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► **To cite this version:**

Catherine Lerouge, Nicolas Maubec, Guillaume Wille, Christine Flehoc, Catherine Guerrot, et al.. In-situ long-term interactions between different concrete formulas and CO_x claystone in a deep disposal context. Clay conference 2024: International Conference on Clays in Natural and Engineered Barriers for Radioactive Waste Confinement, Bundesgesellschaft für Endlagerung (BGE); Bundesanstalt für Geowissenschaften und Rohstoffe (BGR), Nov 2024, Hannover - Germany, Germany. hal-04519824

HAL Id: hal-04519824

<https://brgm.hal.science/hal-04519824v1>

Submitted on 25 Mar 2024

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***In-situ* long-term interactions between different concrete formulas and COx claystone in a deep disposal context**

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Many deep disposal concepts for radioactive wastes in natural clay formation use cementitious materials as structural support material for access galleries and disposal drifts of cells (e.g. concrete/shotcrete), backfill and waste matrix. Thus, cementitious materials can be in contact with clay host rock. Due to contrasting chemical properties between cementitious materials and clays, chemical gradients occur at concrete-clay interface involving chemical and mineralogical perturbations. Nevertheless, long-term in situ mineralogical evolution remains poorly documented in the literature.

In 2009, five experiments were placed between -5m and -7m below the concrete invert of the main drifts of Andra's underground research laboratory to be dismantled at five deadlines (1-2, 5, 13 years). For each experiment, a 101 mm-diameter borehole was drilled in the Callovian-Oxfordian clay rock (COx). Three concrete formulations (CEM I, CEM V and low pH) were poured, separated by bentonite/sand compacted interlayers (Figure 1a). The interlayers were saturated with synthetic pore water between each concrete emplacement. In 2021, 12 years after the beginning of the experiment an overcoring was carried out on one of the borehole to characterize the concrete/COx interfaces.

A multi-technical approach including micro X-ray fluorescence, X-ray diffraction (XRD), SEM observations and electron microprobe mapping was used to investigate mineralogical and chemical changes in clay host rock and concrete materials. Additional cation exchange capacity, anion leaching, strontium isotopes on the clay exchanger, and (C, O, Sr) isotopes on calcite were conducted on the clay host rock at different distances from the interface, to further investigate chemical changes of clay and calcite fraction in the clay host rock.

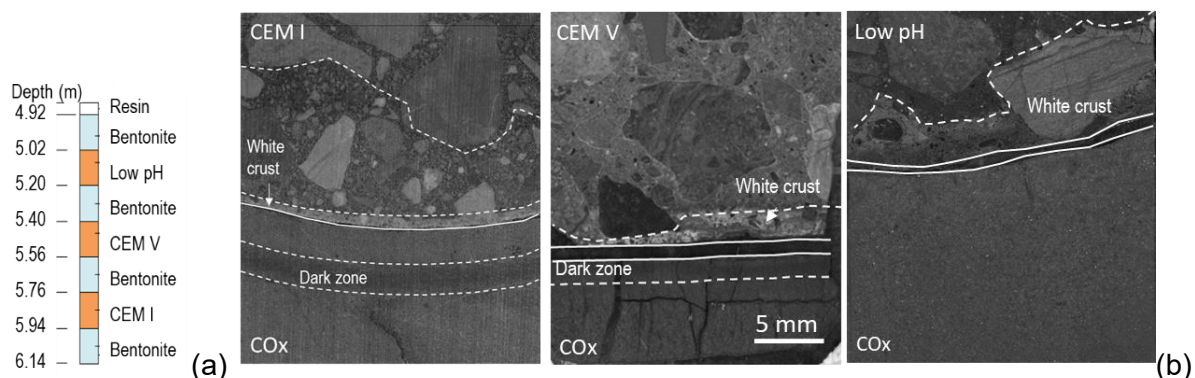


Figure 1: (a) Sketch of the in situ experiment; (b) Photographs of the interfaces between COx and the 3 concretes (CEM I, CEM V, Low pH).

Macroscopic observations

Visible perturbations at interface between concrete and COx are limited and depend on the cement type (Figure 1b). The CEM I/COx and CEM V/COx interfaces are marked by a white crust on concrete side (0.5 to 3 mm), and a dark zone on COx side (up to 5mm from contact with concrete for the CEM I/COx interface). No evidence of perturbation is visible at interface between the low pH concrete and COx.

Mineralogical perturbations

COx in contact with the three concretes does not show major mineralogical change, even in the dark zone developed in clay at interfaces with CEM I and CEM V concretes. However, XRD and electron microprobe mapping provide evidence of the small presence of smectite at interface (0-100 μm) with the CEM I and CEM V concretes, and of gypsum at interface with the CEM V and low pH concretes. Observations in optical cathodoluminescence show a decrease of the luminescence in the dark zones, suggesting a lower calcite content.

On the concrete side, white crusts are rich in calcite; a little further concrete is rich in ettringite. In the low pH concrete, a 2-3 mm zone in contact with COx consists of saponite, calcite with CSH (Figure 2).

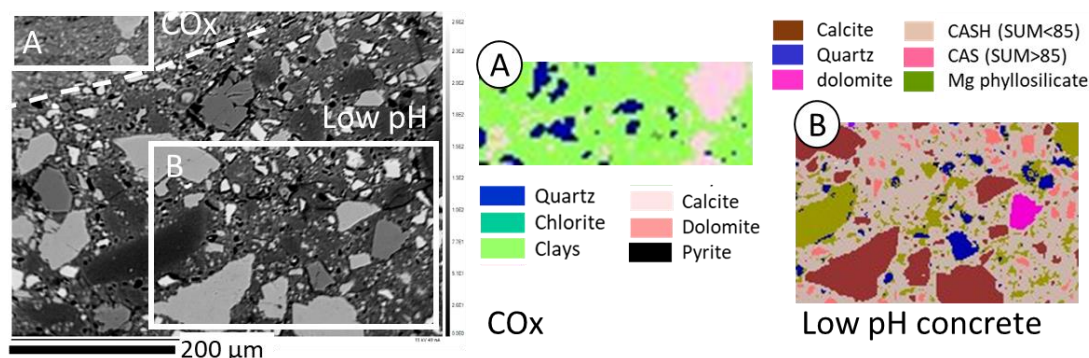


Figure 2: BSE image of the low pH-Cox interface and mineral maps obtained by treatment of electron microprobe mapping of COx (A) and low pH concrete (B).

Chemical perturbations

Chemical perturbations detected by micro-XRF and electron microprobe are very limited on the both sides of the interfaces. The white crust developed in CEM I and CEM V concrete show a sulfur depletion, followed by an enrichment in sulfur associated to the presence of ettringite. In the low pH concrete, the 2-3 mm zone in contact with COx is highly rich in Mg (up to 14 wt% MgO) associated to the presence of saponite, and poor in sulfur. On the COx clay side, the dark zone observed near interfaces with CEM I and CEM V are rich in Mg (~7 wt.% MgO) compared to natural COx (~2-3 wt.%). A similar Mg enrichment was identified in COx in contact with the low pH concrete, but this zone is limited to the first 100-200 μm .

Leaching experiments of COx with deionized water do not show any significant change of the concentration of chlorides dissolved in pore waters of COx in contact with the three types of concretes, while sulfate concentrations are abnormal (~x10) in pore waters of COx near CEM V and low pH concretes. What is consistent with the observation of gypsum.

Cation exchange capacity and cation distribution on the clay exchanger are not significantly modified. An enrichment of the clay exchanger in Mg is associated to the dark zones observed in COx near the interfaces of CEM I and CEM V. A Ca enrichment is also locally measured when concentrations in dissolved sulfates increase. At the interface of the CEM I/COx sample, the $^{87}\text{Sr}/^{86}\text{Sr}$ isotopic ratio of the clay exchanger is highly contrasted to that of concrete. It is almost homogeneous and very similar to natural clay exchanger.

The (C, O) isotopic composition of the calcite fraction analysed in the first 15 cm near the interfaces with the three concretes do not give evidence of reactivity beyond the first millimetre. The $^{87}\text{Sr}/^{86}\text{Sr}$ isotopic ratios of the calcite fraction analysed in the first 15 cm near the interface with the CEM I concrete do not give evidence of reactivity beyond the first millimetre.

Such long interaction time for an in situ engineered analogue provides a bridge between laboratory-derived data and the long time scale of safety assessment modelling [1]

[1] A. Jenni, U. Mäder, C. Lerouge, S. Gaboreau, B. Schwyn. "In situ interaction between different concretes and Opalinus Clay" *Physics and Chemistry of the Earth* 70–71 (2014) 71–83.