Physicochemical Reactivity in Clay-Rich Materials: Tools for Safety Assessment

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Résumé — **Réactivité physicochimique des argiles : outils pour l'évaluation de sûreté** — Les matériaux argileux naturels ou industriels sont omniprésents dans les concepts de séquestration des gaz acides, de confinement des polluants et déchets radioactifs, ainsi qu'en couverture de réservoirs géologiques d'hydrocarbures. La fonction de piégeage repose sur des propriétés telles qu'une très faible perméabilité, une capacité élevée d'échange ionique et de sorption, et, dans certains cas, sur un fort pouvoir de gonflement. En raison de la petite taille des pores et de leur tortuosité élevée, mais aussi de par leur surface spécifique très élevée et leur charge électrique importante (particulièrement les smectites), les matériaux argileux développent de telles propriétés de confinement. Dans le cadre des évaluations de performance et de sûreté, la persistance de cette fonction de confinement doit être assurée sur le long terme. Les matériaux argileux et l'ensemble des matériaux d'origine anthropique (béton, acier, verre, etc.) vont interagir physicochimiquement au cours du temps. Les argiles vont également être soumises à des perturbations dues au dégagement de chaleur (notamment dans le cas du stockage des déchets radioactifs) ainsi qu'à des transferts hydriques (eau et vapeur). L'ensemble de ces perturbations couplées est susceptible d'engendrer des transformations irréversibles dont il convient d'estimer l'impact sur le comportement à long terme.

Pour aborder la complexité de ces phénomènes, nous combinons des méthodes de caractérisation multi-échelles et multitechniques (infrarouge moyen et lointain, diffraction des RX, microscopie électronique à balayage, microscopie électronique à transmission) sur des échantillons provenant d'expériences de laboratoire et d'analogues naturels. Ensuite, les résultats sont intégrés au travers de la modélisation du transport réactif. La sensibilité élevée des smectites est décrite dans le cas des interactions entre les argiles et le fer métallique, expérimentalement et par l'étude d'analogues naturels. Cette étude montre l'existence d'un seuil de rapport de masse fer/argile au-dessus duquel les smectites tendent à être transformées en de nouveaux minéraux à 7 Å, riches en fer, dont les capacités de gonflement et d'échanges cationiques sont largement inférieures à celles des smectites initiales, et ceci de manière irréversible. À titre d'illustration, la méthodologie est également appliquée pour décrire l'illitisation thermique d'une argilite due à une intrusion basaltique.

Malgré le travail de caractérisation et de compréhension, la prévision de l'évolution à long terme de tels systèmes complexes est encore sujette à caution. Modéliser le comportement global des matériaux argileux reste une tâche difficile en raison du fort couplage, présenté par la suite, entre les phénomènes chimiques, mécaniques et de transport, potentiellement contrôlés par une phase de gel smectique, physiquement délicate à prendre en compte.

Abstract — Physicochemical Reactivity in Clay-Rich Materials: Tools for Safety Assessment —
Natural or engineered clay-rich materials are ubiquitous when it comes to achieving sequestration of
acid gas, confinement of pollutants or high level radioactive waste (HLRW), and trapping hydrocarbon
oil and gas in geological settings. The sequestration, confinement, and trapping functions rely on proper-
ties such as low permeability, high sorption and ion exchange capacity, and, in some cases, on swelling
abilities. Clay-rich materials contain specific clay minerals possessing these properties due to the small
size and high tortuosity of the pores as well as the very high specific surface area and the surface charge
of these minerals (especially smectites). For performance and safety purposes, the persistence of this ini-
tial sealing function has to be ensured over time, as the clay minerals of interest and the foreign anthro-
pogenic materials (concrete, steel, and other clay materials in situ) will undergo physicochemical inter-
actions and may lead to irreversible transformations. The clay minerals will also be subjected to
perturbations due to the heat release of waste packages in the case of HLRW repository, and liquid water
and vapour transfers.

To tackle the complexity of these phenomena, we combine multi-scale and multi-technique characterisa-
tion (middle and far Fourier transform infrared, X-ray diffraction, scanning electron microscopy (SEM)
and transmission electron microscopy (TEM)) on samples coming from laboratory experiments and
natural analogues, and integrate the results through reactive transport modelling. As an example, the
characterisation methodology is used to establish the illitisation of claystones due to a basaltic dyke
intrusion. The approach is compared with classical ones and the application to diagenetic clay sequences
for petroleum exploration is discussed. We also explore the high sensitivity of smectic (gel phase)/smec-
tite properties as a function of water content/composition and temperature by investigating the interac-
tions between metallic iron and smectitic clays. This comprehensive study reveals an iron/clay mass ratio
threshold above which the smectites tend to be altered into 7 Å Fe-rich clay minerals with much lower
swelling and cation exchange capacity.

With a comprehensive description and understanding, the prediction of the long-term evolution of such
systems seems to be at hand. However, modelling the overall behaviour of clay-rich materials remains a
difficult task because of the strong, multi-scale coupling between chemical, mechanical and transport
phenomena, potentially mediated by a smectitic gel phase.

INTRODUCTION

The sequestration, confinement and trapping of substances such as acid gas, oil, radioactive wastes and pollutants share a set of common materials and complex phenomena that need to be studied by interdisciplinary research groups. The results must be integrated at the industrial level in order to reach operational efficiency. The natural or engineered materials involved in these fields of activity often include clay-rich materials (CRM) because of their useful properties: low permeability, high sorption and ion exchange capacity, and swelling abilities. The sealing function conferred to clayey materials qualifies them as efficient caprocks for trapping and sequestration, or host-rocks for confinement.

The prediction of the long-term behaviour of these systems constitutes a challenging task and, for an important part, requires the understanding of the reactivity of CRM with the "foreign" materials used for man-made seals and structures (concrete, steel, engineered clays). The impact of the gas injection (CO_2, H_2S) and/or gas production by corrosion processes (*e.g.*, H_2) or by irradiation (*e.g.*, HCl) is also of great importance for the mechanical stability of the underground installations (see Marshall *et al.*, this issue).

The range of physical conditions we are looking at is quite large: low to high temperature, from 25 to 80 or 100°C with atmospheric to low pressure for radioactive waste disposal and acid gas sequestration in saline aquifers, whereas for reservoir exploitation and acid gas sequestration in hydrocarbon fields, we expect moderate to high temperature (up to 180 or 200°C) with moderate to high pressure (up to 800 bar). The characteristic time scales associated with the installation life depend on the stage considered, from the start of the exploitation to the long-term behaviour. We may expect decennial life expectancy for oil and gas well exploitation, centennial for the nuclear waste disposal safety assessment and geological time for other disposals performance assessments and sequestration activities.

This paper focuses on the chemical reactivity of CRM, leaving the gas phase for further developments but keeping in mind that interactions with gas are equally important for the chemical and mechanical behaviour of clay-rich materials. One of the major remaining challenges is to understand the coupling between phenomena occurring when different materials (concrete, steel, clays) are put into physical contact.

After describing the global methodology, applications to steel corrosion in clay materials and reactivity of claystone

under thermal gradient are presented. The coupled processes occurring in clay will be also discussed to underline the further developments needed for the global modelling of the long term behaviour of clays.

1 METHODOLOGY AND APPROACH

In order to assess the clay material behaviour, the characterisation method used has to take into account a wide scale of investigation: from the global system of the sedimentary basin to the metric or decimetric scale of an experimental device. Claystone presents heterogeneities at these scales (Marshall *et al.*, this issue), some of which can impact the material behaviour as a confinement barrier or a caprock. Centimetric to micrometric scales are necessary to represent the texture of the clay material *(Fig. 1)* and to reach the elementary reaction, one has to look at the nanometric reactive level. At this last scale, the identification of the significant physicochemical processes impacting the macroscopic behaviour is complex since they involve the coupling between thermal, hydraulic, mechanical, chemical, and electrical (THMCE) phenomena *(Fig. 2)*. To tackle this problem, a multi-disciplinary and multi-scale approach is used to identify these processes and to determine the crucial parameters controlling the transformations *(Fig. 3)*. The approach consists of a combination of investigative techniques: global methods such as spectroscopy (IRTF, Mössbauer, EXAFS, etc.), X-ray diffraction, and thermal analysis associated with chemical analyses and completed with local microscopic characterisation from optical and electron microscopy (SEM-EDS and TEM-EDS). We use samples coming from laboratory experiments, to obtain parametric data, as well as a large variety of systems representing natural and archaeological long term behaviour analogues for the repository. The study of natural analogues allows us to identify the governing parameters of the reactive systems on time scales and space scales not accessible to laboratory experiments.

In parallel with the characterisation results, a priori numerical modelling focusing on mineralogical reactivity is carried out to help determine the key processes and to reveal a possible lack of crucial data. In the systems we are dealing with, we use multicomponent reactive transport models which:

– require a complete speciation of aqueous species reflecting the pH and Eh conditions;
– involve reactions such as dissolution and precipitation of mineral phases, sorption and exchange of ions.
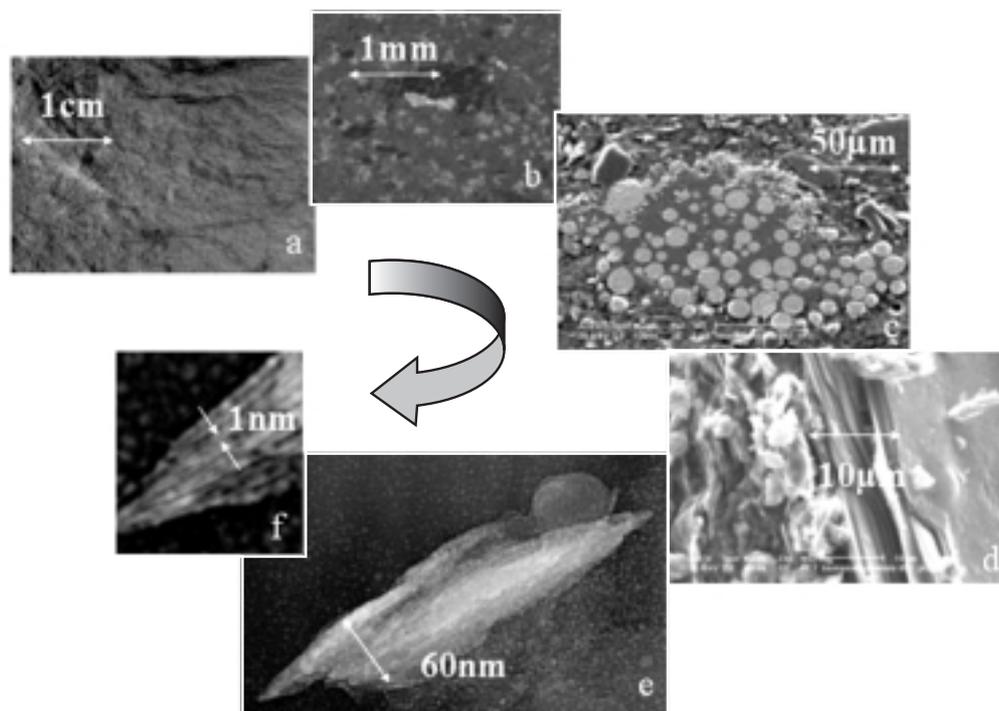

Figure 1

The multi-scale nature of clay rich material: case study of Tournemire marl; optical microscopy of marl (a) and accessory minerals (b), SEM micrographs of pyrite and calcite assembly (c) and layered structure of micaceous minerals (d), TEM micrographs of illite particles (e) and a illite stacking sequence (f).
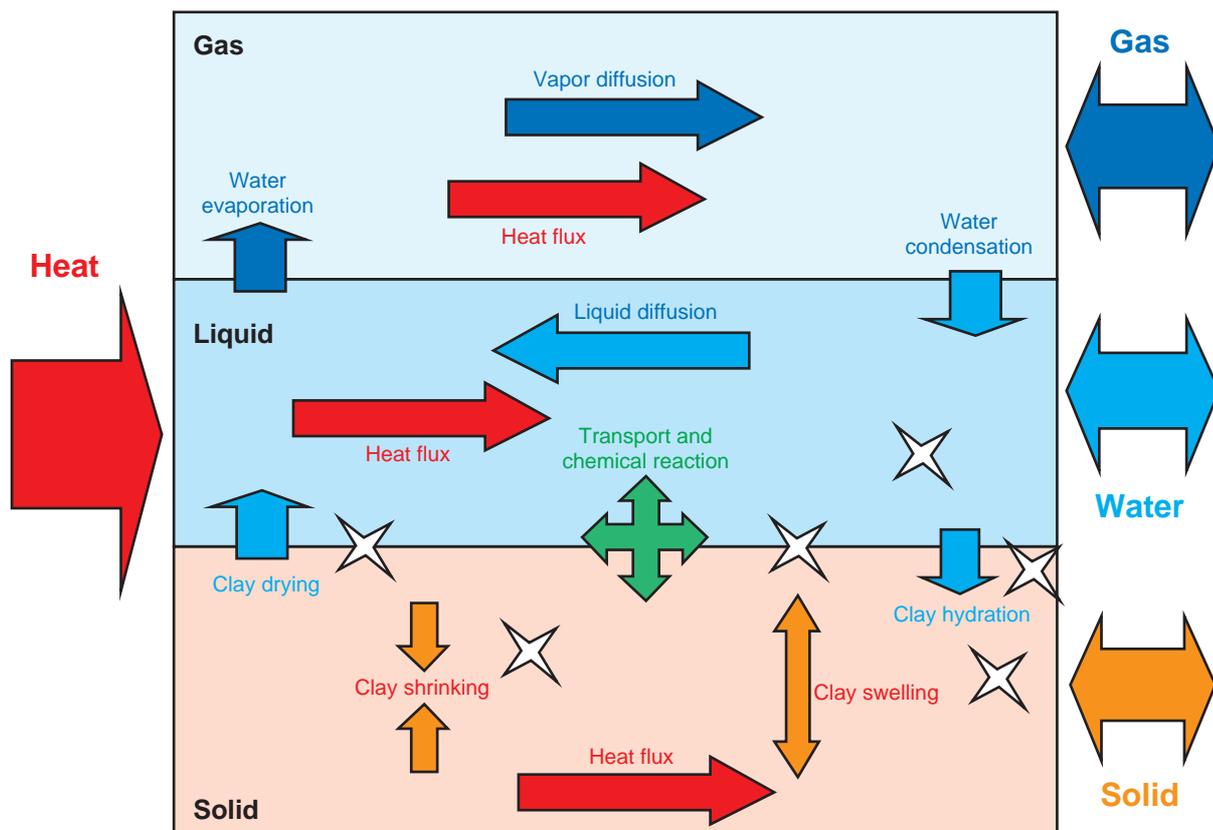
Figure 2

Macroscopic manifestation of couplings between processes occurring in clay-rich materials. Single arrows represent transfers (heat, matter, etc.) and double arrows represent exchanges (gas, water and solids). White stars express electrical phenomena (surface complexation, double layer phenomena, etc.).
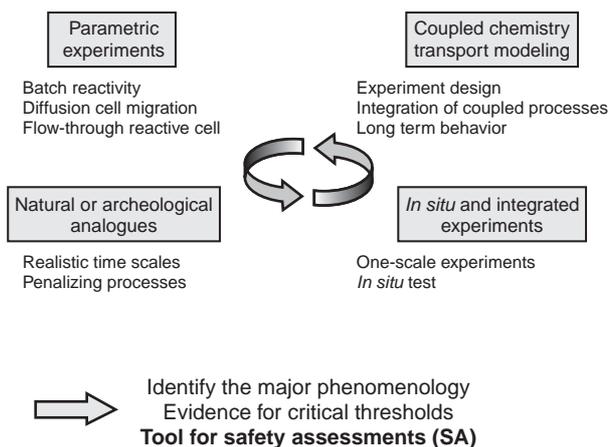

Figure 3

The coupled multi-scale and multi-disciplinary approach applied to the clay study.

The feedback effect of the coupling between chemical reactions and flow/transport is an important point and appears as a result of the precipitation and dissolution of minerals. The mineral transformations affect the surface area (and the number of sorption sites) and may change the porosity and the concentration of dissolved species. These changes may in turn modify the permeability and the effective diffusion coefficients affecting the flow rate and the transport of dissolved species (Lichtner *et al.*, 1996; Steefel and Van Cappellen, 1998). The way a particular feedback acts in the system is crucial to determine if an initial perturbation will be attenuated or amplified. This feature has been investigated in the case of porosity clogging in concrete-clay systems (Lagneau *et al.*, in press; Trotignon *et al.*, this issue). These studies helped to design an experimental device which is proposed as a basis for consistent code benchmarking (Trotignon *et al.*, this issue). In contrast, some systems show the opposite behaviour, where local porosity enhancement can lead to the creation of preferential transport pathways. This is potentially the case in the iron-clay system where the

initial clay material (smectite) is irreversibly transformed in a new phase (berthierine-like phase) with smaller molar volume; swelling and ion exchange capacity (see next section).

In general, the understanding of such complex systems requires continuous iterations between the different methods, going from experimental studies (including full scale experiments when possible), to characterisation of analogues and numerical modelling. Modelling may also be used to narrow down the field of investigation, to highlight the crucial questions and to validate the data previously acquired. This approach is illustrated with examples of iron/clay interactions and the thermal perturbation caused by a basaltic intrusion in claystones. In these studies, we attempt to address key questions such as: what are the transformations expected of the clay materials? What are the mineral phases, reaction processes and their kinetics influencing the long-term behaviour of the system? What are the implications for the confinement capabilities of the near field in a repository?

2 APPLICATION TO STEEL CORROSION IN CLAY

The purpose of this section is to identify physicochemical couplings occurring in the context of deep geological disposal, involving metallic iron and clay, and possibly leading to transformations in mineral composition and alteration of the confinement properties such as swelling and retention capacity. In the repository context, components made of different materials are put into contact. Waste packages with thermal output, such as vitrified wastes or spent fuel, will be contained in stainless steel canisters and possibly over-packs. In some concepts, clay materials will be used to confine these packages: either bentonite from the engineered barrier system (EBS) or claystones from the host-rock (concept without EBS). During the first hundred years, the clay material in the near field of the repository will be subjected to a thermal load and to resaturation (or hydration). The aqueous corrosion of the canisters and over-packs will then lead to the first chemical perturbation of the system, changing parameters such as redox potential and pH, and releasing large amounts of iron into the system (Papillon *et al.*, 2003). In the long term, the waste packages will in turn be affected by incoming water leading to the alteration of the nuclear glass and, consequently, to the release of its components (mainly silica, sodium, boron, aluminium, calcium, etc.) and the radionuclides. At each step in the evolution of the near field, the chemical perturbation will cause transformations in the clay material and may affect both the lifetime of the waste packages and the performances of the multi-barrier system.

In this study, we are looking for evidence of threshold values for parameters such as the iron/clay ratio, possibly causing adverse transformations impacting the performance

and safety of the repository. The mineralogical transformations of the clayey materials are studied through natural and batch-type experiments. After identification of the phenomenology such as neocrystallisation and/or dissolution of minerals and textural modifications, the key parameters (temperature, physicochemical conditions, etc.) are inferred and tested with geochemical and reaction-transport modelling.

2.1 Natural Analogues for the Iron-Clay System

In natural systems, the geochemical control on the iron cycle is the result of competition between reactions involving sulphur, carbonates and clay minerals. The reactions with sulphur are predominant, leading to the formation of iron sulphide minerals. In carbonate diagenetic environments with very low sulphur content, precipitation of siderite ($FeCO_3$) dominates. This carbonate is often observed in cases of aqueous corrosion and plays an important role in the long-term behaviour of the steels and low cast iron because it could form a protective layer (passivation effect). In clayey sedimentary and diagenetic environments, in addition to the two former transformations, iron can also be incorporated in the structure of nonswelling Fe-Mg phyllosilicates such as berthierines and chlorites. These three types of formation (sulphides, carbonates, and phyllosilicates) may actually occur simultaneously at different locations of an argillaceous system. This is confirmed by observations showing that for a large range of temperature and redox conditions the most stable mineral phases are 14 Å-type Fe-Mg chlorites, containing more or less aluminium, and iron-rich 7 Å-type serpentines and berthierines. These diagenetic environments allow us to define key parameters and mineral phases able to occur in multi-barrier confining system, *i.e.* clays and steel in our case.

It is important to consider iron in its metallic form and not only in the aqueous phase, in order to check the coupled corrosion/clay reactivity. The study of natural analogues gives us hints about the key parameters of the reactivity of iron-clay systems. It stresses the importance of the amount of iron entering the clay material, the presence of minerals able to buffer pH and redox conditions, the amount and accessibility of water, and the nature of the initial clay minerals. The only existing analogues, to the authors' knowledge, are carbonaceous chondrites. Chondrites are meteorites mainly composed of metallic iron and nickel, silicates and accreted water. During their extraterrestrial evolution, they underwent alteration and the interactions between iron and clays led to the formation of significant amounts of phyllosilicates *(Fig. 4)*. The conditions of alteration in terms of temperature (20-150°C), pressure, redox (reduced conditions) and solid-solution ratio are close to those expected in the near-field of a repository. Again, the final products of the alteration are iron-rich serpentines (berthierine, cronstedtite, etc.): the same type of mineral phases is expected in our experiments.
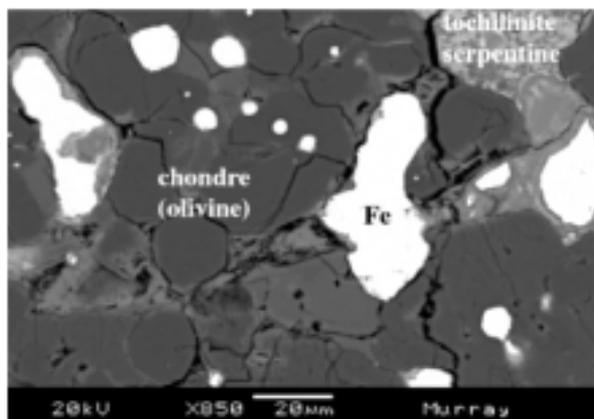
Figure 4

Carbonaceous chondrites illustrating iron corrosion and silicate contact with formation of Fe-rich serpentine *(courtesy of B. Devouard, Univ. Clermont-Ferrand, France).*
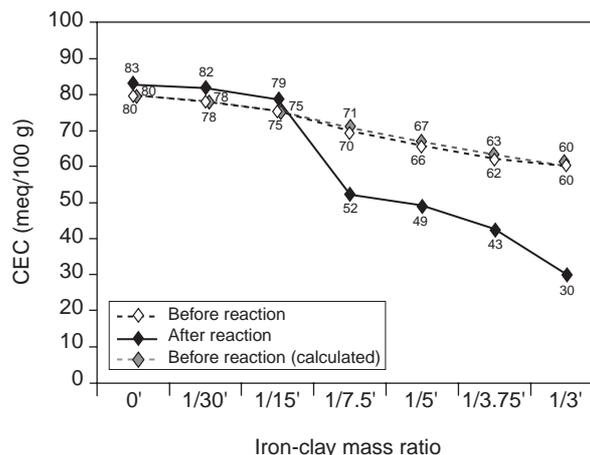

Figure 5

Decrease of cation exchange capacity after reaction between FoCa bentonite and metallic iron at 80°C as a function of the iron/clay mass ratio (Perronnet *et al.*, submitted).

2.2 Batch Type Experiments

An extensive experimental program consisting of batch-type systems was set up to study the reactivity of metallic iron (powder) with clay minerals. A large range of CRM were studied such as natural clay minerals (montmorillonites, beidellites, nontronite, illite, kaolinite), industrial clay materials (French FoCa and Forez I/S, USA Wyoming MX 80), and naturally occurring argillaceous material (Tournemire, France). Experimental conditions ranged from 25 to 150°C, with different redox environments (Lantenois *et al.*, 2003; Perronnet *et al.*, submitted).

In particular, the reactivity of FoCa7 bentonite has been investigated in the presence of metallic iron in *Évian®* mineral water. Experiments in test tubes lasted 45 days at 80°C. The iron/clay mass ratio (I/C) ranged from 0 to 1/3 with a clay/solution mass ratio maintained at 1/16.7. The mineralogical evolution of bentonite was studied using XRD and HR-TEM and the chemical variations measured by EDS-TEM microanalyses. The evolution of iron components was obtained by ^{57}Fe Mössbauer spectroscopy and the cation exchange capacity was measured using the Cu-ethylenediamine method. This study shows that for I/C values above 1/7.5, kaolinite and smectites are partially consumed as shown using HR-TEM and XRD. As a result, the exchange capacity significantly decreases *(Fig. 5)* and, as the iron consumption increases, new 7 Å Fe-rich phases grow in small tabular crystals in the Si-Al-Fe gels formed by the alteration of smectite and kaolinite. A phenomenon of smectitic corrosion is invoked to explain this variation of reactivity and the existence of an I/C threshold ratio (Perronnet *et al.*, submitted).

As a general conclusion, the results of the batch experiments show the very high reactivity of the iron-clay system and demonstrate the formation of iron-rich 7 Å phases like berthierine, cronstedtite or odinite *(Fig. 6)*. These experiments allowed the reaction mechanisms to be identified and threshold values to be established, in terms of temperature and supply of iron (Perronnet *et al.*, submitted), for which the initial clay minerals are destabilised, and in certain conditions completely consumed (Lantenois, 2003). This work also provided the first evidence of the presence of a gel phase resulting from the clay dissolution *(Fig. 6)* and its role as medium for nucleation and growing of new phases. Irreversible transformations resulting from such reactivity could induce possible loss of confinement function in the case of the decrease of retention capacity or the creation transport preferential pathways or short-cut between waste or gas and aquifers or surface.

2.3 Numerical Modelling

Coupled reaction-transport codes are used here as tools to investigate the effect of steel corrosion in a clayey environment (*e.g.*, Trotignon *et al.*, 1998a). The results of the modelling are interpreted and provide the basis for new simulations in the light of the conclusions from the experimental observations (see above). Figure 7 shows a 1D domain for the numerical simulation of the repository near field with three different components: a steel canister, a 0.8 m thick bentonite engineered barrier, and the undisturbed claystone from the geological medium. In this case study, the corrosion rate is held constant (0.1 μm/year). The transport of aqueous species is purely diffusive and the simulations are performed over a 10 000 year period. The calibration of the model is
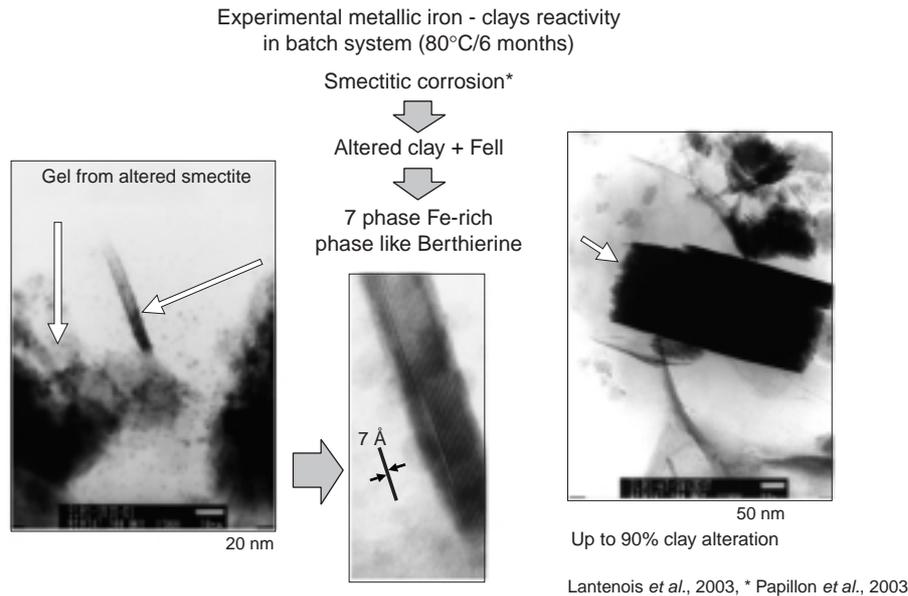
Experimental metallic iron - clays reactivity
in batch system (80°C/6 months)

Smectitic corrosion*

Gel from altered smectite

Altered clay + FeII

7 phase Fe-rich
phase like Berthierine

7 Å

20 nm

50 nm

Up to 90% clay alteration

Lantenois *et al.*, 2003, * Papillon *et al.*, 2003

Figure 6

TEM micrograph showing the alteration of FoCa clay with crystallization of bertherine *(courtesy of S. Lantenois, Univ. Orleans, France).*
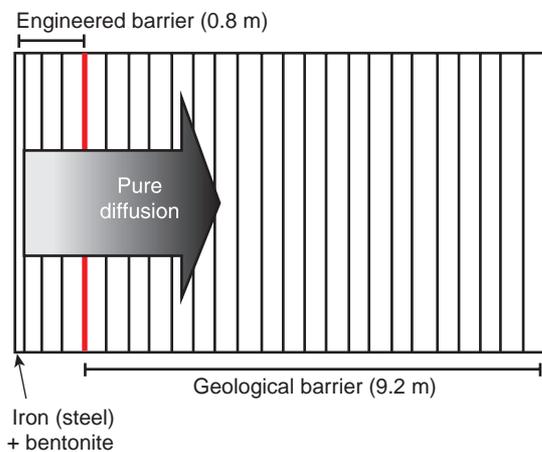
Engineered barrier (0.8 m)

Pure
diffusion

Geological barrier (9.2 m)

Iron (steel)
+ bentonite

Figure 7

1D simulation domain for the simulation of corrosion of a steel canister in a repository concept including a bentonite engineered barrier in an argillaceous geological medium.

achieved in a "trial and error" mode, starting with parameters available from the literature such as thermodynamic and kinetic data for minerals, transport parameters, etc. These parameters are then modified to fit the observations, which usually involve a certain amount of experience from the operator. In this particular case, the results indicate that the reactivity (*i.e.*, the dissolution kinetics) of the initial clay material must be set to a high value in order to simulate the transformation of montmorillonite (*e.g.*, in this case MX80

bentonite) into iron-rich 7 Å berthierine-type minerals (chamosite-7 Å), along with the precipitation of siderite *(Fig. 8)*. They also show that the transformation affects only a few centimetres of the argillaceous material in contact with iron in the case of a homogeneous CRM. If other, highly reactive alumino-silicate minerals, such as kaolinite, are initially present in the clay material, they will have the highest reactivity, providing the critical source of aluminium, silica reacting to a lesser extent.

Other chemical perturbations of clays have also been evaluated using reactive transport codes, in particular the influence of concrete degradation (Trotignon *et al.*, 1998b) or the reequilibration of clay engineered barriers with site groundwaters (Cranga *et al.*, 1998). In the latter case, the multisite ion exchange reactions occurring at the clay surface are coupled to carbonate and pH evolution in the near field.

3 THERMAL BEHAVIOUR OF CLAY

As an example of another physicochemical perturbation to CRM, we looked at a natural analogue for the response of clay minerals to heating, representing the thermal output of the high level radioactive waste (HLRW) canisters in a repository setting. Four million years ago, a basaltic plume intruded a clay rich medium (marl) at Laumiere in the middle Toarcian of Causses (Massif Central, Aveyron, France) and heated the clay minerals in the neighbouring rock. In order to isolate the thermal effect of the intrusion from other perturbations, we took unaltered reference samples in the same sedimentary series located under the experimental platform of the
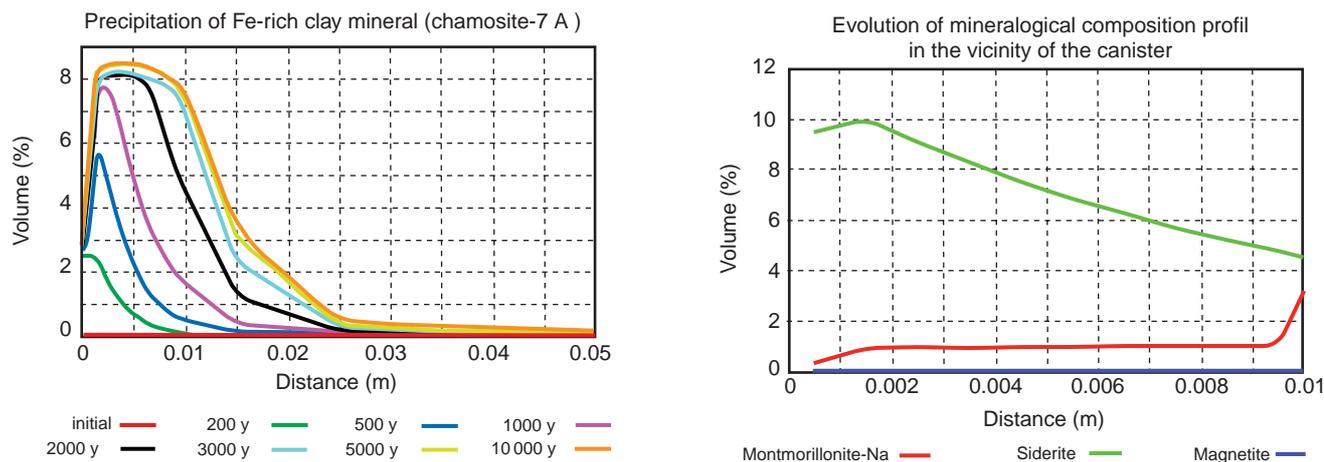
Figure 8

Evolution of the volume fraction of minerals as a function of the distance to the canister: iron-rich phase vol% as a function of time (left), composition profile in the first cm after 10 000 yr (right).

Institut de radioprotection et de sureté nucléaire, IRSN, at Tournemire. The Tournemire and Laumiere sites are situated in a Mesozoic marine basin in Aveyron, in southern France. The middle Toarcian of Tournemire is a deposit comprised between two series of limestone and dolomite. This marl layer leans on carbonaceous shists ("*schistes cartons*") that constitutes the inferior Toarcian. These marls are composed mainly of illite and inter-layered illite-smectite minerals (I-S). The marl also contains kaolinite (20%) and chlorite (approximately 10%), there is a cementing by calcite (20%) and quartz (20%). The organic content is very low (1% of TOC).

This kind of diagenetic or sedimentary series has already been extensively studied using the smectite illitisation approach *e.g.*, Kubler (1967), Kubler and Jaboyedoff (2000), Srodon (1980), Reynolds (1980, 1992), Lanson and Besson (1992), Lanson and Velde (1992), Lanson and Bouchet (1995), Lanson *et al.* (1998). This process deals with the illitisation of surface smectite clays with diagenetic phenomena during burial. The smectite to illite transition is defined, according to X-ray diffraction studies (XRD), by the transformation of mixed-layer illite-smectite (smectite rich) to highly ordered minerals (illite rich). The I-S index constitutes a standard measure of diagenetic transformation.

In Laumiere, the marls have been sampled in depth along a dry and oblique drilling reaching the basaltic intrusion *(Fig. 9a, 9b and 9c)* in addition to a sampling at the surface *(Fig. 9d)*. For surface samples, the chemical and water content analysis show that the smectitisation is limited to the clay/basalt vicinity (10 cm). For deep samples, the variation of the chemistry, water content and ion exchange capacity are weak along the drilling. The FTIR spectrometric characterisation of modified clay (using tetramethyl ammonium exchange of smectite components) show a decrease of smectite content

close to the basalt contact. The illite content in the I-S is very high (around 90% of illite) as measured by classical method ($\Delta°2\theta$ in the XRD pattern of ethylene glycol oriented paste). The direct observation of the variation of illite and smectite content in these kind of I-S is difficult and required the development of a new methodology which combines spectroscopic tools such as infrared spectrometry (far infrared domain, FIR) with XRD on oriented air dried samples.

XRD and FIR diagrams are decomposed according to the same mineralogical composition with variable proportions: chlorite, mica, illite-smectite and poorly crystallised illite-smectite (PCI). For DRX experiments, the set of components are peak distance (in Å or $\Delta°2\theta$) and full width at half maximum (FWHM). These components are crystallographic parameters that vary with the illite proportion and particle size distribution. For FIR experiments, components are peak wavenumber and FWHM that reflect the potassium vibration in interlayer. The vibration of the potassium corresponds to its parallel movement with regard to the (a, b) crystallographic plane of the di-trigonal oxygen cavity (Ishii *et al.*, 1967). The energy level of potassium vibration, called mode A, is proportional to consecutive illite layer content (Laperche, 1991; Diaz *et al.*, 2002).

The parameters used for the "illitisation state diagram" are chosen after the exclusion from those that are too much connected to the experimental artefacts or that are not univocal (Kohler *et al.*, *Am. Min.*, in process of publication). The parameters for FIR and XRD are the energy level of potassium vibration and the FWHM of PCI *(Fig. 10a and 10b)*. The produced diagram is an analysis chart that describes the level of illitisation with two structural indexes: the crystallinity and the consecutive illitic layer content of the PCI only *(Fig. 11)*.
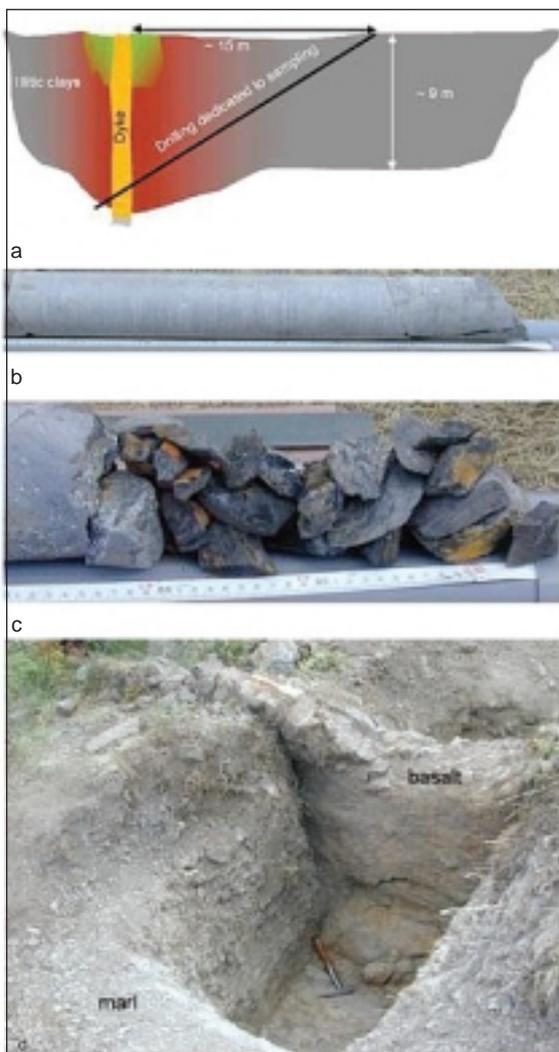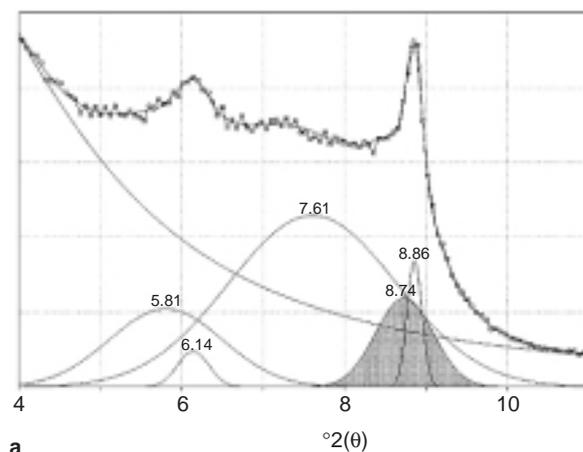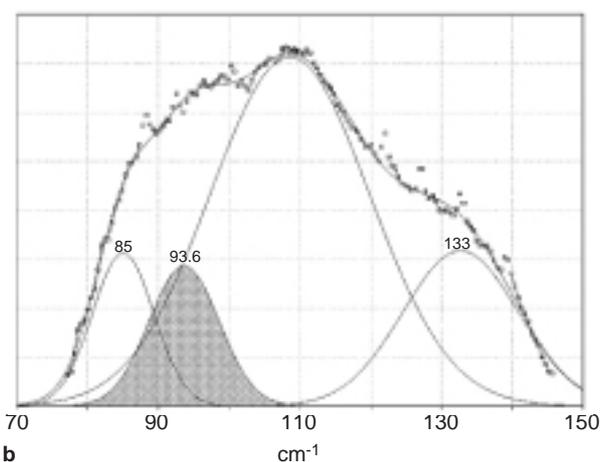
Figure 9

Sampling locations at Laumiere (Aveyron, France).

Figure 10

Decomposition procedure to extract XRD (a) and FIR (b) indexes of PCI (gray) for the contact sample at surface.

The distribution of measurements does not display any clear tendency of a correlation between the "illitisation state" and the distance to basalt contact *(Fig. 12a and 12b)*. Nevertheless, samples at the contact are described in the diagrams by the higher level of illitisation. These results show that thermal impact is the cause of an increase of illite content. This confirms and refines previous study (Bouchet *et al.*, 1993).

This phenomenon has important consequences on the clay materials properties and has an impact to safety of HLRW repository. The smectite formation observed at surface is not connected only to thermal event as shown by its absence in depth. But the smectite is formed in the vicinity of the basalt, not only at contact, and could be the consequence of the feedback of matrix change, by illitisation, on meteorological alteration of basalt. The thermal illitisation is not linearly connected to the distance from the basalt. It could be influenced also by the sedimentary heterogeneities and by the tectonic fractures. These structures could increase the local reactivity by opening the reactive system to the foreign fluids. In these conditions, illite and smectite formations show the impact of textural and mechanical feedback on the physico-chemical reactivity of clay rich materials. When these processes are well developed along homogeneous and complete diagenetic series, the coupled approach presented here could be a useful tool to understand the fine illitisation reaction in order to determine, for example, the precise thermal conditions of illitisation in potential hydrocarbon fields.
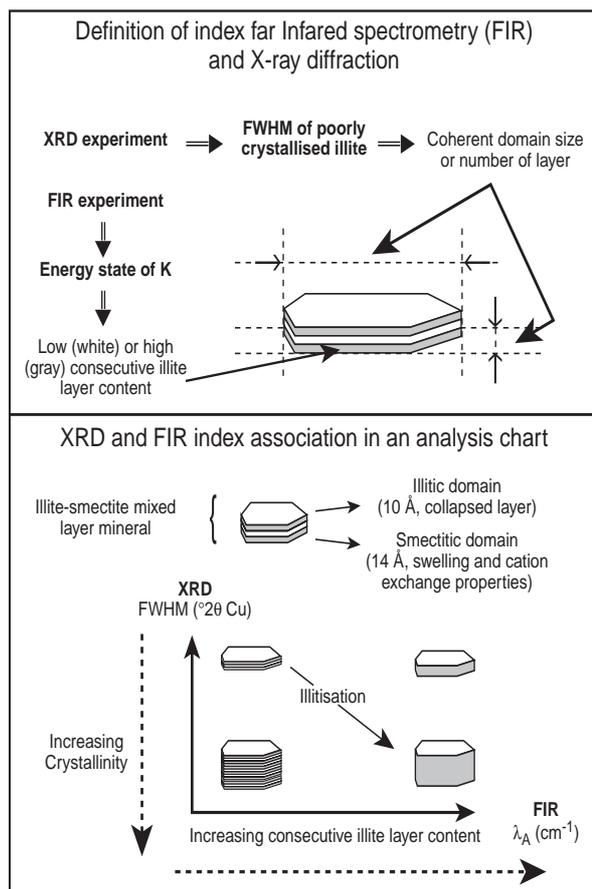
Figure 11

Analysis chart to identify smectite illitisation in illite-rich media.

4 WATER BEHAVIOUR IN CLAY RICH MATERIAL

The chemomechanical reactivity of CRM is strongly influenced by the hydration state and may be mediated by water (free, adsorbed) and by the gel phase present in the pore space. The hydration processes are also intimately linked to the mechanical behaviour of CRM, leading to the swelling pressure in smectites. The water uptake in clay-rich materials essentially differs from a "granular" porous media due to the multiscale distribution of the pore size and its evolution when swelling occurs. The multiscale nature of clays can be characterised using a micro-, a meso-, and a macroscale (Norrish, 1954; Sposito and Prost, 1982; Yong, 1999; Bihannic *et al.*, 2001; Pusch and Yong, 2003).

The **microscopic scale** is the scale of the aluminosilicate layers and the interlamellar space where cation solvation occurs and crystalline swelling (up to d ~ 2 nm) takes place *(Fig. 13)*. Swelling beyond 2 nm occurring for the most common monovalent cations (Na, K) is attributed to osmotic phenomena (according to the IUPAC nomenclature, the interlayer spaces should then be defined as mesopores). At the **mesoscopic scale**, clay particles or tactoids reveal stacks of layers and contain mesopores (2 to 50 nm) inside the particles (*e.g.*, Van Damme, 1998; Bihannic *et al.*, 2001) and in between the particles *(Fig. 14)*. Water movement and swelling is thought to be controlled by the diffuse double layer phenomena associated with the osmotic potential. The **macroscopic scale** is the classical scale of the representative elementary volume (REV) in porous media. It is the scale pertinent to clay aggregates (~ 1 µm) and macropores (> 50 nm) filled with "free" water responding to capillary phenomenon (unsaturated case) or pore pressure (saturated case).
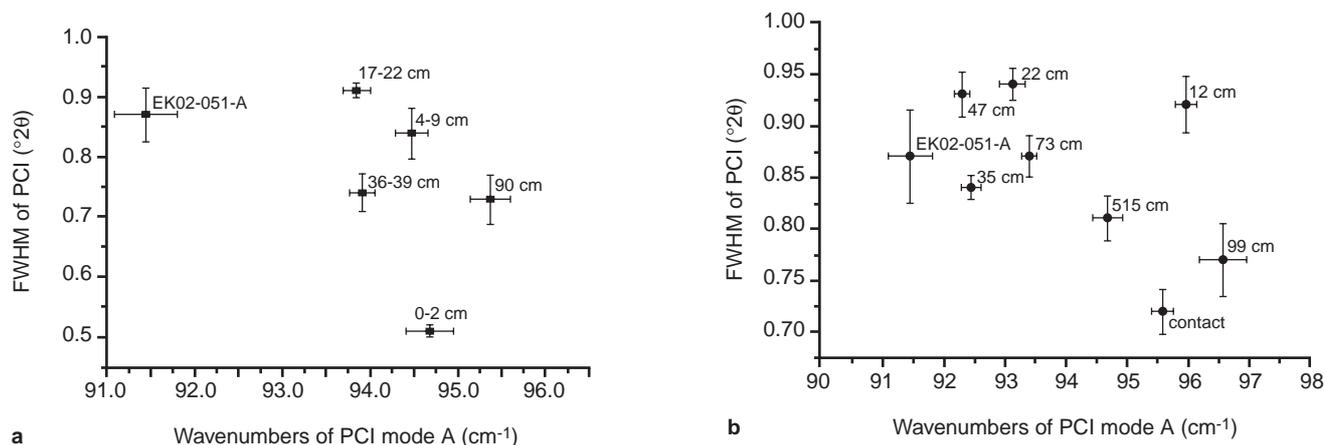

Figure 12

Analysis charts of samples from Laumiere (labelled by distance from contact) and Tournemire (EK02-051-A), (a) surface samples, (b) deep samples.
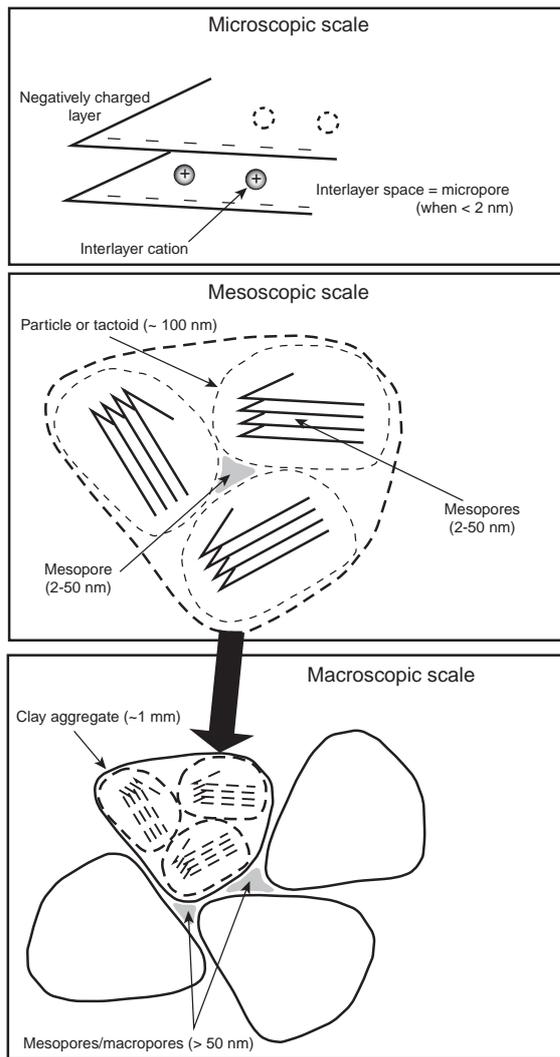
Figure 13
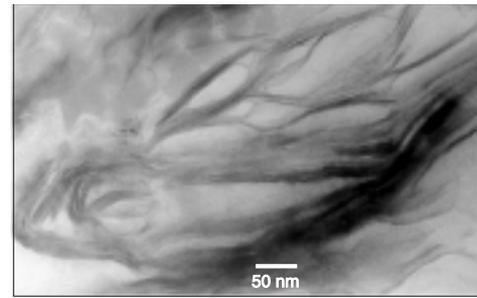
Micro-, meso-, and macroscales in clays.

Figure 14

TEM micrograph of MX 80 bentonite from Wyoming (ultra thin section) showing mesoporosity (2-50 nm). JEOL 2000 FX – CEA Cadarache.
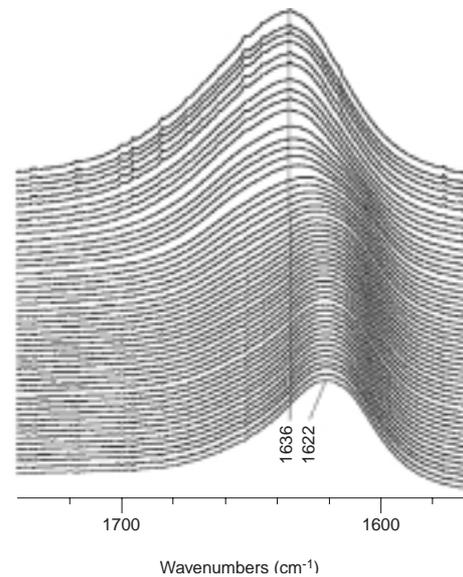

Figure 15

From top to bottom (every 25 s), drying process of Orduartikli smectite film (free water peak at 1636 cm^{-1}, adsorbed water peak at 1622 cm^{-1}).

The origin, sampling, and conditioning of the clay material affects the distribution of the porosity and the mechanical behaviour: crucial parameters include compaction in engineered bentonites and cementation in natural occurring argilite. Upon compaction the macroporosity usually decreases, but the meso- and microporosity are not affected (*e.g.*, Robinet *et al.*, 1996). Macropores are generally present in natural shales due to the existence of secondary mineral particles preserving porosity by resisting compaction, but mesopores usually dominate the porosity volume (Romero *et al.*, 1999; Sammartino *et al.*, 2003; Villar, 1999). In engineered bentonites and natural clay (with high clay content), upon resaturation, the macropores tend to be filled with gel so that almost no "free pore water" is present in the system (Pusch and Yong, 2003).

Associated with the different porosity types are different "states" of water in clays, which will have specific properties with regard to transport. The hydration processes and the rate at which they occur are linked to the structure of clays. In the early stages of water uptake, water moves into the macrospores by capillary suction and through film boundary transport to form at least one layer of water molecules. At this stage water enters the clay particles and the interlayer space through a diffusion-like process driven by matric and osmotic potential gradients at the meso- and microscopic scale (Pusch and Yong, 2003; Yong, 2003). At low water content, intercrystalline swelling occurs first (the interlayer adsorbs up to 3 or 4 molecular layers of water, depending on the interlayer cation), followed by osmotic swelling. Then, additional layers of water build up on the external surface of

the aggregates and water starts moving under capillary forces. For intercrystalline swelling, the hydration at the microscopic level in the aggregates is controlled either by interlayer counterion solvation or by adsorption of water on the clay surface (*e.g.*, Marcial *et al.*, 2002), depending on the hydration energy of the cation (low for Na^+, K^+, and Cs^+; high for Li^+, Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}).

The transformation or the formation of new clay minerals has an influence on location and state of water for the same hydrous conditions in a site. This evolution can be observed directly in the laboratory by FTIR (Johnston *et al.*, 1992) but the identification of the real physical phenomenon is complex. The macroscopic water content can be decomposed into free and bound water states (Madejova *et al.*, 2002). These two states are identified by the vibratory properties linked to water-crystal interactions. The water may be adsorbed either on interlamellar cations or on charged surfaces. An example of an experiment that shows two distinct kinds of water is provided by the observation of smectite drying with the state of water as molecular probe. A wet film of Orduartikli smectite (see Kohler, 2001; and Lantenois, 2003, for characterisation of Orduartikli smectite) deposited on a ZnSe window is dried in the low vapour pressure atmosphere of the analysis cell of the IR spectrometer (0.5 % RH à 25°C). A series of spectra are acquired during the drying of the sample (every 25 s) and compared with a reference spectrum *(Fig. 15)* acquired after 12 h of drying (*e.g.*, equilibrated with the dry atmosphere of the cell). During the drying, intensity variation of two bands of water (bending vibration) could be observed (see Pelletier *et al.*, 1997, for static experiments). The free water vibration wavenumber is higher than that of the bound water vibration. These two kinds of water are components of microscopic to mesoscopic scale domains that depend on clay film texture obtained by sedimentation in aqueous phase. By analogy, we can infer that during the dehydration stage in the repository history, the smectite will lose first free water and then, in a second stage, the adsorbed water. The two kinds of water are connected and there is a potential feedback during desorption of these two kinds of water.

The modelling of hydration of CRM is a challenging task. The methodology to be used for the mathematical model is known but complex (*e.g.* Mathieu-Balster and Sicard, 1999; Revil and Leroy, 2004):

– write balance equations for the system (mass, charge, energy, momentum) and entropy variation for each phase (Gibbs relation);

– express the thermodynamic fluxes and forces and the constitutive and state equations.

One of the major difficulties encountered when developing such models is to use appropriate constitutive equations and the relevant relationships linking the microscopic phenomena to the macroscopic behaviour. Some authors use homogenisation techniques to change scale, others use "mesoscopic" phenomenology to link scales, *e.g.*, the macroscopic mechanical behaviour linked to the microscopic electrochemical phenomena using the DDL theory (Loret *et al.*, 2002; Dormieux *et al.*, 2003). In order to achieve a practical use of such models, a crucial step is to express the equations in terms of measurable macroscopic parameters (*e.g.*, Moyne and Murad, 2002a, 2002b; Leroy and Revil, 2004). A good example is the study of the chemo-mechanical behaviour of the Ponza bentonite and the Bisaccia clay showing the influence of the water chemistry on elastic-plastic behaviour (Di Maio, 1996; Loret *et al.*, 2002).

CONCLUSION

Clay-rich materials have useful properties for deep geological disposal and represent suitable candidates for host-rocks as well as for the engineered barrier system. The expected confinement capacity relies on properties such as low permeability, sorption properties and high ion exchange capacity, as well as swelling abilities. These properties are due to the small size and high tortuosity of the pores as well as the surface charge and very high surface area of specific clay minerals (especially smectites). For performance and safety assessment, it is crucial to ensure the durability of these properties with regard to impact of THMC perturbations on the long-term behaviour.

The clay minerals will also be subjected to perturbations due to the heat release of waste packages in the case of HLRW repository, and liquid water and vapour transfers. These complex phenomena are studied by combining multi-scale and multi-technique characterisations (middle and far infrared Fourier Transform spectrometry, X-ray diffraction, scanning electron microscopy and transmission electron microscopy) on samples coming from laboratory experiments and natural analogues, and by integrating the results through reactive transport modelling.

This global approach represents a useful tool to describe the multi-scale physicochemical reactivity of clay rich material. The method represents a project-like point of view of these materials, combining specialist teams from experimentation, characterisation and modelling. This federative approach is necessary to obtain operational data, in a short time, for multiple applications, from waste management to acid gas sequestration.

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