Modeling experimental results of diffusion of alkaline solutions through a compacted bentonite barrier

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ABSTRACT

The interaction between concrete/cement and swelling clay (bentonite) has been modeled in the context of engineered barrier systems for deep geological disposal of high-level radioactive waste. The geochemical transformations observed in laboratory diffusion experiments at 60 and 90 °C between bentonite and different high-pH solutions (K–Na–OH and Ca(OH)$_2$-saturated) were reconciled with the reactive transport code CrunchFlow. For K–Na–OH solutions (pH = 13.5 at 25 °C) partial dissolution of montmorillonite and precipitation of Mg-silicates (talc-like), hydrotalcite and brucite at the interface are predicted at 60 °C, while at 90 °C the alteration is wider. Alkaline cations diffused beyond the mineralogical alteration zone by means of exchange with Mg^{2+} in the interlayer region of montmorillonite. Very slow reactivity and minor alteration of the clay are predicted in the Ca(OH)$_2$-bentonite system. The model is a reasonable description of the experiments but also demonstrates the difficulties in modeling processes operating at a small scale under a diffusive regime.

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1. Introduction

Concrete and compacted bentonite are being studied as components of engineered barrier systems to isolate high-level radioactive waste in geological disposal. These materials should conserve the physical and chemical characteristics for what they have been designed until the radioactive waste and the spent nuclear fuel decrease their radioactivity levels to near the natural background. However, both materials will evolve over time due to their different compositions. The high-pH (13–14) fluids emanating from OPC-type concrete will interact with the bentonite barrier where these two materials will be placed in direct contact. The initial composition of the concrete porewater is dominated by K$^+$ (0.2–0.5 M), Na$^+$ (0.05–0.2 M) and OH$^-$ (0.3–0.7 M), and will evolve to Ca-(OH)$_2$ solutions after the alkali-leaching period [1–3]. At laboratory scale these situations are simulated with two types of synthetic alkaline solutions: an early cement water, mainly Na–K–OH with pH ~13.5 at 25 °C, used to simulate early repository conditions, and an Evolved Cement Water, saturated with respect to portlandite (pH ~12.5, at 25 °C), that represents the conditions expected to prevail for a very long time in a repository. The duration for which the barrier should conserve its retention properties for radionuclides is 10^5 to 10^6 years.

Numerous laboratory experiments [4–13], natural analogues [14–19] and modeling studies [20–26] confirm and detail the alteration of clays by interaction with alkaline fluids. These studies agree on the following processes related to cement/bentonite systems:

1. Concrete or cement (Ordinary Portland Cement: OPC) reacts initially with bentonite due to the high-pH porewater. Montmorillonite dissolves under hyperalkaline conditions, precipitating zeolites and leaving a Mg-rich residual clay.
2. Bentonite is able to buffer the hyperalkaline pH (13.6–13.0, for OPC) to pH ≤ 12.5. Portlandite is then slowly dissolved at the interface, forming C–S–H gels (Ca-Si-hydrate). Crystalline C–S–H gels of tobermorite-type form at temperature higher than 80 °C at laboratory time scales.
3. Some of the dissolved Ca^{2+} is incorporated in the exchangeable complex of bentonite, displacing Mg^{2+}, which precipitates as brucite [Mg(OH)$_2$] or hydrous magnesium silicate and hydrotalcite depending on the temperature of reaction.

Diffusion experiments with alkaline solutions and compacted bentonite columns show the coupling between the changing porosity due to cementation processes at the interface, and the retardation of alteration in the cemented layer, as well as the decrease in the cation exchange capacity of bentonite due to montmorillonite dissolution as the main geochemical reactions [27]. The reactive transport geochemical code CrunchFlow is used in this study to investigate numerically the same system, with the aim to reproduce the alteration reactions observed experimentally with special focus on

cation exchange and mineralogical transformations in order to confirm and clarify key processes, and provide insight into expected system behaviour over long periods of time. In order to achieve relevant results that permit the interpretation of the experimental observations, some of the key parameters were selected based on available published data but some others were adjusted to obtain numerical convergence (reaction rates, diffusion coefficients, etc.).

2. Experimental conditions and main results

The experimental system consists of a cylindrical compacted bentonite column in contact with a 0.6 M MgCl₂ solution at one end and a synthetic alkaline solution at the other end of the column (Fig. 1). To maintain an almost constant source of alkalinity, the alkaline solution is constantly circulated from a 0.5 L solution reservoir by a peristaltic pump. No circulation was applied to the MgCl₂ solution since the only objective was to maintain saturated conditions during the course of the experiment. A set of 12 experiments were performed under these conditions over 6, 12 and 18/24 months, applying a constant temperature of 60 °C (6, 12, 24 months) and 90 °C (6, 12, 18 months), and using 2 different alkaline solutions: Young Cement Water (YCW) and Evolved Cement Water (ECW).

The clay material was pre-treated to saturate the exchangeable complex of montmorillonite in Mg^{2+}; but the mineralogical composition of bentonite was not modified. Most soluble salts, such as gypsum or halite, were washed out from the bulk clay during the saturation process but some calcite remained in bentonite after Mg-saturation. This pre-treatment permits to study the mineralogical transformations in the first millimeters of the alkaline interface since exchangeable Mg^{2+} is displaced from the interlayer of montmorillonite under alkaline conditions, precipitating as brucite or incorporating itself in the internal structure of silicates in a non-exchangeable form [7,13,28].

At 60 °C, diffusion of the hyperalkaline plume (YCW: K/NaOH solution) through compacted bentonite (1.6 g/cm³ dry density) produced a domain of mineralogical alteration characterized by a cemented rim of 2 mm thickness, developed in 6 months. The thickness of alteration did not evolve thereafter despite the nearly constant input solution composition owing to an increased surface area and reduced porosity that caused a strong retardation of diffusion. Montmorillonite was partially dissolved and formation of brucite, Al- and Mg-chlorite-type silicates were observed within this domain. XRD diffraction suggests intercalation of hydroxides and hydrotalcite-type structures (7.5 Å). Zeolites were not observed.

At 90 °C, the alteration zone had a larger extent, and this was observed as a hardening of the bentonite column and partial occlusion of the connected porosity, retarding the diffusion of alkaline cations. Only traces of analcime were detected at the interface with the YCW.

The pH was buffered efficiently by montmorillonite dissolution at 60 and 90 °C as evidenced by only small amounts of brucite precipitation. Brucite would be the main secondary phase if pH was maintained at the initial 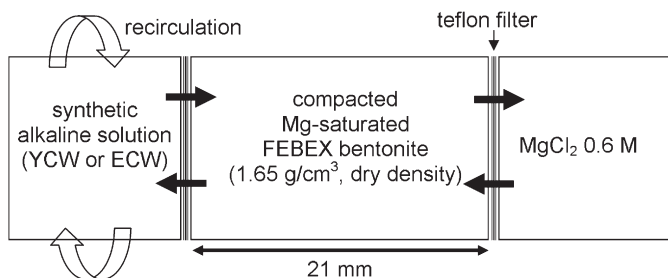value. Disturbance of the ion exchange complex extended deeper than the mineralogical alteration; substitution of Mg^{2+} by K^+ was detected even at 60 °C and after 6 months along the entire column of bentonite (2.1 cm).

Further details of the experiments are reported in [27].

3. Physical model and approach

Modeling was carried out using the geochemical computer code CrunchFlow [29–31] that can be operated in two modes: using the Sequential Iteration Approach (SIA) which solves the transport and chemical equations sequentially, or the Direct Substitution Approach (DSA) which solves the transport and chemical equations simultaneously. Geochemical evolution in CrunchFlow is modeled using user-defined kinetic rate laws for mineral reactions, and chemical equilibrium for aqueous speciation and surface reactions. The code takes into account aqueous speciation, mineral dissolution/precipitation, surface complexation, ion exchange, and transport processes. Transport in the system may optionally be coupled to or decoupled from the evolving porosity when minerals precipitate or dissolve. Aqueous species can be constrained by mineral or gas equilibrium and charge balance. Reactions given in the database are temperature dependent extending up to 300 °C but several inconsistencies had to be resolved and supplementary data supplied (see details below).

In analogy to the laboratory experiments, the model considers an alkaline solution (either YCW or ECW; Table 1) diffusing through the bentonite column, which is divided into 21 cells of 1 mm each, with the same initial mineralogical composition and porewater composition (Table 2). The alkaline solution is located outside the column, adjacent to the bentonite domain. At the end of the column, 2 cells of 1 mm are added for a 0.6 M MgCl₂ solution. The transport is limited to diffusive interaction between the infinite source of alkalinity and the bentonite and MgCl₂ domains. Mineral dissolution/precipitation, aqueous speciation and ion exchange selectively associated to montmorillonite are the geochemical processes included in all scenarios. The DSA mode was used in this study which will allow for larger time stepping and better performance.

3.1. Initial considerations

A model in one dimension was preferred due to the approximate homogeneity of the domains involved in the system and for simplicity in order to express the results as a function of distance from the alkaline interface.

Watson et al. [32] performed predictive modeling of the diffusion of cementitious water in bentonite with a sensitivity study of input parameters, using the code Raiden-3 [33]. They observed different behaviours in the system as a function of the size of the alkaline reservoir. The larger the reservoir, the longer it took for montmorillonite dissolution to start, but when it did it was at a faster dissolution rate. For an infinite reservoir, montmorillonite dissolution started before other cases examined and was more rapid. A dependency on the alkaline reservoir size is also observed in this study with CrunchFlow; but the alkaline fluid has been considered an infinitely large reservoir out of the domain. This fact disagrees with the

Fig. 1. Experimental set-up of diffusion experiments.

Table 1
Synthetic concrete porewater compositions (mol/kg solution).

Aqueous species	YCW	ECW
OH⁻ (charge balance)	4.27E−2	4.00E−2
K⁺	3.54E−1	
Na⁺	1.02E−2	
Ca²⁺	7.36E−4	2.00E−2
SO₄²⁻	1.53E−2	
O₂(aq)	1.00E−8	1.00E−8
pH	12.4 (60 °C)	11.447 (60 °C)
	11.8 (90 °C)	