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Geochemistry of Callovo-oxfordian argillite at 80°C: batch experiments and modeling

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Introduction

A repository of high-level nuclear wastes in the Callovo-Oxfordian (COx) clayrock will lead to a temporary increase in temperature locally around the disposal cells, up to about 80°C. Thermally induced modifications of the pore-water chemistry of the clayrock 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). In the present study, carried out as part of a collaborative BRGM/Andra research program, the results of long-term batch experiments performed at 80°C, are compared with compositions predicted using a model based on the one developed for 25°C. These experiments include a previous study (Gailhanou et al., 2012) that is completed by recent long-term batch experiments in order to verify the reproductibility of results and better understand the reactivity of the COx rock-solution system at 80°C. In this aspect, selectivity coefficients for exchange reactions Na/K, Na/Ca, Na/Mg and Na/Sr in the clay-porewater system have been acquired at 80°C and have been considered to model the experiments.

Batch experiments

A first series of two experiments were performed with COx rock samples in contact with synthetic water, at 80°C, for durations at 6 and 20 months (Gailhanou et al., 2012). Few changes were detected in the mineralogy between initial and final solids. The only noticeable change was the formation of needles of nanocrystalline goethite on pyrite particles in the 20 months experiment (Gailhanou et al., 2012). A new series of experiments is being conducted to follow the reactivity of the clayrock-solution-gas system at 80°C for durations from 20 months to 10 years. The results at 20 months are presented here and are compared with the previous ones. In addition, a last experiment was carried out with an initial CO₂(g) partial pressure in the gaseous phase fixed at a higher value than the value predicted by modeling approach ($\log p_{CO_2} = -0.6$ instead of -1.1). This new 20 months experiment aims at verifying that the carbonate system re-equilibrates or not with the whole system independently of the initial pH. All these experiments were prepared at 25°C under anoxic atmosphere in closed reactors, with solution compositions close to the predicted pore water composition (Gaucher et al., 2009). Afterwards, each system was heated at 80°C. p_{CO_2} was monitored during the experiments. At the end of the experiments, the suspension was filtered at 0.1 µm at 80°C, under anoxic atmosphere. The pH was measured at 80°C; major cations (Ca, Mg, K, Na, Sr) and anions (notably Cl, SO₄), TIC and minor and trace elements (notably Si, Al, Fe, Zn, Pb) were analysed.

In addition, selectivity coefficients were obtained for Na/K, Na/Ca, Na/Mg and Na/Sr cation exchange at 80°C on the clay fraction (< 2 µm).

Modelling of batch experiments

The predictive model of composition as a function of temperature was developed based on the model from Gaucher et al. (2009) and using the PHREEQC code and Thermoddem database (Blanc et al., 2012). Modelling prediction were in fairly good agreement with the results of the first series of experiments, at 6 and 20 months, if the following primary mineral assemblage was considered: quartz, pyrite, carbonates (calcite and dolomite), sulfates (celestite), aluminosilicates (chlorite and illite) and goethite (Fig. 1). This model differs from the model of Gaucher et al. (2009) at 25°C by the replacement of siderite by goethite (Fig. 1). This modification led to a noticeable improvement of the Fe concentration prediction. The introduction of goethite in the model instead of siderite, is in agreement with the presence of nanogoethite detected in the initial sample and in the solid after 20 months experiment.

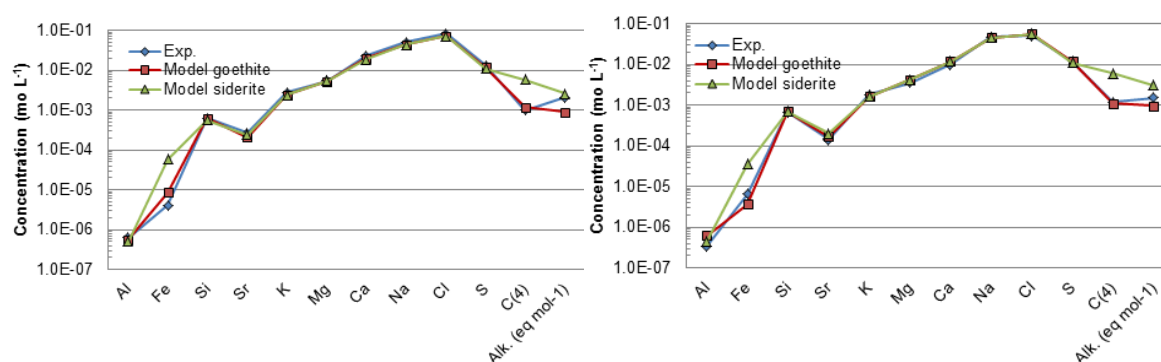


Fig 1. Results of the first series of experiments. Comparison between experimental and modeled concentrations (a) at 6 months at 80°C and (b) at 20 months at 80°C.

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