

# Mineral Reaction Front Developed in a 4.5 Years Test for the Study of Concrete-Bentonite Interface

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## INTRODUCTION

The European Commission has supported during the last decades scientific research programs focused on chemical processes occurring in the concrete-bentonite interface (ECOCLAY I, II and NF-PRO), since they can affect the feasibility of the clay barriers implemented for the isolation of nuclear wastes. The experiments performed focused on the stability of the bentonite in contact with concrete pore solutions. During the concrete degradation, highly alkaline waters from the concrete will diffuse through the clay barrier. The high pH (12.5 to 13.4) of the pore waters of concrete contrasts with the pH (7 to 8) of the pore waters in bentonite. This may produce structural transformations in the bentonite (smectite), dissolution/precipitation of minerals in the bentonite/concrete interface and, consequently, changes in the bentonite properties. Particularly, the studies carried out with the FEBEX bentonite in contact with concrete (CEM I, SR-type) showed montmorillonite dissolution, precipitation of zeolites (phillipsite-analcime), Mg-smectite, CSH gels and brucite  $[Mg(OH)_2]$ . These studies focused mainly in a highly reactive alteration environment ( $pH > 13$ ), (Cuevas et al., 2006).

During the NF-PRO integrated project the concrete-compacted bentonite interaction was also studied containing the materials and conditions as close as possible to real ones, with simultaneous heating and hydration. Several experimental cells were designed and mounted at a time in CIEMAT, starting in 2006. Three of them were already dismantled at different times up to 1.5 years. The main results were reported in Torres et al. (2009). Presently, in the context of the PEBS project, another cell has been dismantled after 4.5 years.

The results obtained in this long-term cell are the subject of the present abstract.

## EXPERIMENTAL PROCEDURE

The tests were performed in cells especially designed in CIEMAT for the experiments (Enresa, 2008; Fig. 1). Blocks of FEBEX bentonite were compacted with its hygroscopic water content (14%) at a dry density of  $1.65 \text{ g/cm}^3$ . At the bottom of the cell, the bentonite block was inserted just in contact with the heater ( $100 \text{ }^\circ\text{C}$ ).

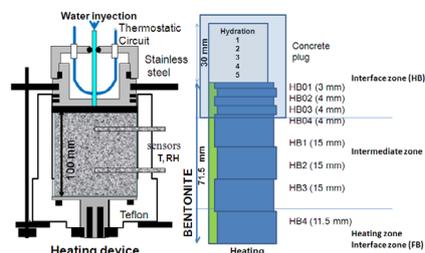


fig 1. Experimental cell and environmental conditions for the concrete-bentonite interaction tests. Sampling of the concrete-bentonite block.

On top of this, a 30-mm thick concrete block was placed. The hydration occurred through the concrete block. In a few days after the beginning of the test the sensor placed at the concrete-bentonite interface recorded stable relative humidities of 100% and temperatures of  $45 \text{ }^\circ\text{C}$ . The 4.5 years cell (HB4) was dismantled with the aim to preserve the concrete/bentonite interface. Then, the 30 mm piece of concrete and 15 mm of bentonite were isolated from the laboratory ambient. The remaining part of the compacted bentonite cylinder was cut in four sections. Later on, a detailed sampling of the concrete/bentonite interface and the cement matrix of the concrete was performed for mineralogical, microscopy, and geochemical

characterization (Fig. 2).



fig 2. Calcium (aluminite) silicate hydrates (CASH) needles and fibers (SEM).

## MATERIALS

The concrete used was manufactured following the specifications by CSIC-Torroja CEM-I, SR. The water injected to hydrate the concrete/bentonite cells is a synthetic clay water, representative of a Spanish clayey formation. Its composition is mainly  $\text{SO}_4^{2-}$ ,  $\text{Cl}^-$ ,  $\text{Na}^+$  and  $\text{Mg}^{2+}$ , at pH 7.5, close to 0.2 M global concentration. The FEBEX bentonite is high-grade bentonite (> 90 wt.% in smectite). The physico-chemical properties of the FEBEX bentonite, as well as its most relevant geochemical characteristics obtained during the projects FEBEX I and II are summarized in the final reports of the project (Enresa, 2006).

## CHARACTERIZATION

Each of the bentonite zones was used to analyze soluble elements in 1:8 (105  $^\circ\text{C}$  dry solid: deionized water) aqueous extract solutions. Major cations and anions were analyzed by Inductive Coupled Plasma - Optical Emission Spectrometry (ICP-OES) and ion chromatography, respectively. To determine the exchangeable cations of the samples, a  $\text{CsNO}_3$  solution was used to displace the exchangeable cations.

**palabras clave:** Bentonita, Hormigón, Frente reactivo.

**key words:** Bentonite, Concrete, Reaction front.

Mineralogy was studied by Fourier transform IR (FTIR) spectra and X-ray diffraction (XRD). XRD patterns were recorded on random powder samples of bulk bentonite and oriented < 2µm clay size fraction. In order to complete the geochemical characterization, a resin indurated polished vertical section of the concrete-bentonite interface was prepared. This block was used to analyze profiles of the chemical composition along the column axis as measured by Scanning Electron Microscopy with Energy Dispersive X-ray spectrometry (SEM-EDX). BET specific surface area was measured by N<sub>2</sub> adsorption. External specific surface area at the interface is almost identical to the original FEBEX bentonite (61 ± 2 m<sup>2</sup>/g), but it decreases to < 20 m<sup>2</sup>/g close to the heater, which is related to thermal drying phenomena.

## RESULTS

Soluble salts, both migrating through the concrete plug and those already present in the bentonite, concentrate as a function of time towards the heater zone. Cl<sup>-</sup> and Na<sup>+</sup> became more concentrated compared to SO<sub>4</sub><sup>2-</sup> and other cations. The behaviour of exchangeable cations is affected both by exchange reactions and dissolution/precipitation processes. Calcium and sodium increased in the bentonite-concrete interface with time. The uptake of calcium is favoured by the dissolution of the cement matrix and the increase of sodium is consistent with its prevalence in the percolating porewater. However, magnesium, decreases sharply at the interface zone and increases near the heater. Sodium exchanges by magnesium in the saturated areas, although some precipitation of Mg-rich phases at the alkaline interface cannot be discarded.

In spite of the change in the distribution of exchangeable cations, total cation exchange capacity of the interface area is within the original bentonite values (102 ± 2 meq/100g), which indicates a low degree of physical-chemical alteration at this interface.

Mineralogy was investigated by means of sampling at different levels: (1) Precipitates at the upper concrete interface; (2) at the concrete matrix, scrapped at several depths; (3) in crusts within the concrete-bentonite interface and (4) in mm sections practiced near the interface. The precipitates at the

hydration source are composed of brucite and aragonite, which indicated that carbonates and magnesium precipitated at the hydration-concrete interface and, consequently these components have been "filtered" by the concrete disc. FTIR spectra of the concrete matrix show a generalized carbonation of the matrix, indicated by the presence of calcite bands. Calcite was identified by XRD in all of the cement matrix samples. Ettringite was identified also in cement matrix samples near the interface and was observed precipitated at cement vesicles (SEM-EDX), which suggested that also sulphates determined in porewater have been retained in the concrete disc.

Crusts at the concrete/bentonite interface are composed of carbonates mixed with calcium (aluminate) silicate hydrates (CASH). New XRD sharp reflections have been assigned preliminary to a low Ca/Si anorthite-like phase (CASH-like phase). The interface bentonite samples displayed the typical FEBEX bentonite XRD pattern, but bentonite FTIR characteristic Al-Mg-Fe bands at 1000 and 700 cm<sup>-1</sup> showed changes and suggested the presence of new-formed or modified clay minerals. The montmorillonite XRD 1.498 Å peak is prevalent in all samples, but the clay within the crusts sampled showed peaks in the range of (060) tri-octahedral clays (1.53-1.52 Å), in agreement with FTIR data. These data suggest the formation of new tri-octahedral clays in small quantities, which should be further confirmed in the long-term experiments.

The presence of CSH 1.1 Å tobermorite phases was not conclusive. The bentonites near the interface have well-developed XRD peaks at near 14.5 Å and 12-11 Å, which is in agreement with the sodium enrichment of the exchange complex and hide the CSH signal. In contrast, the bentonite near the heater, HB4 4 shows virtually a unique reflection peak at 14.4 Å (Ca-Mg montmorillonite). The XRD study of Mg-saturated clay films displayed the normal behaviour of smectites, indicative of negligible alteration of the montmorillonite in the first 3 mm of interface.

A detailed observation of the interface in the backscattering electron SEM mode reveals the existence of 1 mm thickness portion of the bentonite interface that is crossed by sub-parallel bright veinlets, characteristic of calcium enrichments. A

fresh fractured chip of these rims was studied. Calcite, aragonite, and CASH compounds varying Ca/Si ratios (0.5-1.5) have been determined. These minerals appear as a sort of parallel crusts (presumably amorphous) confining microcrystals with different habits (laths, needles and fibres; Fig. 3). In addition, high magnification EDX chemical profiles confirm the concentration of calcium and also magnesium in the first 1-1.5 mm of bentonite from the interface.

This concrete-bentonite interaction long-term test has been conducted under relevant environmental conditions in a nuclear waste repository. FTIR, XRD and SEM-EDX results have reveal that mineralogical alteration of compacted bentonite in contact with a CEM-SR concrete merely affects to its first 3mm thickness. However, chemistry of porewater and exchangeable cations changes affected longer thickness than mineralogical changes. The interaction of this geochemical front with the thermal gradient is currently under research.

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