Modelling of the COx/glass interactions: case of the long term MVE experiment

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High-level nuclear waste (HLW) is confined in a glass matrix packaged into stainless steel canister and carbon steel overpack. The Callovian–Oxfordian (COx) claystone layer located in the north-eastern Parisian basin is currently investigated as a potential host-rock. As the COx contains minerals that can feed the near-field with soluble elements (e.g. Mg) that can enhance the glass alteration, the study of the COx/glass interactions is of primary importance to evaluate the containment capacity of the glass over the time period required to the decrease of the radioactive elements. Several studies focused on clay behavior in temperature (Gailhanou et al., 2017), on the glass behavior (Gin et al., 2012) and on integrated system: glass/iron/clay (Schlegel et al., 2016) but no modelling study of the COx/glass interactions in situ at the temperature of the COx formation had already been made.

This work aims at studying the glass alteration in presence of the COx in purely diffusive conditions. The studied glass is called SON68 and is the inactive analogous of the of the French R7T7 HLW glass. The vertical descending borehole is twelve meters deep and contains a two meters high test chamber with a series of three stacked clay blocks. Those blocks were drill in order to be filled with glass powder separated from the COx by sintered stainless steel filters (Linard et al., 2015). The test interval was then closed and saturated with synthetic porewater representative of the host-rock (Gaucher et al., 2009). To reach diffusive conditions, the pressure in the test interval was rose to 40 bars close to the expected pressure of the COx formation. **A** flow rate equal to 15 mL/minute between the interval and a module located in the drift is maintained. The pH, Eh, electrical conductivity, temperature and mass are measured online and samples can be collected at chosen time.

A diffusive transport model based on the model developed by Appelo et al. (2008) was built. The hydrological parameters were implemented according to this work and to the particularity of the test (Linard, 2010). The model considers the COx whose parameters (minerals, exchangers) are based on the model published by Gaucher et al. (2009) and the glass (SON68). A glass alteration model based on the work of Frugier et al. (2008) has been implemented in Phreeqc.

First the deuterium tracer was modeled with a porewater diffusion coefficient of 8 10^{-10} $m^2.s^{-1}$. The porosity of the formation was set to 0.18. Because of the complexity of the perturbation that occurred during the whole test, every external change influences the test is not yet considered in the modelling. Thus, the current model does not enable to reproduce the higher deuterium and iodine concentrations measured at 546 days (Figure 1.a) but match all the bromide data. Despite the difficulties on the hydrological parameters, the pH reaches a steady state in the modelling once the COx buffered the pH (Figure 1.b). The initial high pH is close to 9 that is the value imposed by the glass dissolution. This gap occurs because the system is closed in the model the first 427 days of reaction. However, it appears that several water entrance from the formation lower the pH in the system toward values usually encountered in the clay (pH 7.2). The modeled chlorine agrees with the measured one (Figure 1.b). This element is only influenced by the porewater chemistry and is not modified during the test. A difference appears for the sodium that is underestimated and remains at the value of the porewater

injected at the beginning of the test. This discrepancy can be attributed to an underestimation of the water coming from the formation that is richer in sodium than the injected water and/or from the glass dissolution that is currently underestimated (Figure 1.b). The first explanation is assumed because the porewater measured in the field varies in function of the samples (Vinsot et al., 2008), so a difference with the injected water can occur. The second hypothesis is linked to the first one as a higher solution renewal will lead to higher glass dissolution and then to higher boron, lithium and sodium release in solution. Furthermore, desaturation process occurring during the drilling and leading to salt precipitation cannot be discarded. Those salt will dissolve during the entrance of the water coming from the formation (Vinsot et al., 2013). It is worth noting that the Si concentration is in equilibrium with cristobalite. Furthermore, modelling tests proved that secondary phases usually considered like hydroxyapatite or sepiolite highly influence the results and cannot be considered at thermodynamic equilibrium otherwise glass dissolution is overestimated.

This model is a first step to investigate the interaction between the COx and the glass SON68. The several perturbations occurring during the test (water entrance, leakages, and thermal variations) have to be considered more accurately because they highly influence the system and then the glass dissolution. Improvements concerning these matters are already under progress.

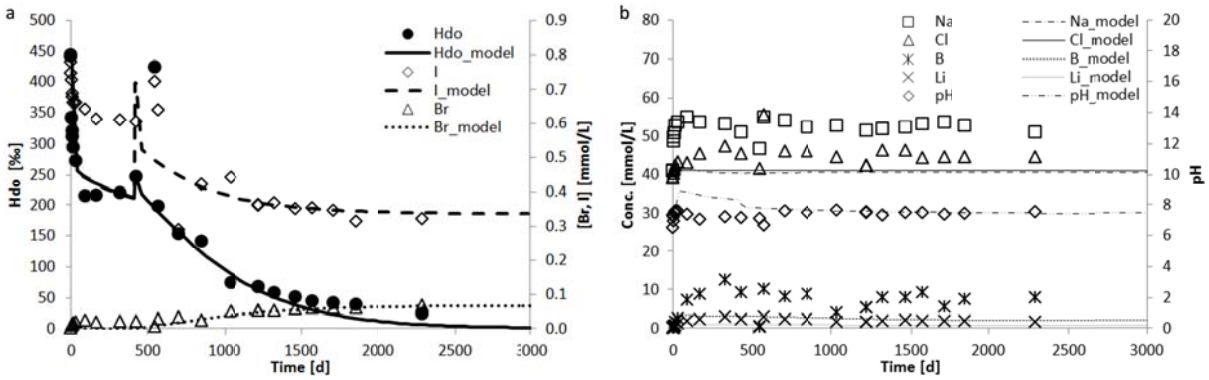

Figure 1. Comparison of experimental data measured over the time in the MVE long term test to the modeling results obtain with the GRAAL model and Phreeqc; a. deuterium, iodine and bromide; b: sodium, chlorine, boron, lithium and pH.

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