

Fe(0)-CLAYS INTERACTIONS AT 90°C UNDER ANOXIC CONDITIONS: A COMPARATIVE STUDY BETWEEN CLAY FRACTION OF CALLOVO-OXFORDIAN AND OTHER PURIFIED CLAYS

**C. Rivard^{1*}, M. Pelletier¹, F. Villieras¹, O. Barrès¹, J. Ghanbaja²,
A. Kohler², M. Galmiche¹, N. Michau³**

- 1. Laboratoire Environnement et Minéralurgie (LEM), UMR 7569 CNRS-INPL, Ecole Nationale Supérieure de Géologie, Vandœuvre-lès-Nancy, 54501, France
(camille.rivard@ensg.inpl-nancy.fr)**
- 2. Service Commun de Microscopies Electroniques et de Microanalyses (SCMEM), Université Henri Poincaré Nancy université, 54506, Vandœuvre-lès-Nancy, France**
- 3. ANDRA, 1/7 rue Jean Monnet, 92298, Châtenay-Malabry Cedex, France
(nicolas.michau@andra.fr)**

In the context of the geological disposal of high-level radioactive waste it is of prime importance to understand the interactions between the saturated clay formation and steel containers. This can be achieved through an in-depth analysis of iron-clay interactions. Previous studies on the subject investigated the influence of solid/liquid ratio, iron/clay ratio, temperature and reaction time [Guillaume (2002), Lantenois (2003), Perronnet (2004)].

The aim of the present study is to explain Callovo-Oxfordian-Fe(0) interactions by determining the role of each mineral phases present in the Callovo-Oxfordian (clay minerals, quartz, carbonates and pyrite) on the mechanisms of interaction between metal iron and clay particles. In that context, it is especially important to understand in detail the influence of clay nature and to obtain some insight about the relationships between interaction mechanisms at the molecular scale and crystallographic properties (particle size, TO or TOT layers, amount of edge faces...). The influence of the combination of different clays and the addition of other minerals must also be studied.

In a first step, the Callovo-Oxfordian argillite from the Andra's underground research laboratory was purified to extract the clay fraction (illite, illite-smectite, kaolinite and chlorite). Batch experiments were carried out in anoxic conditions at 90°C in the presence of background electrolyte (NaCl 0.02 M.L⁻¹, CaCl₂ 0.04 M.L⁻¹) for durations of one, three or nine months in the presence of metallic iron powder. Experiments without iron were used as control. The iron/clay ratio was fixed at 1/3 with a solid/liquid ratio of 1/20. The above mentioned experiments were also carried out in parallel on other purified clays: two smectites (Georgia bentonite and SWy2 from the Clay Minerals Society), one illite (illite du Puy) and one kaolinite (KGa2, from the Clay Minerals society).

At the end of the experiments, solid and liquid phases were separated by centrifugation. For the liquid phase, pH and Eh measurements as well as chemical analyses were carried out. The solid fraction was characterized using a combination of classical techniques (chemical analyses, X-ray diffraction, Fourier Transform Infrared spectroscopy, scanning and transmission electron microscopy, nitrogen adsorption and XPS and Mossbauer analyses). Additional observation tools, based on the use of synchrotron radiation (Scanning Transmission X-ray Microscopy (STXM) and Micro-X-ray Absorption Spectroscopy (μ -XAS)) were used to obtain more detailed data on the status of iron and location in individualized clay particles.

The combination of all these experimental techniques and comparison between reference clays and Callovo-Oxfordian clay fraction provides information about the evolution of pristine iron and clay minerals and newly formed phases.

In a second step, quartz, calcite or pyrite were added to Callovo-Oxfordian clay fraction and the same experimental procedure was applied in order to evaluate the impact of these accessory minerals on the evolution of clays fraction and iron.

In addition, two other physicochemical parameters were investigated: the role of physical contact between metallic iron grains and clay particles, and the influence of gas exchanges. Indeed, these parameters can modify the kinetics of the reaction between iron and clay, and consequently, change the nature of newly formed minerals.

References:

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