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Influence of temperature on the geochemistry of Callovo-Oxfordian argillite: batch experiments and modelling at 80°C

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Introduction

A repository of high-level nuclear wastes in the Callovo-Oxfordian (COx) clay rock 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 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). The chemistry of COx pore water has been studied at ambient temperature (~ 25°C) using modelling approaches constrained by parameter values measured on core samples (Gaucher et al., 2006, 2009) and by measurements of pore water collected by means of specially designed in-situ experiments (Vinsot et al., 2008). In particular, the predictive model from Gaucher et al. (2009) reproduces the measured, in situ pore-water composition without any estimated parameters.

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.

Batch experiments

Two batch experiments have been performed with COx rock samples in contact with synthetic water, for respectively 6 and 20 months. The experiments were prepared at 25°C under anoxic atmosphere in closed reactors, with solution compositions close to the pore water composition. Afterwards, each system was heated at 80°C. During the experiments, measurements of P_{CO_2} were carried out as this parameter is considered as an indicator of the reactivity of this carbonate-dominated system. At the end of the experiments, the suspension was filtered at 0.1 µm at 80°C, under anoxic atmosphere. The pH was also 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.

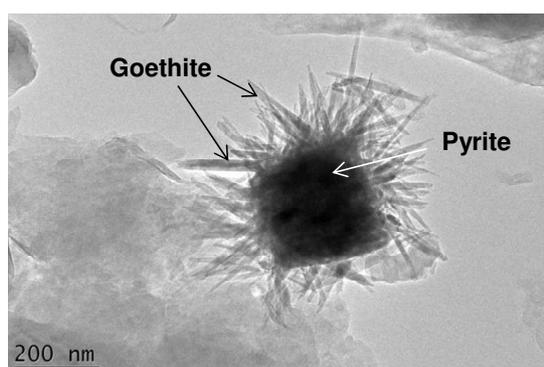
Concerning the solids, some minor changes were detected in the mineralogy between initial and final solids, essentially partial dissolution of celestite and a small increase in the amount of dolomite. Besides, an interesting change was observed by TEM with the formation of needles of nanocrystalline goethite on pyrite particles for the solid from the 20 months experiment (see figure). Such needles were not observed on the initial solid, although magnetic measurements at low temperature on the sample revealed the presence of nanocrystalline goethite. Moreover, an increasing of the Fe²⁺/Fe³⁺

ratio in the octahedral environment of clay minerals, compared with initial ratio, was evidenced by ^{57}Fe Mössbauer spectrometry.

Modelling of batch experiments

The predictive model of composition as a function of temperature was developed, based on the Gaucher et al. (2009) model and using the PHREEQC code and Thermoddem database (Blanc et al., submitted). As a first approximation, the model considers a primary mineral assemblage with quartz, pyrite, carbonates (calcite, dolomite and siderite), sulfates (celestite), aluminosilicates (chlorite and illite). Moreover, the model takes into account exchange reactions and dissolution reaction kinetics for the potentially more reactive minerals.

For both cases, at 6 and 20 months, the comparison between estimated and observed concentrations of ions in solution are in rather good agreement for pH, Si, Al, major cations (Ca, Mg, Na, K, Sr) and for sulphates and chlorides. The calculated concentrations of Fe are, on the other hand, too high compared with the measured concentrations, for both experiments. The control on the Fe(II) solubility by siderite was already questioned in Gaucher et al. (2009). This problem is being studied, notably by considering the presence of nanogoethite detected in the initial sample and in the solid after 20 months experiment.



TEM image of needles of nanocrystalline goethite on a pyrite particle, after 20 months experiment at 80°C.

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