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# Magnesium perturbation in low-pH concretes placed in clayey environment—solid characterizations and modeling

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# ABSTRACT

In the framework of the CI project, the interaction of two different low-pH cements (ESDRED and LAC) with Opalinus Clay (OPA) at Mont-Terri rock laboratory was studied. SEM-EDS analyses showed after 2.5 and 5 years of interaction a Mg-enriched zone associated with a decalcification of the C-S-H near the OPA contact zone of both cements. TGA and XRD investigations indicate that hydrotalcite and brucite predict classically in modeling are not formed. <sup>29</sup>Si NMR and FTIR analyses showing a high polymerization degree of the Si-network typical of a sheet-like structure as observed for M-S-H. TEM/EDS investigations of the Mg enriched zone of both concretes indicate that the formed Mg phase exhibits a gel-like structure. New reactive transport modeling with the HYTEC code corroborates the formation of M-S-H at the interface.

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## 1. Introduction

The radioactive wastes disposal design in France foresees the storage in a clayey rock to contain radionuclides and to protect the human and its environment. Whatever kind of exogenous materials will be placed in contact with the surrounding clayey rock, the perturbations of the containment and retention properties must be minimized. ILLW cells are envisaged to be constituted by cementitious materials (liner, confinement plugs, and wastes containers) while the sealing zone of each cell and of each gallery entrance will consist of a bentonite plug placed between two concrete barriers, such that a large number of clay/concrete interfaces would be created [1].

The natural interstitial water in the clayey rock will cause physicochemical modifications in the concrete matrix (carbonation, leaching, ettringite precipitation) due to its neutral pH value and the high concentrations of sulfates, carbonates, and magnesium [2–6]. On the other side, the hyper alkaline pore solution of Portland-based cementitious material will alter the degraded clayey materials and change its porosity [7–11].

In order to limit the alkaline disturbance in clayey rocks, new cementitious binders, so-called low-pH cements, were developed based on Portland cement blended with pozzolanic materials such as silica fume and/or fly ashes in binary or ternary mixes [12–15] to destabilize portlandite, form additional C-S-H (calcium silicate hydrate) and reduce the pH values in the pore solution.

Studies concerning the evolution of low-pH cementitious materials in clayey environment are scarce and our understanding of the physico-

chemical evolution of low-pH cementitious materials in clayey environment is very limited.

It has been observed that for low-pH cement in contact with clayey environment, mainly leaching and carbonation occur [6,11,16,17]. Leaching leads to a partial [11] or total [6] decalcification of C-S-H to amorphous silica resulting in a decrease of strength and the formation of macroporosity. The carbonation is linked to the precipitation of calcite [6,11,16,17] and thus the decalcification of C-S-H. Additionally, a magnesium enrichment in the decalcification area is reported. Jenni et al. [11], Dauzères et al. [6], and Garcia Calvo et al. [16] linked this Mg perturbation to formation of hydrotalcite and the possible formation of M-S-H (magnesium silicate hydrates). On the formation of M-S-H could only be speculated due to its amorphous nature. Attempts to model this magnesium perturbation using available thermodynamic data (without M-S-H thermodynamic data) suggested the formation of hydrotalcite [18]. However, the recent determination of the solubility data for M-S-H phases [19] makes it now possible to account for the possible formation of M-S-H in thermodynamic modeling of the perturbation of a low-pH concrete in clayey environment.

This paper is focused on the evolution of two low-pH concretes placed in contact with the Opalinus clay in the Mont-Terri underground research laboratory (Switzerland) as part of the CI (cement–clay interaction) experiments, especially on the magnesium perturbation zone. Samples of the in situ interfaces are characterized by XRD, TGA, FTIR, <sup>29</sup>Si-NMR, SEM, and TEM/EDS analysis and compared to synthetic reference M-S-H described in detail [19–21]. The experimental results are





compared with the results of reactive transport modeling with the HYTEC code.

#### 2. CI experiment, materials, methods, and numerical approach

#### 2.1. The CI experiment

The long-term CI (cement-clay interaction) experiment in the Mont-Terri underground laboratory (Switzerland) aimed to investigate the physico-chemical interactions between cementitious material (CEM I or low-pH) and clayey materials (Opalinus clay and bentonite), which contain a multionic solution.

Two low-pH concretes have been emplaced: a concrete named ESDRED (60% CEM I + 40% silica fume), a low alkali cement named LAC (90% CEM III/B + 10% nanosilica). Sand and gravels used for aggregates for the both cements were rounded river sediment according to SN EN 12620. The in situ experimental device consisted of two vertical boreholes until 9 m depth in the Opalinus clay (OPA) filled with these two low-pH cements, a CEM I, and a bentonite plug (Fig. 1).The diameter of each borehole was equal to 37.5 cm as detailed in Jenni et al. [11]. Samples extraction was performed by drilling (diameter 80 mm) parallel to the rock stratification ( $45^\circ$  compared to the tunnel base surface) after 2.5 and 5 years of interaction. The studied interfaces in this paper, after 5 years of interaction, were originated from the BCI-13 (LAC/OPA interface) and BCI-14 (ESDRED/OPA interface) boreholes. A more detailed protocol of sample extraction and preservation procedures is given in Jenni et al. [11].



**Fig. 1.** In situ experimental device of the CI experiment, with the different sampling campaign by slanted drilling (parallel to the rock stratification): after 2.5 years of interaction (white) and after 5 years of interaction (telescoped) [11].

# 2.2. Concretes

The concretes were prepared on site and poured in the boreholes, to obtain a perfect interface between the host rock and the cementitious materials. For ESDRED a water/solid ratio of 0.5 and for LAC of 1.08 were used. In both cases, an aggregate (silica and calcareous aggregates) / cement weight ratio of 8.5 was used.

The composition of the two used low-pH cements (without aggregates) is fully detailed in two papers: for the LAC in [22] and the ESDRED in [23], including the chemistry of the different components, the evolution of the pore solutions compositions during the hydration, and the hydrate compositions. The present paper summarizes only the cementitious matrix general properties and the data used for the modeling.

# 2.2.1. LAC

The LAC cement was a mix of 90% of CEM III/B 42.5 L (66% of slag + 34% of clinker) with 10% of nanosilica corresponding to a ternary mix of 10% of nanosilica, 59% of slag, and 31% of clinker. A polycarboxylate-based superplasticizer was used, and a w/b (water on binder ratio) of 1.1. The chemical composition of the binder, the pore solution and the cement paste are detailed in the Table 1.

The hydrated material was composed mainly by C-S-H or C-(A)-S-H. The measured Ca/Si ratio by SEM-EDS in the matrix varies between 0.8 and 1.3 and the Al/Si ratio was closed to 0.1. The pore solution had a higher alkali concentration than the ESDRED pore solution and a pH value equal to 12.2.

## 2.2.2. ESDRED

The ESDRED cement was a binary blend of 40% silica fume with 60% CEM I 42.N with a w/b equal to 0.5. The same polycarboxylate-based superplasticizer and an aluminum sulfate-based set accelerator were added to the water during the preparation, as detailed in the Table 2. Experimental investigation and thermodynamic modeling [23] indicated that low Ca/Si C-S-H and ettringite were the main components of the hydrated material; small quantities of hydrotalcite, calcite, and FH<sub>3</sub> are also present. The Ca/Si ratio of the matrix varied between 0.8 and 1.2 and the Al/Si ratio was inferior to the 0.1 (detection limit). The pore solution after 1310 days of hydration contained a relatively high concentration of calcium ( $\approx$  30 mmol/L) and very low alkali concentrations resulting in a pH of 11.7.

For the modeling, aggregates were considered as non-reactive solid phases.

## 2.3. The environmental conditions

The Opalinus clay (OPA) formed 170 million years ago is mainly composed by clayey minerals: illite, illite/smectite mixed-layer, chlorite, and kaolinite, as well as calcite and quartz as described in detail in [24] and summarized in Table 3.

The mineralogical composition is very variable and depends on the location in the tunnel. In order to have a representative composition for the modeling, an average composition was chosen. The pore solution contained in a porosity of 18% has a high concentration of sodium, chloride, sulfate, and magnesium and a pH value of 7.2, in equilibrium with a carbonated system and a  $CO_2$  fugacity of  $1 \times 10^{-2}$  atm.

Synthetic C-S-H and M-S-H samples and LAC and ESDRED pastes hydrated for 3.5 and 7 years were analyzed for comparison. The M-S-H and C-S-H preparation properties are described in Lothenbach et al. [21], the preparation and hydration of the LAC paste are detailed in Lothenbach et al. [22] and of ESDRED in Lothenbach et al. [23].

# 2.4. Analytical methods

Samples extracted from the perturbation zone between low-pH concrete and OPA were polished and used for TEM and SEM analysis. Download English Version:

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