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Constraints from sulfur isotopes on the origin of gypsum at concrete/claystone interfaces

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ABSTRACT

Two in situ concrete/claystone interfaces were sampled at the laboratory level in the Andra Meuse/Haute Marne (France) Underground Research Laboratory (URL) in order to study five years of interactions between Callovian–Oxfordian (COx) claystone and two cementitious materials (concrete bottom slab and shotcrete on the walls of the main gallery), with a specific focus on sulfur. Combined mineralogical, chemical and sulfur isotopic investigations were carried out to define the degree of the perturbation of the sulfur system in the claystone and in both the cementitious materials. At both interfaces, results show that the main perturbation on the claystone side is the formation of scarce μm-sized gypsum, the sulfur content of which is essentially derived from pyrite oxidation. The distribution of gypsum is highly correlated with the fissure network of the damaged zone due to excavation of the gallery. Its presence is also often associated with a loss of cohesion of the concrete/claystone interface. Due to the small amounts of gypsum and its μm-size, measurements were performed by ion microprobe. Adaptations were needed on account of the reactivity of gypsum and sulfates in general under the beam. The use of ion microprobe analysis provided evidence of high local isotopic heterogeneity that could be attributed to kinetic fractionation effects. Some analyses suggest a minor contribution of dissolved sulfates in pore water of claystone and possibly of concrete. The perturbation on the concrete side is marked by a significant increase in the bulk sulfur content within three millimeters of the interface with the claystone, showing a sulfur gradient from claystone to concrete. The main objective of this work was to define the extent of the chemical and mineralogical perturbations, taking into account in situ URL conditions, i.e. hydrodynamic conditions (shotcrete sprayed on the gallery walls and subjected to ventilation of the galleries), damaged zone of claystone induced by excavation and multi-scale heterogeneity. This identifies the relevant parameters to better constrain predictive reactive transport models of concrete/claystone interactions at a realistic scale.

1. Introduction

Concrete is used in the design of deep disposal facilities for nuclear waste storage in natural clay formations, not just for access structures, galleries and disposal cells but also as waste containment material (ONDRAF/NIRAS, 2001; Nagra, 2002; ANDRA, 2005; SKB, 2006). Upon contact, modifications in the mineralogy and physical properties of the clayey and cementitious materials are expected, due to their contrasting chemical properties. For this reason, considerable research effort has been dedicated to (i) understanding concrete/claystone interactions and (ii) predicting the evolution of the system over long time-scales that are representative of nuclear waste disposal. This includes laboratory cement/clay interaction experiments (Claret et al., 2002, 2012; Gaucher et al., 2004a; Fernandez et al., 2006; Devol-Brown et al., 2007; Dauzères et al., 2010), predictive reactive transport modeling studies (Savage et al., 1992; Gaucher et al., 2004a; De Windt et al., 2008; Marty et al., 2009; Trotignon et al., 2009) and natural analog studies (Khoury et al., 1992; Alexander and Smellie, 1998; Techer et al., 2006; Elie et al., 2007; Fourcade et al., 2007; Savage et al., 2010; Savage, 2011). Additionally, mineralogical, chemical and physical characterizations of samples collected from in situ

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concrete/claystone interfaces originating from Underground Research Laboratories (URL) provide constraints on the reaction paths and on the extent of perturbation for short time interactions (Hades URL (Mol): Read et al., 2001; Tournemire URL: Tinseau et al., 2006; Dauzères et al., 2010; Gaboreau et al., 2011; Techer et al., 2012; Mont Terri, URL; Meuse Haute Marne URL: Gaboreau et al., 2012; Jenni et al., 2014).

Three major chemical and mineralogical reactions are expected at Portland concrete/claystone interfaces: dissolution/precipitation of silicates, carbonation and reactivity of the sulfur system. Mineral changes among silicate phases are marked by precipitation of calcium silicate hydrates (C–S–H) with low Ca/Si ratios on the concrete side and by dissolution of primary minerals such as montmorillonite or quartz accompanied by the formation of secondary minerals such as C–(A)–S–H or zeolite on the claystone side (Bérubé et al., 1990; Savage et al., 1992; Cuevas, 2004; Ramírez et al., 2005). The carbonation process essentially develops as a thin calcite + low Ca/Si C-S-H zone on the concrete side and is associated with portlandite dissolution in the cement (Hodgkinson and Hughes, 1999; Dauzères et al., 2010; Gaboreau et al., 2012), and with the gradient of CO_2 partial pressure (P_{CO2}) from the clay formation (high P_{CO2}, near neutral pH) to the concrete (low P_{CO2}, high pH) (Gaboreau et al., 2012; Techer et al., 2012). This kind of observation is in agreement with results from predictive reactive transport modeling (Marty et al., 2009; Trotignon et al., 2009).

The reactivity of the sulfur system is much more complex and may have significant consequences on the chemical and physical properties of both materials. At interfaces between concrete and sulfur-bearing materials such as marine claystone, a sulfate gradient towards the concrete is expected. This sulfate supply to the concrete side (external sulfate attack) initiates the precipitation of secondary needle-shaped ettringite ($3CaO{\cdot}Al_2O_3{\cdot}3CaSO_4{\cdot}32H_2O$), with minor gypsum ($CaSO_4{\cdot}2H_2O$) (Brown and Taylor, 1999; Dauzères et al., 2010; Jenni et al., 2014; Lothenbach et al., 2010; Kunther et al., 2013; Ramírez et al., 2005; Santhanam et al., 2001), but also of thaumasite ($CaSiO_3{\cdot}CaCO_3{\cdot}CaSO_4{\cdot}15H_2O$) in concrete containing a source of carbonate (Blanco-Varela et al., 2006; Freyburg and Berninger, 2003; Schmidt et al., 2008). Such reactions have a strong influence on the physical integrity of the medium, because both gypsum and ettringite are expansive phases that can cause degradation of concrete. On the claystone side, physical and chemical deterioration of clayrock may be triggered by the presence of sulfur minerals stable in natural reducing environments but which become unstable under atmospheric and alkaline conditions (Caldeira et al., 2010; Czerewko et al., 2003, 2011). A major problem is pyrite oxidation, which causes significant volumetric and mineralogical changes and may affect nearby materials (Cripps et al., 1993; Woo et al., 2013), but also acts as a local sulfate supply to the chemical gradient towards concrete.

In the non-disturbed (i.e. representative of the far field) in situ conditions, gypsum is under-saturated in COx pore water. Unsaturated conditions at the interface may have favored pore water evaporation and $CaSO_4$ salt precipitation (Gaboreau et al., 2012). Saturation of gypsum may also be attained at such interfaces in other different ways, including: (i) oxidation of pyrite in claystone due to diffusion of atmospheric O_2 originating from the gallery, which would supply dissolved sulfate from the clay towards the interface, or, quite the opposite, (ii) a supply of dissolved sulfate from freshly deposited concrete slurry to clay.

In order to tackle this issue and to elucidate the dominant reason for gypsum precipitation (the hypotheses formulated above are not mutually exclusive), a mineralogical, chemical and isotopic study focused on sulfur was performed on two five year old cementitious materials (shotcrete and concrete bottom slab/COx clay interfaces). These interfaces are of major interest for two reasons. Firstly, they are not derived from an experiment but concern part of the actual wall from the main gallery of the URL. Consequently, these interfaces have been subjected to in situ chemical and physical conditions occurring in a tunnel, i.e. partial de-saturation of claystone associated with the excavation damaged zone, re-saturation by clay formation and the interface between claystone and concrete subjected to atmospheric conditions. Secondly, as discussed by Gaboreau et al. (2012), the precipitation of gypsum is locally present in claystone and at the interface between clay and concrete. Consequently, the concrete/claystone interface provides degradation information on both materials by sulfate attack, under in situ conditions.

Mineralogical and textural observations of sulfur-bearing phases in claystone were performed to determine their stability and the major reactions involved at the interface on the claystone side. Micro-X-ray fluorescence (μ-XRF) was used to measure bulk sulfur content and identify the chemical gradient at the interface. The sulfur isotopic composition of gypsum at both the cementitious materials/COx clay interfaces was measured by ion microprobe and compared to sulfur isotopic compositions of the main sulfur reservoirs in claystone: porewater sulfate (Vinsot et al., 2008), pyrite (Lerouge et al., 2011), and sulfates in concrete. All this information was gathered to build a coherent framework of the processes taking place at the concrete/claystone interface and leading to gypsum precipitation.

2. Materials and methods

2.1. Materials

2.1.1. Concrete/claystone interface

Samples originate from the Underground Research Laboratory (URL) of Bure, operated since 2004 by the French National Radioactive Waste Management Agency (ANDRA). The URL is located in the Eastern part of the Paris Basin in a thick clay-rich formation of Callovian–Oxfordian age (ANDRA, 2005).

Cementitious materials were used for the construction of the URL. Among them, concrete (also called shotcrete) was sprayed onto the walls of the access drifts and onto the walls of the galleries; the thickness of the concrete varies from 10 to 30 cm, depending on the position of the wall. Concrete (also called concrete bottom slab) was also poured onto the floor of the galleries. The concrete used was composed of 67% millimeter-size alluvial aggregates, 18% of CEM I binder, 3% of fly ash, and 0.4% of plasticizer added to 10% of water.

A first interface (shotcrete, called wall 1) was sampled on the wall of an access drift at the laboratory level ($Z_{NGF} \sim -124$ m). The claystone in contact with the concrete is located in the excavation damaged zone (EDZ). A second interface (concrete bottom slag, called floor 2) was sampled on the floor of the gallery ($Z_{NGF} \sim -124$ m). The concrete of both interfaces is five years old. The drift is ventilated; consequently the interfaces are considered partially unsaturated (e.g. Trotignon et al., 2009). Owing to the low mechanical strength of the interfaces, exacerbated by the fact that the clayey side is in the excavation damaged zone, samples were embedded with a thick coating of viscous Araldite resin to preserve cohesion and to limit oxidation from atmospheric O_2. Detailed sampling procedures and major chemical, physical and mineralogical data on the wall 1 interface are available in Gaboreau et al. (2012).

Eighteen small pieces of samples, thirteen at wall 1 interface and five at floor 2 interface, were collected and prepared for mineralogical characterization. Two pieces (one of each interface) were selected for sulfur isotope measurements by ion microprobe. Coarse-grained gypsum material in fissures crosscutting the claystone was separated by handpicking for sulfur isotope analyses