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CLAY-BASED MATERIALS FOR ENGINEERED BARRIERS : A REVIEW

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I. INTRODUCTION

The potential importance of backfilling and plugging in underground radioactive waste repositories has led differents research institutions around the world (SKB in Sweden, CEA in France, AECL in Canada, etc.) to carry out extensive studies of swelling clay materials for the development of engineered barriers. These materials, which have to be emplaced in underground conditions, should combine a variety of complementary properties from both the hydro-thermo-mechanical and geochemical viewpoints: impermeability, swelling ability in order to fill all void space, heat transfer and retention capacity for the most noxious radionuclides. For years, the scientific community has acknowledged the fact that smectite clays best exhibit these properties and, thus, most of the research effort has been devoted to this type of materials. The aim of such studies is to try and link the microscopic characteristics of the material (mineralogy, geochemical properties, microstructure, etc.) to its macroscopic behaviour (swelling properties, etc...).

II. HISTORICAL PERSPECTIVE

Before reviewing the information acquired on such clay materials, investigated for more than a decade either for reprocessed wastes or for spent fuel, we think interesting to underline the fact that the concept of engineered barriers dates back to the end of the 70's. Indeed, the idea of disposing radioactive wastes in geological formations has a very long history but, until the mid-70's, the concept promoted in several countries was restricted to the waste form (usually glass since reprocessing was a common option at that time), its canister and the host rock (see for instance Petit, [1] for a sociotechnical analysis of this field). In a paper, where the authors were questioning the capability of the geological formation to confine radionuclides, as well as the ability of the geologist to model it, de Marsily et al. [2] insisted on the geochemical properties of the host rock, and in particular its retardation capability, due to a variety of mechanisms (sorption, ion exchange, etc.). They first introduced the idea that such a function could be reinforced by "an artificial one set up around the wastes. It could be possible, therefore, to reinforce the confinement locally by means of a complementary physical barrier". However no particular suggestion was made about the possible constituents of such an artificial geochemical barrier.

Later on, Ringwood [3] suggested that the long-term geological stability of the Synroc constituents (basically titanate minerals) as well as of the Ni_3Fe canister he was promoting (a material analogue to some meteorites) could be best guaranteed in particular geochemical conditions. Indeed, the remarkable corrosion resistance in groundwaters of these compounds has only been observed in well defined geochemical environments and Ringwood's idea was to artificially generate or maintain such favourable conditions in the repository. Crushed serpentine as well as magnesium oxide were proposed as buffer materials to fill the repository cavity. Again, the geochemical function of such materials was stressed. However, Ringwood also noted that, in contact with groundwaters, the magnesium oxide would transform into a hydroxide having swelling capacities and thus able to seal voids.
Simultaneously, a Swedish law of 1977 forbid any new development of the nuclear programme until the nuclear industry could demonstrate that a reliable and definitive solution to the disposal of radioactive wastes could be found. This official statement obliged the nuclear industry, not only to develop a concept and to discuss scientific

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issues, but to actually propose a feasible engineered solution to this socio-technical and political problem. Through the two reports of the company in charge [4, 5], it is quite clear that the Swedes soon realized that circulation of groundwaters would be unavoidable in a granitic formation (practically the only type of host rock available in this country for the purpose of disposing radioactive wastes) and that a priority would be to introduce an efficient hydraulic barrier in their concept. Some scientists then remembered the known high swelling capacities of smectite-based clays, which reflects their ability to absorb great amounts of water, and thus their sealing properties. It was also stressed that such natural materials, which should be geochemically compatible with the granitic host rock, are also well known for their high exchange capacities and their ability to sorb a number of cations, thus presumably acting as a retention barrier for radiotoxic nuclides escaping the waste form. Finally, the addition of certain compounds could improve the limited thermal conductivity of clay-based materials. The necessary optimization of all these functions led the Swedish engineers to transform these natural materials into an actual engineered barrier (by mixing sand to clay, compaction, etc...). Specialists in all countries have then followed the Swedes along this line of research and development.

In this paper, we will review the investigations carried out on such clay-based engineered barriers and, as far as it is possible, we will make an intercomparison between the results obtained in different countries on similar materials. The scope of this paper will be restricted to the initial properties of these engineered materials and, therefore, we will not tackle the important issue of their long-term behaviour. This is essentially due to the fact that an intercomparison was quite difficult amongst the different materials selected due the disparity of experiments carried out. A larger overview of materials properties, on both short and long terms, will be given in Lajudie et al. [6]. In the present paper, we will describe the physical and chemical properties, as well as the influence of additives which may be used to improve the performance of the materials. Because new options are now being considered for the disposal of radioactive wastes (e.g. in France reversibility), such materials are expected to fulfill additional requirements, notably from the point of view of their mechanical properties, thus renewing the R&D programmes. The future developments of these research activities in this field will be outlined.

III. RESULTS AND DISCUSSION

In this paper, we are dealing with five smectite clays selected by five major nuclear countries to best fit the combination of properties (swelling, heat transfer, retention) sought for their particular disposal concept: Avonseal montmorillonite for Canada, MX 80 montmorillonite in the case of Sweden, Montigel montmorillonite for Switzerland, S-2 montmorillonite for Spain and Fo-Ca interstratified kaolinite/beidellite for France.

III.1 - ORIGIN AND COMPOSITION OF SAMPLES

We will give a brief indication on the origin of each clay, its mode of formation, whenever known, its main composition (table I) as well as the marketing company, where appropriate.

Table I: Mineralogical composition of the different clays (in %)

Clay	Fo-Ca [7]	MX 80 [8]	S-2 [9]	Montigel [8]	Avonseal [10]
Montmorillonite		75	84	66	79
Interstratified kaolinite/beidellite	80 ± 2				
Kaolinite	4 ± 2	<1			
Illite			4.6	2	9.5
Mica		<1		12 to 15	
Quartz	6 ± 1	15.2	3.6	8.3	5
Cristobalite			1.7		
Goethite	6 ± 1				
Hematite	0.25				
Feldspath		5 to 8	6.1	2 to 4	3
Pyrite		0.3			
Calcite	1.4 ± 0.2	1.4			1.5
Gypsum	0.4				2
Others		2		2 to 3	
Organic matter	0.1	0.4	0.1	0.03	0.3

Fo-Ca: This is a sedimentary clay from the Paris Basin, extracted in a site near to the Vexin region. The major component of the clay fraction is an interstratified clay made up of 50% calcium beidellite and 50% kaolinite [11]. This clay is not commercialized.

MX 80: This well known Wyoming clay is formed by the decomposition of volcanic rocks. It is a sodium montmorillonite purchased by American Colloids [8].

S-2: This is a clay from the Almera region, formed by the hydrothermal decomposition of volcanic rocks. The major component is a calcium montmorillonite with plagioclase, black mica and quartz. It also contains some fragments of volcanic rock and silica [9]. This clay is not commercialized.

Montigel: This is a Bavarian clay essentially made up of a calcium montmorillonite, marketed by the company Sud Chemie [8].

Avonseal: This upper Cretaceous sedimentary clay, from Saskatchewan, Canada, is probably derived from a volcanic ash like MX 80. It is a naturally occurring sodium montmorillonite, as shown by the predominance of exchangeable ions (table I). This clay is commercially available from Avonlea Mineral Industries [10].

The selected clays are swelling clays of the smectite type and they all, as can be seen in table I, have montmorillonite as their main component, with the exception of Fo-Ca, which is made up of interstratified beidellite and kaolinite. Non-swelling clays are also present, in particular illite in S-2 and Avonseal, and kaolinite in Fo-Ca and Montigel. Fo-Ca is the only clay to contain iron in the goethite and hematite forms. Montigel is the only one to contain mica. All clays, except Fo-Ca, contain varying quantities of quartz and feldspar.

III.2 - SODIUM OR CALCIUM CONTENT OF CLAYS

We are in presence of two types of swelling clays, according to the nature of the major interfoliar cation: sodium or calcium (table II). When clay hydration occurs, Na^+ cations are surrounded by more molecules of water than Ca^{2+} ones, and thus Na^+ cation have a larger radius. Then, the liquid limit w_L (which it is the water content adsorbed by the clay to reach the liquid state) and the plastic limit w_P (water content adsorbed by the clay to form a paste) are higher for sodium clays. This is clearly showed on the figure 1: a good correlation exists between the geomechanical parameter (the liquid limit) and the chemical one (the Na/Ca ratio).

Table II : Main physico-chemical characteristics of the five selected clays

Clay Origin		Fo-Ca Vexin (France)	MX 80 Wyoming (USA)	S-2 Almeria (Spain)	Montigel Bavaria (Germany)	Avonseal Saskatchewan (Canada)
< 2 µm fraction	(%)	90	80 to 90	70 to 80	70 to 77	65
Ambiant water content	(%)	10 to 12	8 to 14	10 to 13	7 to 11	6 to 9
Specific weight	(g/cm³)	2.67	2.70	2.78	2.85	2.75
Specific area	(m²/g)	430	562	569	493	631
Liquid limit *wL*	(%)	112	400	213	140	257
Plastic limit *wP*	(%)	50	70		50	49
CEC	(meq/100g)	71	79	88	62	82
Exchangeable cations (meq/100g)	Ca^{2+}	73.1	30.1	42.0	37.6	39.5
	Mg^{2+}	6.5	15.6	26.0	22.4	7.0
	Na^+	3.6	56.0	18.0	1.8	48.5
	K^+	0.8	2.3	2.0	0.2	0.7
Na^+/Ca^{2+} ratio		0.05	1.86	0.43	0.05	1.18

The MX 80 clay contains the highest sodium concentration, at 56.0 meq of exchangeable Na^+ per 100g of clay, resulting in a very high liquid limit W_L of 400% [12, 13]). Avonseal also has a very high exchangeable sodium ion content corresponding to 46.5 meq/100 g for 39.5 meq/100 g of Ca^{2+} only. The average of the various liquid limit values W_L is 257% [10, 14].

Almost all the other clays have a high calcium content, S-2 has 42 meq/100g of Ca with a fairly high liquid limit of 213%, owing to the presence of fewer exchangeable sodium ions (18 meq/100 g) than calcium ions, a value which is still high [15]. The two clays with little or no Na and a large quantity of exchangeable Ca ions (37.6 in the case of Montigel, and 73.1 meq/100 g in the case of Fo-Ca) also have the lowest liquid limits: 130% and 112% for Montigel and Fo-Ca respectively [7, 8].

III.3 - THERMO-HYDRO-MECHANICAL PROPERTIES

Thermo-hydro-mechanical properties are extremely dependent on the density of the materials. In the case of the different clays, measurements have been performed at different density ranges, which do not always coincide. So, in order to make a comparison between the various clays, the dry specific gravity of 1.75 was adopted, a value for which the greatest number of results were available. An additional reason

for choosing this value is that it should approximately correspond to the density of the actual engineered barrier (table III).

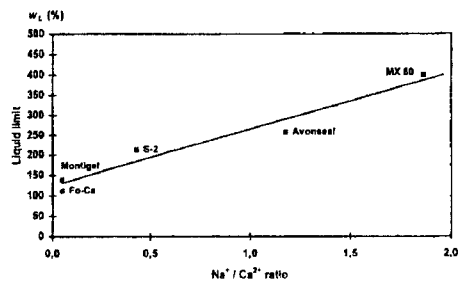

Figure I : Correlation between liquid limit and Na^+ / Ca^{2+} ratio

Table III : Thermo-hydro-mechanical properties of the five clays for the reference dry density of 1.75

Clay		Fo-Ca	MX 80	S-2	Montigel	Avonseal
Swelling pressure	(MPa)	13 [16]	13 [17]	11 [15]	15 [18]	16 [19]
Hydraulic conductivity	(m/s)	5.10-14 [7]	2.10-14 [20]	1.10-13 [15]	< 2.10-13 [21]	2.10-13 [22]
Thermal conductivity	(W.m-1.K-1)	0.95 [23]	0.93 [23]	0.89 [9]	0.66 [24]	

III.3.1 - Swelling pressure

Smectites swell in the presence of water by a process of interfoliar cation hydration. When clays are maintained within a constant volume, for instance in oedometric cells, pressure is brought to bear on cell walls. In this type of cell, there is no opportunity for radial deformation and the state of the stress can be determined using a single factor: the pressure on the cell piston named swelling pressure.

The pressures obtained for the materials are fairly similar and depend mainly on the density of the clay. In general, the swelling pressure drops by a factor 30 to 40 when the dry density varies between 2 and 1.4 (figure II). So, in the case of the reference specific gravity, 1.75, only 5 MPa separate the clays which swell the most (Avonseal and Montigel), from the clays which swell the least (Fo-Ca, MX 80 and S2) ; (figure II and table III). As part of a study into swelling within a given volume, the nature of the exchangeable cation which prevails in the clays (sodium or calcium) is not indicative of the material's ability to swell. Their high density must be considered as minimising the porous spaces; under these conditions, any increase in the volume of the clay layer fills the space available in the pores and brings about a sudden increase in the pressure exerted by the material. On the other hand, in the case of swelling in an open space, the calcium or sodium content of the clay plays a significant role. Sodium clays increase much more in terms of volume that calcium clays, since the hydrated sodium montmorillonite base clay layer are thicker than the hydrated calcium montmorillonite layer.

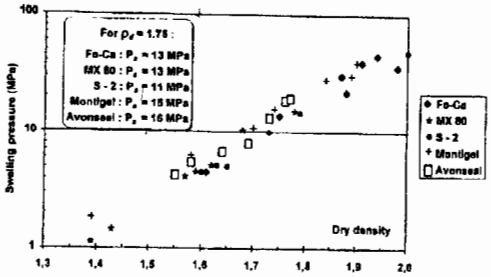

Figure II : Swelling pressure of the different clays

III.3.2 - Hydraulic conductivity

There are two main methods of measuring the hydraulic conductivity of clay samples: the first is the oedometric method, the sample is pressed in a cell and the water extracted is mesured in fonction of time, the second uses a permeameter, which is a special cell for measuring water transfer through the sample for a given injection pressure.

At specific gravities greater than 1.75, the hydraulic conductivities are always very low ($\leq 2 \times 10^{-13}$ m/s) (table III). The Wyoming MX 80 clay has the lowest hydraulic conductivity, followed by Montigel, the other clays all having similar values (figure III).

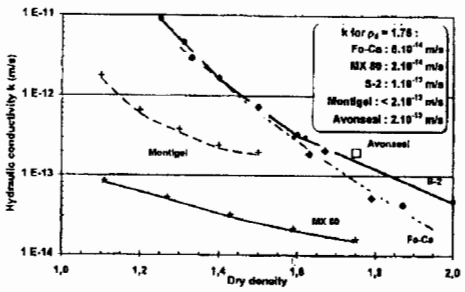

Figure III : Hydraulic conductivity of the different clays versus dry density

The microstructure of the materials is an important factor in the hydraulic conductivity of clays: pore diameter, tortuousness etc. These data should shed light on the significantly different behaviours of the five clays selected. It can be seen that

the compacting method used to increase the density of the clay has a significant effect on the hydraulic conductivity measured. Compacting along a single axis induces greater orientation of the clay layer than isostatic compacting. Therefore, if during measurement the flow of water is perpendicular to the layer (compacting along a single axis), the hydraulic conductivity is lower than for a sample which has been compacted isostatically, as it is well shown by figure IV in the case of Fo-Ca clay.

III.3.3 - Thermal conductivity

The thermal conductivity of a given clay is primarily a function of its density as well as the type and quantities of non argilaceous minerals it contains [23]. The thermal conductivities of the different clays are fairly similar, but figure V shows a few notable differences.

Fo-Ca has the highest values (0.95 W/m.K for ρ_d = 1.75, table III), which can be explained by the presence of both the goethite and hematite forms of iron which are minerals of high density. The Wyoming MX 80 montmorillonite also has a good thermal conductivity (0.93 W/m.K for ρ_d = 1.75), owing to the presence of a larger quantity of quartz (15.2%) than other materials (table I). We can observe that the thermal conductivities obtained for the different clays are much lower than those of the host environment (e.g. granite: λ = 3.5 W/m.K). So, research organizations are currently carrying out studies to identify, substances which, when added to these clays, would improve the transfer of heat through the engineered barrier.

Quartz is the simplest material which can be added to clays to increase their thermal conductivity. The possible deleterious effects of the addition of quartz have been studied [15]. Indeed, when the quartz content is not in excess of 30 - 40%, there is no real effect on the clay's ability to swell or conduct water. In the case of S-2 montmorillonite, adding quartz does not increase the hydraulic conductivity which remains below 10^{-12} m/s (for densities < 1.45 g/cm^3), or reduce the swelling pressure which remains above 10 MPa (for a density of 1.7 g/cm^3). When there is a low quartz content, individual grains are not in contact with each other. They are distributed within the clay medium without affecting the macroporosity. Conversely, when quartz content is higher, the gaps between the large quartz grains are no longer filled with clay particles, thereby forming prefential paths through the grain clusters. This phenomenon is also observed in the case of the other clays [19].

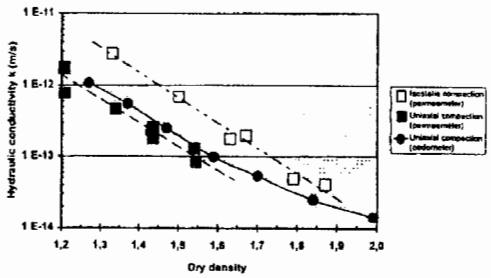

Figure IV : Influence of the compacting method upon hydraulic conductivity
(Example of the Fo-Ca clay)

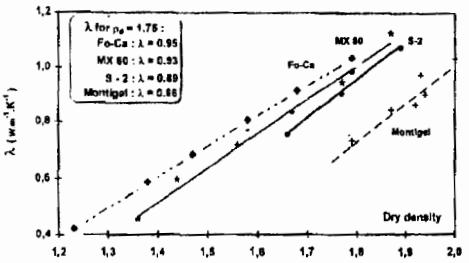

Figure V : Thermal conductivity of the different clays (at their ambiant water content)

III.4 CHEMICAL PROPERTIES : FROM PASSIVE TO ACTIVE GEOCHEMICAL BARRIERS

Retardation capabilities of clay-based engineered barriers are a consequence of the structural and textural properties of clay minerals. Nevertheless, they have seldom been considered as a major feature of clay-based EB compared to hydraulic and mechanical properties. This can be illustrated by the approach carried out in many integrated studies on clay bakfill materials ; during the eighties, the diffusion properties of radionuclides have been experimented in diffusion cells, in which bentonite was compacted at various degrees [26, 27, 28]). Such experiments were generally associated with batch sorption experiments, in order to determine independently the retardation coefficients, which can also be derived from diffusion coefficients. Many problems and discrepancies arose, owing to (1) the complexity of sorption processes and their dependence upon the chemistry of interstitial fluids ; (2) an uncomplete evaluation of physical diffusion processes and parthways in compacted bentonite, especially for in situ conditions. In addition, commercial bentonites are complex mixtures of natural minerals, the individual sorption properties of which must be evaluated.

Consequently, diffusion experiments in compacted bentonite delivered consistent and unambuguously interpretable results only for non-interacting radionuclides (iodide, pertechnetate, etc...). To summarize, the prediction of long term retardation properties of clay based EB is rather difficult because :

- the response of each mineral fraction to chemical changes of interstitial fluids must be evaluated,
- the individual sorption properties (ion exchange and anion exclusion mostly) of major and trace mineral constituents must be experimented and properly modeled,
- the additivity of sorption properties of each constituent must be checked, in reference to the tecture of highly compacted bentonite,
- the long term mineralogical, textural and structural transformation of the mineral phases repository conditions must be evaluated.

As many countries, we have been characterizing global diffusion/retention properties of our EB reference clay [27]), but we are now in a process in which the following steps are progressively evaluated :

- individual sorption properties of mineral constituents, precise experimentation and intrinsic modeling of ion exchange phenomena [29],
- additivity of ion exchange properties in complex systems, modeling of multiphase sorption properties, validation on natural materials.
- controlled diffusion experiments in representative physical and chemical conditions (fluid composition, Eh and pH),
- in situ tests, which will be achieved in the future French underground laboratory (1998-2000).

Together with such an integrated approach, we are developing new concepts in which geochemical processes are active, and progressively contribute to a better confinement of radionuclides, as early suggested [25]. Among such processes are : chemical buffers, chemical getters, chemical getters which would be activated after water saturation, clogging or sealing evolutive mineral assemblages. The stability and long term properties of such chemical barriers should be envisaged with a reference to natural geological systems (natural analogues, and a general concept of buffering : coming back to an initial equilibrium after a perturbation.

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EFFECTS OF SMECTITE ILLITIZATION ON TRANSPORT OF ACTINIDES THROUGH ENGINEERED BARRIERS OF HLW REPOSITORIES

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ABSTRACT

Effect of smectite illitization on mass release rate from the bentonite-filled buffer of the engineered barriers is analyzed based on experimental results of sorption of americium and neptunium onto illite-smectite mixtures, and on mathematical models for smectite illitization by K^+ diffusion, water flow through the engineered barriers, waste glass dissolution, and transport of americium and neptunium including solubility sharing with two major americium isotopes and moving boundary effect of the neptunium precipitation region. Numerical results for mass release rates of americium and neptunium as well as time-dependent pore velocity and glass dissolution rate are shown. Illitization effect is negligible with parameter values assumed here.

INTRODUCTION

This paper presents effects of smectite illitization on transport of americium and neptunium through the bentonite-filled buffer region of engineered barriers of a high-level radioactive waste repository.

Due to elevated temperature and presence of potassium ion in groundwater, smectite, the major mineral in the buffer, changes into illite. As the illite content in the buffer increases, hydraulic conductivity of the buffer will increase and sorption capacity of the buffer will decrease. Increase in hydraulic conductivity enhances water flow in the engineered barriers, resulting in faster waste glass dissolution and faster radionuclide transport. Furthermore, gradual decrease in sorption distribution coefficients with increasing illite content may result in increase in mass release rates of radionuclides at the outer boundary of the engineered barriers.

Experimentally obtaining the sorption distribution coefficients of americium and neptunium for various illite-smectite mixtures, we propose the quantitative relation between sorption distribution coefficients and the illite content in the buffer. With the experimental result and the reported reaction rate constant for smectite illitization [1], sorption distribution coefficients can be written as a function of time.

With time-dependent hydraulic conductivity and sorption distribution coefficients, mathematical models are established for (1) groundwater flow in the engineered barriers, (2) waste glass dissolution, and (3) mass transport through the buffer. Analytical solutions are obtained for the pore velocity of groundwater in the buffer and the glass dissolution rate as a function of the illite content, and so of time. Mass release rates of Am and Np at the outer boundary of the buffer are obtained numerically, and effects of smectite illitization on the performance of the engineered barriers are shown quantitatively.

SMECTITE ILLITIZATION

Still, further studies are necessary for quantitative formulae of density, porosity, permeability and sorption distribution coefficients as a function of illite content. Here we utilize the results by Altaner [1]. He estimated values of a potassium diffusion coefficient, smectite illitization reaction rate constant, and a Darcy velocity in a bentonite layer by interpreting zoned K-bentonite with illite-rich contacts and smectite-rich interiors as products of potassium metasomatism. He established a mathematical model of K^+ transport, assuming the smectite illitization as $K^+ + X$-Smectite $\rightarrow$ I/S + Quartz + X^+, where X^+ is an exchangeable cation such as Na^+ or Ca^{2+}, I/S mixed-layer illite/smectite. He reported that potassium diffusion coefficient is in the order of 10^{-7} cm^2/sec and that the reaction rate constant varies from 10^{-15} sec^{-1}(50°C) to 10^{-10} sec^{-1} (150°C).

The mathematical model for potassium transport and smectite illitization is given in the reference [1] and cited here: