MODELLING OF LONG-TERM DIFFUSION-REACTION IN A BENTONITE BARRIER FOR RADIOACTIVE WASTE CONFINEMENT

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ABSTRACT
Bentonites have been proposed as buffer material for barriers in geological disposal facilities for radioactive waste. This material is expected to fill up by swelling the void between the canisters containing the waste and the surrounding ground. However, the bentonite barriers may be submitted to changes of humidity, temperature variation, fluid interaction, mass transport, etc. This could modify the physico-chemical performance of the barrier, mainly on the interface with the steel container and with the geological barrier. The engineered barrier development necessitates thus the study of the physico-chemical stability of its mineral component as a function of time under the conditions of the repository in the long-term. The aim of this paper is double: simulation of the chemical transformations into the engineered barrier and of the chemical-elements diffusion impact under repository conditions and then to apply a simplified method (volume balance in a saturated medium) to evaluate the swelling capacity evolution of the bentonite barrier because of their geochemical transformations. For that, a thermo-kinetic hydrochemical code KIRMAT (Kinetic Reactions and Mass Transport “1D”) was used.

The system modelled here is considered to consist of 1 m thick zone of water-saturated engineered barrier. This non-equilibrated system is put in contact with a geological fluid on one side, which is then allowed to diffuse into the barrier, while the other side is kept in contact with a source of metallic iron. Reducing initial conditions ($P_{O_2}=0$; $Eh=-200$ mV) and a constant reaction temperature (100°C) were considered.

In the current study the variation of swelling capacity was considered directly proportional on the montmorillonite dissolution (or chemical transformation), taking into account that this variation may be partially compensated by the precipitation (or neo-formation) of others swelling clays.

The results show that Na/Ca-montmorillonite-to-Ca-montmorillonite conversion is the main chemical transformation in the bentonite barrier. The neo-formation of illite, saponites, chlorites and Na-montmorillonite were also observed. In addition, the swelling capacity of the engineered barrier is not drastically affected after 10 000 years of diffusion-reaction. Due to the precipitated (or neo-formed) volume of swelling clays is almost directly proportional on the dissolved (or transformed) volume of montmorillonite. In fact, this simple approach predicted that the decay of swelling capacity of the engineered barrier is drastically affected near from the geological barrier-engineered barrier interface then the swelling capacity decay lies between 1 and 15% when the montmorillonite is completely transformed in the system.

Keywords: Engineered barrier, MX80 bentonite, Swelling capacity, Modelling, KIRMAT code, Geochemical transformations, Diffusion.
ABSTRACT
An important part of the nuclear waste disposal concepts of many European countries is a geotechnical barrier (buffer and/or backfill) consisting of clay material. It makes use of the swelling capacity of clay minerals that is expected to lead to sealing of drifts or boreholes when water is taken up from the host rock. Obviously, monitoring of the water content of clay barriers is of particular interest when such barrier systems are tested. Water content of clay is also of special importance if clay formations represent the geological barrier in an underground repository. The water content may be influenced by temperature rise in a HLW repository or by repository ventilation during operation, which could again influence the hydraulic behaviour of the rock.

For many rocks or technical materials, water content is the primary parameter determining the electric resistivity. Thus, geoelectric measurements can be used for monitoring of the water content of such materials. By using techniques like geoelectric tomography, larger portions of rock or backfill can be monitored in-situ. Conductivity is also influenced by solution composition and temperature. Therefore, calibration measurements with the actual boundary conditions have to be performed in the laboratory if resistivity tomograms are to be interpreted in terms of solution content. Although clay materials have a somewhat more complex electric behaviour than other types of rock, the same measuring and calibration techniques can be applied.

GRS has successfully tested the geoelectric method in various types of rock (salt, granite, clay rock) and backfill materials. The measurement and evaluation techniques employed are presented in this paper, together with the results obtained in projects dealing with geotechnical and natural clay materials.

A project involving geotechnical clay materials is the Swedish Prototype Repository Project, which incorporates disposal boreholes with bentonite buffer in a drift backfilled with a bentonite/crushed granite backfill. Here, the water uptake of the backfill has been measured by geoelectric tomography since October 2001. The continuous increase of saturation from the drift walls proceeding inward could be made clearly visible. Measurements in the buffer were started in May 2003. The results of these measurements show that water enters the buffer from the backfilled drift rather than via the borehole wall.

Geoelectric measurements in clay rock have been performed at the Mont Terri URL. Water content changes due to heating or ventilation have been monitored in the Heater Test HE-B and the Ventilation Test VE, respectively.

Heating had no significant effect on the clay water content. Throughout the heating period no resistivity increase was detected. Post-test laboratory investigations on rock samples from the heated region have confirmed this result.

An evolving desaturated zone around the ventilated VE microtunnel could, however, be well assessed. Ventilation with dry air by half a year resulted in the formation of a 40 to 50 cm wide zone which was desaturated down to about 50 % saturation.
DIFFUSION COEFFICIENTS
OF SOME CATIONS IN A MUDROCK
SAMPLE FROM THE BURE SITE

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Clayey materials exhibit attractive features as barrier for radioactive waste confinement, such as low permeability, high retention capacity, long-term stability, etc. The low permeability of such materials often makes diffusion the principal mechanism for migration of radionuclides potentially released from waste canisters. Therefore, diffusion of dissolved species has been extensively investigated in clay-based porous media. The purpose of this work is to investigate the diffusion of alkaline cations (Li⁺, Na⁺, K⁺, Rb⁺ and Cs⁺) in a mudrock sample from the Bure site (Meuse/Haute-Marne, France).

According to previously published data, positively charged solutes exhibit high diffusion coefficients compared to neutral species. Some authors assign this observation to the particular migration of ions within the electrical double layer, next to mineral surfaces. The occurrence of this surface diffusion mechanism is still an open debate. Furthermore, the extent of enhanced diffusion appears to depend on the considered cation.

Available data are mainly measured in compacted bentonite samples, involving Cs or Sr as tracers. The objective of this work is to evaluate if an accelerated diffusion is actually observed with alkaline cations in Bure mudrock and, if so, in what extent this effect vary for the considered cations.

The material is a natural rock, mainly composed of interstratified illite/smectite, quartz and calcite. It is saturated with a Na-Cl-dominated synthetic solution with a ionic strength of 57 mM and a pH ~8.0. The effective diffusion coefficients (Dₑ) for the cations are determined from their steady-state flux through mudrock slices at 23°C (through-diffusion technique). HTO diffusivities are systematically measured as well.

The results of HTO diffusion measurements are homogeneous: the mean value of Dₑ(HTO) is found to be $2.5 \times 10^{-11}$ m² s⁻¹ (± 30%). According to the pore diffusion model, the effective diffusion coefficient depends both on the diffusion coefficient in water, and on a formation factor. This latter parameter accounts for the structure of the porous network accessible to the considered solute. The accessible porosity in clay media is currently assumed to be similar for both cationic and neutral species. Therefore, the effective diffusion coefficient for a cation M⁺ can be calculated from water diffusion coefficients by:

$$D_e(M^+) = D_e(HTO) \cdot \frac{D_o(M^+)}{D_o(HTO)}$$

This equation is widely used to estimate the diffusivities of cations. Values calculated by this way for alkaline cations in Bure mudrock are found to be systematically lower than measured data. Moreover, this observation appears to depend on the considered species: the ratio between measured and calculated effective diffusion coefficients ranges between factor two for lithium and nearly one order of magnitude for rubidium and cesium.

The differences between calculated and measured Dₑ is found to continuously decrease with increasing ion radius. The correlation observed between effective diffusion coefficients and cation radii –if it is confirmed with other species- could be profitably used for the assessment of diffusion coefficients.
Thus, predicting the diffusion coefficients for cations appears to be tricky. Estimations can yield errors as large as one order of magnitude. Unfortunately, for some highly sorptive species, measuring the diffusion parameters is not achievable to laboratory study over reasonable time scale. It is concluded that some care must be taken with calculated diffusion coefficients in clayey media for positively charged species.
A HIGH-RESOLUTION ABRASIVE METHOD FOR DETERMINING DIFFUSION PROFILES OF SORBING RADIONUCLIDES IN DENSE ARGILLACEOUS ROCKS

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INTRODUCTION
It is common practice that the diffusion of radionuclides is measured in the laboratory on small-scale rock samples. Preferentially through-diffusion is chosen because the effective diffusion coefficient, \( D_e \), and the rock capacity factor, \( q \), can be determined independently. Moreover, for non- or weakly sorbing tracers the breakthrough occurs within a reasonable time span, i.e. days to months. In the case of strongly sorbing radionuclides, however, the breakthrough is very slow (up to years) and through-diffusion techniques become no longer practicable. Therefore alternative methods have to be developed in order to measure the diffusion properties of strongly sorbing tracers in argillaceous rocks. In-diffusion, combined with profile analysis, has been used for this purpose in the past for diffusion of radionuclides in compacted bentonite (Yu and Neretnieks, 1997; and references therein). Because bentonite is plastic, thin layers of material can easily be removed by cutting. In the case of a stiff material, the removing of thin layers is much more difficult. Andersson et al. (1981) and Albinsson et al. (1993) used an abrasive technique for analysing the diffusion profiles of Cs in concrete. The method proposed in this work is based on the idea of Andersson et al. (1981) and was further refined in order to remove much thinner layers of material for obtaining a higher resolution. This is important for strongly sorbing tracers such as tri- and tetravalent actinides that have sorption coefficients up to 1000 m\(^3\) kg\(^{-1}\) resulting in typical in-diffusion distances smaller than 1 mm for diffusion times of several years.

RESULTS
The diffusion of \(^{134}\)Cs\(^{+}\) and \(^{22}\)Na\(^{+}\) in Opalinus Clay was studied by in-diffusion laboratory experiments. The diffusive tracer profiles in the rock were determined using a high-resolution abrasive peeling method. The tracer concentrations of the radionuclides in the grinding swarf were measured directly via \( \alpha \)-spectrometry. By choosing the appropriate abrasive paper, a resolution down to 15 µm can be achieved. This is important when analysing strongly sorbing radionuclides such as tri- and tetravalent actinides that show steep diffusion profiles. In this study, a resolution between 30 and 70 mm was selected which was sufficient for spatial resolution of the diffusion profiles.

Both the effective diffusion coefficient and the sorption value of the radionuclides could be determined applying a single reservoir method with decreasing source concentration for a semi-infinite case. In the case of \(^{22}\)Na\(^{+}\), an effective diffusion coefficient \( D_e=1.8\times10^{-11}\) m\(^2\) s\(^{-1}\) and \( D_e=1.6\times10^{-11}\) m\(^2\) s\(^{-1}\) for Benken OPA and Mont Terri OPA, respectively, were derived. The distribution coefficients were 2.4x10\(^{-4}\) and 1.0x10\(^{-4}\) m\(^3\) kg\(^{-1}\), respectively. For Cs the effective diffusion coefficients were higher, i.e. \( D_e=3.5\times10^{-11}\) m\(^2\) s\(^{-1}\) for OPA from Benken and \( D_e=3.4\times10^{-11}\) m\(^2\) s\(^{-1}\) for OPA from Mont Terri. The sorption values determined were \( K_d=0.17\) m\(^3\) kg\(^{-1}\) for Benken and 0.30 m\(^3\) kg\(^{-1}\) for Mont Terri. Comparison of the data obtained for the weakly sorbing \(^{22}\)Na\(^{+}\) with that from earlier through-diffusion experiments, showed that there is an excellent agreement between the two methods. In the case of \(^{134}\)Cs\(^{+}\) such a comparison was not possible because of lacking through-diffusion data. Experiments with \(^{60}\)Co\(^{2+}\) and \(^{154}\)Eu\(^{3+}\) are in progress and first results are expected by beginning of 2005.
CONCLUSION
Through-diffusion methods cannot be applied to study the diffusive behaviour of strongly sorbing tracers because of the corresponding long break-through times. In-diffusion combined with high-resolution abrasive peeling was shown to be an excellent alternative for measuring diffusion properties of strongly sorbing tracers in dense argillaceous rocks. The proposed method is a simple and fast one, and requires a low cost equipment.

References


A WAVELET APPROACH TO ROBUST SOLVER FOR THREE DIMENSIONAL CONTAMINANT MASS TRANSPORT

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INTRODUCTION
Numerical modeling of the contaminant transport especially in three dimensions is considerably difficult. Transport model is not only vulnerable to numerical errors such as numerical dispersion and artificial oscillation, but also requires much of the computer memory and execution time. There is obviously need for a new mathematical approach to develop a computer code that is virtually free of numerical dispersion and oscillations, simple to use and flexible for a variety of field conditions, and also efficient with respect to computer memory. The physical phenomena taken in account in this model are advection, dispersion, chemical reaction, radioactivity, dissolution, sorption and precipitation. The mathematical formulation of the mass transport is defined by:

$$\frac{\partial (\theta C^k)}{\partial t} = \frac{\partial}{\partial x_i} \left( \theta D_{ij} \frac{\partial C^k}{\partial x_j} \right) - \frac{\partial}{\partial x_i} (\theta v_i C^k) + \sum Q - \lambda \theta C + \sum R_n$$

WAVELET DISCRETIZATION
The WCMT transport model uses a wavelet Galerkin discretization to solve the mass transport model efficiently. Since the scaling functions are compactly supported, only finite number of the connection coefficients are non, the resultant matrix has a block diagonal structure and it can be inverted easily (Nasif, 2003).

The system is treated as a fully Galerkin procedure. Our procedure uses a class of compactly supported scaling function introduced by Daubechies. We define wavelet series expansion within each region for the unknown concentration as

$$C(x) = \sum_{k=-N+1}^{2^j} c_k 2^j \phi(2^j x - k)$$

RESULTS AND DISCUSSION
The model has been tested for several problems ranged from one dimension to three dimensions. The results are compared to the results of the same cases, which solved using different numerical schemes. Three test cases have been carried out to prove the validity and applicability of this code to solve contaminant mass transport problems. First test case is to find the concentration of $^{135}$Cs radionuclide in the geosphere of the proposed Japan HLW repository as stated in H12 report. The second test case is the case introduced by (Sudicky, 1989) for mass transport in 2D system. The third and final test case is a 3D heterogeneous field study case and it used for ELLAM model verification (Heberton, 2000). The accuracy of the solution is calculated using the Discrepancy term. The total mass is calculated at each transport step to provide summarized information on the total mass in and out of the system. A good agreement between the results obtained using WCMT code and other codes has been proved.
H12 report test case, \(^{137}\text{Cs}\) Release From the Host Rock

(Sudicky, 1989) 2D filed test case

Concentration breakthrough curves as calculated from WCMT Vs Concentration breakthrough as calculated using ELLAM code.

References:


CAN THERMAL OSMOTIC TRANSPORT OCCUR UNDER STATIONARY CONDITIONS AFTER CANISTER LIFETIMES ARE EXCEEDED?

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According to Derjaguin et al. (1987), thermal osmosis is a flow of fluid driven by a temperature gradient due to a variation in the specific enthalpy of water depending on the distance to charged surfaces of solid phases. Thermal osmosis has a pronounced effect in clays and might therefore be a relevant transport process in a repository for heat producing radioactive wastes in which clays are present in the engineered barrier or in the host rock. Previous assessments have yielded that after resaturation of a repository, thermal osmosis might dominate both diffusion and advection, at least if one does not consider interactions between those transport processes. Yet, it has commonly been stated, that there is no effective thermal osmotic transport as soon as quasi-stationary flow conditions have been established. This is being explained by the fact that, due to the mass conservation of the fluid, thermal osmotic fluxes give rise to reverse advective fluxes of equal strength provided that flow conditions are stationary and no fluid sources are present within the flow domain. This mechanism of compensation would strongly reduce the importance of thermal osmosis since it is of no relevance during the nonstationary resaturation phase of a repository in which radionuclides are held back by the waste canisters.

However, uncompensated thermal osmotic fluxes might occur even if flow conditions are stationary and the flow domain is free of fluid sources. They might appear if a heat source causes temperature differences between boundaries representing fluid sources or sinks or if thermal osmotic or hydraulic conductivities are inhomogeneously distributed thereby giving rise to circulating currents (The flow vector field then does not need to be irrotational). In the study presented here, the effect of uncompensated thermal osmotic fluxes is investigated using a simple 2-dimensional numerical model for advective and thermal osmotic flow assuming stationary conditions and constant fluid density and viscosity. The transport effect of thermal osmosis is compared to that of diffusion by calculating particle transport accounting for a time-dependent heat production rate. Calculations are performed for a repository system (Fig. 1) containing a layer with high conductivity (e.g. a sandy interlayer or a damage zone) and for an emplacement chamber containing a bentonite buffer (not illustrated here). The calculations show that heat sources are able to induce significant thermal osmotic transport within the investigated parameter range (Fig 2 left). It was observed that even small temperature gradients are capable of causing significant particle transport when acting over long periods of time (Fig 2 right).

The study shows that the mechanism of advective compensation does not necessarily inhibit an effective thermal osmotic transport due to heat producing wastes. The finding of previous assessments that thermal osmosis might produce higher fluxes than diffusion and advection must therefore be regarded as a problem. This is affirmed by the simulation results which show that thermal osmotic transport can be significant even if radionuclides are held back by the canisters for several thousand years. Therefore, there still is need for further research on the relevance of thermal osmosis. Presently, there is an essential lack of data concerning thermal osmotic conductivity for clays and conditions relevant to repository systems. The study points out the necessity to narrow down the expected range of this parameter by experiments. Also, improved conceptual and numerical models have to be applied.
Figure 1: Top: 2D-model for a horizontal clay layer confined by aquifers and containing an extended permeable structure. Bottom: Calculated orientation of flow vectors showing circulating flow. The permeable structure acts as a fluid source near the heat source owing to the advective recharge at lateral parts of the domain.

Figure 2: Particle transport calculations (injection at heat source). – $kt^* := m Q_0 / \lambda k_t$ is a model parameter called “initial rescaled thermal osmotic conductivity (IRTC)” with $m$: number of canisters, $Q_0$: initial heat production rate [W], $\lambda$: heat conductivity [Wm$^{-1}$K$^{-1}$], $k_t$: thermal osmotic conductivity [m$^2$K$^{-1}$s$^{-1}$].
LARGE-SCALE GAS INJECTION TEST (LASGIT) AT THE ÄSPO HARD ROCK LABORATORY IN SWEDEN

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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, over time, will draw in the surrounding groundwater and swell to close up construction gaps. Once hydrated, the bentonite 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 and include high sorption capacity, very high plasticity and excellent fracture self-sealing characteristics. These severely limit the migration of any radionuclides released from a canister after closure of the repository. Because of the important pH-buffering effect of the bentonite on the porewater, this engineered barrier is often referred to as the clay buffer.

The metal canisters are expected to have a very substantial life in the repository environment. However, for purposes of performance assessment (PA), we must consider the possible impact of groundwater penetrating one of the canisters. 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 gas will accumulate in the void space of the canister. Gas will enter the bentonite when the gas pressure exceeds some 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 aimed at the development of safe disposal technologies, 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. Both the porewater pressure and the total stress acting within the clay are strongly affected by the passage of gas. The laboratory work has highlighted a number 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 will be undertaken at the Äspö Hard Rock Laboratory (HRL), around 360km south of Stockholm in the municipality of Oskarshamn. The HRL consists of a network of underground tunnels, totalling over 3600m in length, at an average depth of around 460m. 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, has been drilled into the gallery floor. Canister defects will be mimicked by placing thirteen circular filters of varying dimensions on the surface of a copper canister to provide point sources of gas. These filters will also be 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 have been installed, the borehole will be capped with a conical concrete plug retained by a reinforced steel lid. The lid will be held down by rock anchors designed to withstand over 5000 tonnes of force. Additional instruments will 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 will enable remote control and monitoring to be undertaken by staff at BGS Headquarters in Keyworth and will also allow 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. The experiment is scheduled to run continuously over the next 5 years.
NON-ISOTHERMAL MULTIPHASE SOLUTE TRANSPORT IN PARTIALLY SATURATED BENTONITE

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ABSTRACT
Clay-rich material, e.g. bentonite, has been selected as backfilling material in the geotechnical barrier system in different concepts for the final disposal of high-level radioactive waste in many countries. In such a subsurface system bentonite is subjected to effects from coupled thermal (T), hydrogeological (H), mechanical (M) and chemical (C) processes.

In order to analyse and understand the bentonite behaviour under these complicated conditions, a concept of external combination of two existing numerical codes, namely GeoSys/RockFlow [1] and PHREEQC2 [2], has been developed. GeoSys/RockFlow is a code based on the finite element method developed originally by the University of Hanover together with the BGR for simulating thermal, two-phase-flow, deformation, and solute transport processes in fractured porous media [3, 4, 5]. PHREEQC2 is a computer program written in the programming language C by USGS that is designed to perform aqueous geochemical calculations at low temperature. Using this concept and corresponding tools, a variety of aspects concerning THMC coupled problems can be considered.

As validation example, a laboratory experiment conducted by Cuevas et al. 1997 [6] was simulated. In the experiment, highly compacted FEBEX-bentonite was simultaneously subjected to heating and hydration, in order to investigate the possible changes in pore water chemistry resulting from thermal gradients and hydration processes.

A 1D model was used to calculate the distribution of temperature, water content, and concentration of different chemical specimens. The results show a good agreement of simulated and measured pore water chemical compositions (Figure 1) [5]. The following conclusions can be drawn:

Figure 1: Comparison of simulated with experimental results after 2619 hours by non-isothermal reactive transport in two phase flow (EXP – Experimental)
1. Temperature affects both the multiphase flow and geochemical reactions. Around the heated end, the sample was dried by heat and can be well observed at the beginning stage while water from the bottom did not reach there. Consequently, capillary pressure was increased and thus favoured the flow transport. The effect on chemical reactions was also observed in the simulation. With increase of temperature, concentrations of elements in pore water change, for example, the concentration of Na increases.

2. Within the duration of an experiment the chemical composition of pore water in bentonite can be strongly determined by relatively soluble minerals like calcite, halite, gypsum, etc., which are normally of small quantities in bentonite. Consequently, porosity change resulting from mineral dissolution/precipitation remains small within a relatively short period (experiment).

3. The swelling effect is an important phenomenon in bentonite. With swelling under constrained conditions, effective porosity and thus effective permeability of the bentonite will be changed. The swelling potential can also be influenced by variation of the chemical composition. For such modelling more exact material parameters are required [7].

References:
TRANSPORT THROUGH SHALES.
THERMODYNAMIC APPROACH,
IMPORTANCE OF THE MICROSTRUCTURE,
AND COMPARAISON WITH EXPERIMENTAL DATA

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The transport properties of shales or argillaceous rocks is complicated by the existence of a variety of coupling transport phenomena. For example, when a macroscopic disturbance like a salinity gradient is applied through such a material, it generates a ionic flux, an electrical current density and a fluid flow through the porous material. In shales, most of the coupling phenomena owe their existence to the smallness of the pores, the high specific surface and the excess of electrical charge located in the close vicinity of the mineral-water interface, in the so-called electrical-double layer associated with the charge excess or deficiency of the clay minerals. We have developed a consistent model of ionic transport in water-saturated porous shales (Revil and Leroy, 2004). This model is based at the macro-scale on the use of an extension of the theory of linear irreversible thermodynamics of Prigogine and De Groot and Mazur. The material properties entering into the macro-scale phenomenological relationships are obtained from a micro-macro homogenization by volume-averaging the local equations (Nernst-Planck and Stokes equations) in the case of a binary symmetric electrolyte like NaCl or KCl. The thermostatic state (equilibrium situation) is described using a modified Donnan equilibrium model. In this model, we account for the spatial distribution of the counterions in an electrical triple-layer model (Leroy and Revil, 2004). All the materials properties entering the macroscopic constitutive equations are explicitly related to the porosity of the shale, to its cation exchange capacity, and to some textural properties like the electrical formation factor. We suppose that the size of the diffuse layer can be on the same order of the magnitude than the size of the throats controlling transport though the connected pore space, which is a good assumption for low porosity shales. We assume the porous medium homogeneous and isotropic at the scale of the measurements.

Clay-rich composites act as semi-permeable membranes that restrict the passage of charged and uncharged solutes. Reinvestigating some recent data from the literature (Malusis and Shackelford 2002), we explain for the first time, from first principles and not from empirical considerations, the observed relationship between the chemico-osmotic efficency coefficient, $\varepsilon$, and the effective diffusivity $D^*$ of the salt through such barrier (geosynthetic clay liner). The effective diffusivity $D^*$ of the salt calculated increases from $6\times10^{-11}$ m$^2$ s$^{-1}$ to $2.3\times10^{-10}$ m$^2$ s$^{-1}$ and the chemico-osmotic efficency coefficient $\varepsilon$ calculated decreases form 0.8 to 0.1 with the increase of the salinity ($4\times10^{-3}$ to $4\times10^{-4}$ mol L$^{-1}$) here.

The samples analyzed in this work come from the Callovo-Oxfordien formation at the underground laboratory of Bure (Meuse, France). These samples were extracted from a depth of approximately 500 meters. The clay content is approximately 40 % and the clay fraction is composed of illite, chlorite and mixed layer illite/smectite clays.

• When the samples are perturbed by a fluid pressure gradient, electric gradients are generated through the samples. These streaming potential measurements yield electro-filtration coefficients. The streaming potential exhibits a relaxation associated with the variation of the pressure front through the pore, which is related to the sample length and the hydraulic diffusivity of the material.
• When the samples are submitted to a salinity gradient, electric gradients are generated through the samples: membrane potential. These measurements yield the macroscopic Hittorf number. The predictions are in good agreement with the experimental data. The amplitude of the Hittorf number and of the electrofiltration coefficient decrease from 0.8 to 0.46 and 3.5 to 1 respectively when the salinity increases (1.5x10^{-2} to 7.5x10^{-2} mol L^{-1}). We observe the relaxation of the membrane potential. The relaxation time is directly dependent on the sample length and on the effective diffusivity of the salt.

We have developed a finite difference algorithm to estimate the retardation coefficient for cations Na^+ and anions Cl^- including the electrical triple layer model.

In summary, some important parameters for describing ionic migration in shales like the effective diffusivity of the salt, the macroscopic Hittorf number, the streaming potential coupling and the hydraulic diffusivity coefficient have been determined experimentally and compared with the model of ionic transport in shales. This new model developed by (Revil and Leroy 2004) can also be applied to non isothermal conditions and in anisotropic media. Extension and future work involve unsaturated media, multi-component electrolytes and irreversible deformations.

References:


MODELING OF TRACER BEHAVIOUR AND DOMINANT REACTIONS DURING THE PORE WATER CHEMISTRY (PC) EXPERIMENT IN THE OPALINUS CLAY, SWITZERLAND

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The Pore Water Chemistry (PC) Experiment at Mont Terri Rock Laboratory (Switzerland) aimed to gain more insight into the reactions and processes that dominate the chemistry of the pore water in the Opalinus Clay. For that purpose, a long-term diffusive exchange experiment was set up in a packed-off borehole interval, which intersects the bedding plane at an angle of roughly 45°. To minimise oxidation, the borehole was drilled with N₂ and filled with Ar prior to equipment installation. On March 22, 2002, artificial water was filled into the interval and allowed to equilibrate with the formation pore water. The artificial water was designed by geochemical modelling to be in equilibrium with the mineralogy and cation exchange properties of the rock and traced with Cl, Br, SO₄, H₂,¹⁸O, and ¹³C. Water samples were taken for chemical analysis 12, 116, 264, 529, 600 and 807 days after start.

In view of the dominating diffusion along the bedding, we analysed the tracer data with a 2D solution. The plane parallel to the bedding intersects the borehole in form of an ellipse. We simplified this geometry by assuming a radial symmetry, where the circular borehole area (radius $a' = 0.032$ m) has the same circumference as the ellipse. The diffusion equation for this radial system, including the borehole area, was solved in Laplace space and inverted numerically with the Talbot algorithm. The solution in Laplace space is

$$\hat{\epsilon}(r,s) = \frac{a' K_0(q r)}{q D_p \left[ a' q K_0(a' q) + \alpha K_1(a' q) \right]}$$

where $r \geq a'$ is the radial distance from the centre, $s$ the Laplace transform variable, $\alpha$ two times the rock capacity per rock area divided by the borehole capacity per borehole area, $D_p$ the pore diffusion coefficient, $q = (s/D_p)^{1/2}$, and $K_0$ and $K_1$ modified Bessel functions of order zero and one.

Diffusion coefficients for Opalinus Clay samples from Mont Terri were determined in lab experiments within other projects. As a first estimate, we used the value of $D_e = 4.3 \times 10^{-11}$ m² s⁻¹ obtained for HTO parallel to the bedding (all values were adapted to a temperature of 15°C) for HDO and for H₂¹⁸O. We performed also simulations with a five times lower value of $D_e = 8.7 \times 10^{-12}$ m² s⁻¹ representing diffusion perpendicular to the bedding, as well as with the geometrical mean of the two values ($D_e = 1.9 \times 10^{-11}$ m² s⁻¹). For Cl and Br, the laboratory value for ³⁶Cl of $1.3 \times 10^{-11}$ m² s⁻¹ (parallel), and values of $2.5 \times 10^{-12}$ m² s⁻¹ (perpendicular), and $5.7 \times 10^{-12}$ m² s⁻¹ (geometrical mean) were used. A porosity $\alpha$ of 0.17 m⁻³ was assumed for the water tracers, and of 0.082 m⁻³ for the anions. Note that $D_p = D_e / \varepsilon$. The capacity ratio $\alpha$ was 9.2 $\varepsilon$.

Measured concentrations of tracers in the water follow more or less the simulation for a $D_e$ of about $2 \times 10^{-11}$ m² s⁻¹ and a porosity of 0.17 m⁻³. The $D_e$ value is somewhat lower than typical values reported for diffusion along the bedding for Mont Terri samples. This may be because the experiment was located in the fault zone, where the bedding is slightly disturbed. The concentration changes of the anionic tracer Br can be described approximately by using a $D_e$ of about $6 \times 10^{-12}$ m² s⁻¹ and a porosity of 0.082 m⁻³. Again, the $D_e$ value lies between those expected for diffusion parallel and perpendicular to the bedding. Cl shows the same tendency, but has very large measurement uncertainties.
Modelling of the dominant reactions in the system was performed utilising the one dimensional reactive transport model PHREEQC. The modelling domain was divided into 30 cells, 29 out of which correspond to the clay formation and the remaining cell corresponds to the test borehole. The length of each cell was 0.03 m.

Diffusion was the only transport process accounted for. The right boundary of the system, with the cell representing the experimental borehole, was assumed a no flow boundary, whereas diffusion was allowed across the left boundary of the system, assuming a constant initial pore water composition within the Opalinus Clay. Effective diffusion coefficients \( D_e \) of \( 1-3 \times 10^{-11} \) m\(^2\)s\(^{-1} \) were used.

The chemical composition of the initial pore water within the Opalinus Clay was that corresponding to water sampled in long-term experiments. The initial water composition in the borehole was the in-filled artificial water.

The water-rock reactions modelled within the formation were mineral precipitation and dissolution and cation exchange reactions. The solid phases present in the Opalinus Clay include calcite (6-39 wt.%), dolomite (0.6-2.7 wt.%), quartz (6-30 wt.%), celestite (0.02-0.06 wt.%), and pyrite (0.7-3.2 wt.%), beside the dominating clay minerals (45-76 wt.%). Aragonite, dolomite and gypsum were allowed to form as secondary phases as soon as they oversaturated in the system, while the precipitation of amorphous FeS was permitted according to a kinetic rate law. The initial carbonate concentration in the formation pore water was fixed to be in equilibrium with a pCO\(_2\) of \( 10^{-2.85} \) bars according to experimental values.

The degradation of dissolved organic matter was included in a kinetic Monod-like fashion. Sulphate was assumed to be the only electron acceptor species. Organic matter was conceptualised by the generic formula CH\(_2\)O. According to this process, the reaction included in the code was

\[
2\text{CH}_2\text{O} + \text{SO}_4^{2-} \rightarrow \text{H}_2\text{S} + 2\text{HCO}_3^- 
\]

with the following rate law

\[
R = k_{\text{max}} \frac{ED}{K_{ED} + ED} \frac{EA}{K_{EA} + EA}
\]

where \( k_{\text{max}} \) stands for the maximum rate of the metabolizable organic fraction and \( K_{EA} \) and \( K_{ED} \) are the half-saturation concentration of the electron acceptor (\( \text{SO}_4^{2-} \) in this case) and of the electron donor (dissolved organic matter), respectively. In the absence of site-specific data on the parameters included in the rate law, we conducted a sensitivity analysis to obtain the values of those three parameters that best reproduce the on-line measured data.

The comparison between the model results and the measured data shows that master variables of the water (pH and redox potential) are fairly well represented by the model. The model is also able to describe the redox evolution of the system, indicating the adequacy of considering the role of bacterially mediated organic matter oxidation.

An apparent discrepancy between data and calculation appears when dealing with sulphate and TIC. Although the model describes the patterns of these two components, the extent of sulphate decrease and TIC increase is much lower in the model compared to the actual observations. This can be a direct effect of the fact that the parameterisation of the kinetics of organic matter decomposition was conducted without \textit{in-situ} specific data.
DYNAMICS OF CONFINED WATER IN COMPACTED CLAY SYSTEMS

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Compacted clays and argillaceous rocks are used worldwide as barriers around disposal sites of hazardous wastes. The clays have well-suited physico-chemical and hydrological properties (i.e., large retention capacities and low hydraulic conductivities). Water plays a central role in the transport of radionuclides through clay rocks. Solute can move via molecular diffusion through the thin water films that wet the clay particle surfaces and interfaces. The physical and chemical properties of water films in clays may be different as compared to bulk liquid water, which affects also the diffusion of solutes. In order to predict the rates of diffusive transport and design effective barriers, it is essential to understand the characteristic properties of pore water in clays.

Our aim was to characterise the following properties: the self-diffusion of pore water, the activation energy of this process, and the freezing behaviour of pore water in well-defined compacted clays. All of these properties are very likely influenced by interactions of the pore water with the clay surfaces and the cations and thus probably differ from the corresponding properties of bulk water. Self-diffusion is, in addition, also influenced by the geometrical arrangement of primary particles in the compacted clays, and thus depends on the scale of observation. In this contribution, we present first results of this ongoing work.

Three different clays were investigated because of their different behaviour in contact with water: Montmorillonite, illite, and kaolinite. In the case of montmorillonite, water is located in between particles and in the interlayer space. In illite, water is found only in between particles, because the interlayer surfaces are tightly linked by potassium cations. The layers of kaolinite are uncharged and, consequently, water is also located only in between particles.

Diffusion of water through these clays was studied at two spatial scales in order to infer the effect of the geometrical arrangement of the primary particles. First, macroscopic diffusion experiments were performed at different temperatures using clay samples of about 1 cm thickness and HTO as a tracer. These experiments allow to determine porosities, diffusion coefficients or tortuosities, and activation energies of the diffusion process. Diffusion coefficients at this scale are strongly affected by the geometry of the pore space. Second, diffusion of water was studied at a microscopic level by quasi-elastic neutron scattering (QENS) at the time-of-flight spectrometer FOCUS (SINQ, Paul Scherrer Institut). QENS can give information about the dynamics of water molecules over a time scale of about $10^{-12}$ to $10^{-9}$ s. At this scale, the dynamics is influenced by the local environment only, that is, mostly by the clay surfaces and cations, but not the geometrical arrangement of the particles. The data were analysed preliminarily using a simple jump diffusion model, which allows to extract the local self-diffusion coefficient of water and the time in between jumps of a water molecule. The experiments were performed at different temperatures to be able to estimate also the activation energy of the diffusion of confined water.

In order to link the diffusion measurements at the two spatial scales, the structure and texture of the clay samples were characterised by various methods. Particle sizes were estimated from SEM images and with a zeta sizer, particle orientation with an x-ray goniometer, and clay layer spacing with x-ray diffraction.
The freezing behaviour of the water in the clays was investigated by QENS at the IN10 backscattering instrument at ILL (Institut Laue-Langevin, France). Measurements were performed over a temperature range from about 140K to about 320K. The amount of frozen water was estimated from the intensity of the elastic peak.

As expected, macroscopic self-diffusion coefficients of water were strongly influenced by the geometry of the pore space, being roughly 50 times smaller than those of bulk water. The activation energy for the macroscopic self-diffusion of pore water was slightly larger than the value for bulk water. It seems so far that local diffusion coefficients are similar, but the times in between jumps are larger for pore water in the clays as compared to bulk liquid water. However, the parameter values obtained are rather sensitive to the choice of models to analyse the spectra, and a refined analysis will be required. It was observed that water in clays did freeze at considerable lower temperatures than bulk water. The width of the distribution of freezing temperatures did clearly depend on the type of the clay sample, with montmorillonite exhibiting the broadest range.
DIFFUSION AND ACTIVATION ENERGIES OF I− AND Cs+ IONS IN COMPACTED SMECTITE

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In safety assessment of the geological disposal of high-level radioactive waste in Japan, a role as a barrier function of the buffer material (bentonite) composing multi-barrier system is quite important. The authors have reported in previous studies that clay particles orientate in the perpendicular direction to the compacted direction of bentonite for a bentonite (Kunipia-F®) which is almost 100 wt.% smectite [e.g., 1] and that both diffusivities of tritium and deuterium are different between parallel and perpendicular directions to the orientated direction of clay particles [1, 2].

In this study, the author studied the anisotropy in the apparent diffusivities (Da) of I− and Cs+ ions in compacted smectite and the effect of ionic strength on those parameters, and discussed the effect of porewater chemistry on diffusive pathway and microstructure.

The experiments were curried out by in-diffusion method. The Na-smectite was prepared by further purifying a Na-bentonite, Kunipia-F® (Kunimine Industries Co. Ltd.), of which smectite content is over 99 wt.%. The diffusion experiments were performed as a function of smectite’s dry density (0.9–1.4 Mg/m³), ionic strength ([NaCl]=0.01, 0.51 M), temperature (22–60°C) and diffusion direction to the orientated direction of smectite particles.

Figure 1 shows dependencies of Da for both ions on smectite’s dry density at 22°C together with Da data for I− [3], Cl− [4] and Cs+ [3, 4] ions in Kunipia-F® (DW: distilled water) reported up to date. The Da for both ions in the parallel direction to the orientated direction of smectite particles showed a tendency to be higher than those in the perpendicular direction to the orientated direction of smectite particles at low ionic strength ([NaCl]=0.01 M). The Da for I− ions showed different trends depending on diffusion direction and dry density at high ionic strength ([NaCl]=0.51 M), but Da for Cs+ ions increased with an increase of ionic strength in both diffusion directions over the dry density.

Figure 2 shows dependencies of activation energies (∆Ea) for both ions on smectite’s dry density together with ∆Ea data for Cl− ions and Cs+ ions in montmorillonite reported up to date [4]. The ∆Ea for I− ions, slightly higher than that of the diffusivity for I− ions in free water (D°) (∆Ea =17.36 kJ/mol) at low ionic strength, similar level to that of D° at high ionic strength, increased with an increase of dry density. On the contrary, ∆Ea for Cs+ ions, clearly higher than that of D° for Cs+ ions (∆Ea =16.47 kJ/mol) for all conditions, increased with an increase of dry density. Since it is known that basal spacing and interstitial pore aperture depend on both dry density and ionic strength, contributing diffusive pathway is considered to differ depending on the charge of diffusion species. At the present, further diffusion experiments are on going, and the author will discuss in more detail, added those data at the conference.

References:
**Figure 1:** Dependencies of $D_a$ for $\Gamma^-$ (left) and $\text{Cs}^+$ ions (right) on smectite’s dry density at 22°C

**Figure 2:** Dependencies of $\Delta E_a$ for $\Gamma^-$ (left) and $\text{Cs}^+$ ions (right) on smectite’s dry density
TIME-COURSE VARIATION
IN HYDRAULIC CONDUCTIVITY
OF CLAY-SAND COMPACTED SPECIMENS
USING CALCIUM RICH WATER

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ABSTRACT
Time-course variations in hydraulic conductivity of compacted specimens consist of clay samples and siliceous sand was monitored using permeameters with flexible wall cells. The clay content to whole solid was fixed at 11.5 % w/w, and the mixtures were compressed in a mold to be disk compactions. Inlet liquid was initially distilled water and it was switched to Calcium Chloride aqueous solution whose Chloride concentration was 1,000 ppm at long-term measurements. It was observed that initial 45 days using distilled water as the inlet water the hydraulic conductivity did not show clear time-course trends but some fluctuations in average value of 1.08 x 10^{-9} cm/s, it was shown that Ca^{2+} loading from inlet water slightly increases hydraulic conductivity for 40 days (1.38 x 10^{-9} cm/s in average), but after that hydraulic conductivity was getting lowered drastically in a few days. After this decline, no significant change in hydraulic conductivity observed. More than 150 days, the hydraulic conductivity had been stable at low value (1.31 x 10^{-10} cm/s in average).

The ion exchange by Calcium has been estimated to be a cause of decline in the impermeability. There is a tendency for sodium type bentonite to have higher expandability than that of calcium type bentonite. Actually, the increase in hydraulic conductivity of clay – sand compaction using Ca rich bentonite specimen was reported in previous studies. The different result of hydraulic conductivity using Ca^{2+} rich water was obtained in this study, a drastic fall of hydraulic conductivity was shown and it was kept in a low value for a long time. The drastic fall of the conductivity may be explained as follows. As ion exchange by Ca^{2+} proceeded, the compaction specimen got to be sparse because of the poorer expandability of Ca^{2+} bentonite. As the result, the specimen was further compacted by a cell pressure, giving a denser compaction with less water channels. The compaction was observed indirectly as a simultaneous rise in inlet and outlet levels. Applying a cell pressure to the compaction is the important factor, according to the real condition in landfills that isotropic pressure from the ground will compress the compaction. This result suggests a long-term barrier performance of the Na type bentonite – sand compaction under Ca-rich circumstance.
AN ALTERNATIVE EXPERIMENTAL SET-UP FOR DIFFUSION EXPERIMENTS APPLICABLE TO IN-SITU STUDIES.

M. García-Gutiérrez, M. Mingarro, T. Missana, P.L. Martín

Clay formations are being considered as potential host rocks for radioactive waste disposal in many countries. Since clays have a very low hydraulic conductivity, diffusion is the main transport mechanism for radionuclides released from the canisters.

Diffusion is a process by which the matter is transported from one part of a system to another by random molecular motion. The mathematical description of diffusion is based on the Fick's laws, which has to be modified for porous media, as clays, because several interactions between the solid and solutes exist. The nature of the ions, the porous medium itself and the specific geochemical conditions, influence the diffusion process.

Thus, the understanding of the diffusion processes and the determination of diffusion parameters, for many critical radionuclides, is crucial for the performance assessment of a deep geological repository. Experimental studies on diffusion are mainly performed in laboratory but some “in-situ” tests are planned in underground rock laboratories (URL).

Mont Terri URL, is situated in a service gallery of the Mont Terri motorway tunnel, near St. Ursanne in north-western Switzerland, drilled in a Opalinus Clay (OP A) formation. OP A clay is currently under investigation as a potential host rock for a high-level radioactive waste repository in Switzerland. In this laboratory, few in-situ diffusion tests have already been carried out, in the framework of an international multidisciplinary project running since 1996.

In all these tests, a similar experimental design was used. In fact, generally, the classic experimental set-up for in-situ diffusion studies includes the injection of a tracer diluted in reconstituted formation water into a packed off section of a borehole. The packed off section is formed by a stainless steel sinters of high and known porosity. Between the sinter chamber and the wall of the borehole a void volume is always left. In this configuration, a true contact between the chamber and the clay formation does not exist, and a possible deformation of the clay material near the injection chamber and density losses could occur. Furthermore, the introduction of a chamber filled of water could modify the properties of the saturated clay in the first centimetres near the clay/experimental chamber interface, just where radionuclide diffusion is expected to take place.

In this paper, a novel experimental set-up that could overcome the abovementioned problems and that could allow to carry out in-situ diffusion experiments in more realistic conditions is presented. This configuration would simplify in-situ studies because the sampling or monitoring would be not necessary, as well as the installation of packers and surface instrumentation; furthermore, if radioactive elements are used, less radiological control is needed because the system is isolated. Finally, no vessel or tubing exists, in which the sorption of certain elements could bias the results.

To show the feasibility of diffusion experiments using this “new” experimental set-up for diffusion studies, a large cylindrical sample (30 x 30 cm) of the consolidated OP A clay was used in this work. In the centre of the cylinder an hole was drilled (38 mm diameter and 20 cm of depth). A certain amount of clay
obtained in the borehole drill was mixed with clay pore water to which the dissolved tracer was added. The clay mixed with the traced water, compacted at the same density of the consolidated block, was introduced in the hole. Finally, the system was sealed and diffusion started taking place. Scoping calculations were carried out to calculate the diffusion distances, in the cylindrical geometry of the test, and the experimental time was decided. After that time, different clay samples were extracted from the cylinder, at different distances from the cylinder axis and at different heights. The activity in the solid samples was measured to obtain the diffusion profiles.

Using this experimental set-up the diffusion of neutral, anionic and cationic species (HTO, $^{36}$Cl and $^{85}$Sr) was studied. In parallel, “conventional” laboratory experiments were carried out with the same radionuclides, for comparison. In all cases a synthetic groundwater simulating the Mont Terri groundwater is used for the clay saturation (Pearson, 2000).

Different types of “conventional” experiments were carried out. Through diffusion-experiments were done for determining the effective diffusion coefficient, $D_e$, of HTO and Cl. Apparent diffusion coefficient, $D_a$, of HTO was obtained by means of out-diffusion experiments. As HTO is a conservative specie ($K_d = 0$), the ratio between $D_e$ and $D_a$ provided the value of the sample porosity. Apparent diffusion coefficient of Cl$^-$ was determined by means of in-diffusion experiments. Finally, apparent diffusion coefficient of Sr$^{2+}$ was determined using a filter paper impregnated with the tracer between two saturated clay plugs. After a given time, the clay plugs were cut into slices and the activity measured. The $D_a$ is obtained by fit the experimental profile to theoretical curves.

In all the cases, the internal consistency of the transport parameters obtained using different methods ($D_a$, $D_e$, porosity, rock factor, distribution coefficient...) was verified and discussed.

References:

Acknowledgement:
This work has been partially supported by the ENRESA-CIEMAT association.
ABSTRACT
The fluid advancement in unsaturated highly compacted clay materials is determined by the hydration and swelling behaviour of the clay minerals as well as by the resulting capillary and permeability behaviour of the clay material.

Small-scale, technical experiments were performed in connection with the development of moisture detecting cable sensors for the investigation of fluid advancement within several compacted clay material/ Kupfer et al., 2004/. Based on these investigations the processes of saturation and flow in compacted clays were analyzed and empirical approaches for the modeling of the main processes were developed. The resulting modeling concept allows the prediction of the fluid flow within clay based sealings and barriers in shafts and drifts.

SMALL-SCALE, TECHNICAL EXPERIMENTS
In co-operation with the Department of Mining and Special civil engineering of the Freiberg University of Mining and Technology bentonite filled columns of a diameter up to 800 mm and a length up to 2000 mm were hydraulically tested in vertical direction. Figure 1 schematically shows the test configuration.

The hydraulic tests were performed on bricks, granules and a binary mixture (pillows and granules) produced from MX-80 as well as Calcigel. Water and NaCl-solution were used as flow fluid. The clay materials were filled in with a defined clay bulk density. There was no confinement pressure applied to the columns. The hydraulic tests were performed at maximum fluid pressures of 10 MPa and a duration of maximal 150 days. Rate of flow, pressure, temperature and cumulative fluid volume were measured and recorded during the whole test. During some tests the swelling pressure were additionally recorded at different levels within the bentonite bodies. After testing the samples were dismantled and the moisture distributions were determined within the clay bodies.

PROCESS ANALYSIS AND MODELLING
The fluid advancement within compacted clays is determined by:
• changes in the effective phase permeabilities as a result of the pore saturation,
• changes in the density / porosity of clay materials due to:
  - swelling of clay minerals – redistribution of the pore space,
  - secondary compaction and / or decompaction (axial displacement) of the clay body – changes in density,
• reaching of an equilibrium between the moisture content or the pore saturation with fluid and the relative atmospheric humidity in the atmosphere or the pore gas.
The permeability of the saturated clay material is the highest possible permeability. Therefore, the flow within the saturated clay is determining the long-term flow within the whole sealing barrier. Based on the knowledge about the properties of the used clay materials and test parameters as well as results from the test rebuilding a modelling concept was developed considering following processes:

- two phase flow in the unsaturated pore space,
- single phase flow in the saturated pore space,
- changes in the intrinsic permeability of clay materials due to swelling and consequently modifications of the pore structure \( n_{\text{mobil}} \rightarrow n_{\text{immobil}} \),
- changes in the intrinsic permeability caused by the secondary compaction and decompaction and consequently changes in density of the clay materials.

This modelling concept was taken to calibrate the model using the measured moisture distribution in the performed tests by the variation of the intrinsic permeability. Figure 2 shows an example for the calibration between the model and test results for a test with Calcigel (binary mixture) and water. As result of this it can be demonstrated that the developed modelling concept is capable to simulate flow and saturation processes in clay materials. Thus, it is possible to predict the moisture advancement in large-scale, clay based sealing systems by numerical modelling.

**Figure 2:** Model results (clay material: calcigel, binary mixture; fluid: water)

**Overview of presentation**

The presentation will focus onto the following thematic priorities:

- general overview of the performed tests, test conditions and results,
- explanation of the modelling concept for the numerical simulation of measured saturation processes in highly compacted clay bodies,
- presentation of the simulation results and their interpretation,
- conclusions.

**Acknowledgement:**

This work was supported by the Federal Ministry of Education and Research (BMBF) under the registration number 02C0800. The authors also express their gratitude to the MFPA Weimar and to the department Entsorgung of PtWT+E at the Forschungszentrum Karlsruhe for the coordination of the research project. Kupfer et al., 2004: Entwicklung eines Messsystems zur Wassergehaltsbestimmung von Bentonit in salinarer Umgebung. BMBF-Förderkennzeichen: 02C0800, 2004
Flow and transport properties of an argillaceous rock are largely determined by its microstructure, that is by the spatial arrangement of solids and pore water. Our goal was to characterise the pore structure of Opalinus Clay and to derive parameters relevant for solute transport, such as porosity, mobility of the pore water, and accessibility of the pore water for a given tracer. Opalinus Clay is a moderately consolidated argillaceous formation of middle Jurassic age and occurs throughout northern Switzerland and southern Germany. Maximum burial (ca. 1650 m b.g. at the Benken site in NE Switzerland) was reached during the Miocene; since then, about 1000 m were eroded. The pore space is largely unaffected by diagenetic cementation, with the exception of sandy/calcareous laminae that are strongly cemented by calcite.

A number of different methods were applied to characterise the pore space. Densitometric and water-loss data yielded average porosities of ca. 0.11 for Benken. Data based on through-diffusion and diffusive equilibration experiments resulted in water-accessible porosity of ca. 0.12-0.15. The slight discrepancy to the densitometric and water-loss data is explained by the fact that the latter methods involve sample drying, which, for clay-rich samples, is not completely achieved at a drying temperature of 105°C. Porosity of cm-size sandy/calcareous laminae, which occupy a small volume fraction of the total formation, is smaller due to diagenetic cementation.

**Table 1:** Estimations of the fraction of bound water, based on different data and assumptions

<table>
<thead>
<tr>
<th>Approach</th>
<th>Experimental data needed as input</th>
<th>Surfaces considered</th>
<th>Bound water [m^3/m^3]</th>
<th>Bound water (% of physical porosity)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calculation assuming 2 layers of bound water on external and 1 layer on each internal surface</td>
<td>External surface area (BET)</td>
<td>external</td>
<td>0.040</td>
<td>32</td>
</tr>
<tr>
<td></td>
<td>Total (EGME) and external (BET) surface area</td>
<td>internal</td>
<td>0.044</td>
<td>36</td>
</tr>
<tr>
<td></td>
<td>Total (EGME) and external (BET) surface area</td>
<td>total</td>
<td>0.084</td>
<td>68</td>
</tr>
<tr>
<td>Calculation assuming that bound water is represented by hydration shells of cations sorbed on clay surfaces</td>
<td>Cation exchange capacity (CEC) and type of sorbed cations</td>
<td>mainly internal</td>
<td>0.021</td>
<td>17</td>
</tr>
<tr>
<td>Calculation based on water ad-/desorption experiments, assuming that at a relative vapour pressure of 0.68 pore water is present as 2 layers on external surfaces and 1 layer on each internal surface</td>
<td>Water ad-/desorption isotherms</td>
<td>total (desorption)</td>
<td>0.075</td>
<td>60</td>
</tr>
<tr>
<td></td>
<td></td>
<td>total (adsorption)</td>
<td>0.055</td>
<td>48</td>
</tr>
<tr>
<td>Frenkel-Halsey-Hill formalism</td>
<td>Water ad-/desorption isotherms</td>
<td>total (desorption)</td>
<td>0.083</td>
<td>67</td>
</tr>
<tr>
<td></td>
<td></td>
<td>total (adsorption)</td>
<td>0.057</td>
<td>46</td>
</tr>
</tbody>
</table>
Hg intrusion, N\textsubscript{2} and H\textsubscript{2}O adsorption isotherms show that about 45 to 65 \% of the pore space are mesopores with equivalent radii of 1 to 25 nm. This finding is corroborated by relating water contents and measured total and external specific surface areas. Due to the dominance of very small pores, interactions with solid surfaces affect a substantial part of the water and the solutes present in the pore space. From Table 1, it is evident that a substantial part (45 - 70 \%, neglecting the value based on CEC, which represents only part of the bound water) of the pore water is represented by bound water, and only the remaining 30 - 55 \% can be considered as free or mobile pore water. These numbers are a simplification in the sense that, from an energetic point of view, there is no sharp distinction between bound and free water because the electrostatic potentials decrease gradually as a function of distance from the clay-mineral surface.

The small pore sizes and the negative charges of clay-mineral surfaces also affect the accessibility of the pore water for solutes. While neutral species (e.g. water tracers) and cations can access the whole pore space, anions are excluded from a considerable part of it. Table 2 shows the porosities available to Cl in comparison with water-accessible porosity. Only ca. 30-70 \% of the available pore space is accessible to Cl.

Table 2: Water- and Cl-accessible porosities in Opalinus Clay

<table>
<thead>
<tr>
<th>Methodology to derive Cl accessible porosity</th>
<th>Site</th>
<th>Cl accessible porosity</th>
<th>HTO Diffusion accessible porosity</th>
<th>Cl accessible porosity / water-loss porosity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Derived from through diffusion experiments</td>
<td>Mont Terri</td>
<td>0.09</td>
<td>0.15</td>
<td>0.62 (0.47-0.75)</td>
</tr>
<tr>
<td></td>
<td>Benken (2 samples only)</td>
<td>0.04-0.05</td>
<td>0.14-0.15</td>
<td>0.31 (0.33-0.29)</td>
</tr>
<tr>
<td>Calculated from Cl concentrations obtained by squeezing or direct sampling</td>
<td>Mont Terri</td>
<td>0.09</td>
<td>0.16</td>
<td>0.58 (0.50-0.74)</td>
</tr>
<tr>
<td></td>
<td>Benken (2 samples only)</td>
<td>0.07</td>
<td>0.13</td>
<td>0.55 (0.35-0.74)</td>
</tr>
</tbody>
</table>

There are a number of implications related to the small pore sizes and the negative charge on clay mineral surfaces:

• Evaporation of pore water (thermal displacement) occurs over a range of temperatures, depending on the binding energy on clay-mineral surfaces.
• In Opalinus Clay, the displacement of pore water by air occurs only at relatively high pressures (air entry values > 5 MPa at Benken).
• Advection may occur only in a fraction of the physical porosity. In order to displace bound water by advection, the binding energy of the water must be surmounted. Higher hydraulic gradients may mobilise a larger fraction of bound water than small gradients, where Darcy’s law may no longer apply. This has implications for the extrapolation of laboratory and in-situ tests (with gradients typically > 1000) to the natural system (typical gradients < 1).
• The proportion of bound water is about 45-70 \% of total pore water, compared with a proportion of about 30-70 \% from which Cl is excluded. Considering the various analytical and conceptual uncertainties that underlie these data, to a first approximation, the region adjacent to clay-mineral surfaces where water is bound can also be considered as the region that is largely free of anions. At the present stage, this conclusion cannot be generalised because both proportions depend on ionic strength, and the precise relationship is not currently clearly established.
A FAST AND SENSITIVE METHOD FOR EVALUATING NUCLIDES MIGRATION CHARACTERISTICS IN ROCK MEDIUM BY USING MICRO-CHANNEL REACTOR CONCEPT

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ABSTRACT

Experimental effort to evaluate the barrier performance of geologic disposal requires relatively long testing periods and chemically stable conditions. For example, a through diffusion experiment of cesium through a 5mm thick granite disc runs several months in the constant atmosphere to obtain the meaningful data. It is normally time consuming and resulting cost-effectiveness is low. We thus have developed a new technique to present a fast and sensitive method to measure both nuclide diffusivity and sorption coefficient simultaneously within a day to overcome such disadvantage of the conventional method.

In this method, a Teflon plate having a micro channel (10-200 µm depth, 2mm width) is placed just beneath the rock sample plate, radionuclide solution is injected into the channel with constant rate. The breakthrough curve is being measured until a steady state. The outlet flux in the steady state however does not meet the inlet flux because of the matrix diffusion into the rock body. This inlet-outlet difference is simply related to the apparent diffusion coefficient ($D_a$) of rock sample. Then, we adopt a fitting procedure to speculate the sorption coefficient ($K_d$) and the effective diffusion coefficient ($D_e$), simultaneously by comparing the observation to the theoretical curve of the two-dimensional diffusion-advection equation.

In the present study, we measured $D_e$ of $^3$H by using both the new method and the conventional through-diffusion method for comparison. The obtained values of $D_e$ by two different ways for granite sample (Inada area of Japan) were identical: $6.0 \times 10^{-12}$ m$^2$/s and $5.8 \times 10^{-12}$ m$^2$/s but the testing period was much different: 10hrs and 3days, respectively. We also measured the breakthrough curve of $^{85}$Sr and the resulting $K_d$ and $D_e$ agreed well to the previous study [1] obtained by the batch sorption experiments with crushed samples.

Features of the new method are summarized as follows.

(1) **High sensitivity:** According to the very much high solid/liquid ratio ($1 \times 10^4$ m$^3$/m$^3$), the concentration drop due to the matrix diffusion is drastic and easy to detect such difference thus a large sample surface area is not necessary.

(2) **Short testing period:** The solution volume is very small and only several days are enough to reach the steady state even if the case of large $K_d$. 

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International Meeting, March 14-18, 2005, Tours, France
Clays in Natural & Engineered Barriers for Radioactive Waste Confinement
(3) **Simple setup:** The apparatus is small and constructed only by an injection syringe pump and sample plate (40 mm × 25 mm × 10 mm) connected with a channel plate (40 mm × 25 mm × 0.2 mm). It is easy to handle and easy to mount into a glove box to maintain a stable atmosphere.

(4) **Simultaneous measurement:** Both $K_d$ and $D_e$ values can be obtained in a single experiment.

The experimental evidence and the above features reveal that our new method based on the microreactor concept is powerful and much advantageous when compared to the conventional method.

**Reference:**

THE \textit{IN-SITU} GAS MIGRATION TEST (GMT) 
AT THE GRIMSEL TEST SITE: GAS INJECTION AND SYSTEM HYDRAULIC TESTS


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The Gas Migration Test in Engineered Barriers (GMT) is performed in Nagra’s Grimsel Test Site in Switzerland under the leadership of the Japanese Radioactive Waste Management Funding and Research Center (RWMC). The project focuses on issues related to waste-generated gas migration through the engineered barriers in a silo-type disposal system. The main objectives of GMT are: 1) to assess the function of the system “EBS and adjacent geosphere” as a whole with respect to migration of waste-generated gas, and 2) to evaluate models (conceptual and numerical) applicable to gas migration through barriers under realistic in-situ conditions.

The components of the field experiment (see Figure 1) are: a silo cavern, a concrete silo emplaced within the cavern, a gas vent in the top of the concrete silo, bentonite/sand buffer around the silo (20% bentonite and 80% sand) and, finally, sand/gravel backfill in the upper cavern above the silo cavern. The bentonite/sand was emplaced as a series of “lifts” which were compacted \textit{in-situ}. At the tops of selected lifts, monitoring instruments were located, defining a series of Levels and associated Layers numbered 2-12. The bentonite/sand in Layers 8-10 was traced with lead-nitrate for a gas flowpath visualisation experiment which was performed during a second set of gas tracer injection tests (not described in this paper).

Saturation of the EBS started in August 2001 by water injection into Layer 1 and the backfill. During flooding and pressurisation of the backfill it was found that piezometers and Time Domain Reflectometers (TDRs) between Levels 7 and 10 showed much faster responses than at other levels, indicating preferential saturation of Layers 8-10 around the vent and silo top. This was probably due to reduced swelling of the bentonite caused by the presence of lead nitrate. Saturation in other layers was slow due to the low permeability of the untraced 20/80 buffer. The saturation phase of the experiment was ended at the start of October 2002 as the region expected to be the focus of gas flow was highly saturated, although parts of Layers 2-6 and 11 had shown little increase in saturation since the start of the saturation phase.
Pre-Gas Water Test (WT1) – Prior to gas injection a series of pumping tests were performed to determine hydraulic properties of the EBS. The tests included injection and withdrawal tests from the concrete silo and pumping tests in the backfill.

Gas Injection Phase (RG11-RGI3b) – Nitrogen was injected into the silo at increasing mass flow rates from 0.025 to 5 mg/s starting in January 2003 (see Figure 2). The injections were designed to target different processes: dilution, two phase flow, interface opening and pathway dilation. The first responses to gas injection were seen in TDRs on the silo sides and later within the bentonite/sand above the silo. During the higher rate gas injections, instrument responses became focused in Layer 8 (close to the silo top) at the North side of the silo. Pressure breakdowns were seen at the start of RGI2a and RGI3a, that corresponded to periods of low effective stress on the silo top. During high rate gas injections the backfill pressure rose strongly, indicating an influx of gas.

Post-Gas Injection Activities – After shut-in of the gas injection, an upper cavern injection test was performed to determine any change in compressibility due to the presence of free gas. Free gas was also removed from the silo to determine the volume of water displaced during gas injection. Finally the pressure in the upper cavern was reduced so that it was similar to that prior to WT1.

Post-Gas Injection Water Test (WT2) – Repeat water testing after the reduction in EBS pressure showed the influence of residual gas in the bentonite/sand and an increased resistance to flow in/out of the silo.

Second Gas Injection Phase with Gas Tracers (RGI4) – A second series of gas injections using nitrogen and selected gas tracers was performed between January and April 2004, following which the system was depressurised and is now being carefully excavated and characterised.

Preliminary conclusions – Interpretation and characterisation work is ongoing but preliminary conclusions can be drawn: a) It was possible for high rates of gas to migrate from the silo under relatively low pressure gradients, probably controlled by the effective stresses, and b) No significant increase in EBS permeability due to gas migration was observed.

Figure 2: Pore pressure, effective stress and volumetric water content at selected sensors during gas injections RGI1-RGI3b
A DISCUSSION OF THE APPLICABILITY OF WATER/AIR TWO-PHASE FLOW MODELING TO IN-SITU GAS MIGRATION BEHAVIOR IN ENGINEERED BARRIER SYSTEM

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INTRODUCTION

Gas migration in Sand/Bentonite (S/B) mixture is of great interest issue in radioactive waste geological disposal. Understanding and predicting the gas migration behavior in S/B both experimentally and numerically is important for design of Engineered Barrier System (EBS). Radioactive Waste Management Funding and Research Center (RWMC) in Japan have been conducted the in-situ Gas Migration Test (GMT) by using large-scale EBS in Grimsel Test Site (GTS) in Switzerland [1]. This in-situ experiment, including several stages: construction of the EBS, resaturation tests and gas injection/migration tests etc, has been initiated from 1996. By the end of FY2004, the EBS dismantling will terminate. Many instruments have been installed into EBS and monitored pressure, water content and temperature and so on.

International modeling/comparison study have been done by several numerical simulation codes: TOUGH2, ROCKFLOW, CODE_BRIGHT, MERLIN and GETFLOWS, which based on different organizations, conceptualizations, dimensionality and numerical analysis schemes. Some of those numerical codes are traditional water/air two-phase flow models based on the generalized Darcy law, and some of that are fully- or pseudo- mechanical coupling flow models in this study.

In this paper, we discussed the reproducibility of the observed data at the in-situ GMT by 2-phase numerical fluid flow simulator GETFLOWS. A full 3D model is used for discretizing the EBS and surrounding rock body, and for reproducing the whole processes dynamically. In the simulation, gas dissolution to water and pressure-dependent pathway-dilation model of EBS are considered. Through trial and error runs, good matching is attained for the observation at resaturation stage, and at gas injection stage qualitative applicability of the proposed pressure-dependent model is indicated.

GMT SITE IN GRIMSEL

GMT site is mainly composed of the upper and lower caverns, and is located at overburden around 400m depths in granite host rock, including shear zone partially (Fig.1). Upper and lower caverns are circular-type pits, which have different height and diameter. Pseudo-waste matrix is emplaced in the middle part of lower cavern and 20wt% sand-bentonite mixture is buried around it. Gas is injected from the top of the pseudo-waste matrix. In order to detect fluid flow movement in EBS, many instruments such as pressure sensors and TDR sensors are installed in and around EBS.

This in-situ experiment has been done through several stages, such as opening cavern, emplacement of EBS, natural and artificial resaturation, hydraulic testing, gas migration tests and noble gas tracer tests. Gas injection was performed after that the major part that the injected gas migrates becomes almost
fully-water saturated. During gas is injecting, pressure responses in EBS shows that not only a standard 2 phase flow but also a gas dissolution to water and/or a failure of S/B pore structure occurred.

**Figure 1:** Schematic View of GMT

**DISCUSSION OF NUMERICAL MODELING AND REPRODUCTION**

GETFLOWS (GEneral-purpose Terrestrial fluid-FLOW Simulator), which was developed by H.TOSAKA [2], have been applied to GMT modeling study. A full 3D model is used for discretizing the EBS and surrounding rock, and for reproducing the whole processes dynamically. GETFLOWS is the 3D multi-phase and multi-component, flow and transport fully coupled simulator. Corner-pointed finite difference scheme is employed for the expansion of system equations and for the flexible expression of complex geology or artificial materials. Fast and robust matrix solver by preconditioned conjugate residual algorithm with SLP (Successive Locking Process) technique is provided for easy and quick trials. SLP is a method that was devised to attain rapid solution through successive reduction of the size of the problem by excluding the system equations for certain grid block by the use of blockwise differential convergence phenomena observed in multi-unknown Newton-Raphson iteration scheme.

A sequence of experiment data was completely traced by GETFLOWS through the trial and error history matching runs. Simulation result shows good agreement with the observed data. Also, we found that "pathway dilation" could be one of the most important processes in order to reproduce the gas migration behavior in S/B mixture. "Pathway dilation" in numerical model was considered as the pressure-dependent permeability and porosity changes.

For the future, new experimental data that will be obtained through the EBS dismantling may provide us additional information about gas migration pathway. Based on that new information, we aim to establish toward practical usage of numerical model focused on the reproducibility and possibility of prediction.

**References:**


DIFFUSION OF STRONTIUM$^{85}$ IN HIGHLY COMPACTED MONTMORILLONITE: VARIATION OF SAMPLE THICKNESS AND IONIC STRENGTH

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INTRODUCTION
Diffusion and sorption are the dominant transport and retardation mechanisms for dissolved radionuclides in the buffer material of a repository for high-level wastes [1]. However, the diffusion behaviour of anionic and cationic species is not well understood in detail. No conceptual models exist that are able to describe the key diffusion and retardation parameters, such as effective diffusion coefficients ($D_e$), rock capacity and sorption distribution factors ($R_d$), as a function of degree of compaction and the chemical composition of the equilibrium pore water. The present contribution is a very first step in the direction of elucidating such interrelations. The diffusion of Sr$^{2+}$ — as a typical representative of moderately sorbing cations — in compacted montmorillonite has been investigated as a function of sample thickness and the ionic strength of the saturating solution. The experiments follow two independent lines: (i) The aim of investigating the influence of sample thickness is to clarify whether through-diffusion tests for strongly sorbing tracers are feasible on reasonable time scales. For a 10 mm sample it can be expected that the observation time for obtaining experimental data in the steady-state phase of diffusion, i.e. where the tracer flux is constant, may be of the order of a few months, e.g. for $D_e$ and $R_d$ values of $10^{-10}$ m$^2$ s$^{-1}$ and $10^{-2}$ m$^3$ kg$^{-1}$, respectively. Reducing the sample thickness will reduce the experimental times, because these are proportional to the square of the sample thickness. However, with decreasing sample thickness, diffusion processes in the filter plates, which confine the sample and produce a uniform contact of the solutions containing the tracer under investigation and the sample, will become increasingly important. (ii) Varying the ionic strength of the saturating solution is a first step in addressing the question of the influence of the chemical composition of the external pore waters on the diffusive properties of Sr$^{2+}$ in compacted clay minerals. The sorption of Sr$^{2+}$ on clay minerals is governed by ion-exchange [2]. If the external pore water composition has an influence on the properties of the interlayer space of montmorillonite, it might be expected that the overall diffusive properties of Sr$^{2+}$ would be influenced, because the diffusion of Sr$^{2+}$ in montmorillonite is hypothesised to occur mainly through the interlayer structure at high degrees of compaction [3].

MATERIALS AND METHODS
Commercially available montmorillonite (Milos) was brought to the sodium form by repeatedly equilibrating with solutions of 1 M NaCl, washing with deionised water and finally freeze-drying the samples. Known weights of Na-conditioned montmorillonite were compacted to a dry bulk density of ~1950 kg m$^{-3}$ in stainless steel diffusion cells connected to two solution reservoirs through a continuous flow system. The samples were equilibrated with solutions of NaClO$_4$ (0.5, 0.7 or 1.0 M) for ~1 month, after which $^{85}$Sr was added to one of the solution reservoirs. The solution reservoirs were regularly sampled, whereby the downstream reservoirs initially devoid of $^{85}$Sr were replaced by fresh solutions, in order to keep the activity concentration at very low levels. Sample activities were measured by $\gamma$-counting. The tracer flux and the total amount of diffused tracer were calculated as a function of time from these measurements. Best-fit parameters for effective diffusion coefficients and rock capacity factors were evaluated using a computer code, which accounts for (i) time-dependent boundary conditions and (ii) the diffusive properties of the tracer in the filter plates.
RESULTS

First results of this ongoing investigation are presented for the experiments using a 5 mm thick sample. The results are unexpected in two respects: (i) $D_e$ values are dependent on the ionic strength of the external solution, i.e. they are decreasing with increasing ionic strength. (ii) Ionic strength variations do not appear to effect the initial phase of the diffusion experiments. If the sorption of $^{85}$Sr was dependent on the external ionic strength, it would be expected that the tracer breakthrough would be delayed with decreasing ionic strength, because the sorption of $\text{Sr}^{2+}$ would be increasing. However, the results may be interpreted in terms of both the diffusion and sorption properties of $^{85}$Sr being affected by changes in ionic strength. The quotients of $D_e$ values and rock capacity factors suggest that these effects may compensate each other, resulting in apparent diffusion coefficients which are independent of the external ionic strength. Owing to the preliminary character of the modelled diffusion parameters, and to the fact that the steady-state phase has not yet been reached in all experiments, no attempt has been made yet to compare the results obtained from experiments carried out with clay samples of different thickness.

Additional information on the test systems will be obtained by following the out-diffusion of the tracer and by separately analysing the tracer distribution in the samples.

References:


PORE NETWORK CONNECTIVITY
ANISOTROPY IN JURASSIC ARGILLITE
SPECIMENS FROM EASTERN PARIS BASIN
(FRANCE)

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In order to scientifically test the feasibility of storage of high activity nuclear wastes, ANDRA, the French radioactive waste management agency, gave us the opportunity to study entirely preserved specimens of Jurassic clay-rich rocks from eastern Paris Basin. The collection was realised in the frame of a reconnaissance study that now leads to the building, under progress, of a ~400 m-deep Laboratory, close to the village of Bure. The rocks under study consist in dark- to light-grey silty marls, or clay-stones, that were deposited during the Callovian and the beginning of the Oxfordian, called Cox (Callovo-Oxfordian) argillites. According to pyrolysis data of the organic fraction and to fluid inclusion studies, these argillites never reached 50°C in temperature nor have been buried deeper than 800 m, hence retain most of their original physical and chemical properties that were examined through microstructural and SEM observations.

Core-specimens belonging to the top and basal parts of the Callovo-Oxfordian were subjected to anisotropy measurements of both the pore network connectivity (APNC) and the magnetic susceptibility (AMS). In terms of total connected porosity, the basal COX (richer in clay) has more constant and higher values (average 10%) than the top of the COX (4 to 8%). Surprisingly, the porosities positively correlate with the magnetic susceptibilities, themselves likely controlled by the clay/calcite fraction (Figure 1).

![Figure 1](image-url)

Figure 1
The APNC was studied by cutting cubic specimens along the three main AMS axes (K1>K2>K3), and by using epoxy to impose the mercury to flow parallel to these axes. For specimens with a measurable magnetic anisotropy, the AMS and APNC axes coincide, the higher pore connectivity being parallel to K1 and the lower connectivity parallel to K3 (Figure 2: 337-3C). By contrast, in specimens having a weak magnetic anisotropy, no pore connectivity anisotropy is observed (Figure 2: 455-11A).

We conclude that the APNC reflects the organization of the clay fraction: the low connectivity being normal to bedding and the high one parallel to bedding. The highest connectivity is parallel to the magnetic lineation K1, that likely corresponds either to the zone axis of the clayey fraction during deposition or to differential compaction during diagenesis.

Worth noting is the specimen (Figure 2; 337-4B) where an inverse correlation between AMS and APNC is observed, the maximum connectivity being normal to bedding. In sections parallel to bedding of this specimen, tension gashes are observable under the microscope, as well as many extension features of objects (lithoclasts, …). These subvertical gashes may control the connectivity, and thus explain the local “inversion” between the AMS and the APNC axes.

In conclusion, the APNC technique appears to be robust and rather unexpensive to characterize the “microstructuration” of such homogeneous clay-rich materials.
GAS FLOW MECHANISM IN AN ENGINEERED BARRIER SYSTEM

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ABSTRACT

The gas flow in a complex 3-dimensional engineered barrier system (EBS) and its surrounding rock is studied by means of hydro-mechanical-coupled numerical simulations using different conceptual hypotheses. The results of the numerical simulations are compared to experimental findings.

For the three phase hydro-mechanically coupled calculations, the numerical code MEHRLIN is used, which is based on the continuum theory of mixtures and treats the EBS as a three phase porous medium (solid, liquid and gas). The principal field variables are solid deformations, liquid and gas pressure. The gas phase is governed by the ideal gas law, and the flow of the two fluid phases (water and gas) is governed by Darcy law and non-linear capillary pressure-saturation and relative permeability relationships are used. The resulting system of equations is discretized in space using the finite element technique and in time using an implicit formulation.

The experimental comparison is provided by the Gas Migration Test (GMT). The GMT experiment, initiated by the Japanese Radioactive Waste Management Funding and Research Center RWMC, is located at the Grimsel underground rock laboratory in Switzerland (GMT: http://www.grimsel.com/pdfs/flg_gmt.pdf). It studies the gas migration through a sand-bentonite engineered barrier system under conditions mimicking those expected in a real repository for radioactive waste in a crystalline host rock. The experiment started in 1997 and is currently being dismantled. After natural and artificial resaturation of the barrier system, several gas injections were carried out and resulting porewater and total pressures as well as saturations have been measured continuously at various locations within the engineered barrier.

The experimental setup consists of a concrete container with a permeable gas vent (mortar), surrounded by an engineered barrier system made of a 20/80 % bentonite/sand mixture, which has been placed in layers, a gravel backfill in the upper cavern and a concrete plug. In total, 12 different materials are considered in the numerical model. As the surrounding rock matrix is very impervious, only a relatively high-permeable shear zone intersecting the setup is considered for flow outside of the EBS. This represents a 3D situation, in particular due to the hydraulic connection to the shear zone and a drift nearby the GMT location, which is of importance for the pressure level and flow patterns found in the experimental setup. Therefore a full 3D finite element model has been used, containing about 61’000 3D tetrahedral elements.

The material parameters are based on independent laboratory tests for the sand-bentonite mixture, on results of independent in-situ tests and on literature values for the other materials. In a first modelling step, the concepts of Darcy’s flow and a linear elastic material law were used to reproduce the resaturation phase. In a further step, the gas injection phases are simulated.
Based on the results of the numerical simulation, the different modelling hypotheses were investigated. In particular, the importance of the mechanical influence on the functioning of the system under the specific conditions was assessed.

Several possible mechanisms of gas flow in the EBS and more specifically in the sand/bentonite buffer material surrounding the gas source were analysed. This is done on the one hand using classical continuum based approaches and elastic constitutive laws for the materials involved. On the other hand, a material model with damage development is used to evaluate mechanical effects on gas breakthrough phenomena as observed in this real scale EBS in a tight rock formation.

The obtained results are analyzed in light of experimental findings (measurements during the gas injection test and measurements/observations during the dismantling phase) in order to assess the flow mechanisms that occurred in the setup at the different phases of the experiment.

Both mechanisms, two phase Darcy flow and preferential flow along damaged zones of bulk material or along interfaces between them, are used to explain characteristic features of the experimental findings and it is not yet clear which hypothesis should be preferred.
WATER TRANSPORT IN BENTONITE: EVALUATION BY MOLECULAR DYNAMICS, HOMOGENIZATION ANALYSIS AND SIMILITUDE LAW

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The major scenario of transport of radioactive nuclides is due to groundwater flow in most HLW projects. The phenomena of water flow and diffusion of chemical species in a bentonite buffer and surrounding rock mass have been treated mainly based on the classical porous media theories under the Darcy’s law and Fick’s law.

The classical theories involve the following difficulties: 1) True velocity field is hard to be identified, especially in microscale sense. Note that it essentially affects the transport of chemical species. 2) The classical theories are not applicable to the problems in which experimental data are not available. Thus, the very long time behavior cannot be proven.

We commonly recognize that the water flow in bentonite and mudstone is strongly retarded. It is highly doubtful whether the above classical theories are applicable for such very low permeable materials.

In this work we first show that the velocity and diffusion fields in pure smectite bentonite can be calculated by a coupled molecular dynamics (MD) simulation and the homogenization analysis (HA). The true velocity field can be calculated by applying HA to the Navier-Stokes equation, and the local distribution of viscosity used in this HA is obtained by MD. The diffusion field is also calculated under the same procedure of MD/HA by using the local diffusion equation with diffusivity calculated by MD. See in details Ichikawa, et al. (2002)

Next, in order to clarify the dominant phenomena in saturated bentonite we introduce the similitude law to the Navier-Stokes equation under incompressible condition and the diffusion equation, and obtain the Peclet number. Here we apply the above MD/HA to specify the local profiles of water flow and diffusion characteristics. The important point of the procedure presented here is that in the sense of HA the characteristic length which plays an essential role in the similitude law is uniquely given. That is, the size of a unit cell of the HA model exactly gives the characteristic length. Note that the method to specify it has not been discussed clearly, so in most case studies it is arbitrarily introduced, for example, as an underground cavern size, see, e.g., JNC (1999). Thus, the Peclet number becomes also arbitrary in the conventional analyses. In our MD/HA-similitude analysis this ambiguity is resolved. The results shown in Table 1 imply that the mass transport in bentonite is extremely diffusion-dominant, since the calculated Peclet numbers are of order $10^{-14}$.

¹ HA is a perturbation method, which introduces a periodic microstructure, called a unit cell. Then, we can identify both the macroscale and microscale profiles of field variables simultaneously. See Fig. 1.
Table 1: Calculated results for pure smectite bentonite, Kunipia F (Kunimine Kogyo, Co.).

<table>
<thead>
<tr>
<th>$\rho_d$ (Mg/m$^3$)</th>
<th>$L$ ($\times 10^{-8}$ m)</th>
<th>$v^H$ ($\times 10^{-17}$ m/s)</th>
<th>$D^H$ ($\times 10^{-10}$ m$^2$/s)</th>
<th>Pe ($\times 10^{-14}$)</th>
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<tr>
<td>1.8</td>
<td>3.67</td>
<td>0.433</td>
<td>0.412</td>
<td>0.386</td>
</tr>
</tbody>
</table>

$\rho_d$: Dry density,

$L$: Unit cell length,

$v^H$: Homogenized velocity,

$D^H$: Homogenized diffusivity

Pe: Peclet number

References:


Figure 1: Domains for the two-scale HA.
EXPERIMENTS ON WATER SORPTION AND DILATATION

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Previous studies of water sorption and dilatation were concerned on syntetic zeolites (mainly clinoptiolite). Sorption and dilatation curves are characteristic for groups of swelling materials and natural/syntetic zeolites.

The aim of this study is to determine the behaviour of smectite-rich clay materials during sorption and dilatation experiments. Eight sets of clay materials were used in the experiments. Six samples represent bentonites s. s. (argillized pyroclastics). These materials were sampled at Rokle deposit, Nepomysl deposit, Trebusice deposit, Cerný vrch deposit, Krasný dvur deposit and Stránce deposit (Czech Republic). All studied bentonites contain mainly montmorillonite with Ca\(^{2+}\) and Mg\(^{2+}\) as dominant interlayer ions. Kaolinite and illite are subordinate. Two samples represent sedimentary montmorillonite-rich clays from Marsov and Zelená deposit near Skalná (Czech Republic). These clays contain smectite \(\geq\) illite \(\geq\) kaolinite.

Homogenized bulk clay samples (particles > 0.5 cm were removed) were dried in the circulated atmosphere (40°C) for 72 hours. Samples (0.5 g) were placed to the glassy U – tube and covered with glassy grater containing a referent point and heated to 115°C (2°C / 1min) using a heating device. The U – tube containing studied sample was subsequently saturated with nitrogen. Desorption humidity curves were calculated according to the following formula:

\[
m_D = \int_0^t F g dt
\]

\(m_D\) – desorption water, \(F\) – flow of nitrogen (ml/min), \(t\) – time (min), \(g\) – absolute humidity (g/m³).

Desorption curves are plotted in fig. 1.

Figure 1: Desorption curves of bentonite (Rokle deposit) and montmorillonitic clay (Zelená deposit)

The absolute humidity (AH) increases with temperature rise (fig.1). The humidity increase has two stages: Absolute humidity increases rapidly during the first stage. However, the second stage is represented by slow increase until point A, where all of the interlayer water is released.
Absorption experiments followed the desorption. The U – tube containing studied clay sample was put into the 30°C aqueous bath and connected with humidified flow of nitrogen (AH\text{max} = 40 \text{ ml/min}). Remaining humidity of the clay sample was measured using a SENSORICA hydrometer. Absorption humidity curves were calculated according to the following formula:

\[ m_a = F \cdot (g_{\text{max}} \cdot t_k - \int_0^t g dt), \]

\( g \) – absolute humidity (g/m\(^3\)), \( g_{\text{max}} \) – maximal absolute humidity (g/m\(^3\)), \( m_a \) – absorbed water (mg), \( F \) – flow of nitrogen (ml/min), \( t \) – time (min), \( t_k \) – const. time (min).

Absorption curves are plotted in fig. 2.

![Figure 2: Absorption curves of bentonite (Rokle deposit) and montmorillonitic clay (Zelená deposit)](image)

The C – D interval represents gradual adsorption of hydrate shells to the surface of clay minerals (fig. 2). At the same time, the water also fills the interlayer. After filling the interlayer, the humidity reaches maximal value, which is equal to the input value (point E).

![Figure 3: Dilatation curves of bentonite (Rokle deposit) and montmorillonitic clay (Zelená deposit)](image)

Dilatation measurements consist in evaluation of the swelling ability of clay materials. Fig. 3 shows dilatation curves which increases with time. The ability to dilate (expressed in % of ΔL/L) depends on the water sorption to the surface and into the interlayer of clay minerals. The maximum is reached in point B, where ΔL/L reaches 2.4 % (Rokle bentonite) respectively 1.2 % (Zelená montmorillonitic clay). In this point, the interlayer of clay minerals is totally filled with hydrate shells.

The behaviour of clay materials can be estimated using water sorption and dilatation measurements. These methods give also the possibility to determine the percentage of smectites. (The higher values ΔL/L or the longer C – D interval in the absorption curve, the higher amount of smectites in studied materials.)

The advantage of water sorption and dilatation consists in the quick evaluation of studied clay with precise estimates of physico-chemical properties (e.g. cation exchange capacity, specific surface area, porosity).
QUALIFICATION OF ASTER_CODE FOR THE SIMULATION OF TWO-PHASE FLOWS IN POROUS MEDIA. APPLICATION TO MASCILIA EXPERIMENT

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Within the framework of the nuclear waste storage in deep geological layers, the behavior of the saturated grounds in contact with the heating waste package is studied to ensure the short, average and long-term safety of the installation.

However, experiments in geological ground, including heterogeneities, difficult to characterize, take a long time and are expensive.

Therefore, the numerical simulation, which is a powerful tool to study the storage behavior versus space and time, became impossible to circumvent in order to analyze the radioactive waste management in porous media.

In that prospect, the Thermo-Hydro-Mechanics (THM) modules of Code_Aster were complemented by a two-phase thermal-hydraulics model, devoted to porous media. Such new developments intended to simulate the physical phenomena of un-saturation and re-saturation that occur in porous, permeable and initially saturated media, representative of worked engineer barriers or rock host. The concerned application is related to the storage of long-lived nuclear waste in deep geological layers.

A qualification of Code_Aster was previously carried out, using experimental results in porous media (worked Bentonite barrier and clay of storage) with a system of water-steam-air. The current paper deals with a new qualification of Code_Aster based on another experimental configuration, the CEA-Cadarache MASCILIA one. In this experiment, a tank of very pure sand, saturated with water is heated by means of an electric heater to simulate the thermal action of a nuclear waste package, and temperature profiles are measured.

Moreover, the results of Code_Aster simulation are compared to those got by running two other computers codes, the CEA (MC3D-repo) and the Marne La Vallée University (ULMV) ones. These two-step processes should allow the further use of Code_Aster to simulate realistic storage configurations.

Code_Aster is a Finite Element Method (FEM) code which has been developed by EDF. It includes modules to solve coupled problems involving thermal heat transfer, hydraulics and mechanics. The present study consists only in testing THV (Thermal-Hydraulic-Vapor) module which deals with water-steam two-phase flows, in rigid porous media, then the motion of the two phase flows is governed by Darcy’s law. In the article, the equations implemented in Code_Aster to simulate heated two-phase flows in porous media are developed, prior to the calculation presentation, to allow a relevant analysis of the numerical results obtained.

A first Code_Aster calculation set was carried out on the MASCILIA configuration with two different package powers (500 and 900 W), three modelings were considered in turn:
• the 2-D plane model, fast to compute, to study the sensitivity of the results versus various parameters: refinement of the meshes, physical properties of the porous media and of water,
• the axisymmetric model, more reliable, but more time consuming, for comparisons with the experimental results on one hand, and with the results obtained with CEA MC3D-repo code on the other hand,
• a 3-D model, more representative but heavily time consuming, for comparison with the experimental results and the results of Marne La Vallee (ULMV) code.

Simulations by Code-Aster made it possible to distinguish the two-phase zone (heat pipe effect) from the saturated water zone. The temperature results are qualitatively correct, but they show some weaknesses on the quantitative point of view, as do the MC3D-repo and ULMV codes:
• the dissymmetry of the temperature profile between the upward and downward vertical directions, due to gravity effect, is insufficiently marked in the numerical results: calculations over-estimate the temperatures below the heater and underestimate them over it,
• in the two-phase zone, calculations show a slight decrease on the profile of temperature, according to the distance from the heater package, whereas measurements indicate a near constant temperature,

A possible origin of such shortcomings can be found in the knowledge of closure laws: capillary pressure function of saturation and relative permeability laws. Although the closure laws used are definite in experiments from tests carried out on the sand of the experiment, they concern a field still badly known for the porous media used (sand) and the studied configuration (without air).

In order to get calculation results closer to experimental results, new laws of sorption (capillary pressure according to saturation) and of relative permeability of the steam, have been tested, running the 3-D model. The results showed the strong influence of these laws on the extent of the two-phase zone and the saturation temperature. These new laws result in a better agreement between the experimental and calculated profiles, but some points still remain to be improved:
• complete un-saturation, implying the appearance of an overheated steam zone, must be better taken into account, because it makes numerical convergence difficult to achieve,
• on a physical point of view, the saturation temperature difference (~2°C) between the upward and the downward zone observed in experiments, which would correspond to a pressure steam gradient, is a phenomenon to be better evaluated in the comparison between numerical and experiment results.
EFFECT OF HOMOGENIZATION ON THE EXCLUSION OF CHLORIDE IN COMPACTED BENTONITE

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In our earlier study of non-homogenized clay (Muurinen et al. 2004), it was concluded that chloride is excluded from compacted bentonite. At low chloride concentrations, where anion exclusion is most pronounced, the measured chloride concentrations were clearly higher than the values calculated with the Donnan model. A potential explanation for this discrepancy was the model’s inability to take account of the non-homogenous microstructure of the bentonite. Consequently, an attempt to explicitly incorporate the effects of clay microstructure, with the total porosity divided into interlayer and interparticle porosity, into the Donnan model was made, which resulted in a considerably better agreement between experimental and model results.

In the present work, an attempt was made to prepare more homogenous bentonite samples than in Muurinen et al. (2004). The experiments were performed with MX-80 bentonite, from which easily dissolving components had been removed to ensure that the excess ions in the pore water came from the external solution alone. The bentonite was homogenized by first dispersing the clay powder in deionized water with ultra sound. The bentonite-to-water ratio in the homogenization was 0.2 g/ml. The extra water was squeezed out in order to obtain the desired clay density. The samples were closed in cells and equilibrated with 0.1 M NaCl solution through filter plates at one end of the cells. The concentrations in the pore water were determined by dispersing the sample in deionized water.

Figure 1: Chloride concentrations measured in the pore water of homogenized and non-homogenized compacted bentonite equilibrated with 0.1 M NaCl solution. The solid line is calculated with the Donnan model.

The results are compared in Figure 1 with those obtained previously for non-homogenized samples (Muurinen et al. 2004) and with values calculated using the Donnan model. It can be seen that the concentrations in the pore water are clearly lower than for the non-homogenized samples, and, at lower densities, the measured values are in line with model results. At higher densities, the values obtained with
the homogenized clay approach those obtained with the non-homogenized clay, however. This probably indicates a difficulty of obtaining well-homogenized samples when the density increases and the clay flakes are no longer able to re-arrange themselves freely, and also a potential limitation of the Donnan approach to describe the exclusion in highly compacted clay.

References:

Keywords: bentonite, nuclear waste, porosity, exclusion, microstructure, Donnan model
MODELLING THE OVERPRESSURE REGIME IN THE OPALINUS CLAY, AT BENKEN (CH).
IMPACT OF THE DEVELOPMENT OF THE TOPOGRAPHIC RELIEF THROUGH A 2D ANALYSIS.

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A promising area in the Zurcher Weinland (North Switzerland) has been identified by Nagra, potentially suitable for hosting a high-level radioactive waste repository [1]. The geologic setting would be a slightly over-consolidated claystone layer of Jurassic age, about 100 m thick, known as Opalinus clay. In-situ characterisation of the Opalinus clay formation at the Benken exploratory site indicates that it may be overpressured. Key numbers are a present day porosity of about 11 %, associated with a porewater overpressure of 0.5 - 1.5 MPa and vertical hydraulic conductivity estimates in the range of $10^{14}$ ms$^{-1}$. Some modelling work was therefore undertaken to identify a possible mechanism, responsible for such observations. Compaction of poorly permeable materials during the geologic history was examined in a preliminary study on compaction processes [2]. A more refined 1D modelling of the history of drainage and compaction of the Opalinus clay, including the uplift/erosion sequence since the Miocene period, up to the present time was then discussed [3]. Because the maximum overburden, estimated to 1600 - 1700 m, was reached about 10 MY ago, the possibility of inheriting large pressures from the late geological history of this basin was firstly investigated. Additional physical processes were gradually accounted for to respectively (i) assess the importance of horizontal stresses due to ongoing tangential Alpine tectonics, and the numerical code was adapted to account for the amplitude and the duration of a compressive phase and (ii) measure the potential impact of a time-dependent visco-plastic rheology, that may candidate to explain a porosity reduction during the cretaceous period where sedimentation rates and burial depth were moderate.

A major discrepancy is still remaining and concerns the numerically calibrated Opalinus clay permeability which is found at least one to two order of magnitude smaller than the in-situ permeability estimates.

Owing to the difficulties to match simultaneously the whole set of data, a new piece of work was undertaken, using the same basin modeling approach as was done in [3], but based on the analysis of a two dimensionnal NW-SE vertical cross section of the area. The selected portion of the section is about 25 km in length, starting some 10 km NW to the Benken bore hole, at a location where the Opalinus clay is outcropping under some quaternary deposits. A quite sub-horizontal bedding, slowly deeping toward the south is observed and the section is more or less aligned with the direction of the recent compressive stress regime. The objective is to evaluate the impact of the late tertiary uplift evolution explaining the present day topographic relief, on the hydrogeologic regime in the potential host rock and surrounding layers. For modelling purposes, visco-plasticity and lateral stress are again assumed as a possible options for compaction phases, while an elastic behaviour is used during the unloading sequences.

References:
MONTE CARLO SIMULATION OF NaCl SPECIES IN Na-MONTMORILLONITE INTERLAYERS

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Highly compacted bentonite plays a decisive role in the design of underground repositories for high-level radioactive waste since it is a very efficient diffusion barrier for the migration of radionuclides. While the effectiveness of bentonite as a diffusion barrier is undisputed, a detailed understanding of the transport mechanisms of aqueous species in bentonite, and of the factors which influence them, is still missing.

Much of the water present in compacted bentonite and clay systems is likely to be adsorbed on the internal and external surfaces of clay minerals, so that the physical and chemical properties of water are largely affected by interfacial phenomena. The dielectric and diffusional properties of water confined to nanoscale spaces are significantly different from those of bulk water. It is known from experiments that the dielectric constant of water ($\varepsilon$) in clay-water systems decreases systematically as the water content is reduced. The reduction of $\varepsilon$ increases the effective electrostatic forces between cations and anions, favoring the formation of neutral or low-charge ion pairs or complexes. This results in an increase of the corresponding stability constants. Geochemical modeling of porewaters in compacted clays using stability constants determined for bulk water may therefore not be appropriate. Furthermore, a reduction of $\varepsilon$ may also influence diffusion in compacted clays. In all 2:1 clays (apart from talcs and pyrophyllites) the substitution of Si$^{4+}$ by Al$^{3+}$ in tetrahedral layers and of Al$^{3+}$ by Mg$^{2+}$ in octahedral layers leaves the TOT layers negatively charged. This is compensated in the interlayer by diffuse double layers of charge-compensating cations close to the surfaces of the TOT layers. If a clay is sufficiently compacted, the diffuse double layers of adjacent surfaces may overlap, preventing the diffusion of anions (Donnan exclusion). Consequently, the formation of neutral ion pairs or positively charged complexes, due to the reduced $\varepsilon$, may enhance diffusion in places where double layers overlap, since neutral or positively charged species are not subject to Donnan exclusion.

In order to investigate the potential formation of such species in the interlayers of compacted clays, we have started a series of Monte Carlo simulations of NaCl in the interlayer of Na-montmorillonite. The simulation cell consists of a 31.7 x 36.6 Å sheet of Na-montmorillonite, where the interlayer is sandwiched between two TOT half-layers. The composition of the simulation cell is Na$_{18}$[Si$_{186}$Al$_{6}$]tet(Al$_{84}$Mg$_{12}$)oktO$_{480}$(OH)$_{96}$·aH$_2$O · bNaCl. The number a of water molecules in the interlayer was systematically reduced from 1000 to 144 (resulting in a decrease of the layer thickness from about 35.7 to 14.5 Å), while the number b of NaCl in the interlayer was correspondingly adjusted from 42 to 6 in order to keep the interlayer solution constant at 2.3 molal. Monte Carlo simulations in the NpT ensemble at 10$^5$ Pa and 25° were performed with program MONTE v. 5.4 (developed by N.T. Skipper, University College, London) using the TIP4P water model.

Preliminary results indicate that the proportion of neutral NaCl ion pairs increases as the amount of interlayer water is reduced. At low water contents, positively charged higher order NaCl complexes or clusters are formed. The formation of such species has also been predicted by BRODHOLT (1998), DRIESNER, SEWARD & TIRONI (1998), and SHERMAN & COLLINGS (2002) in molecular dynamics simulations of bulk aqueous NaCl solutions at high temperatures, where $\varepsilon$ of water is also significantly reduced. It is thus conceivable that anionic radionuclides (like Cl$^-$) may diffuse through the interlayer despite Donnan exclusion by forming neutral ion pairs or positively charged complexes.
VALIDATION AND USE OF A REACTIVE TRANSPORT CODE IN POROUS MEDIA

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INTRODUCTION
The French Nuclear Agency (CEA) and the French Agency for the Management of Radioactive Waste (ANDRA) are jointly developing a software platform called ALLIANCES. Its purpose is to produce a tool for the simulation of nuclear waste storage and disposal repository. This paper deals with the validation and the use of the chemistry-transport model included in ALLIANCES. This model solves iteratively a geochemical model coupled to a transport model. It has been qualified and validated on numerous configurations involving aqueous speciation, dissolution-precipitation, sorption, and surface complexation. Nowadays, the reactive transport numerical tool is used to simulate realistic configurations. We will present two such applications: the migration of uranium in a soil with various redox conditions and tritium/helium age dating in an aquifer.

PRESENTATION OF THE COUPLED REACTIVE TRANSPORT CODE
The model describes the spatial and temporal evolution of a set of chemical species that are, on one hand, submitted to transport phenomena and, on the other hand, submitted to chemical reactions. Chemical reactions may be in equilibrium or under kinetics, in liquid, solid or sorbed phases. More precisely, in addition to the usual homogeneous reactions occurring in the liquid phase such as aqueous complex formation, acid-base and redox reactions, heterogeneous reactions that exchange matter between the liquid and the solid phase are also taken into account. The main heterogeneous reactions considered are precipitation-dissolution of minerals and sorption such as cation exchange or surface complexation. The code relies on the libraries of two geochemical codes solving the complex ensemble of reacting chemical species: CHESS, developed by CIG (France) [Lee (2002)] and PHREEQC, developed by USGS (US) [Parkhurst (1999)]. Hydrological processes involved are the transport by convection, dispersion and/or diffusion in 1D/2D/3D with structured and unstructured meshes. Several codes are available to simulate hydraulic flow and transport: Cast3M, developed by CEA (France) [Dabbene, (1998)][Bernard-Michel (2003)] and Modflow/MT3D, developed by U. Alabama (US) [Zheng (1998)]. The coupling algorithm is sequential iterative [Yeh (1989)].

VALIDATION OF THE COUPLED REACTIVE TRANSPORT CODE
In a first step, several analytical test cases have been defined and used to validate the reactive transport code. Numerical results have been compared to analytical solutions. In a second step, more complicated configurations have been simulated [Mügler (2004)]. The code is now used to model and simulate real configurations of reactive transport. Among those, this paper focuses on two applications: the migration of uranium in a soil with various redox conditions the second one dealing with tritium/helium age dating in an aquifer.

MIGRATION OF URANIUM IN A SOIL WITH VARIOUS REDOX CONDITIONS
Measurements performed in a polluted site have shown that the dissolved uranium concentration varies in time: it increases in winter and decreases in summer according to variations of redox conditions. The numerical platform ALLIANCES has been used to model and simulate the site. In the simulation, water in equilibrium with the oxygen atmosphere infiltrates a subsurface aquifer and leaches a zone enriched in uraninite. Several simulations have been performed with an increasing complexity for the soil geochemistry, including nitrogen and sulfur aqueous redox chemistry. Reactive transport modelling shows the dissolution...
of uraninite and the subsequent migration of uranium in the environment. When thiosulfate ions are present in the soil, the solubility of uranium increases due to dissolved uranium complex formation. As a consequence, the uranium concentration is greater than without thiosulfate ions. Numerical results are in qualitative agreement with experimental measurements and show the interest of the use of a coupled reactive transport code.

TRITIUM/HELIUM AGE DATING IN AN AQUIFER

ALLIANCES has been used to model an aquifer in two space dimensions in order to simulate the degradation of $^3$H to its daughter $^2$He. Time varying boundary conditions have been introduced to take experimental measurements into account. A kinetic law is describing the decay rate of Tritium to Helium. First results will be presented showing the capacity of the coupling tool to treat complex realistic configurations.

CONCLUSION

A coupled transport/chemistry simulation tool has been developed and validated against numerous configurations. It is now successfully used to model and simulate real configurations of reactive transport.

References:
DETERMINATION OF THE MINIMAL SAMPLE THICKNESS FOR DIFFUSION EXPERIMENTS WITH STRONG SORBING TRACERS

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The long-term risk assessment of underground repositories for radioactive waste requires among others diffusion coefficients of actinides in bentonite to account for the steady state diffusion process after exhaustion of the limited sorption capacity of the bentonite sealing. The determination of effective diffusion parameters of strong sorbing tracers such as actinides in laboratory diffusion experiments is very time consuming. For that, the sample thickness has to be reduced to a minimum. However, falling below a critical distance may lead to a disturbance of the clay texture and to inadequate boundary conditions and thus, to a misinterpretation of the diffusion data. Our work focuses on the dependence of the diffusion parameters of tritiated water (HTO) in bentonite on the sample thickness.

MX-80 bentonite samples were compacted in pressure cells of 50 mm inner diameter to a dry bulk density of 1.6 g cm\(^{-3}\) and a final sample thickness of 2.5, 5.0, 7.5, and 10.0 µm, respectively. Titanium filter plates of 5 mm thickness and 10 µm pore size were used. The samples were saturated with synthetic Opalinus Clay pore water applying a hydraulic pressure of maximal 10 MPa in order to verify the sealing function. After dropping the pressure the through-diffusion of HTO was investigated using a stationary technique. After attaining the steady state diffusion over an appropriate time the out-diffusion of the tracer was measured. The parameter estimation is based on analytical solutions and was performed by linear regression in the case of through-diffusion and a nonlinear fitting routine in the case of out-diffusion.

The experimental data show that the clay plugs used are representative concerning their sealing behavior. No fluid break-through occurred under hydraulic pressure. The swelling pressure was nearly constant over the duration of the diffusion experiments. No formation of cracks or channels was observed which would have led to an abrupt increase of the diffusive flux. The diffusion coefficients (\(D_e\)) derived from through-diffusion experiments for the different thickness show that the \(D_e\) values at 7.5 and 10.0 mm are in a good agreement (1.05·10\(^{-10}\) m\(^2\) s\(^{-1}\)). A slightly (within uncertainty) decreased \(D_e\) was found at 5.0 mm, whereas a significant drop of \(D_e\) was observed at 2.5 mm. In the case of out-diffusion the discrepancy was lower, especially at the low concentration side.

We conclude, that the clay plugs are mechanically stable and fulfill the hydraulic sealing function. From the relationship between sample thickness and \(D_e\) we see that the filter plates exert a significant influence on the boundary condition as soon as sample and filter plate are of the same thickness. Filter plates should be of about 1 to 2 mm thickness to resist the swelling pressure. Thus, a sample thickness in this dimension is possible to work with strong sorbing tracers minimizing the duration of the diffusion experiment and providing representative results.

Based on literature values for MX-80 pore water chemistry and sorption data of Uranium on montmorillonite a distribution coefficient \(K_d\) was estimated. This approach utilized the surface complexation model and a respective data base (RES\(^3\)T). Computations were performed with the FITEQ 3.2 code. The calculated \(K_d\)’s range from 30 to 300 ml g\(^{-1}\). This enables a blind prediction of the accumulated diffused activity for different sample thickness. A time frame of at least one year will be necessary to reach steady state. This will be checked by respective long lasting diffusion experiments.
DIFFUSION OF HUMIC COLLOIDS IN COMPACTED BENTONITE

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ABSTRACT

In Sweden, as in many other countries, compacted bentonite will surround the encapsulated spent nuclear fuel in a deep bedrock repository. Bentonite gives mechanical support and minimizes the water flow over the deposition holes. The retardation for cationic radionuclides escaping a faulted canister is high in saturated compacted bentonite, since cationic radionuclides sorbs strongly on the bentonite surface, and the only plausible transport mechanism is diffusion. Sorption and diffusion of radionuclides in the bentonite barrier has been extensively studied, and sorption and diffusion coefficients are well established. There is a lack of knowledge as well as data for effects of colloids on radionuclide mobility and transport in the bentonite barrier. In a deep bedrock repository, colloids, particles in the size range of 1-1000 nm, will be present, however in very low concentrations. The colloids origin from eroded bedrock and filling material, mineraloxids, clay, degraded organic compounds and micro-organisms etc. The bentonite barrier is regarded to be an efficient filtering barrier for colloids. With the widely spread micro-structure with pores in between the montmorillonite flakes in the size range of nm, and the inter particle voids partly gel filled of µm sizes, colloid transport seems unlikely. In a Japanese diffusion study on gold colloids no breakthrough of the colloids was detected [1]. However, to reject the possibility of enhancement of transport of radionuclides by colloids, more data from diffusion studies on other types of colloids in compacted bentonite are needed.

Therefore diffusion experiments of Humic Colloids (HC), in the size range of 1-10 nm, were performed. Stability experiments on HC were initially performed as well as sorption of HC on bentonite. The bentonite was compacted to the dry densities between 0.6-1.8 g/cm³ and saturated with 0.01 and 0.1 M NaClO₄-solutions for eight weeks. The diffusion cells were of 5 and 10 mm length. 0.1 g/l HC and 0.01 and 0.1 M NaClO₄-solutions initially analysed with Photon Correlation Spectroscopy (PCS) for the HC size distributions were connected to the diffusion cells. The diffusion of HC was studied for 60 days and the humic concentration in the outlet solutions was measured at time intervals by optical absorption at 278 nm. Water from the bentonite equilibration was used as blank, to avoid to artefacts of organic material leaching out from the bentonite. In parallel a number of diffusion experiments were performed with Co(II) and Eu(III) in the absence and presence of HC. Since Co(II) and Eu(III) are in principle immobilized by sorption on bentonite, the presence of HC could potentially mobilise these radionuclides. Sorption experiments with Eu(III) on bentonite at different pH and ionic strengths were run parallel to the diffusion experiments. Bentonite was compacted to 0.6, 1.2 and 1.8 g/cm³ dry density and equilibrated with 0.01 and 0.1 M NaClO₄-solutions for eight weeks. The diffusion of Co(II) and Eu(III) was monitored by analysing the outlet solutions at time intervals by γ-counting using a germanium detector and multichannel analyser. At the end of these experiments, each diffusion cell was dismantled and the bentonite sliced into thin sections. Each section was dried and weighed and the activity measured by γ-counting. The experimental breakthrough curves as well as the HS, Co(II) and Eu(III) profiles in the bentonite were simulated with the finite difference based computer code ANADIFF.

Regardless of the compaction and ionic strength of solutions, HC diffused through the compacted bentonite with apparent diffusivities, Da, in the magnitude of 10⁻⁸ cm²/s. HC diffused through the compacted bentonite without any strong physical hindrance. Any filtering effect of the bentonite is very low. The effects of HC on both Co(II) and Eu(III) sorption and diffusion were significant. Co(II) is mobilised when HC is
present in the system. The $D_a$ increases significantly for Co(II) when HC is present. For example $D_a$ increases from the magnitude of $10^{-10}$ cm$^2$/s, to $10^{-9}$ cm$^2$/s in bentonite compacted to 1.8 g/cm$^3$ and ionic strength 0.1 M in the equilibrating solutions when HC are present. From ANADIFF simulations it can be seen that the $K_d$ decreases from 2400 g/cm$^3$, to 850 g/cm$^3$ under these experimental conditions. Eu(III) is also mobilised significantly by the presence of HC. For example $D_a$ increases from the magnitude of $10^{-10}$ cm$^2$/s, to $10^{-8}$ cm$^2$/s in bentonite compacted to dry density 1.8 g/cm$^3$, and ionic strength 0.1 M of the equilibrating solutions, when HC is present. The $K_d$ accordingly decreases from 7000 to 10 g/cm$^3$.

The results from this study indicate that HC, in the size of 1-10 nm, diffuse rather unhindered and the bentonite does not function as an efficient filter for these colloids. Radionuclides are complexed by the colloids and transported further into the compacted bentonite, than when HC are not present.

Further investigations are needed to understand the factors controlling colloid transport in compacted bentonite, as well as studies of the microstructure of compacted bentonite.

Reference:
MULTISCALE, COUPLED T-H MODEL FOR SYSTEM STUDIES

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INTRODUCTION
One of the most important issues in any high-level nuclear waste repository is the effect of heat that affects the safety and performance of the facility. Firstly, the heat is the main, lasting disturbance upon the natural system in addition to the fracturing of the host rock during the construction of the facility. The host formation may be restored after the waste is emplaced by sealing and backfilling the openings. However, the heat further generates a thermal pulse that lasts for several hundred years, causing thermally-induced processes in the natural and engineered barrier systems. Secondly, the effect of heat, i.e., the resulting temperature rise is slow in development. The evolution of the maximum temperature may be delayed by hundreds of years. Errors in the model prediction of the thermal pulse may cause long-lasting and perhaps uncorrectable consequences since remedial actions are nearly impossible after the repository is sealed. Thirdly, the long time period relates to large host rock volume and dimensions, much larger is size than that of the construction area. At the same time, the near-field areas close to the heat and potential emission source is the most affected by the temperature field. This multi-scale nature places great challenges to the modeling and prediction of the thermal responses.

DESCRIPTION OF THE WORK
A multiscale, coupled thermo-hydrologic model is developed for supporting conceptual design and thermal loading system studies. According to the literature, the interactions between the mechanic-thermal (M->T) and the hydraulic-thermal (H->T) model-elements are usually negligible, making it possible to uncouple the thermal equation from the mechanical and the hydraulic equations. However, the thermal properties of the host rock are known to be strongly dependent on the moisture content. In addition, any thermally-induced moisture movement in the matrix and fracture of the rock may be the most significant close to the emplacement drift where the thermal gradient is the highest. Therefore, it is most appropriate to use a fully-coupled H↔T hydrothermal model from the start of the model formation. The present work applies NUFT (Nonisothermal Unsaturated-saturated, Flow and Transport model), a Lawrence Livermore National Laboratory software product. The M->(T↔H) interaction may have a cross-effect that can be consecutively included in the model by adjusting porosity and fracture properties under stress conditions. The T-H model includes conduction and convection in a porous and fractured rock formation, general enough for incorporating any potentially variable thermal conductivity and related diffusivity for temperature prediction.

Another important modeling issue is the analysis of the potential development of conduction-convection-vapor migration-condensation mechanism in the engineered barrier system and the damaged host rock zone during the partially saturated phase of the operation. A continuous steam cycle may form between the central, relatively hot, and the distal, relatively cold repository areas in such a system during the thermal pulse. A steam cycle is possible under certain conditions, namely, if the backfill buffer material cannot saturate and the damaged zone cannot re-saturate due to vapor-phase water loss to the cold, condenser areas of the repository. The coupled modeling of this scenario during the conceptional design phase is a target point for model configuration. Preferential pathways and single-fracture flows are difficult to incorporate in a large-scale model due to the large number of nodes involved. A new coupling technique is used that allows for incorporating overlapped model-elements within the same domain. This new, NTCF technique is used in MULTIFLUX, developed at the University of Nevada, Reno. The NTCF
technique allows for massive node reduction and multi-scale solutions. MULTIFLUX is used with NUFT as a porous- and fractured-media model, and a Computational Fluid Dynamic or heat and flow network element model as the overlapped domain model(s).

MULTIFLUX with the multi-scale NTCF technique is used to solve the coupled thermohydrologic problem for a large model domain that includes the maximum temperature area in the central part of a repository panel, while it stretches out to the unheated zone. Within the large, mountain-scale domain, the model represents tunnel-scale as well as waste container-scale domain elements, with fine enough division to depict temperature and moisture concentration variations along a single waste container. The multi-scale model domain is shown for a conceptual arrangement in Figure 1 for spent nuclear fuel emplacement.

RESULTS AND CONCLUSIONS
The paper will describe the input data and assumptions of the model; and the temperature and moisture/humidity results for a time period of 10,000 years. The model results will include a pre-closure time period of 20 years during which the facility is ventilated and artificially kept dry for construction and emplacement; and the entire post-closure time period during which the facility first heats up to its maximum temperature while at the same time re-saturates, and subsequently decays toward its ambient conditions. Conclusions will be provided relative to the spatial and temporal temperature and moisture/humidity variations for a conceptual arrangement. The expected thermal goals will be evaluated.

**Figure 1:** Horizontal conceptual emplacement. (a) repository panel; (b) enlargement of emplacement area; and (c) multi-scale model building block.
HEAT AND WATER MASS TRANSFER IN UNSATURATED SWELLING CLAY BASED BUFFER: DISCUSSION ON THE EFFECT OF THE THERMAL GRADIENT AND ON THE DIFFUSION OF WATER VAPOUR

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Transfer of dry air and water under thermal gradient and capillary (e.g. suction) gradient in unsaturated compacted swelling clays consider evaporation, migration and condensation. These transfers take into account the capillary effect (Gens, A. et al. 1998), (Code Aster. 2001), (Robinet, J.C. et al. 1999), (Robinet, J.C., Ducoulombier, A. & Plas, F. 1999), (Villar, M.V., Fernandez, A.M. & Cuevas, J. 1997). This effect is an evaporation of liquid water in the hot part for temperature higher than 100°C associated with a, diffusion of water vapor towards cold part then condensation, and convection of liquid water with gradient of suction in the opposite direction of the water vapour diffusion. High values of the diffusion coefficient of the vapour water are considered about 10⁻⁷ m²/s (Olivella, S. & Gens, A. 2000).

Some thermal experiments related (i) low values of the water vapour diffusion coefficient in compacted swelling clays, 10⁻⁹ to 10⁻¹⁰ m²/s (Takeuchi, S., Hara, K. & Nakano, M. 1995), (Suzuki, H., Chijimatsu, M. & Fujita, T. 1999 Robinet 2004) and (ii) a significant drying associated with a water transfer even for temperature lower than 100°C (Suzuki, H., Chijimatsu, M. & Fujita, T. 1999). Other enhancement phenomena are used to explain these data and observations:
• The vaporization is a continuous process. At short term the mechanism of drying at short term is the thermal effect on the capillary pressure (e.g. surface tension depending of temperature).
• The thermal gradient is a driving force. When a temperature gradient is applied, diffusion occurs in order to reach equilibrium, e.g. to make the chemical potential (m) of each component uniform throughout. This mechanism is called thermal diffusion (e.g. Soret’s effect) (Jones, R.C. & Furry, W.H. 1946), (Grew, K.E. & Ibbs, T.L. 1952) for aqueous solutions (Costeséque, P. 1985), (Thornton, B.C. & Seyfried, W.E. 1983) and clay material (Robinet J.C, Bui T.D, Dang K.D, Trinh Q.V & Plas F 2004).

This paper proposes a discussion on (i) the effect of the temperature and the gradient of temperature on the water transfer and (ii) the diffusion of water vapour, in unsaturated compacted swelling clays. This discussion is based on experimental data and modelling data. Simulations using Soret’s effect and low values of water vapour diffusion coefficient give profiles of water saturation similar to those obtained with classical approach.
References:
MICROSTRUCTURE AND POROUS NETWORK CHARACTERISATION OF CALCAROUS AND CLAYEY ROCKS USING HIGH RESOLUTION X-RAY MICROTMOTOMOGRAPHY AND PETROPHYSICAL TOOLS

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ANDRA has developed a model for radionuclides and chemical pollutant migrations in the Callovian-Oxfordian argillite formation and its inclosing limestone beds. This model is based on the petrophysical properties of the studied materials, and on phenomena and transport processes that can probably happen within their connected porous networks. The morphological properties of this last and the associated spatial organization of minerals govern the physico-chemical processes that are realistically considered. In the view of the heterogeneity of the studied rock facies and the extent of the constituent dimensions (clay particle to detrital minerals, and molecular scale pores to macropores), it is necessary to implement appropriate imaging techniques to reveal their multi-scale structural organization.

ERM has developed imaging techniques allowing to characterize the microstructure of finely divided heterogeneous media. These innovative tools such as porosity mapping from autoradiograph and mineral mapping from scanning electron microscopy, are bi-dimensional. Despite they constitute a progress in the study of clay rock microstructure, they do not prejudge of their volume properties such that the connectivity of the porous networks and the preferential fluid pathway distribution for migration process; volume properties that however are necessary in order to construct transport models. Therefore, it is useful to implement three-dimensional tools in addition to bi-dimensional image acquisition. The high resolution X-ray microtomography from synchrotron radiation constitutes the adapted technological means provided by the European Synchrotron Radiation Facility (ESRF, Grenoble, France).

As the pore size distribution in clayey compacted rocks (chalk clays, marls or clayey limestones) tend to be nearby sub-micrometric, common microscopy and even high resolution microtomography are limited to define the pore sizes, except those of macroporosity as defined by petrographs. Indeed, one pixel (or one voxel in 3D) gives an average value, integrating porosity features and minerals that contains the analyzed micro-volume. For a more precise definition of the effective porous system, one determines the pore size distribution of the connected porosity in rock sample volumes, until nanometric pore sizes, by mercury porosimetry. Obviously, one difficulty lies in the link to be made between mercury porosity distributions and mappings describing the sample microstructure in one hydrated state nearby the water saturation.

The main goals of our study is firstly to give a realistic three-dimensional description of the microstructure and the micro-heterogeneities of the studied sample facies. This characterization implies to compare porosity and mineral spatial distributions in 2 and 3 dimensions. Secondly, the objective is to determine, using this approach, the relevant parameters that could be used in the construction of radionuclide migration models. This study is based on four limestone samples and one argillite sample; this last one is studied as a demonstration of the feasibility of this global approach at the laboratory scale.
NUMERICAL SIMULATION
OF THE HYDROGEN MIGRATION
OUT OF INTERMEDIATE LEVEL
RADIOACTIVE WASTE

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ABSTRACT

Due to corrosion processes, hydrogen is produced by intermediate level radioactive waste, during the
post closure phase of a radioactive waste repository in an argillaceous formation (i.e. within a time
frame of at least several 1000 years after closure of the repository). The potential impact of the hydrogen
production on the pressure (gas and water), water saturation and dissolved hydrogen is demonstrated by
means of numerical simulations of increasing geometrical complexity (1-D, 2-D and 3-D). The simulations
are performed with the TOUGH2-Multiphase code (Pruess, 1999) and based on the following assumption:
• Darcy flow of the two phases: gas and water, including capillary pressure and relative permeability-
saturation relationships
• Storage of fluids in the materials according to their fluid compressibility and the material stiffness
• Diffusive and advective mass transport of hydrogen in the gas and water phases
• Isothermal conditions

The general disposal configuration under study is presented in figure 1.

In a first step, a series of simulations based on a simplified cylindrical geometry (one-dimensional radial
grid, no gravity) was performed. The waste package is embedded in a concrete backfill, a construction
void exists between waste package and the concrete, the surrounding rock is divided into 3 radial zones
of decreasing permeability: a fractured zone, a disturbed zone and the undisturbed argillaceous formation.
The impact of i) the hydrogen production rate, ii) the desaturation phase due to the drift ventilation during
the operational phase and iii) the hydrogen production scheme, on the pressure build-up within the
emplacement drift and the gas saturation level in the surrounding rock was investigated. Given the
parameter values assumed, all simulation cases provided maximum pressure at the emplacement drift
less than 11 MPa.

In a second step, a vertical cross-section of the emplacement-drift and the surrounding rock was studied
by means of a 2-dimensional grid resolving the waste package and its high performance concrete overpack.
The boundary conditions correspond to the potential site conditions (hydraulic potential). The impact
of the overpack of the waste packages on the pressure and saturation levels was found to be low.

The third step was to simulate a complete 3D-configuration with the backfilled emplacement-drift,
bentonite-sealing and the access drift.

For all simulations cases (1D, 2D and 3D) the level of overpressure in the emplacement drift depends on
the permeability and thickness of the argilite, the gas-filled pore volume and the hydrogen production rate.
The results of the simulations showed no pressures larger than the theoretical frac-limit at the site conditions. Furthermore, the penetration depth of the hydrogen gas phase into the undisturbed argillite rock was found to be small.

Figure 1: Vertical cross section of the emplacement drift, with access drift and distribution drift

References:
Pruess et al., 1999: TOUGH2 user's guide
FROM U-SERIES DISEQUILIBRIUM MEASUREMENTS IN CLAYEY SEDIMENTS TO RADIONUCLIDE MIGRATION PROCESSES

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The uranium-series equilibrium state of borehole core samples from the deep Callovo-Oxfordian argillite layer and its surrounding low-permeability Bathonian and Oxfordian limestone formations (Eastern Paris basin) was examined in order to improve our understanding of naturally occurring radionuclide behaviour in such geological settings. The COX clayey layer is the potential host rock for reconnaissance work carried out by ANDRA in eastern France, whose objective is to design and build an underground research laboratory to study the aptitude of the Callovo-Oxfordian clay layer for radioactive waste storage.

With respect to bulk concentrations, the U and Th contents in the labile fraction are particularly low in the COX argillites. This behaviour suggests that, given the extremely low permeability of the rock, any transfer of solutes could only have taken place by diffusion – a very slow mechanism that favours water-rock interactions. The variations in the concentrations of U and Th, and the $^{234}\text{U}/^{238}\text{U}$ and $^{230}\text{Th}/^{234}\text{U}$ activity ratios (AR) with depth in the sedimentary column were studied (Casanova et al., in press) to obtain information of U migration processes in the rock matrix and to estimate the timing (or age limit) of potential events induced by groundwater. If no hydrological disturbance affects the rock over a period exceeding five times the $^{234}\text{U}$ half-life, the radionuclides from the $^{238}\text{U}$ decay chain attain secular equilibrium, and both the $^{234}\text{U}/^{238}\text{U}$ and $^{230}\text{Th}/^{234}\text{U}$ AR equal unity. Numerous studies have, however, indicated that sediments do not form a closed system for uranium. Fractionation can occur between the parent-daughter radionuclides pairs $^{238}\text{U}$/$^{234}\text{U}$ and $^{234}\text{U}$/$^{230}\text{Th}$, and the resulting disequilibria indicate migration over the last 1.5 Ma, and 350 ka, respectively. Since $^{230}\text{Th}$ is comparatively immobile under ambient conditions, the disequilibria are assumed mainly to be due to the bulk removal of uranium or the preferential removal of $^{234}\text{U}$.

A working hypothesis to relate observed absolute uranium release and isotopic fractionation between isotopes $^{234}\text{U}$ and $^{238}\text{U}$ is based on the radioactive decay induced oxidation of $^{234}\text{U}$ to U(VI), which is the most soluble oxidation state of uranium. In this situation the oxygen concentration in groundwater plays an important role. In presence of a large oxygen concentration it can actually oxidise and release the bulk of uranium that would not lead to marked isotopic fractionation. If there are small amounts of oxygen, the already oxidised $^{234}\text{U}$ is easier to remove, leading to clear isotopic fractionation. If, finally, there is few or no oxygen, it would have no effect, even for $^{234}\text{U}$, and there would be neither absolute release nor preferential $^{234}\text{U}$ release. Taking into account that direct ejection of recoiling nuclei into intergranular space only concern the first 20 nm of clay surfaces, it is assumed that preferential leaching originating from changes in the valence state of $\alpha$-recoil $^{234}\text{U}$ and enhanced by $^{234}\text{U}$ location in radiation-damaged sites is the main mechanism of $^{234}\text{U}$ mobility from a mass balance viewpoint.

Most data points discussed here (HTM101, HTM102 and EST106) lie within ±2σ of secular equilibrium. However there is a tendency for these points to have AR values significantly deviated from unity and therefore to provide an indication of the potential radionuclide migration in recent time. The first case to be taken into consideration is $^{234}\text{U}$ depletion in rock samples. In this case, the $^{234}\text{U}/^{238}\text{U}$ AR is less...
than unity and indicates that preferential leaching of $^{234}\text{U}$ by groundwater occurred during the last 1.5 Ma. When $^{234}\text{U}$ depletion is associated with a $^{230}\text{Th}$ excess, the chemical release of $^{234}\text{U}$ occurred recently (< 350 ka). When $^{234}\text{U}$ depletion is associated with a $^{230}\text{Th}/^{234}\text{U}$ AR at or close to secular equilibrium, the process responsible of $^{234}\text{U}$ leaching occurred between 350 ka and 1.5 Ma. Finally, the complex situation with coexisting $^{234}\text{U}$ and $^{230}\text{Th}$ depletion has not been encountered over the studied core length.

The second case to be considered corresponds to a $^{234}\text{U}$ excess (i.e. $^{234}\text{U}/^{238}\text{U} > 1$) in rock samples and indicates precipitation of $^{234}\text{U}$ from a solution depleted in $^{238}\text{U}$ over the last 1.5 Ma. Here again the value of the $^{230}\text{Th}/^{234}\text{U}$ AR provides a better constraint on the age limit of the related hydrological disturbances. When $^{234}\text{U}$ excess is associated with a $^{230}\text{Th}$ deficit, the chemical accumulation of $^{234}\text{U}$ occurred recently (< 350 ka). When $^{234}\text{U}$ excess is associated with a $^{230}\text{Th}/^{234}\text{U}$ AR at, or close to, secular equilibrium, the process responsible of $^{234}\text{U}$ accumulation occurred between 350 ka and 1.5 Ma. Finally, the complex situation with coexisting $^{234}\text{U}$ and $^{230}\text{Th}$ excess has not been encountered over the studied core length.

The third case to be considered corresponds to a $^{234}\text{U}/^{238}\text{U}$ AR at, or close to, secular equilibrium, indicating that no process, implying an isotopic fractionation of uranium, occurred over the last 1.5 Ma. When $^{234}\text{U}/^{238}\text{U}$ secular equilibrium is associated with a $^{230}\text{Th}$ excess, a congruent U release occurred recently (< 350 ka). When in contact with oxidising groundwater, U will be congruently dissolved and drained away. When $^{234}\text{U}/^{238}\text{U}$ secular equilibrium is associated with a $^{230}\text{Th}$ deficit, a bulk U-accumulation occurred recently (< 350 ka). When $^{234}\text{U}/^{238}\text{U}$ and $^{230}\text{Th}/^{234}\text{U}$ AR both exhibit secular equilibrium, it is assumed that the studied sediments have formed a closed system for uranium over the last 1.5 Ma. This last situation is the most frequently encountered over the studied core length and particularly in the COX argillites. This result is convergent with those recently obtained by Deschamps (2003) and provides indication of the confining capacities of the target formation in the current settings.

Within the carbonate-rich part (Bathonian and Oxfordian to Tithonian) of the section, the $^{234}\text{U}/^{238}\text{U}$ ratios slightly divert from secular equilibrium and are interpreted as chemical U release and deposit related to groundwater circulation. According to oxygen concentration in groundwater, uranium mobility indicates either congruent U release or preferential $^{234}\text{U}$ solution-precipitation processes. Preferential removal of $^{234}\text{U}$ in these zones is also indicated by some $^{230}\text{Th}/^{234}\text{U}$ activity ratios higher than unity. In contrast, most of the samples from the Callovian-Oxfordian argillites plot on or close to the secular equilibrium line. This result suggests an uranium immobility in the target formation and provides indication of the confining capacities of the COX formation. The observed isotopic disequilibria from samples taken on either side of the interface between the clay formation and the carbonated country rock, indicate a $^{234}\text{U}$ deficiency relative to $^{230}\text{Th}$ and correspond to bulk U-dissolution.

References:
Casanova J., Négrel Ph., Brulhet J. Behaviour of trace elements and U-series disequilibrium in clayey sediments: application to the Late Jurassic record from the eastern Paris Basin Journal of Geochemical Exploration (in press).

EXTENSION OF THE DESATURATED ZONE AROUND STRUCTURES IN THE TOURNEMIRE ARGILLITE BY MEANS OF PETROPHYSICAL MEASUREMENTS COUPLED TO GAS TESTS

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Studies carried out on URL constructed in compacted argillaceous formations like in Mont Terri and Tournemire have demonstrated the occurrence of a rock de-saturation around tunnels or drifts as a consequence of excavation works and drift ventilation.

The Tournemire URL owns structures realized at three distinct periods: a century-old tunnel and drifts excavated in 1996 and 2003. It is also characterized by the appearance of desiccation fractures in the drifts. This behavior has conducted IRSN to record since 1999 the properties (Relative humidity and temperature) of the air ventilating the different structures. Time series have shown seasonal cycles for the Relative Humidity and temperature that are negatively correlated with a mean annual RH and temperature values of ca 70% and 10°C, respectively. These variations produced hydration/dehydration cycles at the structure walls since their excavation. These cycles explain the shrinkage/swelling behavior of the rock and the subsequent opening and closure of inter-layers spaces (Valès et al., 2004). However, the too short periods of saturated-air conditions did not allow a complete re-saturation of the rock at the structure wall that progressively de-saturates. This study aims to assess the extension of this de-saturation with time and location by means of densitometric petrophysical measurements coupled to pneumatic tests.

This abstract presents the main results of the first 2m borehole dedicated to this study and that was drilled parallel to bedding in the most recent drift excavated in 2003.

The volumetric weight of the humid samples was determined on core samples sawed immediately after drilling to avoid any evaporation and sample relaxation. Weights were measured with an accurate scale on wet samples and on samples dried on site at 105°C till temperature stabilization after 3 days. The humid and dry volumetric weight of the wet and dried samples were deduced from the total volume determination following the Archimede’s principle by using kerdane as described in Monnier et al. (1973). This method has allowed the determination of the water content, the water-loss porosity, the total porosity and the degree of saturation. Errors on each of these functions were calculated from propagation of the errors’ variance following the Gauss formula (Theoria combinationis 1821).

Pneumatic tests were performed by using a MMPS (multi-mini-piezometers) device from Solexperts under constant flow rate, with the aim of estimating the extent of the de-saturated area. This device has also allowed the determination of the water permeability in the saturated area.

Degree of saturation is reported in figure 1 as a function of the distance to the drift wall. De-saturation concerns the very first 30cm and the limits of cores identified as A to F where evaporation takes place preferentially due to heating during drilling. The remaining samples are saturated. Location of gas test intervals is also given in figure 1 with the corresponding values of gas permeability in intervals 4, 3 and 2. A water-bearing fracture observed at around 180cm from the drift wall has not allowed the realization of gas tests in the last interval. This figure shows that the extension of the de-saturated area determined from petrophysical measurements is shorter than that obtained from pneumatic tests indicating saturation.
from 57 cm (interval 2). The bigger de-saturation area obtained from pneumatic tests is assumed to be due to the presence of fractures.

**Figure 1**: Comparison of de-saturated areas obtained from petrophysical measurements and pneumatic tests

The same approach will be applied to five other boreholes located in the three kinds of structures (2 boreholes per structure) in the Tournemire URL and will give a good sight of the extension of de-saturated area.

Results will be used as fundamental inputs for assessing magnitude of hydromechanics coupling phenomena.
TREATMENT AND EXPLOITATION OF TIME SERIES OF PRESSURE AND TEMPERATURE OBTAINED IN THE TOURNEMIRE URL

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Compacted argillaceous semi-permeables are potential geological formations for the deep repository of radioactive wastes, due to their very low permeability and to their capacity of radionuclide retention. In this framework, IRSN develops its own research programmes in its experimental station of Tournemire (Aveyron, France). This laboratory is located in a century-old tunnel crossing an argillite formation 250m thick from Toarcian and Domerian.

Since 1990, 18 boreholes have been realized with the aim of acquiring among others, the hydraulic characteristics of the argillaceous formation and of its bounding aquifers. Seven boreholes, equipped with twenty sensors, have been followed for the pressure and temperature of the pore and fracture waters with an acquisition each half of an hour. The barometric pressure and temperature in the tunnel were also recorded in the same period.

The aim of this work was to treat all of these time series by means of mathematical tools with the goal of extracting signals emitted at the massif scale and likely to inform us about its global hydraulic functioning. This information will be compared to that acquired, at the very local scale, by hydraulic tests.

From an instrumentation point of view, temperature measurements obtained by thermistance have required a correction that has demonstrated a strong instability to low frequencies and have not allowed their full exploitation. In the future, it is recommended to use platinum probes. All the data were submitted to a multiple treatment including: spectral and correlation analyses, 1/f noise analysis, continuous wavelets analyses, simple and crossed multi-resolution analyses, and at last, reconstructed attractors analyses.

The analysis of borehole pressure and temperature data has revealed the influence of Earth tides (fig.1) in the unfractured semi-permeable and its bounding aquifers constituted by the Carixian and Aalenian formations.

Figure 1: Example of spectral analysis showing the influence of the Earth tides on pressures
This result demonstrates that these formations show a captive behaviour. On the contrary, boreholes having crossed water-bearing fractures in the semi-permeable do not show any influence of the Earth tides. This result could suggest a connection of these fractures with the surface as indicated by geochemical data. Besides, it was possible to determine the specific storativity and the kinematic porosity from the pressure data under the influence of the Earth tides. Specific storativity is homogenous with values of $2.5 \times 10^{-7}$, $5 \times 10^{-7}$ and $1 \times 10^{-6}$ m$^{-1}$ for the lower aquifer, the semi-permeable and the upper aquifer, respectively, and shows a decreasing trend with depth. Kinematic porosity is more heterogeneous (from 1 to 14%) and varies with time. It is to note that the specific storativity values are in a quite good agreement with those determined by hydraulic tests. This result also demonstrates that despite their short-range radius around the borehole the hydraulic tests give a quite good estimate of this coefficient.

The short-term variations, of random nature, present a certain structure. The analysis of this structure was carried out by means of the reconstructed attractors’ method. This method has permitted to propose an attractor dimension of 2.8. This signature implies five degrees of freedom, like for the thermal convection. However, thermal convection is incompatible with the hydraulic conductivities estimated from hydraulic tests in the matrix (from $10^{-14}$ to $10^{-15}$ m/s). If this process is confirmed by modelling, this could mean that bigger permeabilities exist locally in the unit constituted by the semi-permeable and its bounding aquifers. These higher permeabilities could therefore be linked to the presence of fractures like the regional fault of Cernon. Convection could appear in these permeable zones and pass on the semi-permeable/aquifers unit as a consequence of the observed confining.

The application of mathematical tools on time series has demonstrated the influence of several phenomena on pore and fracture water pressures (Earth tides, thermal convection) that could have never been found from classical tools. Information obtained in this study has permitted to complete that deduced from hydraulic tests and has allowed a better understanding of the hydrogeological functioning of the multi-layer system. It is also another way to valorize a huge amount of data.
ASSESSMENT OF GEOCHEMICAL STABILITY OF THE SPANISH REFERENCE CLAY BY HYDROGEOCHEMICAL AND REACTIVE TRANSPORT MODELING

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A hydrogeochemical model has been used to infer the chemical composition of the Spanish Reference Clay (SRC) pore water at the natural conditions of the formation. The model accounts for the processes suffered by clay samples during a long period of storage prior to chemical sampling. The model considers simultaneously the following processes: evaporation, oxidation, degassing and major geochemical processes. The conceptual geochemical model considers acid-base, aqueous complexation, redox, mineral dissolution/precipitation, cation exchange and dissolution/ex-solution of gases, and includes 12 primary species, 56 aqueous complexes, 6 minerals, 4 exchangeable cations and 2 gases. The model has been tested with measured chemical composition of 8 water samples from IC-1 borehole obtained by squeezing at high pressures. Modelling has been performed with the reactive transport code, CORE2D V4. Except for chloride, most chemical species present large discrepancies between measured and inferred concentrations. Measured concentrations are generally greater than inferred concentrations. Model results indicate that sample C-290 suffered significant CO$_2$(g) degassing and oxidation which caused pyrite oxidation (4.63·10$^{-2}$ moles/L), a decrease in pH which induced calcite (8.15·10$^{-2}$ moles/L) and dolomite (5.81·10$^{-2}$ moles/L) dissolution and gypsum precipitation (1.88·10$^{-2}$ moles/L). An increase in exchanged Ca$^{2+}$ concentration (from 9.33 meq/100g to 11.74) is induced by the increase in dissolved Ca$^{2+}$, which in turn provokes a release of exchanged Na$^+$ from the exchanged complex to the aqueous solution (from 5.92 meq/100g to 3.79). The effect of evaporation is generally small except for sample C-203, in which evaporation was nearly of 40% of the total water content. This sample requires consideration of evaporation, otherwise errors in concentrations would be of 61% for chloride, 25% for potassium and 46% for sodium.

Inferred chemical composition of clay porewater at several depths have been used to analyze the chemical stability of the formation during the last 40 Ma by using a 1-D reactive solute transport model. The model has been used to evaluate the consistency between hydrodynamic and hydrochemical data. The depth of the column ranges from 50 to 540 m. The model assumes an upwards water flux and a variable diffusion coefficient which decreases with depth. Calculated results for most of the chemical species reproduce measured values (see Fig. 1).
OSMOTIC ORIGIN OF OVERPRESSURES IN SHALE FORMATIONS: IMPACT OF OSMOTIC EFFICIENCY MODELS

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The ongoing research on the construction of a possible geological nuclear waste repository in shale formations raises the issue of the electrochemical interactions extensively studied in soil science between pore waters, solutes and clay mineral surfaces. These interactions are related to the negatively charged surfaces of clay platelets which generate the presence of the so-called electric double layer and the occurrence of anion exclusion. This feature suggests that clay formations may have a membrane behaviour. The assumption is supported by extended experimental works on samples in the 1970’s and 1980’s and more recently by field experiments proving the existence of osmotic behaviour in shales at the field scale i.e. in geological media. The osmotic theory developed in biophysics has been extended to geological situations through the observation that shales can behave as semi-permeable membranes.

If the geological membrane is perfect, only water can flow in response to salinity gradients. In most case studies, the semi-permeable layer is not an ideal membrane and some solute transport takes place. Osmotic flow occurs when there is a concentration gradient within the geological medium which causes solute transport dominated by diffusion. The chemical potential drives the fluid flow from the low-concentration zones to the high-concentration ones. In order to account for this chemical potential driving force, an osmotic pressure term \( \pi \) (Pa) has to be added to the hydraulic potential \( h \) to describe fluid flow. Darcy’s law in one dimension is then modified as follows:

\[
q_i = -K \frac{dp}{dx} + s \pi \frac{d\sigma}{dx}
\]

where \( s \) is the dimensionless reflection coefficient, or osmotic efficiency which characterizes the membrane properties (i.e., the difference from ideality) of the medium.

Osmotic effects are sometimes proposed to explain “abnormal pressures” in shales. The values of excess pressures that can be obtained by such processes are highly dependent on the \( \sigma \) value. This efficiency coefficient is determined from electrochemical or mechanical analyses of the interaction between solutes and clay platelets. Different theories predicting the possible values of these coupling parameters are available. The different theories providing predictive laws for \( \sigma \) are tested in this presentation with a sensitivity study using a numerical model of fluid and solute transport in shales. The effects of such models on overpressure estimates for different shales described in the literature are analysed. This numerical approach emphasizes the value of experimental work to improve an osmotic efficiency model that applies to our case study.
IN-SITU CHEMICAL OSMOSIS EXPERIMENT IN BOOM CLAY AT THE UNDERGROUND RESEARCH LABORATORY OF MOL

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Clay rich layers have traditionally been regarded as natural protective covers in regional aquifers because of their low permeability. In the absence of water conducting features, these deposits provide the low flow environment required for waste containment. Comprehensive understanding of the physical and chemical processes that control water and solute transport through low permeability argillaceous formations and to the environment is a key factor for assessing their suitability as host rocks. The Boom Clay, an over-consolidated marine Oligocene deposit, is considered as a potential host rock for radioactive waste disposal. For more than two decades, extensive hydraulic and hydrochemical research has been carried out in the Boom Clay at the HADES Underground Research Laboratory (URL) in Mol (Belgium). The main objective of the experiments conducted at the HADES URL has been to characterize the in-situ hydrogeological conditions, to determine the hydraulic parameters, and to study the mechanisms controlling the chemistry and the composition of the Boom Clay porewater.

For some mudrock environments the common hydrogeological assumptions (validity of Darcy’s law and steady-state systems) may not hold. There exists conclusive evidence for long-term transient flow in low permeability sedimentary basins. Moreover, water and solute flow and transport, may be associated with several types of driving forces, or gradients (chemical, electrical, thermal), in addition to the hydraulic forces, resulting in the so-called coupled flows. Fluid flow caused by driving forces different than hydraulic gradients is referred as osmosis. Chemical osmosis is the pore-fluid flow induced by a chemical gradient across a semi-permeable membrane. Osmotically-driven fluid flow occurs from low to high solute concentrations and tends to raise and lower fluid pressure at the outflow and inflow sides of the membrane, respectively. Osmosis, therefore, tends to induce an opposing hydraulic counter flow, and the net flow may cease when osmotic equilibrium is reached, in what case both flows are of finite and equal magnitude.

Extensive practical evidence exists on the semi-permeable membrane behaviour of clays. The extent to which a low-permeability material acts as a membrane is indicated by the efficiency of the membrane, or reflection coefficient σ, which varies from 0 for non-ideal membranes to 1 for ideal membranes. Smectite-type clays and compacted clays containing low salinity pore water act more efficiently as semi-permeable membranes. Osmotic properties (e.g. efficiency) of clays have been broadly quantified in small scale laboratory experiments on remoulded, or undisturbed, clay samples. In contrast, for the field scale, conclusive evidence for the membrane behaviour of clays and shales is scarce. Direct experimental evidence for osmosis has been obtained at the field scale in the Cretaceous-age Pierre Shale in South Dakota and in the Jurassic-age Opalinus Clay at the Mont Terri Rock laboratory.

This might also be the case for the Boom Clay. Two questions thus arise: (i) does the Boom Clay exhibit osmotic behaviour, and (ii) to what extent is it relevant for the radioactive waste disposal.

Studies on the compatibility with Boom Clay of large amounts of bituminized medium level waste (3 200 tons of Eurobitume ML W produced by the former Eurochemic fuel reprocessing plan at Dessel, Belgium) have recently raised a particular interest for osmosis. Does there exist a risk to create high
pore pressures susceptible to damage the near-field of MLW galleries, if osmotically-driven flows are produced by the release of 700 tons of NaNO$_3$ in the formation?

To attempt to answer this question, and to assess the osmotic efficiency of Boom Clay, an *in-situ* osmosis experiment has been conducted at the *HADES* URL. A recently developed chemical-osmosis flow continuum model has been applied:
(i) to aid the design of the osmosis experiment using existing piezometers at the HADES URL, and,
(ii) to interpret the obtained measurements.

The osmosis experiment was achieved in one of the filters of an existing piezometer located at the ring 85 of the Test Drift of the *HADES* URL. The clay water initially present inside the filter chamber was replaced – without pressure drop – by a 0.15 mol dm$^{-3}$ NaHCO$_3$ solution, 10 times more concentrated than Boom Clay porewater. The fast solution exchange (10 minutes) in the filter was made with a gear pump starting to operate at the local pressure value of the filter. Long-term monitoring of the water pressure was carried out, showing after 2 hours an increase in pressure within the filter containing the more saline water. We interpret this pressure increase by a water inflow from the clay formation into the filter due to osmosis because the filter and the clay were initially in hydraulic equilibrium. The increase in water pressure considerably slows down after 15 hours and the conditions at that time seem to be these of osmotic equilibrium. The maximum increase of osmotically-induced pressure corresponds to 2 m water column (0.2 bar), followed by a long pressure decay (months).

From modelling, the osmotic efficiency for the *in-situ* porewater salinity (0.015 mol dm$^{-3}$) is 35%, while for the high-saline solution (0.15 mol dm$^{-3}$) its value is only 4%. Modelling also provided additional constraints for the intrinsic permeability, $k = 1.75 \times 10^{-19}$ m$^2$, specific storage coefficient, $S_s = 4 \times 10^{-6}$ m$^{-1}$, and, effective diffusion coefficient, $D = 2 \times 10^{-11}$ m$^2$ s$^{-1}$. Experimental data could be reproduced quite accurately by the model, and the inferred parameter values are consistent with independent determinations for Boom Clay.

The experimental results obtained confirm the *in-situ* occurrence of non-hydraulic flow phenomena (chemical osmosis) in low permeability plastic formations as Boom Clay.

**Acknowledgments:**
This work is undertaken in close co-operation with, and with the financial support of, NIRAS-ONDRAF, the Belgian Agency for Radioactive Waste and Enriched Fissile Materials. The research here presented is also funded by the Netherlands Organization for Scientific Research (TRIAS grant number 835.80.032.). The support and the fruitful discussions with G. Volckaert, M. Van Geet, and X. Sillen and the TRIAS project partners have been highly appreciated. H. Moors, F. Vandervoort, and L. Van Ravestyn are also gratefully acknowledged for their assistance during the experiment.
INFLUENCE OF IONIC STRENGTH ON THE TRANSPORT PARAMETERS OF TRITIATED WATER AND IODIDE IN BOOM CLAY

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To fulfil its role as main barrier for High and Medium Level radioactive waste (HLW and MLW), Boom Clay relies on its advantageous capacity to minimise radionuclide transport by its slow diffusion– and high retention properties.

One of the key parameters in the radionuclide dispersion process is the diffusion accessible porosity ($\eta_{acc}$). Diffusion accessible porosity, is a transport parameter that is linked to the properties of each dispersing radionuclide and the geochemical conditions of Boom Clay.

Disposing radioactive waste in Boom Clay will inevitably cause perturbations of which some can generate changes in the Boom's Clay pore water chemistry. One effect of these chemical perturbations will be the increase of ionic strength of the pore water in the vicinity of a repository. This paper synthesises the results of the experimental work done to obtain the transport parameters of tritiated water and iodide for Boom Clay at different ionic strengths.

The ionic strength of pore water is a crucial parameter as it controls the thickness of the Electrical Double Layer (EDL) that surrounds the host rock minerals. On its turn, the changing characteristics of the Electrical Double Layer will likely influence the diffusion accessible porosity. Therefore, SCK•CEN started already in 1988 with preliminary migration tests, studying the impact of increasing salt concentration on radionuclide transport. In accordance with NIRAS/ONDRAF, the study was extended and continued until 1998.

To study the influence of a change of ionic strength on the diffusion accessible porosity of Boom Clay, pulse injection methodology has been applied. The dispersion of the injected pulses is monitored by labelling the pulse solutions with $^3$H and $^{131}$I. All pulse injection experiments have been done using the same three Boom Clay cores, with known stratification: two perpendicular (vertical) and one parallel (horizontal) to the bedding plane. These three Boom Clay cores have served as reference material throughout this study.

The experimental chronology relevant for the study on ionic strength is the following: first, preliminary tests have been done using only Real Boom Clay pore Water (RBCW) as percolation feed water. Secondly, the clay cores are flushed with RBCW feed water of changing ionic strength, starting from high saline (1 mole per litre NaCl) towards low saline (0.1 mole per litre NaCl). Once the clay cores were modified with each of these feed waters, a series of pulse injection experiments is executed. Finally, pulse injections under normal RBCW (0.015 mole per litre bicarbonate) feed water conditions have been repeated.

For iodide, the results clearly indicate that an increase of the ionic strength leads to an increase of the diffusion accessible porosity. A subsequent decrease of the ionic strength towards the RBCW level, restores the diffusion accessible porosity to its initial value. These observations are in agreement with
what is expected: a collapse of the electrical double layer diminishes the anion repulsion. The influence of the changes in ionic strength on the apparent diffusion coefficient are not clearly present. However, the two fold anisotropy of the apparent diffusion coefficient between vertical and horizontal stratified Boom Clay is always observed. The influence of changes in advection velocity or consolidation pressure seems to be much stronger than changes in ionic strength.

For tritiated water, variations of the diffusion accessible porosity are within the error limits of the pulse injection methodology. This observation was expected, as ionic strength variation are not supposed to have an effect on the diffusion accessible porosity of neutral molecules. As for iodide the two fold anisotropy of the apparent diffusion coefficient between vertical and horizontal stratified Boom Clay is present.
DESIGN AND DIMENSIONNING OF IN-SITU DIFFUSION EXPERIMENTS AT BURE

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INTRODUCTION
Radionuclide migration in the Jurassic-age Callovo-Oxfordian argillites is a main topic of the multidisciplinary research and investigation program initiated by Andra for studying the feasibility of radioactive waste disposal in this deep geological formation.

This research topic includes:
• Characterisations performed on core samples taken from the shafts of the underground laboratory or in deep boreholes (diffusion tests, characterisation of porosity properties, chemical retention measurements);
• Characterisation of the profiles of natural tracers;
• Phenomological modelings;
• in-situ diffusion experiments (DIR) in the underground laboratory.

The objective of the DIR scientific program is to determine the predictive capacity of the diffusion-retention models based on data obtained on core samples. This objective must be achieved for three migration behaviors of diffusion: inert, anionioic and cationic solutes. The variability (horizontal and vertical) of the lithological properties could modify the behavior of the tracers. Consequently, the in-situ diffusion experiments will be carried out at different depths in the underground laboratory and one deep borehole is drilling at 250 m away from the others experiments.

EXPERIMENTAL CONCEPT
The tracers are diluted in reconstituted formation water and introduced into a packer off section of a borehole located at a 15 m distance in the saturated rock. Pressure in this interval is kept close to the pore pressure of the surrounding rock to prevent any hydraulic gradient around the borehole. This equipment is connected to the underground gallery by a closed circuit to homogenize the traced solution and to monitor the evolution of the tracer concentration over time. After several month of diffusion, overcoring the claystone surrounding the interval will allow to measure the tracer concentration profiles in the rock.

DIMENSIONNING OF THE EXPERIMENTS
The detailed characteristics of the experiments (tracer cocktails, activities and concentrations of tracers, duration of the experiments, total volume of solution in the closed circuit) were chosen taking into account the following information:
1. The results of the long term diffusion experiments (DI and DI-A) carried out at the Mont Terri URL;
2. The diffusion and retention parameters of tracers deduced from column and classical through diffusion experiments on core samples;
3. Numerous 3D predictive modellings performed with CASTEM 2000 computer code (see fig 1.);
4. The assessment of the detection limits of the radioactive tracers;
5. The results of sorption tests of tracers on the materials constitutive of the injection system.
CONCLUSION
According to the design calculations, the first *in-situ* experiment start in November 2004 at Bure. This test is the first one in the world to be carried out from the surface in a 500 m deep borehole. Two successive tracer injections are planned: The first cocktail is composed of stable caesium, nickel and cobalt. The second cocktail mix HTO, $^{36}$Cl and $^{134}$Cs. And, in the Bure’s URL, six *in-situ* diffusion experiments are planned: 3 in the experimental niche and 3 in the main gallery level. The selected tracer cocktails are: HTO, $^{36}$Cl, $^{125}$I and HTO, $^{22}$Na and $^{134}$Cs. The duration of each experiment is about one year.

![Figure 1](image_url): results of 3D predictive modelling performed with CASTEM 2000: calculated HTO concentration in the argillites after a 6-month diffusion duration with two experimental concepts.
OSMOTIC FLOW AND OVERPRESSURES WITHIN THE CALLOVO-OXFORDIAN ARGILLITE IN THE EASTERN PART OF THE PARIS BASIN

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A middle Jurassic shale, the Callovo-Oxfordian argillite (420-560 m b.g.), is currently being intensively investigated at the Andra site, about 300 km eastern from Paris, and particularly with respect to its hydrogeological and hydrochemical properties. The argillite rests between the Oxfordian Limestone above and the Dogger Limestone below.

Observations from the different deep boreholes located at the site can be summarized as follows:
(1) the measured apparent hydraulic head across the Callovo-Oxfordian argillite show excess values of several tens of meters in comparison to the upper and lower aquifers (see figure 1), a fact which is referred to as “anomalous overpressure” in the shale literature (e.g. Neuzil, 2000)
(2) The salinity of the pore water in the Callovo-Oxfordian argillite and the Dogger is much larger than that of the Oxfordian. The salinity levels in the Callovo-Oxfordian and the Dogger are similar.

Among all physical processes which can be proposed as explanation for the formation of overpressure in shales, osmosis driven by a chemical potential (total dissolved solids) gradient is a possible candidate (Gonçalvês et al., 2004). As a matter of fact, the presence of contrasts in water composition and clay minerals content, as observed here, lead to osmotic effects (e.g. Bresler, 1973, Neuzil, 2000).

This paper presents the results of simulations using steady-state approximations and transient simulations (software OSMO, a numerical simulator developed by the British Geological Survey). It is shown that based on the extensive database of argillite measurements applicable to the study (including porosity values, specific surface determinations, pore water compositions, and effective diffusion coefficients), the chemo-osmosis is a process which can at least explain partly the “anomalous overpressures” observed.

The sensitivity of the simulation results to the interrelated effects of water chemistry, osmotic efficiency, diffusive transport, and argillite hydraulic properties was investigated. The large overpressures observed in the upper part of the Callovo-Oxfordian, where salinity contrasts are greatest, are consistent with the simulation results.
Figure 1: Measured hydraulic head profile in the Callovo-Oxfordian

References:


NUMERICAL SIMULATION OF THE HYDROGEN MIGRATION OUT OF INTERMEDIATE LEVEL RADIOACTIVE WASTE

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ABSTRACT

Due to corrosion processes, hydrogen is produced by intermediate level radioactive waste, during the post closure phase of a radioactive waste repository in an argillaceous formation (i.e. within a time frame of at least several 1000 years after closure of the repository). The potential impact of the hydrogen production on the pressure (gas and water), water saturation and dissolved hydrogen is demonstrated by means of numerical simulations of increasing geometrical complexity (1-D, 2-D and 3-D). The simulations are performed with the TOUGH2-Multiphase code (Pruess, 1999) and based on the following assumption:

• Darcy flow of the two phases: gas and water, including capillary pressure and relative permeability-saturation relationships
• Storage of fluids in the materials according to their fluid compressibility and the material stiffness
• Diffusive and advective mass transport of hydrogen in the gas and water phases
• Isothermal conditions

The general disposal configuration under study is presented in figure 1.

In a first step, a series of simulations based on a simplified cylindrical geometry (one-dimensional radial grid, no gravity) was performed. The waste package is embedded in a concrete backfill, a construction void exists between waste package and the concrete, the surrounding rock is divided into 3 radial zones of decreasing permeability: a fractured zone, a disturbed zone and the undisturbed argillaceous formation. The impact of i) the hydrogen production rate, ii) the desaturation phase due to the drift ventilation during the operational phase and iii) the hydrogen production scheme, on the pressure build-up within the emplacement drift and the gas saturation level in the surrounding rock was investigated. Given the parameter values assumed, all simulation cases provided maximum pressure at the emplacement drift less than 11 MPa.

In a second step, a vertical cross-section of the emplacement-drift and the surrounding rock was studied by means of a 2-dimensional grid resolving the waste package and its high performance concrete overpack. The boundary conditions correspond to the potential site conditions (hydraulic potential). The impact of the overpack of the waste packages on the pressure and saturation levels was found to be low.

The third step was to simulate a complete 3D-configuration with the backfilled emplacement-drift, bentonite-sealing and the access drift.

For all simulations cases (1D, 2D and 3D) the level of overpressure in the emplacement drift depends on the permeability and thickness of the argillite, the gas-filled pore volume and the hydrogen production rate. The results of the simulations showed no pressures larger than the theoretical frac-limit at the site conditions. Furthermore, the penetration depth of the hydrogen gas phase into the undisturbed argillite rock was found to be small.
Figure 1: Vertical cross section of the emplacement drift, with access drift and main drift

References:
Fractures and fracture networks determine the permeability of many natural rocks, and their behaviour has attracted attention in various fields such as the oil industry, but also water resources and waste storage. The major purpose of this communication is to summarize our work in the field and to show how to predict the macroscopic properties of such media starting from simple measurements.

First, monodisperse fracture networks are addressed. The fracture density \( r \) is the number of fractures per unit volume. A basic concept is the excluded volume \( V_{ex} \) of an object \( F \) which is defined as the volume into which the center of another object may not enter if overlap of the two objects is to be avoided (Balberg et al., 1984). For randomly oriented flat convex objects 1 and 2, \( V_{ex} \) is equal to (Adler and Thovert, 1999)

\[
V_{ex} = (A_1 P_2 + A_2 P_1)/4 \tag{1}
\]

This concept serves to introduce a dimensionless fracture density \( \rho' \). This density is equal to the number of fractures per excluded volume

\[
\rho' = \rho V_{ex} \tag{2}
\]

Topological properties of these networks are then numerically studied and they are shown to be independent of the fracture shape when the data are expressed as functions of \( \rho' \). For instance, the percolation threshold is a constant independent of the fracture shapes. A universal curve is also obtained for the number of blocks cut into the solid matrix by the network as it can be seen in Fig.1a. This independence on the shape is very important in practice.

Then, single phase flow is analysed. A new parameter \( \sigma' \) is introduced which is the ratio between the fracture permeability \( \sigma \) and the porous medium permeability \( K_m \)

\[
\sigma' = \sigma /RK_m \tag{3}
\]

where \( R \) is a measure of the lateral extension of the fracture. The macroscopic permeability \( K \) depends on \( \sigma' \) and on the fracture density. However, it is also shown that the effect of the fracture shapes is taken into account almost completely by \( \rho' \). This conclusion applies whether the solid matrix located in between the fractures is permeable or not. This is illustrated in Fig.1b.

The next problem consists in the practical determination of \( \rho' \). We demonstrated that \( \rho' \) can be derived from data which are simple to obtain on the field, such as the intersection with a single line. Of course, this line may be a well.

The most elementary version of this property can be illustrated by the intersection of a family of fractures with a line of length \( L \) which is parallel to the unit vector \( p \). Consider a particular fracture of surface \( A \) of normal \( n \) and of in-plane orientation \( \omega \); this object does not intersect the line when its center is located out of a surface of area \( A \) (cf Fig.1 of Sisavath et al., 2004). Since this is valid for any in-plane orientation, the excluded volume of the line and of the surface is equal to \( A L |p.n| \). Hence, the average number of intersections \(<n_i>\) per unit length between such a line and an isotropic network of a monodisperse family of fractures is

\[
<n_i>=A \rho /2 \tag{4}
\]

where \(<\cdot>\) denotes the statistical average. Of course, the major interests of this formula are that it does not depend on the precise shape \( S \) of the fractures and that \( \rho \) can be deduced from \(<n_i>\) and \( A \). Some
additional relations were given by Sisavath et al. (2004) for anisotropic networks. Moreover, if some information is given on the fracture shapes, $\rho'$ can be derived and the data presented in Fig.1 can be used to predict the overall properties of the fractured medium.

This first part is illustrated with the example of a real fracture network where the predictions of our methodology are successfully compared with the real data.

The second part of our talk will be devoted to various extensions of the previous results. The stereological analysis relative to a plane can be extended to convex fractures. Moreover, some results will be presented relative to multiphase flows and to polydisperse fracture networks.

**Figure 1**: Monodisperse fracture networks. (a): the number of blocks per excluded volume cut by the network in the solid matrix as a function of $\rho'$ for different fracture shapes. (b): the macroscopic permeability of a fractured porous medium as a function of $\rho'$ for different ratios between the fracture permeability and the porous medium permeability; data are for: hexagons (solid lines), squares (▲), rectangles with aspect ratios 2 (●) and 4 (■), hexagons (□) and 20-gonal fractures (☆). $\sigma'$ is equal to $10^{-4}$, 10, $10^2$, $10^3$ and $10^4$.

**References:**


STEREOLOGICAL ANALYSIS OF FRACTURE NETWORKS

GdR FORPRO: J.-F. Thovert², A.K. Gupta¹, P.M. Adler¹

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Fractures influence in a decisive way the macroscopic properties of geological media (Bogdanov et al., 2003). A crucial feature in this respect is the percolating character of the networks.

Fractures are always present in geological formations over a large range of scales and their characterization is drastically limited by the virtual impossibility of measuring them in-situ. Therefore, most analyses are based on 1D and 2D measurements of fracture traces along boreholes or on exposed outcrops which necessitate extrapolation by stereological techniques to 3D. Such extrapolations have already been made for specific fracture shapes by Warburton (1980a, b), Piggott (1997), Berkowitz and Adler (1998) and Sisavath et al. (2004) (see also the references therein).

The purpose of this communication is to survey our recent works in this field.

Let us consider in the 3D space a set of fractures which are portions of plane surfaces. When its shape S is specified, each surface can be located in space when the position of a particular point x which can be called its center, the normal \( n \) to the surface and the orientation of the fracture \( \omega \) in the fracture plane are known. The points \( x \) are assumed to be uniformly distributed with a volumetric density \( \rho \); the shapes S are always convex. The lateral extension of the fractures is measured by some length R. The probability density of the number of fractures is denoted by \( n(R) \), their area by \( A(R) \) and their perimeter by \( P(R) \).

A basic concept is the excluded volume \( V_{ex} \) of an object F which is defined as the volume into which the center of another object may not enter if overlap of the two objects is to be avoided (Balberg et al., 1984). For randomly oriented flat convex objects 1 and 2, \( V_{ex} \) is equal to (Adler and Thovert, 1999)

\[
V_{ex} = \frac{(A_1 P_2 + A_2 P_1)}{4}
\]

Our general methodology can be illustrated by the intersection of a family of fractures with a line of length \( L \) which is parallel to the unit vector \( p \). Consider a particular fracture of surface A of normal \( n \) and of in-plane orientation \( \omega \); this object does not intersect the line when its center is located out of a surface of area A (cf Fig.1 of Sisavath et al., 2004). Since this is valid for any in-plane orientation, the excluded volume of the line and of the surface is equal to \( A L |p.n| \). Hence, the average number of intersections \( <n_I> \) per unit length between such a line and an isotropic network of a monodisperse family of fractures is

\[
<n_I> = A \rho /2
\]

where \( <> \) denotes the statistical average. Of course, the major interests of this formula are that it does not depend on the precise shape S of the fractures and that \( \rho \) can be deduced from \( <n_I> \) and A. Some additional relations were given by Sisavath et al. (2004) for anisotropic networks.

The major results obtained by Berkowitz and Adler (1998) for disks intersecting an observation plane could be recently generalized to fractures of convex shapes. Some overall relations are given in Table 1. \( \Sigma_t <c> \) and \( \Sigma_p \) denote the surface density of traces, the average length of the intersections and the surface density of chord intersections in the observation plane.
The major interest of these formulae is to try to use them to derive the macroscopic quantities $\rho$, $\langle A \rangle$ and $\langle P \rangle$. It is easy (and frustrating) to realize that only two of these quantities can be obtained. An additional relation is thus necessary to derive these quantities such as a shape factor.

<table>
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<tr>
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<th>Isotropic 3D</th>
<th>Anisotropic 3D</th>
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<td>$\langle n_I \rangle$</td>
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<td>$\rho \langle A</td>
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<tr>
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<td>$\frac{P}{\pi}</td>
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<td>$\langle c \rangle$</td>
<td>$\pi \langle A \rangle \langle P \rangle$</td>
<td>$\pi \langle A</td>
</tr>
<tr>
<td>$\Sigma_P$</td>
<td>$\frac{\pi}{16} \rho^2 \langle A \rangle^2$</td>
<td>$\frac{1}{2} \rho^2 A_{12}$</td>
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Table 1: The major stereological relations for convex fractures intersecting a plane.

When the fractures are disks, the radii distribution can be derived from the trace distribution.

These results were recently extended to the important case of traces on a gallery by Gupta and Adler (2004) following Mauldon and Mauldon (1997). Exact and approximate analytical formulae were derived for the numbers of partial or full intersections. These predictions were verified by Monte Carlo calculations. Then, trace length distributions were studied mostly by numerical techniques for various disk distributions. These simulations showed that the differences between the various disk distributions are very small when the trace length distributions are compared with the same average and the same standard deviations.

All these theoretical developments are illustrated by real examples.

References:
The chemical parameters used in reactive transport models are not known accurately due to the complexity and the heterogeneous conditions of a real domain. A reactive transport model needs five kinds of inputs: the hydraulic properties of the domain, the chemical reactions occurring and the chemical parameters, the boundary and initial conditions. We will focus here on the chemical part of the problem. To describe a reactive transport model, a set of chemical reactions is first chosen and after that the corresponding parameters are obtained, whatever the way. Nevertheless, the required chemical parameters are not known exactly. Because the described phenomena are non linear, low precision on the determination of the parameters can lead to rejection of an accurate set of reactions. Moreover it is not possible to determine if the divergence between the experimental results and the calculated one is due to a wrong set of reactions or to a insufficiently precise determination of the parameters. Today, parameter estimation is mainly done using batch experiments under unique experimental conditions with tools like FITEQL (Westall, 1982). Estimated parameters are then accurate for batch reactor and for a given experimental state such as imposed pH or fixed ionic force. Extrapolating these parameters to a natural uncontrolled systems is then very hazardous.

We will present the development of an efficient algorithm in order to estimate the chemical parameters using Monte-Carlo method (Aggarwal and Carrayrou, 2004). The objective is to estimate these parameters using multi-conditional experiments. It will then be possible to make predictions under variable conditions (pH, ionic strength) which are more representative of natural systems.

By fitting the results obtained from the model to the experimental curves obtained at various experimental conditions, the problem of parameter estimation is converted into a minimisation problem. Monte-Carlo methods are very robust for the optimisation of the highly non linear mathematical model describing reactive transport. It involves generating random values of parameters and finding the best set. Unfortunately, the number of realisations to do is very high. We develop an optimisation algorithm which uses less number of realisations and, therefore, reduces the CPU time. Moreover, other improvements are used to reduce CPU time, such as:

(i) a combination of discontinuous and mixed hybrid finite elements method for the transport operator resolution (Carrayrou et al., 2003 ; Siegel et al., 1997) and;
(ii) a combined algorithm using the chemically allowed interval and positive continuous fractions methods for the chemical operator resolution (Carrayrou et al., 2002).

Reactive transport of TBT through natural quartz sand at 7 different pHs is taken as test case (Bueno et al., 1998). We will compare results from various optimisations to choose the most efficient one. Finally, our algorithm will be used to estimate the chemical parameters of the sorption of TBT onto the natural quartz sand (Table 1).

In this work, we prove that the chemical comportment of an heterogeneous surface cannot be describe by a single sorption site model, whatever the parameters are (Figure 1). An accurate modelling of reactive transport should then use a complete description of chemical phenomenon at the solid-water interface including surface heterogeneities.
Table 1: Morel Tableau for the TBT reactive transport test-case

<table>
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<tr>
<th></th>
<th>H⁺</th>
<th>Cl⁻</th>
<th>NO₃⁻</th>
<th>Na⁺</th>
<th>Im</th>
<th>TBT⁺</th>
<th>=S-OH⁻</th>
<th>ΨS</th>
<th>Given log (K)</th>
<th>Estimated log (K)</th>
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<td></td>
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</table>

Initial condition (M) fixed 0.0 0.1 0.1 10⁻³ 0.0
Injection (M) fixed 8.6 10⁻⁶ 0.1 0.1 10⁻³ 8.6 10⁻⁶
Leaching (M) fixed 0.0 0.1 0.1 10⁻³ 0.0

Given specific area $S = 0.200 \text{ m}^2\cdot\text{g}^{-1}$ (Bueno, 1999), estimated $S = 0.346 \text{ m}^2\cdot\text{g}^{-1}$.
Bolt parameters will be estimated.

Figure 1: Experimental and calculated elution curves for the reactive transport of TBT onto a natural quartz sand. Calculated elution curves are obtained after optimizing the chemical parameters.
References:
This paper presents the application of so-called gas threshold pressure tests (GTPT) to assess the behavior and two-phase flow properties of clay-rich sedimentary rocks under investigation for disposal of high-level radioactive (HLW) and spent fuel (SF).

Nagra and Andra are the organizations carrying out this type of site investigation in Switzerland and France respectively. In both cases, clay-rich sedimentary rocks (e.g. argillites, shales, claystones) with low permeability are being considered as possible repository host rocks. The favorable hydraulic characteristics of these rock types restrict the flow of groundwater through the repository and imply that transport by pressure-driven advective flow may be negligible compared with diffusion effects (GAUTSCHI, 2001; NAGRA, 2002a).

The radioactive wastes will produce a significant amount of gas due to corrosion and degradation processes. Gas generation will continue for a long period after repository closure. Accumulation of the gas may lead to unacceptable build-up of gas pressure in the disposal tunnels, if the gas cannot escape through the low permeability host rock. Furthermore, gas could be the driving-force for forcing contaminated water from the disposal zone and contaminant transport in the gaseous phase could occur. In this context, the two-phase flow properties of the host rock formation are important parameters for the simulation of the gas pressure build-up in the backfilled disposal tunnels and the assessment of the pressure build-up on the long-term performance of the disposal system consisting of engineered and geological barriers (NAGRA, 2002b & 2002c).

In the early site investigation phase, the only access into the host rock formation is normally the drilling of deep boreholes, which provides the opportunity to perform gas tests - in particular the so-called gas threshold pressure test - to obtain an in-situ data set and information on the two-phase flow properties of the host rock.

**GAS THRESHOLD PRESSURE TEST (GTPT) CONCEPT**

With the gas threshold pressure test (Figure 1), the gas entry threshold pressure and two-phase flow parameters are determined. A common GTPT consists, in the beginning, of a single-phase hydraulic test sequence performed to derive the hydraulic parameters of the test interval, namely transmissivity, formation head and the valid flow model. The water phase in the test interval is then displaced by gas, keeping the test interval pressure as stable as possible. Afterwards, gas injection starts and the gas threshold is detected. The final stage comprises a shut-in with a pressure recovery phase.

**GTP-TESTS AT BENKEN (SWITZERLAND) AND BURE (FRANCE)**

The test in Switzerland was performed in the Benken borehole, drilled in 1998-1999; the borehole encountered the Opalinus Clay at a depth between 540 and 650 meters. The test interval was located between 600 to 603.5 m bgl (NAGRA, 2001). The interpretation reveals a best estimate hydraulic conductivity of $1 \times 10^{-14}$ m/s. The GTPT analysis suggests a gas entry pressure value > 4.3 MPa.
The argillites of the Callovo-Oxfordian formation at Bure are at a depth of between 420 – 550 m below ground level and the GTP-Test in borehole EST 363 was conducted in September 2004 in a test interval located between 490 – 495.15 m below surface. The preliminary interpretation reveals a best estimate hydraulic conductivity of $4 \times 10^{-13}$ m/s and a gas entry pressure of around 3.3 MPa (ANDRA, 2004).

Figure 1: General test sequence example of a GTP-Test

RESULTS AND CONCLUSIONS

The results of the tests in the two different formations fit well with the empirical relationship between gas entry pressure and permeability, compiled for a wide range argillaceous formations (NAGRA 2002a). The GTP-Test results support the general system understanding of the two-phase flow properties of host rock formations. In the Nagra case, visco-capillary flow and pathway dilation provide a suitable conceptual framework for describing gas release through the Opalinus Clay (NAGRA, 2002a).

References:


ESTIMATION OF THE STORAGE IMPACT ON THE FLUIDS MOVEMENT IN THE CALLOVO-OXFORDIAN GEOLOGICAL LAYER

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Around the MHM site, and for the last tens of thousands years, the natural flow in the Callovo-Oxfordian layer can be considered at equilibrium, and so should be for the next tens of thousand years. However, the digging of the storage will modify the hydraulic heads around all shafts and galleries.

The hydraulic behavior is largely influenced by the presence of an EDZ around the excavations. Radially, this mechanically damaged zone can be divided into two parts:

• one fractured zone just outside the galleries walls, which permeability is 4 to 5 orders of magnitude higher than the permeability of the sound argillites,
• one micro fissured zone, externally of the fractured zone, which permeability is 1 to 2 orders of magnitude higher than the one of the sound rock.

Except for EDZ generation, mechanical effects on hydraulic flow can be neglected.

Another major characteristic influencing the hydraulic behavior of the argillites around the excavation is the ventilation of the tunnels. The relative humidity of this ventilation air is around 50%. So a desaturation zone will develop around the tunnel walls, especially in the EDZ.

The thermal load of certain types of waste will also have a significant impact on the flow scheme. During the rising temperature phase, an over pressure can be generated some tens of meters away from the galleries. Another effect of temperature is to accelerate the resaturation process. Significant impact of thermal load on water flow will last some thousands of years.

Some hundreds of years after repository closure, gas production by corrosion of the metallic parts present mainly in the storage cells will begin to influence the water flow. A gas phase will by individualized inside each cell and gas pressure will build up until it reaches the gas entry pressure of the EDZ. The gas will then expand into the galleries. Gas generation process will last some tens of thousands of years, and the gas phase will need some additional thousands of years to dissipate by dissolution in the surrounding water.

From this analysis, one can evaluate that the general impact of the storage on the hydraulic behavior of argillites around excavation walls will be significant for at least some tens of thousands of years, more probably for one hundred of thousands of years.
MULTIDOMAIN SIMULATION OF FLOW AND TRANSPORT AROUND THE BURE SITE

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Studies for a possible deep underground repository for nuclear waste require fast and accurate simulation of contaminant transport. Indeed for performance assessment of the site the same code is run several hundred times with varying coefficients. At the same time, as studies become sharper and sharper, the models used in performance assessment get more and more complex. Therefore there is a strong need for improving the computer performance of codes. Multidomain simulation is one technique that can be used to achieve this purpose.

A large scale simulation around the Bure site is run in a domain with several geological layers whose rock properties are very different and for which, consequently, permeability and diffusion coefficients vary with several orders of magnitude. In order to speed up the simulation, one will divide the domain into several subdomains which are fairly homogeneous so that fast solvers can be used on the subdomains.

The two main ingredients for multidomain simulation are domain decomposition and subdomain time stepping.

A domain decomposition method is an iterative procedure using subdomain solvers for calculating the solution of the global system. In order to calculate the flow (assumed to be incompressible), we used a domain decomposition method for elliptic equations based on Robin-Robin transmission conditions. A similar method is used in order to calculate the diffusion contribution to transport.

Since the transport coefficients vary strongly from one subdomain to the other, the subdomain time scales vary in the same manner and the time steps in the subdomains should be calculated accordingly. Current codes do not possess this capability and use instead the smallest time step required by the fastest time scale to perform a calculation in the whole domain. In order to save computational costs, subdomain time stepping allows for a choice of a time step per subdomain which is appropriate for the time scale of the physical phenomena occurring in the subdomain.

The two main techniques for multidomain simulation, domain decomposition and subdomain time stepping, will be illustrated by a flow and transport simulation around the Bure site.