CatClay
(Contract Number: Grant Agreement 249624)

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Reporting period: 01/06/10 – 31/05/12

Date of issue of this report: 03/12/2012

Start date of project: 01/06/2010

Duration: 48 Months

Project co-funded by the European Commission under the Seventh Euratom Framework Programme for Nuclear Research & Training Activities (2007-2011)

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Abstract

The European CatClay project aims at describing the cation migration processes in natural clay rocks. The project is structured along three RTD workpackages, combining modelling and experimental studies from a “simple”, analogous system (monophasic compacted clay system: illite) to clay rocks (Callevo-Oxfordian claystones, Opalinus Clay and Boom Clay). Two main objectives, since the start of CatClay in June 2010, were achieved. Firstly, a knowledge base was provided regarding the diffusion and sorption behaviour of the cations of interest towards the studied pure clay mineral, i.e. Illite du Puy, and its physical, chemical, thermodynamic and surface speciation properties. Secondly, most of the required experimental and modelling developments were done for allowing the acquisition of reliable data and their relevant interpretation. Techniques for imaging the texture of the clay materials (illite + clay rock) led to preliminary promising results. Moreover, the different methods developed for acquiring tracer profile in clay materials have clearly demonstrated that they could create new opportunities for investigating diffusion at µm scale (µLIBS, TRLFS, µ-abrasive technique coupled to µ-diffusion cells).

Introduction

In the framework of radioactive waste repository, clay rock formations are foreseen as barrier materials due to their high confinement properties. In clay materials, the dominant transport mode is diffusive and depends mainly on parameters such as the mobility of the species in water, the accessible porosity, the pore space geometry and the retardation, if any. Within this context, the overall objective of CatClay is to provide a scientifically well grounded answer to the following question: Can the migration of actinides and other strongly sorbing radionuclides in clay rock 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 answer is of prime importance for Safety Cases for clay rock formation-based radioactive waste disposal concepts.

The project takes as its starting point experimental observations showing that certain cations known to form highly stable surface complexes with sites on mineral surfaces, migrated more deeply into clay rock than expected (Altman et al., 2012). This suggests that current models may not be correct for these cations.

The understanding (data, models) of highly sorbing elements (e.g. Sr, Zn, Eu) in clay rock geological barriers requires various scales of investigation, which combine model and experimental developments. Assuming that diffusion and retention processes in clays are the first controlling phenomenon for cation transport in clay rocks, a good understanding at the nanometric level is necessary to quantify the diffusion and sorption coupled processes at the clay particle surface (physico-chemical approach). Therefore, the research program is organized around three major topics: (1) development of model for covalently complexing cation diffusion in compacted clay materials, (2) experimental determination of the “surface diffusion” on clays (illite type), which is based on the investigation of the coupled diffusion-sorption processes at the nm-µm scale; (3) determination of diffusion pathways in clayey rocks based on µm to mm investigation. In addition, a specific effort will be invested in synthesizing, and ‘up-scaling’ project results for use in Safety Cases for radioactive waste disposal.

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disposal concepts in clay rock formations. The present paper has followed these three main topics in its structure.

1. Development of Models and Integration

One of the first prerequisites of the project was to furnish the essential state of the art input data. Remind that CatClay is focused on understanding diffusion of cations forming surface complexes with clay rock mineral surfaces, in particular amphoteric edge sites on clays. Therefore, the coupled sorption-diffusion models used to predict and interpret experimental data require information on the nature (stoichiometry, structure), equilibrium (MAL) and reversibility of $\text{Zn}^{2+}$ and $\text{Eu}^{3+}$. In this sense, an extensive literature review was provided under the form of two deliverables, accessible in the CatClay website (www.catclay.org).

Moreover, new transport and porosity models for compacted clay were proposed, a part of which having been published in Geochimica and Cosmochimica Acta. (Tournassat and Appelo, 2011). In this study, a model that considers clay microstructure changes as a function of bentonite compaction and ionic strength was developed to reproduce observed trends in the data for all experimental conditions within a single model. Our predictive model excludes anions from the interlayer space and relates the interlayer porosity to the ionic strength and the montmorillonite bulk dry density. This presentation offers a good fit for measured anion accessible porosities in bentonites over a wide range of conditions and is also in agreement with microscopic observations (Figure 1).

In the same time, the tools required for modelling the diffusion experiments with the software PHREEQC were provided: a window HELP file was created and the Bradbury and Bayens model describing the sorption of Ni, Co, Eu, and Sn on illite with 2 sites, the protolysis, the non electrostatic 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.

![Figure 1](image)

**Figure 1:** Anion accessible porosities in bentonite as a function of the dry density and the NaCl concentration in an external solution. The black dashed lines are from a model with a single Donnan-type porosity (Birgersson and Karlsson, 2009), full red lines are from the model 1 ($n_c = 8.4$, Donnan volume = non interlayer porosity), dash-dot red lines are from model 2 ($n_c = 2.48$, Donnan volume extending up to two debye lengths from the montmorillonite surface, if possible, else equal to the non interlayer porosity), dotted blue lines are from model 3 ($n_0c = 1.5$; $d_{pore} min = 5.5 j 1$), full blue lines are from model 4 ($n_0c = 1.5$; $d_{pore} min = 5.5 j 1$, $h_{intmin} = 0.33 \text{ nm}$) (Tournassat and Appelo, 2011).
2. Diffusion experiments in Illite du Puy

In a modern conception of cation diffusion in clays, the diffusive flux of the tracer under investigation depends on the chemical composition of the pore water. Cations sorbed by outer-sphere complexation (cation-exchange) are prone to diffuse by surface diffusion in clays with negatively charged surfaces. Nothing is known about the diffusion of cations sorbed by inner-sphere complexation (surface complexation). Two experimental techniques are used to investigate the behaviour of the cations of interest.

On one hand, at the µm scale, in-diffusion experiments allow for the comparison of the diffusion in illite of the cations sorbed by inner sphere complexation (e.g. Zn\(^{2+}\), Eu\(^{3+}\)) with the diffusion of Sr\(^{2+}\), a typical representative of cation sorbed by outer-sphere complexation. Various chemical conditions are investigating, taking into account also the role of natural organic matter as complexing agent. On the other hand, microscopic techniques (Transmission Electronic Microscopy, FIB-SEM) have been used to investigate the textural properties of illite and relate them to measured tracer profiles in micro-diffusion cells.

2.1. Diffusion in Illite

The achievement of the goal of this part, i.e. the determination of the diffusive properties of some strongly sorbing cations in pure illite, with a special focus on the chemical state of the sorbed species, has required (i) a concerted action by all project partners for using the same prepared Illite du Puy material, (ii) the acquisition of some complementary sorption isotherms, and (iii) several experimental developments, e.g. for ensuring the intended saturation of the illite samples.

Zn-sorption isotherms experiments are being performed by SCK-CEN under different chemical conditions (var pH, var CO\(_2\), presence/absence of humic substances). The influence of humic substances on the Zn sorption on Illite du Puy was clearly identified: the higher the the DOC (Boom clay extracted humics), the higher the Zn sorption (Figure 2).

![Figure 2: sorption isotherms of Zn on dispersed CatClay Illite du Puy as function of different chemical conditions. In blue and red: Influence of carbonate and organic matter (16 mM NaHCO3, 0.4% CO2, 10 and 50 mg DOM/L). In green: Inert atmosphere, with no Inorganic Carbon, no Organic Carbon. In purple: Influence of carbonate (16 mM NaHCO3, 0.4% CO2, pH~8)](image-url)
Moreover, several diffusion experiments have been already started. PSI carried out first diffusion tests with Sr$^{2+}$ and HTO at pH = 5 and 9 by investigating the effect of the ionic strength. PSI shows that the dependence of the $D_e$ values of $^{85}$Sr$^{2+}$ on the external salinity clearly shows that “sorption-enhanced diffusion” is important for this radiotracer in compacted illite both at pH 5 (Figure 3) and pH 9. Consequently the approximation of cation diffusion data in this clay mineral simply based on measurements of HTO diffusion only may lead to erroneous predictions.

Lastly, KIT performed two experiments for 152 days with Eu(III) and Sr$^{2+}$ with the emphasis on testing protocols for compacted Illite du Puy impregnation, in close cooperation with BRGM (Kupcik et al., 2012). Analysis of the various alcohol/water mixtures and the epoxy resin revealed no mobilization of Eu during this preparation steps and opens a way for post-processing (microstructure analysis including spatial resolved laser fluorescence studies) of diffusion experiments (Figure 4).

\[ D_e = 1 \times 10^{-10} \text{ m}^2 \text{ s}^{-1} \text{ and } R_d = 52 \text{ mL/g} \text{ for Ionic strength=0.1M} \]

\[ D_e = 1 \times 10^{-10} \text{ m}^2 \text{ s}^{-1} \text{ and } R_d = 52 \text{ mL/g} \text{ for Ionic Strength=1.0 M} \]

**Figure 3**: Through-diffusion (left) and profile (right) data for the diffusion of $^{85}$Sr$^{2+}$ through Na-Illite (1700 kg m$^{-3}$ bulk-dry density) at pH 5 and external salinities of 0.1 M (top) and 1.0 M (bottom). The values of the estimated diffusive parameters are given above each of the graphs.
2.2 Techniques for imaging the texture of illitic material in compacted state

When imaging a rather fragile material like illite, one of the first challenges is to be able to preserve the actual state of the material, such as in the diffusion cells systems, e.g., without losing the clay confinement. For that purpose, four different monomers were tested for the resin impregnation procedure: a styrene, two acrylates (LR white and Methyl MethAcrylate: MMA) and an epoxy. The choice was done based on the size of the molecule, the viscosity of the monomer, the polymerization process, the stability under the ion beam and the facility to implement. Finally, only two monomers have been retained: the LR White and the MMA.

On one hand, Transmission Electronic Microscopy (TEM) images were performed on compacted illite with a dry density of 1.7 g/cm³ with a calculated porosity of 0.39. TEM size resolution gives us the possibility to threshold the total pore space. Others information like 2D morphological analysis of pores (orientation, size, morphology) could also be extract from this TEM images (Gaboreau et al., 2012).

On the other hand, Focused Ion Beam coupled to Scanning Electron Microscopy (FIB/SEM) was tested to evaluate the potential in representing a 3D geometry of pore space in clay samples (Illite Du Puy). Image processing and analyses were then performed in order to reconstruct a 3D volume from the 2D sectional acquisition (Figure 5). This technique is appropriated to illustrate a 3D volume of clay in compacted state at nm scale. The accessible pore space is however limited to a segmentation of more than 3 pixel size, i.e., 15 nm which implies only 20 to 30% of the total pore space.

Figure 5: 3D reconstruction of the analysed volume based on FIB SEM images
3. Diffusion experiments in clay rock

Diffusion of Sr, Zn, and Eu will be investigated in three real ‘clay rocks’ (Callovo-Oxfordian argilites, Opalinus Clay and Boom Clay), by using in- or –through diffusion experiments, according to the cation of concern. These experiments are performed to depict, in clay rocks, the role of clay minerals on diffusion, as derived from the two previous parts. However, given the complexity of such materials, several experimental developments have been required for fine-tuning the future experiments.

3.1. Diffusion in clay rocks

The reliability of the Laser-Induced Breakdown Spectroscopy (LIBS)developed by CEA for acquiring Zn and Eu solid profiles on Callovo-Oxfordian clay rocks was successfully demonstrated, leading to consistent data set. Figure 6A shows for instance the Zn mapping acquired from µLibs on the sample having undergone the diffusion experiment with [Zn(II)]\text{ini} equal to 4 \times 10^{-5} \text{ mol L}^{-1}. Note the occurrence of Zn hot spots inside the sample, related to Zn-bearing minerals. The corresponding profiles exhibit a well-know diffusion shape on the two sample sides, which are consistent with the data obtained from the abrasive peeling method (Figure 6B) (Savoye et al., submitted). The natural background content of zinc in the Callovo-Oxfordian rock is close to 0.5 \mu mol g\(^{-1}\) of rock.

A filter-free system was also successfully developed by PSI for limiting the cation sorption on the materials. The effect of the ionic strength on the diffusive behaviour of cobalt and zinc was preliminary investigated by means of this new device with the Swiss clay rock, the Opalinus Clay. Figure 7 shows the zinc rock profiles acquired by the abrasive peeling method and the associated simulation curves for two ionic strengths 0.17 M and 1.07M. A decrease of the effective diffusion coefficient with the increase of the ionic strength can be observed suggesting an evolution of this cation close to those sorbed by outer-sphere complexation such as Sr\(^{2+}\).

![Figure 6: (A) Zinc mapping from µLibs and (B) comparison of the Zn profile obtained by µLibs (blue and purple curves) and by abrasive-peeling (red curve).](image-url)
CEA also performed diffusion experiments with this cation, i.e., $^{85}\text{Sr}^{2+}$ through the Callovo-Oxfordian claystones at three ionic strength values, and evidenced a reduction of the effective diffusion coefficient by a factor of four (Figure 8).

**Figure 7:** zinc rock profiles obtained in OPA samples at two ionic strengths (on left: 0.17 M; on right: 1.07M).

Preliminary in-diffusion with Zn was also launched on the Boom Clay by SCK-CEN for estimating the potential artefacts, capable of jeopardizing the interpretation of the...
experiments. They observed an uptake of zinc by the system (e.g. stainless steel material).

3.2. Techniques for imaging the texture of the three clay rocks

While illite should be a material easy to cut, COx, OPA, and Boom clay samples contain minerals such as quartz that could make difficult the use of ultra-microtome. The first part of the project has been dedicated to develop procedures to handle these samples.

In order to preserve the texture of claystone during the different steps of impregnation, specific cells were developed by BRGM. These cells allow to work at constant volume by considering the fact that claystone contain swelling clay layers (∼5%). The intercalation of monomer inside the interlayer space could induce swelling and create damage in the texture of the clay.

TEM images were obtained from the first section test performed on the COx claystone impregnated with PMMA (Figure 9). These images are the first observations never done on the claystone in compacted state at such a high resolution. The difficulties encountered during the sectioning, lied to the presence of quartz, make the claystone sections very brittle and break apart. The section fragments are OK for high resolution TEM imaging. An overview or even 3D reconstruction of serial section should not be possible.

Figure 9: TEM images of COx claystone in compacted state.
Conclusions and Future work

The understanding (data, models) of highly sorbing elements (e.g. Sr, Zn, Eu) in clay rock geological barriers requires various scales of investigation, which combine model and experimental developments. Therefore, three main research axes were investigated within the CatClay project: (1) development of model for covalently complexing cation diffusion in compacted clay materials, (2) experimental determination of the “surface diffusion” on clays (illite type), which is based on the investigation of the coupled diffusion-sorption processes at the nm-µm scale; (3) determination of diffusion pathways in clayey rocks based on µm to mm investigation.

At mid-period, the main achievements are as follows. A knowledge base was provided regarding the diffusion and sorption behaviour of the cations of interest towards the studied pure clay mineral, i.e. Illite du Puy, and its physical, chemical, thermodynamic and surface speciation properties. Most of the required experimental and modelling developments were achieved for allowing the acquisition of reliable data and their relevant interpretation. Techniques for imaging the texture of the clay materials (illite + clay rock) led to preliminary promising results. Moreover, the different methods developed for acquiring tracer profile in clay materials create new opportunities for investigating diffusion at µm scale (µLIBS, TRLFS, µ-abrasive technique coupled to µ-diffusion cells).

Therefore, these experimental and modelling advances are allowing us to perform diffusion experiments more representative of the actual conditions, so as to better address the issue of the CatClay project about the determination of appropriate sorption–diffusion models for highly sorbing cations in clay rocks.

Acknowledgement

The research leading to these results has received funding from the European Union's European Atomic Energy Community's (Euratom) Seventh Framework Programme FP7/2007-2011 under grant agreement no 249624 (CATCLAY project).

References


