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**CEMENT/CLAY INTERACTIONS – A REVIEW:
EXPERIMENTS, NATURAL ANALOGUES, AND MODELING.**

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Abstract

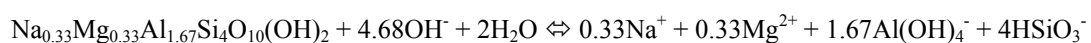
The concept of storing radioactive waste in geological formations calls for large quantities of concrete that will be in contact with the clay material of the engineered barriers as well as with the geological formation. France, Switzerland and Belgium are studying the option of clayey geological formations. The clay and cement media have very contrasted chemistries that will interact and lead to a degradation of both types of material. The purpose of this review is to establish an exhaustive list of laboratory experiments so as to identify the reaction sequences in the evolution of both the clay minerals and accessory minerals during their alteration in an alkaline environment. We review the data on clay dissolution kinetics in this environment, and include an invaluable study of natural analogues that allow one to correlate the phenomena in time. The available data and experiments make it possible to construct predictive numerical models. However, as the quality of the data is inhomogeneous, we recommend a continuation of the thermodynamic and kinetic data acquisition. It is obvious that the numerical modeling of the alkaline disturbance will be more relevant if it can combine the advantages of the different detailed models: mineralogical completeness, combined modeling of the clay and cement media, evolution of the porosity, consideration of the pCO_2 and all the surface reactions.

Keywords : Cement, Clay, Alkaline perturbation, Experiments, Natural analogues, Modeling.

1. Introduction

It is likely, for the deep storage of radioactive waste, that significant use will be made of hydraulic binders for concrete, used as support material for the access galleries and certain storage cells, as well as containment material for low to moderately active wastes. These cement materials will be in contact with both the geological clay formation and the bentonite barriers. Due to their very aggressive nature, they will chemically disturb both the clay minerals and accessory minerals of the clay barriers (quartz, calcite, etc.). The concrete will begin to evolve as soon as it is saturated with pore water from the geological formation whose initial pH is close to neutral. This saturation will occur after the storage cells have been sealed. If commercial materials are used, the concrete degradation will initially generate a high-pH water (pH >13) rich in K, Na, Ca ions. This first period will be followed by a period in which the pH is dominated by equilibrium with portlandite, Ca(OH)₂, (pH = 12.4), and finally by an equilibrium with the CSH-type minerals (pH ≥10) (Berner, 1992; Taylor, 1997). This sequence of concrete-degradation states can be modified by using special "low pH"-type concretes that would lessen the destabilizing effects where the clays are concerned (Glasser, 1996).

The clay barrier's geochemistry, mineralogy and texture will be modified near the concrete/clay interface because concrete degradation generates a diffusive alkaline plume. Takase (2004) suggests the following rough calculation to initially determine the dimension of the montmorillonite/concrete interaction. If we take the following dissolution reaction for montmorillonite in an alkaline medium:



the dissolution of one mole of montmorillonite consumes 4.68 moles of OH⁻, 1 m³ of concrete (OPC + unreactive aggregate) produces 8000 moles of OH⁻, and one finds 1500 moles of montmorillonite in 1 m³ of barrier (Kunigel V1 70% + sand 30%; dry density 1.6 g/cm³); taking a molar volume of 220 cm³/mol for this montmorillonite therefore gives 4500 mol/m³ in a mineralogically pure barrier with no porosity. These figures show that approximately 1 m³ of montmorillonite is required to buffer 1 m³ of concrete. In fact, things are much more complex because the dissolution of the barrier's accessory phases and the precipitation of secondary phases will also modify the pH. For example, the precipitation of tobermorite consumes 4 moles of OH⁻ per mole precipitated, whilst the precipitation of analcime liberates 2 moles of OH⁻ per mole precipitated. Finally, carbonation of the concrete is a well-known phenomenon that plays an essential buffer role with respect to the alkaline disturbance. In sedimentary formations the partial pressure of CO₂ (pCO₂) can be more than 10 to 100

times greater than atmospheric pCO_2 at 25 °C (Coudrain-Ribbstein *et al.*, 1998; Gaucher *et al.*, 2005). We are therefore dealing with a complex and evolutionary system whose initial state we need to be know in detail and whose reaction pathways, taking into account the pH gradients and elemental concentrations, lead to a varied mineralogy.

The scientific community has used several tools to tackle this problem:

- laboratory experiments, to understand the reaction pathways and acquire thermodynamic and kinetic constants;
- characterization of artificial and natural analogues of the cement/rock interaction to describe the phenomena in temporal and spatial terms;
- numerical modeling of the alkaline disturbance to model the experiments and determine a predictive approach.

Many articles have been published on this subject, and it is now time to compile a working synthesis that can be used to analyse the performance of future radioactive waste storage. We start by discussing the experiments dealing with alkaline alteration of the clays used for the barriers, as well of their accessory minerals, and follow this with a summary of the experiments that have provided kinetic constants for the dissolution of montmorillonite. We then describe the work on natural analogues in Jordan where alkaline fluids have been circulating within limestone and marly limestone for some 100,000 years. Together, the experiments and the observations of natural analogues have enabled us to draw up a list of reaction pathways involving mineral evolution during the interaction between concrete and engineered clay barriers. In the last part, we discuss the numerical modeling aimed at assessing the importance of the clay-barrier degradation in time and space, detailing the uncertainties involved in this type of calculation.

2. Minerals and reaction pathways involved in the alkaline disturbance

The clay barriers will be made up mainly of smectite-type swelling clays. As these clays are natural materials, they will include accessory minerals that are both clays (illite(s), kaolinite, chlorite(s)) and non-clays (quartz, cristobalite, feldspar(s), mica(s), carbonate(s), sulfate(s), sulfide(s)). These minerals will have different stability under alkaline conditions and answer to a varied range of dissolution kinetics. The ions liberated by the

dissolutions will in part be "reused" in the formation of new, more stable, mineral phases. The clays with the large reactive surfaces will also be subject to sorption reactions that will modify the chemistry of the clay pore water. We can thus expect the following reactions:

- **modification of the adsorbed cation populations.** The clay, which may initially be sodic, becomes more potassic and calcic given the greater affinity of these cations for clay and the presence of high K and Ca concentrations in the alkaline fluid. This evolution depends on Na/K and Na/Ca ratios in the alkaline fluid in function of the cement type. The precipitation of low-solubility magnesian phases causes desorption of the Mg fixed on the clays through the law of mass action. It should be noted that the clay's silanol and aluminol edge functional groups will ionize in an alkaline medium and may be involved in the adsorption reactions (Gaucher *et al.*, 2001; de Windt *et al.*, 2004);
- **a dissolution of the clays** (smectites, illites, mixed layer clays, kaolinite). These clays disappear completely next to the cement/clay interface. This dissolution has a significant buffer effect limiting the pH rise within the barrier;
- **a dissolution of the accessory minerals** (quartz, cristobalite, amorphous glass, feldspars, plagioclases, micas, dolomite). The accessory minerals should not be disregarded because they can have an important buffer role with respect to the pH. Their dissolution liberates elements that favour the precipitation of certain phases (zeolites, CSH, CSAH);
- **an important role of the pCO_2** in establishing the chemical conditions. This parameter can be fixed internally by an equilibrium with the mineralogy or externally by a diffusive flow from the geological formation. It is essential that this factor is taken into consideration when assessing the development of the high-pH zone, because $CO_{2(g)}$ is an acid gas. It should be noted that the pCO_2 of sedimentary rocks is generally high ($\log pCO_2 > -2$ bar) and that it exceeds atmospheric pCO_2 by two orders of magnitude (Coudrain-Ribstein *et al.*, 1998);
- **a distribution of the neogenic minerals** (cement phases, zeolites, carbonates, clays, silicates) as a function of distance from the concrete/bentonite interface and consequently, affects the pH gradient.

3. Review of the experiments on mineral alteration in an alkaline medium

Table 1 lists the published experiments relating to the alkaline alteration of minerals present in engineered barriers. The synthesis of these observations on the mineralogical transformations has allowed us to formulate the following conclusions.

Alteration of the montmorillonites generally begins with a modification of their adsorbed cation population (Ramirez *et al.*, 2002, 2005), and then continues with a beidellitization or an illitization (Mosser-Ruck and Cathelineau, 2004; Bouchet *et al.*, 2004; Karnland, 2004; Bauer and Berger, 1998). The trend toward one or the other of the two reaction pathways depends mainly on the activity of K within the system. One notes a decrease in Cation Exchange Capacity (CEC) with illitization (Eberl *et al.*, 1993). This is the only case in which the CEC is lowered: precipitation of beidellite, zeolites and CSH tends to result in a strong CEC increase (Ramirez *et al.*, 2002, 2005; Bouchet *et al.*, 2004; Karnland, 2004).

The next stage in the alteration of the smectites is generally the formation of zeolites, the most common being phillipsite and analcime (de la Villa *et al.*, 2001; Ramirez *et al.*, 2002, 2005; Bouchet *et al.*, 2004; Cuevas, 2004; Bauer and Berger, 1998; Nakayama *et al.*, 2004; Chermak, 1993). Analcime requires higher Na levels than phillipsite in order to precipitate. One also notes the formation of variably well crystallized CSH and CASH (Ramirez *et al.*, 2002, 2005; Cuevas, 2004; Bouchet *et al.*, 2004; Bérubé *et al.*, 1990; Braney *et al.*, 1993). Dissolution of the quartz by the cement waters enables the precipitation of CSH minerals such as tobermorite, hillebrandite, foshagite (Bérubé *et al.*, 1990; Savage *et al.*, 1992; Bateman *et al.*, 1999), while dissolution of the Al-bearing micas and feldspars enables precipitation of CASH-phases as hydrogrossular in addition to CSH (Bérubé *et al.*, 1990; Savage *et al.*, 1992; Bateman *et al.*, 1999; Hodgkinson and Hughes, 1999). The Ca will thus be trapped by three phase types, i.e. CSH, CASH, CAH. Where magnesium is concerned, one notes an absence of brucite in most of the experiments. While the Mg-chlorites appear to be stable under alkaline conditions, they do contain brucite interlayers (Bérubé *et al.*, 1990). In the presence of Si and Al, therefore, the Mg-chlorites are phases of the alkaline systems. Saponite or hydrotalcite can also trap the Mg (Cuevas, 2004).

Finally, of note is the solubilization of organic matter in the high-pH clay systems. In the Callovian-Oxfordian argillite, for example, organic matter can form a weak acid buffer of the order of 0.1 mol/kg for the water-soluble organic acids (Brevet *et al.*, 2005). In addition, Claret *et al.* (2002) have shown that organic matter can preserve clays from dissolution.

4. Dissolution kinetics of montmorillonite in an alkaline medium

Among the experiments dealing with the dissolution of montmorillonite in an alkaline medium, some have endeavored to determine the kinetic laws; Bauer and Berger (1998), Cama *et al.* (2000), Huertas *et al.* (2001), Huertas *et al.* (2004), Yamagushi *et al.* (2004), Madé and Michaux (2005) and Tsutsui *et al.* (2005). Temperature and pH are two factors that accelerate the dissolution of montmorillonite. Figure 1 interprets the evolution the dissolution rates as a function of pH based on the results of Huertas *et al.* (2004) (dashes). These authors identified a first acceleration inflection at around pH 11 and a second acceleration inflection with a very steep slope at around pH 13.0-13.4. Madé and Michaux (2005) also find an increase of 2 orders of magnitude in the dissolution rate of the FoCa clay (interstratified kaolinite/smectite) between pH 7 and pH 12.2. This interpretation of a strong increase in the dissolution rate of the smectites with the most alkaline pH (>13) is not indicated by the earlier work of Bauer and Berger (1998) who found a fairly gentle evolution slope with the highest pH. However, the values ($\log \text{molSi}/\text{m}^2/\text{s}$) given by Bauer and Berger (1998) between pH 13 and 14 were already very high, being close to -11 at 35°C and close to -10 at 80°C . Also their beidellite smectite (Ibecco) has lower dissolution rates than Wyoming montmorillonite.

Cama *et al.* (2000) shows how difficult it is to obtain kinetic constants. For a single pH of 8.8 at 80°C , their values ($\log \text{molSi}/\text{m}^2/\text{s}$) range between -11 and -14 (Figure 1). The Si content is a dissolution inhibitor. As one approaches equilibrium with smectite, the dissolution rate reaches its lowest values. This is an important result for the study of clay barriers where, due to the very low porosity, the water/clay ratio favours rapid equilibration. The work of Yamagushi *et al.* (2004) using compacted clays is probably the closest to actual barrier conditions in its approach. These authors also noted that their dissolution rates are lower than those of Bauer and Berger (1998), who worked with high solution/solid ratios. Finally, Tsutsui *et al.* (2005) shows that one must not use the total specific surface (BET) of the clays when calculating dissolution rates in an alkaline medium, but only the surfaces of the sheet edges at which preferential clay dissolution takes place. A quantification of these surfaces has been done by Bickmore *et al.* (1999, 2001) for kaolinite and hectorite, and by Tournassat *et al.* (2003) for montmorillonite. These new results should make it possible to re-evaluate the previously obtained dissolution rates in terms of the reactive area.

In conclusion, existing kinetic studies show the difficulty in obtaining dissolution rates; values scatter. It is clear that temperature and pH increase the dissolution rate. Conversely, it is necessary to undertake a study similar to that of Cama *et al.* (2000) to determine the effect of the silica content on the dissolution rate between pH 11 and 13.5. The use of kinetic constants for the smectites in numerical models seems to us to be premature, or at least

very imprecise, in the absence of such data. Most authors who have undertaken kinetic modeling are well aware of the difficulty of evaluating kinetics (Savage *et al.*, 2002; Vieillard *et al.*, 2004).

5. Underground laboratory experiments and natural analogues of the alkaline disturbance

Underground laboratory experiments give access to the full-scale complexity of the natural system and usefully complement off-site experiments, even though the interpretation is at times more difficult. The study of natural analogues gives access to very long interaction times, which is invaluable for evaluation and understanding the durability of the materials.

- Read *et al.* (2001) report experiments made at the Mol laboratory (Belgium). Cylinders of different concretes (CPA, CPA + fly ash, aluminous cement, etc.) were placed in the Boom Clay (smectite, illite, illite/smectite, chlorite, quartz, calcite, pyrite, feldspar, organic matter) at 85 °C for 12 to 18 months. Overcoring enabled the concrete/clay interface to be sampled and characterized. The results show a zoning in element distribution; the clay alteration zone, 100 to 250 µm thick, is impoverished in Al, Si, Mg and enriched in Ca with respect to the unaltered clay. On the other side of the interface, the concrete alteration zone shows a reverse trend with a loss of Ca and an enrichment in Mg, S, Al, Si with respect to the unaltered concrete. The contact between the two media is marked by a Mg-Al-Si-rich zone (10 µm) containing a weakly crystalline gel whose composition could correspond to hydrotalcite and sepiolite.
- The study by Tinseau *et al.* (2005) gives us access to the results of 125 years of interaction between tunnel masonry and the Tournemire argillite (France). The interaction has taken place in both the water-saturated and -unsaturated zones. The saturated system is clearly the more reactive due to the constant water supply. The system has remained open to the atmosphere throughout the entire period and is oxidizing. The major interaction has been pyrite oxidation with a precipitation of iron oxides. However, pyrite is a minor phase in this system. Carbonate (calcite and dolomite) precipitation is noted at the interface, the waters of the adjacent formation being in equilibrium with these two phases. Quartz and kaolinite have been dissolved and the Fe-chlorites oxidized. Variations in the proportions of illite and illite/smectite are seen up to 17 cm from the interface. The saturated zone also reveals a precipitation of zeolites and calcium sulfates at the interface, plus a recrystallization of K-feldspars. An interesting aspect has arisen from the experimental study of alkaline alteration in the Tournemire argillites carried out at the same time by Devol-Brown *et al.*

(2005). These authors found the same overall mineralogical evolution during the accelerated tests they undertook in the laboratory.

- Hodgkinson and Hughes (1999) studied the Roman mortar of Hadrian's Wall dating from 1800 years ago. They found cement paste in different states of preservation. The initial binder was an amorphous CASH gel sometimes exhibiting a fibrous texture. The gel appears to have evolved little at low temperature, and in places has been preserved from carbonatation. The authors emphasize the role of CO₂ gas and carbonate waters on the evolution of the concretes. Calcite precipitation is very present in Hadrian's Wall. Where in contact with flint, the CASH product is Si rich; the paste/flint contact is diffuse and its porosity has been filled. The Si-rich halos are more resistant to carbonatation than the cement paste. Where in contact with dolerite (feldspar, pyroxene, olivine, quartz), the paste has provided CASH and a C₄AH_n. C₄AH_n is known to be metastable with respect to hydrogarnet and in fact converts slowly to hydrogarnet during cement curing (Lea, 1970). Its persistence in a very old mortar implies a very low kinetics of reaction at low temperature. The maximum extension of reaction in the non-carbonate zones is 2.5 mm over 1800 years. Carbonatation limits the size of the disturbance through a buffering effect.
- At Maquarin, in northern Jordan, the dissolution of natural portlandite, derived from the *in situ* combustion of bituminous marl, has given rise to circulating hyperalkaline waters. The "metamorphic" zone, in which the combustion of the bituminous marl took place, corresponds to the top of a thick marl unit and the base of the overlying impure limestone unit. The combustion was followed by rehydration and carbonatation that locally gave a mineralogy close to that of Portland cement. The water circulating through this "metamorphic" zone acquires a chemistry very close to the cement waters with a high pH (12.1 – 13.5) and a high Ca content (Smellie, 1998). Downgradient from this zone, the hyperalkaline waters circulate through fractures in a clayey biomicrite. The fracture edges show dissolution of calcite, kaolinite, silica, traces of illite, albite and organic matter. Within the fractures themselves, different opening/closing episodes may have taken place to give a complex mineralogy. Aragonite precipitated first, followed by an ettringite-thaumasite solid solution and gypsum. Reactivation of the fractures then enabled the precipitation of CSH (tobermorite and jennite). Zeolites corresponding to a last stage of mineralization are seen locally; these are yugawaralite, mordenite, diachardite for the quartz supersaturated waters, laumontite and epistilbite for the quartz equilibrated waters, and chabazite for the undersaturated waters. Intense alteration of the rock matrix extends for 1 to 4 mm with precipitation of thaumasite and ettringite. The area of influence of the

disturbance can be assessed at 40 mm from the fracture for roughly 100,000 years of interaction (Smellie, 1998; Milodowski *et al.*, 2001; Cassagnabère *et al.*, 2001). However, it is not for sure that the rock/water contact was constant during the whole period as “dry periods” could have occurred.

6. Numerical modeling of the alkaline disturbance

- Intercomparison

Numerical modeling of the alkaline disturbance can be broken down into three categories: (i) simulations reproducing laboratory experiments (Vieillard *et al.*, 2004 – KINDIS code), (ii) simulations of observed natural analogues (Steefel and Lichtner, 1998 – GIMRT code), and (iii) "predictive" simulations (Steefel and Lichtner, 1994 – 1DREACT code; Savage *et al.*, 2002 – PRECIP code; Soler, 2003 – modified GIMRT code; de Windt *et al.*, 2004 – HYTEC; Gaucher *et al.*, 2004 – PHREEQC code; Mäder and Traber, 2004 – CRUNCH code). The authors select either a purely thermodynamic approach (de Windt *et al.*, 2004; Gaucher *et al.*, 2004), or a mixed kinetic and thermodynamic approach (Steefel and Lichtner, 1994, 1998; Savage *et al.*, 2002; Soler, 2003; Vieillard *et al.*, 2004; Mäder and Traber, 2004). All authors using the kinetic approach recognize the difficulties inherent in manipulating kinetic rates. Vieillard *et al.* (2004) mention that few data are available for highly alkaline environments. The kinetic approach requires sensitivity tests, either through varying the reactive surfaces to be considered (Steefel and Lichtner, 1994, 1998; Soler, 2003), or through considering variable kinetic rates or laws (Savage *et al.*, 2002). De Windt *et al.* (2004) and Gaucher *et al.* (2004) consider that, in view of the very long interaction times (>1000 years) and very low water/rock ratio, simulations can be made using a purely thermodynamic mode. In view of the low porosities of the clayey media, these are the most suitable for attaining the thermodynamic water/rock equilibrium.

The studied geometries are more or less complex (1D, 2D), depending on the authors, with variable porosities being taken into account. Nevertheless, this aspect has relatively little impact on the data presentation and conclusions concerning the mineralogical sequences. As mineral reactions induced by chemical gradients have to be calculated for small (interface) volume, the discretization of the spatial grid is important and must be finest as possible.

Two articles deal with temperature-based simulations after adapting the thermodynamic database (120 °C: Vieillard *et al.*, 2004; 70 °C: Savage *et al.*, 2002). Savage *et al.* (2002) were obliged to estimate a certain number of temperature-controlled dissolution or precipitation rates due to a lack of satisfactory data.

The pore diffusion coefficients used by the authors range between 10^{-9} m²/s and 10^{-11} m²/s. This large range comes from porosity differences in the clay materials that are considered or to maximize the extension of the perturbation with the largest coefficients. Gaucher *et al.* (2004) made a sensitivity test on the amplitude of this variation range and suggested an empirical law to determine the extension of the disturbance in relation to time and the numerical value of the pore diffusion coefficient.

All the simulations give mineral phases with a higher molar volume than that of the original rock minerals. The PRECIP, GIMRT, 1DREACT, HYTEC, CRUNCH codes enable a return effect on the porosity during a phase's dissolution or precipitation. In extreme cases, the porosity can be sealed by the precipitation of minerals with high molar volumes. This results in modifying the transport conditions and can stop the transport in case of sealing. The calculations enabling this porosity return effect all indicate a total sealing of the porosity, sometimes within a very short period; 15 years in the case studied by Steefel and Lichtner (1994). These authors also noted an unexpected consequence of the porosity sealing. Once the porosity was sealed at a certain distance from the cement/clay interface, the continued cementation had the effect of preventing the diffusion of OH⁻ ions within the geological formation, thus confining the alkaline pH front toward the cement medium. Savage *et al.* (2002) show that the Ca content in the alkaline fluid, rather than the pH of the solutions, that possibly dominates sealing the porosity. Steefel and Lichtner (1994) show that the interdiffusion of Ca²⁺ from the cement medium and CO₃²⁻ from the geological formation causes a localized precipitation of calcite that seals the porosity at 1.5 cm from the fracture containing the alkaline solution. Sealing of the groundmass porosity appears to be well established in the case of the Jordanian natural analogues. The experiments of Melkior *et al.* (2004) show a decrease ($D_e/1.5$ to $D_e/2.0$) in the diffusion coefficients of the tritiated water during a year-long alkaline disturbance; the authors explain this decrease as being due to pore blocking. Finally, precipitation of the cement phases with a large molar volume could have mechanical consequences on the barriers, because the volumes exceed those of the rock porosity (Gaucher *et al.*, 2004).

In simulations, the alkaline medium is represented by (i) pure solutions (NaOH at pH 13.5, KOH at pH 13.8, CaOH₂ at pH 12.5; Vieillard *et al.*, 2004), (ii) "young" alkaline-rich concrete solutions with pH >13.2 (Savage *et al.*, 2002; Soler, 2003; de Windt *et al.*, 2004), (iii) evolved concrete solutions (Steefel and Lichtner, 1994, 1998; Savage *et al.*, 2002; Gaucher *et al.*, 2004) in equilibrium with the portlandite (pH 12.5), and (iv) degraded

concrete solutions (Savage *et al.*, 2002) in equilibrium with a CSH gel (pH 11.2). Comparing the simulations shows that, in the absence of porosity sealing, the alkaline disturbance will extend roughly 10 times further when the pH is one order of magnitude higher. Of note is that none of the authors models the combined evolution of a complete concrete. Two articles consider the evolution of the cement medium (de Windt *et al.*, 2004; Mäder and Traber, 2004). De Windt *et al.* (2004) introduce a cement paste (without aggregate) with only three phases: portlandite, ettringite and a 1.8 CSH. Mäder and Traber (2004) consider a complex concrete with portlandite, CSH (Ca/Si = 1.79), ettringite, hydrotalcite and hydrogarnet. The aggregate is quartz. As this last phase cannot be in equilibrium with the cement system, a dissolution kinetic control is applied. Combined modeling of the cement and clay media undeniably marks a significant progress.

Three models consider the surface reactions (ion exchange, surface complexing). Thus, de Windt *et al.* (2004) consider the ion exchange on three types of site for the 2:1 clays, one type of site for clinoptilolite and one surface complexing site for the CSH. Some of these sites may play a role in the buffer effect of the alkaline pH by liberating H⁺ ions. Gaucher *et al.* (2004) use a less complex ion exchange model based on the constants put forward by Fletcher and Sposito (1989) for the Wyoming montmorillonite; this model does not enable the pH to be buffered. Mäder and Traber (2005) use the ion exchange constants proposed by Appelo and Postma (1999) for Na, K, Ca, Mg. This choice is unfortunate because ion exchange constants were acquired specifically by Waber *et al.* (2003) for the Opalinus Clay considered in these models.

- Completeness of the considered mineralogy

A major difference between the various articles on alkaline disturbance simulation is the completeness of the mineral list that was used. First of all, for the clay systems, one must accommodate all the mineral phases present. Then, in the context of modeling the disturbance, one must provide the model with a sufficient number of mineral phases so that it is not "forced" to accept a unique solution.

In this respect, the replacement of illite by muscovite is doubtless prejudicial to the representation of the phenomena in the articles by Savage *et al.* (2002), Steefel and Lichtner (1994, 1998), and Soler (2003). The logK_{eq} given for the muscovite is 11.02 for Savage *et al.* (2002) and Soler (2003), but 13.59 by Steefel and Lichtner (1998), although in all cases the data were taken from the EQ3/6 database. These values are to be compared with the logK_{eq} of illite which is 9.02 in this database. As the muscovite used by these authors is much more insoluble than illite, an artificial "resistance" is introduced for the clay barrier. Steefel and Lichtner (1994) also replace the rock's chlorite by kaolinite in their model. Again, this replacement is prejudicial because Mg-

chlorite is stable in an alkaline medium (cf. §2) and can precipitate during the dissolution of montmorillonite by taking up Mg. The description of the reaction pathways is thus that much the poorer.

Supplying the chemical/transport code with a list of minerals that is too short can bias the response because it does not give the model any choice in the mineral phases. Savage *et al.* (2002) included only 12 minerals in their simulations, including leucite which is a volcanic mineral phase. Steefel and Lichtner (1998) used a restricted list (16 minerals), but one which corresponds to the analogue they were modeling (except for the muscovite). The mineral lists of Steefel and Lichtner (1994), Soler (2003), de Windt *et al.* (2004) and Mäder and Traber (2004) consist of 18-20 phases that include a good number of calcic phases, but which are deficient in magnesian minerals. The number of considered clay phases is generally very low. The phase lists proposed by Vieillard *et al.* (2004; 35 minerals) and Gaucher *et al.* (2004; 48 minerals) are much richer and leave the model to find the best solution. De Windt *et al.* (2004) show that when their model includes its maximum number of phases (CSH, zeolites, sepiolite), the pH is strongly buffered and is very different from the earlier simulations with less phases. All the diffusion modeling carried out by the authors that we have cited show a succession of mineralogically contrasted zones. Starting outward from the concrete/clay interface, we pass through a zone of precipitation of cement phases, a zeolite zone, and then a zone in which the original clay minerals are altered. However, we shall only discuss the simulations carried out by Gaucher *et al.* (2004) using the PHREEQC code (Parkhurst and Appelo, 1999) because, in view of the large number of phases involved, they give a fairly complete picture of the expected reaction sequence (Figure 2). They model the diffusion of an evolved cement water of pH 12.5 within a barrier engineered in Wyoming bentonite MX80. The chemistry of the cement water is assumed to be constant in order to maximize the barrier degradation. From the intact barrier up to the bentonite/concrete interface we find (1) a zone of accessory-mineral (calcite and cristabolite) dissolution with the appearance of potassic zeolites; ion exchange phenomena are intense in this zone with a conversion of Na-montmorillonite to Ca-montmorillonite (1'). This is followed by (2) a zone of smectite zeolitization and illitization, then (3) total dissolution of the clays in favour of zeolites and saponites (4'). At the interface contact (4), the zeolites disappear and we find purely cement phases of CSH (gyrolite, tobermorite, afwillite with an evolutionary sequence in their Ca/Si ratios), CASH (gismondine), hydrogarnet (katoite), carbonates (calcite and hydrotalcite) and sulfates (ettringite). There is an absence of hydroxides (portlandite and brucite) in the simulation results; although these phases are in the list of minerals likely to precipitate, they do not appear. The absence of portlandite can be explained by the pH being lower than 12.4. The absence of brucite is due to the presence of large amounts of Al and Si that hinder the formation of this phase, which has practically never been encountered under experimental conditions or during

the study of natural analogues. The Mg of the smectites is thus reused to precipitate saponites, then Mg-chlorites and finally hydrotalcite, preventing brucite from reaching saturation. To be noted, however, is that the Mg-chlorites (clinochlore) contain a "brucite" interlayer. Some authors force a precipitation of brucite in their models because they consider it to be practically the only phase for trapping the Mg in an alkaline medium, although they propose a number of phases for trapping the Ca (De Windt *et al.*, 2004; Soler, 2003; Steefel and Lichtner, 1994). This is unfortunate because montmorillonite liberates a lot of Mg on dissolution, and so the reaction dynamics of the Mg is not computed as well as it could be. This has consequences on the computation of the carbonate system (Ca, Mg, C) and thus on the manner in which the pCO_2 is fixed in the system, which appreciably modifies the buffer effect on the pH of a clay system "open" to the geological formation. In the simulations of Gaucher *et al.* (2004), the $\log pCO_2$ is established at -2.4 bar at 25 °C within the unaltered MX80. This value drops by several orders of magnitude in the alteration zone where the mineralogical buffer has been destroyed. The pCO_2 is a fundamental parameter for these simulations, but only Steefel and Lichtner (1994) and Gaucher *et al.* (2004) discuss it in detail. As a complement to this description of the altered clay medium, the simulations by Mäder and Traber (2004) show the related alteration of the concrete. These authors note the disappearance of the portlandite and a sequence of CSH with decreasing Ca/Si ratios in the direction of the concrete/clay interface. Ettringite is also totally dissolved next to the interface.

7. Conclusion on the impact of the alkaline disturbance

Although it appears premature to conclude definitively on the consequences of an alkaline disturbance in a clay medium, analysis of the scientific literature in this field allows us to identify the following elements. The mineralogical consequences of an alkaline disturbance are fairly well known as a result of a large number of laboratory experiments. Efforts are nevertheless still required in order to improve our knowledge of the thermodynamics of the clays, zeolites and cement phases. Large uncertainties remain where our studies of the dissolution kinetics and mineral precipitations are concerned. Multiparameter experiments are still necessary to fix the dissolution kinetics laws of the montmorillonites, principally for constraining the inhibitor effects and taking into account the specific surfaces of the sheet edges. The studies made on natural analogues and in underground laboratories show a fairly limited spatial extension of the alkaline disturbance that is of the order of 4 cm per 100,000 years at Maqarin. All these studies have made it possible to numerically model of the phenomenon. The simulations will become increasingly representative inasmuch as we are able to take into

account a specific geometry, the complexity of the concrete and bentonite mineralogical systems, to incorporate the surface chemistry of the clays, zeolites and CSH, and to consider a mineralogical control of the pCO_2 and the evolution of the porosity. Combined modeling of the cement and clay media also appears to be a promising approach.

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Table 1: Summary of literature data concerning the alkaline alteration of clay barrier minerals. Question marks report a doubt of the authors concerning the validity of an observation.

Reference	Initial mineral (or rock)	Chemistry of the pore solution	Temperature (°C)	Time (days)	Pressure (atm)	Resultant minerals	Evolution of the CEC
DE LA VILLA <i>et al.</i> , 2001	Bentonite Febex (Spain) 93% montmorillonite, 2% quartz, 2% K-feldspar, 1% plagioclase, 2% calcite, 1.5% volcanic glass, cristobalite.	pH 13.5; Na 0.17M, K 0.33M, Ca 4.07M	35, 60, 90	30, 90, 180, 360	1	Na-phillipsite	
DE LA VILLA <i>et al.</i> , 2001	Bentonite Febex (Spain) <2 µm montmorillonite	pH 13.5; Na 0.5M, Ca 4.1M	60, 90	30, 90,	1	Na-phillipsite, analcime	
RAMIREZ <i>et al.</i> , 2002	Bentonite Febex (Spain) 93% montmorillonite, 2% quartz, 2% K-feldspar, 1% plagioclase, 2% calcite, 1.5% volcanic glass, cristobalite.	pH 13.5 to 10; several tests with Na, Ca, K at different concentrations.	30, 60, 90	7 to 365	1	Phillipsite, analcime, Mg- smectite, CSH-gel phases	Loss of Mg and Na replaced by Ca and K.
CUEVAS, 2004	Bentonite Febex (Spain) 93% montmorillonite, 2% quartz, 2% K-feldspar, 1% plagioclase, 2% calcite, 1.5% volcanic glass, cristobalite.	NaOH 0.1M, 0.25M, 0.5M + Ca(OH) ₂ at saturation	25, 75, 125, 200	30, 180, 365, 540		Analcime, tobermorite or CSH- gel, gyrolite, phillipsite, saponite	
EBERL <i>et al.</i> , 1993	MX80: montmorillonite, quartz, cristobalite, calcite, feldspar, pyrite, gypsum.	KOH 3M	35	270	1	Illite (+25%)	diminution
EBERL <i>et al.</i> , 1993	MX80: montmorillonite, quartz, cristobalite, calcite, feldspar, pyrite, gypsum.	NaOH 0.5M	35	270	1	I/S _{R=0} in non-swelling sheets	diminution
BOUCHET <i>et al.</i> , 2004	MX80: montmorillonite, quartz, cristobalite, calcite, feldspar, pyrite, gypsum.	NaOH 1M	60, 90, 120	1, 7	1 P >1 atm at 120 °C	Analcime, beidellite	Increase from 75 to 110 meq/100 g
BOUCHET <i>et al.</i> , 2004	MX80: montmorillonite, quartz, cristobalite, calcite, feldspar, pyrite, gypsum.	KOH 1M	60, 90, 120	1, 7	1 P >1 atm at 120 °C	Phillipsite, beidellite	Increase from 75 to 110 meq/100 g
BOUCHET <i>et al.</i> , 2004	MX80: montmorillonite, quartz, cristobalite, calcite, feldspar, pyrite, gypsum.	CaO 0.5M	60, 90, 120	1, 7	1 P >1 atm at 120 °C	Portlandite, CSH-gel, gypsum, beidellite	Increase from 75 to 110 meq/100 g
KARNLAND, 2004	MX80: montmorillonite, quartz, cristobalite, calcite, feldspar, pyrite, gypsum.	NaOH 1.0 to 0.3M NaCl 1.0 to 0.3M	23	70	1	Beidellite	Increase of the CEC from 74 to 94 meq/100 g.
BAUER AND BERGER, 1998	Smectite (Ceca and Ibeco)	KOH >4M	35		1	Initial product (1) illite (+45%) sequence (2): mica, phillipsite, K-feldspar, quartz	diminution
BAUER AND BERGER, 1998	Smectite (Ceca and Ibeco)	KOH >4M	80		1	Initial product (1) illite (+90%) sequence (2): mica, phillipsite, K-feldspar, quartz	diminution

NAKAYAMA <i>et al.</i> , 2004	Montmorillonite + quartz	pH 13 to 14; type Na, K	50 to 170	up to 125	1	Analcime	
MOSSER-RUCK and CATHELINEAU, 2004	Na-Ca smectite, Na-smectite, Ca-smectite	pH 12; NaOH	150	60	5 to 150 bar	No evolution. Buffer effect of the final clay pH = 9	
MOSSER-RUCK and CATHELINEAU, 2004	Na-smectite,	pH 11.7; K ₂ CO ₃ 2M	150	60	5 to 150 bar	Na-K ion exchange, illitization? or bedellitization; Na-merlinoite (Na-phillipsite)	
MOSSER-RUCK and CATHELINEAU, 2004	Ca-smectite,	pH 11.7; K ₂ CO ₃ 2M	150	60	5 to 150 bar	Ca-K ion exchange, illitization? or bedellitization, CSH-tobermorite	
MOSSER-RUCK and CATHELINEAU, 2004	Na-Ca smectite, Na-smectite, Ca-smectite	pH 11.8; KOH + KCl 1M	150	60	5 to 150 bar	Na-K, Ca-K ion exchange; illitization? or beidellitization?	
MOSSER-RUCK and CATHELINEAU, 2004	Na-Ca smectite, Na-smectite, Ca-smectite	pH 11.7; KOH + KCl 3M	150	60	5 to 150 bar	Na-K, Ca-K ion exchange; illitization? or beidellitization?	
BÉRUBÉ <i>et al.</i> , 1990	Metabentonite (S-rich I/S)	pH 12.5; CaOH ₂ at saturation	23	265	1	CASH	
ADLER <i>et al.</i> , 1999	Opalinus Clay (Mont Terri), kaolinite, illite, I/S, chlorite, micas, calcite, quartz, pyrite, dolomite, siderite, K- and Na-feldspar.	pH 13.2; type K, Na, Ca	30	up to 540		Calcite, CASH, CaOH ₂ , Ca-zeolite (mordenite), illite, FeOOH, Fe-rich chlorite, gypsum, alkaline sulfates: syngenite and glauberite	
CHERMAK, 1992	Opalinus Clay (Mont Terri), kaolinite, illite, I/S, chlorite, micas, calcite, quartz, pyrite, dolomite, siderite, K- and Na-feldspar.	pH 13 and 12; NaOH	150, 175, 200	40		Analcime, vermiculite, Na-rectorite	
CHERMAK, 1993	Opalinus Clay (Mont Terri), kaolinite, illite, I/S, chlorite, micas, calcite, quartz, pyrite, dolomite, siderite, K- and Na-feldspar.	pH 13 and 12; KOH	150, 175, 200	50		Phillipsite, K-feldspar, K-rectorite	
CLARET <i>et al.</i> , 2002	Callovian-Oxfordian deposits	pH 13.2; type K, Na, Ca	60	360	1	Illite/smectite, tobermorite, solubilization of organic matter	
ELIE <i>et al.</i> , 2004	Callovian-Oxfordian deposits after 384 to 1024 hours oxidation.	pH 12.7; Portland Cement type solution	20	4	1	Solubilization of organic matter. Extraction of n-carboxylic acids.	
RAMIREZ <i>et al.</i> , 2005	Callovian-Oxfordian clays (<2 μm)	Ca(OH) ₂ 0.05mM, 5mM, 0.5M	60, 90, 120	1, 7	1 P >1 atm at 120 °C	Tobermorite, katoite	Increase from 40 to 600(?) meq/100 g
RAMIREZ <i>et al.</i> , 2005	Callovian-Oxfordian clays (<2 μm)	NaOH 0.1mM, 10mM, 1M	60, 90, 120	1, 7	1 P >1 atm	Analcime, phillipsite, chabazite, beidellite	

		KOH 0.1mM, 10mM, 1M				at 120 °C		
BRANEY <i>et al.</i> , 1993	Clashach Sandstone: quartz, K-feldspar, illite, iron oxides	pH 12.5; CaOH ₂ at saturation	25	280		1	CSH (jennite, tobermorite)	CECx3
DEVOL-BROWN I. <i>et al.</i> , 2005	Tournemire Argillite: kaolinite, illite, I/S, chlorite, calcite, quartz, pyrite, dolomite, siderite, K- and Na-feldspar, micas	pH 13.25; NaOH 0.08M, KOH 0.1M Oxidation	25, 70	30, 60, 90		1	Calcite, siderite, iron oxide, Ca-Na-zeolites, Na-zeolites, clays(?)	
BÉRUBÉ <i>et al.</i> , 1990	Quartz	pH 12.5; CaOH ₂ at saturation	23	265		1	CSH	
SAVAGE <i>et al.</i> , 1992	Quartz	pH 13.0; K, Na, Ca	70	1 to 100	1 to 300 bar		Amorphous CSH, Ca/Si 0.5 to 1.0, (okenite, tobermorite type)	
BATEMAN <i>et al.</i> , 1999	Quartz	pH 12.5; CaOH ₂ at saturation, or pH 13.22: K, Na, Ca	70	25		1	CSH: hillebrandite, foshagite, tobermorite	
BATEMAN <i>et al.</i> , 1999	Muscovite + quartz	pH 12.5: CaOH ₂ at saturation, or pH 13.22: K, Na, Ca	70	25		1	CSH: hillebrandite, foshagite, tobermorite + CASH	
BÉRUBÉ <i>et al.</i> , 1990	Mg-chlorite	pH 12.5: CaOH ₂ at saturation	23	265		1	No neogenesis; this phase is stable in an alkaline medium	
HODGKINSON and HUGHES, 1999	Fe-chlorite (chamosite)	pH 12.5: CaOH ₂ at saturation	85	33		1	CASH, katoite	
BÉRUBÉ <i>et al.</i> , 1990	Feldspar	pH 12.5: CaOH ₂ at saturation	23	265		1	CASH	
SAVAGE <i>et al.</i> , 1992	Microcline	pH 12.5: CaOH ₂ at saturation	70	1 to 100	1 to 300 bar		Hydrogrossular	
BATEMAN <i>et al.</i> , 1999	Albite	pH 12.5: CaOH ₂ at saturation, or pH 13.22: K, Na, Ca	70	25		1	CSH: hillebrandite, foshagite, tobermorite + CASH	
SAVAGE <i>et al.</i> , 1992	Albite	pH 13.0: K, Na, Ca	70	1 to 100	1 to 300 bar		Amorphous CSH, Ca/Si 1.5, (jennite type); CASH (tacharanite type)	
HODGKINSON and HUGHES, 1999	Anorthite	pH 12.5: CaOH ₂ at saturation	85	33		1	CASH, katoite, tobermorite or jennite	
HODGKINSON and HUGHES, 1999	Muscovite	pH 12.5: CaOH ₂ at saturation	85	33		1	CASH, CSH gel.	
BÉRUBÉ <i>et al.</i> , 1990	Biotite	pH 12.5: CaOH ₂ at saturation	23	265		1	CASH	

SAVAGE <i>et al.</i> , 1992	Biotite	pH 12.5: CaOH ₂ at saturation	70	1 to 100	1 to 300 bar	Hydroandratite	
BÉRUBÉ <i>et al.</i> , 1990	Pyrite	pH 12.5: CaOH ₂ at saturation	23	265		1 No neogenesis; this phase is stable in an alkaline medium	
BÉRUBÉ <i>et al.</i> , 1990	Goethite	pH 12.5: CaOH ₂ at saturation	23	265		1 No neogenesis; this phase is stable in an alkaline medium	
KAWANO and TOMITA, 1997	Obsidian	pH >10: KOH	150, 200			1 Smectite, merlinoite, sanidine	
KAWANO and TOMITA, 1997	Obsidian	pH >10: NaOH	150, 200			1 Phillipsite, rodosite(?)	
BÉRUBÉ <i>et al.</i> , 1990	Dolomite	pH 12.5: CaOH ₂ at saturation	23	265		1 Calcite + brucite	
ZHAO <i>et al.</i> , 2004	Kaolinite KGa-1 KGa-2	NaOH 1.4 & 2.8M, NaNO ₃ 3.7M, NaAlO ₂ 0.125 & 0.25M.	50, 80	60		1 NO ₃ -sodalite; NO ₃ -cancrinite	

Figures

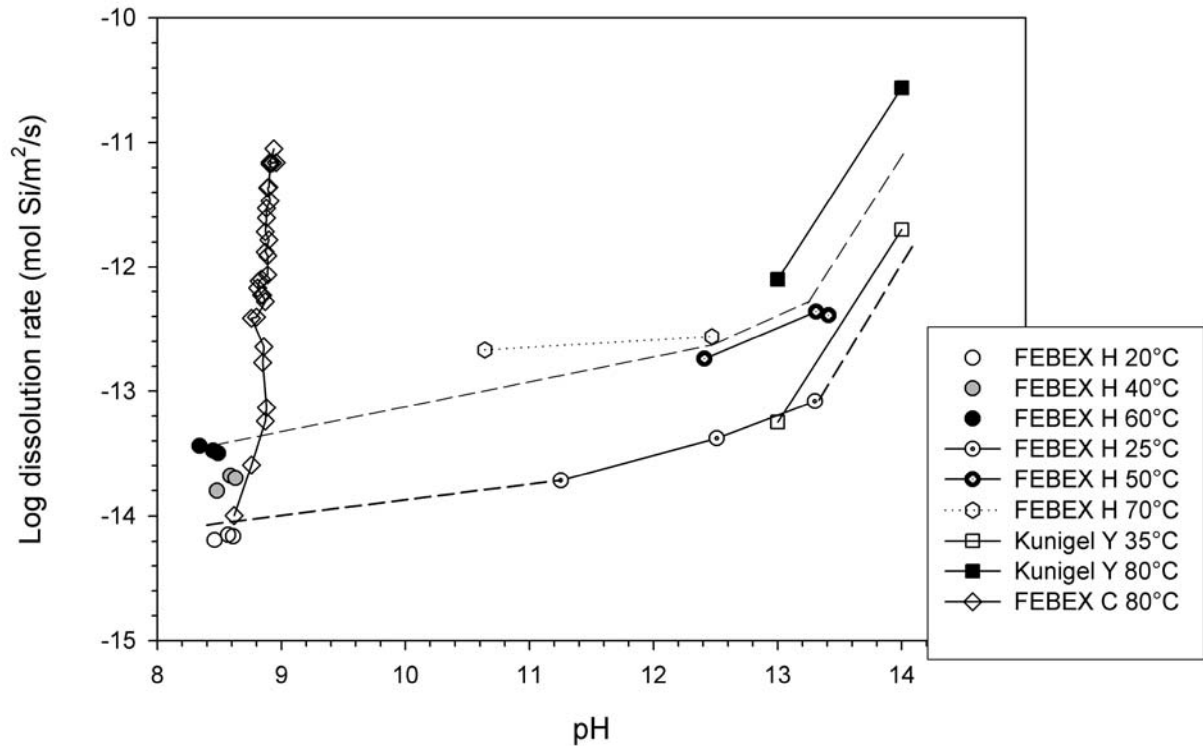


Figure 1: Dissolution rate as a function of pH (data from Huertas et al., 2001, 2004: FEBEX H 20 – 70 °C; from Cama et al., 2000: FEBEX C 80 °C; and from Yamagushi et al., 2004: Kunigel Y 35 – 80 °C).

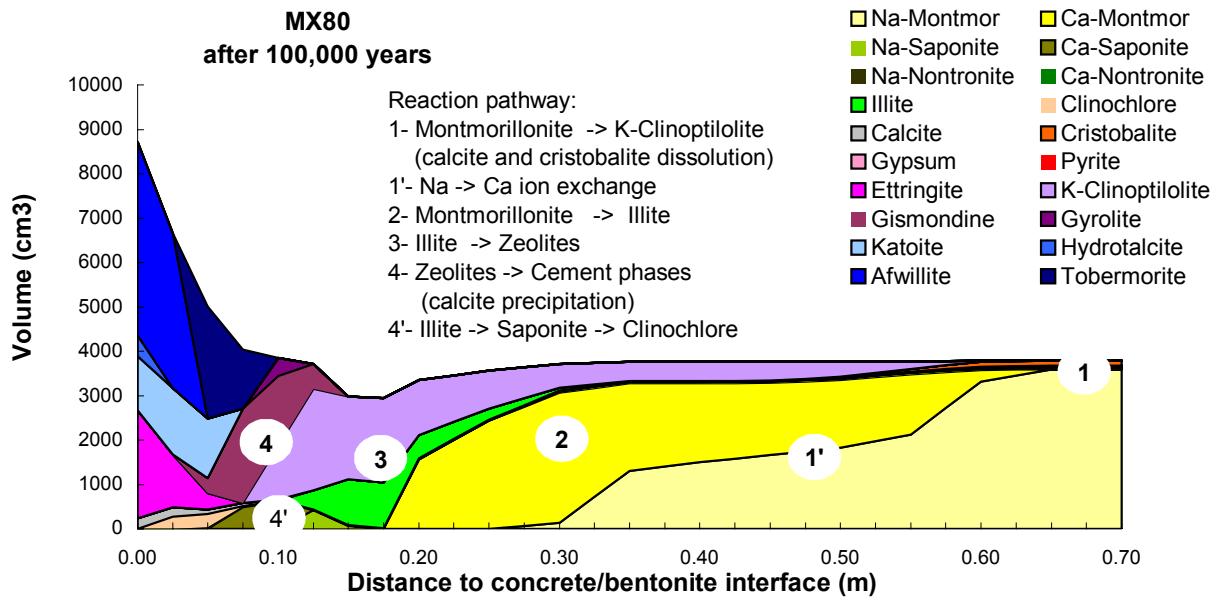


Figure 2: Composition of a clay barrier after 100,000 years of interaction with an effective diffusion coefficient of $10^{-11} \text{ m}^2/\text{s}$.