Poster [MT]

Mass Transfer
SCALE EFFECTS IN MODELING ADSORPTION

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Retention processes are especially significant when analyzing transport in clay formations. Considering the simplest case of equilibrium adsorption with a linear isotherm, retention can be represented by a retardation factor, which is function of the partition coefficient. The influence of the spatial variability of the retardation factor in the overall distribution of travel times at the field scale, and the existence of an equivalent retardation factor that can be used at a large scale to predict some representative average behavior have been subject of study during the last decade. We present a summary of the major findings in this area and investigate the dependency of an equivalent retardation factor upon known retardation values at a smaller scale. We assume steady statistically uniform flow or convergent flow in a porous medium with heterogeneous conductivity characterized by various types of statistical models. The method proposed could be used to derive equivalent retardation factors at the performance scale from laboratory data, or from short scale field experiments.
INFLUENCE OF INTERLAYER CATION IN SWELLING AND SHRINKAGE OF BENTONITE MX80

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Introduction
Bentonite is expected to be used as buffer material around the waste storage site due to its interesting physico-chemical properties. Among them, swelling is very important and directly related to the nature of the interlayer cation. Many studies showed the role that play interlayer cations in the adsorption capacity of swelling clays. Most of these studies refer to adsorption experiments and macroscopic changes. In this work we observe and measure the swelling at the microscopic scale, and the different behaviours of bentonite saturated by 5 different cations (Na, Li, Mg, Ca, K) in hydration and dehydration conditions. In addition, for the same exchanged samples we studied the water sorption capacity by adsorption curves. Microscopic observations of hydrated clays were possible thanks to a new tool, the environmental microscope (ESEM). Its great advantage is to keep samples in hydrated states and the possibility to change relative humidity and temperature in the observation chamber. This enables to proceed to dynamical studies.

Samples and experimental conditions
MX 80 sample is an industrial bentonite containing about 80% low charge montmorillonite, biotite and accessory minerals (iron oxides and hydroxides and carbonates). MX bentonite was prepared in order to exchange the smectite interlayer cations and obtain homoionic smectites in the samples. Each exchanged sample was submitted to hydration and dehydration in the ESEM by progressive relative humidity change, from the dry state to the saturated state ; for each step, observations of swelling were done when equilibrium was reached, and digital image analyses (DIA) were performed on images to measure the changes in aggregates. These measurements lead to the elaboration of swelling and shrinkage curves whose informations are compared to those obtained from sorption isotherms. Swelling kinetics could also be approached by swelling measurements.

Results
Swelling curves could be established from 2.5 % HR to 80 % HR which was the maximum relative humidity before clay aggregates loose cohesion and finally disintegrate. They show strong differences between the exchanged samples as was expected and already described in the literature. Swelling as well as adsorption are greater for divalent cations (Ca and Mg) at low HR, and for monovalent cations (Na and Li) at higher HR. However adsorption starts at lower HR than swelling which corresponds to a first water filling in greater pores of the aggregates. In the second stage where swelling is measurable and increases, corresponds to the adsorption in smaller pores and interlayer sites. At this point Na and Li exchanged samples show a strong increase in adsorbed water amount whereas only Na shows great changes in swelling. Li-exchanged sample shows a peculiar behaviour as swelling increases lately at high HR.
Shrinkage curves compared to swelling curves show an hysteresis which may be related to the aggregate deformation and pore distribution changes inside the aggregate during swelling. This phenomenon is enhanced in Na-exchanged sample where the initial aggregate size was not recovered after dehydration.

**Conclusion**

Coupled ESEM-DIA is a good tool to observe and measure changes during swelling and shrinkage of bentonite aggregates and to point out the influence of interlayer cations on the swelling and shrinkage behaviour. Great differences are pointed out, in swelling behaviour and kinetics, depending on the exchanged cation which are comparable to those observed in adsorption curves. Moreover ESEM-DIA shows the influence of the exchanged cation on the recovery of the initial aggregate size after deformation during swelling.

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ELECTROMIGRATION OF SODIUM IONS AND ELECTRO - OSMOTIC FLOW IN WATER - SATURATED, COMPACTED NA - MONTMORILLONITE

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Introduction

In the deep-underground disposal of both high-level radioactive waste and a part of TRU waste, compacted bentonite is a promising buffer material. The bentonite is quite suitable for long-term assessment of the migration of radionuclides, because diffusion is predominant process on the migration of radionuclides due to impermeability of the bentonite. The diffusion coefficients of many radionuclides in compacted bentonite have been reported. However, the diffusion process is not sufficiently clarified; several subjects have been left for the further understanding of the material, and hydraulic and chemical aspects of water in bentonite. In the present work, it was studied that the electromigration of sodium ions and electro-osmotic flow measured with dissolved helium as a tracer in water-saturated, compacted sodium montmorillonite. The dispersion coefficients and dispersivity parameters of each chemical species were obtained from their concentration profiles.

Experimental

Montmorillonite powder, which is a product of the Kunimine industries Co. Ltd., Kunipia-F, was used to prepare water-saturated, compacted sodium montmorillonite specimens. The clay powder dried in an oven was compacted in an acrylic resin cell 20 mm in height and 20 mm in diameter. The dry densities of the specimens were 1.0 and 1.6 \times 10^3 \text{ kg m}^{-3}. The compacted montmorillonite was immersed in 0.1 M NaClO_4 solution for 30 d and saturated. Then, a tracer $^{22}\text{Na}$ was applied to compacted montmorillonite as thin layer source using the same type of cell developed by Maes et al. A voltage was applied to the montmorillonite specimens for 4.0 and 6.0 h at the constant current of 3.0 and 5.0 \times 10^{-2} \text{ A}. On the other hand, electro-osmotic flow using helium as a tracer in montmorillonite was carried out as follows. The water-saturated, compacted Na-montmorillonite was contacted with dissolved helium in 0.1 M NaClO_4 solution for 14 d to prepare helium-saturated pellets. The specimen for experimental setup consists of these pellets with saturated helium and those without helium. Applying a voltage under the same condition as in the case of electromigration, helium migrated in compacted montmorillonite by electro-osmotic flow. After migration of these chemical species, the concentration profiles of $^{22}\text{Na}$ and He were obtained by $\gamma$-spectrometry and mass-spectrometry, respectively.

Results and Discussion

A typical example of concentration profiles of $^{22}\text{Na}$ and He in water-saturated, compacted Na-montmorillonite is shown in Fig. 1. The apparent dispersion of chemical species $i$ in compacted montmorillonite can be expressed by the advection-dispersion equation,

$$\frac{\partial C_i}{\partial t} = D_i \frac{\partial^2 C_i}{\partial x^2} - U_i \frac{\partial C_i}{\partial x}.$$  (1)
The initial conditions, i.e., for migration of $^{22}\text{Na}$ ions are $C(0, 0) = \infty$ and $C(x, 0) = 0$, $|x| > 0$, and the boundary condition, b.c., is $C(\pm\infty, t) = 0$, $t > 0$. The i.c. for helium migration are $C(x < 0, 0) = C_0$ and $C(x > 0, 0) = 0$, and the b.c. is $C(\pm\infty, t) = 0$, $t > 0$. Based on these equation, the concentration profiles of $^{22}\text{Na}$ and He are described by the relations,

$$C_{\text{Na}} = \frac{M}{2\sqrt{\pi D_{\text{Na}}}} \exp \left\{ -\frac{(x-U_{\text{Na}}t)^2}{4D_{\text{Na}}t} \right\} \quad (2)$$

$$C_{\text{He}} = \frac{C_0}{2} \text{erfc} \left( \frac{x-U_{\text{He}}t}{2\sqrt{D_{\text{He}}t}} \right) \quad (3)$$

The dispersion coefficients can be determined by a least-squares fit, using eq. (2) and (3). At dry density of $1.0 \times 10^3$ kg m$^{-3}$, the dispersion coefficient of sodium ions is $1.0 \times 10^{-10}$ m$^2$ s$^{-1}$, while that of helium is $1.0 \times 10^{-9}$ m$^2$ s$^{-1}$. The apparent diffusion coefficient of $^{22}\text{Na}$ reported is $7.4 \times 10^{-11}$ m$^2$ s$^{-1}$ (3) and that of He is $3.6 \times 10^{-10}$ m$^2$ s$^{-1}$ (2). The difference between the dispersion coefficients and diffusion coefficients means that not only diffusion but also mechanical dispersion occur, resulting from electromigration and electro-osmotic flow in the montmorillonite. The dispersivity parameters of Na$^+$ and He, obtained were $7.2 \times 10^{-5}$ m and $2.4 \times 10^{-3}$ m, respectively. It is found that helium is more dispersible than Na$^+$ in compacted montmorillonite. It is likely that helium can migrate in larger space, such as a pore, while Na$^+$ is restricted in relatively smaller space.

Fig. 1: Concentration profiles of $^{22}\text{Na}$ and He in water-saturated, compacted Na-montmorillonite at $1.0 \times 10^3$ kg m$^3$, 0.1 M NaClO$_4$ and 298 K

TRANSPORT THROUGH SHALES. THERMODYNAMIC APPROACH, IMPORTANCE OF THE MICROSTRUCTURE, AND COMPARISON WITH EXPERIMENTAL DATA

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The understanding of ionic transport in porous media is both a complex and well-studied field with numerous applications in geosciences. The study of salt filtration is especially important in the study of ionic species migrations in mudrocks, which are used as hydraulic and chemical barriers for containment of contaminants such as low-level radioactive wastes. This paper is concerned with the modeling of ionic transport in low-porosity two-phase (fluid and solid) porous media possessing a high specific surface area. Water-saturated shales are some examples of such media.

One of the most complex issues in the study of ionic transport in these porous media concerns the modeling of the coupling effects between the various thermodynamic forces and fluxes. Generally speaking, one must expect from thermodynamics theory of open systems that all the fluxes and their conjugate forces are coupled [e.g., Prigogine, 1949]. In porous materials, most of these coupling phenomena owe their existence to the excess of electrical charge located in the close vicinity of the mineral water interface, in the so-called electrical double layer. Indeed, all minerals see their surface the site of electrochemical disturbances when in contact with water. Clay minerals, for example, exhibit deficiency of electrical charges due to isomorphic substitutions inside their crystalline framework plus chemical speciation between their surface reactive groups (e.g., silanols and aluminols) and the ions from the pore water. The charge deficiency of the clay minerals is counterbalanced by an excess of charge of opposite sign (the "counterions") populating the pore water. Usually this electrostatic and ionic densities disturbances are restricted to the pore water fraction in the close vicinity of the mineral water interface (< 0.1 µm). However in low-porosity shales, the size of the electrical double layer can be on the same order of magnitude than the size of the throats controlling transport properties in the connected porosity. So models based on the thin electrical double layer assumption are not valid. It follows that the pore water of a shale does not follow strictly the electroneutrality condition or that the electroneutrality condition in the pore water needs to be modified to include the charge deficiency of the clay minerals.

There has been quite a number of works in modeling ionic transport in porous materials. However, most of the past works remains mainly phenomelogical theories in which the material properties are not specified as a function of the constituent properties and microstructural parameters. In addition, when the influence of the microstructure is specified, the models are always based on the thin electrical double layer assumption that we wish to avoid here. In this paper, the continuum equations known to applied to the ions, the solvent (water), and solid phase are volume-averaged to obtain the macroscopic equations at the scale of a representative elementary volume. The Onsager reciprocal relationships valid at the macroscopic scale are shown to result from linearisation of the local equations. At the local scale, the concentrations inside the pore water of the shale are assumed to obey to the Donnan
distribution as an alternative to the use the Poisson-Boltzmann distribution in the equilibrium (thermostatic) state.

To keep our theory as simple as possible, we make the following assumptions. (1) In the thermodynamic equilibrium state, ionic concentrations obey Donnan distributions. (2) We assume only linear disturbances in the vicinity of thermodynamic equilibrium. It follows that we will use the formalism of irreversible linear thermodynamics developed by De Groot and Mazur [1984]. (3) The pore water is assumed to be an ideal electrolyte, which is a relatively correct assumption for dilute electrolyte (<1 Mol L⁻¹). The porous medium is assumed to be isotropic and homogeneous at the scale of the representative elementary volume (anisotropy will be discussed shortly). (4) We will assume the porous medium behaves as a rigid body. Comparison with various experimental data (ultrafiltration, diffusivity, electrical conductivity...) indicate the validity of the new approach. Deformation and chemical reactions will be incorporated in a forthcoming work.
DIFFUSION BEHAVIOUR OF SELENITE AND HYDROSELENIDE IN COMPACTED BENTONITE

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Research has been performed to investigate the geochemistry and radionuclide migration in buffer materials and geosphere at JNC. Experiments and modelling studies have been carried out related to the geological disposal of high-level radioactive waste. Although much data have been reported with respect to diffusion and sorption of radionuclides in bentonite so far, almost all data have been obtained under air condition. Data for redox sensitive elements obtained under reducing conditions, reflecting conditions for a deep geological environment, are limited. Selenium, important for dose evaluation in safety assessment, is one of the redox sensitive elements. However, quantitative data and information on the effect of redox potential on retardation properties in compacted bentonite as well as thermodynamic data for Se diffusion are lacking.

In this study, the apparent diffusivities (Da) for Se, among other redox sensitive elements, for diffusion in compacted bentonite are obtained under reducing conditions and compared with Da values obtained under anaerobic conditions. The Da values under reducing conditions are obtained also as a function of temperature. In this paper, the effect of the redox potential and activation energy (ΔEa) on diffusion of Se is discussed.

The experiments were carried out by an in-diffusion method [1]. A Na-bentonite, Kunigel-V1 with Na-smectite content of 46-49wt% (Kunimine Industries Co. Ltd.), was used in a series of diffusion experiments. The diffusion experiments were performed at a dry density of 1.6 Mg/m³ as a function of silica sand content. Since Se is redox sensitive, all diffusion experiments were carried out in a controlled N₂ atmosphere glove box. The experiments were furthermore carried out at room temperature (22.5°C) and 60°C in order to discuss diffusion behaviour thermodynamically.

Although the Eh of the solution contacted with bentonite rose a little as time evolved for the diffusion experiments at 60°C, it was stable at around -400mV at 22.5°C. The dominant species of Se in the porewater of bentonite under these conditions is predicted from Eh-pH diagrams to be HSe⁻ [2].

The Da values for Se were determined based on the Fickian law [3]. The effects of silica sand content and temperature on Da are overall summarized as follows:
(1) the Da values show a tendency to increase with increasing silica sand content,
(2) the Da values show a tendency to increase with increasing temperature,
(3) the increasing rate of Da with temperature is approximately constant, independent on silica sand constant.

The obtained Da values for HSe⁻ under reducing conditions were compared with those for SeO₃²⁻ obtained under anaerobic conditions. The Da values for HSe⁻ are about one order of magnitude smaller than those for SeO₃²⁻. Therefore, Se is strongly retarded under reducing conditions. This trend is in good agreement with that of distribution coefficients obtained by
batch method. The reason might be explained by the fact that different sorption processes for different species in the porewater are related to different redox conditions. Correlations between $Da$ values for HSe$^-$ and smectite partial density, which is defined only by density of the smectite aggregates in bentonite were discussed. The $Da$ values were well correlative with smectite partial density for both temperatures. This indicates that Se diffusion is predominantly controlled by the properties in part of smectite.

The $\Delta E_a$ values for $Da$ values of HSe$^-$ were calculated from the temperature dependency of the $Da$ values. Figure 1 shows Arrhenius plot for the $Da$ values. The calculated $\Delta E_a$ values are in a range of 17 to 32 kJ/mol and are slightly higher than that (15.3 kJ/mol) of ionic diffusivity in free water ($D^o$) for HS$^-$, which takes the same species as HSe$^-$ in solution. A reason might be that the properties of the porewater of compacted bentonite are different from that of free water.

![Figure 1: Arrhenius plot for $Da$ values for HSe$^-$ and $D^o$ for HS$^-$](image)

APPLICABILITY OF WAVELET GALERKIN METHOD TO CALCULATE RADIONUCLIDE TRANSPORT FOR LOW LEVEL RADIOACTIVE WASTE THROUGH DIFFERENT BARRIERS

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The disposal concept, which is based on the multibarrier system, is expected to be applicable for various types of waste and a wide range of geological conditions. However, performing an assessment of all possible combinations of these parameters would require a vast amount of effort. Therefore, in this work the newly developed wavelet technique for low-level radioactive waste repository is introduced. Radionuclides leaching from the waste form transport through the engineered barrier system to the water bearing fracture around the repository to the natural barrier reach the biosphere. The problem is diffusion-advection type in both engineered and natural barrier systems with highly varying parameters and a very concentrated nature of the spatio-temporal source.

The wavelet Galerkin method (WGM) represents the solution as a summation of Daubechies’ scaling functions. The Daubechies’ scaling functions have the properties of orthagonality, high smoothness and compactly supported.

We tested our WGM algorithms with several radionuclides in both near and far fields of the repository. The solutions agree well with a proper selection of wavelet order and dilation order.

Introduction

This paper presents numerical results for the performance assessment of a low level radioactive waste repository using wavelet Galerkin method. The purposes of the present study are to investigate transport of radionuclides inside the low level radioactive waste repository and the mass transfer to the surrounding geological medium and to obtain the amount of radionuclides reach the biosphere from the geological medium around the waste repository.

Model Formulation

The modeling of radionuclides transport includes the transport of the radionuclides through the engineered barrier system and the natural barrier of geological medium around the repository. EBS model for radionuclide transport can be written as follows:

\[ \chi^b \frac{\partial A^b}{\partial t} = \frac{\partial}{\partial x} \left( e^b D^b \chi^b \frac{\partial C^b}{\partial x} \right) - \frac{\partial}{\partial x} \left( g^b e^b \chi^b C^b \right) - \lambda e^b \chi^b A^b \]

Where, \( C \) is the concentration we want know, \( W \) is the source distribution, and others are standard. The Concentration can be expanded in terms of the wavelet scaling function as follows, \( C(x) = \sum_{k=N+1}^{2j} c_k \phi(2^j r - k) \), Where \( \phi \) is the scaling function; \( c_k \) is unknown we have to calculate and \( j \) is the dilation order. We use Leapfrog for the time discretization.
Results
Figures 1 and 2 shows the release rate of C14 and I129 from the EBS and Natural barrier respectively. The high release rate of C14 at the early time is due to its high inventory in the Waste, then its concentration fall down due to its short half-life. I129 is long-lived isotopes but it has low inventory in the waste.

Conclusion
Wavelet Galerkin method is devised to be a very useful tool for solving the system of partial differential equations arising from the model formulation of the radionuclide transport for low level radioactive waste.

References

Figure 1 : Release rate of C14 and I129 from the EBS of the repository without and with bentonite

Figure 2 : Release rate of C14 and I129 from the Natural Barrier of the repository without and with bentonite
CONTRIBUTION OF DIAGENETIC CHLORITE TO PHYSICAL PROPERTIES OF SILICICLASTIC RESERVOIR

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This paper reports an investigation of the influence of chlorite content and its microtexture on the petrophysical properties of the siliciclastic reservoir. The pore-lining chlorite is a diagenetic clay mineral that commonly coats the surface of detrital grains in sandstone. Its earliness, continuity and thickness around the grains prevent the subsequent precipitation of quartz overgrowths saving very good reservoir properties, especially, the porosity (Fig. 1). On the contrary, when the chlorite content is high, the permeability decreases.

Figure 1: SEM images of chloritic sandstone reservoir in different magnifications
A, B: SEM images on thin section with pore-lining chlorite. Qz: quartz; Ch: chlorite
C, D: SEM images on fractures with pore-lining chlorite

The Hg-injection analysis of pore-throat size distribution and capillary pressure versus saturation on several samples show a two/three-modes structure of porous medium and a high irreducible saturation due to the pore-lining chlorite. From Hg-injection method, we calculated the microporosity developed by pore-lining chlorite. The micro-geometry and the morphology of pores system (primary and secondary porosity) were quantified from petrographic image analysis as a 2D technique. From that, we obtain the 3D petrophysical properties of an argillaceous sandstone pore system. More than four orders of magnitude are integrated in PIA method, from a submicron to a millimeter scale and enables
to measure petrophysic properties such as porosity, specific surface area, average pore diameter, capillary pressure versus porosity, distribution of pore size, electrical properties. The permeability increases with the macroporosity (intergranular pore-type) and decreases with the microporosity associated to the chloritic micro-texture. Hence, the permeability results from the competition between macro and microporosity. The different laboratory measurements show that the chlorite shows a low cationic exchange capacity due to surfacic charges and low specific surface area. Ca$^{2+}$ cations play the main role in exchange cations. Hence, a low influence of chlorite mineral on the electrical properties.

Two electrical models (Waxman’s model and Dual-water model) are used to understand the chlorite effect. The difference between the Qv values measured by laboratory chemistry measurements and calculated from two electrical models shows the influence of micro-texture of chlorite in porous medium on electrical behavior. The chlorite content and its texture increases both the formation factor and the cementation exponent for the same lithofacies and porosity. The database comes from some cores of different chlorite content and indicates that for a higher chlorite content (lower permeability, higher specific surface area) and a higher pore-lining presence the saturation exponent decreases gradually when the brine saturation decreases.
GAS TRANSFER AND MECHANICAL INCIDENCE IN SATURATED STORAGE BARRIERS

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Context
In deep geological repositories, the hydrogen produced by the corrosion of the steel container protecting the nuclear waste represents a risk of damage for the surrounding engineered and geological barriers. Under the assumption that the vicinity of the waste package is re-saturated when the corrosion starts, the comparison between the corrosion kinetics and of the dissolved gas outflow through the barrier will indicate the risk of gas pressure accumulation with time and, finally, of a potential breakthrough of the barrier.

Modelling
Such a prediction relies on the existence of a clear modelling of the transfer and coupling phenomena. The situation described in our study is made of liquid water and dissolved gas, making a perfect liquid mixture (solution). Both of the two components of the mixture (namely: the water and the dissolved hydrogen) migrate through the barriers under diffusive and convective flow. At the same time, the constitutive equations describing the mechanical interaction of the solution (water+dissolved gas) with the solid phase (engineered barrier or rock) are derived from simple and clear physical assumption. The mechanical influence of the dissolved gas is proved to be a simple osmotic pressure leading, in practical cases, to a very low increase of the total pressure and of the correspondent mechanical stress.

Operational conclusions
The main tendencies of the first results derived from the application of the model to very simple descriptions of a storage are: (i) the pressure and stress increase due to gas production is highly smaller than described by previous authors (see Bonin et al.); (ii) the consumption of water with corrosion could be, on a mechanical point of view, the dominant and major phenomenon, creating an important decrease of water and total pressure. These two conclusions are summarised in the figures below, in terms of permeability and diffusion coefficient domains which correspond: (i) to a water consumption dominant, (ii) with a potential critical situation.

Of course, the importance of the water consumption stresses out the limits of such a simple model: due to water depression, the porosity of the rock will desaturate and the whole analysis would have to be reformulated in unsaturated conditions. However, some first tendencies can be proposed on the influence of desaturation upon corrosion gas effects.
SIMPLIFIED EVALUATION ON HYDRAULIC CONDUCTIVITIES OF SAND-BENTONITE MIXTURE BACKFILL

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Sand-bentonite mixtures are currently planned to be used as backfill materials for high-level nuclear wastes disposal in Japanese projects. The design and development of backfill materials, which fill up the tunnels of disposal facilities, are important for developing the technology of high-level nuclear wastes disposal (see Fig. 1). Sand-bentonite mixtures are attracting greater attention as backfill materials because they have very low permeable and high swelling properties. To design the specifications, such as dry density and bentonite content, of backfill materials, we must investigate the hydraulic properties by experiments and evaluate quantitatively the hydraulic-conductivities of sand-bentonite mixtures.

For the purpose, this study investigated the hydraulic conductivities at the different bentonite content and dry density by the experimental works. The hydraulic conductivity of backfill of which bentonite content is less than 50% was measured by the triaxial test apparatus with some improved parts (see Fig. 2). This study used commercial bentonite, which is called as Kunigel-V1, produced at the Tsukinuno Mine in Japan. The dry density of backfill was in the range of 1.43 to 1.79 Mg/m³. From the experimental results, the hydraulic conductivity of backfill was in the range of $2.66 \times 10^{-10}$ to $4.85 \times 10^{-12}$ m/sec for 5-20% bentonite content and was within $6.87 \times 10^{-12}$ to $1.21 \times 10^{-12}$ m/sec for 30-50% bentonite content (see Fig. 3).

We also discussed on the relationship between hydraulic conductivity and bentonite content from the viewpoint of bentonite-swelling in voids of backfill. The observation shown in Fig. 4 indicates that the hydraulic conductivity of backfill is strongly dependent on the swelling of montmorillonite in bentonite.

On the basis of the consideration described above, this study proposed the simplified evaluation for hydraulic conductivity using the parameter "Swelling volumetric strain of montmorillonite", which was proposed by the author (see Fig. 5). The evaluation method can obtain the hydraulic conductivity of backfill materials at various dry densities and bentonite contents. Therefore, the evaluation method can be used for designing the bentonite content and compaction density from the viewpoint of "very low permeability".
The disposal facility is currently planned to be constructed to a depth of several hundred meters.

Figure 1. An example of disposal facility and pit for high-level radioactive wastes in Japan

Figure 2. Test apparatus
Figure 3: Experimental results

Figure 4: Swelling behavior of bentonite in the mixture (bentonite content 50%)

Figure 5: Relationship between k and $\varepsilon_{sv}^*$
THERMODIFFUSION IN COMPACT CLAYS

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1. Introduction

When a concentration gradient $\nabla C$ and a temperature gradient $\nabla T$ are applied simultaneously, the evolution of the concentration field is governed by the classical diffusive transport and the Soret effect. The latter generates concentration gradients in response to an applied temperature difference. Within a domain sufficiently close to equilibrium and for ideal dilute solutions, the solute flux $J_1$ and the thermal flux $J_q$ can be expressed as [1]

$$J_1 = -\rho D \nabla C - \rho C S_T D \nabla T$$
$$J_q = -\lambda \nabla T - \frac{p R T^2 S_T D}{M} \nabla C$$

(1)

where $\rho$ is the fluid density, $T$ the temperature, $C$ the concentration, $M$ the molecular mass, $\lambda$ the thermal conductivity, $R$ the gas constant, $D$ the macroscopic diffusion and $S_T$ the Soret coefficient. The major objective of this work is to determine $S_T$.

2. Materials and measurements

The thermodiffusion cell is schematized in Figure 1. The material, supplied to us by ANDRA, is a block of argillite from the East part of France (see [2]). It has been used in order to obtain either clay powder or solid samples of 12 mm in diameter and 2 mm in thickness. NaCl, obtained from SIGMA (purity 99.5 %), was used as the principal solute. Pure water was used as solvent.

The temperature of each reservoir was measured by heat-resistances. The resistance data were converted to temperature by a calibration curve. The salt concentration was obtained from conductivity measurements. The conductivity of an electrolyte is known to vary with concentration and temperature. To obtain these variations, calibration curves were used. Each experiment was divided into two periods:

(I) a concentration difference $\Delta C$ was imposed at a constant temperature and measured as a function of time.

(II) after approximately 200-300 hours, a temperature difference $\Delta T$ was superposed on the concentration gradient. This temperature gradient was imposed in the same direction as the concentration gradient ($\nabla C \cdot \nabla T > 0$) or in the opposite direction ($\nabla C \cdot \nabla T < 0$). Experiments have been conducted at various temperatures ranging from 285K to 311K, with an associated different average temperature $\overline{T}$ and at various concentrations ranging from $5 \times 10^{-4}$ M to $10^{-1}$ M to obtain the dependence of $S_T$ with $\Delta T$, $\overline{T}$, $\Delta C$ and $C$.

3. Results and discussion

During the first period (I) in the absence of any thermal gradient, the evolution of the concentration profile during the diffusive process is described by the classical diffusion equation [3].

During the second period (II), the Soret coefficient was obtained from the experimentally measured concentration difference by means of a numerical program described in [4].
In Figure 2, we show an example of the evolution of $\Delta C$ with time. In (I), a concentration difference ($5 \times 10^{-4} \text{ M} - 10^{-3} \text{ M}$) was imposed ($T = 25^\circ \text{C}$). During (II), a temperature difference $\Delta T = 10^\circ \text{C}$ was superposed to $\Delta C$ in the same direction. Mass transfer is clearly influenced by the Soret effect. Values of $|S_T|$ against the diffusive formation factor are reported in Figure 3. It was found that the magnitude and the sign of $S_T$ depend on the sign of $(\nabla C \cdot \nabla T)$ and also on the average concentration $\overline{C}$.

References
DIFFUSION OF TECHNETIUM IN COMPACTED BENTONITE

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A repository for high-level radioactive wastes will be constructed in the bedrock at a depth of several hundred meters below ground surface. The gap between the container and the wall of borehole drilled on the floors of emplacement rooms of the repository is filled with a buffer material. The present design concepts of the repository consider use of compacted bentonite as the buffer material [1-3]. When a compacted bentonite is used for the buffer, it is installed to minimize the hydraulic conductivity and thus to control the transport of radionuclides by diffusion process. Understanding the characteristics of radionuclide diffusion therefore is essential in the assessment of radionuclide release through the buffer of a repository. In the present study, in-diffusion tests are carried out to determine diffusion coefficients and to investigate the effect of dry density on the diffusion of technetium in compacted bentonite considering as a candidate buffer material for a HLW repository in Korea.

The bentonite used for the diffusion tests is Ca-type. Its chemical composition is 56.8 % SiO$_2$, 20.0 % Al$_2$O$_3$, 6.0 % Fe$_2$O$_3$, 2.6 % CaO, 0.8 % MgO, 0.9 % K$_2$O, 1.3 % Na$_2$O, 0.2 % FeO, 1.3 % SO$_3$, and 0.8 % TiO$_2$. It has a cation exchange capacity of 57.6 meq/100g, and the predominant exchangeable cation is Ca$^{2+}$. The bentonite contains montmorillonite (70 %), feldspar (29 %), and small amounts of quartz (~1 %). $^{99}$TcO$_4$ as radioactive tracer and a synthetic groundwater were used for preparing the experimental solution. The diffusion tests were conducted under oxidizing condition and the dry densities of compacted bentonite were 1.4 Mg/m$^3$, 1.6 Mg/m$^3$, and 1.8 Mg/m$^3$.

Under the oxidizing conditions the technetium existed as TcO$_4^{-}$ and had no sorption on the bentonite. The apparent diffusion coefficients of technetium measured ranged from $3.46 \times 10^{-11}$ m$^2$/s to $9.46 \times 10^{-11}$ m$^2$/s, and they decreased with increasing the dry density. With no sorption on the bentonite, the diffusion of technetium was dependent on the pore structure of compacted bentonite, and it was also affected by anion exclusion between the technetium in the form of TcO$_4^{-}$ and the bentonite particle with negative surface charge. The results obtained will be used for the safety assessment of a repository.

References
DIFFUSION OF RADIONUCLIDES AND MICROSTRUCTURE OF COMPACTED BENTONITE OBSERVED WITH MICRO-CT

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Introduction
Compacted bentonite is a candidate buffer material for the geological disposal of high-level radioactive waste. Therefore, the diffusion behavior of radionuclides in the compacted bentonite is a key issue for the safety assessment of the geological disposal. The diffusion behavior has been considered to be affected by the microstructure of the compacted bentonite, such as vacancies (pores) between bentonite grains. However, conventional observation using TEM and SEM require sample preparations such as drying or freezing that alter the microstructure of water-saturated samples. In addition, these methods provide only sample surface information. A microfocus X-ray computerized tomograph (micro-CT, X-ray microscope) that has a high-resolution image, several µm, is expected to be useful to observe the microstructure of compacted bentonite samples in dry and water-saturated states[1]. Then, in this study, nondestructive, three-dimensional images of the internal microstructures of compacted bentonite samples obtained with this method were analyzed with a computer graphics, and the relationship between the internal microstructure and the diffusion behavior of radionuclides will be discussed here.

Experimental
The microfocus X-ray computerized tomograph system used in this study is a SkyScan-1072 (Skyscan, Belgium). This system is comprised of an X-ray source (80 keV sealed microfocus tube with spot size less than 8 µm), a cooled, 12-bit, X-ray CCD camera with a resolution of 1024 x 1024 pixels, and a precision object manipulator. The detectable spatial resolution of this system is about 6 µm.
Bentonite used is Kunipia-F supplied by Kunimine Industries, Japan. The bentonite contained montmorillonite (> 99wt%) and minor components. The bentonite was purified into homoionic Na⁺-type, ground by mortar and pestle, and sieved. After the purification, the bentonite sample was compacted into a cylindrical shape using a acrylic cell (7 mm in internal diameter and 10 mm in height) or an aluminum cells (5 mm in internal diameter and 10 mm in height) to obtain a dry density of 1.0 Mg m⁻³. Water-saturated bentonite samples were prepared by contacting the samples with distilled water through sintered stainless steel filters. The microstructure of the sample in the cells were directly observed by micro-CT. All samples were examined while being rotated 180 degrees in 0.2-degree steps. Data acquisition time was approximately 30-50 min for each sample. Images obtained by 3D-reconstruction processes consist of 1024 x 1024 pixels with 8-bit attenuation values.
Results and discussion
A typical horizontal plane, two-dimensional, micro-CT image of a dry bentonite sample at a dry density of 1.0 Mg m\(^{-3}\) is shown in Fig. 1. Black circle and dark dapples in this figure correspond to the wall of the aluminum cell and bentonite grains, respectively. The size distribution of the dark dapples in a portion of Fig. 1 was analyzed by means of computer graphics by supposing a certain threshold of brightness by which bentonite grains can be distinguished from vacancies (air). The size distribution of the dark dapples analyzed by computer graphics reasonably agrees with the size of the sieves (75-150 µm) and also agrees with the grain size distribution determined by laser diffraction/scattering particle size analysis[2]. This suggests that the combination of micro-CT and computer graphics enables high-resolution evaluation of the three-dimensional microstructures of the dry compacted bentonite samples. Based on the apparent diffusivities of some radionuclides that were experimentally obtained [2], the effects of the microstructure on the diffusivities will be discussed here.

References
INFLUENCE OF CATIONIC EXCHANGES ON CLAY SANDSTONE PERMEABILITY.
THERMODYNAMICS OUT OF EQUILIBRIUM OF EXCHANGES

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I. Introduction
Clay bed formations are frequently used as geological barrier because of their impermeability. But the coming in to contact of an effluent with clay formations to a variation in the permeability due to exchanges in clay minerals. Being in a dynamic system, i.e, without equilibrium, these exchanges cannot be studied through classical thermodynamics. We have then suggested a model reflecting dynamic exchanges based on the du Basty’s concept (1963).

II. Experimenting
1. Water / cation exchange
A sample of clay mineral was submitted to a continuous percolation of solution (at I = 0,01) of the water / KCl / water / NaCl / water / CaCl2 / water / MgCl2 / water cycle (figure1 as an example).
It can be noted that each water flow resulting a 40 to 60 % decrease in permeability whereas salk flow leads to an increase permeability in the same order.

2. Cation / cation exchange
The same sample is then submitted to a continuous percolation of the following solutions. Variations of the permeability are much weaker here (table I).
Permeability increases during the monovalent / divalent cation exchange. It decreases during inversed exchange, and it is practicaly constant during the exchanges of the cations of the same valence.

Results interpretation

| Tableau I. : Permeability and potential variations during cation exchanges. |
| Exchange    | Ca++/Mg++ | Mg++/K+ | K+/Na+ | Na+/K+ | K+/Mg++ | Mg++/Ca+ |
| Δk (%)      | - 0,4     | - 6,9   | - 0,3  | 0      | + 5     | - 0,5    |
| Ψd (mV)     | 240       | 233     | 410    | 410    | 250     | 242      |
We can see these exchanges are realised in a dynamic system since contaminating cations take the place of compensatory cations fixed on a solid surface during percolation. To treat these exchanges, one uses electroneutrality conservation of the system (equation 1), liberated energy during an exchange (equation 2), numbers of cationic charges conserved during an exchange (equation 3):

\[
\frac{d^2 \Psi}{dx^2} = \frac{F}{\varepsilon} \left[ \left( u_1 C_1 e^{\frac{\rho_1 \Psi}{RT}} + u_2 C_2 e^{\frac{\rho_2 \Psi}{RT}} \right) - \left( u_1 C_1 + u_2 C_2 \right) e^{\frac{\rho_1 \Psi}{RT}} \right] \tag{1}
\]

\[
AF \frac{\sum}{\varepsilon} \left[ \left( 1 + \frac{1}{k_1 C_1 e^{\frac{\rho_1 \Psi}{RT}}} + \frac{1}{k_2 C_2 e^{\frac{\rho_2 \Psi}{RT}}} \right) \right] = \frac{d \Psi}{dx} \tag{2}
\]

\[
\frac{1}{C_1 \left( 1 + k_1 C_1 e^{\frac{\rho_1 \Psi}{RT}} \right) + k_2 C_2 e^{\frac{\rho_2 \Psi}{RT}}} = \frac{\sum}{A} \int e^{\frac{\rho \Psi}{RT}} dx \tag{3}
\]

Where \( F \) is the Faraday’s constant, \( \varepsilon \), the permittivity of the media, \( x \), the distance of the potentiel barrier (shear plane of the fixed and moving layers). \( C, k, v, w \), respectively the cation concentration, the speed constant, the cation valence and the reaction energy, \( A \), the total number of compensatory cations which take part in the equilibrium, \( V \), the liquid phase, \( R \) the inert gases constant, \( T \), the absolute temperature.

The resolution of these equations permit the calculation of the variations of the potential barrier. The potentiel barrier is higher for monova lent cations than for bivalent cations. The potential is constant during and exchange of cations of the same valency. It increases when there are bivalent / monovalent cation exchanges and decreases during inverse exchange. Only the double layer repulsion energy varies in this cycle. Thus, potential and permeability stay constant. When potential increases, repulsion energy increases also favoring free particule dispersion in porous media. These particules obstruct the pores therefore the permeability decreases. When potential increases, the process is inversed.

References
CORRELATION OF HYDRAULIC CONDUCTIVITY OF CLAY - SAND COMPACTED SPECIMENS WITH CLAY PROPERTIES

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Hydraulic conductivity of compacted specimens consist of one of 17 clay samples and Toyoura standard sand (Yamaguchi, Japan) was measured using permeameters (Hojun Type D) with flexible wall cells designed based on ASTM D 5084-90. Clay samples studied were eight natural bentonites (WyomingA, WyomingB, China, Gunma-Ak, Gunma-As, Gunma-Ha, Gunma-Ho, and Gunma-N), one purified montmorillonite (KunipiaP; Kunimine Kogyo), five standard clay samples(SHCa-1, Syn-1, SAz-1, Tsukinuno, and Mikawa), one synthetic hectorite (SWN; Co-op Chemical Co.), and two cation exchanged bentonites (Na-WyB, Ca-WyB). Clay content was fixed at 13 % w/w. The clay/sand mixtures were compacted to be 16mm thick, 100mm diameter disks using a mold and a rammer. The compaction was carried out in conformity to JIS A1210. The wet density varied from 1.798 to 2.023 g/cm³, and the dry density ranged from 1.563 to 1.710 g/cm³. There is a tendency for Na type bentonites to have higher densities suggesting a dense structure without many water paths.

Hydraulic conductivity at 288 K (k_{288}) of Toyoura standard sand was determined at 1.433×10^{-2} cm/sec by constant head test, and it shows a good agreement with literature data. On the other hand, k_{288} of clay/sand specimens determined by falling head test were below than 3.6×10^{-7} cm/sec demonstrating a capability of the mixed material as a hydraulic impermeable barrier. The k_{288} varied from 3.6×10^{-7} to 3.3×10^{-10} cm/sec showing the dependence on characteristics of the clays. Especially, in the cases of natural bentonites, k_{288} value below than 10^{-8} cm/sec was measured. Moreover, extremely low k_{288} value below than 10^{-9} cm/sec was observed for Kunipia P and Tsukinuno specimens which have high smectite content. A marked tendency was observed that clays with higher Ca/Na ratio resulted in higher k_{288}. This result is consistent with reports that Ca type bentonite has higher hydraulic conductivity than the case of Na type bentonite. This was clearly demonstrated by WyomingB sample which was changed to Na form (Na-WyB) and Ca form (Ca-WyB) by cation exchange. The original WyomingB and the Na-WyB had almost the same k_{288} while the Ca-WyB had more than 5,000 larger k_{288} than that of Na-WyB.

The k_{288} of some of the compactions was also measured at an inlet pressure of 10 and 20 kPa to evaluate the impermeability on the assumption that up to 2 meters deep water lies on the barrier material. The k_{288} increased to some extent when pressure was applied, but it didn’t exceed 7×10^{-9} cm/sec in any cases.

Then measured k_{288} is correlated with additive properties of the clays such as, chemical concentrations, chemical ratios, methylene blue adsorption, and weight loss by drying at 383 K using multiple regression analysis. As the result, following linear polynomial correlation was obtained with a regression coefficient of 0.996.

\[ \ln k_{288} = - 19.57 + 0.027 \text{ Ca/Na} + 12.76 \text{ Al/Si} + 0.746 \text{ MgO} + 0.866 \text{ K}_2\text{O} + 0.467 \text{ CaO} + 0.217 \text{ Na/Ca} - 0.008 \text{ MB} - 0.184 \text{ Al}_2\text{O}_3 \]
Where Ca/Na is a ratio of CaO to Na₂O concentrations determined by X-ray fluorescence analysis [-]. Similarly Al/Si and Na/Ca are ratios of Al₂O₃ to SiO₂, and Na₂O to CaO, respectively. MgO, K₂O, and CaO are also concentrations [w/w %]. MB is methylene blue capacity [mmol/100g]. The predictors are arranged in decreasing order of significance, that is, Ca/Na ratio had the most significant effect to k₂₈₈ and Al₂O₃ the least. This equation can be used to estimate k₂₈₈ of clays or clay mixtures whose impermeability is unknown, because the predictor variables are all simple additive analysis data.
INSTRUMENT FOR MEASURING PORE PRESSURE AND PERMEABILITY IN LOW PERMEABILITY CLAY

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The Institute for Radioprotection and Nuclear Safety (IRNS) develops research programmes with the aim of establishing and furthering its expert understanding of the hydraulic characteristics of clay formations. Within this context, IRNS asked ANTEA in 2000 to design and install a first experimental instrument in a borehole drilled in Toarcian argillite from a tunnel in the experimental station at Tournemire (Aveyron). The instrument was to make highly accurate measurements of the hydraulic characteristics (hydraulic head and conductivity, and storage coefficient) of this specific formation. A second aim of the instrument was to help in evaluating the chemical composition of the pore fluid, by collecting water trapped in the probe chamber after a sufficiently long equilibrium time. The formation is characterised by a low matrix permeability ($10^{-14} < K < 10^{-13}$ m/s), known from measurements on samples, that requires recordings over at least several months to obtain stabilized head measurements.

The measuring instrument
The instrument can be inserted in boreholes with a diameter of 96 mm, at depths over 100 m. It consists of:

- a probe (fig. 1) with absolute-pressure and temperature sensors is emplaced in the measuring cavity, linked to the surface by two stainless-tubings and the sensor cable. A porous element ensures a large contact surface between the annular space around the probe and the pressure sensor. The probe is installed at the end of a string of watertight steel rods, that hold the tubings and sensor cable,

- a surface manifold (fig. 2) in a housing allows the measuring circuit to be put under a vacuum, to be filled with water, or to be pressurized. The manifold also contains absolute-pressure and temperature sensors,

- a high-resolution data-acquisition logger records the pressure and temperature values, as well as the barometric pressure and the pressure within the aquifers around the clay formation (fractured Aalenian – above – and Carixian – below – limestones). Teletransmission via a modem makes it possible to monitor parameter evolution from a distance.

Installation of the instrument
Once the borehole has been drilled, the probe is lowered into the 1-m-long measuring cavity and the annular space around it is filled with a porous and clean supporting material (acid-washed Fontainebleau sand) that serves to prevent the cavity wall collapse. A resin plug is then poured on top of the sand, followed by several metres of cement-based slurry. This operating method, which was tested in the laboratory, ensures a very good tightness of the cavity. After creating a strong vacuum ($\approx 60$ hPa), the chamber is saturated with water through the tubings. The water is a synthetic variety with a chemical composition as close as possible
to that estimated for the formation water. The tubing is closed after filling of the circuit and bleeding off the air within it.

**Interest of the instrument**
The monitoring of pressures on surface and at depth provides information on the possible re-saturation of the surrounding formation and on the return to equilibrium of pore pressure. Pulse tests are conducted to determine the hydraulic properties, i.e. transmissivity and storage coefficient, of the formation. The instrument can also be used for sampling part of the water in the chamber; by applying a slight fluid-overpressure at the end of one of the two tubings, it is possible to recover from the other line on surface at least part of the fluid contained in the measuring circuit. The instrument was installed in October 2000 in a first borehole, PH1, at 40 m below the tunnel floor. Monitoring the measurements until January 2002, including a pulse test, showed that the instrument functioned properly and provided very promising preliminary results.

![Figure 1: Borehole probe (cross-section)](image1)

![Figure 2: Schematic layout of the measuring system](image2)

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<td>1</td>
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<td>Temperature sensor</td>
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<td>Sintered inox porous sleeve</td>
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<td>Absolute pressure sensor</td>
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Figure 1: Borehole probe (cross-section)

Figure 2: Schematic layout of the measuring system
THE PERMEABILITY OF CLAY ROCKS.
CONSEQUENCES ON NOTION OF GEOLOGICAL BARRIERS

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I. Introduction
Airtightness of geological barriers is measured by the permeability of its constituent formation. Thus, permeability is a parameter that depends on fluid measure. Liquid permeability is of macroscopic value resulting solely from viscous flow. Gaz permeability can result from three types of flow: viscous flow, pore surface diffusion and free molecular flow. We have determined the contribution to permeability by each type of flow for clay rock, by comparing the mean free path of the gas molecules with the pore sizes.

II. Reminders
Viscous flow is verified by Darcy’s Law and is produced when the mean free path of the gas molecules is smaller than the pore sizes.
If this mean free path of the gas molecules is a fraction of the pore diameter (for example by diminishing pressure), a flow occurs by pore surface diffusion.
If it is much larger than the diameter, viscosity no longer intervenes, the molecules don’t move around except by shocks in the walls, due to free molecular flow (or to Knudsen flow).
This free process of diffusion occurs in each constituent by a mix according its own partial pressure even if the total pressure is heightened. One conceives here of the danger of emitting radioactive propagation whose partial pressure is weak.

III. Measures Of Permeability
In the case of viscous flow, gas permeability is measured with the aid of a constant load permeameter given as: \( k = \frac{2Q_P \eta L}{S(P_{up}^2 - P_{down}^2)} \), where: \( Q_P \) is the flow of gas measured at the pressure \( P \), \( \eta \) the viscosity of gas, \( L \) the length of the sample, \( S \) the section, \( P_{up} \) and \( P_{down} \), the respectively measured pressure upstream and downstream of the sample. By introducing a coefficient \( n \) in the difference of squares of the pressure, one can prove Darcy’s Law: \( k = \frac{2Q_P \eta L}{S(P_{up}^2 - P_{down}^2)} \) or: \( \ln(Q_P) = n \ln \Delta P + \lnk + \frac{\lnk S}{2 \eta L} \), with: \( \Delta P = (P_{up}^2 - P_{down}^2) \). If \( n = 1 \), Darcy’s Law is proven and the flow is laminar, if \( n \neq 1 \), the flow is no longer laminar.

The flow contributions by pore surface diffusion and/or free molecular flow are determined by Klinkenberg’s (1941) and Schofield’s et al (1990) methods. Klinkenberg’s methods (1941), confirmed by Jones and Owens (1980), consists of correcting the measure of permeability \( k \) by a coefficient \( (\beta) \) determined by tracing the curve of permeability by the measure of the inverse of the mean pressure: \( k = k_c (1 + \beta \tilde{P}) \), \( k_c \) is the corrected permeability of Klinkenberg. Schofield’s method (1990) depends on the fact that in viscous flow the flow is proportional to the product of the mean pressure by the pressure difference applied between the two faces of the sample \( Q+P_m \Delta P \). In the case of pore surface diffusion and/or free molecular flow, it is only proportional to the pressure difference \( Q+\Delta P \).

If we apply an exposant to the mean pressure equal to 1 in the case of viscous flow, or 0 in the case of free molecular flow and if we vary it between, one tries to correlate \( Q \) and \( P_m \Delta P \) by diminishing squares method. When the correlant’s coefficient is closest to 1, the exposant corresponds to the proportion of viscous flow (figure).
IV. Results. Conclusion
The resulting measures on diverse sandstone drilling give free molecular flow percentages between 5 to 30 %. This shows that rocks with small pores although reputedly airtight are capable of letting gasses pass through them by molecular diffusion. This shows that the notion of airtightness is a relative notions.

References
Klinkenberg, L.J., 1941. The permeability of porous media to liquids and gases. Drilling and Production Practice Ed.
RELATIONSHIP BETWEEN HF PERMITTIVITY AND MICROSCOPIC FLUID DISTRIBUTION IN CLAYEY GEOMATERIALS

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Since the relative permittivity of water is significantly higher than that of other materials commonly found in soils and rocks, there has been much interest in employing the relative permittivity of geomaterials, $\varepsilon$, as an "indirect" measurement of water content, $\theta$. In particular, capacitance sensors, time domain reflectometry (TDR) probes and ground-penetrating radar (GPR) have been developed in few dozen of MHz to 1 GHz frequency range and allow to obtain a high frequency (HF) permittivity measurement.

In order to improve the inversion of relative permittivity data for swelling clayey geomaterials, a good understanding of the effect of water distribution and the soil texture on the permittivity is required. Indeed, it is well known that numerous macroscopic properties of smectites are mainly controlled by microscopic processes (swelling and shrinkage properties, hydraulic conductivity).

Two theoretical approaches were used to investigate the effect of microscopic fluid distribution on HF dielectric permittivity of unsaturated clayey geomaterials: (1) the moment method, which is based on a numerical solution of Maxwell's equations written at a microscopic scale; (2) differential effective schemes (DES) corresponding to an effective medium approximation.

Both modelling approaches lead to the following results:

1. An anisotropic distribution of water microvolumes leads to an anisotropic macroscopic dielectric response (Fig. 1). Therefore, a deep claystone, associated with a clear anisotropic microstructure will show a significant anisotropic dielectric permittivity,

2. Calculations are strongly sensitive to bound water permittivity value, which is between that of ice (3.5) and free water (80). This key parameter is poorly constrained and a better understanding of the relationship between $\varepsilon$ and $\theta$ requires further experimental and theoretical investigations (eg. Fig. 2),

3. By considering spherical grains and platelet-shaped grains, DES models were applied to calculate dielectric permittivities measured on swelling clayey soils with clay contents up to 38 %. The results suggest that the soil particle shape has a secondary order effect on the relationship $\varepsilon-\theta$ in natural clayey soils (Fig. 3),

Concluding remarks

Hence, surveys of this type may be useful to determine and to monitor the distribution of the water in the unsaturated zone of clayey geomaterials. It allows to separate bound water content i.e. immobile water and free water content i.e. mobile water.

The permittivity of clayey geomaterials depends on texture (fine-grained materials) and electro-chemical/interfacial effects. Both parameters lead to the following features: (a) High content of bound water with low permittivity value (Figure 1); (b) a frequency dependent dielectric response; (c) a significantly high imaginary part of the permittivity (permittivity has to be considered as a complex quantity with a real and imaginary component). The high imaginary part values are due to energy dissipation associated with polarization and electrical conductivity processes.
Fig. 1. : Relationship between the effective permittivity and the water content when two perpendicular anisotropic distributions of water microvolumes are considered.

Fig. 3. : Relationship between the effective permittivity and the water content when two shapes (disk and sphere) of soil particle are considered. Experimental data are taken from Saarenketo (1998).

Fig 2. : Relationship between permittivity and water content considering the different states of water in clayey swelling geomaterials. The solid line (Topp et al. curve) is an empirical equation usually used in soils with low clay content. Note the significant difference between Topp et al. curve and the swelling geomaterials data (Dirksen & Dasberg, 1993) due to the low value of bound water permittivity.
ACTIVATION ENERGY OF THE SELF-DIFFUSION OF WATER IN COMPACTED CLAY SYSTEMS: A CASE STUDY WITH OPALINUS CLAY

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Clays are widely used as – natural or engineered – barriers to retain pollutants within a disposal site. In highly compacted clay systems, the pore water is quasi stagnant and molecular diffusion through this stagnant water is the main transport mechanism for pollutants. Because pores in compacted clay systems are so narrow, only a few water layers can build up. It is known that water in close vicinity to the surface of clay minerals has properties different from bulk liquid water (LOW 1976, ICHIKAWA et al. 1998, MERCURY et al. 2001).

Figure 1: Properties of bulk and confined water and their potential effect on thermodynamic properties and transport.

The properties of water in compacted clay systems will largely affect thermodynamics and the diffusive behaviour of pollutants and therefore, a detailed understanding of the structure of water in such systems is important for a mechanistic understanding of the fate of pollutants in argillaceous rocks and clay systems.

The activation energy of self-diffusion of water depends on the structure of the water. In bulk water, the interaction of a water molecule with its neighbours is, to a large extent, of a hydrogen-bond type. In order to move, these hydrogen bonds have to be broken. The corresponding energy required for breaking these bonds is reflected in the activation energy of self-diffusion of water. The value for the activation energy of self-diffusion of free liquid water is ~18 kJ/mole (MILLS 1973, FRIPIAT et al. 1984) whereas in ice-I the activation energy is ~57 kJ-mol⁻¹. When a water molecule is in an environment different from the bulk water, e.g. in a compacted clay system (Figure 1), it can be expected that the activation energy of the diffusion of water in such an environment is different from that of self-diffusion in bulk water.
This study focuses on the measurement of the activation energy of the self-diffusion of water in an argillaceous rock from the northern part of Switzerland (Opalinus Clay). Two methods were used: i) through-diffusion/out-diffusion of HTO at different temperatures and ii) time-of-flight neutron spectroscopy (TOF-NS). The temperature range covered by the experiments was between 5 and 70 °C. The values measured for Opalinus Clay (OPA-Benken) were compared with the values for bulk liquid water. In the case of Opalinus clay, the activation energy is slightly higher (22 kJ·mol⁻¹) than in bulk liquid water (18 kJ·mol⁻¹) indicating that the structure of water in OPA is slightly different from bulk liquid water.

References
LONG - TERM DIFFUSION EXPERIMENT AT MONT TERRI (DI-A) : FIRST RESULTS FROM FIELD AND LABORATORY DATA

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Introduction
Argillaceous formations are envisioned as host rocks for radioactive waste disposal in a number of countries. For the last few years a large number of investigations have been performed on the Opalinus Clay, a Mesozoic shale formation, at the Mont Terri Rock Laboratory (Thury & Bossart, 1999). All results on the geochemical properties and migration behaviour confirm that diffusion is the dominant transport process of this clay formation. Several studies have focussed on the diffusion of non-reactive tracers under in-situ conditions (Palut et al., 2002). On the other hand, reliable diffusion data for reactive tracers are lacking so far.

In this study (DI-A), the diffusion behaviour of sorbing tracers is investigated and compared to the one revealed by non-reactive tracers. We show first results from the diffusion of Na-22 and cesium in addition to HTO and iodide. Also, data from diffusion experiments performed under laboratory conditions will be presented.

Experimental procedures
The in-situ experiment consists of a single-borehole through which artificial formation water including the tracers is continuously circulated. Diffusion into the rock occurs in the packed-off test interval. A hydrotest performed prior to tracer injection indicated a hydraulic conductivity of 3E-13 m·s⁻¹ and a pore pressure of about 3 bar of the rock adjacent to the test interval. The concentrations of tracers in the borehole are regularly monitored. At the end of the experiment tracer profiles of an overcored section will be analysed. The interpretation of the results will be performed through numerical modelling. The aim is to obtain values for diffusion coefficients, accessible porosities and sorption parameters, and to compare them with the results from small-scale laboratory experiments (upscaling). Through diffusion experiments on sliced samples parallel to the bedding plane were performed at two laboratories, PSI and CIEMAT. The break-through and subsequent steady-state flux were studied for HTO, iodide, Cl-36 and Li-6. Two different techniques were used here. A radial through diffusion technique and a one-dimensional through-diffusion technique (Van Loon et al. 2002).
First results and conclusions
Results from water analyses in the borehole indicate tracer-dependent decrease with time. The composition of the artificial water remained rather constant, thus indicating that it reflects the actual in-situ composition fairly well. The decrease of Na-22 and cesium can be explained by concomitant diffusion and sorption processes, as was predicted in the case of Cs in scoping calculations.

First results from the laboratory through-diffusion experiments showed that diffusion parallel to the bedding is faster by a factor of 4-5 compared to diffusion perpendicular to bedding. The different $D_e$ values must be due to differences in tortuosity.

The results obtained so far demonstrate the feasibility of the experimental design to study the migration of non-reactive and reactive tracers. Long term experiments (>3 years) are necessary for studying the realistic diffusion behaviour of strongly sorbing tracers in low permeability clay formations.

References
DIFFUSION COEFFICIENTS AND ACCESSIBLE POROSITY FOR HTO AND $^{36}$Cl IN COMPACTED FEBEX BENTONITE

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Performance assessment of spent fuel repositories have shown that doses are controlled by non sorbing anionic species ($^{129}$I and $^{36}$Cl). As a consequence, it is necessary to have an in depth knowledge of the behaviour of anionic species in the compacted bentonite used as backfill material of the disposal galleries. Diffusion of anionic species in compacted clays is affected by electrostatic forces between the negatively charged clay surface and the anions, this phenomenon being called anionic exclusion, since it results in a smaller volume of pore water available for their transport. Effective diffusion coefficients and accessible porosities for HTO and $^{36}$Cl in FEBEX bentonite were determined by means of through-diffusion experiments. The behaviour of HTO (neutral and conservative tracer) was compared with that of the anionic $^{36}$Cl and the accessible porosities for both tracers were obtained by means of saturation experiments for several clay densities.

Clay plugs of 50 mm diameter of different thickness (10 mm for HTO, 5.3 mm and 8.3 mm for $^{36}$Cl) were compacted at different densities (from 1.0 to 1.7 g/cm$^3$) into a stainless steel ring and placed between two sinters. The diffusion cells were connected to two reservoirs (inlet and outlet) where the solution was continuously stirred. After the saturation of the clay plugs with water, the tracer was spiked into the inlet reservoir. The concentration evolution in both reservoirs was measured periodically.

The effective diffusion coefficient, $D_e$, was estimated using two methods: a) by fitting the evolution of the concentrations in the reservoirs to the theoretical evolution using numerical methods and b) using the analytical formulation proposed by Wolfrum et al., 1988:

$$D_e = \frac{\ln \Delta C_0 / \Delta C}{\beta \cdot t}$$

where $\Delta C_0$ and $\Delta C$ represent the concentration difference between the two reservoirs at initial and time $t$ respectively, and $\beta$ is a coefficient that takes into account the cross-sectional area, the thickness of the sample and the volumes of the reservoirs. Both methods gave similar results.

The effective diffusion coefficient for HTO, varied from $2 \cdot 10^{-10}$ m$^2$/s for a density of 1.1 g/cm$^3$ to $5 \cdot 10^{-11}$ m$^2$/s for a density of 1.7 g/cm$^3$. Whereas the effective diffusion coefficient for $^{36}$Cl decreased more significantly when varying the density from 1.0 to 1.65 g/cm$^3$.

Accessible porosities for HTO and $^{36}$Cl were obtained by means of saturation experiments. In these experiments the water saturated bentonite samples were introduced in a reservoir with the tracer until equilibrium concentration is reached. The measurement of the tracer activity contained in the clay pore water gives a direct measurements of the accessible porosity. Time evolution of concentration in outlet reservoirs in through-diffusion experiments provided a redundant, although less precise, methods to estimate the accessible porosity.

The accessible porosity obtained for HTO always agreed very well with the theoretical total porosity, which implies that all the pores in compacted bentonite are available for diffusion of neutral species (Muurinen and Lehikoinen, 1995). Different results were obtained in the case...
of Cl\textsuperscript{-}, for which the accessible porosity was significantly smaller than the total one, even at the lower densities. 

Taking into account the relationship between effective and apparent diffusion coefficients for conservative species, distribution coefficient, \( K_d \), equal at zero (Yu and Neretnieks, 1997):

\[
D_e = D_a (\varepsilon + K_d \rho_d) = D_a \varepsilon
\]

where \( \varepsilon \) is the accessible porosity and \( \rho_d \) the dry density, apparent diffusion coefficients for HTO and \({ }^{36}\text{Cl}\) in compacted bentonite can be also calculated if \( D_e \) and \( \varepsilon \) are measured.

**References**


**Acknowledgement**

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DIFFUSION EXPERIMENTS WITH COMPACTED POWDER / PELLETS CLAY MIXTURES

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Geological disposal of the high-level radioactive waste is currently considered as a safe solution to ensure the long-term isolation from the biosphere. The backfilling and sealing of shafts and galleries is an essential part of underground repository design.

A mixture (1:1) of pellets and powdered FoCa bentonite is being investigated by SCK CEN (Belgium) as a possible sealing material. One of the possible advantages of this mixture consists on the fact that it can be used to backfill irregular shaped volumes, obtaining an homogeneous material when saturation is reached.

In the frame of the RESEAL project (Dereeper et al., 2001), Ciemat carried out laboratory experiments to determine the diffusion parameters of conservative tracers in this mixture and to compare its properties with those of a powdered compacted material. HTO and iodide were selected as tracers in order to investigate the behaviour of a neutral specie and the behaviour of an anionic one that may suffer anion exclusion.

The diffusion coefficients through the powder/pellets mixture were obtained by means of through-diffusion experiments with constant concentration gradient. The “time lag” method and saturation experiments were used for the determination of the accessible porosity. The difference obtained with the two methods will be discussed.

The pellets and powder were placed inside a stainless steel ring by alternated layers and the mixture was uniaxially compacted inside this ring. The clay in the cell (diameter 10 cm and thickness 3 cm) was sandwiched by porous filters. The water used for the clay saturation was synthesised on basis of the composition of the Boom (site for the in situ experiments) clay pore water.

For through-diffusion experiments, carried out with a constant concentration gradient, an analytical solution is given by Crank (1975). Experimentally, the constant gradient is obtained using a high volume in the tracer inlet reservoir and a little volume in the measurement reservoir, which is periodically replaced. The diffusion process is initially characterised by a transient stage until the tracer flow through the sample becomes constant and reaching the steady state. The graph of cumulative mass recovery vs time, at the steady state, is a straight line from which slope the diffusion coefficient can be obtained. From the intercept of this straight line with the time axis, the accessible porosity can be theoretically calculated and this method is known as the “time lag” method.

An alternative method to measure the accessible porosity is to saturate the clay with the tracer, in fact the measurement of the activity of the tracer in the water within the clay plug allows its direct estimation.

The diffusion tests were carried out at different dry densities for the mixture: 1.34, 1.43 and 1.49 g/cm³. The effective diffusion coefficient, measured for HTO, varied between 5.1·10⁻¹¹ and 3.2·10⁻¹¹ m²/s decreasing with the increasing of the dry density. The values obtained are only slightly lower than those obtained in similar experiments with the compacted powdered material. Even at sight, upon the experiment, the pellet / powder seems to be homogeneous, it is not unlikely that regions with small differences in density still exist (initially the pellets have a dry density of 2.05 g/cm³).
The diffusion coefficient for iodide varied between $3.0 \times 10^{-12}$ and $5.8 \times 10^{-13}$ m$^2$/s from lower to higher dry densities and it was at least one order of magnitude lower than that of HTO for the same densities.

The theoretical porosities, calculated considering a clay specific weight of 2.67 g/cm$^3$, are 49.8, 46.4 and 44.2 % for the densities of 1.34, 1.43 and 1.49 g/cm$^3$ respectively. The accessible porosity for HTO estimated by the 'time-lag' technique varied between 45.8 and 30.8 % for HTO and between 10.8 and 2.5 % for iodide.

The experimental values obtained by the saturation method with HTO agreed satisfactorily with the theoretical porosity values for all the densities studied. These differences are probably due to the analytical approximation. The constant concentration gradient method, that has been largely used because an analytical solution can be used for the determination of transport parameters, allows to determine quite precisely the diffusion coefficients, in fact small variations in the slope of the tracer cumulative mass recovery vs time curve do not lead to significant changes in the calculated diffusion coefficients. On the contrary, it is very sensitive to the possible errors in the estimation the intercept of this straight line with the time axis, and small variation can lead to very different accessible porosity estimations.

References

Acknowledgement
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CLAY AS A PHYSICAL BARRIER TO RADIONUCLIDE MIGRATION

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This paper is a novel approach focused on clay performance as an engineered barrier that depends on the bond configuration and bond energy for effective retention rather than on the chemical processes of sorption. The performance is assessed in terms of bond susceptibility to radiolysis. Depending on the radiated energy by a radionuclide, the clay configuration can collapse. The research showed that clays susceptible to bond collapse due radiolysis add a physical aspect of obstruction to radionuclide migration from the near field especially when in colloidal form. Colloids migrate partly due to charge contrast and when the chemical structure of clay collapses the pathways are physically closed. The phenomenon enhances clay performance and is more evident in clays characterized by sheet configuration. It is one of the reasons why montmorillonite is regarded as an ideal buffer for isolation of high-level waste (HLW).
MODELLING OF WATER UPTAKE IN HIGHLY COMPACTED BENTONITE FOR ENVIRONMENTAL SEALING BARRIERS

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One alternative to close a radioactive waste repository in rock salt is the construction of a “Cross Section Closure (CSC)” sealing barrier. The proposed material for the CSC is highly compacted bentonite. To investigate the swelling behaviour of a highly compacted bentonite a large number of laboratory tests were performed. In addition, large scale model tests (Fig. 1) were carried out to demonstrate the development of a nearly homogeneous and isotropic swelling pressure. The results of the large scale model tests were interpreted numerically based on the models for stress-strain behaviour and water uptake which are implemented in the finite element codes FEST03 and HYDOPO. The investigations show a good agreement of the results of the model tests and the corresponding analyses (Fig. 2) and show that the theoretical models are capable of describing the behaviour of sealing structures based on highly compacted bentonite.

References

Fig. 1: Bentonite masonry
Fig. 2: Measured and computed swelling pressure
ION CONCENTRATION CAUSED BY AN EXTERNAL SOLUTION INTO THE POREWATER OF COMPACTED BENTONITE

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As part of a swelling-pressure study, the concentrations caused by the external solution into the porewater of compacted bentonite were studied. The tests were carried out with clay (MX-80), from which easily dissolving components had been removed in order to ensure that the ions in the porewater came from the external solution. The dry densities of the samples varied from 0.7 g/cm³ to 1.7 g/cm³. NaCl solutions of different concentrations were used as the external solution for saturation. The concentrations in the porewater were determined by two methods. The first one was based on the direct analysis of the squeezed porewaters. In the second method, the chloride concentration in the porewater was calculated on the basis of the total chloride content in the bentonite determined by dispersing the sample in deionized water. The latter method gives average concentrations in the porewater.

The results were first interpreted by the Donnan model. According to the model, the cation concentration $C_{ce}$ caused by the external concentration $C_e$ can be calculated from the Donnan equilibrium between the clay and solution using Eq. (1)

$$C_{ce} = \frac{-C_e \pm \sqrt{C_e^2 + 4 * C_e^2}}{2}$$

where $C_{ce}$ means the concentration caused by the exchangeable cations and can be evaluated from the cation-exchange capacity and water content in the clay. The method assumes the bentonite and porewater form a homogenous mixture and that there is only one type of porewater. The measured points and modelling curves are presented in Figure 1. It is obvious that at high concentrations the model can predict the concentrations in the porewater rather well. At low concentrations, where the exclusion is stronger, the measured concentrations are clearly higher than the modelling values. A possible explanation for this discrepancy is that the microstructure of bentonite is more complex than the homogenous structure assumed in the simple Donnan model, and an attempt to include the effects of the microstructure was made.

In the second modelling it was assumed that there are two pore types, interlamellar and external (large) pores. The dimensions for the microstructure were obtained from SAXS and BET surface area measurements. It was also assumed that there are two Donnan membranes in the system. The first one is the sinter between the external solution and the large pores, the second one is between the large pores and the interlamellar pores. Figure 2 compares the measured values with the modelling curves. In this case, the fitting is much better, which supports the assumption of different pore types in bentonite.
Figure 1. Chloride concentrations in the porewater as a function of the dry density of the sample and the concentration of the saturation solution. The concentrations were determined by the dispersion method (points). The modelling curves are based on the Donnan model.

Figure 2. Chloride concentrations in the porewater as a function of the dry density of the sample and the concentration of the external solution. The concentrations were determined by the dispersion method (points). The modelling curves are based on coupling the microstructure and the Donnan model.
CHARACTERIZATION AND MODELING OF DIFFUSION PROCESS FOR MASS TRANSPORT THROUGH THE TOURNEMIRE ARGILLITES (AVEYRON, FRANCE)

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Argillites are one of the geological formations studied by the IRSN for their confining properties for isolation of radioactive wastes. One of the main objectives is the study of water transport through rocks with very low water content and hydraulic conductivity by modeling of tracers’ profiles. This paper presents the protocol developed and applied for acquiring data of chloride content in the interstitial water of the Toarcian argillites at the Tournemire site (Southern France). This protocol is based on laboratory experiments involving diffusion process, and on modeling. Experimental data obtained during the transient and the steady parts of diffusion allow respectively the assessment of the diffusion coefficient and the initial concentration of pore water. Using this protocol, profiles for both of these data have been acquired along the geological sequence (fig. 1). Taking into account the present knowledge of the geological and hydrogeological history of the Tournemire massif, a conceptual model granting the main role for mass transport to diffusion has been proposed. According to this conceptual model, a one-dimensional numerical model was built for simulating the mass transport of chloride through the sedimentary column, over 53 Ma. The good agreement between experimental data and calculated values for both diffusion coefficients and concentrations of chloride, confirms that the diffusion is high likely the main process for mass transport in the massif. This model was also tested with the deuterium content of interstitial water as tracer, applying variable concentrations at the aquifer system boundaries for reflecting the thermal dependency of isotopic composition in precipitation. These simulations also reveal the likely important role of heterogeneities, such as fractures, in the variability of tracers’ concentrations with regards to a simple diffusion profile.
Fig. 1: Profiles of pore water concentrations in chlorine and of effective diffusion coefficients along the sedimentary column at Tournemire underground laboratory. Dots: measured values with error bars, from laboratory experiments, red lines: computed values using a 1D diffusion model.
1D REACTIVE TRANSPORT MODEL FOR THE OPALINUS CLAY AT MONT TERRI UNDERGROUND LABORATORY

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Pore waters from the Opalinus clay at Mont Terri show a compositional trend as a function of the distance to the formation limits, being the more saline waters those found in the centre of the formation and becoming more diluted as they are closer to the formation limits. The ratios of conservative components, such as Br/Cl, are equivalent to that of seawater. Considering that the Opalinus clay has a very low permeability, it could be assumed that seawater was trapped during sedimentation or at the first stages of diagenesis. According to this assumption, it is clear that the present-day porewater composition is the result of outward diffusion of the original porewater components, inward diffusion of groundwaters from the surrounding formations (Jurensis marls and lower Dogger limestones) and water-rock reactions.

We developed a geochemical model that considers groundwater diffusive transport in the Opalinus Clay, considered to be initially saturated with seawater. This process together with the relevant mineral equilibria and the appropriate cation exchange processes determine the main processes governing pore water evolution. Groundwater circulation and associated diffusion in the Opalinus Clay started after sedimentation of the marine sequence during the Triassic-Cretaceous period. This implies that any model concerning the hydrogeochemical evolution of the Opalinus Clay pore water should start after this period.

The comparison between analytical data and modelling results, based on conservative components, indicate that the best agreement is when considering a total evolution time of the system ranging between 4 and 5 million years. For longer time periods the calculated salinity is lower than that of the analytical data.

The agreement between the measured data and the modelling results is also satisfactory for major cations as calcium, sodium, potassium, and magnesium. In the case of sodium and potassium, the diffusive transport and the cation exchange control their concentration. Magnesium and calcium concentrations are in addition controlled by the equilibrium with calcite and dolomite respectively.

Strontium is also an important component in the Opalinus Clay system. Its behaviour is controlled by equilibrium with the cation exchanger and celestite. The model results also fit reasonably the analytical data.

The problem arises when comparing the results for the carbonate evolution and pH with the measurements. In both cases there is a systematic disagreement between modelling results and analytical data. This systematic difference could be the result of CO₂ loss during the long time period of water seeping into the packer zone in boreholes or in the case of the squeezing experiments at atmospheric conditions. This would allow CO₂ to escape resulting in a decrease of the total carbonate concentration relative to its in situ value. This has an
immediate effect on pH, which increases proportionally to the amount of CO₂ loss. In order to test this loss of CO₂, we simulated the effect of adding CO₂ to the samples. In this simulation we added CO₂ up to a pressure of log pCO₂ of −1.5 bars, which is the mean value obtained during the model calculation, and equilibrate the resulting waters with calcite. The results from this simulation are in agreement with the reactive transport modelling results.

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ILLUSTRATION OF THE ALLIANCES PLATFORM
CHEMISTRY/TRANSPORT
COUPLING CAPACITIES THROUGH THE SIMULATION
OF A CEMENT / CLAY INTERACTION

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One mission of Andra is to contribute to both national and international R&D projects related to deep repositories for Long-Lived High Level radioactive waste (HLW-LL). Andra will submit a report including proposals for HLW-LL disposal in deep geological to the French government by 2006. This report corresponds to the second research area described in the French law of December 1991 and entrusted to Andra. Therefore, safety studies have to be provided which involve numerical simulations. Stating the lack of numerical tools in this field, Andra decided to launch the Alliances project which aim is to create an user friendly numerical tool enabling the simulation of multi-phenomenology through numerical couplings. Among those ones, it has been decided to promote the transport chemistry coupling in a multidimensional space. The goal of this presentation is to give an overview of this coupling on a practical interface clay/cement study in one and two dimensions of space.

For the chemistry, the PhreeqC and Chess codes have been chosen. The phenomenology which can be involved includes:
- Speciation
- Ion exchange
- Surface complexation
- Oxydo-reduction
- Kinetic laws

For the transport, parabolic equations with advection / diffusion / dispersion terms are taken into account, the convection / diffusion/ dispersion operator \( L \) being:

\[
L(C_j) = C_j \nabla \vec{U} - \nabla \left( \frac{D}{\phi} \nabla (C_j) \right)
\]

within the global transport equation for species concentration \( C_j \)

\[
\frac{\partial C_j}{\partial t} + L(C_j) = Q_j, \quad j = 1, \ldots, N
\]

\( Q_j \) represents the source term obtained through speciation, \( N \) the number of involved species and \( \phi \) the porosity. It is worth to note in this formulation that, due to the mathematical formulation of the problem in terms of component species, \( \frac{D}{\phi} \) must be independent of the \( C_j \).

The coupling of the two phenomena occurs through a well known two steps operator splitting technique. Using a transient explicit scheme, the convergence is ensured by the numerical stability criterion, while in the case of an implicit discretization, a so called CC Picard iterative algorithm is used to meet convergence.

To illustrate this in the chemistry coupling field, we will focus on a clay / cement interface in a two dimensional field with an ion exchange linked to the Ca-Montmorillonite. This case has been defined at Andra to be used as a reference test case for chemistry coupling.
We will present the way the whole case is built up in terms of chemistry:
- database modifications and additions
- aqueous states definition
- ion exchangers characteristics
in terms of transport:
- geometry definition and meshing
- physical and numerical transport characteristics
and in terms of postprocessing by presenting the way information can be retrieved from the simulation.

An overall presentation of the open source part of the platform will also be given focusing on the chemical solver PhreeqC and the way information is exchanged, especially concerning the splitting algorithm enabling the PhreeqC chemistry part to be coupled with any multidimensional space porous media transport codes.