Poster [MTPM]

Mass Transfer & Porous Media
INTERLAYER / MICROPOROUS EXCHANGE OF WATER AND IONS IN CLAYS: A MOLECULAR DYNAMICS STUDY

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INTRODUCTION

Mobility of ions through geological barriers is greatly affected by their interactions with the minerals. This is especially true for clay minerals, because of their negatively charged surfaces. Depending on their charge, ions explore a different fraction of the porosity: It is now admitted that cations can enter into clay interlayers by exchanging with natural counterions, while anions remain in larger porosities (>nm). Therefore the diffusion pathways should be different for cations and anions. Understanding cationic exchange and anionic exclusion is necessary to provide a consistent picture of ionic transport through clay minerals. This is particularly important in the context of geological storage of toxic or radioactive waste, where the geological medium acts as a barrier preventing the release of waste into the biosphere (ANDRA 2005).

The present study consists in the modelling of ionic exchange and anion exclusion at the microscopic scale, using molecular dynamics (MD) simulations.

MOLECULAR SIMULATIONS

Water and ionic exchange between clay interlayers and micropores was studied by simulation of a system containing both clay particles (with interlayer porosity and counterions), and a bulk salt solution (micropore). A snapshot of the simulation box is given in Figure 1. The interactions between all atoms were described using a modified version of the force field of Smith for the bulk clay atoms, the SPC/E water model and parameters of Koneshan for the ions (Marry et al. 2003). For the clay edges, the structure (including electronic density) was first determined using ab-initio simulations. Then partial charges on the edge atoms were determined from the electronic density.

Equilibrium MD simulations in the NVT ensemble (fixed number of particles, volume and temperature) were done using the DL_POLY software. Within a few nanoseconds, Cs⁺ ions near the lateral surface of the clay particle can enter into the interlayer, while Na⁺ counterions are released into the micropore. Water exchange between interlayer and micropore is also observed at this timescale, whereas no anion was found to enter into the interlayer during the 10 ns simulation.

Figure 1: Simulation box containing clay particles (with interlayer porosity and Na⁺ counterions in blue) and a bulk CsCl solution filling a micropore (Cs⁺ in orange, Cl⁻ in pink).
The free energy cost of forcing an anion into the interlayer was estimated using a set of biased simulations combined with an unbiased scheme named Weighted Histogram Analysis Method (Roux 1995). The relatively high value of this penalty (about 30 kJ/mol, that is 12 times the thermal energy at 298K) confirms that anions are excluded from the interlayer.

CONCLUSION
This study gives the first microscopic insights into the dynamics of exchange of water and ions between interlayer porosity and microporosity. It will allow to better understand the different diffusion mechanism of water, cations and anions in clay minerals.

References:
MULTI-SCALE CHARACTERISATION OF MINERAL AND TEXTURAL SPATIAL HETEROGENEITIES IN CALLOVO-OXFORDIAN ARGILITE AND ITS CONSEQUENCE ON SOLUTE SPECIES DIFFUSION MODELLING

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The French National Agency for radioactive waste management (ANDRA) investigates the Callovo-Oxfordian argilite of the Eastern Paris Bassin as the host rock for high-level radioactive waste repository in deep geological formation. The modelling of radionuclides return times in the biosphere is carried out from parameters controlling the migration of radionuclides through this barrier (permeability, diffusion coefficient…). Diffusion is assumed to be the main transport mechanism governing radionuclide migration through this rock. Classically, the parameters controlling the diffusion processes (diffusion coefficient, porosity, sorption…) are obtained by bulk analyses considering the samples as homogeneous. Theses parameters are then included into simulation models of solute species diffusion processes.

Nevertheless, in recent studies, mineral and textural spatial heterogeneities have been visualised and quantified at different scale in the Callovo-Oxfordian argilite by imaging techniques adapted to clay rocks (autoradiographs, SEM images analysis, electronic microprobe analysis, μLIBS, tomography…) [1, 2, 3].

The aim of this study is to set up, gauged and validated a methodology allowing the highlight and the understanding of the relation between the solute diffusion and the spatial distribution of minerals and texture in clayey rocks.

First, a multiscale characterisation from centimeter to micrometer were performed for a core sample of COx (DIR 1003 - EST 26059) using all of theses imaging techniques. In addition, classical bulk analysis (DRX, carbonate contents, chemical analysis…) were also achieved for the same core. Different mineral and porosity maps are obtained using this combining approach. Second, direct simulations of diffusion experiment have been done from these maps using a random walk method in time domain (Time Domain Diffusion method [4]). Third, the distribution of diffusion parameters within the COx was obtained by an inversion method applied on experimental in diffusion maps for Eu and Cu tracer obtained using μLIBS analysis.

References:
DIFFUSION OF IONS IN UNSATURATED CLAY-ROCKS: THEORY AND APPLICATION TO THE CALLOVO-OXFORDIAN ARGILLITE

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INTRODUCTION
The intrinsic permeability of low-porosity clay-rocks is usually much below \(10^{15}\) m\(^2\) and therefore the dominant mechanism of transport of the ions in these media is by diffusion of the ionic species through the connected porosity. The problem of predicting the effective diffusion coefficient of ions in porous media is currently attracting attention, especially in clay-rich materials because of their application to nuclear waste storage. In this contribution, we extend the theoretical model of transport developed by Revil and Linde (2006) under saturated conditions to include the influence of unsaturated conditions upon diffusion of ionic species in clay-rocks. This theory provides a new way to predict the effect of the saturation on the diffusion coefficient and to make an application to the EDZ (Excavated Damaged Zone) matrix of the COx (Callovo-Oxfordian) argilite.

THEORY
In a salinity gradient, the diffusion of ions through the connected porosity of a clay-rock is influenced by the charged nature of the interface between the pore water and the clay minerals. This influence is exerted through the generation of a macroscopic electrical field called the diffusion or membrane potential. This electrical field depends on the excess of counterions located in the pore space to counterbalance the charge density of the surface of the clay minerals.

Revil and Leroy (2004) and Revil et al. (2005) derived recently a new set of constitutive equations to study the transport of ions in a water-saturated clay-rock. Their model was able to explain successfully the influence of the pore water chemistry and tortuosity of the pore space upon the diffusivity coefficient of a salt through a water-saturated clay-rock or a compacted bentonite.

In unsaturated clay-rocks, we have to consider (1) the effect of the charged nature of the air / water interface, (2) the increase of the counterions density as the counterions are packed in a smaller volume when the saturation of the non-wetting phase (air) increases (Figure 1), and (3) the influence of the water saturation upon the tortuosity of the water phase. In this contribution, we volume average the Nernst-Planck equation to determine the coupled constitutive equations for the diffusion flux and the current density of a multi-component electrolyte in unsaturated conditions with water being the wetting phase for the grains.

The work by Hunt and Ewing (2003) is a recent effort to include the influence of the water content upon diffusion in soils based on percolation theory. They have shown that the diffusion coefficient decreases with the desaturation and vanish at threshold moisture content. We include this observation in our theory.

APPLICATION TO THE COX
The material considered for the sensitivity analysis is the argillite clay-rock from the Callovo-Oxfordian geological formation under consideration in the eastern part of France for a deep geological disposal facility for radioactive wastes. We compute the effect of the water saturation upon the effective diffusion coefficient of a binary salt (like NaCl or KCl) in this clay-rock. The sensitivity analysis was made using the data provided by Leroy et al. (2007). The result shows a decrease of the diffusion coefficient by a factor four when relative water saturation decreases from 100% to 60% (Figure 2).
Figure 1: Distribution of the ionic species in pore space of a clay-rock. The Stern layer of adsorbed counterions is considered to be part of the solid. a. At high water saturations, the excess charge density of the pore water is relatively low. b. At low water saturations, the counterions are packed in a smaller volume and therefore the excess charge density of the pore water is higher.

Figure 2: Influence of the saturation \( s_w \) upon the diffusion coefficient of NaCl of the Callovo-Oxfordian argillite. a. For different values of the partition coefficient \( f_0 \) of the counterions between the Stern and the diffuse layers (for a salinity of 1 mol L\(^{-1}\)). b. For different values of the salinities \( c_w \) (for a partition coefficient of 0.94).

Reference


POROUS MEDIA CHARACTERIZATION WITH RESPECT TO GAS TRANSFER IN CALLOVO OXFORDIAN ARGILLITE

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Gases, especially hydrogen, will be generated by corrosion and radiolysis of the high radioactive waste containers. Pressure build up, resulting from those long processes along the lifetime of the installation, have to be study to evaluate the risk of fracturation of the geological barrier and the potential creation of preferential pathways for radionuclide migration. This work is interested in the Callovo-Oxfordian argillite (500m depth) characterization regarding gas transfer mechanisms. Furthermore, within the framework of this characterization, permeability experiments are performed in experimental cells with hydrogen.

Mercury intrusion experiments were performed to have a first comprehension of how argillite reacts to gas intrusion. It was completed by water sorption isotherms. Due to evapo-condensation process the results were different from the mercury intrusion curves. The methods reveal that a trapped porosity exists (diameters between 20 nm and 1 μm). Large pores are connected by smaller pores of 20 nm diameter which represent the capillary barrier to gas breakthrough. A network model XDQ, based on the connectivity and pore size distribution obtained from the previous experiments, is set. It shows a high Klinkenberg effect on such network and few connected pathways for gas migration in a partially saturated pore network.

Gas diffusion experiments on partially saturated and saturated argillite samples were performed to estimate permeability and diffusion coefficient. The main difficulty is to maintain the water content constant within the sample since water is displaced and gas pressure increases. Permeability and gas diffusion are very sensitive to sample volumetric water content, especially near saturation. A simple numerical model of gas transfer computed on the COMSOL software (1D gas flow combining diffusion/advection) is used to identify both the permeability and diffusivity coefficients from the hydrogen outflows. Permeation is due to the pressure difference between the two sample faces. The model solves the two coupled gases diffusion and advection equations, i.e. one for hydrogen and one for total gas. The model shows that advection hydrogen flux can predominate hydrogen diffusion flux when the pressure difference is up to 5 Bar. Whereas a low pressure difference does not affect the diffusion fluxes. This affirmation will be confirmed by the ongoing experiments.
PREDICTIONS ON A 2-D CEMENTATION EXPERIMENT IN POROUS MEDIUM: INTERCOMPARISON ON THE COMEDIE PROJECT

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INTRODUCTION

The work reported here aims at contributing to validate simulation tools for reactive transport in porous media, where porosity and texture of the porous medium are strongly affected by chemical reactions. This kind of situation is met, for instance, at the interface between materials in condition of deep geological disposal (concrete/argillite, iron/bentonite) or in different chemical barrier designs (e.g. carbonation of cements). The ComEDIE project specially concerns the investigation of the chemical-transport coupling when significant variations of porosity occur (Lagneau 2000). Such variations of local porosity/permeability in the porous media induce variations of intensity and direction of the flow field which may affect the way reactants in solution are transported. The present report is dedicated to a numerical benchmark based on the simulation of the ComEDIE-2D experiment. The use of various numerical tools such as Hytec (van der Lee, De Windt et al. 2003) and Crunch (Maher, Steefel et al. 2006) will provide predictions of the physico-chemical evolutions that are expected during the future experiments in the laboratory.

EXPERIMENTAL CONCEPT

A 2-D cementation experiment in a porous medium was previously proposed with Hytec (Trotignon, Didot et al. 2005). The selected experimental design involves the successive precipitation and perforation of a clogging obstacle made with calcium oxalate mineral. Reactants (oxalate ions) are injected with a constant flux in a porous medium, which locally contains portlandite. The chemical reaction between the inlet solution and the mineral phase leads to the precipitation of calcium oxalate following the reaction:

\[
C_2O_4^{2-} + \text{portlandite} + nH_2O \Rightarrow Ca\cdot\text{oxalate} + 2H_2O
\]  

The experimental chamber is a squared box with two inlets and one outlet for fluid circulations (see figure1). The porous medium is heterogeneous, since a rectangular zone located in the middle of the box is composed of quartz (considered as a chemically inert phase in the simulations) and portlandite grains, while the other part contains only quartz.

Several of the physical laws governing chemistry and transport are not identically described in both codes and this point will have to be considered in the interpretation of results. The most significant difference concerns the dissolution/precipitation law. In Crunch, the only possibility is to use an explicit kinetic rate law to describe the mass transfer between the solution and mineral phases. In Hytec, it is possible to use the same kinetic formulation, and also, in the case of fast reactions, the hypothesis of local equilibrium between minerals and the solution. In this study, the sensibility to some parameters (dispersion coefficient, injection rate and cementation exponent) is evaluated with respect to the reaction pathways and the final scenario.
RESULTS AND INTERPRETATION

In the reference experiment first simulated with Hytec (equilibrium hypothesis), the clogging obstacle is predicted to progressively grow in a first stage and then suddenly perforate after 2.8 months from the upper part of the obstacle wall. Whereas Crunch results show the oxalate wall to be perforated starting from the lower part. This study reveals also that predictions made with Crunch are more sensitive to particular parameters.

When the assumption of thermodynamic equilibrium is made, Crunch and Hytec do not predict equivalent scenarios. These differences must at least partially come from the nonstrictly valid hypothesis of local equilibrium in Crunch when portlandite begins to dissolve.

This comparative study also raises the problem of a priori models used to describe variations of reactive surface area with porosity. Actually, with the assumption of kinetics controlled processes, some discrepancies in the predictions can be attributed to the different conceptual models implemented in Crunch and Hytec.

Finally, analyses of all these results provide an original feedback on coupling algorithms between transport and chemistry.

References


LARGE-SCALE GAS INJECTION TEST (LASGIT) AT THE ÅSPO HARD ROCK LABORATORY IN SWEDEN

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INTRODUCTION

In the Swedish disposal concept, canisters containing spent nuclear fuel will be placed in large diameter disposal boreholes drilled into the floor of the repository tunnels. Each full canister will weigh up to 27 tonnes. The canister consists of a 50mm thick outer copper skin, which acts as a corrosion barrier in the oxygen-poor groundwater of the crystalline rock selected for disposal, and a nodular iron insert to provide strength and rigidity. The space around each canister will be filled with pre-compacted bentonite blocks which, once hydrated, will act as a low permeability diffusional barrier. The unique physico-chemical properties of the bentonite depend on its colloidal behaviour and enormous specific surface. These include high sorption capacity, very high plasticity and excellent fracture self-sealing characteristics, severely limiting the migration of any radionuclides released from a canister after closure of the repository.

The metal canisters are expected to have a very substantial life in the repository environment. However, for purposes of performance assessment (PA), the possible impact of groundwater penetrating one of the canisters must be considered. Under anoxic conditions, corrosion of the steel inner will lead to the formation of hydrogen gas. Radioactive decay of the waste and the radiolysis of water will produce some additional gas in the container. Depending on the gas production rate and the rate of diffusion of gas molecules in the pores of the bentonite, it is possible that gas will accumulate in the void space of the canister, entering the bentonite when the gas pressure exceeds the critical entry pressure specific to this material. Since water penetration of the canister is a prerequisite for the occurrence of hydrogen gas in the buffer, the timing of gas movement in the clay might coincide with that of radionuclide release into the buffer porewater. The possibility of an interaction between gas and radionuclide migration therefore emerges as an important issue in PA.

As part of an ongoing programme of research, the Swedish waste management company SKB commissioned BGS to undertake a series of detailed laboratory studies aimed at resolving specific issues relating to the gas migration process. It has been shown that gas moves through the clay following pressure-induced pathways. The clay tends to dilate when these pathways are formed with both the poros water pressure and the total stress acting within the clay, strongly affected by the passage of gas. The laboratory work has highlighted a number of uncertainties, notably the sensitivity of the gas migration process to experimental boundary conditions and possible scale-dependency of the measured responses. These issues are best addressed by undertaking a large-scale gas injection test or "Lasgit".

Lasgit is being undertaken at the Åspö Hard Rock Laboratory (HRL), around 360km south of Stockholm in the municipality of Oskarshamn. The underlying diorite formation is representative of the geological conditions likely to be encountered in a Swedish conceptual nuclear repository. Lasgit is a full-scale demonstration project conducted in the Assembly Hall Area of the HRL at a depth of 420m. This is a "mock test" which does not use any radioactive materials. A deposition hole, 8.5m deep and 1.8m in diameter, was drilled in to the gallery floor. Canister defects are mimicked by placing thirteen circular filters of varying dimensions on the surface of a copper canister to provide point sources of gas. These filters are used to inject water during the initial hydration phase. Helium gas will be used as a safe substitute for hydrogen during gas testing. Once the pre-compacted bentonite blocks were installed, the
borehole was capped with a conical concrete plug and retained by a reinforced steel lid. The lid is held down by rock anchors designed to withstand over 5000 tonnes of force. Additional instruments record variations in the relative humidity of the clay, the total stress and porewater pressure at the borehole wall, the temperature, any upward displacement of the lid and the restraining forces on the rock anchors.

The state-of-the-art experimental monitoring and control systems for Lasgit are housed in the “Gas Laboratory” which is a self-contained unit designed and assembled by BGS within a modified shipping container. A customised graphical interface based on National Instruments LabVIEW™ software enables remote control and monitoring to be undertaken by staff at BGS Headquarters in Keyworth and also allows the project's international partners to access data using their desktop computers. Lasgit will provide the industry with important new information on the mechanics of gas flow in buffer bentonite. The numeric data will be used in the development and validation of process models aimed at repository performance assessment.

RESULTS
The Lasgit deposition hole was closed on the 1st February 2005 signifying the start of the hydration phase. At present monitored porewater pressures within the clay remain rather low ranging from 100 kPa to 430 kPa. This is in contrast to the water pressure measured at the face of the deposition hole which ranges from 1160 kPa to 2575 kPa. Monitored radial stress around the canister continues to increase steadily ranging in value from 1500 kPa to 5130 kPa, with an average value of 3900 kPa. Analysis of the distribution in radial stress shows a narrow expanding zone of elevated stress propagating vertically upwards from the base of the hole. Stress measurements on the canister surface indicate radial stresses in the range 4430 kPa and 4630 kPa, which are comparable with the values of radial stress monitored on the rock face. Axial stress is significantly lower at 3200 kPa. Axial stress within the clay ranges from 4488 kPa to 5750 kPa and is non-uniformly distributed across the major axis of the emplacement hole. The average axial total stress within the bentonite is now greater than the initial pre-stress applied by the lid. Movement and distortion of the steel retaining lid has occurred following the installation and initial closure of packered intervals within the pressure relief holes. Estimates of effective stress (swelling pressure) at the rock face suggest values in the range of 180 to 3240 kPa with an average of around 2075 kPa. Suction data from devices located within the buffer above and beneath the canister indicate that a significant amount of the clay remains in suction.

Analysis of the flow data from the artificial hydration system suggests a disproportionately large flux from the canister filters compared to the hydration mats. This can be explained by a number of factors including compression of the filter mats (i.e. a reduction in permeability) or a zone of elevated permeability around the canister.

During 2007 a preliminary gas injection history will be performed with a view to verifying the operation and data reduction methodologies for the experiment, providing qualitative data on hydraulic and gas transport parameters. The test will be designed in such a way as to minimise the effect of reintroducing gas and will be performed in one of the lower filter arrays where the bentonite is locally saturated. The remaining filters on that level will be isolated from the artificial hydration system and their pressure allowed to evolve to provide temporal data on local porewater pressures within the buffer clay. Simultaneously artificial hydration will continue through all remaining canister filters and hydration mats.

The test has now been in successful operation for in excess of 740 days and continues to yield high quality data amenable to the development and validation of process models aimed at repository performance assessment.
SIMULATING THE GEOCHEMICAL COUPLING BETWEEN VITRIFIED WASTE, CANISTER AND NEAR-FIELD ON THE ALLIANCES PLATFORM

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INTRODUCTION
The simulation of the alteration of waste glass and associated geochemical interactions in the near field of a deep geological disposal is an important issue for evaluating the long term release of fission products and actinides in the geosphere. Among difficulties encountered when attempting such simulations is the fact that the glass and iron canister cannot, as opposed to the clay barriers or to the host rock, be considered as true porous media (Bildstein et al., 2006, 2007). Description of the coupling of geochemical fluxes at the interface between alteration fronts moving inside materials and the porous surrounding rock therefore requires specific adaptation and development in the simulation tools.

The approach described here was developed in the Alliances simulation platform (Bengaouer et al., 2003) in order to represent with a greater accuracy the successive and progressive alteration of thick iron canisters and waste glass blocks in the HLW near-field.

SIMULATION APPROACH
The underlying idea for the selected approach stems from the observation that in usual reactive transport simulation tools, the reaction rates affecting solid phases are computed from local chemical conditions, i.e. inside a given discretization cell. Also, usual reactive transport simulation tools assume that all cells are part of the porous medium and contain fluid. In order to avoid complex adaptative mesh approaches, a simple algorithm was devised in which a solid phase reacts according to the conditions prevailing in the surrounding cells. The dissolution of a mineral at a specific location would, for instance, depend on the chemical conditions in nearby cells. This approach enables to describe the progression of a dissolution front in a non porous solid and is in addition easily adaptable to 2D and 3D geometries and to situations in which multiple layers of heterogeneous and non porous materials are present. The chemical coupling between the porous medium, the progressively larger alteration zone (corrosion products, gel) and the local zone where the matrix begins to dissolve are described using the reactive transport algorithm implemented in the platform.

TESTS AND APPLICATIONS
Tests are presented in 1D and 2D geometry with a simplified chemistry in order to demonstrate the topographic capabilities of this new approach (Fig. 1). A more complex application is then presented, showing the evolution in 1D geometry of the interface between argillite and a thick carbon steel overpack.
**Figure 1:** Illustration on a simple 1-D case of the alteration of a waste package included in a canister. The initial situation is depicted in the top profile: the simulated glass is included in a canister that is thicker on the right side. The two figures below illustrate the evolution of the canister, dissolving progressively from the outside and when perforation is reached on the right side, allowing glass to begin to dissolve.

**References:**


TOWARD RADIONUCLIDE TRANSPORT CALCULATIONS ON WHOLE RADIOACTIVE WASTE DISPOSAL WITH CAST3M PLATFORM

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INTRODUCTION

In the context of high-level nuclear waste repository safety calculations, the modelling of radionuclide migration is of first importance. Three dimensional radionuclide transport calculations in geological repository need to describe objects of the meter scale embedded in geologic layer formations of kilometer extension. A complete and refined spatial description would end up with at least meshes of hundreds of millions to billions elements. The resolution of this kind of problem is today not reachable with classical computers due to resources limitations. Although parallelized computation appears as potential tool to handle multiscale calculations, to our knowledge no attempt have been yet performed.

DOMAIN DECOMPOSITION APPROACH

One emerging solution for repository safety calculations on very large cells meshes consists in using a domain decomposition approach (Gerardo-Giorda et al, 2004) linked to massive parallelized computer calculation. In this approach, the repository domain is divided in small elementary domains and transport calculations are performed independently on different processor for each elementary domain.

Before to develop this possible solution, we performed some preliminary calculations with Cast3m platform (http://www-cast3m.cea.fr/) in order to access the order of magnitude of cells needed to perform converged calculation on one elementary disposal domain and to check if Finite Volume (FV) (Aavatsmark et al, 1998; Le Potier, 2004) based on Multi Point Flux Approximation (MPFA) spatial scheme or more classical Mixed Hybrid Finite Element (MHFE) (Brezzi and Fortin, 1991; Dabbene, 1998) spatial scheme were adapted for those calculations in highly heterogeneous porous media.

RESULTS AND INTERPRETATION

The elementary domain selected for this study was defined considering on one hand that the disposal concept presents a high degree of symmetry and on the other hand that the cell is the elementary brick of the disposal (Fig. 1).

![Figure 1: Over view of a vitrified radioactive waste disposal concept (left) and closer top view of disposal units (right)](image-url)
The mesh of the elementary calculation domain is presented on Figure 2 for a coarse refinement. Two finest refinement levels leading to 200,000 and 1,600,000 cells were used for calculations.

Radionuclide transport calculations performed for each refinement level mesh were analyzed by comparing time dependent fluxes at the upper domain boundary outlet.

Our mesh and time step convergence calculations point out that MHFE and VF schemes applied on non-parallelepipedic hexahedral cells for flow and transport calculations in highly heterogeneous media gave satisfactory results. Mesh refinement level as well as time step required for converged calculations were exhibited an analyzed in term of cpu time needed.

Figure 2: Coarser mesh refinement level of calculation domain (24,000 cells).

References:
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EXPERIMENTAL STUDY OF THE WATER PERMEABILITY OF A PARTIALLY SATURATED ARGILLITE

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INTRODUCTION

To increase the knowledge about the hydro-mechanical behaviour of indurated clays as host rock for the underground disposal of radioactive waste, a series of laboratory experiments has been undertaken. The experiments focused on the water permeability of the argillite for a large range of saturation states.

Water permeability measurement is currently realised on saturated clayey materials or indurated clays. For the determination of such property as a function of the saturation degree, two main methods are identified: (i) the non-destructive survey of the evolution of the water content along a column of clay submitted to an uniaxial drying or imbibition process; (ii) the survey of the transient behaviour of a clay sample submitted to a little variation of suction, this measurement being repeated many times along the suction range. In this paper focus will be given on the second type of experiment. Associated with an H-M model the experimental data provide the water permeability of the argillite along a drying path. Considering the wide range of suction which is studied, the transfer of water occurs in vapour phase. So in fact this method can be considered as a means of determining the vapour diffusion coefficient.

EXPERIMENTAL METHOD

The principle of the experimental technique is the following. A core sample from the Callovo-Oxfordian argillite has been cut into many cylindrical sub-samples. The core sample has been preserved from both drying and decompression thanks to a special cell. At the beginning, the core sample is considered as almost saturated. In order to control the starting point, a stabilization step was made at 97% relative humidity. Five groups of four samples have been submitted to a series of suction levels, along a drying path, from 97%, 92%, 90%, 84% and 80% relative humidity to 6.4% relative humidity for the last group. For each step, the suction is controlled inside a glass vessel thanks to a saturated saline solution. When the surrounding suction is changed, a careful survey of the mass variation of the sample is made. So the kinetics of the transient phase is recorded. The next step is undertaken only after complete equilibrium of the sample. A special care is devoted to the control of temperature to 25°C during the whole experiment.

The preparation of the samples includes a watertight coating placed on the lateral face and on the bottom face. So the experiment takes place in uniaxial conditions making possible the interpretation with a 1-D model. Because the draining length is equal to the thickness of the cylinders, the duration of the transient drying phase is maximized. So the survey of the mass variation is easy.

Each group of samples gives four measurements of mass variation at each step. The different groups follow a part of the drying path, so for each suction step many measurements are realized. The organisation of the experimental campaign provides a redundancy of the measurements.
Moreover, using another sample, radial and axial strains were recorded during each transient phase. The effective value of the relative humidity imposed by the saturated salt solutions was continuously recorded. A third set of samples was submitted to the same drying path allowing the determination, by destructive measurements, of the moisture content and the bulk density for each suction level. This study provides the capillary curve of the argillite.

**INTERPRETATION OF THE RESULTS**

The second part of the work concerns the permeability determination. More precisely, a coefficient for moisture transfer in the argillite is deduced from both experimental results and calculation. A model for water transport in uniaxial conditions is proposed. This model is based on the following assumptions: isotropic permeability, linear behaviour (small suction variation), small transformation hypothesis, small gas pressure variation, vapour relative diffusion into gas is neglected, strain and mass have same evolution, Darcy law is applicable [Olichitzky, 2002]. Using this model, the calculated behaviour is compared to the experimental behaviour. Fitting the curves provides the value of the water permeability of the argillite.

This method was developed by [Olichitzky, 2002] who studied a bentonite. A detailed presentation of the model and the analytical solution can be found in [Imbert, 2005]. A similar experimental work has been undertaken on a deep argillite by [Koriche, 2004]. The values of permeability they obtain are in good agreement with those of the present paper. [Homand, 2004] and [Giraud, 2006] have improved the method and proposed both a linear and a non-linear modelling approaches.

Finally, these results of water permeability for partially saturated states are compared to the permeability of the saturated argillite.

**References:**


MIXED HEXAHEDRAL FINITE ELEMENTS
FOR DARCY FLOW CALCULATION
IN CLAY POROUS MEDIA

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We are concerned with the problem of developing a numerical simulator for modeling flow and contaminant transport in the vicinity of an underground nuclear waste repository for use in performance assessment. Clearly reasonably accurate and reliable simulators are needed, but as performance assessment requires many simulations, it is also important that the simulators be very efficient. The method developed here is the Kuznetsov-Repin mixed finite element method which is designed to handle nonrectangular hexahedral meshes for Darcy flow calculations.

INTRODUCTION
The Darcy flow equation is an elliptic equation coupling a conservation equation with Darcy’s law. As the Darcy velocity is the unknown of interest and we are concerned with problems with large changes in the permeability coefficient, we use a mixed finite element method. However standard mixed finite elements do not work on general hexahedral grids because the space of discrete velocities does not contain the constant velocities [5]. To correct this situation some solutions were proposed in two dimensions in [1, 2, 7]. We will instead use a new mixed finite element method for hexahedrons proposed by Yu. Kuznetsov and S. Repin (KR) [3, 4].

In this paper, following the ideas of Kuznetsov and Repin, we develop a composite element specifically for a convex hexahedron. This element is obtained by dividing the hexahedron into five tetrahedra [6].

EXPERIMENTAL CONCEPT
The Kuznetsov-Repin mixed finite element method was proven to be convergent, it was used to calculate the pressure and velocity field around a nuclear waste disposal. The domain of calculation is made up of 13 geological subdomains with permeabilities changing with up to three orders of magnitude from one subdomain to the other. The mesh was provided by engineers from ANDRA and is made of about 500 000 hexahedrons which for the most part are not parallelepipeds.

RESULTS AND INTERPRETATION
Since the Darcy velocity is actually the important quantity that is needed for the transport, we show in Figure 1 the norm of the velocity on an horizontal cross section, the velocity calculated with RTN finite elements (left) and KR mixed finite elements (right).

As one can observe, there are significant differences in the calculated velocity. In particular the norm of the velocity calculated with RTN mixed finite elements show a rough behaviour which is clearly unphysical for regions with constant permeabilities. This will necessarily have a strong impact when this velocity will be used in transport calculations.

We constructed a new mixed finite element for general hexahedral grids based on Kuznetsov’s and Repin’s general procedure for composite mixed finite elements. This new mixed finite element provides an elegant and simple way to implement mixed finite elements for general hexahedral discretizations. Theoretical convergence was proven and numerical convergence was observed. The method was applied to the calculation of a Darcy velocity which will be used for the simulation of the transport of radionuclides around a storage site.
Figure 1: Horizontal cross section of the norm of the Darcy velocity for the RTN (left) and KR (right) mixed finite elements.

References:
DIFFUSIVE PROPERTIES OF STAINLESS STEEL FILTER DISCS BEFORE AND AFTER USE IN DIFFUSION EXPERIMENTS WITH COMPACTED CLAYS

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INTRODUCTION
Porous stainless steel filters are frequently used for the purpose of confining compacted samples of expanding clays in diffusion studies. The typical sandwich-type of arrangement applied, viz. filter–clay–filter, allows for an even contact to be made between the liquid phase and the clay. For a proper evaluation of the diffusion coefficients of the clay it is important to know the diffusive properties of these filters. Depending on the geometrical differences in the pore structure of the filters and the clays, the diffusive resistance of the filters may be negligible in some cases. However, if the permeability of the filter discs is of similar order of magnitude as the one of the clay, the filter disc has a significant impact on the tracer concentration at the clay boundaries. Neglecting this effect may lead to an underestimation of diffusion coefficients of the clay.

In recent work (Glaus et al., 2007) we described diffusion measurements, where the diffusive resistance of the clay was a function of the salt concentration in the liquid phase contacting the clay. Such cases require a sufficient knowledge of the diffusive properties of the filters and a careful optimisation of the dimensions of clay and filters. Otherwise such experiments may not be carried out in reasonable time and with adequate accuracy.

In the present contribution measurements of the diffusive properties of porous stainless steel filters are reported for a series of diffusants before and after use of the filters for diffusion experiments with different clay minerals. The results are discussed in the light of optimisation of the experimental setup and the impact of the uncertainties in the filter properties on the overall uncertainties involved in the calculation of the diffusion parameters of the clays.

EXPERIMENTAL
Through-diffusion measurements were carried out using in-house manufactured acrylic glass two-chamber diffusion cells, in which the chambers were separated by the filter disc. The filter discs were laterally supported with FKM-elastomer flat seals in order to prevent advective transport along the filters or liquid loss from the diffusion cells. Filters were either used as received from the manufacturer or taken from the diffusion experiments with the various clays as described in Glaus et al. (2007) after being in contact with the Na-montmorillonite (Na-mom), Na-illite (Na-ill), or kaolinite (kao) for a minimum of 50 days up to 400 days at a dry density of ~1950 kg m⁻³. Diffusion was started by adding a concentrated solution of the diffusant under study to one of the chambers. HTO and ²²Na were used as radioactive tracers, whereas the diffusion of Sr and Cs was measured using stable isotopes.

RESULTS AND DISCUSSION
Figure 1 shows a comparison of breakthrough curves for the through-diffusion of Sr through a filter used as-received and others after being previously used in diffusion experiments with various clays. For the filter used as received an effective diffusion coefficient for diffusion in the filter, Df, of (1.1 ±0.1)×10⁻¹⁰ m² s⁻¹ was calculated, whereas this value was reduced to (0.61 ±0.02)×10⁻¹⁰ m² s⁻¹ for Na-mom, (0.50 ±0.04)×10⁻¹⁰ m² s⁻¹ for Na-ill and (0.79 ±0.02)×10⁻¹⁰ m² s⁻¹ for kao. Two explanations are feasible for the increased diffusive resistance of used filter discs: (i) the mechanical stress of the expanding clay or (ii) small clay particles
infiltrating the filter pores leading to a reduced geometry for diffusion (viz. reduced constrictivity or tortuosity). The second interpretation is rather supported by the experimental findings, because Na-mom and kao differ largely in their swelling behaviour. Further it was observed that the increase in diffusive resistance of the filter was almost independent on the clay thickness used in the preceding diffusion experiment with clay, which also supports the second interpretation.

$D_i$ values measured for the diffusion of HTO, $^{22}$Na, Sr and Cs in fresh and used stainless steel filter discs correlated fairly well with the respective molecular diffusion coefficients in bulk water. Although such correlations are inherently associated with some uncertainties, they generally allow for a reasonable estimate to be made for diffusants, for which no $D_i$ values are available. The present contribution further shows how the overall uncertainty of an effective diffusion coefficient in compacted clay may be assessed from the individual sources of uncertainty. Such considerations are helpful to decide, whether, for a given experimental setup, the uncertainty of $D_i$ may be critical for the overall uncertainty of diffusion in clay. If this sensitivity is relatively small, it is sufficient to rely on correlations with bulk water diffusion coefficients, which are readily available in the literature (e.g. Li and Gregory, 1974). Time-consuming measurements of the diffusive resistance of the filter discs may thereby be avoided.

References:

**Figure 1:** Accumulated mass of Sr, $n_r$, diffused across stainless steel filter discs as a function of time. The filter discs were previously used in diffusion experiments with compacted clays (~1950 kg m$^{-3}$) according to the legend.
STRUCTURAL ORGANIZATION OF POROSITY IN THE OPALINUS CLAY AT THE MONT TERRI ROCK LABORATORY UNDER SATURATED AND UNSATURATED CONDITIONS

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INTRODUCTION
The construction and the operational phases of a high-level radioactive waste repository include the ventilation of the underground drifts since excavation until the waste emplacement and their subsequent backfilling and sealing. This ventilation that will occur over a significant period of time will induce a rock desaturation that may have an important impact in the near field of the clay barrier. Microstructure of argillaceous rocks is related to the spatial distribution of minerals (mainly swelling clay minerals) and pores and consequently with that of water. The effects of desaturation on the microstructures of the Opalinus clay were investigated by visualizing and quantifying the organization of minerals and porosity of core samples taken under assumed saturated and unsaturated conditions.

EXPERIMENTAL CONCEPT
Two boreholes were drilled from the microtunnel of the Mont Terri URL dedicated to the Ventilation Experiment phase II framed in the NF-PRO RTD Component 4, WP4.3 EC project. The two boreholes about 1.2 m long each were air core-drilled, 30° upward and subparallel to the bedding at a distance of about 20cm from each other along the same beddings. The first borehole (BVE-96) was assumed to be representative of the saturated conditions as it was realized at the end of a 16 months natural resaturation period without ventilation (VE phases I + II; Mayor et al., 2005). The second borehole (BVE-103) was drilled at the end of the second desaturation period (VE phase II) after one year of a high flowrate (60m3/h) and dry air (1<RH<3%) ventilation and was therefore assumed to be representative of unsaturated conditions. For each borehole cores were sawed for obtaining 3×15cm samples in the very first 45cm and a 15cm sample at the borehole end (between 105 and 120cm). In addition of a drillcore mapping a combination of techniques was applied for each sample among which, petrophysical determinations by water content measurements at 150°C, SEM observations, XRD, autoradiographs and high resolution X-ray tomography.

RESULTS AND INTERPRETATION
Values of degree of saturation (Figure 1) estimated from water content and volume measurements indicate a water loss in the rock mass for the first borehole (giving assumed initial conditions) with values of saturation circa 70% and attributed either to an artifact due to an evaporation process during drilling and the subsequent handling during mapping or to a residue of desaturation due to the former VE experiment. Samples taken from the 2nd borehole at the end of the desaturation period (final conditions) show a much bigger desaturation with values reaching 50% in the very first 20cm and a resaturation trend between 80% and 100% further. For both boreholes the combination of techniques has revealed the occurrence of micrometric cracks parallel to the bedding. These cracks have a frequency that decreases with the distance.
from the borehole head and are quantitatively well correlated to the degree of saturation especially for the BVE-103 borehole. Theses cracks are therefore attributed to desaturation cracks. Autoradiographs obtained after rock fragments impregnation with a $^{14}$C-radioactive resin enabled us to quantify the role of fracturation in total porosity by comparing matrix porosity to total porosity. The matrix porosity decreases up to about 40cm then slightly increases in the borehole end. This reduction of matrix porosity was also observed around drifts excavated in the well compacted Tournemire argillite submitted to a natural dry-air ventilation and was attributed to the reduction of volume by water loss (Altinier, 2006; Matray et al., 2007).

High resolution X-rays tomography was performed with the aim of visualizing the organization of porosity in 3D at a micrometric scale and quantifying porosity and minerals. The proportions of minerals estimated by this method are consistent with the known mineralogy of Opalinus Clay (Gautschi, 2006). It also enabled us to verify the occurrence of desaturation cracks and to quantify their contribution to the total porosity that appeared in good agreement with estimates of fracture and matrix porosity deduced from autoradiographs.

References:


EVALUATION OF PORE STRUCTURE IN COMPACTED SATURATED BENTONITE USING NMR RELAXOMETRY

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INTRODUCTION

The permeability and diffusivity of a compacted bentonite, which is a candidate buffer material in various Japanese geological disposal system, have been examined to assess its barrier performance and provide input for tailoring engineering barriers to specific geological environments. Despite considerable accumulation of experimental data in the past, the relationship of pore structures (both the interlayer pores of the clay and the intralayer pores resulting from particle aggregation) to aqueous pathways in compacted saturated bentonite is not yet fully understood. In order to clarify some of the factors involved, we have applied NMR relaxometry (relaxation distribution analysis of ²H NMR) to saturated compacted bentonite.

NMR RELAXOMETRY AND EXPERIMENTAL PROCEDURE

The proton longitudinal relaxation time, $T_1$, measured by NMR of fluids in porous media, is strongly influenced by fluid-solid interaction. One interesting application of such relaxation measurements is the determination of the surface-volume ratio of pores,

$$\frac{1}{T_1} = \rho_i \frac{S}{V}_{\text{pore}}$$

where $\rho_i$ is the surface relaxivity, $S$ and $V$ are the surface area and volume of the pore. In saturated clays, $(S/V)_{\text{pore}}$ corresponds to the surface-volume ratio of pores filled with water. A possible source of surface relaxation is the presence of magnetic impurities along the pore wall, in this particular application paramagnetic ions like Mn³⁺ and Fe³⁺ in clay.

Measurements were performed using an NMR spectrometer (Maran Ultra, Resonance Instrument, UK) at 23.4 MHz. A saturation recovery sequence with 256 recovery values from 0.1 to 52 ms was used. The decay of nuclear magnetization obtained from these measurements was analyzed numerically using an inverse Laplace transformation (Provencher, 1982) to derive the $T_1$ distribution.

MATERIAL

The bentonite material examined is Kunigel VI, which is a Na-bentonite provided by Kunimine Industries Co., Ltd. Kunigel VI contains 47 wt% montmorillonite, 37 wt% chalcedony, 4 wt% plagioclase, 3 wt% analcime, 2 wt% calcite 2 wt% dolomite, 0.6 wt% quartz, and 0.6 wt% pyrite (total 96.2 wt%). Due to its high surface area and content of magnetic impurities, the relaxation time measured is expected to be due to the montmorillonite component. Do you think it is worth adding this sentence? Compacted bentonite samples with dry densities, $\rho_c$, of 1.33 and 1.80 Mg/m³ were prepared. After compaction, saturation of the samples with distilled water was carried out at fixed volume over a period of 2 months. Montmorillonite soils and gels were also prepared by adding distilled water to Kunipia F, which is a purified bentonite containing over 98 wt% montmorillonite, to estimate the surface relaxivity of the clay component of the Kunigel.
RESULTS
First, we estimated \( \rho_i \) of montmorillonite through \( T_1 \) measurements of dispersed montmorillonite sols and gels. A single \( T_1 \) value was observed for these uncompacted samples. All the high water content – e.g. 6.7% sample illustrated below systems. The \( (S/V)_{\text{pure}} \) in these systems is determined by the specific surface area, \( S_0 \), of montmorillonite and the solid/liquid ratio by weight \( [(\text{clay})/(\text{water})] \). C; that is, \( (S/V)_{\text{pure}}=S_0C \), where \( \rho_y \) is density of bulk water. \( S_0 \) was measured as 700 m²/g by the EGME (ethylene-glycol-monoethyl-ether) method (Kozaki et al., 1999). A simple linear regression analysis of C against \( 1/T_1 \) for 13 samples with C<0.5 resulted in \( \rho_i = 0.212 \text{ nm/ms} \) (standard fitting error 0.47%) I think it is valuable to add this information.

Results of relaxation distribution analysis for saturated \( \rho_i = 1.33 \) and 1.80 Mg/m³ samples and Kunipia F with water content 6.7 wt% are shown in Fig. 1. The relaxation distribution of the Kunigel samples indicate two peaks within the relaxation time ranges of 0.1-1.0 ms (range A) and 1.0-10 ms (range B), which are clearly dependent on \( \rho_y \). The peak position in range A is 0.546 ms for the Kunipia F powder sample, interpreted as surface monolayer water. The peak positions in range B are 1.7 and 3.7 ms for \( \rho_i = 1.33 \) and 1.80 Mg/m³, respectively. For the assignment of these peaks, results of X-ray diffraction (XRD) for compacted Na-montmorillonite saturated with water are used (Kozaki et al., 1998). A 3-water molecule interlayer hydrate of Na-montmorillonite with a basal spacing of 1.8 nm was observed for \( \rho_i = 1.3 \) Mg/m³, and a 2-molecule hydrate with a basal spacing of 1.5 nm for \( \rho_i = 1.8 \) Mg/m³. The basal spacing is easily convertible into interlayer space dimensions by subtracting the thickness of montmorillonite layers (about 1 nm), and thus these results can be directly related to the relaxation times determined in this study. If an extended planar pore water distribution between montmorillonite layers is assumed, \( (S/V)_{\text{pure}} \), I think it is better to use S/V here as this has been used in all discussion up to this point calculated from the relaxation time is equal to [1/(hydrate layer thickness)]. On this basis, the relaxation times calculated by equation (1) using XRD dimensions of the 2- and 3-layer hydrate are 2.6 and 4.1 ms, respectively. These results are slightly larger than the maximum peak positions in range B in this study. This could be due to effects of interlayer cations or surface diffusivity of water, but we can clearly assign relaxation time in range B to interlayer water in compacted bentonite.

We are also trying to extend the NMR relaxometry method to compacted bentonite with changes of key parameters influencing diffusivity and permeability - such as sand content and composition of water. Some perspectives on the associated relaxometry approach will be given.

References:
DIFFUSION COEFFICIENTS MEASUREMENT IN CONSOLIDATED CLAYS: A COMBINATION OF MICRO-SCALE PROFILING AND SOLID PORE STRUCTURE ANALYSES

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Consolidated clays are considered suitable geological formations to host a high-level radioactive waste repository. They are low permeability media and diffusion is the main mechanism for radionuclide (RN) transport. Thus, the determination of RN diffusion coefficients is required to evaluate the safety of the clay barrier. Experimental methods to measure diffusion coefficients for elements that suffer no or small retardation exist but, almost no data are available for elements presenting high sorption onto the clay, as the majority of actinides and several fission products.

In this study, the nuclear ion beam technique Rutherford Backscattering Spectrometry (RBS) is tested to evaluate RN concentration profiles within the Opalinus consolidated clay from the Mont Terri rock laboratory (Switzerland). This technique, widely used in material science is scarcely applied to measure diffusion coefficients in geological materials, and it is suited to evaluate concentration gradients of heavy elements in the near surface region (several micrometers) in samples mainly composed by light elements.

To relate the measured apparent diffusion coefficients to the porosity of the clay samples, clay porosity was determined by impregnation technique. Furthermore, the porestructure was studied in detail by electronmicroscopy (SEM) on the impregnated sample. The poly-methylmethacrylate (PMMA) method involves impregnation of clay samples here with ³¹H labelled methylmethacrylate (³¹H-MMA), irradiation for polymerisation, autoradiography and optical densitometry evaluation of the tracer, by digital image-processing techniques. In our samples, the average measured porosity was 19 %.

Diffusion experiments were performed with Sr and Eu that are respectively low and strongly sorbing elements onto the clay. Commercial gold colloids of 2 nm in diameter were also selected, to define the lowest limit of diffusion coefficient within the clay. Colloid diffusion is expected to be hindered because of having higher diameter than solutes and because both the colloids and the clay are negatively charged.

Papers were spiked with Sr or Eu solution or the 2 nm Au colloids suspensions and were placed on the clay samples previously hydrated with synthetic water (Pearson water), simulating the Opalinus clay pore water. Once the selected contact time passed (ranging from 5 minutes to 7 days), the traced-papers were removed, and the samples were analyzed by Rutherford Backscattering Spectrometry (RBS).

As example, Figure 1 presents the RBS spectra obtained on the MtTerri clay samples after contact with Eu (Figure 1- left) or Sr (Figure 1-right). Comparatively, in Figure 1 (left) undoubted asymmetric Eu peaks are detected in the RBS spectra indicating Eu access into the clay. In Figure 1 (left) the Eu peak shape is rather narrow at higher channels, suggesting Eu retention on the surface caused by sorption, but also, the Eu peak showed a tail going towards lower channels, indicating that Eu was going deeper in the sample.
The time dependence of the Eu peak height and tail was in agreement with a diffusion process. Similar behaviour was observed for Eu and for the 2 nm Au colloids, but in comparison, the gold signal was lower than that of Eu and its profile thinner, suggesting slightly slower diffusion. However, different behaviour is observed for Sr in Figure 1 (right). In this case, even after 5 minutes, the Sr signal is plane, overlapping its tail with the signal of lighter elements, indicating faster Sr diffusion than that of Eu (Figure 1) or 2 nm Au colloids.

From the RBS spectra simulation, considering an average clay composition, and introducing a concentration gradient of the selected element (Eu, Au or Sr), diffusion lengths were determined, and it was possible to evaluate apparent diffusion coefficients for Eu, Sr and Au colloids. Diffusion coefficients were measured for Eu (D_Eu 2.5E-16 m²/s) and Au colloids, being 10¹⁷ m²/s. Since Sr presented faster diffusion, the signal was plane even after only 5 minutes (Figure 1 right), so it was only possible to evaluate an inferior limit for diffusion coefficient (D_s > 4E-14 m²/s). Through the porosity values, effective diffusion coefficients (D_eff) were calculated and the values are compared to that reported in the literature.

Experimental times required with the methodology presented here are clearly shorter (days) than those required with conventional experiments (months-years). The applicability and (or) limitations of this new methodology to other relevant solutes are also discussed.
NUMERICAL INTERPRETATION OF IN SITU DIR DIFFUSION EXPERIMENTS ON C-OX CLAY AT BURE SITE

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The Callovo-Oxfordian argillite is under investigation as a potential host rock for high-level waste repository at Andra Underground Research Laboratory in Meuse/Haute Marne (France). DIR (Diffusion and Retention) is an experimental program which aims at characterizing diffusion and retention of radionuclides in clay rock. Several boreholes were drilled to perform in situ diffusion experiments in order to determine diffusion and retention properties of radionuclides such as tritium (\(^{3}\)H), iodine (\(^{125}\)I), chloride (\(^{36}\)Cl), sodium (\(^{23}\)Na), and cesium (\(^{137}\)Cs). DIR diffusion experiments were performed in vertical boreholes drilled perpendicular to bedding. Bure clay exhibits mild diffusion anisotropy due to stratification. In situ diffusion experiments DIR2001, DIR2002 and EST208 were interpreted using data on the decrease of tracer activity in the testing interval. All the analysis were performed by CEA DPC Saclay. These experiments could not be interpreted with analytical solutions because they do not account for the presence of the filter, the gap between the casing and the borehole wall and an excavation disturbed zone which here will be denoted as EdZ.

DIR experiments were interpreted using numerical inverse models with INVERSE-CORE (Dai and Samper, 2004). Numerical interpretation of DIR experiments requires the use of 3-D models due to diffusion anisotropy. However, symmetry with respect to borehole axis allows the use of 2-D axisymmetric models. Comparison of the results of a 2-D anisotropic model with those of a 1-D model indicates that concentrations at the testing interval computed with both models are similar and are not sensitive to the diffusion anisotropy ratio. Therefore, 1-D axisymmetric models were used to interpret DIR diffusion experiments. Numerical models were used to: 1) Compute numerical sensitivities of concentrations to model parameters; 2) Analyze parameter identifiability and parameter estimation errors with synthetic experiments and 3) Interpret real DIR experiments. Here we report on the results of the numerical interpretation of real DIR experiments.

Real diffusion experiments relied on results of sensitivity runs and identifiability analysis of synthetic data. They were interpreted using a systematic approach according to which: 1) \(D_e\) fiber and \(D_e\) gap were estimated first using mostly early-time 2) \(D_e\) fiber and \(D_e\) gap were fixed to the estimated values and \(D_e\) EDZ and \(\phi\) EDZ were estimated using mostly concentration data measured and 3) \(D_e\) clay and \(\phi\) clay were estimated using all concentration date while \(D_e\) fiber, \(D_e\) gap, \(D_e\) EDZ and \(\phi\) EDZ were fixed at the values estimated in precious steps. This sequence of steps led to excellent fits to measured data. In addition, this approach worked well for all tracers and all experiments, providing robust results in all cases.

Model results indicate unambiguously that a model without EdZ cannot fit measured data with values of \(D_e\) clay and \(\phi\) clay within the range of values determined in lab experiments. In fact, measured concentration data can only be fitted with values of \(D_e\) clay and \(\phi\) clay much larger than measured values. Therefore, HTO data allow us to conclude that data are clearly affected by an EdZ and such data cannot be explained without resorting to such hypothesis. Several sources of parameter uncertainty have been evaluated. By adopting a volume of water in circulation system 5% smaller than the reference value, data can be fit equally well as with the reference volume, but with slightly smaller values of \(D_e\) clay, \(\phi\) clay and \(\phi\) EDZ. This means that a small (5%) error in the volume of water in the circulation system has no major effect on...
estimates of $D_{c,clay}$ and $\phi_{clay}$. Our estimates of $D_{c,clay}$ for HTO in DIR2001, DIR2002 and EST208 experiments are 30% larger than those obtained by CEA (Radwan et al., 2005) for DIR2001 and DIR2002.

$^{36}\text{Cl}$ and $^{125}\text{I}$ data from DIR2001 experiment and $^{36}\text{Cl}$ data from EST208 experiment cannot be explained without an EdZ. Several sources of parameter uncertainty were evaluated. By adopting a volume of water in the injection system 5% smaller than the reference value, data can be fit equally well as with the reference volume, but with slightly smaller values of $D_{c,clay}$, $\phi_{clay}$ and $\phi_{EdZ}$. This means that a small (5%) error in the volume of water in the injection system has no major effect on estimates of $D_{c,clay}$ and accessible $\phi_{clay}$ for $^{36}\text{Cl}$ and $^{125}\text{I}$.

UDC estimates of $D_{c,clay}$ for $^{36}\text{Cl}$ are similar in DIR2001 and EST208 experiments. CEA $D_{c,clay}$ estimates, however, show a rather large range for DIR2001 and DIR2002. Contrary to CEA who fixed accessible porosity and estimated only $D_{c,clay}$ we obtained estimates for both $D_{c}$ and porosity. Our estimate of $D_{c,clay}$ for $^{125}\text{I}$ in experiment DIR2001 is within the range of CEA values.

Model results indicate that $^{134}\text{Cs}^{+}$ data can be fit equally well with several combinations of parameters: large $K_{a}$ with a small $D_{EdZ}$ and small $K_{a}$ with a large $D_{EdZ}$. Therefore, a model without EdZ can fit measured data, but with values which are similar to those estimated for the EdZ. Several sources of parameter uncertainty were evaluated for $^{134}\text{Cs}^{+}$ data including the volume of water in the injection system, the porosity of the gap and $D_{c}$ of filter. Numerical model fits data both at early times (which is best visualized in a semilog c-log plot) and late times (which is visualized in the c-t plot) (see Fig. 1). Parameter estimates are consistent with parameter estimates obtained by CEA, except for the $K_{a}$ of $^{22}\text{Na}^{+}$ for which our estimate is twice as large as CEA estimate.

References


IDENTIFICATION OF RELATIVE CONDUCTIVITY MODELS FOR WATER FLOW AND SOLUTE TRANSPORT IN UNSATURATED COMPACTED BENTONITE

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INTRODUCTION
Underground facilities are being operated by several countries around the world for performing research and providing demonstration of the safety of a deep geological high level radioactive waste (HLW) repository. The Grimsel test site at Switzerland is one of such facilities launched and operated by the Swiss Nuclear Waste Management Company (NAGRA) where various in situ experiments have been carried out in fractured granites. One of them is the FEBEX (Full-scale Engineered Barrier EXperiment) in situ experiment which is part of a larger demonstration and research project launched by ENRESA for the engineered barrier of a high level radioactive waste repository. FEBEX is based on the Spanish reference concept for radioactive waste disposal in crystalline rock according to which canisters are emplaced in horizontal drifts and surrounded by a compacted bentonite clay barrier. This bentonite comes from the Cortijo de Archidona deposit, exploited by Minas de Gádor, S. A., at Serrata de Nijar (Almería, Spain). This deposit was selected by ENRESA (Empresa Nacional de Residuos Radioactivos, S. A.) prior to the FEBEX project (Huertas et al., 2000) as the most suitable material for the backfilling and sealing of a HLW repository. FEBEX bentonite has very high montmorillonite content, large swelling pressure, low hydraulic conductivity, good retention properties and is easy to compact for fabrication of blocks. Compacted bentonite is packaged as homogeneous as possible. Homogenization reduces model uncertainties (Huertas et al., 2000). Predictions of water flow and solute transport in the unsaturated compacted bentonite are essential for the repository of potentially hazardous chemicals to minimize the potential of groundwater contamination. In order to establish an effective prediction model of water flow and solute transport in unsaturated bentonite, We developed an inverse methodology to estimate bentonite hydraulic parameters and identify its relative conductivity function from infiltration experiments using transient cumulative water inflow and final water content data. Model identification criteria developed in the context of information theory have been used to select the best relative conductivity function among four candidates, including that of Irmay (1954) and three proposed by van Genuchten (1980).

RESULTS AND DISCUSSION
Five infiltration experiments were performed by CIEMAT on FEBEX compacted bentonite samples with the steel cylindrical cells of 5 cm of inner diameter and 2.5 cm of length. Compacted bentonite samples were confined between two porous sinters. They were hydrated from the upper end under a constant water pressure of 1 MPa. Infiltration rate was recorded with time. At the end of the test, the sample was taken out of the cell. Final water content (w) and dry density (ρd) were measured at five sections located at different distances to the hydration front.

A 1-D numerical model was used to simulate the infiltration experiments and estimate unsaturated flow parameters. Four relative conductivity functions including that proposed by Irmay (1954) and three of van Genuchten (1980) are tested with our inverse model INVERSE-CORE²⁰ (Dai and Samper, 2004) and compared using model identification criteria. Table 1 summarizes the estimated parameters from the five experiments. Mean, standard deviation (SD) and coefficient of variation (CV) of each estimated parameter
Table 1: Summary of estimated parameters from the five tests

<table>
<thead>
<tr>
<th>Model</th>
<th>$K_i$ (m/d)</th>
<th>$m$</th>
<th>$\alpha$ (m$^{-1}$)</th>
<th>$\phi$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>mean</td>
<td>SD</td>
<td>CV</td>
<td>Mean</td>
</tr>
<tr>
<td></td>
<td>4.98·10^{-9}</td>
<td>3.56·10^{-9}</td>
<td>0.07</td>
<td>0.266</td>
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<td>0.25</td>
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<tr>
<td></td>
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<td>0.773</td>
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<td></td>
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<td>0.265</td>
</tr>
<tr>
<td></td>
<td>6.77·10^{-9}</td>
<td>1.47·10^{-9}</td>
<td>0.22</td>
<td>1.813</td>
</tr>
<tr>
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<td>6.87·10^{-9}</td>
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<td></td>
<td>0.204</td>
</tr>
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<td>0.594</td>
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<tr>
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<td>5.9·10^{-9}</td>
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<td>0.259</td>
</tr>
<tr>
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<td>1.44·10^{-3}</td>
<td>2.43·10^{-4}</td>
<td>0.17</td>
<td>0.421</td>
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<tr>
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<td>0.4·10^{-3}</td>
<td>0.16</td>
<td>0.04</td>
<td></td>
</tr>
</tbody>
</table>

($K_i$ is saturated conductivity; $m$ and $\alpha$ are parameters defining the retention curve; $\phi$ is porosity)

were computed from values estimated in the five infiltration experiments. Irmay model has one more parameter ($n_r$) than other models and its mean, standard deviation and coefficient of variation are 3.03, 0.432 and 0.14, respectively.

Although the computed values of the objective functions and the model selection criteria are various from data to data, the overall evaluations of the results indicate that even though Irmay model has a better fit to the observation data, the general van Genuchten model (vG-M1) is the best model for the relative conductivity, since it minimizes the three model selection criteria. The better fit from Irmay model may come from the fact that it estimates more parameters. The uncertainty from the inverse modeling which involves more parameters is usually much larger than those with few parameters. From the point of model parsimony, the other two van Genuchten models (vG-M2 and vG-M3) with more complex function structures are not the attractive alternates for the general van Genuchten model, even though they have very similar performance. Therefore, we identify the general van Genuchten function as the best model for water flow and solute transport in the unsaturated compacted bentonite.

ACKNOWLEDGMENTS:
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References
DIFFUSION EXPERIMENTS
IN CALLOVO-OXFORDIAN CLAY
FROM THE BURE SITE, FRANCE:
1 EXPERIMENTAL SETUP
AND DATA ANALYSES

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INTRODUCTION

Clay formations are being considered potential host rocks for radioactive waste disposal in many countries. The French National Radioactive Waste Management Agency (ANDRA) is performing research at the Meuse/Haute-Marne Underground Research Laboratory (URL) located at Bure (300 km east of Paris) to evaluate the use of the Callovo-Oxfordian (COx) argillite formation as a potential host rock for high-level radioactive waste repository in France. The argillaceous COx formation is a 130 m thick argillite lying at depth between 420-560 meters at the laboratory site. The host formation contains 30 to 55 % clay minerals, associated with 20 to 30% carbonates, 20 to 35% quartz and a small percentage of subordinate minerals (J.-L. Gaussen, 2002). Since clays have a very low hydraulic conductivity (<1E-12 m/s), diffusion is the main transport mechanism for radionuclides released from the canisters. Understanding diffusion processes and determination of diffusion coefficients for critical radionuclides are crucial for the performance assessment of a deep geological repository.

In situ diffusion experiments are being carried out to confirm the results obtained in the “real system” with those obtained in classical laboratory tests, where small thickness samples, generally about 1 cm. thick are used.

EXPERIMENTAL CONCEPT

The “classical” experimental set-up of in situ diffusion experiment includes the use of a tracer diluted in reconstituted formation water into a packed-off borehole section. The packed-off section contains a stainless steel sinter of high porosity. In general, between the sinter chamber and the wall of the borehole a void volume is always left, and a decrease in the clay density and an increase of porosity is expected at the clay/chamber interface. As a consequence, the introduction of a chamber filled with water could modify the properties of the saturated clay in the first few centimetres, near the clay/ experimental chamber interface, just where radionuclide diffusion is mainly expected to take place. In particular, at the clay/ chamber interface, a decrease in the clay density and an increase of porosity can take place.

In this study we present both small-scale laboratory diffusion experiments in samples of 1 cm thick, and large-scale diffusion experiments performed in a cylindrical sample of 30x30 cm, using a methodology described in M. García-Gutiérrez et al. 2006. This last method could overcome the abovementioned problem and could allow carrying out in situ diffusion experiments in more realistic conditions.

Laboratory diffusion experiments in the smaller samples were performed using the through-diffusion (TD) method. In this method the 1 cm. thick sample is located in between two reservoirs, “in” and “out” reservoirs, where constant and zero concentration are maintained. Both reservoirs were filled with a
Figure 1: Experimental HTO spread at four different horizontal planes (from left to right, 6 to 8 cm, 8 to 10 cm, 10 to 12 cm and 12 to 14 cm).

The synthetic solution representative of the site groundwater (T. Melkior, 2004). TD diffusion experiments were performed with HTO (neutral), $^{36}$Cl$^-$ (anionic) and $^{22}$Na$^+$ (cationic) as tracers.

In the large-scale diffusion experiments, a re-compacted clay/radionuclide mixed solid source was placed in the centre of a large clay block, allowing the tracer to diffuse into the closed system. At the end, a thorough sampling of the rock provided a 3D distribution of the tracer activity, evidencing the diffusion paths. Experiments using HTO and $^{85}$Sr$^{2+}$ were finished but experiments with $^{137}$Cs$^+$, $^{60}$Co$^{4+}$ and $^{152}$Eu$^{3+}$ are still ongoing. Figure 1 show HTO experimental results obtained at four different horizontals planes.

These experiments demonstrated that the methodology proposed for large-scale diffusion studies is feasible. Results showed that it is possible to obtain a good three-dimensional representation of the diffusion process that allows analysing the anisotropy of diffusion.

The proposed experimental set-up could simplify the design and performance of an in situ diffusion experiment, eliminating the need for continuous monitoring and avoiding the alteration of the clay (due to contact with water) in the proximity of the source of the tracer.

ACKNOWLEDGEMENTS

This work has been carried out in the frame of the ENRESA-CIEMAT association and partially funded by the EU within the FUNMIG (Fundamental Processes of radionuclide Migration) Project (Ref. FP6-516514).

References:


TRANSPORT IN ORGANO-MONTMORILLONITES: IN SITU DIFFUSION EXPERIMENTS USING ATR-FTIR SPECTROSCOPY

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INTRODUCTION
Bentonites are preferentially used in engineered barriers of waste deposits repositories. Usually the retardation capacity for anions is low. Bentonites modified by certain organic cations have the capability to adsorb anions too. The resulting anion exchange capacity takes values of up to 0.5 mol, kg⁻¹ (Darder et al., 2003). The use of organo-clays as material of barriers in waste repositories is thought to improve the retardation capacity for hazardous anions. Modification of the clay by organic cations results in change of surface charge and wettability, and it might as well have an effect on diffusion coefficient. In this work diffusion coefficients for protons in modified, compacted montmorillonites are examined in a cell attached to a FTIR-ATR spectrometer.

EXPERIMENTAL CONCEPT
A commercial Wyoming bentonite (MX-80) was modified with the monovalent organic cations hexadecylpyridinium (HDPy), benzethonium (BE) and tetraphenylphosphorium (TPP) in amounts corresponding to 2-400 % of the cation exchange capacity (CEC). Uptake of the organic cations was calculated by the C-content. Surface charge was quantified by polyelectrolyte titration in a cell of a particle charge detector. Wettability was determined with a dynamic contact angle tensiometer by the Wilhelmy-Plate-Method. The effect of surface charge on microstructure was defined by flocculation properties and electron microscopy.

Figure 1: Scheme of the ATR-cell

Figure 2: H⁺ diffusion in HDPy-montmorillonite (HDPy applied: 80 % CEC): Comparison of experimental data (squares) and fits (lines).
Diffusion experiments were carried out in situ in an ATR-cell attached to a FTIR-spectrometer (TENSOR 27, Bruker, Germany). The samples are compacted by a pressure of 690 bar on the ATR diamond (Ø 1.8 mm, Fig. 1). First samples are saturated with D₂O afterwards H₂O is applied to the external surface of the clay sample. The diffusion of protons results in an increase of the absorbance of the O-H stretching frequency at 3380 cm⁻¹ and a decrease of the absorbance of the O-D stretching frequency at 2480 cm⁻¹. Diffusion coefficients were calculated by fitting the integrated and normalized OH-stretching as a function of time. The diffusion coefficient is assessed by comparing the time dependent absorption-intensity with simulated diffusion coefficients (Fielderson and Barbari, 1993) (Fig. 2).

RESULTS AND INTERPRETATION

By the modification with organic cations the surface charge of the clay shifts from negative to positive values. TPP is adsorbed on the external surfaces of montmorillonite as a monolayer and, in contrast to HDPy- and BE-montmorillonite, no positive surface charge was observed. Highest hydrophobicity occurs in samples close to the point of zero charge (Tab.1). Surface charge and the resulting wettability were found to have an effect on the diffusion coefficient: In the range of zero and high positive surface charge the proton diffusion is one order of magnitude faster than for samples with negative surface charge. Besides the effect of hydrophobicity of the samples, this might also be related to the modified microstructure. There is evidence, that diffusion of protons is not affected by the amount of organic cations adsorbed onto the external surface of montmorillonite.

<table>
<thead>
<tr>
<th>Added amount of HDPy [% of CEC]</th>
<th>Surface charge [mmol/kg]</th>
<th>Contact angle [°]</th>
<th>Diffusion coefficient [cm²/s]</th>
</tr>
</thead>
<tbody>
<tr>
<td>40</td>
<td>-19.3</td>
<td>52</td>
<td>9.4 × 10⁹</td>
</tr>
<tr>
<td>80</td>
<td>-0.3</td>
<td>91</td>
<td>2.5 × 10⁸</td>
</tr>
<tr>
<td>400</td>
<td>213.9</td>
<td>35</td>
<td>3.4 × 10⁸</td>
</tr>
</tbody>
</table>

The diffusion cell attached to the ATR-FTIR-spectrometer allows a fast determination (~2-8 h each) of diffusion coefficients of samples with different properties. Due to continuous recording of diffusion profiles, detailed analyses of diffusion processes are possible. Experiments with organic anions and temperature-depending studies will be accomplished.

References:


ACKNOWLEDGMENT:
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UNSATURATED FLOW AROUND HIGH-LEVEL LONG-LIVED RADIOACTIVE WASTE REPOSITORY DRIFT SEAL WITH ALLIANCES PLATFORM

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INTRODUCTION

In the context of high-level radioactive waste disposal, the modelling of the processes of host rock desaturation and host rock, backfills, seals and engineered barriers saturation is of first importance (Andra, 2005).

The desaturation processes are strongly coupled with mechanics, and can induce host rock confinement properties changes. The physico-chemical behaviour of the repository is highly dependent on the time scale of the repository components saturation. Indeed, the saturation processes mainly control corrosion and other geochemical processes responsible initially for waste canister failure and thereafter for waste dissolution (Andra, 2005). Therefore, radionuclide source term depends on saturation processes.

The objective of this paper is to evaluate the occurrence of air entrapment in the repository due to early repository drift seal saturation.

UNSATURATED FLOW AROUND REPOSITORY DRIFT SEAL

We considered a scholastic modelling exercise where the drilling of a repository drift intercepts a geological system composed of an argillaceous host rock topped by a permeable layer considered as an aquifer. The drift excavation leads to an hydraulic decompression of the geological layers system as well as its desaturation as long as the drift stays open, namely for the repository exploitation duration expected to be of the order of 100 years.

The repository is closed by the sealing of the drifts with several argillaceous swelling plugs. For this modelling exercise, we consider that the plug totally seals the drift. After closure, the system constituted of the geological layers and seal will saturate and will reach a new hydraulic steady state.

The time scale for the full saturation of the back fields and engineered barriers inside the repository is expected to be of the order of 100,000 years (Andra, 2005). We are interested in the drift seal saturation time scale.

RESULTS AND INTERPRETATION

Computations were performed using the Alliances Platform (Montarnal \textit{et al}, 2006) where a common form of the Richard’s equation including specific storage coefficient (Miller \textit{et al}, 1998) is considered.

The three-dimensional mesh used for computation is presented in Figure 1.

Desaturation calculation was conducted over a period of 100 years. After what, a seal with initial unsaturated conditions is introduced inside the drift and saturation calculation performed over a period of 100 years.
The calculations results show that during the desaturation phase the host rock desaturation extension around the drift is small. But the more important result is that, due to the presence of a more permeable layer at the top of the host rock, the total saturation of the repository drift seal is very fast. The air enclosed in the backfills of the repository is then expected to be entrapped. Due to this air entrapment, the use of Richard’s model to evaluate saturation time of components of the repository like backfills or engineered barriers may be not relevant and the use of a two phase flow model including air dissolution should be considered.

References:
NUMERICAL INTERPRETATION OF GAS TRANSPORT EXPERIMENTS ON WATER-SATURATED SAMPLES OF OPALINUS CLAY

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INTRODUCTION

The understanding of gas transport processes through the host rock forms a key issue in the assessment of long-term safety of radioactive waste repositories in argillaceous formations (Marschall et al., 2005). The gas transport capacity of such ultra-low permeability rock formations can be tested in the laboratory by gas breakthrough tests on core samples. A series of gas breakthrough tests using either Helium or Argon on small cylindrical samples (Ø2.4cm, height = 2cm) of the Opalinus Clay (Mont Terri, Switzerland) has been conducted by Krooss and Alles, 2006. The experimental data and conditions were carefully reviewed and an interpretation was performed taking into account both two-phase flow (water and gas) and diffusive transport of gas in the aqueous phase by means of numerical simulations.

EXPERIMENTAL DATA, ANALYSIS METHOD AND RESULTS

A schematic of the triaxial flow cell is presented in Figure 1. The sample is confined with an axial and radial confining pressure of 6 MPa. A water permeability test is performed on each sample prior to the gas test. At the beginning of the gas test an air-filled volume is created at the downstream end of the sample by withdrawing a definite volume of water using a syringe. Gas (He or Ar) is then injected at high pressure into the upstream compartment (tubing + porous disc) and closed. The pressure evolution in the two compartments is continuously monitored over time: A steady decrease is observed in the upstream compartment, a steady increase at the downstream compartment, respectively. This type of experimental set-up has been thoroughly tested and has also been used by Hildenbrand et al., 2002.

The simultaneous acting of different transport processes required adopting a stepwise approach for the analysis of the experiment. The following steps were performed: i) A model identification step based on TOUGH2 simulations (a two-phase flow and transport code, Pruess et al., 1999) in order to investigate the effects of the different transport processes on the pressure evolutions in the upstream and downstream compartments. ii) A sensitivity analysis on two-phase flow and diffusion parameters of the samples and on initial and boundary conditions using iTOUGH2. iii) A parameter estimation step by inverse modelling using iTOUGH2.

The prevailing processes influencing the measured pressure evolution have been identified and quantified. These are: Storage of gas and water in the upstream and downstream compartments, advective transport
of water through the sample at early times, and – at later times – advective transport of the injected gas (He or Ar) through the sample and diffusion of both the injected gas (He or Ar) and air (initially present in the downstream compartment) through the sample in opposite directions.

The parameter estimation comprised diffusion coefficients of the dissolved gases and the two phase flow parameters according to van Genuchten’s parametric model of capillary pressure and the van Genuchten/Mualem model of relative permeability.

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CALLOVO-OXFORDIAN FORMATION AT THE MEUSE/HAUTE-MARNE URL: CONSISTENCY BETWEEN MEASURED HYDRAULIC CONDUCTIVITY AND THE DRAINAGE EFFECT OF THE EXPERIMENTAL DRIFTS

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INTRODUCTION
Andra is currently investigating the Callovo-Oxfordian argillaceous formation as a potential host rock for the deep disposal of high level radioactive waste at the Meuse/Haute-Marne URL (Andra, 2005). A large number of geomechanical and hydraulic measurements are performed in instrumented boreholes (Delay et al., 2006a and b). In particular, hydraulic tests were performed in test intervals of these boreholes and allowed the determination of the hydraulic conductivity and of the formation pressure at small scale (max. of a few decimetres due to the low permeability). Furthermore, the porewater pressures perpendicularly to the drift wall situated at ~490 m bgl were measured continuously at distances between a few decimetres up to 20 meters from the drift wall over more than one year. Figure 1 presents a 3D view of the experimental boreholes and a schematic of measurements of the quasi-stabilized pressures. The aim of the work was to investigate the consistency of the small scale hydraulic conductivity measurements and the observed pressure distribution around the drifts GEX and SMR1.1 in the rock mass located outside the Excavation Damaged/disturbed Zone (Measurement points situated at distances larger than 5 m from the drift wall, floor or roof) with the darceen drainage effect due to the atmospheric pressure in the experimental drifts.

RESULTS AND INTERPRETATION
The pressure data collected between the end of 2005 and the end of 2006 at the 8 measurement points borehole intervals of the PEP, DIR and SUG experiments were carefully examined in terms of degree of reliability and measurements characteristics; a synthesis of quasi-stabilized pressure values was obtained. The drainage effect of the experimental drifts GEX and SMR1.1 has been investigated by means of 2D-vertical flow simulations.

Outside the EDZ/EdZ of the drifts (i.e. at most a few meters from the drift wall) the pressures measurements at PEP, DIR and SUG boreholes show that, once the perturbation impact of drilling declines, a quasi-stabilized pressure profile occurs, with a global pressure gradient directed towards the drift (drainage effect).

Transient single-phase (water) 2D vertical flow simulations were performed based on a simplified 2 homogeneous zones model: a first zone represents the EDZ/EdZ with an enhanced hydraulic conductivity compared to the intact rock. The second zone is the intact rock, with permeability values fixed at references as determined with the hydraulic tests (5x10⁻¹³ m/s). The drainage effect due to the drift is simulated by specifying an atmospheric pressure at the drift wall. Suction effects related to the lowered relative humidity due to ventilation are neglected, as they only impact the first few decimetres around the drift. The preliminary conclusions can be drawn from the flow simulation performed:
The simulated transient vertical and horizontal pressure profiles over the first half year of monitoring are consistent with the observed pressures. This indicates a good degree of consistency between the permeability determined on the 10 cm scale and the one at metric to decametric scale, which determines the pressure response due to the drainage effect of the drift.

However, at a later stage, a significant mismatch exists between the experimental data and the flow simulation: the observed time evolution of the pressure profile after around 6 months observation following the excavation of the drift, presents a very slow increase or decrease (less than 1 bar in 6 months); on the other hand, the simulations results predict much larger decrease over time (several bar in 6 months). This indicates that the conceptual model should be enriched with additional processes in order to better explain the observed pressures: several effects like mechanical compaction or perturbations in the nearfield of the boreholes might influence strongly the measurements and should be taken into account in a further interpretation step.

Globally, the results obtained in the study indicate that the permeability determined by the hydraulic tests in the boreholes on the several 10cm scale might represent an upper bound of the permeability at a larger scale in the Callovo-Oxfordian.

References:
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IN SITU DIFFUSION TESTS PERFORMED IN THE CALLOVO-OXFORDIAN MUDSTONE IN THE BURE URL: EXPERIMENTAL DATA AND NUMERICAL INTERPRETATIONS

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INTRODUCTION

Several countries (Switzerland, Belgium, France,…) are studying deep argillaceous formations as potential host rocks for radioactive waste disposal due to their confinement properties (low permeability and retention capacity of the rock), that are favourable to limit the migration of radionuclides. In such an environment, the transport is dominated by diffusion processes. To investigate and quantify the diffusion properties of the Callovo-Oxfordian argillite, studied in the French URL located at the limit of Meuse and Haute-Marne departments, seven vertical boreholes have been drilled by Andra in geological layers with different mineralogy (Illite/Smectite type R0 and Illite/Smectite type R1). Six short boreholes have been performed from the drifts of the URL and one deep borehole (EST208) has been carried out from the surface (Figure 1).

First, this paper presents the experimental data obtained from in situ tests that were monitored over one year and more. Secondly, it presents a first estimation of the diffusion coefficients that is based on the 1D radial modelling of the tracers’ concentrations decreases in the fluid circulating in contact with the rock.

EXPERIMENTAL CONCEPT

The tests are carried out in vertical down boreholes in whose a packed off interval is initially filled with synthetic water. To avoid a saline gradient, the composition of this synthetic water is close to that of the natural pore water. At the bottom of the borehole, the circulating synthetic water is in contact with the rock. Tracers are added to the synthetic water when chemical and hydrostatic equilibrium are roughly reached. The tracers injected are radioactive (HTO, ¹²⁵I, ³⁵Cl, ²²Na, ⁸⁵Sr, ¹³⁷Cs) and representative of the chemical and physical behaviours of the different radionuclides in the waste. A circulation pump is maintaining a homogeneous concentration of the tracers in the interval. Tracer contents in the circulating fluid are regularly measured by water sampling and analysing. The decrease of activities is monitored over time. At the end of the experiment, the rock around the injection chamber where tracers diffused, is retrieved by overcooring to analyse tracers’ concentration profiles within the rock. This last step is not yet performed in the Bure URL.

RESULTS AND INTERPRETATION

The decrease of the relative tracers’ activities versus time is different from one tracer to another due to its chemical or physical behaviour. Compared to tritiated water, which is considered as a reference, the relative activity of anionic species decreases more slowly. At the opposite, the relative activity of cationic species decreases faster than that of tritiated water. This is in good agreement with results obtained by...
through-diffusion experiments on samples of 1 cm width. This difference of behaviour could be explained by the anionic exclusion effect for anions and by the chemical retention for cations. For each tracer injected, we observe no significant difference of behaviour between I/S type R0 and I/S type R1 mineralogy. In a first approximation, without overcored samples, we can say that the ratio between smectite and illite content doesn’t influence much the diffusion properties (Figure 2).

A first estimation of the diffusion parameters was derived from the monitoring data set. The numerical model used is a radial code. The numerical interpretation shows that it is imperative to take into account a drilling disturbed zone around the borehole of 2-3 cm thickness with a higher porosity than the bulk rock. Beyond 3 cm around the wall of the borehole, the diffusion parameters obtained are consistent with those obtained from drill core samples and are representative of the undisturbed rock. The overcoring of the tests, analyses of the rock samples and data treatment using numerical inverse modelling, will allow us to consolidate this first interpretation.

References


Figure 2: Monitoring of the $^{134}$Cs relative activity versus time for both mineralogies of Callovo-Oxfordian geological formation.
INFLUENCE OF HUMIC COLLOIDS ON THE MIGRATION OF U(VI) IN COMPACTED CLAY

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Clay minerals and organic substances are widespread components of many soils, sediments, and rocks. As humic acids (HA) possess a strong ability for metal complexation, they can influence the migration of radioactive and toxic metal ions in clayey environments. However, the migration behavior of humic colloids and its impact on the actinide migration in clay formations is poorly understood.

Former studies discuss the influence of HA on the radionuclide migration in clays controversially. Wold and Eriksen [1] reported the diffusion of humic colloids through compacted bentonite without strong physical hindrance mobilizing metal ions. In contrast, Wang et al. [2] found a significant immobilization of Eu(III) by humic substances. Maes et al. [3] stressed the reversibility of the interaction between radionuclides, organic matter, and clay. The competition of the adsorbents for radionuclides is kinetic and determines their distribution between mobile and immobile phase.

In the present study we investigated the diffusion behavior of humic colloids in compacted clay as a function of compaction and pH. The impact on the uranium transport was studied by comparing the uranium diffusion in presence of HA.

Kaoinite KGa-1b and a \textsuperscript{14}C-labeled synthetic HA type M42 [4] in a 0.01 M NaClO\textsubscript{4} / 1 mM NaN\textsubscript{3} medium were used. We studied steady-state through-diffusion applying a constant concentration gradient. The clay was compacted in diffusion cells to bulk dry densities $\bar{d}$ of 1.32 to 1.67 g/cm$^3$ and equilibrated at pH 5 or 7. HA was used at a concentration of 12 mg/L. For the experiments involving U(VI), a UO\textsubscript{2}\textsuperscript{2+} concentration of 1-10$^{-6}$ M (238U) was used, whereas 239U was employed as tracer in the experiments with humic substances. The tracer activities in the high and low concentration reservoirs were periodically analyzed by liquid scintillation counting and by ICP-MS. After the end of the experiments, in-diffusion profiles of HA and uranium were taken. Modeling based on Fick’s second law yields the effective diffusion coefficient $D_e$ [m$^2$/s] and the rock capacity factor $\alpha$ [-].

The migration of HA in compacted kaoinite was found to be governed by diffusion. A constant diffusive flux established after a transient state of 8 to 30 days. The size distribution of HA in the high and low concentration reservoir suggests that the mean particle size shifts from 50 kD in the high to less than 1 kD in the low concentration reservoir. Only small HA molecules are able to pass the kaoinite pore system, which demonstrates a filtration of colloidal particles in the clay.

The effective diffusion coefficients decrease with increasing clay density. The values of HA ($5.1 \cdot 10^{-12}$ m$^2$/s to $1.2 \cdot 10^{-10}$ m$^2$/s) are always lower than those of HTO ((1.6 - 2.7) $\cdot 10^{-10}$ m$^2$/s). The effective diffusion coefficients of HA were found to be higher by a factor of four to six at pH 7 compared to pH 5. Here, differences in the free diffusion coefficients $D_e$ of the macro molecules are assumed. Lead et al. [5] observed an increase in the $D_e$ of Suwannee river humic acid by a factor of about 1.2 when increasing the pH from 5 to 7. This effect has been attributed to an aggregation of humic colloids at pH below 7. Surprisingly, a stronger adsorption of HA has been found at pH 7, where the electrostatic repulsion between the deprotonated HA and the negatively charged clay surface increases.
Figure 1: U and HA distribution in the clay plug at pH 5 (a) and pH 7 (b). (Absence of HA: 70 d (pH 5), 64 d (pH 7); presence of HA: 78 d (pH 5 and 7)).

The diffusing low molecular fraction of HA diffusing through the clay plug was not found to transport uranium within the experimental duration. Possibly, the uranyl humate complex dissociates in the pore system due to competition between humate and surface complexes. Alternatively, the mobile low molecular HA fraction is not able to complex U(VI) due to structural and functional dissimilarities.

The in-diffusion profiles of both tracers are illustrated in Fig. 1. HA is immobilized at the high concentration boundary. In presence of HA, the U(VI) concentration is permanently lower compared to the HA free system (see insets in Fig. 1). The bulk of U(VI) is immobilized in association with HA at the solution-clay boundary. Comparing pH 5 and pH 7, a deeper penetration of U(VI) was observed at pH 5. This is in concordance with the penetration depth of HA, the complexing agent, and U(VI) in absence of HA. From the diffusion profiles of U(VI) in presence of HA it becomes clear that HA penetrates the clay deeper than U(VI) (see Fig. 1). This is in agreement with the observed through-diffusion behavior of the low molecular HA fraction.

The migration of HA in clay is governed by diffusion. It is influenced by the colloidal behavior of HA. At higher clay bulk densities, size fractionation affects the diffusion parameters. In presence of HA colloids U(VI) is immobilized in association with HA near the high concentration boundary.

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References
DIFFUSION OF TRITIATED WATER AND IONS THROUGH THE TOURNEMIRE ARGILLITE (FRANCE) IN PRESENCE OF ALKALINE FLUIDS

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High-pH plumes arising from cementitious leachates are known to alter the mineral assemblage of clayey formations selected to play the role of natural barriers for radioactive waste repositories. Dissolution of constitutive minerals such as smectite and precipitation of secondary phases such as feldspar and zeolite have been reported [1, 2]. These mineral changes are suspected to have a significant effect upon diffusive transport properties, either enhancing or decreasing the mudrock ability for radionuclide confinement. For instance, experiments performed under alkaline conditions have shown a decrease in water diffusion fluxes and an increase in cation fluxes [3].

This study was designed to provide better understanding of the phenomena that govern diffusion processes during the transition between site and alkaline conditions. Experiments involving the use of “through-diffusion” cells were performed to mimic the proceeding of an alkaline plume through different types of clayey materials from the Tournemire experimental site (France). Three kinds of sliced rock material were investigated for the diffusion of both water and major cations (sodium, potassium, calcium and magnesium): i) an unfractured sample, ii) a sample with an opened fracture and iii) a sample with a large tectonic fracture.

An equilibration procedure was required to i) (re-)saturate the rock with water and ii) force its equilibration with a synthetic solution prior to diffusion experiments. It was performed by renewed contacting of the clayey samples with the synthetic background solution every two weeks. The procedure was to be stopped when the composition of the withdrawn solution was similar to that imposed by the synthetic solution, i.e. re-equilibration between the rock and the solution was completed. Once the equilibration steps completed, tritiated water (HTO) considered as a reference species was introduced in the upstream reservoir in order to deduce the HTO diffusion coefficient.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure1.png}
\caption{Photographs of sliced samples (Ø = 6.3 cm) used in the through diffusion cells and displaying: (a) no fractures; (b) an opened fracture (OF); (c) a large tectonic fracture (TF).}
\end{figure}
through each sample. The process for alkaline water diffusions was then somewhat different from the so-called “through-diffusion” process designed to determine the transport parameters of a diffusing species in steady chemical conditions throughout the system (reservoirs + sample). In the experiments presented here, the initial solutions in the upstream and downstream reservoirs were different. Steady chemical conditions were maintained in the upstream reservoir filled with cementitious alkaline solutions (pH 13.5) while the downstream reservoir, initially filled with a synthetic site solution, was left free of any particular constraint. Hence, the composition of the downstream solution was expected to evolve until it reached that of the input alkaline solution, eventually forcing the whole system to equilibrate with it. At last, tritiated water was introduced in the upstream reservoir in order to deduce the evolution of diffusion coefficients for HTO after alkaline fluid diffusion. Microscopic investigations of the solid before and after alteration by the diffusion experiments were also performed for assessing the role of mineral alteration on diffusion processes.

Monitoring of the pH and the concentrations of the major cations showed rapid evolution in the downstream reservoirs. pH and alkaline cations concentrations increased until reaching the values prescribed by the composition of the alkaline solution. Alkaline-earth cations evolved quite differently: their concentrations drastically dropped, probably due to precipitation of carbonate phases.

Diffusion coefficients for HTO decreased of around 30% during the alkaline diffusion process. The pH and the concentrations of major cations were satisfactorily fitted by a geochemical model (PhreeqC…) that combines retention (via cation exchange on a multi-site ion exchanger), dissolution/precipitation of various phases (clays, carbonates,…) and transport (as Fick’s laws description). An evaluation of diffusion coefficients for hydroxyle and the studied cations was proposed.

No significant differences could be observed between the zones displaying no fractures or an opened fracture, showing that the discontinuities induced by the excavation works were readily sealed by the swelling property of the clayey rock when fully hydrated. The tectonic fractured- zone slice showed larger heterogeneity than the two previous samples: it was assumed that the occurrence of calcite and pyrite veins in this zone plays a role in the diffusion processes inasmuch as these minerals reduce both porosity and cation exchange capacity of the stone rock.

References:
REACTIVE TRANSPORT MODELLING
OF IN SITU CEMENT/CLAY INTERACTIONS
ON TOURNEMIRE ARGILLITE

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CONTEXT AND OBJECTIVES
Disposal concepts currently developed in France to host long-lived high-level radioactive waste contain large amounts of cementitious materials. The cement matrix is in strong disequilibrium with the geochemical conditions which prevail in the argillaceous host rock. IRSN has developed an experimental program, which includes the characterisation of so called “engineered analogues” sampled at the Tournemire tunnel site (France), in order to evaluate the perturbations of clays due to the presence of concrete. Argillite samples which experienced 15 years of cement/clay interactions were collected in that purpose by overcoming a vertical borehole sealed by concrete. The upper part of the borehole (sampled between 1 m and 1.30 m in depth), which intersects the EDZ of the main tunnel is slowly drained by water seeping from a small canal located under the tunnel roadbed. The lower part of the borehole (sampled between 1.55 m and 2.60 m) is more representative of argillite/concrete interactions in confined conditions.

The aim of the present modelling study is to simulate the main observations made by a first characterisation stage (Tinseau et al., 2006), which has notably highlighted several fronts of perturbations as well as a potential influence of microstructures as preferential pathways. The microstructures are either unloading joints of the tunnel EDZ or cracks parallel to the bedding all along the borehole. Recent and complementary experimental observations are also discussed in an associated communication at this conference (see Tinseau et al., 2007). Topical background questions concern the balance between kinetic (time-dependent) mechanisms versus local equilibrium reactions and the effects of cement/clay interactions on micro-texture and transport parameters (e.g. crack clogging).

MODELLING FEATURES
The CEM II concrete, which fills the borehole, was modelled by a mixture of 35% Portland cement phases (CSH, sulfo-aluminates and CSH) and 65% calcareous aggregates (calcite) by weight. The interstitial water is a K–Na–OH fluid of pH 13.2 (at 15°C, the average temperature within the tunnel). The argillite in its unperturbed state has a high content in clay minerals, mainly illite (22.5%), interstratified illite/smectite (20%) and kaolinite (12.5%); quartz (27%), K-feldspar (5%), calcite (9.5%), dolomite (0.5%) and pyrite (3%) were also taken into account in the simulations. The pore water has a pH of 8.3 with sodium, chloride and bicarbonate as major ions.

The reactive transport code HYTEC (van der Lee et al., 2003) was used to simulate the perturbation of the argillite around the borehole, considering diffusive transport of solutes and chemical reactions (aqueous chemistry and dissolution/precipitation). An explicit representation of the argillite cracks was found to be more appropriate than a dual porosity approach to investigate the precipitation reactions taking place inside the cracks and the coupling with the argillite matrix alteration. Effective diffusion coefficient values were fixed in a first step of the modelling, then updated with respect to the calculated local porosity change to assess the sealing process. A time-dependent, kinetic formulation was introduced for all dissolution and precipitation reactions. This kinetic formulation depends on the saturation state of minerals, pH and oxygen content (the later, for pyrite oxidation only). The intrinsic rate constants were taken from literature (e.g. Savage et al., 2002). In addition, a sensitivity analysis was performed to the reactive surface areas as well as to rate constants.
FIRST RESULTS
Preliminary calculated sequences of cement/clay interaction is in fair agreement with the mineralogical evolution observed in the upper part of the borehole with dissolution of quartz, massive precipitation of both calcite and dolomite, moderate formation of potassic feldspars and sodic zeolites. The last two minerals correspond to the first stages of the alkaline perturbation characterized by Na-K-OH fluids (though formation of calcic zeolites is also predicted by modelling). Calcite is by far the most common secondary phase, present as a crust at the cement/clay interface as well as deeper within the host rock. The precipitation of dolomite is thought to be specific to this situation since the water seeping through the EDZ has a Ca-Mg bicarbonate source. Kaolinite dissolution and CSH precipitation should also occur according to calculations but were not clearly pointed out by the first characterisation stage. Typical pyrite oxidation patterns, yielding Fe-oxyhydroxide precipitation, were obtained both by analysis and calculation. Alkaline and oxidative perturbations did not seem to interfere between each others, that is to say without forming any mixed alteration products such as nontronites. This statement is still under investigation.

In the lower part of the borehole, experimental characterisation of a typical argillite crack highlighted three successive front zones: precipitation of crusty calcite close to the concrete (0.5 cm width), followed by neoformation of illite/smectite mixed-layers (1 cm), and finally calcite and feldspar overgrowths (1 cm). Preliminary modelling results seem to be significantly different from the experimental ones. Calcite precipitation is spread all over the crack, the second and third mineralogical fronts seem to be switched by comparison to the in situ observations and zeolites are found to be important secondary phases. Study is in progress to better understand the origin of the discrepancies between experimental and modelling results.

References
Tinseau et al. (2007), this book of abstracts.
RESULTS ON PU DIFFUSION EXPERIMENTS IN THE OPALINUS CLAY

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The Opalinus Clay (OPA) is a potential host rock for a repository for spent fuel, vitrified high-level waste and long-lived intermediate-level waste in Switzerland. Owing to its small hydraulic conductivity (10^{-14} - 10^{-13} m^2/s), it is expected that transport of solutes will be dominated by diffusion. Diffusion coefficients are very sensitive parameters in performance assessment (PA). The diffusion process is well understood for non-retarded solutes with simple chemistry, but little is known for retarded solutes such as strongly sorbing actinides. Therefore, the objective of this work is to understand the Pu diffusion in clay mineral-rich geological samples in order to provide support for improved representation of these processes in PA and to enhance safety case credibility.

A sample cell - autoclave system (SCAS) was developed for carrying out actinide diffusion experiments in clay stones under their natural, confining pressure (Fig. 1). To verify our SCAS we performed HTO diffusion experiments. The effective diffusion coefficients of the OPA perpendicular to bedding was found to be 1.6 x 10^{-11} m^2/s, which is in good agreement with the value determined by Van Loon et al., 2003. According to the results of batch sorption data, a strong 239Pu sorption under the experimental conditions of the diffusion experiment is expected. After termination of the diffusion experiments the clay core was cut for autoradiography in two pieces perpendicular to the bedding plane. Autoradiography revealed a very

**Figure 1:** FZK-INE diffusion cell.
heterogeneous distribution of $^{238}$Pu on the inlet surface of the clay sample and also along the cut cross section. In the OPA porewater Pu(V) dominates speciation. If the OPA porewater is circulated over the clay inlet surface, Pu(IV) becomes dominant.

These ongoing investigations will provide the necessary basis for credible description of sorbing radionuclide mobility in clay for the nuclear waste disposal safety case.

Reference:
DIFFUSION OF H$_2$O AND ELECTRO-OSMOSIS IN WATER-SATURATED COMPACTED NA-MONTMORILLONITE USING H$_2^{18}$O AS A TRACER

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INTRODUCTION

Compacted bentonite will be used as buffer material in Japanese high-level radioactive waste disposal. The material has high sorption coefficients based on cation exchange and quite low hydraulic permeability resulting in diffusion control. Therefore, the properties are quite suitable for long-term safety assessment. The mechanistic understanding of cation diffusion is still needed for the assessment and design of an engineered barrier system using the bentonite, in which the thermodynamic and kinetic properties of water and ions existing in interlayer and pore in the bentonite are quite important. In the present study, the kinetic behavior of water, such as migration rate and broadening, was studied by diffusion, electromigration, and electro-osmosis, using H$_2^{18}$O as a tracer.

EXPERIMENTAL

Sodium montmorillonite (Kunipia F) powder was used to prepare the water-saturated compacted montmorillonite. The powder was dried and compacted into pellets of 20 mm in diameter and 20 mm in depth with having dry densities of 1.0, 1.2, and 1.4 Mg/m$^3$. The pellets sandwiched with sintered stainless-steel filters in acrylic cells were immersed in a 0.1 M NaClO$_3$ solution. They were kept for 30 days to saturate the montmorillonite with the solution after evacuation to remove gas. Then some of the pellets were equilibrated with H$_2^{18}$O enriched water. Couples of a H$_2^{18}$O enriched pellet and a normal pellet were used as specimens for the diffusion experiments. The couples were kept at 298 K for 24 h to allow to diffuse H$_2^{18}$O. On the other hand, the specimens for the electro-osmosis experiments consist of two H$_2^{18}$O enriched pellets and two normal pellets in series. The experimental setup for electro-osmosis is given elsewhere [1]. A constant current of 20 mA was applied to the series of the pellets as the H$_2^{18}$O enriched ones are in the anode side and the ones including normal water are in the cathode side. The polarization was carried out for 4-6 h at 298 K. The electric potential gradient was 260 V/m, which was checked using reference Ag/AgCl electrodes in the initial stage of experiments. After the diffusion or electro-osmosis experiments, concentration of H$_2^{18}$O was measured as a function of distance from the contact plane between the H$_2^{18}$O enriched and normal pellets by isotope fractionation.

RESULTS AND DISCUSSION

Figure 1 shows an example of the concentration profiles of H$_2^{18}$O for the dry density of 1.0 Mg/m$^3$ obtained after applying the electric potential gradient. It indicates an electro-osmotic flow toward the cathode in the montmorillonite. The profile is well described by the following advection-dispersion equation,
\[ \frac{\partial C(x,t)}{\partial t} = D_h \frac{\partial^2 C(x,t)}{\partial x^2} - V \frac{\partial C(x,t)}{\partial x} \]  

(1)

where \( C(x,t) \) is the concentration at distance, \( x \), from the contact plane and time, \( t \). Hydraulic dispersion coefficient and advection velocity of \( H_2^{18}O \) are given by \( D_h \) and \( V \), respectively. The concentration profiles of \( Na^+ \) and \( Cl^- \) under electric potential gradient were reported by Higashihara et al. [1] [2]. In order to compare migration behavior in the montmorillonite among species, especially from the view point of electric property, the concentration profiles of \( H_2^{18}O \), \( ^{22}Na^+ \) [1], \( He \) [1] and \( ^{36}Cl^- \) [2] are shown as advection-dispersion from plane source (Fig. 2). The width of the peak corresponds to the hydraulic dispersion. Hydraulic dispersion consists of the two different processes; one is molecular diffusion including sorption and the other is mechanical dispersion. Therefore, a hydraulic dispersion coefficient \( D_h \) can be obtained from the sum of a coefficient of mechanical dispersion \( D_m \) and molecular diffusion coefficient \( D_a \).

\[ D_h = D_a + D_m \]  

(2)

\( D_a \) is related to the velocity of a chemical species, as follows.

\[ D_m = \alpha V \]  

(3)

where \( \alpha \) is the dispersivity parameter of a species and reflects the hydraulic properties of the porous medium for migration of chemical species. Hydraulic dispersion coefficient of \( He \) was definitely larger than that of \( H_2^{18}O \) whose dispersion coefficient is slightly larger than that of \( ^{36}Cl^- \), and much larger than that of \( ^{22}Na^+ \). This fact results from the difference of the dispersivity parameters among chemical species and implies that electrically positive \( ^{22}Na^+ \), negative \( ^{36}Cl^- \) and neutral \( He \) migrated in different paths in water-saturated compacted Na-montmorillonite. The migration paths of the species will be discussed.

References
DETERMINISTIC AND PROBABILISTIC COMPART-MENTAL MODELLING OF NITRATE REDUCTION AND TRANSFER IN A BITUMINOUS WASTE CELL AND THE ADJACENT HOST ROCK

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INTRODUCTION
The oxidation state of radionuclides is of general importance to waste management, regardless of waste type, activity or proposed disposal option. A variety of radionuclides is known to have a higher mobility in the oxidised form compared to the reduced form. U(VI) vs. U(IV), Se(VI) vs. Se(IV) or Tc (VII) vs. Tc(IV) are well known examples. The oxidation state within the waste remains somewhat uncertain. The category of medium activity long lived waste, called B2 waste at Andra, results from the chemical treatment of radionuclides with different reactants, among them nitrates and sulphates. The presence of nitric acid and the generally oxidising conditions of most waste treatment steps, make an oxidized form for redox-sensitive radionuclides more likely. The precipitate is stabilised using bitumen and poured into steel containers. In the Andra Dossier 2005 concept 4 of these primary waste containers are accommodated by a rectangular cement overpack of which 16 fit into the cross section of a B2 waste cell (Figure 1).

After closure of the waste cell, the near-field will slowly start to re-saturate with H₂O passing through the cement engineered barrier and the overpack and then through the permeable lid of the steel containers to contact the nitrate - bitumen mixture, but nitrate dissolution initiates only when relative humidity reaches a value of 74%. The presence of nitrates in solution will have a significant impact on the redox conditions and therefore on the oxidation state of radionuclides released from the waste. Quantifying nitrate reduction and their transport is the main goal of this modelling study. Possible electron donors present in the near-field are indicated in Table 1, with Fe³⁺ as part of the steel container, the two organic molecules representing bitumen and formic acid, the latter an example of the principal bitumen degradation products. Hydrogen gas is produced via radiolysis of the bitumen and via anaerobic corrosion of iron with H⁺ as electron acceptor. Extensive research on nitrates in the biosphere indicates the impact of bacteria on reduction reactions with extremely slow kinetic under sterile conditions (Devlin et al., 2000).

MODELLING CONCEPT
The behaviour of nitrates within a B2 waste cell is quantified using a 1D compartmental approach, with a source compartment represented by the steel waste container, an interface zone between the latter and the cement overpack, a number of cement compartments representing overpack and engineered barrier, a second interface zone between cement and the argillite and finally a series of compartments within the geologic barrier. Inter compartmental fluxes are quantified based on a combined Fickian and mass balance approach. Estimation of electron donor and acceptor concentrations within compartments are based on relevant redox reactions (Tab. 1). Reaction kinetics are considered to be essentially controlled by bacterial respiration, modelled using maximum kinetics influenced by bacterial growth, reaction thermodynamics and the reactant and product concentrations (Jin et Bethke, 2005). Bacterial reactions are assumed to occur principally in the two interface zones, suppressed in the cement compartments by the high pH and in the pristine argillite by the lack of space. Parameter values controlling diffusion and kinetics remain tagged...
Table 1: Cross section of a B2 waste disposal cell showing both the coating and filling cement as well as the support layer at the interface cement - argillite.

Tableau 1: Examples of redox equations governing the reduction of nitrate in the near field.

<table>
<thead>
<tr>
<th>Equation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1) $5 \text{Fe}^3+ + 2\text{NO}_3^- + 6 \text{H}_2\text{O} \rightarrow 5 \text{Fe}^{2+} + \text{N}_2 + 12 \text{OH}^-$</td>
<td></td>
</tr>
<tr>
<td>(2) $\text{C}_4\text{H}_4(\text{CH}_2)_2\text{CH}_3 + 10.8 \text{NO}_3^- + 10.8 \text{H}^+ \rightarrow 10 \text{CO}_2 + 5.4 \text{N}_2 + 12.4 \text{H}_2\text{O}$</td>
<td></td>
</tr>
<tr>
<td>(3) $\text{HCOOH} + 0.4 \text{NO}_3^- + 0.4 \text{H}^+ \rightarrow \text{CO}_2 + 1.2 \text{H}_2\text{O} + 0.2 \text{N}_2$</td>
<td></td>
</tr>
<tr>
<td>(4) $5 \text{H}_2 + 2 \text{NO}_3^- + 2 \text{H}^+ \rightarrow \text{N}_2 + 6 \text{H}_2\text{O}$</td>
<td></td>
</tr>
</tbody>
</table>

with significant uncertainties, which is why we have chosen a simplified model approach which allows extensive Monte Carlo type simulations and associated parameter and uncertainty estimations.

RESULTS AND INTERPRETATION

Pilot model simulations using only organic matter as electron donor for nitrate reduction indicate the importance of three sets of parameters (1) for the degradation kinetics of bitumen (2) for diffusion of both organic matter and nitrates and (3) for determination of maximum bacteria-controlled reaction kinetics. The large abundance of nitrates in the system coupled with bacterial activities restricted to small interface zones explains the probable diffusion of nitrates into the geologic barrier formation.

This simplified model approach has been designed to integrate the combined quantitative knowledge about a complex transport/transformation process. Results of pilot simulations as well as ongoing and planned calculations will help to give direction to both more complex modelling approaches as well as the experimental work destined to reduce parameter uncertainties. In a more comprehensive approach for the system of our study André et al. (companion paper) apply diffusive transport combined with thermo-kinetic modelling.

References:


EXPERIMENTAL STUDY ON GAS PERMEABILITY OF THE CALLOVO-OXFORDIAN ARGILLITE OF MHM

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INTRODUCTION
The very low permeability of the Callovo-Oxfordian argillite formation of MHM (the Meuse/Haute-Marne, France), which is approximately 500 m deep and 130 m thick, is its principal advantage as a medium for waste disposal. Because the permeability depends on the geometry and connectivity of pores, the change in permeability is a representative parameter indicating the structural changes. One can determine the extension and amplitude of disturbance or damage zone around drift by considering the evolution of permeability. Based on this consideration, a transient method of gas permeability on very low permeability rock is developed. Measurements on some samples obtained from the underground research laboratory (URL) of MHM site are realised.

EXPERIMENTAL METHOD AND CONDITION
Transient method has been employed widely in the laboratory and in field to measure the hydraulic properties of rock with low permeability.

Basing on this method, a measurement as illustrated in Fig. A has been designed in the laboratory C.G.I. The measurement consists of a triaxial cell connected to two gas vessels. After the uniform of gas pressure in the system, an incremental pressure between two vessels is applied in the upstream vessel. We choose argon and helium as the gas inert in our tests. The gas pressures are recorded by the captures. The loading and unloading test is possible to realize in this system by GDS. A linear voltage displacement transducer (LVDT) measures axial displacement. The variation of temperature is well controlled in the range of +/- 0.1°C in order to reduce the affect of temperature. After the calibration of system, the minimum permeability that could be measured was determined to be $10^{-21}$m².

For characterising the damage induced by the excavation, argillite cores samples were taken from the different distances (0.07m to 12.73m) to the wall of the main access shaft of the MHM URL. The diameter of samples is about 40mm and their height ranges from 26.20mm to 52.46mm. The confining pressure keeps constant (9MPa or 11MPa) and the axial pressure ranges from 11MPa to 28MPa.

EXPERIMENTAL RESULTS AND INTERPRETATION
Permeability measured on the referenced sample (far away from the wall of the shaft) ranges from $3.10^{-21}$ to $2.10^{-22}$m² under axial loading cycle. This indicates that the permeability decreases with the increasing of the deviatoric stress and the unloading of axial stress show that the permeability reduction is irreversible. (Fig. B). The permeability between the reference sample and the sample near the wall of the shaft doesn’t change significantly, which indicates that the micro-cracks in the near filed induced by excavation of the shaft are very limited.

In order to comprehend the mechanism of transfer of gas within in situ water content samples, we carefully check the changes in mass of samples before and after test. Firstly, we observe the surface connected to the upstream vessel is drier than that connected to the downstream vessel. This difference of humidity at the level of sample faces confirms that the transfer of gas can induce the flow of pore water even if the
difference of applied gas pressure is low (less than 0.5 MPa). Accurate measurements on sample weight and ceramic porous stone weight have been taken and simulations on the mechanism agree with experimental results. The lost weight of pore water relative to the initial weight of pore water is little. It shows that a) the desiccation of sample is negligible in triaxial cell test conditions b) the final change of water content is not linked to water vapour flow exchanges between gas flow and pore water c) it is related to an induced convective flow of liquid pore.

We want also highlight result of one of the tests where the sample was fractured during the loading phase. The origin of the rupture is an artefact of the sample and it is not related to its mechanical behaviour. The measurement of axial strain allows identifying the rupture event during the test, but this is not possible by analyzing permeability measurements. This shows that under the used confining pressure (11 MPa), even if fracture network is continuous form one face to the other, flow of gas is not dramatically increased. One can conclude that closure of fractures under in situ mean stress doesn’t change the global gas permeability of samples with in-situ water content.

Further investigations are necessary for more complete measurements of effective gas permeability of wetted samples by fixing the initial water saturation of samples over large range of saturations.

Reference


GAS INTRUSION IN SATURATED BENTONITE – A THERMODYNAMIC APPROACH

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A thermodynamic description of the response of a saturated bentonite system to changes in external variables has successfully been adopted in several different cases. Examples include correspondence between swelling pressure and water retention properties of unconfined bentonite (Bucher and Müller-Vonmoos, 1989), pressure response due to changes in salt concentration of an external solution (Karmland et al., 2005) and the description of the behavior of confined bentonite below 0°C. In the present work the same thermodynamic framework is used as a starting point for describing gas intrusion in saturated bentonite.

The response to changes in external variables (water pressure, gas pressure, temperature, salinity etc) of a confined bentonite system penetrable to water is a matter of equalization of the chemical potentials of water in the clay and water external to the system. The chemical potential of clay water under isothermal conditions and without added solutes is

\[ \mu_{\text{clay}}(w) = \mu^0 + RT \ln RH_{\text{unconf}}(w) + P \cdot v_w \]

Where \( \mu^0 \) is a reference chemical potential for bulk water in equilibrium with its vapor pressure at the considered temperature, \( RH_{\text{unconf}}(w) \) is a function describing equilibrium relative humidity for the unconfined clay with water content. Here the molar volume of clay water is assumed to be equal to the bulk value, \( v_w \), and independent of pressure.

A homogenous, isotropic model of bentonite is presented which is completely defined by the curve \( RH_{\text{unconf}}(w) \), and the water content at saturation, \( w_{\text{sat}} \). Total pressure at equilibrium in this model is

\[ P_{\text{TOT}}(P_g, P_l) = \begin{cases} P_S + P_l & \text{saturated} \\ P_g & \text{unsaturated} \end{cases} \]

where

\[ P_s = -\frac{RT}{v_w} \ln RH(w_{\text{sat}}) \]

\( P_g > 0 \) is gas pressure and the chemical potential of external water is

\[ \mu = \mu^0 + P_l \cdot v_w \]

which defines liquid pressure, \( P_l \), when \( \mu - \mu^0 < 0 \). The criterion for saturation is \( P_S > P_g - P_l \equiv s \), where \( s \) denotes suction.

It should be noted that the present model is based on thermodynamic equilibrium in a rather strict sense which is not achieved in experiments where the initial state is unsaturated. E.g. the stress build-up in a infiltration test do not follow the equation for total pressure from above. On the other hand, it can be argued based on experimental facts that the model is relevant to adopt when describing gas entry events, where the initial state is a water-saturated system.
The presented theory is exemplified by a modeling of two gas migration experiments using Code_Bright, a 2-phase FEM-code for mass, energy and momentum balance in porous media (CIMNE, 2000). Quantitative agreement with experiment is achieved when adopting a Gas Entry Value (GEV) retention curve, i.e. a constitutive equation relating liquid saturation, , and suction with the property that

\[ S_i(s) = 1 \text{ for all } s \leq P_s. \]

An example of results from such a modeling is presented in Figure 1.

![Diagram](image.png)

**Figure 1:** Results of modeling of gas migration experiments by Horseman and Harrington, 1997. A breakthrough event occurs around day 7, and the gas inflow is turned off at day 14. The Code_Bright model, based on the presented theory, successfully captures the breakthrough, and the subsequent flow rate and pressure level evolution.

**References**


CIMNE, (2000). CODE_BRIGHT. A 3-D program for thermo-hydro-mechanical analysis in geological media. Departamento de Ingenieria del Terreno; Cartografica y Geofisica, UPC, Barcelona, Spain


EVALUATING THE APPLICATION OF ARCHIE’S LAW FOR ARGILLACEOUS ROCKS

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INTRODUCTION
Diffusion is an important transport process in geological systems. Hence, for the safety assessment of potential radioactive waste repositories that might be build in such geological systems, effective diffusion coefficients of various species need to be known. The effective diffusion coefficients strongly depend on porosity. Moreover, previous studies could demonstrate that the effective diffusion coefficients can be estimated using Archie’s law:

\[ D_e = D_{eq} \cdot \varepsilon^m \]  

(1)

where \( D_e \) is the effective diffusion coefficient, \( D_{eq} \) is the diffusion coefficient in bulk water, \( \varepsilon \) is the transport porosity and \( m \) represents an empirical constant depending on the type of porous medium. Boving & Grathwohl (2001) studied the diffusion of iodide (I) in different limestone and sandstone rocks. The exponent \( m \) that fitted the data the best was approximately 2.2. Another study, which focused on chalk, showed that the data for various inorganic and organic compounds resulted in an exponent of around 2.4 (Blum, 2000). A few studies also considered the application of Archie’s law for diffusion in argillaceous rocks. Grathwohl (1998) studied the diffusion of tetrachloroethene (TCE) in natural clays (Figure 1). A good fit with Archie’s law was obtained using the transport-through porosity.

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**Figure 1:** (a) Normalized diffusion coefficient (\( D' \)) of TCE versus overall porosity. (b) Normalized diffusion coefficient (\( D' \)) of TCE versus corrected porosity based on water adsorbed onto dry samples at a relative humidity of 98.8%. The lines represent Archie’s law. km5: Triassic clay (Knollenmergel); ssc: silty-clayey soil; bav: Jurassic clays (Opalinus Clay, Dogger \( \alpha \)); la1: Jurassic clay (Lias \( \alpha 1 \)); aben: activated bentonite.
Furthermore, Van Loon et al. (2003) studied effective diffusion coefficients of tritiated water (HTO) in Opalinus Clay and compared their results with effective diffusion coefficients of HTO for a series of argillaceous rocks (e.g. London Clay, Boom Clay, Wellenberg Marl, Tournemire Toarcian shale). They concluded that the effective diffusion coefficients can be satisfactorily described using Archie’s law with an exponent of around 2.5.

DATA ANALYSIS
Both dissimilar data sets (Grathwohl, 1998; Van Loon et al., 2003) indicate that Archie’s law might be applied for the estimation of the effective diffusion coefficients in argillaceous rocks. However, the value of the accessible or transport-through porosity, respectively, is often not known and therefore Archie’s law will result in imprecise estimates for effective diffusion coefficients. Hence, in the current study, data on effective diffusion coefficients and transport porosities will be collected from diffusion studies (e.g. Henrion et al., 1991; De Cannière et al., 1996; Decostes et al., 2007) performed on various argillaceous rocks (e.g. Opalinus Clay, Callovo-Oxfordian argillites and Boom Clay).

RESULTS AND INTERPRETATION
Comprehensive data sets on diffusion of different tracers (anions, cations and neutral species) in argillaceous rocks will be presented and the applicability of Archie’s law for clays and clay stones will be thoroughly discussed in context of the diffusion (or transport) accessible porosity. The relevance for safety assessment of potential radioactive waste repositories will be highlighted.

References:
COMPARISON BETWEEN RADIAL DIFFUSION AND LEACHING FOR DETERMINING CHLORIDE AND SULPHATE IN TOURNEMIRE ARGILLITE PORE WATER


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INTRODUCTION

Argillaceous rocks are considered as potential host rocks for radioactive waste repositories. The French Institute of Radioprotection and Nuclear Safety (IRSN) develops experimental research programs in such geological formations at the Tournemire site (Aveyron, France). One of the objectives of this project is to evaluate the radionuclide migration through an argillaceous formation (argillites+marls) similar to those studied elsewhere for radioactive waste disposal. In order to estimate the confinement properties of such rocks, it is crucial to characterize the chemical composition of their pore water and its possible vertical variation. Because the argillite porosity is very low (less than 10%) it is impossible to extract directly the water from the rock sample. Therefore, in the present study, we focused on the determination of mobile anion contents (sulphate and chloride) by means of two indirect approaches: the first one based on diffusion and the second one on leaching. After comparing both methods on a single stratigraphic level, we investigated the vertical distribution of anion contents from the upper Toarcian level down to the lower calcareous aquifer.

EXPERIMENTAL CONCEPT

The comparison between the out-diffusion method and the leaching method was carried out on samples collected from an argon-drilled borehole, located in the upper Toarcian level. The samples were immediately sealed in evacuated Al-coated plastic bags under an argon atmosphere and stored in a glove box to limit oxidation of pyrite which could induce an increase of the sulphate amount in the pore water. For the same reasons, all further handlings were carried out in a glove box (~1 ppm O₂).

Radial diffusion cells whose design is described in Savoye et al. (2006) were filled with a synthetic solution (i) with a chemical composition as close as possible to that of the pore water and (ii) spiked with bromide in order to estimate the anion accessible porosity. Anion concentrations were monitored until achievement of equilibrium. At this stage, the concentrations of all major dissolved cations (Na⁺, K⁺, Ca²⁺, Mg²⁺) and anions (Br, Cl, SO₄²⁻, HCO₃⁻/CO₃²⁻) were measured in order to verify the charge balance.

Leaching experiments were performed with deionised water in a glove box with controlled partial pressure of CO₂ equal to 10⁻² atm, which is assumed to correspond to the in situ condition (Beaucaire et al., submitted). The leaching experiments lasted either 24 hours, 7 or 21 days and four solid/liquid ratios, i.e. 0.04, 0.25, 0.6 and 1 g/g, were investigated.
RESULTS
Results show that, on one hand, chloride and sulphate concentrations per kg of rock are identical whatever the solid/liquid ratios and, in the other hand these values are higher than those obtained from radial diffusion. The discrepancy between the two types of methods suggests the following remarks: (i) the anions removed by leaching argillite powder (< 100μm) would not only come from the pore water but also from a second source such as chlorine- or sulphur-bearing minerals, (ii) the contribution of this last source is limited in the radial diffusion method because keeping the rock sample intact (no grounding) prevents the fluid from leaching large reactive mineral surfaces. In addition, it can be mentioned that the radial diffusion method also allows the determination of the argillite anion-accessible porosity, necessary for calculating the mobile anion concentrations in pore water.

For all these reasons, the radial diffusion method was chosen for determining the vertical distribution of mobile anions from the tunnel down to the lower calcareous aquifer by means of a 250m deep borehole recently drilled (winter 2006/2007).

References

A CROSS METHOD OF A NANOSCALE MODEL AND MACROSCOPIC DATA TO ESTIMATE ANION EFFECTIVE DIFFUSION COEFFICIENT IN ARGILLITE

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The Callovo-Oxfordian argillite of the Paris Basin has been proposed as a potential host rock for deep radioactive waste. Because of very low measured permeability, diffusion is assumed to be the main transport mechanism for solute migration. As $^{36}$Cl, $^{131}$I, and SeO$_4^{2-}$ are considered to be the major contributors to the calculated dose rate associated with the long term underground disposal of nuclear waste, this study will focus on the diffusion of anionic species in clayey materials. Such species experimentally exhibits slower diffusion compared to water due to anionic exclusion arising from the negatively charged clay surfaces.

In such materials, the diffusion behaviour of anionic species is known to be related to the diffusion properties of the clayey matrix. The aim of this study is to determine the effective diffusion coefficient of chloride relatively to that of water in argillite at the micrometer scale taking into account the interfacial phenomena in clay due to its negatively charged surface.

A finite element COMSOL Multiphysics code is used to model the diffusion of a species in a 2-D porous media at the nanometric scale. This model correlates the effective diffusion coefficient of anion relatively to that of water in clay to a unique pore size, the ionic strength and the counter-ion valency of the pore solution [1].

Through-diffusion experiments have been carried out on illite clay equilibrated with KClO$_4$ solution. The effective diffusion coefficient of D$_2$O and Cl$,\ Br$, I have been measured for ionic strengths from 0.001 to 0.1 Mol/L. The pore size distribution is obtained by N$_2$ adsorption allowing measurements of pore sizes lower than 180 nm where influence of electrical double layers is likely to occur. CEC and zeta potential have also been determined. All this data have been used to implement an up-scaling method which takes into account the scattering of pore sizes of the clay. The parametric study performed with the nanometric model showed that the pore size is one of the main factors influencing anionic exclusion [1]. The geometrical variability of the clay in terms of pore size distribution is converted to a distribution of effective diffusion coefficient which is randomly implemented into the clayey matrix (figure 1).

In a second step, the up-scaling method is extended to one argillite sample from the Callovo-Oxfordian. Through-diffusion experiments are combined with 2-D mineralogical mapping of a sample of Callovo-Oxfordian argillite obtained by scanning electron microscopy and LIBS microprobe [2]. The three major minerals are identified: carbonates, tectosilicates and phyllosilicates. Carbonates and tectosilicates are described as a non porous media and effective diffusion coefficients are distributed all over the identified clay mineral (figure 1).
Figure 1: Up-scaling method.

References:

NUMERICAL MODELLING OF COUPLED MECHANICS AND GAS TRANSFER

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INTRODUCTION
During long-term storage of high-level nuclear waste, steel containers will be corroded and some organic material will be irradiated. The two processes lead to hydrogen production. This paper deals with the numerical modelling of the gas migration and of its coupling with the mechanical strains and stresses.

The basic equations are recalled. They concern the water transfer, the gas transfer, and the mechanical equilibrium. The storage of water and gas are related to fluid state equation and to porosity changes, including the Biot effective stress, dissolved gas in liquid, water vapour. Perfectly rigid rock, elastic rock and elastoplastic rock cases are compared.

A benchmark exercise has been proposed. Two steps are considered. They refer to a waste disposal in clay, but the disposal geometry is highly simplified. First a simple 1D radial problem is considered: a gallery of 0.35m radius is drilled. Then the state of stress and the water transfers evolve freely during 2 years. Eventually a gas production is considered during 100 000 years. Three different finite element codes (LAGAMINE, MPPSAT and ASTER) have been used and give very similar results, what is a validation of these codes. Secondly a 2D axisymmetric case in modelled (figure 1). Different material properties are here concerned.

The results show that transport of gas in dissolved phase is the most important phenomenon. The water boundary condition plays also an important role. This remains an open question (Gerard et al, 2007). The gas degree of saturation is very low and may induce some numerical difficulties. A classical way to

Figure 1: 2D case – geometry.
Figure 2: Dissolved Hydrogen flux along radial axis.

Figure 3: Gas pressure along radial axis.

improve the numerical convergence rate is to impose at least a minimum degree of saturation, what means that some gas remains always in pores. Such modification of the constitutive equation may modify the numerical answer. This question is discussed and a comparison of results obtained with different numerical strategies is presented.

References:

VERTICAL DISTRIBUTION OF HCO$_3^-$
TRANSPORT PARAMETERS IN BOOM CLAY
IN THE MOL-1 BOREHOLE (MOL, BELGIUM)

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INTRODUCTION

Boom Clay is presently studied as a reference host formation for the disposal of high-level radioactive waste in Belgium. This layer, situated between about -190 m and -290 m deep below the Mol site in the northeast of Belgium, presents various characteristics favorable to the final disposal of radioactive waste. Apart from a very low hydraulic conductivity (around $2.5 \times 10^{-12}$ m s$^{-1}$), it also has a strong sorption capacity for many radionuclides as well as self-sealing properties. A safety analysis of the radiological risks in the biosphere due to the release of radionuclides from the waste requires to calculate the transport rate of radionuclides in Boom Clay. Transport in the Boom Clay is mainly due to diffusion. Because of the very low value of the hydraulic conductivity $K$ and the very low vertical hydraulic gradient (about 2%), advection is negligible and diffusion is dominant in the overall transport. The diffusive transport is determined by (1) the product $\eta R$ of the diffusion accessible porosity $\eta$ and the retardation factor $R$, and (2) the apparent dispersion coefficient $D$. Initially, these parameters have been determined on clay cores taken from the underground research facility Mol, at a depth of -223 m. In 1997, a borehole (Mol-1) was drilled at the Mol site in order to cover the complete profile of the Boom Formation and to analyze the detailed vertical distribution of the transport parameters of non-sorbed tracers as a function of depth and stratigraphy. By performing migration experiments on clay cores from Mol-1, the hydraulic conductivity in the direction perpendicular to the bedding plane, the $\eta R$ product and the apparent dispersion coefficient of iodide and tritiated water have been determined as a function of depth (Aertsens et al., 2004). This study is completed by doing the same for H$^{14}$CO$_3^-$. Other cored boreholes were drilled in northeast Belgium to evaluate the spatial distribution of some of these parameters at a larger scale.

EXPERIMENTAL

For each clay core, the hydraulic conductivity in the direction perpendicular to the bedding plane, the $\eta R$ product, and the apparent dispersion coefficient of H$^{14}$CO$_3^-$ are determined by performing migration experiments (Aertsens et al., 2003) on compact clay cores. For an accurate determination of the migration parameters, it is essential that during an experiment, the water flow rate out of a migration cell is kept constant.

RESULTS AND DISCUSSION

In agreement with previous results (Aertsens et al., 2004), the hydraulic conductivity between -191 m and -281 m can be considered as homogeneous with an average value around $2.5 \times 10^{12}$ m s$^{-1}$. In this region, the product $\eta R$ of H$^{14}$CO$_3^-$ can be considered as homogeneous as well, $\eta R = 0.26$ (standard deviation 0.03). This value lies between that of iodide, $\eta R = 0.16$ and that of HTO, $\eta R = 0.37$ (Aertsens et al., 2004). The reason of the lower porosity of iodide and bicarbonate compared to HTO is due to anion exclusion because of the electrostatic repulsion by the negatively charged clay mineral surfaces. The higher $\eta R$ value of H$^{14}$CO$_3^-$ compared to I could be due to: (i) a different diffusion accessible porosity, or (ii) a slight retardation of H$^{14}$CO$_3^-$. The apparent diffusion coefficient of H$^{14}$CO$_3^-$ can be considered as homogeneous as well with a value around $6 \times 10^{11}$ m$^2$s$^{-1}$. This value complements the values obtained in a similar previous study (Aertsens et al., 2004) for HTO ($2.3 \times 10^{-10}$ m$^2$s$^{-1}$), and iodide ($1.4 \times 10^{-10}$ m$^2$s$^{-1}$).
CONCLUSIONS

Like for HTO and I, the transport parameters of HCO3⁻ can be considered as constant in the depth range between -191 m and -281 m in Boom Clay in the Mol-1 borehole. So, at the level of the Boom Formation at the Mol site, the Transition zone and the members of Putte and Terhagen appear to be homogeneous in contrast to the lower part of the Belsele-Waas member which is also characterised by a higher silt content and a higher hydraulic conductivity.

ACKNOWLEDGEMENTS

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References


DIFFUSION EXPERIMENTS IN CALLOVO-OXFORDIAN CLAY FROM THE BURE SITE, FRANCE: 2 MODEL RESULTS

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INTRODUCTION

Clay formations are being considered potential host rocks for radioactive waste disposal in many countries. The French National Radioactive Waste Management Agency (ANDRA) is performing research at the Meuse/Haute-Marne Underground Research Laboratory (URL) located at Bure (300 km east of Paris) to evaluate the feasibility of constructing a high-level radioactive waste repository in Callovo-Oxfordian (COx) argillite formation. COx clay has a very small hydraulic conductivity and therefore molecular diffusion is the main transport mechanism for radionuclides. Laboratory and in situ experiments are being performed to improve understanding of diffusion processes and determine key diffusion and retention parameters. García-Gutiérrez et al. (2007, in this volume) presented a large-scale diffusion experiment performed in a cylindrical sample of 30x30 cm. which overcomes problems of in situ experiments. A re-compact ed clay/ radionuclide mixed solid source is placed in the centre of a large clay block, allowing the tracer to diffuse into the clay sample. At the end of the experiment, samples along vertical boreholes are taken to get a 3D distribution of tracer activity. Here we present numerical models for the interpretation of experiments performed with HTO and \textsuperscript{85}Sr\textsuperscript{2+}, for which data are already available. Figure 1 shows experimental concentration profiles of HTO along vertical boreholes drilled from top to bottom of the large block at different radial distances from the tracer source. 24 of such concentration profiles were obtained and used to test and calibrate the numerical model.

NUMERICAL MODEL

Solid-source experiments have been interpreted using an inverse model with INVERSE-CORE (Dai and Samper, 2004). Given the symmetry with respect to sample axis, numerical interpretation can be performed with 2-D axi-symmetric anisotropic models. Figure 1 shows the 2-D finite element grid used to model both experiments. Numerical model considers tow material zones: one for the re-compact ed clay containing the solid source and another for intact clay. Prior estimates of transport parameters for compacted clay are available from previous experiments. Therefore, those parameters are fixed. Interpretation of the experiment aims then at estimating diffusion and sorption parameters of clay sample.

Experiments have been modelled using an approach similar to that used for modelling diffusion experiments in Opalinus clay (Samper et al., 2006). Numerical models have been used to: 1) Compute numerical sensitivities of concentrations to model parameters; and 2) Interpret real data. Here we report the results of the numerical interpretation of HTO and \textsuperscript{85}Sr data. Model results indicate that COx clay exhibits mild diffusion anisotropy. In addition to optimum estimates of porosity, effective diffusion coefficient and $K_d$, inverse modelling of these experiments provides estimates of parameters uncertainties and approximate confidence intervals of parameter estimates. Sources of uncertainty related to properties of re-compact ed clay and presence of a damaged zone around the central cylindrical source are also analyzed.
ACKNOWLEDGEMENTS

This work has been funded by ENRESA and EU within FUNMIG (FUNdamental Processes of radionuclide MIGration) Project (Ref. FP6-516514). Partial funding for UDC contribution has been obtained also from Spanish Ministry of Science and Technology (CICYT Projects HID98-282 and REN 2003-8882), Xunta de Galicia (Incentive PGIDT05PXIC11801PM) and University of La Coruña through a research scholarship awarded to Q. Yang.

References:


Figure 1: Experimental concentration profiles of HTO (left) and 2-D finite element grid used for modelling experiments (right). Tracer is emplaced at the central green area.
AN EXPERIMENTAL PROTOCOL
FOR THE INVESTIGATION OF DIFFUSION OF
IONS THROUGH ARGILLACEOUS BARRIERS

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INTRODUCTION
Repositories for radioactive wastes will involve a series of barriers to retard the potential dissemination of radionuclides towards the Hydro- and Bio-spheres. Clays are sought to achieve this objective for both near-field and far-field environments because of their low permeability and high adsorption capacity. In the ANDRA approach the barriers investigated are compacted MX80 bentonite and Callovo-Oxfordian argilite, the first as added clay and the second as host rock formation.

EXPERIMENTAL
In order to investigate diffusive radionuclide transport in argillaceous barriers, we developed an experimental set up which permits either through-diffusion or in-diffusion experiments. Typically, for through-diffusion experiments, the sample is set in a cell at the desired dry density, between two porous plates. Water is circulated through the porous plates (Figure1), the concentration of the element of interest is followed as a function of time in the upstream and downstream reservoirs.

RESULTS
Two types of solids were investigated: MX80 bentonite and argilite (Callovo-Oxfordian). In a first step, the diffusion studies were performed on untreated raw bentonite, and subsequently to obtain representative conditions more rapidly (concerning ionic strength and pH) the bentonite samples were pre-equilibrated for the specific conditions before the experiments. The argilite samples were used, as delivered, under oxygen-free controlled atmosphere.

Four elements (Cs, Ni, Pb, Se) were investigated for conditions either controlled by the argilite (compaction, pH) or imposed on the bentonite (pH, ionic strength, dry density) (Figure 2).

Effective diffusion coefficients (De) were determined and discussed.

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**Figure 1**: Schematic description of the experimental set up.
Figure 2: Through diffusion with argilite.

ACKNOWLEDGEMENTS
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GAZ PERMEABILITY OF AN ARGILITE: MEASUREMENTS AND PARAMETERS IDENTIFICATION

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INTRODUCTION
The effects of gas production due to metal corrosion in a radioactive waste disposal is an important issue. Depending on both rock behavior and corrosion rate, the gas can escape by diffusion in water or water displacement if the capillary pressure reaches the gas entry pressure. If the gas pressure reaches the geostatic stress, rock fracturation could occur. In this paper we present results of gas permeability tests performed under various hydric and mechanical loading on argilite samples cored at different distances of the access well of the future ANDRA URL at Bure.

EXPERIMENTAL PROGRAMM
Two kind of permeability test are performed in order to investigate the gaz permeability and gas entry pressure of argilite samples at different water contents and confining pressures. A first device consists in unconfined gaz permeability tests on hollow cylinders. The experimental set-up is a tight box in which relative humidity is imposed by saline solutions. Two hollow rock cylinders are tested simultaneously. Gas can be injected in the inner cavities when permeability tests are performed. Gas pressure can be imposed by the mean of an electrovalve, and flow rates as low as a few mg/h are measured. One sample can be uniaxially mechanically loaded and the other is continuously weigthed. Strains are also measured in different directions on the samples surface. Permeability tests are performed at hydric equilibrium. In a first step, pressure is suddenly built up in the cavity and held constant. The transient flowrate analysis provide a linearized apparent permeability and a gas porosity. Gas pressure is then built up step by step up to 0.6MPa in order to investigate permeability evolution according to gaz pressure. In a last step, the sample cavity is insulated. The subsequent pressure decay is analysed to identify the intrinsic permeability and the Klikenberg coefficient. Both the Simplexe algorithm (Nelder et al., 1965) and the Levenberg-Marquard algorithm are used to carry out the parameters identification in transient tests. In low permeability porous media, Klikenberg effect and Knudsen diffusion cannot be neglected. Moreover the gas viscosity is poorly dependent on the gas nature contrary to the Klikenberg parameter or Knudsen diffusion coefficient. Different gases (Helium and Nitrogen) are used to discriminate between the microscopic transfer phenomena.

The hollow cylinder being unconfined it is possible that, at some water content, the gas entry pressure overcome the tensile unconfined sample strength, making impossible a permeability measurement: tensile stress of 2 to 5MPa have been measured in this study whereas gaz entry pressure as high than 10MPa may be expected (Thomas et al. 1968, Marshall et al 2005) Confined axial permeability tests in a triaxial cell have been performed to investigate this issue.

RESULTS
Permeability tests have been tests have been performed on samples cored at 1m to 4m and at 12m from the well wall which is 6.3m in diameter. The following partial conclusions can be drawn :

- Samples cored at 1m to 4m were initially fractured. Because the preferential pathways are individual fractures at the sample scale we cannot deal with a sample permeability, but in-situ testing would be more relevant to identify the fracture network.
– Samples cored at 12m were not fractured. The comparison between Helium and Nitrogen permeability tests clearly demonstrate the importance of Knudsen diffusion. At an 66% equilibrium relative humidity, the Klikenberg coefficient ranges from 0.5 to 1.5 MPa for Nitrogen tests, and the intrinsic permeability ranges from $10^{-20}$ m$^2$ to $5.10^{-20}$ m$^2$. The importance of the Knudsen flow regime indicates that the flow occurs in small pores at the microscopic level.

– Confined permeability tests showed a strong influence of the confining pressure. One test performed on an intact sample brought at hydric equilibrium with a 80% relative humidity showed that the differential pressure needed for the gaz to penetrate into the sample is higher than 10MPa when confining pressure is 12MPa. For a sample brought at hydric equilibrium with a 66% relative humidity, a threshold differential pressure of 2.7MPa is observed. This threshold is not observed for unconfined permeability tests. Further testing at lower relative humidities is in progress.

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CORE\textsuperscript{2D} V4: A GENERAL PURPOSE CODE FOR GROUNDWATER FLOW, HEAT AND SOLUTE TRANSPORT, CHEMICAL REACTIONS AND BIOLOGICAL PROCESSES IN POROUS AND FRACTURED MEDIA

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INTRODUCTION

Understanding natural groundwater quality patterns, quantifying groundwater pollution and assessing the effects of waste disposal, require modeling tools accounting for water flow, and transport of heat and dissolved species as well as their complex interactions with solid and gases phases and microbial processes. CORE denotes a series of computer codes developed by the Universit of La Coruña which share the following main description: C0des for modeling saturated/unsaturated water flow, heat transport and multi-component REactive solute transport under both local chemical equilibrium and kinetic conditions. CORE uses the sequential iteration approach to solve the coupled hydrological transport processes and hydrochemical reactions. The finite element method is used for spatial discretization, while general finite difference schemes are used for time discretization. CORE can cope with heterogeneous systems having irregular internal and external boundaries. The code can handle heterogeneous and anisotropic media in 1, 2- and 3-D axysymmetric problems. Both steady-state and transient flow regimes can be simulated. Prescribed head and water flux as well as mixed boundary conditions are included. Both point and areal fluid sources can be specified. In addition, free drainage boundary condition (unit gradient type) is allowed for variably saturated flow. Solute transport processes included in the code are: advection, molecular diffusion and mechanical dispersion. Solute transport boundary conditions include: (1) specified solute mass fluxes, (2) specified solute concentrations and (3) solute sources associated to fluid sources. The code can handle the following types of reactions under the local equilibrium assumption: acid-base, aqueous complexation, redox, mineral dissolution/precipitation, gas dissolution/exsolution, ion exchange (based on the constant charge model) and sorption via surface complexation (using the diffuse double layer model). CORE can take into account any number of aqueous, exchanged and sorbed species, minerals and gases. Heat transport is solved at each time step. Computed temperatures are used for updating equilibrium constants and the constants for calculating activity coefficients. BIOCORE\textsuperscript{2D} (Zhang, 2001) is a version which copes with both thermodynamically-controlled abiotic geochemical reactions and subsurface microbial processes in 2-D while INVERSE-CORE (Dai and Samper, 2004) solves the inverse problem of automatic estimation of flow, solute and chemical parameters.

RECENT DEVELOPMENTS

Here we present CORE\textsuperscript{2D} V4, the most recent version of CORE\textsuperscript{2D} which was developed from CORE\textsuperscript{2D} V2 (Samper et al., 2000) and shares the capabilities of codes within the CORE family such as automatic time stepping, kinetic aqueous complexes reactions, and microbial processes in BIOCORE\textsuperscript{2D} (Samper et al., 2006a) and inverse subroutines of INVERSE-CORE\textsuperscript{2D} (Dai and Samper, 2004). In addition, CORE\textsuperscript{2D} V4 incorporates the following features: 1) Anisotropic diffusion, to deal with diffusion anisotropy of clay media (Samper et al. 2006b), 2) Non-linear adsorption isotherms, 3) Evaporation, 4) Isotopes transport coupled with chemical reactions for the purpose of simulating radionuclide release from a HLW repository, 5) Changes in physical properties of porous medium with time due to chemical reactions, 6) Accurate calculation of mass balances and mass fluxes, 7) Improved SIA and 8) Extending inverse subroutines to estimate flow, transport, chemical and biological parameters.
APPLICATIONS
CORE2D has been extensively used to model laboratory and in situ experiments including CERBERUS Experiment in Boom clay (Samper et al. 2006), interpretation of the Redox Zone Experiment in a fracture zone of the Åspö site (Molinero and Samper, 2004; Molinero et al. 2004; Molinero and Samper, 2006), inverse reactive transport of laboratory experiments and coastal aquifers (Dai and Samper, 2004; 2006), evaluation of oxygen consumption in a HLW repository (Yang et al., 2007) and stochastic cation exchange and reactive transport in aquifers (Samper and Yang, 2006). Codes of CORE series have been used also within the context of performance assessment in the following projects: ENRESA 2000, ENRESA 2003, BENIPA, NFPRO and PAMINA.

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HYPERFILTRATION OF METAL SOLUTIONS THROUGH LOW-PERMEABILITY MEDIA AND ITS EFFECTS ON HYDRAULIC CONDUCTIVITY

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INTRODUCTION
Material of low hydraulic conductivity and high surface charge are likely to exhibit osmotic (membrane) behaviour. Two solutions of differing salt content separated by a membrane tend to equilibrate the concentration gradient by flow of water to the high concentration side. As a result one can measure an osmotic pressure gradient. Pressures in excess of this osmotic pressure applied at the high salinity side cause hyperfiltration (or reverse osmosis): water molecules pass the membrane relatively uninhibited while the dissolved ions remain behind and become concentrated at the high-pressure side. This process is used commercially in desalination plants. Osmosis and reverse osmosis have long been suspected to also occur in geological environments, especially in and around low permeability media, such as clays and argillaceous rocks.

Observations in desalination plants have shown that often precipitates form on the high-pressure side of the membranes. This occurs when solute ion concentrations exceed the dissolution product of its salts. Precipitation of salts in pore spaces leads to a decrease in porosity and thus also in hydraulic conductivity. This hydraulic self-sealing limits further solute migration and decreases the amount of dissolved mobile salts. Potentially the precipitates may be re-dissolved, e.g. after a later pressure-drop.

Hyperfiltration (reverse osmosis) and precipitation of minerals from the hyperfiltrated solution are processes that potentially decrease radionuclide output from leaky radioactive waste containers and lower the hydraulic conductivity of the geotechnical barrier and the near-field. Hydrogen gas originating from corroding containers is envisaged to be the driving pressure source. In this study we tried to assess the effects of precipitation and potential re-dissolution on hydraulic conductivity.

EXPERIMENTAL CONCEPT
The processes of hyperfiltration and salt precipitation were successfully demonstrated using nickel sulphate solutions of differing saturations (10, 30, 50, 70, 90 %), different hyperfiltration flow rates (1, 2, 3, 5 ml/min), and the cretaceous fine-grained Obernkirchen Sandstone as substitute low-permeability material (K = 5·10−8 to 1·10−9 m/s, mean porosity = 17 %). The initial hydraulic conductivity was determined previously using bi-distilled water and several flow rates. After the hyperfiltration, the reversibility of the observed conductivity damage was tested by pumping distilled water at increasing flow rates. Pressures and flow rates and electrical conductivity of the effluent were measured continuously and stored digitally.

RESULTS AND INTERPRETATION
Precipitates were found in small (mm sized) layers at the high-pressure side of the samples where they create zones of lowered hydraulic conductivity. Generally their conductivity is two to three orders of magnitude lower than initial. In our experiments the mass of precipitates is very small compared to the dissolved amount which was passed through the membrane.

Hyperfiltration-induced precipitates and the resulting lowering of hydraulic conductivities were observed at solute saturations as low as 10 %. Nevertheless, at saturations higher than 50 % both the precipitated
mass and the conductivity damage strongly increase (Fig. 1). Full reversibility of the hydraulic conductivity damage was only obtained at low saturations (10%). This indicates that precipitating minerals can completely clog pores. The clogged pores are then inaccessible to solution and the minerals contained within are protected from re-dissolution, except from very slow diffusion controlled processes (Fig. 2).

Hyperfiltration is thus considered a process which potentially limits the transport of contaminants away from the near-field of leaky radioactive waste containers through mineral precipitation and lowering of hydraulic conductivity. Experiments with clay membranes are currently under way.
ARGILLITES THERMAL CONDUCTIVITY VARIATIONS INDUCED BY SEDIMENTARY / DIAGENETIC PROCESSES AND BY MECHANICAL DECOMPRESSION

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INTRODUCTION

Accepting the hypothesis of diffusive heat transport, thermal conductivity (TC) is a decisive parameter that controls the geometry of the deep underground laboratory of Andra, namely the spacing between “alveoles” and the total storage volume. The optical scanning technique, initially developed by Y. Popov from the University of Moscow (Popov et al., 1999), is used to perform thermal conductivity measurements. Examples obtained from argillites will be presented, showing the effect of (1) diagenetic process with calcite cementation using the mapping technique, and (2) mechanical decompression of samples cored at the wall of an experimental gallery using the profile technique.

DIAGENETIC PROCESS WITH CALCITE CEMENTATION

Using the optical scanning technique, TC-maps were produced with a resolution of 1 mm². Mapping was operated on samples cored at the wall of the descending shaft along two directions: perpendicular to bedding (dashed line on the circular section of figure 1) and parallel to bedding (rectangular section). TC values evolve from 1.3 to 2.4 W.m⁻¹.K⁻¹, the highest ones ( > 2) being induced by calcite cement. This diagenetic process seems to be independent of bedding orientation. Hence, thermal conductivity measurement appears to be a good indicator of calcite distribution within the argillites. Parallel to the bedding plane, clay-enriched sectors under sedimentary control seem to parallel the small Kₜ axis of the magnetic anisotropy ellipsoid (Esteban et al., 2006a and b). Kₜ seems to parallel low TC values and to be perpendicular to highest TC ones. These measurements point to a mineralogical and sedimentary control of the TC properties of the argillites. As a consequence, TC-mapping can be used as an indicator of sedimentary and diagenetic processes in mudrocks.

MECHANICAL PROCESSES

Profiles were performed along cores that were drilled from the walls of the underground laboratory. Our measurements show that if a mean TC could be estimated, ranging from 1.2 to 1.5 W. m⁻¹.K⁻¹, large variations were also observed as exemplified in figure 2. Three parallel-to-core profiles were obtained on the core surfaces. On sides of a mean TC value of 1.3 W.m⁻¹.K⁻¹, large variations could be induced by an increase in porosity or by mineralogical variations. A damaged zone was detected with a low TC ( < 1 unity) at the beginning of profile 1, attributed to a high porosity zone. At the end of profile 2, pyrite grains (or framboids) were detected with high TC values (3 W.m⁻¹.K⁻¹).
Figure 1: Thermal conductivity mapping of samples showing a diagenetic control. Upper part, section perpendicular to the bedding (dashed line); yellow to red: calcite cement. Lower part, section parallel to bedding: some variation of the thermal conductivity is observed, between 1.2 (in blue) and 2 W.m\(^{-1}.K^{-1}\) (in green). Using both sections an anisotropy tensor could be reconstructed with a lower value perpendicular to the K\(_1\) axis of the magnetic anisotropy.

Figure 2: TC profiles obtained from the same core drilled at the wall of the underground laboratory. The low TC zone (between 0.5 and 1 W.m\(^{-1}.K^{-1}\)) at the beginning of profile 1 corresponds to the high porosity of a damaged zone. At the end of profile 2 the high TC value is due to pyrite grains and the low TC values correspond to the high porosity alteration zones surrounding the grains of pyrite.

References


POROSITY NETWORK GEOMETRY AND INFERRED PERMEABILITY OF THE CALLOVO-OXFORDIAN ARGILITES FROM MAGNETIC FABRIC AND ORIENTED MERCURY INJECTIONS

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INTRODUCTION
The Jurassic in age, ~130 m thick, gray-coloured and homogeneous argillites that host the Andra laboratory, are a mix of clay minerals (~50%), carbonates (~25%) and silts (~25%). These argillites have been collected at depth (~490 m) by Andra. From a palaeo-climatological point of view, these argilites were deposited during a cold event that lasted ~4 Ma within a globally warm period marked by the carbonate platforms at the base and top of the argilritic formation. In the aim to investigate transfer properties of the material, specimens of the three main lithologies (silty, carbonate and clayey materials) are submitted to a set of combined analyses using magnetic anisotropy axis determination, mercury injection and ferro-fluid saturation. These data are used in a numerical model to infer permeability.

PORE STRUCTURE
The preliminary magnetic anisotropy measurements point out a specific orientation of the main magnetic axis depending on the lithology and are strongly controlled by the mineral fabric (Figure 1). Along the

Figure 1: Structure parameter obtained by ASM and mercury injection. K1, K2, K3 are main magnetic axis (see Bouchez et al. this volume) used for mercury injection (right). Left, ASM orientation after ferro-fluid injection for increasing pressure (4, 8, 14 and 70MPa), the initial orientation is supported by mineral orientation in black. (Esteban et al., 2006a, Esteban et al., 2007)
three main magnetic axis, samples are cored for mercury injection. These measurements show that each magnetic axis has a specific threshold and void volume value indicating a potential anisotropy of flowing parameter. Ferro fluid injections give information about the void shape and void orientation. These measurements are performed for increasing fluid pressure giving access to decreasing threshold values. For clayey material, void orientation and shape are controlled by clay orientation, for silty samples, larger voids are controlled by silt grain and smaller ones are controlled by clay fraction.

**PORE NETWORK MODEL AND INFERRRED PERMEABILITY**

The software “Pore-Cor”(www.pore-cor.com) is used to build a pore network model from mercury injection data (Matthews et al., 2006). This model implies the description of the porous network at a microscopic scale from mercury injection test and at mesoscopic scale from SEM observation. Two kinds of voids are defined, threshold in blue in the fig. 2, controlling the access to voids in orange giving the porosity volume, spaces without voids are associated to volume cemented by calcite (figure 2). Using this geometry a set of transfer properties could be inferred and involves from $10^{-19}$m$^2$ to $10^{-21}$m$^2$ with regard to the direction.

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IDENTIFICATION AND QUANTIFICATION OF LARGE-SCALE DIFFUSION IN A DEEP CLAYSTONE FORMATION (OPALINUS CLAY OF MONT RUSSELIN, SWITZERLAND)

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INTRODUCTION
Natural tracers in pore water of the Opalinus Clay, a claystone formation dating from the earliest Dogger (Aalenian), have been studied in cores drilled from the Mont Russelin emergency exit tunnel near St-Ursanne in the Canton of Jura, Switzerland. The tunnel penetrates an anticline of the thin-skinned belt of the Jura Mountains. Opalinus Clay occurs in the core of the anticline and contains a complex system of thrust faults. In 1991, during the Mont Russelin tunnel construction, a water with a Cl⁻ content similar to that of present-day sea water was collected from an extensometer borehole in a Liassic slice in the centre of the anticline. Water seepages into the tunnel containing fresh water were collected in the Dogger limestone stratigraphically overlying Opalinus Clay. The horizontal distance between the locations where the saline and the fresh water samples were taken is approximately 400 m. The interval between the two locations is largely constituted of Opalinus Clay.

EXPERIMENTAL CONCEPT
In the emergency exit tunnel, 17 boreholes were drilled perpendicular to the tunnel wall, approximately 4 m deep, to cover a profile from the core of the anticline to its southeastern limb. Samples were collected from the Liassic claystone, the Opalinus Clay and the Dogger limestone. Samples for pore-water analysis were taken from the deepest parts of each core, in order to minimize artifacts due to the presence of the tunnel (e.g. evaporation, oxidation and outgassing). The tracers considered included chloride, stable water isotopes and helium. Chloride data were obtained from aqueous leaching and a small number of squeezing tests. The stable isotopic composition of water was obtained by the diffusive isotope exchange technique (Rübel et al., 2002). The amount of ⁴He was measured by mass spectrometry (Pfeiffer QMS 422) after outgassing of the rock samples in a vacuum container over about 3 months.

RESULTS AND DISCUSSION
The chloride-accessible porosity in Opalinus Clay is about 0.55 times the water-loss porosity based on the comparison of the Cl⁻ concentration in the squeezed water with that in the aqueous extract solutions. This value is near-identical to that found for Opalinus Clay in the Mont Terri underground rock laboratory, which is located only 5 km to the northwest in the neighbouring anticline (Pearson et al., 2003). The Cl⁻ distribution in pore water shows a regular and well defined profile, with a conspicuous decrease towards the limestone aquifer in the hanging wall (Fig. 1a). The highest values (approximately 20 g/kg H₂O, similar to the value in present sea water) are found in the centre of the anticline in the underlying Liassic claystones close to the contact with Opalinus Clay.

The spatial distributions of δ¹⁸O, δD and helium concentrations also show systematic variations (Fig.1b for δ¹⁸O). The values are highest in the centre of the anticline and decrease towards the Dogger in the limb. However, in contrast to the Cl⁻ distribution, the stable water isotopes and helium show an anomaly related to a major fault zone close to the contact between Opalinus Clay and a tectonic slice of underlying Liassic claystone.
The available data are consistent with a model considering very old, possibly connate pore water in the centre of the anticline, which undergoes a transition towards fresh water in the limb. Preliminary model calculations yield results indicating that the observed tracer distributions are consistent with diffusion as the dominating transport process. The nature of the anomaly in the faulted zone, identified for water isotopes and helium but not for chloride, is currently not clear. It is yet to be shown whether it represents a natural but geologically young feature or whether it is related to processes since tunnel excavation. Further transport modelling in 1 and 2 dimensions is currently ongoing.

**Figure 1**: Distribution of tracer contents across Opalinus Clay and adjacent formations. Shaded area indicates faulted zone. a) Chloride profile. Open squares: squeezing test; open circles: seepage water; closed circles: aqueous leaching, considering a chloride-accessible porosity of 0.55 times water-loss porosity. b) δ18O profile. Closed circles: pore water; open squares: seepage water.

**References:**
REACTIVE DIFFUSION FRONT DRIVEN BY AN ALKALINE PLUME IN COMPACTED MG-HOMOIONIC BENTONITE

Jaime Cuevas, Raúl Fernández, Laura Sánchez, Raquel Vigil de la Villa, Manuel Rodríguez and Santiago Leguey.


ABSTRACT
Cement - bentonite interactions need to be studied since they will occur in deep geological repositories. They are specifically relevant in the clay host rock reference concept. The reactivity of a Mg-homoionic FEBEX bentonite was studied at 60 °C in contact with a young cement water characterized by the leaching of alkaline hydroxides (K/Na 4/1 -OH, pH = 13.5 at 25 °C) and with an evolved cement water controlled by the portlandite dissolution (Ca(OH)_2, pH = 12.5 at 25 °C). The experimental approach was to run diffusion experiments carried out in a cylindrical compacted bentonite sample, 2.1 cm long with a diameter of 7.0 cm, which is exposed on one circular face to a solution of cementitious water. A second reservoir of fluid is located at the opposite face of the bentonite sample; this contained MgCl₂ solution which was used during the homoionization process. The bentonite sample is maintained at a constant temperature of 60 °C throughout the experiments run for 6 and 12 months.

The key processes investigated were to identify and confirm, considering previous studies (Sánchez et al., 200; Savage et al., 2007), the nature of the newformed mineral phases (i.e., zeolites, CASH and Mg-silicate phases) as a result high pH reactivity of bentonite. This was complemented by addressing the spatial extension affected by mineralogical and geochemical modifications in compacted bentonite, including the extension of cationic exchange.

The diffusion of the hyperalkaline plume (OPC K/NaOH solution) through compacted bentonite (1.6 g/cm³ dry density) produces a mineralogical alteration front characterized by a critically cemented rim of approximately 2-3 mm (Figure 1). The cemented material is characterized by a drastic reduction on its external specific surface (from 80 to 20 m²/g) as well as the CEC (100 to 50 m²/g). The thickness of the rim did not evolve with time, then, diffusion becomes very slow due to the reduction of porosity. The self sealing of the high pH concrete-bentonite interface has been predicted in some models and this process should be taken into account as a potential self-stopped reactivity scenario.

The mineralogical composition of the rim is a mixture of poorly ordered, Mg-rich, clay materials, mainly brucite, hydrotalcite and tri-octahedral Mg-smectite. Montmorillonite is partially dissolved and a part of it remained trapped within the newformed cements. The alteration rim has been accurately measured by means of EDX-chemical profiles in flat polished sections examined under SEM microscopy (Figure 2) Alkali-zeolite have not formed at all as far as no pore-space is available for these lower density silicates. Then, alkaline cations (mainly K⁺) have diffused beyond the altered rim, affecting the whole 2.1 cm length of the compacted bentonite disc. The K⁺ exchange in the montmorillonite is homogeneous in the bentonite probe but it did not saturate completely the exchangeable positions. This can be another indication of the stopped reactivity process. The same studies are being performed at 90 °C in order to compare the extent of the diffusion and reaction processes.

At pH 12.5 and 60 °C there was not detected any significant mineralogical alteration. The main outcome of these experiments evidence the very limited thickness of mineralogical alteration affecting a highly compacted bentonite exposed to the effect of hyperalkaline solutions.
Figure 1: Spatial extension of the cemented mineralogical alteration rim. Dehydration micro-cracks are produced during sample preparation.

Figure 2: MgO % chemical profile measured by SEM-EDX, showing the development of the alteration rim.

References:

TRANSPORT NUMBER OF SODIUM IONS IN WATER-SATURATED, COMPACTED NA-MONTMORILLONITE

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INTRODUCTION
In geologic disposal of both high-level radioactive wastes and a part of TRU wastes, compacted bentonite is a promising material to be used for a buffer material. Radionuclides are not migrated by advection but by diffusion, because of very low hydraulic conductivity of the bentonite. It is important to clarify the diffusion process of the radionuclide as a part of a safety assessment of the geologic disposal.

In the buffer material, the diffusion of the radionuclides may be affected by other ions in the groundwater, because the nuclides as ions diffuse in electrically neutral condition by coupling with counter ions. However, there are quite few reports in which the contribution of these counter ions to diffusion of ions is examined. Nakazawa et al. (1999) suggested that the charge carrier of electrical conduction in the Na-montmorillonite is hydrogen ions rather than Na+ ions. However, the major charge carrier in the compacted bentonite has not been clarified sufficiently, because their conclusion was based on the indirect method such as measurement of electrical conductivities. Measurement of transport number is one of direct methods and is one of the most basic electrochemical properties of materials. The transport number suggests the contribution of counter ions to the migration of radionuclides. The purpose of this study is to propose an experimental method to determine the transport number of the Na+ ions in the water-saturated, compacted Na-montmorillonite to examine possible counter ions to the diffusion of radionuclides in the montmorillonite.

EXPERIMENTAL
The Na-montmorillonite powder was compacted in an acrylic resin cells, 20 mm in diameter and 20 mm in height. The clay columns were saturated with 0.1 M NaClO₄ solution. The transport number was determined using a moving boundary method. To estimate the transport number of Na+ ions in the montmorillonite, two processes are concerned with. One is electromigration of Na+ ions. The migration of the Na+ ions was traced, using ²²Na+ spiked as a thin layer. The other is the electro-osmotic flow of pore water, because it is possible that the Na+ ions migrate together with pore water. The flow of pore water was traced using dissolved helium, because the helium can be regarded as a non-sorbing tracer. For measuring the electro-osmotic flow, a part of the prepared columns were saturated with dissolved helium by bubbling. The osmotic flow was measured using an inflection point of helium distribution in the montmorillonite (Higashihara et al., 2004).

RESULTS
Dispersivity parameters, which were obtained in these experiments, were 10⁻³ m for Na+ and 10⁻³ m for He. This indicates that a property of the migration path for Na+ ions is deferent from one for He. It is quite possible that, in a montmorillonite, the Na+ ions mainly migrate in interlayer space and/or on outer surface, and the He does in pore space, as was suggested previously by Higashihara et al. (2004). Therefore, it is considered that the migration of the Na+ is not affected by the electro-osmotic flow. The transport numbers of Na+ ions were determined taking no account of the contribution of the electro-osmotic flow.
Figure 1: Dry density dependence of migration of $^{22}$Na and He in compacted montmorillonite under an electric potential gradient.

The transport numbers were more than 0.9 and don’t depend on the densities of the montmorillonite. This fact indicates that Na$^+$ ions behave as a dominant species to satisfy the electrically neutral condition during the migration of radionuclides in the montmorillonite.

References:

SWELLING, TRANSPORT AND GAS THRESHOLD PRESSURE OF A SEALING BENTONITE PLUG: EFFECT OF SAND ADDITION

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INTRODUCTION
Compacted bentonite blocks are privileged candidates for sealing nuclear waste repositories (Horsemann et al., 1999). Indeed, when put in place, sodium bentonite swells and thereby ensures proper sealing as in situ experiments prove (Victoria Villar et al., 2006). When dehydrating, sand addition provides resistance against shrinkage and cracking (Graham et al., 2002). Safety assessment of repositories sealing requires to fully identify bentonite swelling pressure and kinetics at given initial compaction and saturation rate. Complementarily, conditions of potential gas release from bentonite sealing plugs need being identified. Therefore, this paper presents an experimental investigation into bentonite swelling pressure and kinetics, and of its gas threshold pressure, when incorporating up to 30% sand in mass.

EXPERIMENTAL METHOD
The experiment consists of placing a specimen inside a triaxial cell and subject it to both confining pressure (Pc) and interstitial gas or liquid upstream and downstream pressures (P1 upstream and P1 downstream). The specimen is designed in order to reproduce an interface between bentonite and a surrounding material. Its geometry is chosen circular cylindrical in order to ensure uniform loading conditions, see Figure 1. At the beginning of each test, a pre-compacted unsaturated bentonite (or sand/bentonite) plug is surrounded by an instrumented tube made of a ductile material and then let to swell in presence of water. The tube is instrumented with four strain gauges which provide an evaluation of the pressure sustained by its inner surface, viz. the bentonite swelling pressure. During all tests, applied pressure levels are taken as determined by experimental in situ investigations: 4 MPa interstitial pressure for bentonite and 12 MPa confinement (also named lithostatic pressure) of the whole specimen.

RESULTS AND ANALYSIS
Swelling pressures of bentonite and (bentonite+30% sand in mass) are presented as a function of time in Figure 2. The time for bentonite (or bentonite+sand) to come in contact with its surrounding tube, viz.
hydraulic cut-off, occurs between 4 and 8 hours after test start only. For bentonite alone, after 12 days swelling under 4 MPa water pressure, an apparent asymptotic swelling pressure of 9.5 MPa is reached. Effective asymptotic swelling pressure is evaluated after 19 days, when interstitial water pressure is lowered to zero: its value is of 7.2 MPa. Interstitial water pressure is increased to 4 MPa again on day 22, and lowered to zero again on day 27: effective swelling pressure remains at 7.2 MPa. For bentonite+30% sand, apparent swelling pressure is of 8.2 MPa, whereas effective swelling pressure (measured after lowering interstitial water pressure on day 22) is of 4 MPa only. Therefore, sand addition provides an immediate and full effect of interstitial water pressure variations whereas 100% bentonite is affected of only half that pressure (with swelling pressure lowered by 2.3 MPa and not 4 MPa when water pressure is off). This is interpreted as an effect of a higher water retention capacity of 100% bentonite compared to bentonite+30% sand. Water permeability and gas breakthrough pressure are also quantified during these tests, they confirm the interpretation proposed.

References:
SPECIES-SPECIFIC TRANSPORT AND REACTIVE TRANSPORT MODELLING OF A LONG-TERM CORE INFILTRATION EXPERIMENT ON OPALINUS CLAY

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INTRODUCTION
Argillaceous rocks have very low hydraulic conductivities, large sorption and ion exchange capacities, and are rather homogeneous. This makes them well suited for deep disposal of radioactive waste. In Switzerland, Opalinus Clay, a Jurassic marine indurated sediment, is considered as a potential host rock for high-level radioactive waste. The claystone has been investigated for the past 10 years in the Mont Terri underground laboratory where it is accessible in a broad anticline of the Jura Mountains.

Because of its low permeability of $10^{-14}$ to $10^{-13}$ m/s, pore water cannot easily be sampled from Opalinus Clay. Thus, mostly indirect methods are employed in order to characterize the chemical composition of the pore water, notably aqueous extraction followed by geochemical modelling of the data on the basis of the mineralogical composition of the rock and ion exchange properties (Pearson et al. 2003). Alternatively, high-pressure squeezing may be applied whereby the rock matrix is deformed.

An alternative to destructive methods is the advective displacement of the preserved porewater from a rock column by injecting a synthetic porewater that can be traced to aid in the data interpretation. The breakthrough and retardation behaviour of chemical constituents can be examined if such a displacement experiment is continued. The results from such an experiment are presented whereby pore water of a drillcore sample of Opalinus Clay was advectively displaced by a traced synthetic pore water over more than 3 years. The objectives were to (1) test and refine this method to obtain little-disturbed samples of the original pore water, and (2) measure the breakthrough of multiple tracers for the determination of species-specific transport properties by (reactive) transport modelling. The method was applied to a core sample from the BPC-A1 borehole, and the work is a task of the PC (Porewater Chemistry) Experiment at Mont Terri. Preliminary results and porewater composition was presented by Mäder et al. (2004, and abstract at Tours 2005 meeting).

METHODS
Drilling parallel to bedding with compressed nitrogen minimized the ingress of oxygen. Sample preparation was done on site. A drillcore (OD = 79 mm, L = 120 mm) was placed in the infiltration apparatus under a confining pressure of 6.2-7.4 MPa. The porosity of the core as estimated from the water loss of adjacent samples was 0.165 m$^3$ m$^{-3}$. The temperature was kept at approximate in situ conditions of the formation of 13-15°C. A synthetic porewater of similar salinity as the in situ pore water was used. It was traced with bromide, deuterium, and $^{18}$O. The infiltration pressure was created by pressurized He in the head space of a closed-volume reservoir.

The sample effluent was collected under protective He atmosphere and extracted periodically. The samples were analysed for chemical constituents (Cl$^-$, Br$^-$, SO$_4^{2-}$, Na$^+$, K$^+$, Ca$^{2+}$, Mg$^{2+}$, and others) and for the isotope tracers. The isotope tracers and Br were used to estimate the degree of mixing between synthetic and original pore water, as well as to estimate the corresponding transport coefficients. These coefficients were
then used in the transport modelling of the reactive components. The hydraulic conductivity was determined periodically from the flow rate, hydraulic gradient and sample dimensions.

RESULTS AND DISCUSSION

Transport modelling of the Br$^\text{-}$ and the $\delta^2$H breakthrough curves: depending on the boundary conditions used for modelling, the pore diffusion coefficient for $\delta^2$H ((1.6±0.2) to (2.2±0.4)·10$^{-10}$ m$^2$ s$^{-1}$) is approximately 0.6 to 0.9 times the value obtained for HTO in the laboratory and scaled to the in situ temperature, whereas for Br$^-$ ((1.9±0.4)·10$^{-10}$ m$^2$ s$^{-1}$) it is about 1.3 times the laboratory value for Cl$^-$ (Van Loon and Soler, 2004). In view of the data and model uncertainties, the differences to the laboratory values are considered to be small. For Br$^-$, the anion exclusion effect is confirmed and leads to an earlier breakthrough (average linear velocity larger by a factor of approximately 1.7) as compared to $\delta^2$H. The column Peclet numbers are approximately 7.4 for Br$^-$ and 4 for $\delta^2$H.

The evolution of the major cations (Na, Ca, Mg, K) in the effluent over the first 2.5 years: Ca increases first slightly above and later decreases towards the input concentration, whereas Mg seems to increase steadily towards the input value. The trend for Na is obstructed by a systematic analytical offset after the first 1.5 months that is presently being resolved. Preliminary results suggest a similar behaviour as Ca with a maximum breakthrough value after 300-400 days that lies above the input concentration. Finally, K does nearly remain constant at the input value. At present, full reactive transport modelling of the data is ongoing to check whether the observed behaviour can be explained by cation exchange processes coupled with a small ionic-strength effect, or any additional contribution from the carbonate system by mineral dissolution or precipitation reactions. Also, alternate approaches to reactive transport modelling in ionic media are examined by either applying uniform or species-specific effective diffusion coefficients, while imposing electroneutrality that in turn leads to transport contributions by electro-migration.

CONCLUSIONS

While earlier work (Mäder et al. 2004) demonstrated the feasibility of the method for porewater extraction, this work focussed on the long-term aspects of core infiltration and monitoring multiple tracer and major component breakthrough behaviour. From the evaluation of the data of the advective displacement experiment we conclude that the method appears to be affected by relatively few chemical and physical artefacts, and offers a promising and valuable alternative to in-situ methods (diffusive exchange, extraction) and laboratory methods (diffusive exchange, leaching, squeezing) for the determination of the pore water composition. It is suggested that several other aspects of ionic transport – including radionuclides – could be addressed by this approach with the objective to obtain parameters that reflect “true” in-situ properties. This would complement costly in-situ experiments and simple and shorter-term laboratory experiments that are often affected by some experimental artefacts. In particular, the ability to apply a quasi-hydrostatic confining pressure to the samples is counteracting some of the possible effects of stress release (micro cracks, uncontrolled swelling or shrinking, relaxation).

References:


MODELLING GAS INJECTION TESTS IN DEFORMABLE CLAY BUFFERS

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ABSTRACT

A significant issue in long term behaviour of clay buffers is its capability to maintain tightness under the expected generation of gases due to canister corrosion and other phenomena. Current research in this important topic, directly related to the long term safety evaluation of a repository, concentrates in understanding the mechanisms of gas transport through a mass of saturated, compacted bentonite, under the confinement stress provided by the host rock. A large proportion of the experimental research performed concerns laboratory tests of gas flow through compacted specimens, fully hydrated. They play the role of “point” tests, although, as explained later, they can be hardly interpreted if they are considered in the Cauchy sense of a homogeneous, small specimen able to provide fundamental constitutive behaviour. A model has been developed in order to simulate in a continuous approach based on finite elements, the presence of embedded discontinuities which are able to simulate gas preferential flow paths. The model is described in Alonso et al, (2006) together with applications of different type, including the simulation of gas flow path formation in heterogeneous fields. Also the large scale test GMT (performed by NAGRA in Grimsel) has already been modelled (Olivella and Alonso, 2005). Yet the simulation of laboratory tests has to provide more insight in the gas flow through clays, and probably, improvements of the constitutive model.

Horsemann and Harrington (1997) have carried out an investigation which includes gas injection tests on saturated clay to understand the gas flow mechanisms. Injection of gas in the center of a cylindrical sample which has sink points in different zones on the external surface.

A 3D domain that represents the laboratory test has been considered for simulating the gas injection tests in these cylindrical samples. The simulation is performed using a hydro-mechanical approach which

Figure 1: Gas pressure (MPa), liquid saturation (-) and gas fluxes (m/s) in a finite element simulation of a gas injection tests. The cylindrical sample is cut through longitudinal and transversal planes for representation.
includes a newly developed model for gas migration in discontinuities. Each of the elements is considered a candidate to develop a discontinuity, and it is assumed that the increase in permeability is isotropic. The medium is assumed to have an initial porosity distribution which is heterogeneous. Injection of gas in the center of the sample creates a gas pressure build up which desaturates the medium and that produces changes of permeability due to hydromechanical interactions (elastic behaviour is considered in this preliminary model). The gas is collected in the sink points which are distributed in 3 rings on the outer surface of the cylinder. Figure 1 shows the distribution of gas pressure, degree of saturation and the gas fluxes at 1250 hours, i.e. after the first peak of gas injection flow rate. Figure 2 shows the evolution of pressures (gas pressure, liquid pressure and stress) and the gas flow rates (prescribed at injection point and calculated at the sinks). The possibility of the permeability. The results show some qualitative agreements with the measurements, but it is clear that the model is still preliminary, and further improvements are required, such as considering elastoplastic response of the material.

The modelling of this type of tests is relevant for the analysis and modelling of large scale in situ tests. At present, gas injection tests are also performed at the UPC Geotechnical Laboratory, which may also be used for further understanding via modelling of the gas flow through clay barriers.

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