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***Recommendations for performing  
radionuclide sorption experiments***

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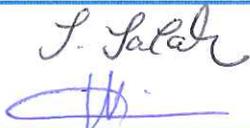
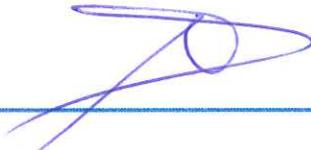
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## **Abstract**

In order to perform sorption experiments in a standardized way, recommendations for performing sorption experiments with radionuclides (RN) on clayrocks or its constituents (e.g. pure clay minerals, organic matter,...) were formulated. The recommendations are based on the OECD guideline (nr 106) 'Sorption – Desorption Using a Batch Equilibrium Method' (OECD, 2000), aiming at estimating the adsorption/desorption behaviour of a substance on soils, on the experience and knowlegde we have built up at SCK•CEN over the years and on the publications of Bradbury and Baeyens from PSI-LES. The guidelines for sorption modelling are based on the NEA publications (NEA 2001, 2005 and 2012).

After explaining how the degree of sorption can be expressed and the general approach of a sorption experiment, recommendations are given for the different components of the sorption experiment: the sorbent, the background solution and the test substance. Further, the requirements for the sorption experiment are amplified and a standard stepwise experimental procedure is proposed. In addition, a brief overview of the different factors that can influence the sorption behaviour, the analytical methods and error propagation are illustrated. At last, a brief description on how to model sorption experiments what is needed for this modeling is given.

## **Keywords**

Sorption, radionuclides, clays, clayrocks, protocol, recommendations

# 1 Introduction

This report provides recommendations for performing sorption experiments with radionuclides (RN) on clayrocks or its constituents (e.g. pure clay minerals, organic matter,...).

**Sorption** includes all processes which take place at the surface (exterior boundary) of solid constituents, or at the interfaces between two phases (e.g. the solid-liquid interface) (Parks, 1990). Sorption itself can be defined as the accumulation of a substance or material at an interface between the solid surface and the bathing solution (Sparks, 2003). The substance to be tested is referred to as **test substance**. The material that accumulates at the interface is referred to as **sorbate**. In this document the test substances to study are mainly radionuclides. The solid surface on which the (ad)sorbate accumulates is referred to as the **sorbent**. In most cases, the sorbent to study is a clayrock or a pure clay mineral, but also the minor components of a clayrock (e.g. organic matter in Boom Clay), can be studied as sorbent.

The OECD guideline (nr 106) 'Sorption – Desorption Using a Batch Equilibrium Method' (OECD, 2000), aiming at estimating the adsorption/desorption behaviour of a substance on soils, served as support to develop the guidelines for the sorption of radionuclides on clay and organic matter. Furthermore, the recommendations are based on the experience and knowledge we have built up at SCK•CEN over the years and on the publications of Bradbury and Baeyens from PSI-LES who are very experienced with sorption experiments. The guidelines for sorption modelling are also based on the NEA publications (NEA 2001, 2005 and 2012).

The document is structured as follows. First it is described how the degree of sorption can be expressed and the general approach of a sorption experiment is given (section 2). Thereafter, the different components of the sorption experiment are described: the sorbent (section 3), the background solution (section 4) and the test substance (section 5). In section 6 the requirements for the sorption experiment are amplified and a standard stepwise experimental procedure is proposed. In section 7 the different factors that can influence the sorption behaviour are discussed briefly. Further, the analytical methods (section 8) and error propagation (section 9) are illustrated. At last, in section 10 it is briefly described how sorption experiments could be modeled and what is needed for this modeling.

## 2 How to measure sorption?

### 2.1 Solid-liquid distribution

The combination of different sorption processes results in a distribution of a specific element between the aqueous phase and the solid phase. This distribution is described by so-called solid-liquid distribution coefficients, which represents a measure for the sorption behaviour of a specific element. This solid-liquid distribution coefficient is expressed in two different annotations in literature, i.e.  $K_d$  and  $R_d$ , and is defined as:

$$K_d \text{ (or } R_d) = \frac{C_{ads}}{C_{sol}}$$

where  $C_{ads}$  is the concentration of an element sorbed on the solid phase and  $C_{sol}$  is the corresponding concentration of the element in the liquid phase. This is in analogy with the description of the equilibrium constant of the following reaction: Solid + dissolved RN  $\leftrightarrow$  Solid-RN. In principle,  $K_d$  is used when the partitioning of an element between the aqueous phase

and a solid phase is in thermodynamic equilibrium, while  $R_d$  is used when the partitioning cannot be assumed to be at equilibrium (the sorption is not fully reversible) or due to kinetic factors.

The term  $K_d$  is used to quantify the sorption described as the surface chemical interactions between aqueous species and solid sorbents. All other processes that may affect RN transport, like precipitation, formation of solid solutions or other physical processes, should not be involved.

## 2.2 General concept of the batch sorption experiment

The most common way to study sorption are batch sorption experiments. The approach of a batch sorption experiment consists of measuring the concentration (non-active isotope) or activity (active isotope) of the test substance before and after bringing the clay in suspension with the solution containing the test substance.

Known volumes of solutions of the test substance, non-active or active, at known concentrations or activities are added to clay samples (or other sorbent material) of known dry weight which have been pre-equilibrated with the solution. The mixture is agitated for an appropriate time. The clay suspensions are then separated by (ultra)centrifugation and, if so wished, (ultra)filtration and the supernatant/filtrate is analyzed. The amount of test substance adsorbed on the soil sample is calculated as the difference between the amount of test substance initially present in solution and the amount remaining at the end of the experiment (indirect method).

In case of using an active test substance, the distribution coefficient is calculated based on the initial and equilibrium activity. The initial activity ( $A_{init}$ ) and the activity in the supernatant after equilibration ( $A_{eq}$ ) are determined by liquid scintillation counting (LSC) (mostly  $\alpha$  and  $\beta$  emitters) or by global-alpha/gamma-spectrometry ( $\alpha/\gamma$ -emitters), depending on the element. The distribution of the active radiotracer on the solid phase and in the liquid phase can then be easily determined by the following equation:

$$K_d = \frac{(A_{init} - A_{eq})}{A_{eq}} \cdot \frac{V}{m}$$

with  $A_{init}$  the total initial activity of the radionuclide in solution (Bq),  $A_{eq}$  the activity at equilibrium of the radionuclide in solution (Bq),  $V$  the volume of the liquid phase (L) and  $m$  the mass of the solid phase (kg). The difference between  $A_{init}$  and  $A_{eq}$  represents the sorbed activity. In case that inactive isotopes are measured instead of radiotracers, activity  $A$  is replaced by concentration  $C$  in the formula.

Batch sorption experiments are designed to produce two main types of data sets which are presented as *sorption edges* and *sorption isotherms*. For the *sorption edges*, sorption is determined at low radionuclide concentration as function of pH. In this case, only a radioisotope is added. For the *sorption isotherms*, sorption is measured at constant pH as function of concentration. In that case, the concerning element is added also in the inactive form to the clay suspensions in order to cover a range of concentrations.

Remark: Another approach of studying sorption is to study the sorption on compacted clay by bringing the clay in contact with a solution containing the RN to investigate until equilibrium. The approach of this method is not described in this TN.

### 3 Sorbents

Three different types of sorbents are described below: natural clayrocks, constituting clay minerals of the natural clayrocks in the pure form and solid organic matter.

#### 3.1 Natural clayrocks

The natural clayrocks of our interest comprise the Boom Clay and the Ypresian clays.

##### 3.1.1 Sampling and pretreatment

Preferably the sample material (e.g. clay core) is non-oxidized and stored under vacuum before using it for sorption experiments.

Before starting the experiment, the moisture content of the clay should be determined (as described in 6.3.7). Depending on the procedure, the clay will be added to the background solution in solid form or in suspension. When added as solid form, the clay should be crushed into fine material (<2mm). If the clay is added as suspension, the clay should be brought into suspension and be vigorously stirred on a magnetic stir plate at least 24h before adding aliquots of the suspension to the sample.

##### 3.1.2 Characterization

A typical characterization of the clay consists of the following analyses:

➤ *Specific surface area*

The specific surface area (m<sup>2</sup>/g) is measured by N<sub>2</sub>-BET-analysis. The Brunauer–Emmett–Teller (BET) analysis is based on the physical adsorption of gas molecules on a solid surface (Brunauer et al., 1938). The equipment used at SCK•CEN is a Micromeritics Tristar® II 3020 Surface Area Analyzer. The experimental procedure applied at SCK•CEN is given in Annex 1.

➤ *CEC*

The cation exchange capacity (CEC – meq/kg) of a clay mineral or clayrock can be determined with different methods. The method mostly used at SCK•CEN is the Cu(trien)-method (Meier and Kahr, 1999). The detailed procedure used at SCK•CEN is given in Annex 2. Another possible method is the cobalt hexamine method (Remy and Orsini, 1976).

➤ *Mineralogical composition*

The bulk mineralogy and clay mineralogy is determined quantitatively and qualitatively by XRD analysis (X-ray powder diffraction).

➤ *Solid organic matter content*

The Total Carbon (TC) content of the solid phase is measured with the SSM-5000AL module for solid phases of the TOC-LCPH Shimadzu equipment.. Total carbon (TC) is

determined by catalytic oxidation of the sample at 680 °C (liquid samples) or 900 °C (solid samples), converting the carbon in the sample to CO<sub>2</sub>. The CO<sub>2</sub> is dispersed into the carrier gas (pure oxygen) and measured by a non-dispersive infrared detector (NDIR). Total inorganic carbon (TIC) is determined by acidification and purging of the sample (at room temperature for liquid samples and at 200 °C for solid samples), converting the TIC to CO<sub>2</sub> and the CO<sub>2</sub> is again measured by the NDIR. The Total Organic Carbon can then be calculated by subtraction (TOC = TC – IC).

➤ *Natural/background concentrations*

Naturally present concentrations of cations in the clayrock can be measured by ICP-MS/AES after total digestion.

## 3.2 Pure clay minerals

Next to the natural clayrocks, sorption can also be studied on the pure constituting minerals of the clayrock. For Boom Clay, the most abundant ones are illite and montmorillonite.

### 3.2.1 Pretreatment

Pure clay minerals can be bought from instances like the Source Clays Repository of the Clay Minerals Society or sampled at specific locations where the clay is present in high weight percentage. The clays are generally purified and conditioned before using in sorption experiments.

Purification is obtained by removing e.g. organic matter, (iron)oxides/hydroxides and carbonate with a multistep process. Mostly, the ground original clay mineral is exchanged into the Na-form. A procedure can be found in Annex 3. Exchanging into the Ca-form is also an option, but Na has as monovalent cation the advantage that it is easier for interpretation than the divalent Ca. Moreover, groundwater in deeper layers are mostly Na dominated waters, which makes Na also more representative.

If the sorption needs to be performed at another pH than the natural one, the clay needs to be titrated to the desired pH.

### 3.2.2 Characterization

A typical characterization of the clay consists of the following analyses:

➤ *Specific surface area*

Description: see above.

➤ *CEC*

Description: see above.

➤ *Mineralogical composition: XRD*

The mineralogical composition of the unpurified clay mineral can be determined with XRD in order to identify any secondary phases. After purification, XRD can be repeated in order to check if the secondary phases were all removed.

➤ *Structural formula*

The mean structural formula can be derived by EPMA (Electron Probe Micro-Analyzer) analysis. Another possibility to derive the formula is to determine the total chemical composition with ICP after acid digestion or fusion with lithium borate or other fluxes. If speciation of Fe is relevant for the mineral in question, an additional extraction is required.

### **3.3 Solid natural organic matter**

Besides to clay and other minerals, Boom Clay contains also a solid organic matter (SOM) fraction. At the Mol site, the SOM varies between 0.5 and 3.5 wt% (Honty and De Craen, 2012). The SOM consists of kerogen (insoluble part) and bitumen (soluble in organic solvents), with kerogen being the largest fraction ( $\pm 80\%$ ) (Deniau et al., 2004). The kerogen fraction can be extracted using e.g. the separation procedure by Durand and Nicaise (1980) developed at IFP (Institut Français du Pétrole). The latter represents however a very laborious (multi-step) and harsh technique (also expensive), which can possibly alter the kerogen fraction. Moreover, it is uncertain if a complete separation of the kerogen can be achieved by the different chemical steps.

Another issue is the fact that it is unsure if sorption on the kerogen fraction is representative for the sorption on the total pool of SOM. It is possible to perform sorption experiments on the isolated kerogen fraction, but as long as it is not known if the other fraction(s) of the SOM may also interact with the RN, uncertainty remains on the results.

The fact that sorption on the solid NOM is difficult to determine, results also in limitations for the application of the component additivity approach (CAA). At this moment, the sorption on the solid NOM is assumed to be negligible compared to the fraction sorbed on the clay. This is probably valid for highly sorbing RN, but it is not sure if this is true for RN which tend to sorb less strong on the clay.

## **4 Background solution**

In the OECD guidelines for determining sorption on soil samples, it is prescribed to use  $\text{CaCl}_2$  0.01 M as a background solution. The claywater in Boom Clay is, however, dominated by Na as main cation, and the pure minerals we study, are mostly brought into the Na-form (3.2.1). Therefore, it is suggested to use natural claywater, synthetic claywater that mimicks the natural claywater or Na-electrolytes as background solution instead of  $\text{CaCl}_2$ . For clayrocks, it is most logic to use natural or synthetic claywater in order to be as representative as possible. Another reason to use Na-electrolytes instead of  $\text{CaCl}_2$  is that the monovalent Na is easier for interpretation than the divalent Ca. When studying clay minerals in the Ca-form, it is of course advised to use  $\text{CaCl}_2$ .

### **4.1 Natural claywater**

If natural claywater is available, it is suggested to use this as background solution. In case of Boom Clay, natural claywater is extracted via piezometers installed in the HADES underground facility. This pore water was referred to as Real Boom Clay Water and abbreviated as RBCW in the past. The composition of the RBCW could however be different, depending on the origin

of the water. Therefore, it is preferred to use the term 'natural Boom Clay water' and mention the piezometer with which the pore water was extracted instead of using the general term of RBCW.

Before, the porewater extracted via piezometer EG/BS in the HADES underground facility was mostly used in sorption experiments (De Craen et al., 2004). The porewater sampled from the EG/BS piezometer differs however from porewaters sampled in other piezometers (i.e. Spring, Morpheus), especially with regard to the size fractions of the dissolved organic matter (DOM) (Durce et al., 2016). The EG/BS piezometer is vertically installed with one of the filters located in the double band layer, where the DOM size distribution is different than the rest of the Boom Clay profile. Therefore, it is preferred for future sorption experiments to use clay water extracted from the Spring piezometer which is horizontally installed at the level of HADES and hence more representative.

The chemical composition of the clay water should be checked before starting the experiments and should consist of:

- *pH measurement*
- *cation analysis by ICP-AES*
- *anion analysis by ion chromatography*
- *(in)organic carbon content by TOC/IC analyzer*

## **4.2 Synthetic solutions**

Besides natural porewater, the sorption of RN on clayrocks can also be studied by using synthetic claywater as background solution. When studying sorption on pure/single clay minerals, Na-electrolytes are generally used. This allows also to study the sorption at varying conditions, e.g. varying ionic strength, presence of (in)organic carbon,...

The composition of the synthetic solution is known from the preparation of the solution, but, should be preferably also measured/analyzed in order to check, if no mistakes occurred when preparing the solution and to screen for impurities in the solution (which can possibly influence the results).

### **4.2.1 Synthetic claywater**

Synthetic claywater is the definition for a solution that mimicks the composition of the natural clay water. For Boom Clay a synthetic solution is composed based on the average pore water composition of the natural claywater, except for the dissolved organic matter (DOM). This synthetic solution is referred to as Synthetic Boom Clay Water and abbreviated as SBCW. The composition is given in Table 1 and the protocol for preparing the solution is described in Annex 4. The composition of this SBCW represents the inorganic composition of the Boom Clay pore water.

Table 1 Composition of the Synthetic Boom Clay Water (SBCW) (De Craen et al., 2004).

Composition	Concentration	
	mg/L	mM
<b>SBCW</b>		
NaHCO <sub>3</sub>	1170	13.9
NaCl	10	0.17
Na <sub>2</sub> SO <sub>4</sub>	0.3	0.002
NaF	11	0.26
KCl	25	0.34
MgCl <sub>2</sub> •6H <sub>2</sub> O	22	0.11
H <sub>3</sub> BO <sub>3</sub>	43	0.70
FeCl <sub>2</sub>	3	0.024
CaCO <sub>3</sub> (s)	saturated	

#### 4.2.2 Background electrolyte

Next to the natural or synthetic claywater, a simple background electrolyte can be chosen too. This is mostly the case when studying single clay minerals like illite. As discussed above, these clay minerals are purified and mostly conditioned to the Na-form. Hence, Na-electrolytes like NaCl or NaClO<sub>4</sub> are suitable in order not to disturb the equilibrium. Ionic strength is generally varied between 0.01 and 1 M, depending on the objectives of the study. This range covers the natural ionic strength of the clays, but also higher ionic strengths in case of scenarios of increased salinity (e.g. seawater intrusion).

In order to fix the pH of the background electrolyte at a certain value, a buffering agent should be added to the suspensions. Table 2 lists buffering agents for the different pH regions, which are known for their insignificant complexation with metals (Perrin and Dempsey, 1974). Buffers are generally used at concentrations around 10<sup>-3</sup> M.

Table 2 Buffering agents for the different pH regions.

Buffer		pKa
AA	acetic acid	4.76
MES	2-(N-morpholino)ethanesulfonic acid	6.15
MOPS	3-(N-morpholino)propanesulfonic acid	7.2
TRIS	tris(hydroxymethyl)aminomethane	8.06
CHES	N-cyclohexyl-2-aminoethanesulfonic acid	9.55

#### 4.2.3 Dissolved organic matter

When studying the effect of dissolved organic matter (DOM) on the sorption behaviour of a radionuclide, sorption experiments should be performed with and without DOM in solution. Therefore, DOM is added to a synthetic background solution. In general, DOM is added in the form of humic acids. As the organic matter fraction in Boom Clay mainly consists of humic acids (70% - Dierckx et al., 2000), they are assumed to be the most representative for the DOM pool. These humic acids can be commercial ones (like Aldrich humic acid) or they can be extracted

from natural Boom Clay water or from solid material via leaching. The protocol to perform a humic acid extraction is described in Annex 5.

The concentration of the DOC is analyzed with the TIC/TOC analyzer (TOC-LCPH Shimadzu). The same method is used as described for the solid TOC (3.1.2), except that the combustion temperature is 680 °C instead of 900°C.

## 5 Radionuclide

The sorption behaviour of radionuclides can be tested with non-active as well as with active isotopes of the element in question, but in general a radio-isotope will be used. When performing a sorption isotherm experiment, a non-active isotope is used to cover the concentration range. Further, the sorbent can contain also non-inactive isotopes as background.

### 5.1 Radio-isotope

The radio-isotopes should be bought from a certified organisation, preferably in a carrier-free (i.e. without added inactive isotope) solution.

The radionuclide concentration is calculated with the specific activity of the radio-isotope (in Bq/g). In case that the radio-isotope source solution contains also carrier, i.e. an inactive isotope of that element, the specific activity is lower than the theoretical maximum specific activity.

Aliquots of the (diluted) radio-isotope source solution will be added to the background solution (before adding the sorbent) or to the suspensions, depending on the followed procedure (more details can be found in section 6). The concentrations of the radionuclide are always trace concentrations ( $< 10^{-7}$  M).

In the case of short half-life tracers, decay corrections should be applied.

### 5.2 Inactive isotope

#### 5.2.1 Natural concentrations

In case that the sorbent contains inactive isotopes of the radionuclide that is studied (e.g. for Ni, Zn, Sr,...), the natural concentration, i.e. background concentration present in the sorbent plays also a role, especially when this is much higher than the radionuclide concentration. In this case, the background concentration should be taken into account for the calculation of the distribution coefficient. The background concentrations in the sorbent can be measured after bringing the sorbent in suspension with the background solution.

Also humic acids extracted from the Boom Clay water can contain amounts of trace elements. These background concentrations should be taken into account too.

Finally, it is advised to check if the synthetic solution (electrolyte with buffer agent) contains a background concentration of the element in question due to impurities.

### 5.2.2 Sorption isotherm

When sorption is studied as function of the concentration, an inactive isotope of the test substance is added in a range of concentrations. The maximum concentration should not exceed the solubility limit under the experimental conditions, otherwise the  $K_d$  will also be influenced by the precipitated fraction.

For the lower limit, the concentration is limited by the detection limit or by the radionuclide concentration, i.e. the concentration calculated with the specific activity of the radionuclide.

## 6 The sorption experiment

This section describes the prerequisites to perform sorption experiments in an accurate way.

### 6.1 Apparatus and chemical reagents

The prerequisites for the apparatus and chemical reagents are given below:

➤ *Chemical reagents*

They should be of analytical grade. The use of non-labeled test substances with known composition and preferably at least 95% purity or of radiolabelled test substances with known composition and radio-purity, is recommended.

➤ *Balance*

➤ *Tubes or vessels to conduct the experiments*

It is important that these tubes or vessels fit directly in the centrifuge apparatus in order to minimize handling and transfer errors and that they are made of an inert material (e.g. polypropylene), which minimizes adsorption of the test substance on its surface.

➤ *Centrifuge*

OECD (2000) prescribes high-speed centrifugation forces  $> 3000$  g, temperature controlled capable of removing particles with a diameter greater than  $0.2 \mu\text{m}$  from aqueous solution. We advise to centrifuge even at least at  $10\,000$  g.

➤ *Oven*

To determine the moisture content of the samples. It should be capable of maintaining a temperature of  $103^\circ$  to  $110^\circ\text{C}$ .

➤ *Filtration device (optional)*

Filters with varying cut-offs, sterile, single use. Special care should be taken in the choice of the filter material, to avoid any losses of the test substance on it; for poorly soluble test substances, organic filter material is not recommended. Some filters need some pretreatment (rinsing). The choice for the cut-off of the filter depends on the purposes of the experiment.

Instead of filtration, ultracentrifugation is also an option to remove particles of a certain size from the solution.

➤ *Analytical instrumentation*

In order to allow for detection and evaluation after partitioning has taken place, the detection limits of the analytical method should be at least two orders of magnitude below the nominal concentration.

## 6.2 Prerequisites for performing sorption tests

### 6.2.1 The selection of optimal solid/liquid ratios

Selection of appropriate soil to solution ratios for sorption studies depends on the distribution coefficient  $K_d$  and the relative degree of sorption desired. The change of the substance concentration in the solution determines the statistical accuracy of the measurement based on the form of adsorption equation and the limit of the analytical methodology, in detecting the concentration of the chemical in solution. Therefore, in general practice it is useful to settle on a few fixed ratios, for which the percentage sorbed is above 20%, and preferably >50%, while care should be taken to keep the test substance concentration in the aqueous phase high enough to be measured accurately. This is particularly important in the case of high sorption percentages. Figure 1 shows the relationship between the S/L ratio and  $K_d$ , assuming a linear sorption equation. The grey zone represents the preferred zone to perform the experiments.

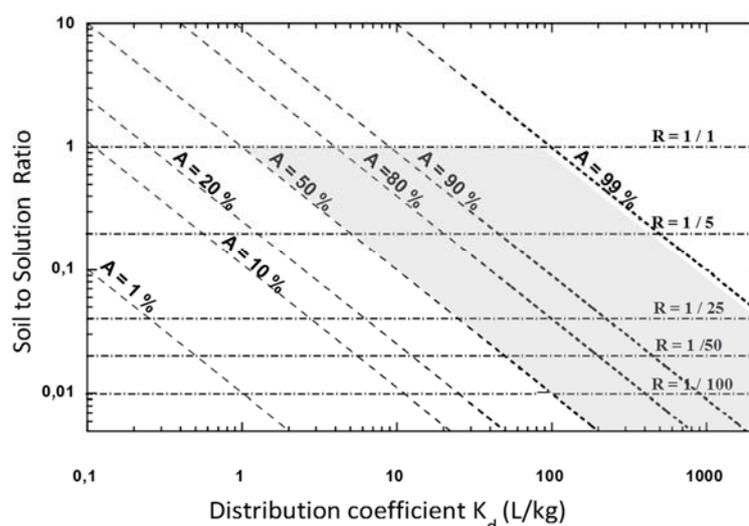


Figure 1 Relationship between soil to solution ratios and  $K_d$  at various percentages of adsorbed test substance. In this plot it is assumed that the sorption equation is linear. The grey zone represents the preferred to perform the experiments.

### 6.2.2 Determination of the equilibrium time

The first step in sorption measurements for a particular radionuclide is to measure the sorption kinetics. The time required to reach an "equilibrium" (steady state) aqueous activity/concentration is then taken as the minimum experimental duration for all the following sorption tests.

In general, sorption equilibrium on clays is reached quite fast ( $\pm 3$  days). In general, minimum 7 days are taken as equilibration time.

### **6.2.3 Sorption on the test vessels and stability of the test substance**

One control sample with only the test substance in the background solution (no sorbent) is subjected to precisely the same steps as the test systems, in order to check the stability of the test substance in the background solution and its possible adsorption on the surfaces of the test vessels.

## **6.3 Performance of the experiment**

### **6.3.1 Test conditions**

All experiments are done at laboratory ambient temperature and, if possible, at a constant temperature between 20 °C and 25 °C.

If the conditions need to be different than the ambient conditions with respect to the partial pressure of oxygen (O<sub>2,g</sub>) and/or carbon dioxide (CO<sub>2,g</sub>), the experiments should be performed in gloveboxes with the desired gas conditions. For Boom Clay, a glovebox with the in-situ conditions of the Boom Clay at depth (anaerobic, 0.4% CO<sub>2</sub>) is preferred. For other sorbents, this depends on the objectives of the experiment.

### **6.3.2 Duration**

The duration should be at least equal to the time needed to reach equilibrium as described in 6.2.2.

### **6.3.3 Solid/liquid ratio**

As mentioned before, the optimal solid/liquid ratio should be determined prior to start the sorption experiments (6.2.1). The higher the sorption, the lower the solid-liquid ratio should be in order to have detectable activities/concentrations of the sorbate remaining at equilibrium.

In principle, a  $K_d$  value should be independent of the solid/liquid ratio. The often found "solid concentration" effect on  $K_d$  is attributed to experimental artefacts rather than real phenomena. The "solid concentration" effect in Boom Clay is at present time considered being caused by the formation of colloids when clay is suspended in a batch experiment. Since colloids are not supposed to be mobile in the compact Boom Clay, they should be treated as part of the solid phase. A careful ultrafiltration or ultracentrifugation should in principle remove the "solid concentration" effect.

### **6.3.4 Blanks**

At least one blank, consisting of the sorbent + background solution (without test substance), must be included, in order to check for artefacts in the analytical method and for matrix effects caused by the sample.

### **6.3.5 Replicates**

It is advised to perform the experiments in duplicate or triplicate. In case of a sorption isotherm or edge, it can also be chosen to study at more concentrations or pH values in the desired range instead of performing duplicates for less concentrations or pH values.

### 6.3.6 Weights/volumes

It is advised to weigh all the solutions and to use this weight as the volume (as can be assumed that the density of the solutions is 1 kg/L) in order to avoid that negligent pipetting would influence the result.

### 6.3.7 Moisture content

For all calculations the mass of soil refers to oven dry mass, i.e. the weight of soil corrected for moisture content. The moisture content of each sample is determined on three aliquots with heating at 105°C until there is no significant change in weight (approximately 12h).

### 6.3.8 Phase separation techniques

After equilibration (agitation) the solid and liquid phase are separated in first instance by centrifugation. Centrifugation conditions should allow the removal of particles larger than 0.2 µm from the solution. This value triggers the smallest sized particle that is considered as a solid particle, and is the limit between solid and colloid particles.

In case of colloid formation (which is valid for Boom Clay when suspended in a batch experiment), the colloids should be removed from the supernatant as well, when the colloids are determining the sorption equilibrium too. Since colloids are not supposed to migrate freely in the compact Boom Clay, they should be treated as part of the solid phase and also be removed from the solution before determining the activity/concentration in solution at equilibrium in order to derive a  $K_d$  applicable to transport in Boom Clay.

Removing the colloids can be done by ultrafiltration or by ultracentrifugation. Ultrafiltration is done by using a filter with a pore size in nanometer range. The disadvantage about filtration is that the filter can break or that the filter possibly retains also particles smaller than the pore size (due to e.g. clogging). Filter materials that have minimal sorption of RN should be selected.

Another option is to remove the colloids from solution via ultracentrifugation. The velocity needed to separate the colloids at a certain cutoff can be determined with the equation of Stokes for a spheric particle with a certain size:

$$v = \frac{d^2(p - L) \times g}{18 n}$$

with  $v$  the sedimentation rate or velocity of the sphere,  $d$  the diameter of the sphere,  $p$  the particle density,  $L$  the medium density,  $n$  the viscosity of the medium and  $g$  the gravitational force. The cutoff between mobile and immobile colloids in Boom Clay has been set at 10 kDa (Durce et al., 2015). The centrifugation speed that separates the particles at this limit, can be calculated with the equation.

## 6.4 Stepwise procedure

Stepwise procedures for sorption edges and sorption isotherms are given below. These are general procedures, which can be adapted according to the needs of the experiment.

Depending on the S/L ratio, clay is added as solid material or as suspension (6.3.3). In case of low(er) sorption, the clay could be added in the solid form, since the required S/L ratio is high

enough. For strong sorbing RN a low S/L ratio should be used. The amount of clay per sample is in that case too small to be weighed accurately and clay is then added as suspension. In the procedures below, it is described how the clay is added as suspension. When adding solid clay, the stepwise procedure should be adapted slightly.

Depending on the desired experimental conditions, all steps of the procedure are performed in the appropriate glovebox, except from centrifugation, which is done outside the glovebox under ambient conditions, but in closed tubes.

#### **6.4.1 Procedure sorption edge**

A sorption edge describes the sorption at low radionuclide concentration as function of pH. In this case, only a radio-isotope is added.

1. *Preparing the solutions (in case of synthetic background solution (4.2.2))*

- a. *Background electrolyte*
- b. *Buffer solutions (Table 2)*

2. *Preparing the clay suspension*

The clay is suspended in background electrolyte at a S/L ratio that takes into account the dilution factor to reach the target S/L in the sorption experiment after adding the suspension to the samples. The suspension is equilibrated by stirring on a magnetic stir plate, at least during 24 h prior to adding.

3. *Weighing the empty tubes*

4. *Transferring the background electrolyte and the buffer solution in the tubes*

The total volume of the solution should not be larger than 40 mL (max volume of the centrifuge tubes).

5. *Adjusting pH with base or acid to the target value*

6. *Adding an aliquot of the RN (active spike) to all the samples*

Take into account that the spike is often dissolved in an acid solution. This can change the pH of the sample. In order to avoid this, an equivalent amount of base could be added.

7. *Weighing the samples*

8. *Equilibration overnight (shaking on the rollerbench or end-over-end)*

9. *Sampling of 0.5-1 mL to measure the initial activity ( $A_{init}$ ) or concentration ( $C_{init}$ ) of the RN in solution*

10. *Adding clay suspension ( $\pm$  1-2 mL) (that is vigorously stirred with a magnetic stirrer) to the samples*

11. *Weighing the samples*

12. *Checking pH after equilibration and adjusting if necessary with acid or base*

13. *Equilibration for at least 1 week (shaking on the rollerbench or end-over-end)*

14. *Measuring pH*

15. *Centrifuging minimum at 15000 g for 1-2 hours*

16. *Sampling of 0.5-1 mL of supernatants to measure the final activity ( $A_{eq}$ ) or concentration ( $C_{eq}$ ) of the RN in solution*

If necessary, the sample is first filtered (0.45  $\mu$ m).

## 6.4.2 Procedure sorption isotherm

A sorption isotherm describes the sorption measured at constant pH as function of concentration. In that case, the studied radionuclide/element is added also in the inactive form to the clay suspensions in order to cover a range of concentrations.

1. *Preparing the solutions (in case of synthetic background solution (4.2.2))*
  - a. *Background electrolyte + the appropriate buffer (Table 2 - 4.2.2)*
  - b. *Stock solutions cold isotope*

2. *Preparing the dilution series*

The background electrolyte is spiked with different amounts of the stock solutions in order to obtain a dilution series covering a concentration range of several orders of magnitude. A subsample of each dilution is taken to check the concentration (measured with ICP-MS/AES).

3. *Preparing the clay suspension*

The clay is suspended in background electrolyte at a S/L ratio that takes into account the dilution factor to reach the target S/L in the sorption experiment after adding the suspension to the samples. The suspension is equilibrated by stirring on a magnetic stir plate, at least during 24h prior to adding.

4. *Weighing the empty tubes*

5. *Transferring the solutions of the dilution series in the tubes*

6. *Adding an aliquot of the RN (active spike) to all the samples*

Take into account that the spike is often dissolved in an acid solution. This can change the pH of the sample.

7. *Checking pH and adjusting with acid or base, if needed*

8. *Weighing the samples*

9. *Equilibration overnight (shaking on the rollerbench or end-over-end)*

10. *Sampling 0.5-1 mL to measure the initial activity ( $A_{init}$ )*

11. *Adding suspension ( $\pm$  1-2 mL) (that is vigorously stirred with a magnetic stirrer) to the samples*

12. *Weighing the samples*

13. *Checking pH after equilibration and adjusting if necessary with acid or base*

14. *Equilibration for at least 1 week (shaking on the rollerbench or end-over-end)*

15. *Measuring pH*

16. *Centrifuging minimum at 15000 g for 1-2 hours*

17. *Sampling of 0.5-1 mL of supernatants to measure the final activity ( $A_{eq}$ ) or concentration ( $C_{eq}$ ) of the RN in solution*

If necessary, the sample is first filtered (0.45  $\mu$ m).

## 6.5 Reversibility

The reversibility of sorption can be investigated by a desorption experiment. After the last stage of the sorption experiment (centrifugation of the soil suspension), the supernatant will be removed and fresh background solution will be added. The clay will be brought again into suspension and will be shaken until equilibrium is reached (minimum a few days). A kinetic test

can be performed to check how fast/slow the equilibrium is established. The concentration in solution is then measured again and the  $K_{des}$  can be defined.

The apparent desorption coefficient ( $K_{des}$ ) is, under the test conditions, the ratio between the content of the substance remaining in the solid phase and the mass concentration of the desorbed substance in the aqueous solution, when desorption equilibrium is reached:

$$K_{des} = \frac{m_{aq}^{ads}(eq) - m_{aq}^{des}(eq)}{m_{aq}^{des}(eq)} \frac{V_t}{m_{sample}}$$

with  $m^{des}$ , the total mass of the test substance desorbed from soil at desorption equilibrium,  $m^{ads}$ , the mass of the test substance adsorbed on soil at adsorption equilibrium,  $V_t$ , the total volume of the aqueous phase and  $m_{sample}$ , the amount of the sorbent (OECD, 2000).

## 7 Factors influencing the sorption behaviour

The solid-liquid distribution coefficient is defined by the affinity of the sorbate for a certain sorbent and by the binding capacity of that sorbent. This is however not a constant and can even vary several orders of magnitude. The prevailing geochemical conditions have an influence on the characteristics of the sorbate and the sorbent and hence also on the solid-liquid distribution coefficient.

The geochemical conditions that can impact the sorption behaviour include the RN concentration, pH, ionic strength,  $E_h$ ,  $CO_2$  conditions (determining the inorganic carbon concentration and pH) and the dissolved organic matter (DOM) concentration present in the system.

### 7.1 Concentration (sorption isotherm)

When the retention of a solute on solid particles is investigated, the remaining solute concentration of the compound  $C$  (mol/L or kg/L) can be compared with the concentration of this compound retained on solid particles  $Q$  (mol/kg or kg/kg). The relationship  $Q = f(C)$  is named the "sorption isotherm" (Limousin et al., 2007).

The sorption isotherm can help to define the total sorption site density for a particular radionuclide. The range of the concentration is limited by the detection limit at the lower concentration side and the solubility limit of the RN at the higher concentration side. In general, the isotherm, i.e. the concentration sorbed on the solid phase (mol/kg) as function of the concentration in solution at equilibrium (mol/L), shows a linear relationship from the trace to intermediate concentration. Further increasing the concentration mostly results in a plateau (decrease in  $K_d$ ) due to the saturation of the sorption sites on the sorbent.

When a sorption isotherm is performed, a non-active as well as an active isotope are used. The radio-labeled test substance is used to determine the  $K_d$ , while the concentration range is obtained by adding inactive isotope in increasing amount.

For more information on sorption isotherms, the reader is referred to Limousin et al. (2007).

## 7.2 pH (sorption edge)

A sorption edge represents the solid-liquid distribution coefficient as function of pH. Clays as sorbent has the characteristic that sorption is low at lower pH and high at higher pH, with a rather steep increase in sorption in the intermediate pH range.

For pure clay minerals, sorption edges can provide information on the different sorption mechanisms. Clayrocks, on the other hand, are generally only studied at their in situ pH and not with varying pH. However, it could be of interest to know how the sorption would change when the pH decreases or increases due to perturbations in the clay (e.g. alkaline plume).

## 7.3 Ionic strength

The sorption of cationic radionuclides that sorb mainly via the 'ion exchange' sorption mechanism, will be influenced by a varying ionic strength of the background electrolyte (competitive sorption of cation with RN). The difference in sorption can be studied for a sorption edge, as well as for a sorption isotherm, but in the latter case this should be at low pH, where ion exchange is playing, while at high pH no effect is expected, as there surface complexation is the dominant mechanism in general.

Caution has to be taken in case of the presence of dissolved organic matter. At higher ionic strength, organic matter can flocculate and this can influence indirectly the sorption of radionuclides, which tend to bind with dissolved organic matter (see also 7.5).

## 7.4 CO<sub>2</sub> pressure

Some RN tend to form (generally very stable) carbonate complexes. Hence, the CO<sub>2</sub> conditions can have a large influence on the speciation of the RN and consequently also on the solid-liquid distribution.

The in-situ CO<sub>2</sub> pressure in the Boom Clay is 0.4%, i.e. 10 times the atmospheric CO<sub>2</sub> pressure. The porewater is a NaHCO<sub>3</sub> solution. An increased CO<sub>2</sub> pressure results in increased carbonate concentration in solution which can result in an increase in carbonate complexation of the RN.

## 7.5 Dissolved organic matter (DOM)

The majority of the cationic radionuclides of interest tend to bind with dissolved organic matter and form soluble complexes. Hence, a smaller fraction of the cations is available to bind on the sorption sites. This way, the sorption will be hindered partially. The effect of DOM on sorption can be determined by comparing the RN sorption in absence and presence of DOM. When using a simple electrolyte as background solution, DOM can be added as humic acids, commercial or extracted from natural Boom Clay water (as described in 4.2.3).

Studying the effect of the DOM on RN sorption on Boom Clay is less obvious. The sorption can be measured with natural Boom Clay water (with [DOC]= ± 100 mg C/L) and with SBCW (without DOM), but in the latter case the Boom Clay will still release some DOM when brought into contact with a synthetic solution (few mg DOC/L) and hence sorption in presence with DOM cannot be compared with a totally DOM-free background solution.

## 7.6 Redox conditions

For redox-sensitive RN, the difference in sorption between anaerobic (glovebox) and aerobic conditions could be interesting to measure. It is however not straightforward to perform accurate experiments at other redox potentials, because it is very difficult to keep the redox potential stable.

## 8 Analytical methods

### 8.1 pH

The pH of the aqueous phase should be measured before and after contact with the sorbent, since it plays an important role in the whole sorption process, especially for ionisable substances. The pH is measured with a pH electrode (in general, glass electrode is used), which is generally calibrated beforehand with pH buffers 4, 7 and/or 9, depending on the pH region under investigation.

### 8.2 ICP

The composition of the background solution and the concentration of the inactive isotope will be measured by ICP-OES (Inductively Coupled Plasma - Optical Emission Spectrometry) or ICP-MS/AES (Inductively Coupled Plasma - Mass Spectrometry).

### 8.3 Radiometry

Depending on the nature of the radionuclide, liquid scintillation counting (LSC) or gamma-radiospectrometry is chosen to measure the activities  $A_0$  and  $A_{eq}$ . In case that the radionuclide emits as well  $\alpha/\beta$  as  $\gamma$ , the technique with the highest counting efficiency is chosen.

#### 8.3.1 Liquid Scintillation Counting

Liquid scintillation counting is generally used for alpha and beta particle detection. An aliquot of the sample is mixed with a liquid scintillator which improves the counting efficiency. The LSC counter in our research group is a TRI-CARB 2100TR from Packard.

#### 8.3.2 Gamma spectroscopy

Radionuclides which emit  $\gamma$  radiation can be measured by gamma spectroscopy. In our research group 'Waste & Disposal' at SCK•CEN, the gamma spectrometer used for these measurements is the Canberra Packard Cobra type 5003.

## 9 Error propagation

The errors should be determined according to the rules of error propagation. For the uncertainty on the  $K_d$ , expressed as  $\partial K_d$ , the general equation looks like:

$$\partial K_d = K_d \sqrt{\frac{(\partial A_{init})^2 + (\partial A_{eq})^2}{(A_{init} - A_{eq})^2} + \left(\frac{\partial A_{eq}}{A_{eq}}\right)^2 + \left(\frac{\partial V}{V}\right)^2 + \left(\frac{\partial m}{m}\right)^2}$$

with  $A_{init}$  the total initial activity of the radionuclide in solution (Bq),  $A_{eq}$  the activity at equilibrium of the radionuclide in solution (Bq),  $V$  the volume of the liquid phase (L) and  $m$  the mass of the solid phase (kg), and  $\partial x$  the uncertainty of the respective parameter.

As the volumes of the suspensions and sample aliquots are determined by weight (6.3.6), the error on the volume is set at 5 times the value of the last significant digit of the balance used.

The uncertainty on the activity measurements is further explained in detail in Annex 6.

According to error analysis studies,  $K_d$  values below 0.3 L/kg cannot be estimated accurately from a decrease in concentration in the aqueous phase, even when the most favourable (from point of view of accuracy) soil/solution ratio is applied, i.e. 1:1. In this case analysis of both phases, soil and solution, is recommended.

## 10 Guidelines for modeling sorption results

Modeling RN sorption under various conditions can be done by use of thermodynamic sorption models (TSMs). TSMs are a useful tool to identify, characterize and eventually parameterize the basic phenomena that are usually described by a  $K_d$  value. The different TSMs share many of the same conceptual building blocks (NEA, 2012). The goal of this section is to list the key parameters needed to build such a TSM.

For modeling the sorption on *pure clay minerals*, different TSMs are already available in the literature. In addition, parameter values exist for different RN and different clay minerals. Ideally, the parameters should be determined experimentally for each type and each batch of clay, as the origin and composition can differ, but this is not in all cases possible, since a comprehensive data set is needed (titration data, sorption isotherms, sorption edges at various conditions). In those cases, the literature values can be applied and - if needed - adapted in order to fit the model to the experimental data.

Modeling sorption on *clayrocks* like Boom Clay with various clay minerals and other components (e.g. organic matter, carbonates, ...) is less straightforward. In this case, two options can be chosen: the component additivity approach (CAA) or the generalized composite approach (GCA). These approaches describe both quantitatively the sorption of a complex mineral assemblage based on principles of chemical equilibrium, but in a different way.

The component additivity approach (CAA) determines the total sorption as the sum of the sorption on the individual sorbents. This approach assumes that the sorption is additive and the individual sorbent, studied as pure mineral, behaves the same when it is mixed with other sorbents in the assemblage. The model combines then the different geochemical models used for predicting the sorption or complexation with the individual components.

The generalized composite approach (GCA) quantifies the sorption on the assemblage as a whole without subdividing according to its real composition. The approach normally assumes that sorption occurs on one or two types of sorption sites without specifying to which mineral(s) these sites belong.

In this section, a brief overview is given of the available geochemical codes, databases, models and approaches. In addition, a summary sheet of the experimentally defined key parameters needed as input for sorption modeling is given.

## 10.1 Geochemical codes and databases

At SCK•CEN, PhreeqC (Parkhurst and Appelo, 1999) and The Geochemist's Workbench (Bethke, 2004) are the most commonly used geochemical codes.

Different thermodynamic databases that can be used, are the database of Lawrence Livermore National Laboratories (LLNL), the chemical thermodynamic database of NAGRA/PSI, the thermodynamic databases of NEA and the in-house developed MOLDATA, etc. For the in-house database MOLDATA more details can be retrieved in the report of Salah & Wang (2014). Important is to use the most up to date database.

## 10.2 Sorption and complexation models

In literature one can find various TSMs and solution complexation models to quantify the sorption of RN on different sorbents and the complexation of cations with dissolved organic matter. Table 3 gives an overview of the most important ones.

The sorption of RN on pure clay minerals has been modeled already extensively in the past. For the sorption of cations, the 2 SPNE SC/CE model (for most cations) of Bradbury and Baeyens (1997) is the most well-known and commonly applied model. This model is similar to the generalized two-layer model of Dzombak and Morel (1990) but without taking into account the electrostatic effect. A concise description is given below.

Only a few anions tend to sorb on clay minerals (under certain conditions). To our knowledge, there is no generally applied model in the literature. The model of Dzombak and Morel (1990) could be a good basis to develop a model for anion sorption on clay minerals.

For the complexation of RN with DOM, currently the NICA-Donnan (Koopal et al., 2005) and the Humic Ion Binding Model VI/VII (Tipping, 1998; Tipping et al., 2011) are both good options. The Humic Ion Binding Model VI (Tipping, 1998) is already implemented in PhreeqC (Bruggeman et al., 2010). The model is briefly described below.

Table 3 Overview of the available geochemical models.

Geochemical model		Literature reference	Interaction type and geochemical phase	RN concerned
<b>Sorption on clay minerals</b>				
3S IEX	3-site Ion exchange model	Bradbury & Baeyens (2000)	Ion exchange on illite	Cs
2 SPNE SC/CE	2-site protolysis non-electrostatic surface complexation/cation exchange	Bradbury & Baeyens (1997) Bradbury <i>et al.</i> (2005)	Ion exchange and surface complexation on illite and montmorillonite	Most cations
<b>Complexation with dissolved organic matter</b>				
HIBM VI/VII	Humic Ion-binding model VI + VII	Tipping (1998) Tipping <i>et al.</i> (2011)	Complexation with humic substances	Most cations
NIC(C)A-Donnan	Non-ideal competitive (consistent) adsorption	Koopal <i>et al.</i> (2005) Kinniburgh <i>et al.</i> (1999)	Complexation with humic substances <sup>a</sup>	Most cations
LCD	Ligand and Charge Distribution model	Weng <i>et al.</i> (2006)	Ternary systems: metals + oxide + humic substances <sup>b</sup>	

<sup>a</sup> Currently unavailable within Phreeqc and GWB code

<sup>b</sup> Currently in a developing phase; it will be investigated whether more conventional models can be used to describe ternary systems)

### 10.2.1 2 SPNE SC/CE model

The 2 SPNE SC/CE model describes sorption of cations on clay minerals by two main uptake mechanisms, i.e. cation exchange and surface complexation. This is described briefly below. For more details, we refer to the literature (Bradbury and Baeyens, 1997; 1998; 2005).

#### Cation exchange

The permanent negative charge of the clay mineral surface is compensated by an excess of aqueous cations held by electrostatic attraction. These electrostatically bound cations can exchange with other cations in solution in reactions which are fast and reversible. The exchange reaction can be written as follows:



with cation B with valence  $z_B$ , cation A with valence  $z_A$ .

The selectivity coefficient  $K'_c$  is then defined as:

$${}^B_A K'_c = \frac{N_B^{z_A}}{N_A^{z_B}} \cdot \frac{[A]^{z_B}}{[B]^{z_A}}$$

with [A] and [B] the molar concentrations in solution of cations A and B.  $N_A$  and  $N_B$  are equivalent fractional occupancies, defined as the equivalents of A and B sorbed per unit mass divided by the cation exchange capacity (CEC).

Cation exchange dominates the sorption in the lower pH region and is dependent on the nature and the amount of cations in the background solution. Selectivity coefficients can be deduced from specific experiments which investigate the cation exchange behavior of RN on clay minerals. In such experiments the uptake of the RN is determined in a bi-ionic system at a fixed pH at a fixed Na concentration (or other major cation) and a low fixed total [RN].

### **Surface complexation**

Next to cation exchange sites, clay minerals like illite and montmorillonite have also surface hydroxyl groups situated along the edges of the clay platelets. Sorption is described in terms of reactions between aqueous species and amphoteric  $\equiv\text{SOH}$  type surface sites. The surface hydroxyl groups undergo protolysis reactions which generate a surface charge whose values vary with pH but as a maximum value equal to the number of binding sites. Values for site capacities and protonation/deprotonation constants are deduced from the modeling of the titration data. Considering the 2 SPNE SC/CE model, three different sites have been identified: a strong site  $\equiv\text{S}^{\text{S}}\text{OH}$  and two weak sites  $\equiv\text{S}^{\text{w1}}\text{OH}$  and  $\equiv\text{S}^{\text{w2}}\text{OH}$ .

The general complexation reaction of a bivalent cation  $M^{2+}$  for these sorption sites can be written as



The intrinsic surface complexation constant is defined as:

$$K_{int}(M) = \frac{[\equiv\text{SOM}^+] \cdot \{H^+\}}{[\equiv\text{SOH}] \cdot \{M^{2+}\}}$$

The parameter values for the three different sites are deduced by a stepwise iterative fitting/modeling procedure, as described in Figure 2 of Bradbury and Baeyens (1997).

*=> When the 2 SPNE SC/CE model is applied for sorption modelling of cations, the parameter values of a certain clay mineral (illite, montmorillonite) determined by Bradbury and Baeyens can be used as approximation, but the user should be aware that these values are determined for a specific batch of these clay minerals and these values can be different for other clay batches. Ideally, these parameters should be determined experimentally for each batch of clay, but as mentioned before, this is a quite extensive task and is not always possible.*

### **10.2.2 Humic Ion Binding Model**

For the complexation of RN with Dissolved Organic Matter, the Humic Ion Binding Model of Tipping (1998, 2011) is proposed as a one of the options. Model VI (1998) has been implemented to the PhreeqC code (Bruggeman et al., 2010) and used to describe sorption data of Eu on illite in presence of DOM. However, it is advised to use the improved Model VII (2011) for future experiments.

The Humic Ion Binding Model VI is a discrete site/electrostatic model for interactions of H<sup>+</sup> and metals with fulvic and humic acids. Proton binding is described with a site density, two median intrinsic equilibrium constants (pK<sub>A</sub> and pK<sub>B</sub>), two parameters defining the spread of equilibrium constants around the medians, and an electrostatic constant. Intrinsic equilibrium constants for metal binding are defined by two median constants, log K<sub>MA</sub> and log K<sub>MB</sub>, which refer to carboxyl and weaker acid sites respectively, together with a parameter ΔLK<sub>1</sub> defining the spreads of values around the medians. A further parameter, ΔLK<sub>2</sub>, takes into account of small numbers of strong binding sites (Tipping, 1998). The most important parameters are given in Table 4. For a complete overview of the parameters we refer to Table II in Tipping (1998). The default parameter values were derived from earlier studies, but for some elements, the datasets are rather limited and hence, the uncertainty on the derived value is larger.

Table 4 Default equilibrium constants for metal binding sites on humic or fulvic acid.

Parameter	
pK <sub>A</sub>	Proton dissociation constant for carboxylic acid groups (type A sites)
pK <sub>B</sub>	Proton dissociation constant for phenolic acid groups (type B sites)
Log K <sub>MA</sub>	Intrinsic equilibrium constant for metal binding at type A sites
Log K <sub>MB</sub>	Intrinsic equilibrium constant for metal binding at type B sites
ΔLK <sub>1</sub>	Distribution term that modifies log K <sub>MA</sub>
ΔLK <sub>2</sub>	Distribution term that modifies the strengths off bidentate and tridentate sites

The proton sites are subdivided in three fractions. For humic acid, the fraction of monodentate binding sites is 0.435, bidentate 0.50 and tridentate 0.065. The calculation of the site abundancies for the different sites are based on the total site capacity, the concentration of organic matter and the specific surface area. The latter depends on the ionic strength (I) and is calculated by the following equation (Appelo and Postma, 2005):

$$A = 159300 - 220800/I^{0.09} + 91260 / I^{0.18}$$

The total site capacity of the dissolved organic matter is equal to the proton exchange capacity (PEC). This parameter can be determined by direct pH titration or by potentiometric titration (Bruggeman and De Craen, 2012). For purified humic acids of Boom Clay water (from EG/BS piezometer), a value of 4.2×10<sup>-3</sup> mol/g has been determined.

Table 5 Parameters for humic acids (HA) and fulvic acids (FA) in the Humic Ion Binding Model VI/VII.

Parameter	HA	FA	Unit
Molecular weight humic acid	15000	1500	g/mol
Generic humic acid rigid sphere radius	1.72	0.80	nm
Total site capacity (number of sites)	To be determined		mol/g

### 10.3 Parameters and summary sheet

This section gives an overview of all the parameters that are needed as input for accurate modeling. Next to the parameters that can be taken from literature or thermodynamic

databases, a list of parameters should be determined experimentally. The latter are summarized in the summary sheet (10.3.6). There is made a distinction between experimental parameters, parameters of the sorbent, parameters of the background solution, parameters of the RN and parameters of other fractions that play a role in the sorption equilibrium, like DOM.

For most of the parameters, it is possible to derive estimates from literature values, chemical analogues,... . They can assist in optimizing experiments or be used as an approximation if no experimental values are available.

### 10.3.1 Experimental parameters

These parameters are chosen by the performer, depending on the objectives of the experiment.

➤ *Temperature*

As chemical reactions are temperature dependent, the temperature is an essential parameter to give as input. There is almost no exceptions that the temperature should be around 25°C because almost all existing sorption data and large part of solution data were derived at 25°C.

➤ *Partial pressure CO<sub>2</sub>*

In cases where the CO<sub>2</sub>/CO<sub>3</sub><sup>2-</sup> equilibrium is influencing the cation speciation, the partial pressure of CO<sub>2</sub> is an important input parameter. This is especially the case for experiments with Boom Clay since they are in general performed in gloveboxes with higher CO<sub>2</sub> pressure (0.4%) than the one in the atmosphere in order to mimic the in-situ conditions.

➤ *Solid/liquid ratio*

This ratio is used as input parameter to calculate the exact amount of sorption sites (cation exchange and surface complexation) in the experimental set-up.

### 10.3.2 Parameters sorbent

A list of parameters of the sorbent are needed for accurate modeling. In the NEA report (phase III) on Thermodynamic Sorption Modeling (NEA, 2012) the key parameters of the sorbent for a Thermodynamic Sorption model (TSM) are listed and described. This section briefly describes these parameters too, but for more details, we refer to the NEA report. The characterization methods for the sorbent (generally clay) are described in section 3.

➤ *Specific surface area (SSA)*

The specific surface area (SSA) of a solid phase, usually expressed in m<sup>2</sup>/g, can be measured by many different methods. The best choice is the BET gas adsorption method (Davis and Kent, 1990), but for clays EGME (ethylene glycol monoethyl ether) adsorption may be an alternative. At SCK•CEN, the N<sub>2</sub>-BET method is available and hence the preferred analysis method.

➤ *Sorption site capacity*

This parameter, expressed in mol/kg, defines the amount of surface sites that are able to sorb cations or RN (surface complexation). These sites are assumed to be equal to the surface hydroxyl groups that are protonated at low pH and deprotonated at high pH. They can be determined by titration. This parameter is multiplied with the

solid/liquid ratio (g/L) in order to determine the exact amount of surface complexation sites of the amount of clay used in the experiment.

➤ *Sorption site density*

The sorption site density or surface site density, expressed by mol/m<sup>2</sup>, can be estimated by dividing the sorption site capacity by the specific surface area. The total surface site concentration can then be divided among different possible binding site types. In two-site models, the sites are referred to as "high affinity" (strong) and "low affinity" (weak) sites. The most common approach in modelling sorption data is to determine the density of "strong" sites by numerical optimization techniques (Davis et al., 1998) and to define the weak sites as the difference relative to the total site concentration. In many RN migration scenarios, the RN is present at an extremely low concentration and therefore knowledge of the density of "strong" sites may be very important in model simulations.

➤ *Surface site hydrolysis (or protolysis constants)*

The acid-base reactions on the mineral surfaces can be described by either one or two protolysis reactions, often referred to as the 1-pK and 2-pK approaches. These reactions can be studied by acid-base titrations.

➤ *Electrostatic double layer (EDL) model*

The EDL can be incorporated in the TSM model in different ways. The different models (DLM, CCM, TLM, BSM and NEM) have different numbers of adjustable parameters. For more details, we refer to NEA (2012).

Bradbury and Baeyens (1997) did not include an EDL model in their TSM. Basically, their model (2 SPNE SC/CE) is essentially the DLM but without electrostatics. They first tried to use the DLM model, but the modeling results were not satisfying. Removing the electrostatic term improved the fittings significantly.

➤ *Formation constants for surface species (or surface complexation constants)*

Formation constants can be determined by performing simple batch experiments at varying pH, RN concentration, ionic strength, S/L ratio, ligand concentration,... A comprehensive sorption data set is needed to estimate the different parameters with the use of numerical optimization codes such as FITEQL (Herbelin and Westall, 1994, 1996 and 1999). It is essential to check for processes other than sorption that remove RNs from solution (precipitation, sorption on container wall,...). In addition, spectroscopic information should be used where possible to constrain choices for sorption reactions.

➤ *Ion exchange: CEC and selectivity coefficients*

The CEC (meq/kg) represents the maximum amount of cations that can bind via cation exchange on the clay, i.e. electrostatic attraction between the permanent negative charge on the clay mineral and aqueous cations close to the surface. It is multiplied with the solid/liquid ratio (g/L) in order to determine the exact amount of exchange binding sites in the experimental set-up.

The selectivity coefficients represent the selectivity of the ion-exchange site with regard to either  $\text{Na}^+$  or  $\text{M}^{z+}$ . The selectivity coefficients of the cation exchange component in the 2SPNE SC/CE sorption model are generally extracted from sorption edges at trace concentrations and low pH (Bradbury and Baeyens, 1997, 2009). Specific experiments can be performed to investigate the exchange equilibrium between a RN (cation) and  $\text{Na}^+$  on mineral surface, e.g., illite, at RN loadings covering 10 to 90 % of the total CEC, i.e. RN fractional occupancies ( $N_{\text{RN}}$ ) ranging from  $\sim 0.1$  to 0.9. The uptake of the RN is then studied in a bi-ionic system at a low fixed total ( $\text{RN} + \text{Na}^+$ ) concentration and at a fixed pH.

The determination of the above described parameters needs an extensive amount of experiments. As alternative or as starting point, literature values or theoretical estimations (based on linear free energy relationships) of the parameters can be used too. For the cation sorption modeling, the 2SPNE-SC/CE model of Bradbury and Baeyens (described in 10.2.1) is a commonly used model. Bradbury and Baeyens determined the above described parameters for various RN's binding on illite and montmorillonite. These parameter values can be used if no experimentally defined parameters are available. When the origin and composition of the clay differs with the one they used for the parameter derivation, the parameters will possibly differ too. If the literature values of the parameters are not able to reproduce the experimental results, the values can in a first step be increased or decreased within the error range of the parameter, and in a second step outside this range, but this should be kept in mind when interpreting the modeling results.

Ion exchange data for Boom Clay, such as the CEC, cation occupancies and selectivity coefficients for K, Ca and Mg with Na have been derived from MORPHEUS water compositions and are summarized in De Craen et al. (2004).

### 10.3.3 Parameters background solution

The composition of the background solution should preferably be given as complete as possible. The basic composition (dominant cation(s) and anion(s), ionic strength and pH) is crucial for the modeling. Consideration of elements which are less abundant is less influential, but can be given for completeness. With respect to the synthetic background electrolyte, the theoretical concentrations could be used too, but preferably the composition should also be determined by analysis.

➤ *Concentrations cations*

The concentrations of the cations (measured with ICP-AES), especially the cation(s) that control(s) the ionic strength, are crucial input parameters.

➤ *Concentrations anions*

In case of cation sorption on clays, the anions that play a role in the aqueous speciation of the cation (e.g. carbonates,...), should be added to the model. Further, they are essential for the charge balance.

➤ *pH*

As surface complexation is a pH-dependent sorption mechanism, this parameter is very essential to obtain good modeling results.

➤ *Ionic strength*

If only the ionic strength is known and not the concentrations of the anions, the ionic strength can be imposed in the model. The anion concentration of the counterion will then be calculated in order to reach a chemical equilibrium.

➤ *Reaction constants (hydrolysis, complexation, solubility) for the elements present in solution*

A thermodynamic database (TDB) is selected from the databases mentioned in 10.1. The TDB should be consistent with the surface complexation model (e.g. the hydrolysis constants need to be consistent with the surface complexation constants). This database should contain all reaction constants of the cations and anions present in solution.

### 10.3.4 Parameters radionuclide

Next to the RN concentration, the reaction constants of the RN with the elements present in the background solution are needed as input.

➤ *Concentration*

The concentration of the radionuclide will be calculated or directly measured. When using only active radionuclide, the concentration is calculated with the specific activity. If inactive isotopes of the RN appear in the background electrolyte, they will be measured and added up to the RN concentration. In case of a sorption isotherm, the cold concentration added is calculated by multiplying the dilution factor with the measured concentration of the spike solutions.

The next parameters are taken from the thermodynamic database selected for the modeling (10.1). They should be consistent with the surface complexation model.

➤ *Aqueous complexation constants*

➤ *Solubility/equilibrium constants*

### 10.3.5 Parameters Dissolved Organic Matter

When the complexation of RN with DOM is involved, additional parameters are needed. The DOM in Boom Clay is generally considered as humic acids.

When using the Humic Ion Binding VI model of Tipping (1998) to model this complexation, the following input parameters are needed:

➤ *Concentration*

The concentration of dissolved organic carbon (DOC) (in mg C/L) measured with the TIC/TOC analyzer or by UV absorption.

➤ *Specific surface area*

Defined by the ionic strength and calculated with the equation described in 10.2.2.

➤ *Proton Exchange Capacity (PEC)*

This parameter is also known as site capacity, i.e. the total amount of functional groups which can (de)protonate. It can be determined by potentiometric titration. If no analysis is performed, values from literature can be taken. For humic acid extracted from the

Boom Clay pore water from the EG/BS piezometer, the PEC amounts to  $\pm 2.85$  meq/g, while the PEC of the original EG/BS amounts to 5-6 meq/g (Dierckx et al., 2000). As mentioned in 4.1, it is advised to use clay water from the Spring piezometer instead of the EG/BS. Values for the Spring clay water or the humic acid fraction are not yet available.

➤ *Protolysis constants humic/fulvic acids*

Protolysis constants of humic acids could be determined experimentally by titration, but are also available in literature e.g. in the publication of Tipping (1998).

➤ *Complexation constants humic/fulvic acids*

The values for the complexation constants for cation binding can be taken e.g. from Tipping (2011) or derived from experimental data.

### **10.3.6 Summary sheet**

The summary sheet consists of all the parameters that could be determined experimentally and which are needed as input parameters for the modeling.

<b>Input parameters</b>	<i>Description (units)</i>	How to determine?
<b>Experimental parameters</b>		
Temperature	(°C or K)	to be measured
Partial pressure CO <sub>2</sub>	(atm or bar)	given parameter
Solid/liquid ratio	(g/L)	calculated
<b>Sorbent parameters</b>		
CEC	# sites available for cation exchange (eq/g)	determination with Cu(trien) method
Specific Surface Area	total surface area of the sorbent per unit of mass (m <sup>2</sup> /g)	BET analysis or derived from geometric SA
Sorption site capacity / density	# sites available for surface complexation (mol/g) / (mol/m <sup>2</sup> )	titration
Protolysis constants *	equilibrium constant for the (de)protonation reaction of the sites	acid-base titration
Selectivity coefficients *	equilibrium constant for the exchange reaction by one cation of another cation on the cation exchange sites	extracted from sorption edges or bi-ionic exp
Surface complexation constants*	equilibrium constant for the surface complexation of a cation on the surface complexation sites	batch sorption exp at various conditions
<b>Parameters background solution</b>		
Concentrations cations	(mol/L)	ICP-AES
Concentrations anions	(mol/L)	Ion chromatography
pH		pH electrode
Ionic strength	(mol/l)	calculated or exp. defined
<b>Parameters radionuclides</b>		
Concentration	(mol/L)	calculated or measured
<b>Parameters Dissolved Organic Matter</b>		
Concentration	(g or mol/L)	TOC analysis
Surface area	total surface area of DOM per unit of mass (m <sup>2</sup> /g)	calculated with ionic strength
Proton exchange capacity*	Site capacity, i.e. total # of functional groups which can (de)protonate (eq/g)	potentionmetric titration
Protolysis constants *	equilibrium constant for the (de)protonation reaction of the functional groups	titration
Complexation constants*	equilibrium constant for the formation of a complex between a cation and humic acid/fulvic acid	complexation exp

\* parameter values are often taken from literature values

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## Annex 1: Analysis of Specific Surface Area with N<sub>2</sub>-BET

The detailed protocol is described in "Instructions for working with the Micromeritics Tristar II 3020 Surface Area Analyzer" with reference IW.FMA.4504.E (internal document SCK•CEN). The short version given here is from Frederickx (2017).

Initial sample preparation starts from bulk clay samples, ground and dried at 60°C. At this temperature, not all water and CO<sub>2</sub> adsorbed to the surface of the clays has been removed. Therefore, the samples need additional degassing at an elevated temperature. Approximately 3 g of bulk sample is introduced into a glass flask. The mass of the empty ( $m_1$ ) and filled ( $m_2$ ) flask is written down to derive the sample mass before degassing. The flask is then sealed by glass wool and a plastic seal frit. The mass of the closed flask is again determined and written down ( $m_3$ ).

The sample is then degassed in the Micromeritics VacPrep 061 in a vacuum for 24 hours at a temperature of 110 °C. After degassing, the mass of the closed flask is again determined ( $m_4$ ). Since the results of the analysis are expressed in units of m<sup>2</sup> per gram of material, it is important to know the true (dry) sample mass. The mass of the dried sample can be determined by the following formula:

$$m_{dry} = m_{wet} - m_{gas} = m_2 - m_1 - m_4 + m_3$$

After degassing, the sample is ready for measurement. The gas adsorption measurements are carried out with the TriStar 3020 device, an automated gas adsorption analyser with ports for simultaneous measurement of three samples. An extra port is reserved for measuring the saturation pressure ( $P_0$ ) continuously. The TriStar device is capable of measuring the adsorption of N<sub>2</sub> at a temperature of 77K in a range from 0 to 950 mm Hg, at a relative pressure range of 0 to 1 P/P<sub>0</sub>. The specific surface area can be measured with a precision of 0.01 m<sup>2</sup>/g.

Three samples are connected to the TriStar ports above a large Dewar flask, which is filled with liquid nitrogen. Prior to initiating the measurement, a flushing routine is carried out to prepare the device for analysis and to equalize the pressure in the sample tubes and the device. Upon starting the measurement, the Dewar flask is automatically raised to submerge the samples in liquid nitrogen, thus ensuring a constant temperature of 77 K.

As a primary quality check, the sorption isotherms are visually inspected. If the desorption branch of the isotherm does not close the hysteresis loop at a relative pressure of P/P<sub>0</sub> = 0.42, the measurement should be discarded and redone. Each sample should be split into two and both subsamples are measured. Additionally a clay mineral standard, Wyoming smectite SWy-2, is included every 10 to 15 measurements. The results of the clay standard are used to determine the 2σ reliability interval for the gas adsorption measurements. Subsequently, it is checked whether the individual measurements lie within the 2σ interval from the average of the duplicates.

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## Annex 2: CEC analysis

The measurement of the CEC (Cation Exchange Capacity) by the Cu(II)-triethylenetetramine method as described by Meier and Kahr (1999).

### Preparation of the stock 0.01 mol/L Cu-trien solution

1 liter of 0.1 mol/L CuSO<sub>4</sub> (15.96 g/L)

0.1 mol/L triethylenetetramine (15 ml/L)

Take 100 mL of each solution, mix together and fill it up to 1 liter by MilliQ water

Standard solution:

40 ml of MilliQ water+ 10 mL of 0.01 mol/L Cu-trien

### Procedure:

1. Weigh 100, 200 and 300 mg of dried (dehydrated clay) clay into 100 mL beakers.
2. Mix the powder with 30 mL of MilliQ water.
3. Disperse the clay in the MilliQ water using the ultrasonic bath.
4. Pour the slurry into 50 mL Falcon tubes.
5. Recuperate thoroughly the solid residuum sticking on the walls of the beakers with another 10 mL of MilliQ water.
6. Add 10 mL of 0.01 mol/L Cu-trien and let it shake for approximately 2 hours ( or overnight).
7. Separate the solid from liquid with the aid of centrifuge.
8. Measure the absorbance of liquid at 577 nm by UV-VIS (3 measurements each sample, take the average).
9. BEFORE each measurement session, measure blank (MilliQ water) and standard solution (3 times each).
10. Standard solution must be measured AFTER the measurements as well.

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### Annex 3: Purification and Na-conditioning of clay minerals

The procedure below is based on the procedure used by Poinssot, Baeyens & Bradbury (1999 – PSI bericht nr 99-06) to purify Illite du Puy. The same procedure was used to purify the illite used in the framework of the EC project of CatClay.

Purification was obtained by exchanging the ground original illite into the Na-form and removing organic matter, free (iron)oxides and carbonate. Purified samples were washed and fractionated.

#### **Flowchart:**

#### 1. Grind the clay to pass a 200 µm sieve

- ~50 g chunks of (solid) illite were put in an agate ball-mill
- Ground at speed 7 – 30 min
- Sieved at 200 µm

This procedure was repeated twice and a total of 150 g was obtained.

#### 2. Bring illite clay into the Na-form

- 2 times 50 g illite clay suspended in 200 mL 1 N NaCl in 2 250 mL centrifuge cups
- Cups are shaken end-over-end for 1 hr
- Centrifugation (JA-14, 12000 rpm, 30 min) – cut-off 75 nm
- Supernatant is decanted

This procedure was repeated once.

#### 3. Oxidation of organic matter (Kunze and Dixon, 1986)

- The content of each cup is brought in a beaker of 1 litre and is allowed to react for 2 hours at room temperature with 500 mL containing 1 part H<sub>2</sub>O<sub>2</sub> (35 weight%) and 4 parts 1 N NaCl
- The beaker is heated to 70°C (water bath) and kept at this temperature for 2 hours; stirring is performed from time to time
- The beaker is heated to 80°C (water bath) and kept at this temperature for 1 hour
- Suspensions are cooled, each beaker is divided over 3 250 mL centrifuge cups
- Centrifugation (JA-14, 12000 rpm, 30 min) – cut-off 75 nm  
*!! precipitation was extremely difficult: gas bubbles from H<sub>2</sub>O<sub>2</sub> keep suspension in solution. Clay was allowed to settle and supernatant was pipetted off rather than decanted !!*
- All clay fractions were recollected in 2 250 mL centrifuge cups and 200 mL 1 N NaCl solution was added to each cup. pH was brought to 7-8 and cups were allowed to stand overnight in the refrigerator.

#### 4. Removal of free iron oxide (Kunze and Dixon, 1986)

- Centrifugation (JA-14, 12000 rpm, 30 min) – cut-off 75 nm
- Supernatant was pipetted off (→ ~100 g wet clay per cup)

- The wet clay in each cup was divided over 5 new 250 mL centrifuge cups (~ 20 g per cup)
- 180 mL 0.1 M NaHCO<sub>3</sub> (8.401 g/L) + 0.3 M Na-citrate (C<sub>6</sub>H<sub>5</sub>Na<sub>3</sub>O<sub>7</sub>·2H<sub>2</sub>O, 88.23 g/L) was added to each cup
- Cups were heated up to 75-80°C in a water bath, and 2 g Na dithionite was added to each cup
- Stirred for 1 min, then allowed to stand for 15 min
- Suspensions were cooled, centrifuged (JA-14, 12000 rpm, 30 min) - cut-off 75 nm, supernatant was pipetted off

Procedure was repeated once.

- 100 mL 1 N NaCl was added to the cups and allowed to stand overnight in the refrigerator

#### 5. Removal of carbonate (Van Reeuwijk, 1986)

- 1 N NaCl solutions were prepared and brought to pH 3.5 with concentrated HCl
- Supernatant solutions were pipetted off and 200 mL 1 N NaCl pH 3.5 was added to the cups
- Suspensions were shaken and brought to pH 3.5 with concentrated HCl
- Cups were centrifuged (JA-14, 12000 rpm, 30 mn) – cut-off 75 nm

Procedure was repeated twice (care was taken not to leave the suspension for longer than 2 hours at a pH of 3.5)

- Suspensions were brought to pH 7.5 with concentrated NaOH, and allowed to stand overnight in the refrigerator

#### 6. Washing the clay

- Suspensions were brought to dialysis-membranes, and 2 drops of a 1 weight% azide-solution was added
- Washing with bi-deionized water until the wash water has a conductivity of less than 20 µS/cm

#### 7. Fractionating the clay (if required)

- The content of the membranes is sieved at 50 µm, the fraction 50-200 µm is kept apart for freeze-drying
- The suspension of the fraction < 50 µm is put in 250 mL centrifuge cups.
- Centrifugation JA-14, 8000 rpm, 25 min 33 sec (9820 g)
- The supernatant, which contains only particles smaller than 0.1 µm, is pipetted. This treatment was repeated twice.
- The cups which contain the suspension of fraction 50-0.1 µm are centrifuged, JA-14, 1000 rpm, 4 min 5 sec (153 g).
- The supernatant, which contains only particles smaller than 2 µm, is pipetted. This treatment was repeated twice.

4 fractions were thus obtained: 200-50 µm; 50-2 µm; 2-0.1 µm; < 0.1 µm

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- Fractions were allowed to stand overnight in the refrigerator

## 8. Freeze-dry the fractions

### **References**

Kunze, G. W. and J. B. Dixon. 1986. Pretreatment for mineralogical analysis. In A. Klute (ed), Methods of Soil Analysis, Part 1, Physical and Mineralogical Methods.

Poinssot, C., Baeyens, B., Bradbury, M.H. (1999). Experimental studies of Cs, Sr, Ni and Eu sorption on Na-illite and the modelling of Cs sorption. PSI Bericht 99-06, Paul Scherrer Institut, Villigen, Switzerland.

Van Reeuwijk, L.P. (Ed) (1986) Procedures for Soil Analysis. International Soil Reference and Information Centre, Wageningen.

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## Annex 4: Procedure of the preparation of SBCW

Boom Clay pore water is basically a NaHCO<sub>3</sub> solution of 15 mM. A 15mM NaHCO<sub>3</sub> solution can thus be used in the experiments.

The directives for the preparation of Synthetic Boom Clay Water Disposal' is described in De Craen *et al.* (2004). The directives are the following:

If you are planning to work in anaerobic conditions, make sure your water is degassed! Always leave the bottle open in the glovebox, to allow the last ppm O<sub>2</sub> to diffuse out. Be aware of the oxygen level while you do that. Then, close the bottle.

To prepare 1 L of synthetic clay water, add the following products to 1 L of high quality water (demineralised, bidistilled, milli-Q...):

Table 6 Weight of salts needed for the preparation of 1 L of SBCW

Salt	Quantity (mg) sorted by descending order	MW	(mol/L)
NaHCO <sub>3</sub>	1 170 mg	83.996	1.39 x 10 <sup>-2</sup>
H <sub>3</sub> BO <sub>3</sub>	43 mg	61.834	6.95 x 10 <sup>-4</sup>
KCl	25 mg	74.555	3.35 x 10 <sup>-4</sup>
MgCl <sub>2</sub> · 6 H <sub>2</sub> O	22 mg (hygroscopic salt !)	203.218	1.08 x 10 <sup>-4</sup>
NaF	11 mg	41.988	2.62 x 10 <sup>-4</sup>
NaCl	10 mg	58.443	1.71 x 10 <sup>-4</sup>
FeCl <sub>2</sub>	3 mg (very sensitive to oxidation !)	126.751	2.37 x 10 <sup>-4</sup>
Na <sub>2</sub> SO <sub>4</sub>	0.3 mg (10 ml of 3 mg dissolved in 100 ml)	142.041	2.11 x 10 <sup>-6</sup>
TDS*	1 284.3 mg (-12 mg H <sub>2</sub> O) = 1 272.3 mg (anhydr.)	—	1.55 x 10 <sup>-2</sup>

\*TDS: Total Dissolved Salts (control of mass balance in Table 2).

- Supersaturation with 1000 mg CaCO<sub>3</sub> to adjust Ca<sup>2+</sup>, followed by one week of stirring.
- Bubbling with 0.4 CO<sub>2</sub> % gas mixture until constant pH (carrier gas Argon or N<sub>2</sub>)
- Always filter through a 0.22 µm filter before use. In case of solubility experiments, perform an ultrafiltration through a 30 000 MWCO filter.
- Bubbling with 0.4 CO<sub>2</sub> % gas mixture until constant pH.

If this SBCW is to be used in the presence of organic matter, organic matter is added AFTER filtration.

We advise to analyse the solution before using it, the minimum analysis required is the Fe, Ca and inorganic carbon (IC) content and pH.

Table 7 Reference to check the analyses of the SBCW

<b>Cations</b>	<b>(mol/L)</b>	<b>MW</b>	<b>(mg/L)</b>
Na <sup>+</sup>	1.44 x 10 <sup>-2</sup>	22.990	330.3
K <sup>+</sup>	3.35 x 10 <sup>-4</sup>	39.098	13.1
Mg <sup>2+</sup>	1.08 x 10 <sup>-4</sup>	24.305	2.6
Ca <sup>2+</sup>	—	40.078	—
Fe <sup>2+</sup>	2.37 x 10 <sup>-5</sup>	55.845	1.3
<i>Sum cations (eq.g.)</i>	<i>1.50 x 10<sup>-2</sup></i>		<i>347.3</i>
<b>Anions</b>	<b>(mol/L)</b>	<b>MW</b>	<b>(mg/L)</b>
HCO <sub>3</sub> <sup>-</sup>	1.39 x 10 <sup>-2</sup>	61.017	849.9
Cl <sup>-</sup>	7.70 x 10 <sup>-4</sup>	35.453	27.3
F <sup>-</sup>	2.62 x 10 <sup>-4</sup>	18.998	5.0
SO <sub>4</sub> <sup>2-</sup>	2.11 x 10 <sup>-6</sup>	96.064	0.2
<i>Sum anions (eq.g.)</i>	<i>1.50 x 10<sup>-2</sup></i>		<i>882.4</i>
<b>Neutral Species</b>	<b>(mol/L)</b>	<b>MW</b>	<b>(mg/L)</b>
B(OH) <sub>3</sub>	6.95 x 10 <sup>-4</sup>	61.834	43.0
TDS (mg/L)			1 272.8

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## Annex 5: Procedure for fractionation and purification of humic acids from natural Boom Clay water

*Procedure from C. Bruggeman based on Stevenson (1982)*

Humic acid is fractionated based on its solubility characteristics. The following stepwise procedure should be followed:

1. Pour ~ 1 liter of natural Boom Clay water into a glass or polyethylene bottle in a N<sub>2</sub>/(H<sub>2</sub>/CO<sub>2</sub>) glove box.
2. Adjust the pH of the natural Boom Clay water to about 1.0 with concentrated HCl (use ~ 6 N HCl in the glovebox to decrease chlorine gas volatilisation)
3. Allow the humic acid to settle (e.g. overnight)
4. Siphon off or decant the excess supernatant liquor (fulvic acid)
5. Redissolve the humic acid in 0.5 N NaOH solution
6. Reprecipitate the humic acid by adjusting the pH of the solution to 1.0 with concentrated HCl (overnight)
7. Siphon off or decant the excess supernatant liquor from the acidified solution
8. Transfer the remaining solution to 3500 MWCO dialysis membranes (these membranes should be thoroughly washed –inside and outside- with distilled H<sub>2</sub>O beforehand; use 24h washing time as a minimum)
9. Transfer the dialysis membranes to a new 1 L bottle and wash with distilled H<sub>2</sub>O until salt-free (check with conductivity meter)  
*Remark: during this step, the dialysis membrane might swell because of the expansion of organic molecules*
10. Transfer the washed humic acid (in H-form) to a glass vial (preferably brown glass) with stopper.

### References

Stevenson F.J. *Humus chemistry – Genesis, composition, reactions* (1982) J. Wiley & Sons, NY.

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## **Annex 6: Error propagation**

*This part will be added later.*