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² The home page of the website should contain the generic European flag and the FP7 logo which are available in electronic format at the Europa website (logo of the European flag: http://europa.eu/abc/symbols/emblem/index_en.htm logo of the 7th FP: http://ec.europa.eu/research/fp7/index_en.cfm?pg=logos). The area of activity of the project should also be mentioned.
CATCLAY EXECUTIVE SUMMARY

The overall objective of the EC CatClay project is to provide a scientifically well-grounded answer to the following question: Can the migration of actinides and other strongly sorbing radionuclides in clayrock be predicted by coupling models of (i) their sorption equilibria on representative clay minerals and (ii) the diffusion-driven mass transport of radionuclide sorbed and dissolved species in compacted masses of these clay minerals?

The scientific approach of CatClay is of the ‘bottom-up’ type, in which simpler, analogous systems (here a compacted clay, ‘pure’ illite) are experimentally studied and modelled, and then the transferability of these results to more complex materials, i.e. the clayrocks under consideration for hosting radioactive waste disposal facilities, is verified. Moreover, the cations of interest have been chosen for covering a representative range of cation families considered in the performance assessment, from a moderately sorbing cation, the strontium, known to be retained by mainly electrostatic interactions with charged clay surfaces, to strongly sorbing cations, two divalent, the zinc and the cobalt, and one trivalent, the europium, known to be sorbed by inner-sphere complexation with clay edge sites.

Because these studied cations have very low transfer characteristics, a major part of the CatClay activities was devoted to developing and applying specific experimental methods needed for acquiring high precision, reliable data. In this sense, new setups have been designed for performing diffusion experiments that are no or less impacted by the presence of filters known to sorb the studied cations and to act as a resistance. For instance, filter-free diffusion techniques are now available for indurated rocks and, for illite, an original diffusion cell confining sample with membrane was successfully tested.

In the project, the sorption and the diffusion of Sr$^{2+}$, Co(II) and Zn(II) were studied with illite and clayrocks under different chemical composition in terms of pH (only for illite system) and background electrolyte concentration of the equilibrium solution in contact with the sample. Decreasing diffusion rates with increasing background electrolyte concentration were unequivocally demonstrated for all cases. It is thus shown that so-called surface diffusion may be an important migration process also for these strongly sorbing radionuclides depending on the specific chemical conditions of the pore water and the speciation of these elements. A modelling approach including diffusion in the diffuse double layer (DDL) promisingly succeeded in reproducing the experimental data under the various conditions. On the other hand, diffusion experiments of Eu(III), only performed through clayrocks, showed that the importance of surface diffusion would be very low. Indeed, no or a limited dependency of diffusion on the ionic strength of the pore water was observed. Finally, it was shown that the transferability of sorption values obtained on dilute systems (crushed rock material, high liquid-to-solid ratio) to dense systems (intact rock, low water-to-rock ratio) was mainly justified in the case of Sr$^{2+}$, suggesting for the other cations, that the role of the competing elements naturally present in rock material and that can block the strong sites needs further attention.

Moreover, actual 3D geometrical pore size distributions of compacted illite, and in less extent, clayrock samples, were successfully determined by combining TEM and FIB-nt analyses on materials maintained in a water-like saturation state by means of an extensive impregnation step. The resolution limitation of FIB-nt previously described by many authors was resolved and allowed to threshold more than 70% of the total porosity of the sample in compacted illite. Therefore, based on this spatial distribution of pores, first numerical diffusion experiments were carried at the pore scale through virtual illite, enabling a better understanding of how transfer pathways are organized in the porous media.

The CatClay Project finally allowed a better understanding of the migration of strongly-sorbing tracers through low permeability ‘clayrock’ formations, increasing confidence in our capacity to demonstrate that the models used to predict radionuclide migration through these rocks are scientifically sound.
A SUMMARY DESCRIPTION OF PROJECT CONTEXT AND OBJECTIVES

Much effort has been invested over the last two decades to measure, understand and model diffusion-driven transfer of radioactive elements in saturated natural or engineered low-permeability porous materials containing large proportions of permanent negative charge swelling and/or non-swelling clay minerals, this mainly to provide support for safety cases for national radioactive waste disposal programs. The materials studied range from swelling clay-(e.g. montmorillonite) rich bentonites foreseen for constructing engineered barrier systems to sedimentary geological formations containing high proportions of illite and smectite-type minerals being studied for hosting potential disposal facilities. The underlying question driving this research can be phrased in a generalized fashion as follows: for a given volume of saturated material under known physical-chemical conditions submitted to a gradient in dissolved concentration (always low to trace) of a given radionuclide, is it possible to predict the radionuclide’s flux through the material over time?

The main features of compacted bentonite and clayrocks influencing RN migration can be summarized as follows (cf. Figure 1):

- The porosity of highly compacted bentonites and clayrocks is dominated by pore spaces in contact with the different categories of clay mineral surfaces: edges, external basal, interlayer (smectite-type only). The pore volume dimensions and the proportioning of total pore space between the external and interlayer fractions vary as a function of bentonite dry density.

- The composition of the pore solution is determined by local (pseudo)equilibrium involving dissolved components, certain mineral phases and clay surface functional groups; the dissolved concentrations of certain components (e.g. Cl-, Na+) may be determined by externally imposed conditions. The dissolved speciation of diffusing trace elements is at equilibrium with the pore solution.

- Clay external and interlayer surfaces possess characteristic densities of permanent negative charge compensated in solution by equivalent amounts of positive charge in the form of cationic species. Cations compensating charge located on external basal surfaces are distributed between two populations: that in direct contact and as dissolved species present in the adjacent solution.

- Electrostatic attraction and repulsion respectively of cations and anions by external and internal surfaces determine the porosities accessible to different species; cations and neutral species can access most if not all of the total connected porosity, while anions are generally assumed to be entirely excluded from the interlayer volumes of highly compacted clay masses and more or less excluded (depending on the ionic strength) from the solution volume immediately adjacent to external basal surfaces.

- The edges of the TOT layers of smectite and illite clay minerals possess functional groups capable of sorbing cationic Me species.
Diffusion-driven transport in porous materials is described in terms of Fick’s laws, adapted to take into account the eventual effects of physical or chemical interaction of the diffusing species with the solid matrix. A common formulation for transient state conditions is:

$$\frac{\partial (Me)}{\partial t} = D_0 \cdot \delta \cdot \frac{1}{1 + \left(\frac{S:Me}{Me}\right)} \cdot \frac{1}{\tau^2} \cdot \frac{\partial^2 (Me)}{\partial x^2}$$  \hspace{1cm} (1)

where $D_0$ is the diffusion coefficient for the species ‘Me’ in free solution; $\delta$ is a factor ($0 < \delta \leq 1$) applied to the total porosity ($\omega_T$) to correct for the effect of physical-chemical phenomena restricting access of Me to some fraction of the porosity; $(S:Me)/(Me)$ represents a fixed (or variable) relationship between the concentrations of dissolved species per pore water volume (Me) and immobile species per pore water volume $(S:Me)$ respectively, resulting from physical-chemical interaction of RN with solid matrix surfaces (if constant this ratio divided by material density / porosity is called $K_d$, i.e. distribution coefficient of immobile and mobile species); $\tau$ is a geometrical factor ($\geq 1$) representing the reduction in the effective concentration gradient $(d(Me)/dx)$ due to the fact that diffusion paths through a porous medium will generally be greater, i.e. more tortuous, than the straight-line distance between the system boundaries, i.e. dx. The corresponding form for steady state conditions is

$$J = -D_e \cdot \delta \omega_T \cdot \frac{1}{\tau^2} \cdot \frac{d(Me)}{dx} = -D_e \frac{d(Me)}{dx}$$  \hspace{1cm} (2)

where $D_e$ is the effective diffusion coefficient.

Experimental data regarding diffusion-driven transport in compacted clay minerals (principally bentonite) and clayrocks concern measurements of the flux, through a given volume of material under fixed physical-chemical conditions, of water molecules (HTO),...
halogen anions (Cl, I) and alkaline and alkaline earth cations (Cs⁺, Sr²⁺…) and show a number of common trends:

- $D_e$ values for HTO decrease with increasing material density (bentonite) and are insensitive to solution composition (Bourg et al., 2006),
- Breakthrough times for anions are generally shorter, and the $D_e$ values smaller, relative to HTO (Glaus et al., 2010; Van Loon et al., 2003),
- $D_e$ values for anions generally decrease with decreasing pore solution ionic strength (van Schaik and Kemper, 1966; Van Loon et al., 2007),
- Cation breakthrough times are generally longer than for HTO (Appelo et al., 2010; Glaus et al., 2010),
- $D_e$ values for alkaline (e.g. Na⁺, Cs⁺) and alkaline earth cations (Sr²⁺, Ca²⁺…) have been found to be significantly higher than for HTO (Glaus et al., 2007; Melkior et al., 2007; van Schaik et al., 1966).
- Diffusion-driven transport of neutral or anionic dissolved species takes place in accordance with equations 1 and 2 with (S:Me)/(Me) = 0 and appropriate $\delta$ and $\tau$ parameter values; the variation of $\delta$ as a function of solution ionic strength can be predicted qualitatively (see above), $\tau$ is (always) a fitting parameter (Ochs et al., 2001; Tournassat and Appelo, 2011).

The conceptual model for cation diffusion-driven transfer is less clear. This is exemplified by the fact that data for diffusion of alkali and alkaline earth cations generally cannot be described simply in terms of diffusion of the dissolved species (Me), i.e. using equations 1 and 2 with HTO as an analogy for the $\delta$ and $\tau$ parameter values and (S:Me) as a simple ‘sink’ (and source) term for immobile Me mass. For these elements, diffusion of cation mass present in surface-associated forms (S:Me) must be considered as contributing to the global Me flux. Diffusion of transition metals, lanthanides and actinides generally show very slow mass propagation through the material. This can be explained in terms of the high solid-solution partitioning ratios, (S:Me)/(Me), for these elements measured during studies in analogous dispersed systems. This sorption-related retardation makes it very difficult to experimentally determine the $D_e$ values for such elements. (Sato et al., 1992; Torstenfelt, 1986)

The overall objective of the work described in this paper, carried out in the framework of the EC Euratom Catclay project, is to increase the understanding and predictability of how different types of ‘surface-association’ affect the diffusion of cationic species in compacted clay systems, in particular for elements of interest to performance assessment other than alkaline and alkaline earths (transition metals, lanthanides/actinides…). This can be summarized by the following question: “Can the migration of actinides and other strongly sorbing radionuclides in clayrock be predicted by coupling models of (i) their sorption
equilibria on representative clay minerals and (ii) the diffusion-driven mass transport of radionuclide sorbed and dissolved species in compacted masses of these clay minerals?" 

Assuming that speciation models for cation sorption on clay materials (illite, clayrock) developed based on the results of measurements in dispersed material systems are valid for the corresponding compacted material, the CatClay project has the following specific objectives:

- Extending, consolidating and testing against experimental data, of theoretical and numerical models for linking the thermodynamic states of electrostatically interacting cations (monovalent, bivalent, trivalent) relative to charged clay surfaces with their corresponding diffusion-driven mobility.

- Evaluation of whether or not the above model framework, after inclusion of appropriate representations of surface complexation reactions for $\text{Zn}^{2+}$ and $\text{Eu}^{3+}$ with illite edge sites (based on available literature data, results of specific measurements), is appropriate for modeling diffusion driven transport of these species. This will be done by comparing model predictions with experimental data on diffusion in compacted illite systems under different conditions. The target question is whether or not translational displacement of covalently bound cations is capable of contributing significantly to RN flux, as is the case for electrostatically interacting cations present in the Stern layer.

- Determination / modelling of the effects of compacted clay and clayrock structure (mineral-porosity-discontinuities, spatial heterogeneity) at the mesoscopic scale (<mm) on diffusion driven transport of strongly sorbing cations.

In order to advance along these lines, the project was guided by the following strategy:

- Selection of illite de Puy as a model clay mineral and several test cations based on known differences in speciation with clay mineral basal and edge sites: $\text{Sr}^{2+}$, $\text{Co}^{2+}$, $\text{Zn}^{2+}$, $\text{Eu}^{3+}$.

- Development / adaptation of conceptual and numerical models (the PhreeqC MCD code) capable of representing the diffusion-driven transport of the above (and other) cations explicitly in terms of their different surface speciation forms with illite, i.e. basal surface species in both Stern layer and diffuse layer forms, ligand exchange complexes with edge sites.

- Use appropriate surface complexation models to calculate the speciation of test cations in illite-containing systems over a range of chemical conditions (pH, competing cations, complexing ligands) selected to modify significantly the relative contributions of basal and edge site species to overall solid-solution partitioning. If necessary, develop an illite de Puy specific model for the cation based on experimental results (batch sorption, spectroscopic…).

- Carry out diffusion measurements for each cation in highly compacted illite equilibrated with different solution compositions (principally pH and ionic strength, but also
carbonate ligand) selected to favour one or the other of the two main types of surface species (edge site complexes; basal plane charge compensation, especially the fraction in diffuse layer).

- Calibrate model for bivalent cation diffusion along basal surfaces (diffuse + solution + Stern?) using data for Sr$^{2+}$ (low pH, low and high ionic strength) and HTO (should be coherent with data for monovalent and anion diffusion). Interpret/improve model

- Predict Co$^{2+}$ diffusion at low and high pH and low and high ionic strength, assuming behaviour identical to Sr$^{2+}$ for basal and immobility of edge complexes. Compare with data, interpret, conclusions regarding Sr$^{2+}$ / Co$^{2+}$ analogy, immobility of edge site species...

- Modify nature of illite surface sites: 100% neutralize basal sites so no Stern+diffuse layer species possible --> is the observed diffusion coherent with model predictions based solely on free species diffusion?

- Modify Me solution speciation (CO$_3$ complexes) --> is observed diffusion coherent with model predictions?

- Characterize compacted illite structure (co-organisation of particles and porosity in oriented samples) plus random walk particle tracking in real sample porosity --> constraints on certain diffusion parameters ($\omega$, $\tau$, $\delta$)

- Carry out, and model, analogous diffusion measurements for each cation in three different clayrocks (Opalinus, Callovo-Oxfordian, Boom Clay).

- Compare the illite and clayrock system results.
A DESCRIPTION OF THE MAIN S&T RESULTS/FOREGROUNDS

Methodology

The scientific approach of the CATCLAY project is of the ‘bottom-up’ type, in which simpler, analogous systems (here a compacted clay, ‘pure’ illite) are experimentally studied and modelled, and then the transferability of these results to more complex materials, i.e. the clayrocks under consideration for hosting radioactive waste disposal facilities, is verified. Moreover, the cations of interest have been chosen for covering a representative range of cation families considered in the performance assessment, from a moderately sorbing cation, the strontium, known to be retained by mainly electrostatic interactions with charged clay surfaces, to strongly sorbing cations, two divalent, the zinc and the cobalt, and one trivalent, the europium, known to be sorbed by inner-sphere complexation with clay edge sites. The understanding (data, models) of these sorbing elements in clays and clay rocks requires various scales of investigation, which combine model and experimental developments. Therefore, the research program has been organized around three major topics: (1) experimental determination of the role of “surface diffusion” in compacted clays (illite type), which is based on the investigation of coupled diffusion-sorption processes; (2) determination of diffusion pathways in clayey rocks (µm to mm scales) and (3) development of models needed for analysing experimental data on diffusion-driven migration in compacted clay materials.

1. EXPERIMENTAL DETERMINATION OF THE ROLE OF “SURFACE DIFFUSION” IN COMPACTED CLAYS (ILLITE TYPE)

1.1. Advances in the experimental issues

Since the June 2010 start-up of this 4-year-long project much effort was devoted to developing and applying specific experimental methods needed for acquiring high precision, reliable data needed to test the alternative hypotheses represented by different conceptual-numerical models.

One of the main experimental issues to be addressed was the use of filters. Indeed, the cations of interest were expected to have an enhanced diffusive behaviour, and in the meantime a sorption affinity from moderate to very strong. This meant that, on the one hand, filters are capable for such species of limiting their diffusion within the clay, acting as a strong resistance and, on the other hand, most of filter are stainless steel made, capable of a strong sorption of the cations onto them. Therefore, the following approaches were proposed:

- For the most enhanced cation when diffusing, i.e., the strontium, the through-diffusion technique was chosen, with filters advectively flushed so that they did not act any more as resistance for the diffusion. Test measurements were performed with strontium and validated its use, in spite of the occurrence of a residual resistance.
For the other cations, owing to their strong sorption, in-diffusion experiments had been the method of choice, for which, the tracer needs to be supplied from a liquid reservoir. This necessitates the use of a mechanically stable interphase between clay and solution, for which the use of the stainless steel sinters was impossible because of their affinity to strongly bind lanthanide ions. Therefore, a first idea was to replace the stainless steel filter by plastic filter, with less affinity and another was to design a miniaturized in-diffusion cell (illite sample with a diameter ~ 6 mm and a length < 15 mm) confined by means of a thin membrane, for which the diffusive resistant is negligible compared to stainless steel filters. In this latter case, previous sorption tests indicated no affinity of europium towards this type membrane filters made from different organic polymers, such as polyvinylidenefluoride (PVDF). Some test measurements were thus performed with strontium and they led to results in satisfactory agreement with those obtained from the classical diffusion cell. Afterwards, this membrane-confined diffusion cell (MCDC) was successfully used to carry out in-diffusion experiments with Co\(^{2+}\) and Zn\(^{2+}\).

![Schematic drawing of the final version of the membrane-confined diffusion cell (MCDC). In contrast to previous versions the supporting slotted titanium disc was left out. An opening of 4 mm provided sufficient mechanical stability to withstand the swelling pressure of the clay sample. As in former versions, saturation of the clay sample can be realised under advective conditions using a stainless steel plate as a support (not shown). After the in-diffusion phase the sample can be extruded from the holder and sliced using an appropriate end-piece (also not shown).](image)

Finally, the investigation of the illite at very small scale for characterizing the pore network organisation also required a lot of developments and tests. Indeed, such investigation is based on the use of two high-resolution imaging techniques: Transmission Electron Microscopy TEM (2D imaging) and Focused Ion Beam/Scanning Electron Microscopy (3D imaging). TEM image analyses give access to the total pore space and 2D morphological information of pores, while FIB-SEM image analyses give 3D morphological information of pores, the connectivity according to the pore diameter. However, these two techniques need to be applied under vacuum conditions and require removing water from pore space without disturbing its geometry. Consequently, several monomers, were tested for consolidating the...
clay material after the polymerization process and it has been demonstrated that impregnation by the MMA monomer led to materials in compacted state which are like the water saturated materials. By means of this approach, the acquisition of images of illite at nm scale with TEM and Fib-SEM has been successfully achieved.

1.2. Advances in the knowledge of the studied strongly-sorbing cations

All experiments reported in the present study were performed on illite collected in the region of le Puy-en-Velay, from the Massif Central region in France. The composition of this illite was first described by Gabis (1963). Because of its natural origin, the clay-rich Puy-en-Velay formation also contains background impurities such as carbonates, feldspars and quartz. As a consequence, this illite was pretreated using a multistep process and saturated in sodium using the method of Baeyens and Bradbury (1997)). The same high purity Na-Form illite du Puy was used for all of the following experiments.

1.2.1. RESULTS FROM DISPERSED DATA

Batch sorption experiments were designed to study the sorption as a function of sorbate (Sr$^{2+}$, Co$^{2+}$, Zn$^{2+}$, Eu$^{3+}$) concentration at constant pH and ionic strength (“sorption isotherm”) and as a function of pH at trace (radio)nuclide concentrations and a fixed ionic strength (“sorption edge”). The sorption isotherm experiments were carried out by three EC CatClay partners (SCK·CEN, KIT-INE and PSI-LES) in an inter-laboratory programme, covering a variety of experimental conditions (pH, ionic strength, inorganic (IC) and organic carbon (OC; present as dissolved organic matter). For a better comparison of the results, some experimental procedures were standardized:

- All experiments were performed in glove boxes under N$_2$ atmosphere (O$_2$ < 0.1 ppm) to (i) prevent a possible influence of CO$_2$ or (ii) to sustain a fixed CO$_2$ atmosphere (e.g. 0.4% CO$_2$).
- Radiotracer solutions used in the different laboratories were purchased from different commercial sources. When a non-carrier free solution was used the concentration of active and inactive isotopes were measured by ICP-MS prior to the experiments, giving a total concentration of the respective metal ion in the (radioactive) stock solutions.
- Buffers were used in the pH range 4-10 to ensure the pH stability during the experiments (2x10$^{-3}$ to 1x10$^{-2}$ M). For strongly acidic (pH< 4) and alkaline conditions (pH > 9), the suspensions were titrated to the target pH with HClO$_4$ or NaOH (SCK-CEN), or aliquots of 1M HNO$_3$ or 0.1M NaOH were added and the solution pH was allowed to evolve with time (PSI-LES). For a detailed description and the effect of the buffers on metal ion sorption see Bradbury & Baeyens (2009a&b) and Perrin & Dempsey (1974). A modification to this protocol was carried out for the Eu$^{3+}$ sorption edge, where no buffer material was used, for a better comparability to literature data and time resolved laser fluorescence spectroscopy (TRLFS) results.
The amount of solid in the tracer containing suspensions, i.e. the solid-to-liquid ratio (S:L ratio) was fixed 1 and 2 g L\(^{-1}\) for the experiments performed by SCK-CEN and KIT-INE, respectively. In the experimental protocol followed by PSI-LES, S:L was varied between 0.25 and 2.0 g L\(^{-1}\). While the former ratio was applied to experimental conditions where a high metal ion uptake was expected (i.e. high pH, low ionic strength), the latter was used at low pH and high ionic strength (i.e. low uptake). This procedure should thus increase the concentration/activity of the radiotracer in solution, leading to more robust statistics.

The contact time of the tracer solutions with Na-illite was at least 7 days.

Phase separation was carried out by ultracentrifugation. Due to the different instrumentation, the centrifugation speed (i.e. the g-value) varied between the different laboratories (600000g, 180800g and 150000g for KIT-INE, PSI-LES and SCK-CEN, respectively). In case of Co(II) and Zn(II), sorption edge data (Kd values) were observed to scatter significantly for similar experimental conditions between 4 < pH < 7, when the phase separation was done at lower separation speed (up to 1.7 log units for experiments performed at similar pH and a phase separation at 180800g). One possible explanation is the presence of small (colloidal?) clay particles with bound radionuclides remaining in the supernatant (due to incomplete phase separation or resuspension during sample transport), which would increase the experimentally determined activity in solution, decrease the log Kd values and lead to scatter in the sorption data. Due to a lack of a better phase separation, a different experimental protocol was used by PSI-LES for additional batch-type experiments (“membrane approach”).

The activities in the supernatant were measured by γ- or liquid scintillation counting (LSC). Labelled standard solutions were counted simultaneously with the supernatant solutions from the batch sorption tests.

A formal estimation of the maximum absolute error performed by Bradbury et Bayeens (1997) yielded an uncertainty in log Kd of ~0.15 log units. However, for conditions where the sorption is very high (i.e. high pH values; > 99% of the radiotracer sorbed), higher uncertainties of ±0.5 log units were used Bradbury & Baeyens (2005).

1.2.1.1. STRONTIUM

Sorption edges for Sr on Na-illite were determined at trace metal ion concentrations (1E-7 – 1E-9M) in 0.01 and 0.1 M NaClO\(_4\) in the pH range between 3-11, while two sorption isotherms were measured in 0.1 and 0.5 M NaCl at pH 5.5 and 8.3, respectively.

Sr sorption edges show clearly that the uptake of Sr is a function of the background electrolyte concentration, as logKd is approximately 1 to 1.5 orders of magnitude higher for the lower ionic strength (0.01 M), thus indicating that cation exchange is the dominating sorption mechanism for Sr on Na-illite. While the decrease in Kd for pH values < 5.5 can be
related to competitive effects from cations released into solution from the illite itself, the increase in sorption for pH ≥ 9 is correlated to surface complexation (Bradbury and Baeyens, 2005). This result is in line with the sorption isotherms, where logKd is observed to be affected by an increase in background electrolyte concentration (0.1 to 0.5 M) rather than by an increase in pH (pH 5.5 to 8.3). In addition, constant logKd values are detected with increasing Sr equilibrium concentration, thus indicating an uptake solely by cation exchange.

Figure 3  Sr sorption edge measurements on Na-illite in 0.01 M (a) and 0.1 M NaClO4 (b) at low Sr concentrations together with literature data (S:L=1.5-1.9 g L⁻¹; [Sr]initial = 1E-9M) (Poinssot et al., 1999). Sr sorption isotherms at different NaCl concentrations at pH 5.5 (c) and 8.3 (d) together with literature data measured at pH 7 (S:L=1.8 g L⁻¹; 0.1M NaClO4; (Bradbury & Baeyens, 2005)

1.2.1.2. COBALT

Co sorption edges and isotherms were performed by PSI-LES and recorded in four different background electrolyte concentrations, i.e. 0.01, 0.03, 0.1 and 1.0 M NaClO4. The sorption behaviour of Co(II) onto Na-illite can be explained by cation exchange and surface complexation mechanisms, the former being dominant at low pH (≤ 6) and low background electrolyte concentrations (0.01 M), while the latter is responsible for metal ion uptake at higher ionic strengths (≥0.1 M) and higher pH values (pH > 6).
Figure 4  pH dependent Co(II) sorption onto conditioned Na-illite at trace Co levels in 0.1M NaClO$_4$ determined by conventional setup and the dialysis membrane approach together with data from Bradbury & Baeyens (2009) (a) $C_{\text{Co}_{\text{initial}}}=1-3\times10^{-6}$ M; S:L=1.6 g L$^{-1}$. Zn sorption edges measured in the membrane approach at different NaClO$_4$ concentrations (b). Co sorption isotherms at pH 5 in NaClO$_4$ concentrations presented as Co sorbed (c) and as logK$_d$ (d) vs. Co equilibrium concentration.

The sorption edge at I = 0.1 M NaClO4 and the sorption isotherm at I = 0.1 M NaClO4 at pH = 5.0 were successfully modelled using a non electrostatic model similar to the one described in the literature (Bradbury & Baeyens, 2009).
1.2.1.3. ZINC

The three labs, involved, i.e. KIT, SCK-CEN and PSI drew for Zinc a consistent picture under different experimental conditions (pH 5, 5.5, 7.0, 8.3, 8.4 and 9, Ionic strength 0.1M, 0.3M, 0.5M, 1.0M, var CO2, presence/absence of humic substances):

- As expected, sorption is much stronger at high pH compared to low pH, but with an extent clearly lower than for the sorption of Zn on Na-montmorillonite (Bradbury and Bayens, 1997);
The effects of the ionic strength are of subordinate importance in all the experiments;

The different CO₂ conditions did not result in significantly different sorption behaviour, while adding organic carbons strongly decreased the Zn sorption extent.

It has to be assumed that sorption is dominated in all cases by specific binding rather than cation exchange.

The sorption edge at I = 0.1 M NaClO₄ and the sorption isotherm at I = 0.1 M NaClO₄ at pH = 5.0 and 9.0 were also successfully modelled using a non electrostatic model similar to the one described in the literature (Bradbury & Baeyens, 2009).

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**Figure 7**  
Zn (II) sorption onto conditioned Na-illite different NaClO₄ concentrations as a function of pH trace Zn levels (a and b) and as a function of Zn equilibrium concentration at pH 5 and 9 (c and d). The sorption edge experiments were performed by the dialysis membrane approach (a, experiments performed at PSI-LES) and by the conventional setup (b, experiments performed at SCK-CEN), while for the sorption isotherms (c and d) only the conventional setup was used (experiments performed at PSI-LES and KIT-INE).
**Figure 8** Sorption edges for Zn on Na-illite in 0.1M NaClO₄. The continuous curves were calculated using the 2SPNE SC/CE model.

**Figure 9** Sorption isotherms for Zn on Na-illite in 0.1M NaClO₄ at pH = 5 and pH = 9. The continuous curves were calculated using the 2SPNE SC/CE model, symbols represent experimental data. The contributions to the overall sorption of the individual Zn surface species are shown by the different curves (black dashed lines): 1: $S_{\text{w}}\text{OZn}$; 2: $S_{\text{w}}\text{OZnOH}$; 3: $S_{\text{w}}\text{OZn(OH)}_2$; 1w: $S_{\text{w}}\text{OZn}^+$; 3w: $S_{\text{w}}\text{OZn(OH)}_2^-$; and cation exchange reaction (red dashed line).
1.2.1.4. EUROPIUM

The pH dependent Eu sorption at trace metal ion concentrations (2x10^{-9} M) was investigated as a function of ionic strength in 0.1 and 0.5 M NaCl. Two distinct areas can roughly be deduced from this figure: (i) an increasing logKd for pH < 7 and (ii) constant logKd above this value. When the background electrolyte concentration is increased to 0.5 M, logKd decreases for pH < 5, whereas it is not changing thereafter. Thus an Eu uptake onto illite is affected by both cation exchange processes (at low pH and ionic strengths) and surface complexation reactions (higher pH values).

In line with these results, similar sorption isotherms are observed at pH 5.5, 7.0 and 8.3. Up to Eu equilibrium concentration of ~1x10^{-7} M a linear sorption behaviour is observed, while logKd decreases by a further increase of the metal ion concentration. Both the sorption edge and isotherm results are in good agreement with published results (Poinssot et al. 1999; Bradbury & Baeyens 2005) on the same Na-illite material.

However, discrepancies are visible for the isotherm recorded at pH 5.5 at intermediate Eu equilibrium concentrations (~1x10^{-7} M). At these conditions, an increased Eu uptake is observed. The reason for this behaviour is not completely understood at the moment, but a minor accessory mineral phase, which was not removed by the condition process, can be responsible for the higher Eu uptake.
1.2.2. RESULTS FROM DIFFUSION DATA

In order to define the underlying mechanisms of cation diffusion in compacted clays, a series of diffusion experiments were performed at various geochemical conditions (CO2, pH, etc.). The results from these experiments include:

- **Figure 10**: Eu sorption edge on Na-illite at trace Eu levels in various NaCl concentrations together with literature data (S:L = 1.8 g L⁻¹; [Eu]₀ = 3x10⁻⁹ M) (Poinssot 1999) (a). Eu sorption isotherms in 0.1 and 0.5 M NaCl at pH 5.5 (b), 7.0 (c) and 8.3 (d) together with literature data Bradbury & Baeyens 2005 (pH 7; S:L = 1.2 – 1.8 g L⁻¹; 0.1M NaClO₄). (e) Comparison of sorption isotherms at different pH in 0.1M NaCl.

The diagrams illustrate the relationship between Eu sorption and pH, NaCl concentration, and the effect of different pH levels on Eu sorption. The data shows a clear trend of increased sorption with decreasing pH and increasing NaCl concentration, indicating the importance of these factors in controlling cation migration in clay rocks.
external salinity, reduced surface charge illite) with Sr, Zn and Co in Na-illite. At PSI-LES, Sr, Zn and Co diffusion was studied at pH 5 and at pH 9 and at ionic strength varying from 0.01 to 1 M. SCK-CEN performed experiments with Sr at different pH (pH 5, pH 7, pH 8.2 & pH 9) and pCO2 conditions (Inorganic carbon at 0.4% and 0.035%), while they carried out diffusion test with Zn at pH 5 and at pH 7 at atmospheric inorganic content (0.035%) and without CO2. Finally, KIT carried out diffusion experiments for HTO, 36Cl and Sr through reduced surface charge illite materials.

1.2.2.1. EFFECT OF CARBONATE CONDITIONS.

According to the speciation calculations, Sr and Zn can form carbonate complexes at higher pCO2 conditions. At the studied conditions (0.4% CO2 = 10x atm pressure, 16 mM NaHCO3), however, only 5% of Sr would complex with carbonates, while 25% Zn could form complexes. At higher pCO2 pressures, the fraction of carbonate complexes increases, but these conditions are not relevant anymore for the geological disposal concept. In case of carbonate complexation, it was expected that sorption would be lower due to less available free metal ion. However, the sorption of Zn was hardly affected by the higher CO2 pressure. For the diffusion experiments, we could only perform experiments at higher CO2 pressure with Sr and not with Zn, since the higher pCO2 results also in a higher pH. There is not yet a suitable diffusion technique to perform the diffusion experiments at higher pH for Zn (sorption problems of Zn on the filter and cell materials). Finally, we observed a slightly higher diffusion coefficient for Sr at higher pCO2, but the higher equilibrium pH (8.2 compared to 7) at these pCO2 conditions is a more plausible explanation for this observation. For Zn, we assume that the diffusion will not be influenced largely by higher pCO2 conditions, based on the very small effect of pCO2 observed in the sorption experiments.

1.2.2.2. EFFECT OF PH.

From the sorption edges, it is clear that strontium mainly binds via ion exchange. However, the sorption of Sr on illite increases slightly at higher pH, which indicates that Sr will partly bind via surface complexation too. The larger sorption at higher pH was also observed in the diffusion experiments (higher α at higher pH). Also the effective diffusion coefficients increased with an increasing pH (factor 2 to 10 between pH 5 and 9).

For Zn and Co, the sorption experiments revealed that surface complexation is the dominant mechanism. This was also observed in the diffusion experiments. The Rd values for Zn and Co showed a strong dependence of pH, again confirming the surface complexation as sorption mechanism. There was, however, no clear effect was observed for the effective diffusion coefficient.

1.2.2.3. EFFECT OF EXTERNAL SALINITY.

As a very simple but important appraisal De values depend significantly on the background electrolyte concentration in the contacting solution. They increase for the three elements tested with decreasing salinity. The fact that De values at the lowest salinity exceed the $D_e$ values of water tracers ($D_e$ for tritiated water is of the order of $2 \times 10^{-10}$ m$^2$ s$^{-1}$, (Glaus et
(al., 2012)) by several orders of magnitude, rules out a simple diffusion model in which the effective diffusion coefficient for a given element is determined by its diffusion coefficient in bulk water and a species-independent geometry factor. Only in restricted ranges of the parameter space, such a model is near reality. An example for this would be Zn diffusion at pH 9 in the presence of rather saline solutions where De values are slightly exceeding a value of $1 \times 10^{-10}$ m$^2$ s$^{-1}$. The De for Zn(II) diffusion in illite would be $\sim 6 \times 10^{-11}$ m$^2$ s$^{-1}$ as expected from the ratio of the diffusion coefficients in bulk water for Zn and HTO and assuming the same geometry factors.

Figure 11 In-diffusion experiments with $^{60}$Co$^2+$ at pH 5 showing the total element concentration (left) and the profile of total element concentration in the clay (right). The initial concentration of the source reservoir data measured at 0.01 M NaClO$_4$ was calculated from the tracer activities using the ratio of stable element to radiotracer in the radiotracer stock solution.
Figure 12 In-diffusion experiments with $^{65}\text{Zn}^{2+}$ at pH 5 showing the total element concentration (left) and the profile of total element concentration (right).

Figure 13 Dependence of $D_e$ and $R_d$ for $^{60}\text{Co}^{2+}$ on the NaClO$_4$ concentration in the contacting solution for the experiments at pH 5 (left-hand plot) and the experiments at pH 9 (right-hand plot).
1.2.2.4. EFFECTS OF COMPETITOR SPECIES REDUCING THE SURFACE CHARGE ILLITE.

As observed above and earlier studies (Glaus et al., 2007; 2010), values for $D_e$ decrease for cationic and increase for anionic tracers with increasing ionic strength. This indicates that an electrostatic shielding of the surface charge (by an increase in ionic strength) is affecting the diffusion properties of charged solutes. An issue related to this subject is, how
these properties are altered if the negative surface charge is occupied by (i) Cs+ or (ii) a high selective organic ligand-metal complex such as copper-ethylenediamine Cu(en)22+. While the former is known to be associated with both the “frayed edges” (FES) and “type II” sites (situated on the permanently charged basal surfaces) (Glaus et al., 2007; Poinssot et al., 1999), the latter was reported to block effectively the planar surface charge in montmorillonites and reduce considerably the access of alkaline-earth metals to these exchange sites (Maes & Cremers, 1979). Thus, Cs- and Cu(en)22+ exchanged illites were prepared and used for multi-tracer (HTO, 36Cl‒ and 85Sr2+) diffusion studies. Additionally, a Cu(en)22+-exchanged montmorillonite was prepared, as effects on charge-reduction on the planar surfaces are expected to be higher for swelling clay minerals (the interlayers of the low-charged montmorillonite are accessible for positively charged solutes (Glaus et al., 2007)).

The multi-tracer diffusion study in Cu(en)22+-illite and -montmorillonite indicate a reduced influence of the negatively charged clay (basal) surfaces on the transport properties of cations and anions. In detail, De and α tend to increase in case of 36Cl, as anions are no longer repelled form the vicinity of the clay surface. This effect is not observed for illite but is significant for montmorillonite, where both the anion accessible porosity as well as De are higher compared to the Na+-form. For the cationic tracer 85Sr, an inverse trend is apparent in the case of illite. Both De and α decrease by Cu(en)22+-exchange, pointing thus to the fact that Sr enrichment in the interlayer (a prerequisite for the enhanced mobility compared to HTO) is reduced due to a neutralization of the negative surface charge. However, a remaining negative charge tends to be still present, as De values for Sr2+ Cu(en)22+-montmorillonite are still higher compared to HTO. Thus, the observed trends are in line with a (partially) neutralized clay surface.

The comparison between Na- and Cs-illite indicates that Cs-exchange does not alter the diffusion properties of anionic tracers. However, this result may also be due to a leaching of Cs+ from the solid in course of the experiments, making the data derived from this experiment less reliable.

1.2.3. RESULTS FOR PARTICLE AND POROSITY ORGANISATION IN COMPACTED ILLITE

The originality of this work was to associate several techniques of pore space characterization, image analysis and morphological in order to provide the actual 3D geometrical pore size distribution. The combination of the different approaches seemed to be consistent. Indeed the morphological analysis calculated from TEM and FIB-nt images showed up anisotropy of the compacted IDP sample.

The main result is that the resolution limitation of FIB-nt described by many authors was resolved by using simple image analysis approach. The proposed approach, among many other potential, allowed to threshold more than 70% of the total porosity of the sample. Moreover, beyond the fact that we detect a large part of the porosity, from the macro to the mesoscopic scale, more than 90% of the pores are interconnected.
Figure 16  Pore size distribution (PSD) of the compacted Illite de Puy. PSD calculated with the different methods (bulk and microscopic) are illustrating. The PSD calculated from the 3D FIB-nt volume is given according the two discussed methods (the present work and Otsu thresholding).

Figure 17  3D visualization of a ROI of 400 x 240 x 180 pixels. (A) Pore components segmented from Otsu thresholding. Each color represents a non-connected pore. (B) Pore components segmented from the present work. (C) Local shape classification, half axis length are computed. The color palette indicates the a/b values. (D) Skeleton representation of the pore volume.
2. DETERMINATION OF DIFFUSION PATHWAYS IN CLAYEY ROCKS (µM TO MM SCALES)

2.1. Advances in the experimental issues

Contrary to the illite, the experimental issue of the filter depends on the type of materials. Indeed, while the Callovo-Oxfordian shales and the Opalinus Clay are quite mechanically stable, the Boom clay, as a plastic clay, requires to be confined by filters. Therefore, several strategies were adopted. For the Callovo-Oxfordian clayrocks, the filters were either omitted in Peek miniaturized cells (diameter ~18 mm and length ~ 10 mm) or replaced by perforated Peek plates. For the Opalinus clay, a diffusion technique was developed on smaller clay cores (diameter ~2.6 mm and length ~10 mm) embedded in epoxy resin and not confined by filter. This approach was published recently (Van Loon et Müller, 2014). Finally, for the Boom Clay, the first experiments were carried out with stainless steel filters, while the last ones with Peek filters, showing less affinity.

The overcoming of the artefact issues for acquiring reliable data, required in addition to the design of new diffusion set-ups, the development or the refinement of analytical tools enabled to probe more accurately the strongly-sorbing cations within the materials. Indeed, the penetration depth of such species are expected to be very small (less than few 100µm), necessitating techniques with a very good resolution. Therefore, a spectroscopic method, the Laser Induced Breakdown Spectroscopic microprobe (µLIBS) was adapted for acquiring both Zn and mineral spatial distribution within Callovo-Oxfordian Clay samples having experienced an in-diffusion test. This is based on the analysis of the optical emission from the plasma created by a focused laser beam. The spatial distribution of elements can be obtained by scanning the laser beam over the surface area, and with a calibration, the concentration of the elements can be determined. Within clay-rich material such as claystones, the spatial resolution is limited to 10 µm.

Finally, by means of this MMA impregnation, the acquisition of images of the Callovo-Oxfordian clayrocks in a water-like saturation state (at nm scale) with TEM has been successfully achieved.

2.2. Advances in the knowledge of the studied strongly-sorbing cations

2.2.1. OPALINUS CLAY

In addition to Co and Zn Sorption experiments, in-diffusion experiments with these species were carried out by PSI by means of a filter-free diffusion set-up. In this case, the effect of the NaCl concentration on their diffusive behaviour was investigated by means of three different diffusion cells. After 16.8 days of in-diffusion, the spatial distribution of both tracers (60Co and 65Zn) was measured. To this end, thin layers of clay were removed using a modified version of the abrasive technique (Van Loon and Eikenberg, 2005) described by Van Loon and Müller (2014).

The diffusion data for Co(II) clearly show the effect of ionic strength: at low ionic strength the sorption value and the effective diffusion coefficient are higher whereas at high
When comparing the Kd value derived from the diffusion experiments with those measured in batch sorption experiments, it is obvious that the sorption on the intact rock is lower than on the crushed rock (Figure 60). In the case of Co(II), the difference is a factor of 2. For Zn(II), the sorption on intact OPA is one order of magnitude less than on crushed OPA.
2.2.2. **THE CALLOVO-OXFORDIAN CLAYSTONES**

* Sorption and diffusion experiments*

The sorption/diffusion of three cations covering a representative range of cation categories taken into consideration in the performance assessment, from a moderately sorbing cation, Sr, to strongly sorbing cations, one divalent, Zn, and one trivalent, Eu was investigated in the Callovo-Oxfordian claystones. The impact on diffusion and sorption of the ionic strength and the partial pressure of CO2 was estimated by means of batch and diffusion experiments. Note that for strongly sorbing cations, such as Zn and Eu, specific approaches were used, and in some cases, developed for improving the reliability of the data acquired.

The batch and through-diffusion experiments carried out with Sr led to a consistent picture for the three ionic strengths explored. Numerical modelling based on the multi-ion exchange model succeeded in well reproducing of these experimental data, using De values varying from 5.2 to 1.35 x 10^{-11} m²/s when the IS increases from 85 to 580 mEq/L. On the other hand, the results derived from the out-diffusion experiments clearly show some inconsistencies with the through-diffusion ones, suggesting that some processes could have taken place for retaining Sr during these long experiments (150 days + 240 days). These processes with slower kinetics than the ion exchange are thought to be either isotopic exchange of 85Sr or incorporation of 85Sr into some Sr-bearing minerals. However, long-term batch experiments (300 days) failed to evidence these processes, likely due to the too high water/rock ratio compared to those of the compacted system.
Figure 19  $^{85}$Sr activity evolution in the upstream reservoir and $^{85}$Sr flux in the downstream reservoir as a function of time in the 0.085 M cell (A), the 0.330M cell (B) and the 0.590 M cell (C) For the Callovo-Oxfordian Claystones. The modelling by an analytical approach is entitled “MIED” and by a numerical approach with the multi-site ion exchange model.

The picture appears more complicated for Zn. For example, its more complex chemistry (complexation, solubility limits, etc…) made its study, especially by µLibs, more tricky, because the Zn initial concentration has to be chosen high enough for acquiring a good µLibs signal and not too high for avoiding any Zn-bearing mineral precipitation. However, first Zn acquisitions by µLibs sound promising. Moreover, all the data obtained by batch
experiments are weakly impacted by the change of the experimental conditions (ionic strength, pCO2), which is unexpected regarding what was estimated by modelling. On the other hand, in-diffusion experiments allowed us to acquire data clearly influenced by the change of the ion strength. And first numerical modellings succeeded in reproducing these data, using De values decreasing when the IS increases.

For Eu, some rough tendencies emerge from the data acquired from the first in-diffusion experiments. The extent of Eu sorption estimated by a simple analytical model seems to be slightly lower than what was previously measured from batch experiments but not impacted by the IS change. Dedicated batch experiments should confirm this trend. Regarding the effective diffusion coefficient, the three in-diffusion experiments carried out with equilibrated water led to consistent values of about 0.3 x 10^-11 m²/s. However, the non-uniform shape of the rock profile derived from one of these cells, using radioactive Eu, suggests that the diffusion process is much more complicated, likely involving the contribution of several Eu species. And among these species, some Eu anionic complexes, occurring in larger amount in the low IS solution, could be responsible for the larger penetration depth than those of the cells with high IS. Finally, it seems that Eu diffusion would be more governed by its chemistry in solution than by some surface diffusion processes. And we hope that the results acquired from the four long-term diffusion experiments (~ 400 days) that are still on-going will strengthen this tendency.

Lastly, the diffusion of Sr, and to a lesser extent, zinc, studying under various experimental conditions, can be described by classical diffusion surface formalisms given in literature. In this case, the extent of the cation diffusion coefficient is clearly correlated to the extent of its sorption.

![Figure 20](image.png) Evolution of the diffusivity as a function of the rock capacity factor or porosity for HTO, strontium, zinc and europium with the increase of the ionic strength in the Callovo-Oxfordian Claystones.
Pore network characterisation

An integrated methodology was proposed to characterize mineral and pore spatial distributions of clay-rich materials from nanometer to micrometer adapted from the methodology developed in the WP2 on compacted illite. Our approach is mainly based on imaging the nano-microscale structural organization (μm- nm) of natural clay-rock from the Callovo Oxfordian using TEM and FIB/SEM imaging techniques and analyzing the resulting set of images to extract information on pore space and mineral spatial distributions. The proposed methodology aims at better identifying and improving several key steps including the sample preparation, images acquisition, image analysis and the final quantification of geometrical parameters such as the pore size distribution.

TEM images were obtained on clay-rocks. These images are the first representations of a clay-rock with a preserved microstructure in a water-like saturated condition. The acquisition was possible due to the resin impregnation techniques developed in the Illite workpackage.

Image stacks obtained either by EsB detection with FIB-nT allowed to display porosity from the surrounding clay matrix and the Pore size distribution (PSD) was retrieved by determining the aperture diameter map. There is good agreement between the PSD obtained with the pore volume extracted from the FIB-nT volume and those calculated from the bulk macroscopic characterization (MIP) until pore diameter of 5 nm. In addition to the characterization of the 3D pore network (pore volume, connectivity, pore size distribution), a 3D geometrical characterization of the compacted clay materials from FIB-nT images was performed to evaluate the anisotropy of the compacted clay plug.
2.2.3. THE BOOM CLAY

The sorption/diffusion of Sr and Zn was investigated in the Boom Clay. The effective diffusion coefficient $D_e$ for Sr determined in the Boom Clay is at least 2 orders of magnitude higher than the effective diffusion coefficient observed for HTO ($\pm 1 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$). This is a strong indication for double layer-enhanced diffusion. A first in-diffusion experiment with Zn was conducted in an early stage of the Catclay project. In this experiment, it was found out that Zn sorbed strongly on the stainless steel filter. In the further course of Catclay, a series of different filter materials were tested. Due to the long time needed to find appropriate filter materials, the second experiment was delayed. Finally, a new experiment was started in a PEEK diffusion cell with flushed filters in polypropylene which is still ongoing.

![Figure 22](image.png)

*Figure 22 Experimental data and best-fit values for the two through-diffusion experiments performed in the framework of EC Catclay with the Boom Clay*
3. DEVELOPMENT OF MODELS NEEDED FOR ANALYSING EXPERIMENTAL DATA ON DIFFUSION-DRIVEN MIGRATION IN COMPACTED CLAY MATERIALS.

Before the acquisition of the large CatClay dataset, transport and porosity models were developed by BRGM and Appelo for anion exclusion in compacted bentonite. This led to a publication in Geochimica and Cosmochimica Acta in 2011. Appelo also provided the tools for modelling the diffusion experiments with Phreeqc. In this sense, the Bradbury and Bayens model describing the sorption of Ni, Co, Eu, and Sn on illite with 2 sites, the protolysis, the non electrostratic surface complexation and the cation exchange, was adapted so that it can be used by taking into account the presence of an electrostatic double layer on clay surfaces. This improvement was necessary to model the different transport modes of cations, anions, and uncharged species in clay pores.

3.1. MODELLING THE DIFFUSION DATA FOR ILLITE

First of all, a sorption model taken into account the cation released by the clay material dissolution was developed, allowing a better description of the Sorption Edge and the Sorption Isotherm given in literature for Sr.

Moreover, a first approach used for the diffusion data obtained on illite was an extension of the model proposed by Gimmi and Kosakowski (2011) for describing the dependence of the De values on pH and concentration of the background electrolyte. The extension comprises two types of surface species, one of these being mobile and the other one immobile. In this case, the mole fraction of mobile surface species, has to decrease with increasing ionic strength and increasing pH and also decreases in the order of elements Sr → Co →Zn corresponding to the trend of these ions to form hydrolysed species (acidity of metal cations). This approach confirms the hypothesis that binding mechanism of Sr2+ on illite is almost pure cation exchange at low pH, whereas an increasing contribution of specific surface complexes becomes noticeable at higher pH (Bradbury and Baeyens, 2005a).

A further modelling approach was realised by deriving De values from thermodynamic speciation calculations in Phreeqc taking into account the presence of mobile species in the electrical double layer (“Donnan layer”) on the charged clay surface. The model uses a subdivision of the pore space into a fraction contains electrically neutral (“free”) pore water, a fraction that has a charged (“Donnan”) solution, which counterbalances the surface charge of illite, and a fraction given by the closest approach that solute ions can come to the surface. De values are calculated using the following relation:

\[
D_e = \frac{c_{DL}}{G} \left( f_{free} + f_{DL} \frac{c_{DL}}{c} \right) D_w
\]

where etot is the total accessible porosity, G a geometry factor lumping together the geometric effects of constrictivity and tortuosity, ffree the fraction of free pore water, fDL the fraction of water in the Donnan layer and cDL the concentration of the diffusion species in the Donnan layer. The latter quantity is the result of the speciation calculation and depends, among others,
on the surface potential, which in turn is a function of the chemical composition of the equilibrium solution. Actually for these calculations a factor (0.4) reducing the mobility of the Donnan layer species had to be introduced to optimise the agreement between the model and the experimental data. Although there are some discrepancies between the experimental data and the model, the agreement is generally good and it would yet be acceptable without the adjustment of this mobility factor. Some of these discrepancies can be explained by the experimental uncertainties in the data at low concentrations of the background electrolyte, which tend to be large at low concentrations of the background electrolyte and at pH 9.

Figure 23  $D_e$ values calculated for Sr, Co and Zn at pH 5 (left) and pH 9 (right) by deriving $D_e$ values from thermodynamic speciation calculations in Phreeqc taking into account the presence of mobile species in the electrical double layer (“Donnan layer”) on the charged clay surface. The model uses a subdivision of the pore space into a fraction contains electrically neutral (“free”) pore water, a fraction that has a charged (“Donnan”) solution, which counterbalances the surface charge of illite, and a fraction given by the closest approach that solute ions can come to the surface.

Based on the spatial distribution of pores extracted from 3D FIB/SEM images in partnership with BRGM, numerical diffusion simulations were performed by Andra at the pore scale for compacted illite material. We modelled numeric “in-diffusion” tracer diffusion experiments from the 3-D digitized volume of the spatial distribution of pores and minerals (spatial resolution: 5 nm). This method is briefly described below; details on it can be found in Robinet et al. (2012). The main steps of the modelling are the following: (i) a constant concentration of particles is imposed on one surface of a cubic volume, (ii) the particles diffuse through using the TDD algorithm, (iii) after a diffusion period the position of each particle is recorded allowing them to be visualized in the 3D volume and the particle concentration profile from the entrance surface to be plotted; (iv) the macroscopic diffusion coefficient (apparent diffusion coefficient $D_a$) is finally determined from the diffusion profile by adjusting an analytical solution assuming an homogeneous media. From the diffusion
coefficient, a geometry factor can be computed (\( G = Da / D0 \) where \( D0 \) is the diffusion coefficient applied in the pores). The diffusion anisotropy was successfully evaluated by modeling diffusion in various diffusion directions imposed by the boundaries at the sample surface. This value was indeed in a good agreement with the mean apparent diffusion obtained from real diffusion experiments.

![Diffusion modeling based on the 3D spatial distribution of pores extracted from FIB/SEM images](image)

Figure 24  Diffusion modelling based on the 3D spatial distribution of pores extracted from FIB/SEM images (a) selected areas used to model diffusion; (b) result of an in-diffusion simulation of 400 000 particles through Volume A; (c) example of a diffusion profile fitted using an homogenous analytical solution.

3.2. MODELLING THE DIFFUSION DATA FOR CLAYROCKS

The multicomponent diffusion model implemented in Phreeqc3 was used for reproducing the Co and Zn diffusion data obtained in Opalinus Clay (Appelo and Wersin, 2007; Appelo et al., 2010). The sorption model developed by Bradbury and Baeyens (2009a) for the sorption of metals on illite was also implemented in the model.

We started with the diffusion of Co(II) in OPA performed with the ordinary synthetic pore water (I = 0.39 M). The diffusion was modeled assuming that there was no Zn(II) present. A first trial with the parameters used to model the sorption isotherm reproduced the measured
diffusion profile reasonably good. The contribution of strong sites is only minimal. This observation is in agreement with the simple diffusion model used before, indicating that only one sorption site is involved in the sorption of Co(II). The diffusion profile for Co(II) in OPA in contact with the dilute synthetic pore water (IS = 0.17 M) could also be well reproduced by the model using identical site densities as for the ordinary pore water. The same was observed for the more concentrated pore water (IS = 1.07 M). The model also predicts the more shallow diffusion profile for the OPA in contact with the concentrated pore water and the less shallow profile for the most diluted pore water. The effective diffusion coefficient derived from the multicomponent diffusion modelling was 3.3 x 10⁻¹¹ m² s⁻¹.

In the case of Zn(II), the situation is different. When using the interaction constants derived from the sorption isotherm (see Table 30) the experimental results could not be reproduced. The calculated diffusion profile is too shallow, i.e. the sorption of Zn(II) on OPA is too high. Only when the constant for the interaction between the weak sites and Zn(II) are lowered from logK = 0.2 to logK = -0.5, a good description of the experimental profile is obtained. However, now the calculated sorption isotherm no longer matches the measured one. It seems that the sorption on the intact OPA is much lower than the sorption on ground OPA. In the case of Co(II), a similar but weaker effect was observed. The observed difference between intact and crushed OPA can only be explained by the fact that new sorption sites are created by the grounding process. Such an effect was not observed in the case of cations sorbing by ion exchange such as Cs(I), Na(I) or Sr(II) (Van Loon et al., 2005; Van Loon et al., 2009).

Another explanation might be the fact that in a compact system, not all sorption sites are accessible (Montavon et al., 2006). It is also possible that the strong sorption sites are blocked by competing cations such as Mn(II) or Fe(II), or that the pH in the pore water of the intact rock is different from that in the contacting solutions. It was recently shown by Wang et al. (2002) that the protonation-deprotonation (pK) behaviour of surface groups on confined interfaces differs from that on unconfined interfaces. Moreover, it could be shown that as pore size is reduced to nanoscale, the adsorption of ions can vary by more than two orders of magnitude compared to unconfined interfaces. Which process explains the observed differences between sorption in confined and unconfined systems is not clear at the moment. Because confined interfaces are not readily accessible, it is almost impossible to directly study effects of confinement on physico-chemical properties such as acidity of surface groups. Model systems such as reverse micelles are therefore used to understand pH in confined spaces (Crans and Levinger, 2012). Albuquerque and Calzaferri (2007) used dye-loaded zeolites and were able to show that - based on the spectroscopic properties of the encapsulated dyes - the pH inside a zeolite could be as low as ca. 3.5.

The effect of ionic strength on the diffusion profiles are matched by the model. The effect can be explained by the dependence of the concentration of cations in the DDL on the ionic strength. The higher the ionic strength, the lower the concentration of cations present in the DDL. As a consequence the concentration gradient in the DDL becomes less as well as the diffusive flux. At low ionic strength values the opposite effect can be observed. The effective diffusion coefficient derived from the multicomponent diffusion modelling was 3.8 x 10⁻¹¹ m² s⁻¹. This value is similar to the value observed for Co(II), in agreement with the similar
values of the diffusion coefficient of both cations in water (DCo = 6.99 x 10^{-9} m^2 s^{-1}; DZn = 7.15 x10^{-9} m^2 s^{-1}; Li and Gregory, 1974).

![Figure 25: Measured and modeled diffusion profiles of Co(II) (Left) and Zn(II) (Right) in Opalinus Clay. The dashed curves represent modeling with the multi-component diffusion model (Appelo et al., 2010).]

**SOME CONCLUSIONS**

The understanding (data, models) of highly sorbing elements (e.g. Sr, Co, Zn, Eu) in clay rock geological barriers required various scales of investigation, which combine model and experimental developments. Therefore, the research program was organized around three major topics: (1) experimental determination of the role of “surface diffusion” in compacted clays (illite type), which is based on the investigation of coupled diffusion-sorption processes; (2) determination of diffusion pathways in clayey rocks (µm to mm scales) and (3) development of models needed for analysing experimental data on diffusion-driven migration in compacted clay materials.

At the end of the project, the development and the application of specific experimental methods allowed the acquisition of data that are more reliable than ever. The Figure 26 shows, for example, the different values of Eu diffusion coefficient estimated within the French Callovo-Oxfordian Clayrocks from 2006 to the present study. In less than 10 years, almost two orders of magnitude have been gained, so that the diffusion of this strongly-sorbing cation significantly slows down.
However, even though the greater mobility previously observed for Europium has not been confirmed by this project, clear indications have been acquired for the other studied cations, i.e. Sr, Co and Zn, both in the simpler system, the compacted illite and in the three clayrocks. For these latter species, the fact that their $D_c$ values at the lowest salinity exceed the $D_e$ values of water tracers by several orders of magnitude, rules out a simple diffusion model in which the effective diffusion coefficient for a given element is determined by coupling sorption behaviour measured in batch systems with assumed diffusion characteristics similar to water molecules. Moreover, for Co and Zn, especially in the clayrocks, the sorption behaviour derived from diffusion experiments within compacted materials was almost one order of magnitude lower than those measured in batch with dispersed materials. This could be related to some competing elements naturally present in the intact clayrocks and that could block strong sorption sites at the expense of the studied cations. Nevertheless, first modelling approach including diffusion in the diffuse double layer (DDL) promisingly succeeded in reproducing the experimental data under the various conditions both in illite and clayrocks, even though some assumptions made have to be verified.

In parallel, actual 3D geometrical pore size distributions of compacted illite, and in less extent, clayrock samples, were successfully determined by combining TEM and FIB-nt analyses on materials maintained in a water-like saturation state by means of an extensive impregnation step. Based on this spatial distribution of pores, first numerical diffusion experiments were carried at the pore scale through virtual illite, enabling a better understanding of how transfer pathways are organized in the porous media.

Finally, the CATCLAY Project allowed a better understanding of the migration of strongly-sorbing tracers through low permeability ‘clayrock’ formations, increasing confidence in our capacity to demonstrate that the models used to predict radionuclide migration through these rocks are scientifically sound.
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DESCRIPTION OF THE POTENTIAL IMPACT AND THE MAIN DISSEMINATION ACTIVITIES AND THE EXPLOITATION OF RESULTS

Belgium, France and Switzerland have chosen to dispose of high- and intermediate-level long half-life radioactive wastes generated in deep underground in low permeability ‘clayrock’ formations. Confidence in these concepts is mainly based on the capacity of the corresponding waste management organisations to demonstrate that the models used to predict radionuclide migration through the respective clayrock formations are scientifically sound. It is crucial for the credibility of future safety cases that the model used for cation migration is as scientifically solid as possible and the CATCLAY project is specifically designed to enhance this understanding.

Moreover, a dissemination workshop was organized at Paris at the end of the Project, gathering more than 40 participants originating from 6 European Countries.

4 oral communications and 11 posters were presented at 5 conferences with international audience; 1 paper was published in proceedings, 2 papers were published in scientific journals and more than 10 papers are in preparation or submitted to scientific journals.
PUBLIC WEBSITE ADDRESS AND CONTACT DETAILS

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