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Effects of a thermal perturbation on mineralogy and pore water composition in a clay-rock: An experimental and modeling study

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The physical and chemical properties of clay-rocks are, at least partly, controlled by the chemical composition of their pore water. In evaluating the concept of disposing of radioactive waste in clay-rock formations, determining pore water composition is an important step in predicting how a clay-rock will behave over time and as a function of external forces, such as chemical and thermal perturbations. Thermally induced modifications of the pore-water chemistry of the clay rock must be assessed since the pore water chemistry can affect the rates of corrosion of metallic materials used in the disposal facility (Gaucher et al., 2009; Altmann, 2008). This study, carried out as part of a collaborative BRGM/Andra research program, aimed to assess experimental and modeling methodology to calculate pore water composition in a clay-rock as a function of temperature (up to 80 °C). The results of these investigations were recently published in the literature (Gailhanou et al., 2017).

Hydrothermal alteration experiments were carried out on clay-rock samples at 80°C, for 6 and 20 months. We conducted comprehensive chemical and mineralogical characterization of the material before and after reaction, and monitored how the chemical parameters in the liquid and gas phases changed. The experimental results are compared with the *a priori* predictions resulting from various models that differ in their hypotheses on the reactivity of the minerals present in the system (in particular, chlorite and Fe-bearing phases). The results between the pore water composition predictions using the various models are similar, so that thermodynamic equilibrium cannot be assessed unequivocally in these experiments. One of the main reasons for this failure is linked to the fact that, contrary to models developed at 25°C (Gaucher et al., 2009; Beaucaire et al., 2012), models at 80°C are not constrained easily by analyzing solid samples having reacted at 80°C, even for a long time. Most of the predicted mineralogy changes were too subtle to be tracked quantitatively. However, from observing the neo-formation of minerals such as goethite (Fig. 1), we were able to assess the prominent role of Fe-bearing phases in the outcome of the experiments, especially for the measured pH and p_{CO_2} values. After calibrating the amount of reacting Fe-bearing phases with our data, we propose a thermodynamic model that is able to predict the chemical evolution of the systems under investigation as well as the evolution of other systems already published in the literature (Beaucaire et al., 2012), with the same clay-rock material but with significant differences in experimental conditions (especially higher initial p_{CO_2} and solid to liquid ratio). This result gave confidence in the model predictions but was not deemed sufficient to be confident in the model adequacy and usefulness in conditions different than the one experimentally tested. To improve our understanding of the equilibria taking place in the Fe-Ca-Mg carbonate system and on kinetics considerations in the models, several

investigations are in progress, notably ten-year equilibration experiments and a dedicated *in-situ* experiment with a thermal perturbation up to 80 °C in the Meuse Haute Marne Underground Research Laboratory (LSMHM).

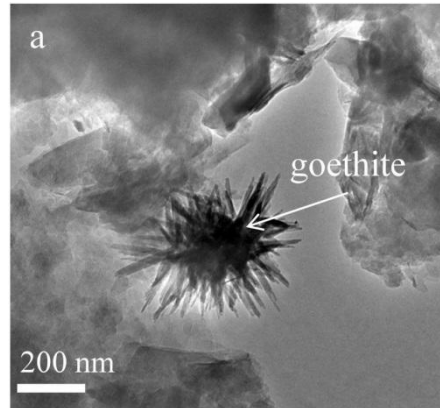


Fig. 1. TEM micrographs of neo-formed goethite in samples reacted at 80°C for 20 months in an anoxic atmosphere.

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