

Evidence of (Ca, Mg) smectite formation at Clay/cement interfaces

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Several experimental and in situ studies have investigated cementitious materials and clay host rock interactions in the ANDRA Underground Laboratory at Bure, France (Gaboreau et al., 2012) and in the Mont Terri channel (Jenni et al., 2014; Mäder et al., 2017). As it has been observed at interfaces between the both materials, the extent of detectable perturbations is highly dependent on the nature of cementitious materials. Adapting the concrete recipe has therefore been a common approach to limit the interactions. Although Ordinary Portland cements (OPC) are considered to be relevant materials for nuclear waste repository condition, “low pH” (~11-12) cement recipes have been developed by adding pozzolan and blastfurnace slag to reduce the alkali content and to limit interactions (Lothenbach et al., 2012).

An interface between low alkali cement (LAC)-based concrete (CEM III/B containing 66% slag and 10% nano-silica) and Opalinus Clay (OPA) was characterized for mineralogy and chemistry in the framework of the CI project (Mont Terri Consortium, Switzerland). Volumes of materials impacted by interactions in term of mineralogy and chemistry do not seem very different from those observed at OPC/Clay interfaces. The first millimeter of the LAC concrete in contact with OPA is a white crust formed of more than 25 % of a Mg-bearing cement phase (also called M-S-H in Dauzères et al., 2016), ~11 weight % of calcite, associated with low Ca/Si ratio calcium silicate hydrates (C-S-H) and other cement phases. The M-S-H is distributed relatively homogeneously along the contact with OPA. A specific mineralogical and chemical focus on M-S-H including electron diffraction combined with transmission electron microscopy and electron microprobe demonstrates that M-S-H is a ditriocahedral (Ca, Mg) smectite with the following average chemical composition:

$(\text{Ca}_{0.5\pm 0.2}) (\text{Mg}_{2.0\pm 0.4}, \text{Fe}_{0.2\pm 0.1}, \text{Al}_{0.5\pm 0.3}, \square_{0.3\pm 0.3}) (\text{Al}_{0.9\pm 0.2}, \text{Si}_{3.1\pm 0.2}) \text{O}_{10} (\text{OH})_2$, \square representing vacancies in the octahedral site.

Some analyses near the LAC concrete/OPA interface show a charge balance highly positive due to very high Mg content. It may be due to (i) a mixing of M-S-H with another Mg-bearing phase, or (ii) the presence of Mg as brucite $[\text{Mg}(\text{OH})_2]$ in the interlayer and the formation of a chlorite-type precursor.

On the clay side, the cation distribution of the clay exchanger is modified in the first centimeters of clayrock near interface; the increase of K charge is lower than in the case of OPC/clay interface, while Mg is less depleted and even increases at the LAC concrete /OPA interface. Assuming that Al, Mg and Si result from the dissolution of

phyllosilicates, as described for OPC/clay interactions, a lower Mg depletion on the clay side should indicate a lower dissolution of phyllosilicates in clayrocks in contact with LAC concrete than in clayrocks in contact with OPC concrete. However, the precipitation of (Ca, Mg) smectite at LAC interface and chemical changes suggest that the diffusion of Si, Al and Mg remains from clay to concrete, even if possible contribution of Mg and Al from slags cannot be neglected. The (Ca, Mg) smectite formation rather indicates an attenuated interaction between both materials, and a relative continuity of the sorption capacities of the materials at the concrete/clayrock interface.

M-S-H present at the interface between LAC concrete and OPA is for the first time described as a (Ca, Mg) smectite. The presence of (Ca, Mg) smectite as product of interaction between natural clayrock and low pH cementitious material is consistent with numerical modeling of OPC concrete/clay interactions (Marty et al., 2015; Trotignon et al., 2007).

Current mineralogical and chemical investigations performed on other kind of interfaces (OPC/clayrock (COx and OPA) and Class G cement/clayrock) combining observations and spot analyses on provide evidence of M-S-H which have very similar chemical composition to (Ca, Mg) smectite identified at the LAC concrete/OPA interface, occurring as small (<100 µm) dark masses disseminated in the cement matrix of low Ca/Si ratio C-S-H and calcite all along the interface with Clay.

References:

- Dauzères, A., Achiedo, G., Nied, D., Bernard, E., Alahrache, S., Lothenbach, B., 2016. Magnesium perturbation in low-pH concretes placed in clayey environment—solid characterizations and modeling. *Cement and Concrete Research* 79, 137-150.
- Gaboreau, S., Lerouge, C., Dewonck, S., Linard, Y., Bourbon, X., Fialips, C.I., Mazurier, A., Prêt, D., Boschenck, D., Montouillout, V., Gaucher, E.C., Claret, F., 2012. In-situ interaction of cement paste and shotcrete with claystones in a deep disposal context. *American Journal of Sciences* 312, 314-356.
- Jenni, A., Mäder, U., Lerouge, C., Gaboreau, S., Schwyn, B., 2014. In situ interaction between different concretes and Opalinus Clay. *Physics and Chemistry of the Earth, Parts A/B/C* 70–71, 71-83.
- Lothenbach, B., Le Saout, G., Ben Haha, M., Figi, R., Wieland, E., 2012. Hydration of a low-alkali CEM III/B–SiO₂ cement (LAC). *Cement and Concrete Research* 42, 410-423.
- Mäder, U., Jenni, A., Lerouge, C., Gaboreau, S., Miyoshi, S., Kimura, Y., Cloet, V., Fukaya, M., Claret, F., Otake, T., Shibata, M., Lothenbach, B., 2017. 5-year chemico-physical evolution of concrete-claystone interfaces. *Swiss Journal of Geosciences*. Accepted for publication.
- Marty, N.C.M., Bildstein, O., Blanc, P., Claret, F., Cochevin, B., Su, D., Gaucher, E.C., Jacques, D., Lartigue, J.E., Mayer, K.U., Meeussen, J.C.L., Munier, I., Pointeau, I., Liu, S., Steefel, C.I., 2015. Benchmark for multicomponent reactive transport codes across a in the context of complex cement/clay interface. *Computational Geosciences* 19, 635-653.
- Trotignon, L., Devallois, V., Peycelon, H., Tiffreau, C., Bourbon, X., 2007. Predicting the long term durability of concrete engineered barriers in a geological repository for radioactive waste. *Physics and Chemistry of the Earth, Parts A/B/C* 32, 259-274.