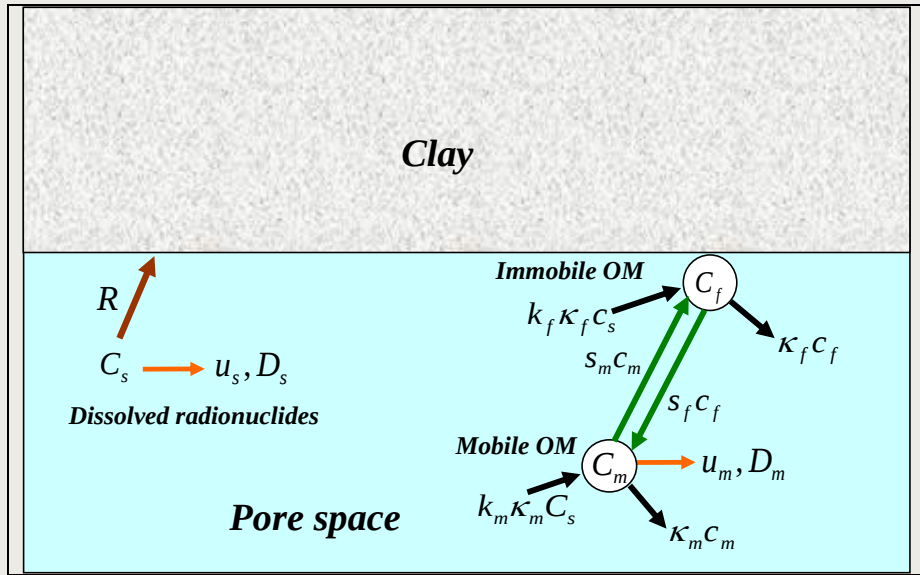


Figure 4-6: Illustration of radionuclide transport processes represented in POPCORN (Hicks, 2008)

The model assumes linear, reversible, instantaneous adsorption of dissolved radionuclides on the clay surface according to the retardation coefficient R . Radionuclide-OM complexation is described by a linear, kinetic model that is analogous to a non-instantaneous adsorption-desorption model. The term κ_m (s^{-1}) is a kinetic constant for the complexation reaction for radionuclides and mobile DOM, and the dimensionless term K_m is effectively a partition coefficient for the reaction, which may be expressed in the form $K_m = K_{dm}a_m$ where K_{dm} (m^3/kg) is equivalent to a distribution coefficient and a_m (kg/m^3) is the mass of mobile DOM per unit fluid volume. The term $\kappa_m(K_m C_s - C_m)$ in **Equation (48)** and **(49)** thus represents mass transfer between radionuclides in the dissolved phase and radionuclides complexed with mobile DOM. Similarly, the term $\kappa_f(K_f C_s - C_f)$ in **Equations (49)** and **(50)** represents mass transfer between radionuclides in the dissolved phase and radionuclides complexed with immobile OM.

Exchange of radionuclides between mobile and immobile OM complexes is characterised by the term $s_m C_m - s_f C_f$, which may represent an OM filtration and detachment process in the clay or an additional dissociation and complexation process. It is assumed that none of these processes affects porosity.

Parameter	Units	Definition
u_s	$\text{m}\cdot\text{s}^{-1}$	Mean fluid velocity, which is U_s/ϕ_s , where U_s ($\text{m}\cdot\text{s}^{-1}$) is the fluid Darcy velocity and ϕ_s is the total porosity.
u_m	$\text{m}\cdot\text{s}^{-1}$	Mean velocity of fluid carrying DOM, which is U_m/ϕ_m , where U_m ($\text{m}\cdot\text{s}^{-1}$) is the Darcy velocity for fluid carrying DOM and ϕ_m is the diffusion accessible porosity for DOM.
D_s	$\text{m}^2\cdot\text{s}^{-1}$	Solute pore dispersion coefficient given by $RD_{sapp} + \alpha_{Ls} u_s $, where D_{sapp} ($\text{m}^2\cdot\text{s}^{-1}$) is the apparent solute diffusion coefficient and α_{Ls} (m) is the intrinsic longitudinal dispersivity.
D_m	$\text{m}^2\cdot\text{s}^{-1}$	Hydrodynamic pore coefficient for mobile DOM given by $D_{mapp} + \alpha_{Lm} u_m $ where D_{mapp} ($\text{m}^2\cdot\text{s}^{-1}$) is the apparent DOM diffusion coefficient and α_{Lm} (m) is the intrinsic DOM longitudinal dispersivity.
λ	s^{-1}	Radionuclide decay constant. Ingrowth is not modelled.
R	-	Retardation coefficient for radionuclides sorbing to the clay surface, which is given by $R = 1 + (1 - \phi_s)\rho K_d/\phi_s$, where K_d ($\text{L}\cdot\text{kg}^{-1}$) is the distribution coefficient for radionuclides sorbing to the clay and ρ (kg/dm^3) is the density of the solid rock.
κ_m	/s	Kinetic constant for complexation of radionuclides with mobile DOM.
κ_f	/s	Kinetic constant for complexation of radionuclides with immobile OM.
K_m	-	Partition coefficient for complexation of radionuclides with mobile DOM, which may be defined as $K_{dm}\alpha_m$, where K_{dm} (m^3/kg) is equivalent to a distribution coefficient for complexation of radionuclides with mobile DOM, and a_m (kg/m^3) is the mass of mobile DOM per unit fluid volume.
K_f	-	Partition coefficient for complexation of radionuclides with immobile OM, which may be defined as $K_{df}\alpha_f$, where K_{df} (m^3/kg) is equivalent to a distribution coefficient for complexation of radionuclides with immobile OM, and a_f (kg/m^3) is the mass of immobile OM per unit fluid volume.
s_m	/s	The rate of exchange of radionuclides between mobile and immobile OM.
s_f	/s	The rate of exchange of radionuclides between immobile and mobile OM.

Table 4-1: Parameters of the POPCORN radionuclide transport model (Hicks, 2008)

The POPCORN model was used mainly to simulate the percolation data and recovery curves of the Am-TROM double labelled experiments performed with different size fractions of DOM in the context of the TRANCOM-clay project (see section 4.3.1). For this end, the model actually appeared quite successful and all experimental data curves could be adequately fitted. Examples of such fits are given in Figure 4-7.

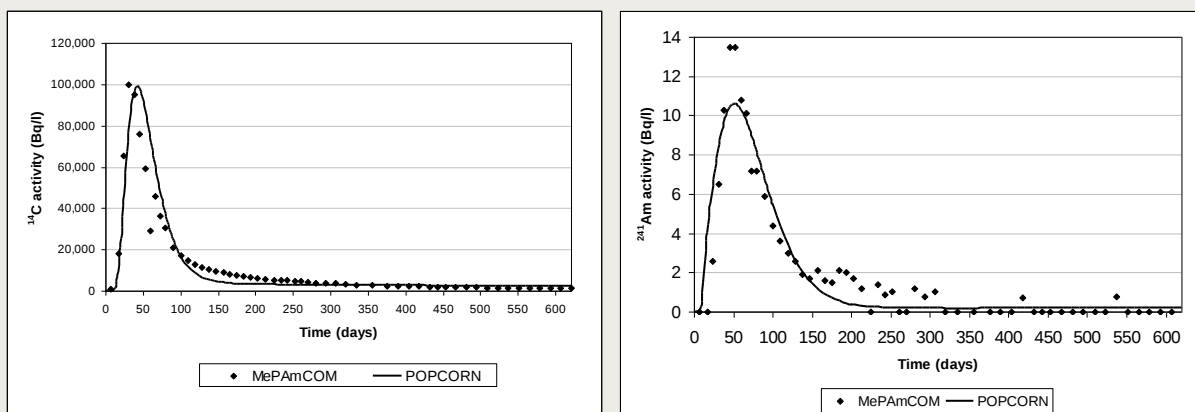


Figure 4-7: ^{14}C (left) and ^{241}Am (right) percolation data (MePAmCOM) and POPCORN results for the medium pressure ^{241}Am -TROM34 experiment (Hicks, 2008)

The kinetic rate constants between radionuclides and (both mobile and immobile) DOM that were fitted to simulate the transport were in the order of $1.0 \times 10^{-7} \text{ s}^{-1}$ to $5.5 \times 10^{-7} \text{ s}^{-1}$.

It is clear that the POPCORN code uses a variety of kinetic parameters to describe both the interaction between a radionuclide and dissolved Boom Clay organic matter and the interaction between mobile and immobile organic matter. This array of kinetic constants was however not independently investigated in experiments and is not straightforwardly compatible with the metal-humic substance interaction formalisms defined in the previous section. Although the POPCORN code was capable of successfully simulating the aforementioned double-labelled migration experiments, it was considered too elaborated and cumbersome to be used in a context of Performance Assessment calculations. Therefore, a more simplified kinetic model was developed that focuses mainly on the slow dissociation kinetics of the metal-humic substance complex.

4.3.4 Sequential column migration experiments: a simplified kinetic model

Long-term sequential column migration experiments with Tc(IV), Cm(III), Np(IV), Pu(III/IV) and Pa(V) through Boom Clay were specifically designed to interpret the organic matter linked radionuclide transport (Maes et al., 2011). The following line of reasoning was assumed with respect to the sequential migration set-up: as the radionuclide (e.g. Pu, Cm) concentration in the eluates of long-term running percolation experiments (Figure 4-8, first clay core) remained constant for many years, the RN-DOM species eluting from the these cores are assumed to be well equilibrated with the Boom Clay pore water.

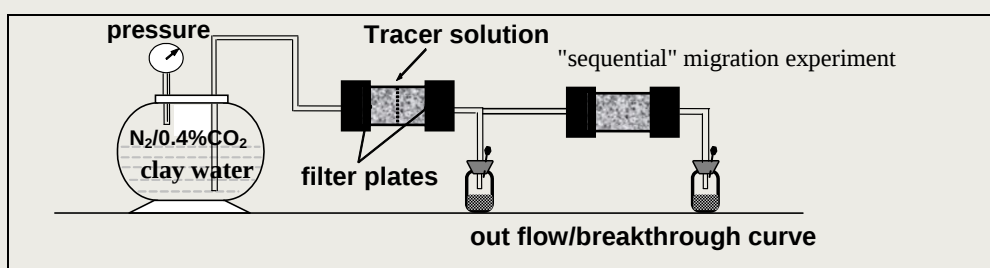


Figure 4-8: Schematic representation of a percolation type migration experiment with radionuclide source sandwiched between two Boom Clay cores. Coupling to a second clay core for the sequential migration experiment uses the constant concentration eluting from the 1st core as input concentration.

Therefore, they were used as input source (constant concentration boundary condition) for a migration experiment through a second clay core (resulting in a sequential column migration experiment). In this way, the transport parameters of the RN-DOM species can be determined and comparison of the radionuclide concentrations in the eluates of the 2nd cores with the input concentration provides information on the dissociation behaviour. If the RN is in the form of a stable (non-exchangeable) DOM complex/colloid, the outlet concentration should approach the inlet concentration after breakthrough; if not, dissociation kinetics plays a role.

The elution curves for the different radionuclides out of the second clay core are illustrated in **Figure 4-9**. It can be seen that they exhibit similar features as the elution curves of the first core. After an initial breakthrough phase, a constant outlet concentration value tends to be reached (which is to be expected). However, this value is for Cm-244 and Pu-238 about one order of magnitude lower than the input concentration. This indicates that the transported species do not behave as a conservative tracer (as otherwise the outlet concentration should equal the inlet concentration) and confirms that the observed concentrations do not correspond to the solubility of a certain solid phase. Instead, the concentration decrease implies that the RN-DOM species eluting from the first core are slowly dissociating. Similar observations can be made for the other radionuclides that associate with DOM (i.e. Np, Pa, Tc).

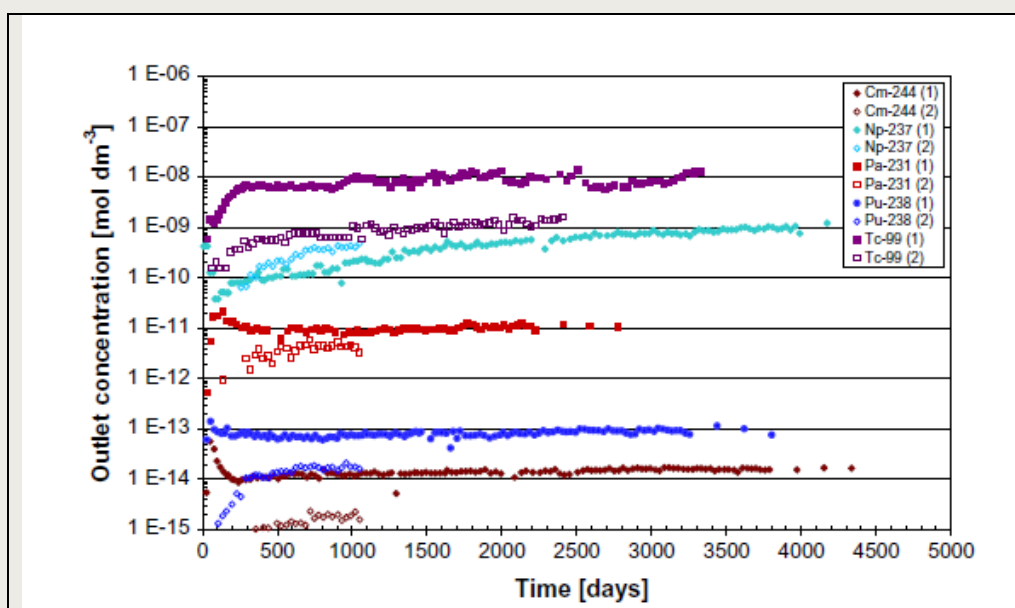


Figure 4-9: Evolution with time of the concentrations measured in the water collected at the outlet of the diffusion experiments for clay core (1) and the sequential coupled core (2)

In order to describe this colloid facilitated transport with dissociation kinetics, a transport model was developed based on the conceptual model described in **Figure 4-10**. Radionuclides in solution will either be present as a mobile RN-DOM complex or "free inorganic" radionuclide species in solution ($[RN_{inorg}]_{liquid}$). The transfer between $[RN_{inorg}]_{liquid}$ and the RN-DOM complex is described by a complexation constant and dissociation kinetics. Both species can interact with the solid phase. It is assumed that this interaction in case of $[RN_{inorg}]_{liquid}$ is mainly due to sorption processes and can be described by a retardation factor (R_{RN}) that can be linked to batch sorption data. In case of RN-DOM the retardation factor (R_{RN-DOM}) is considered as a lumped factor accounting for both sorption and colloid filtration processes (see **section 3.4.3**). Overall, dissolved OM is only poorly retarded within Boom Clay and R_{RN-DOM} is therefore expected to be only of secondary importance to describe RN-coupled transport. Within this transport model, the amount of parameters

remains limited and most of them can be obtained from independent measurements (batch complexation/solubility experiments, batch sorption experiments, DOM transport experiments).

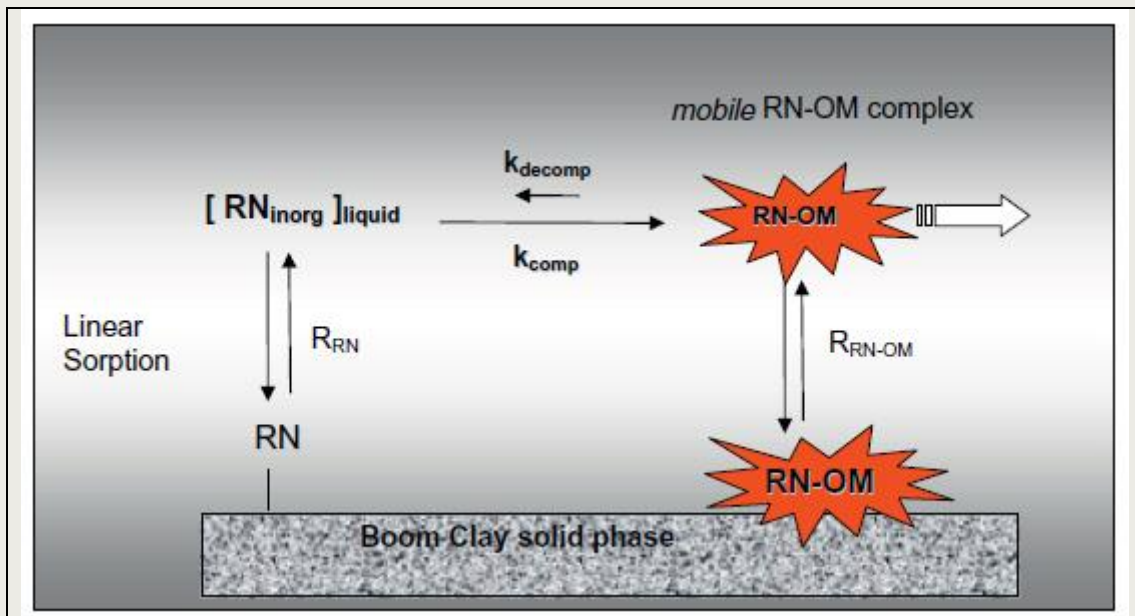


Figure 4-10: Conceptual model used for the interpretation of organic matter linked radionuclide migration in Boom clay (Maes et al., 2011).

The transport of the RN-OM mobile complex is described by:

$$(\eta + \rho_b K_{d,RNOM}) \frac{\partial(c_{RNOM})}{\partial t} - \nabla[\eta D_{p,RNOM} \nabla c_{RNOM} \mu_{Darcy} c_{RNOM}] = -\lambda(\eta + \rho_b K_{d,RNOM}) c_{RNOM} \quad (51)$$

The transport of the free RN-species in solution is described by:

$$(\eta + \rho_b K_{d,RN}) \frac{\partial(c_{RN})}{\partial t} - \nabla[\eta D_{p,RN} \nabla c_{RN} \mu_{Darcy} c_{RN}] = -\lambda(\eta + \rho_b K_{d,RN}) c_{RN} - \eta Q_{sol-OM} \quad (52)$$

where η is the diffusion accessible porosity (-), ρ_b the dry bulk density (kg/m^3), c_{RN} , c_{RNOM} , c_{OM} are the concentrations [M] of the free inorganic radionuclide species in solution, the concentration of the mobile RN-OM complex, and the concentration of the mobile OM (M), respectively.

$D_{p,RNOM}$ and $D_{p,RN}$ are the pore diffusion coefficients (D_p) of the RN complexed to the mobile OM and of the free inorganic RN species in solution (m^2/s), respectively; μ_{Darcy} is the Darcy velocity and γ accounting for radioactive decay.

$K_{d,RNOM}$ and $K_{d,RN}$ are the sorption distribution coefficients (K_d) for the RN complexed to the mobile OM and for the free inorganic RN species in solution (L/kg), respectively. They are related to the retardation factors R_{RNOM} and R_{RN} by the following equation:

$$R = 1 + \frac{\rho_b K_d}{\eta} \quad (53)$$

The mass transfer (Q_{sol-OM}) of the RN between the OM complexed form and the "free" RN in solution is given by:

$$Q_{sol-OM} = k_{comp} c_{RN} c_{OM} - k_{decomp} c_{RNOM} \quad (54)$$

The exchange of the radionuclide between the $[RN_{inorg}]$ and the RN-OM complex is described by a complexation constant (K_{RN-OM}), representing the ratio between the complexation/association and decomplexation/dissociation kinetics:

$$[RN_{inorg}] + [OM] \xrightleftharpoons[k_{decomp}]{k_{comp}} [RN-OM] \text{ and } K_{RN-OM} = \frac{k_{comp}}{k_{decomp}} = \frac{c_{RNOM}}{c_{RN} \cdot c_{OM}} \quad (55)$$

where k_{comp} and k_{decomp} are the kinetic rate constants for the RN-OM complexation/association and decomplexation/dissociation reactions, respectively.

The equations are similar to the equations used in the POPCORN code (Hicks, 2008; Trancom II, 2004), but are more simplified. This approach was chosen because of two reasons: 1) it is assumed that the "fast" association/dissociation reactions are very rapid compared to the time frames typically encountered in these migration set-ups (~ months, years) and certainly with respect to the time frame involved in performance assessment calculations; 2) we consider that the "overall" association/dissociation reactions can be described by a RN-OM interaction constant (K_{RN-OM}) and a kinetic dissociation rate (k_{decomp}).

It should be mentioned that the RN-OM interaction constant (K_{RN-OM}) may refer to different mechanisms, i.e. complexation (Liu et al., 2008) or colloidal interaction (Maes et al., 2003) and in most cases, the exact interaction mechanism is not known. Therefore, K_{RN-OM} is considered as a mathematical constant, which is conditional in nature and is only applicable to undisturbed Boom Clay conditions. Under these conditions, K_{RN-OM} describes the overall reaction between the dominant inorganic aqueous RN species $[RN_{inorg}]$, and dissolved OM.

In order to constrain the modelling, K_{RN-OM} is fixed.

Maes et al. (2003), studied the interaction of uncharged Tc(IV) species, i.e. $TcO(OH)_2$ with dissolved Boom Clay OM and obtained an interaction constant $\log K_{TcOM} = 5.3 \pm 0.3$ which is suitable for our modelling.

Liu et al. (2008) studied the influence of Boom Clay organic matter on the solubility of Eu(III) in order to come to a description of the interaction of trivalent RN with OM.

They successfully described the interaction between Eu(III) and OM using the Humic ion-binding model VI (Tipping, 1998). These data were reinterpreted wrt. the general reaction equation (Equation (55)) in order to derive a "conditional interaction constant" which can be used in the transport model. Based on the available Eu concentrations in equilibrium with an Eu-solid phase at different OM concentrations a generalised $K_{RN-OM} = 4.7 \pm 0.3$ was obtained.

A similar study was done for thorium, solubility (ThO_2) under Boom Clay geochemical conditions at different OM concentrations (Maes et al., 2011) and following the same approach as for Eu, a $\log K_{ThOM} = 6.1 \pm 0.2$ was derived.

For Cm, Np, Pu, and Pa no experimental data are available enabling to estimate the interaction constants for these radionuclides. Therefore, we rely on the "chemical analogy", e.g. between Eu(III) and Cm(III) to constrain the parameters for fitting.

An overview of the other input parameters used in the modelling is given in Table 4-2. The sequential column experiments were fitted for 3 variables: R_{RN} , R_{RNOM} , k_{decomp} . The model

provides excellent fits (**Figure 4-11**) to the experimental data and the fitted parameters are presented in **Table 4-3**.

Table 4-2: Input parameters used for modelling of the sequential migration experiments (Maes et al., 2011)

	Tc	Cm	Np	Pu	Pa
[RN] _{input} [mol/l]	$9.0 \cdot 10^{-9}$	$1.5 \cdot 10^{-14}$	$1.3 \cdot 10^{-9}$	$8.3 \cdot 10^{-14}$	$1.0 \cdot 10^{-11}$
V_{darcy} [m/s]	$9.8 \cdot 10^{-10}$	$1.1 \cdot 10^{-9}$	$1.2 \cdot 10^{-9}$	$1.9 \cdot 10^{-9}$	$1.1 \cdot 10^{-9}$
$\log K_{RNOM}$	5.3	4.7	^(a) 5.3 ^(b) 6.1	^(c) 4.7 (PuIII) ^(b) 6.1 (PuIV)	5.3
[OM] [eq/l]	$3.7 \cdot 10^{-4}$				
$D_{pore,RNOM}$ [m ² /s]	$9.5 \cdot 10^{-11}$				
η_{RNOM} [-]	0.16				
$D_{pore,RN}$ [m ² /s]	$2.0 \cdot 10^{-10}$				
η_{RN} [-]	0.37				

a) analogy with Tc(IV)

b) analogy with Th(IV)

c) analogy with Eu/ (III)

Table 4-3: Summary of the fitted parameters k_{decomp} , R_{RNOM} and R_{RN} . The latter is compared to independent determined sorption data (Maes et al., 2011)

	$\log K_{RNOM}$ (exp.)	k_{decomp} (fit) [s ⁻¹]	R_{RNOM} (fit) [-]	$\log R_{RN}$ (fit) [-]	$\log K_{d,RN}$ (exp.) [log(l/kg)]	^(a) $\log R_{RN}$ (exp.) [-]
Tc(IV)	5.3	$1.7 \pm 0.1 \cdot 10^{-6}$	12 ± 1	4.43 ± 0.05	3.6-4.8	4.3-5.5
Cm(III)	4.7	$1.3 \pm 0.3 \cdot 10^{-6}$	28 ± 6	3.57 ± 0.22	^(b) 2.9-3.9	3.5-4.6
Np(IV)	^(c) 5.3 ^(d) 6.1	$0.7 \pm 0.2 \cdot 10^{-6}$ $0.7 \pm 0.2 \cdot 10^{-6}$	27 ± 4 27 ± 4	3.61 ± 0.14 4.40 ± 0.14	^(e) 2.6-3.9	3.3-4.6
Pu (III)	4.7	$1.0 \pm 0.1 \cdot 10^{-6}$	22 ± 2	4.00 ± 0.23	^(b) 2.9-3.9	3.5-4.6
Pu(IV)	6.1	$1.1 \pm 0.1 \cdot 10^{-6}$	20 ± 3	5.08 ± 0.17	^(e) 2.6-3.9	3.3-4.6
Pa(V)	5.3	$0.3 \pm 0.2 \cdot 10^{-6}$	18 ± 4	3.81 ± 1.22		

a) $R = 1 + \rho \cdot K_d / \eta$ ($\rho = 1.7$ kg/l, $\eta = 0.37$)

b) Based on Am sorption experiments on Boom Clay under relevant geochemical conditions

c) Using the derived logK value for Tc(IV) as analogue

d) Using the derived logK value for Th(IV) as analogue

e) Based on Th sorption experiments on Boom Clay under relevant geochemical conditions

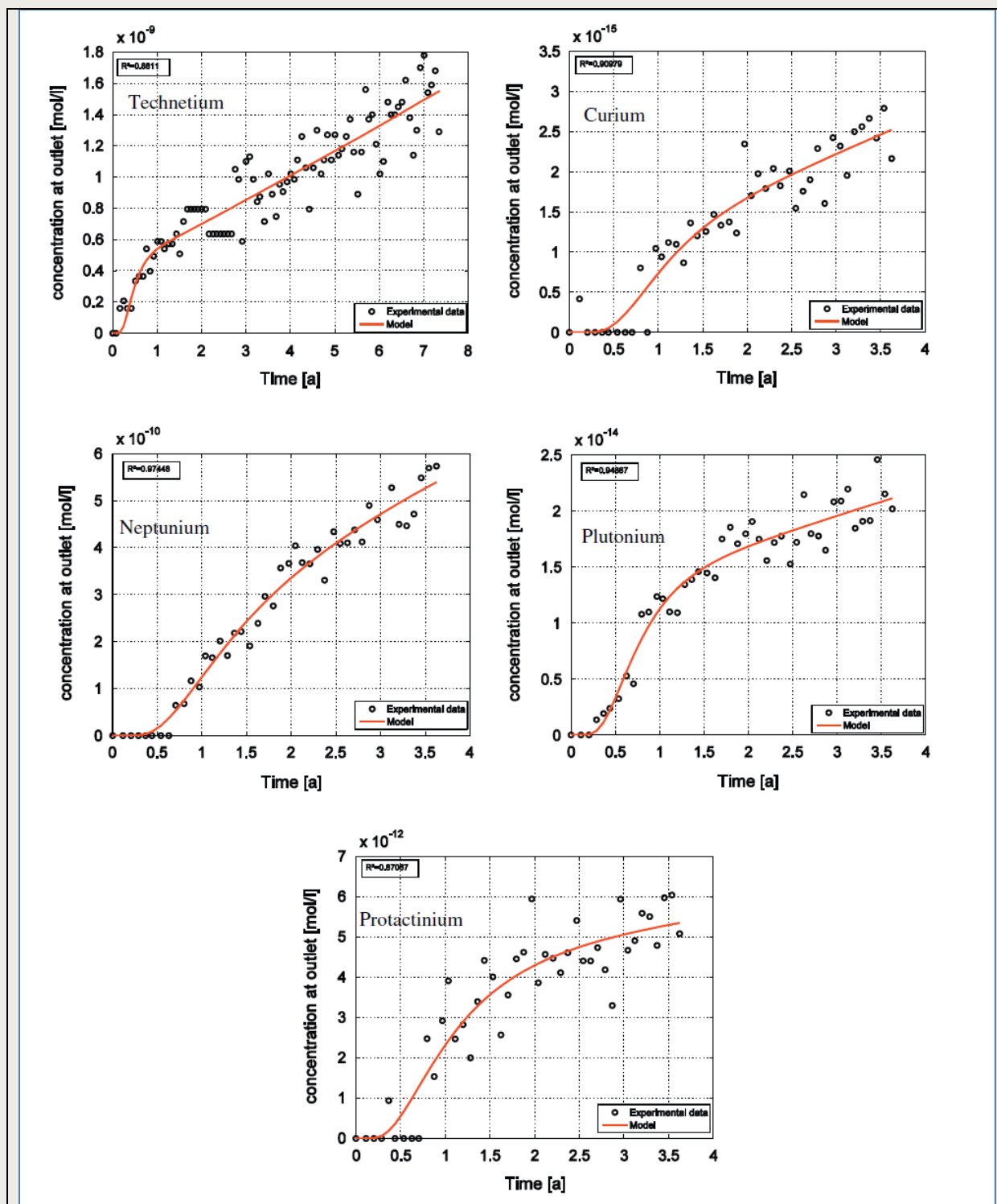


Figure 4-11: Results of the fitting of the outflow profiles measured from the sequential migration experiments using the proposed conceptual model (Maes et al. 2011)

The proposed phenomenological model describes very well the experimental data for Tc(IV), Cm(III), Np(IV), Pu(III/IV) and Pa(V).

Based on OM transport parameters and RN-OM interaction constants that are independently determined for some elements (and using analogy between the elements) the model is well constrained and requires only 3 fitting parameters: k_{decomp} , R_{RN} and R_{RNOM} . The resulting fitted RN dissociation kinetics are found to be in a narrow range ($0.3\text{-}1.7 \cdot 10^{-6} \text{ s}^{-1}$), despite the difference in aqueous speciation. The fitted RN retardation factor (which is along with

the RN-OM complexation constant the most important parameter) was found to be consistent with independently determined sorption data. This agreement provides confidence in the conceptual model.

The dissociation kinetics govern the transfer from RN mobilised by OM to RN sorbed on the solid phase and the kinetic decomplexation leads to an appreciable retardation on the colloid facilitated transport. Despite the relative fast kinetics compared to the long-time scales envisaged, they cannot be ignored and the transport behaviour cannot be approximated by sorption data only.

This conceptual model is an important step forward in the description of OM linked RN transport in Boom Clay and it can be used directly for safety assessment analysis: i) it is process based, ii) the model is easy to implement without oversimplification, iii) elements with a similar OM association behaviour can be described in the same way with a rather narrow range of input parameters.

4.4 *Extrapolation to the Netherlands*

The conceptual model developed by SCK•CEN to describe the DOM-facilitated transport of RN in the Boom Clay is based on a simplification of the physico-chemical processes occurring. It has the strong advantage to facilitate the implementation of laboratory data into performance assessment calculations and to allow the extrapolation of the observed RN migration over time scale of maximum decades to geological time scales. However, because of simplification most of the parameters composing the model are conditional and do not reflect any properties of the Boom Clay, the RN and the DOM. Hence though the conceptual model is in its formalism transferable to the Netherlands, the various parameters and notably $K_{\text{RN-OM}}$ would have to be directly estimated in the physico-chemical conditions met in the Netherlands. It is indeed expected that a change of ionic strength would affect the binding of RN with OM because it affects both the OM (coagulation, compaction/dissociation, charge modification) and in certain case the RN speciation.

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