



Weathering of an argillaceous rock in the presence of atmospheric conditions: A flow-through experiment and modelling study

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ABSTRACT

The construction of a repository for high-level radioactive waste (HLW) in a deep clay formation will produce large volumes of excavated rock that must be stored of at the surface. This material will be weathered for decades to century, and its evolution with time must be assessed in order to decide on its future technological use (i.e. backfill materials of HLW repository) and to evaluate its impact on the surrounding environment (e.g. acid drainage). Predictive modelling that required a consistent set of kinetic data must be used for such evaluation. To this end, the kinetics of mineralogical transformations were investigated on an argillaceous rock from the tailings stored at the surface of an underground research laboratory (Callovian-Oxfordian – COx – argillaceous rock, Bure, France). Mineralogical analysis and flow-through experiments were combined in order to quantify the oxidation kinetics of this material. Deionized water was brought into equilibrium with the atmosphere and was percolated through a suspension of powdered COx rock. Examination of the samples prior to and after the experiments showed that the main transformations were pyrite oxidation associated with calcite and dolomite dissolution. The acidity produced by pyrite oxidation was totally buffered by the dissolution of carbonate minerals that in turn affected the composition of the clay exchanger. Geochemical modelling was used to confirm the relevance of a selected mineralogical assemblage with associated kinetic parameters in order to evaluate the extent of COx rock weathering with time.

1. Introduction

The chemical weathering of argillaceous rocks plays an important role in providing nutrients to ecosystems, controlling river and ocean chemistry, and regulating atmospheric CO₂ over geological time (Kump et al., 2000; Ma et al., 2011). Argillaceous rocks react with meteoric carbon dioxide (CO₂) and oxygen (O₂) from the atmosphere and nested chemical reaction fronts form in the subsurface in response to acid-base and redox reactions (Brantley et al., 2013). The understanding and quantification of the development of these fronts with time is however challenging at large spatial and temporal scales. The use of argillaceous rock formations as a possible host rock for geological disposal of nuclear waste will inevitably result in the store of large amounts of tailings

at the surface. The long-term prediction of the temporal evolution of these clay materials under the influence of meteoric weathering faces the same challenges as the study of natural shale near-surface weathering. In the present study, we aimed to qualify and quantify the reactivity of an argillaceous rock in the presence of meteoric weathering conditions. In the eastern Paris basin (France), Andra (the French national radioactive waste management agency) studies the Callovian-Oxfordian clay formation (COx) as a possible host rock for deep underground storage of nuclear waste (Landais, 2006). For this purpose, an underground laboratory, excavated in COx claystone and located 500 m below the surface, has been in operation since the early 2000s. Construction of the laboratory has produced large volumes of excavated COx rock, and it can be estimated that several million cubic meters will

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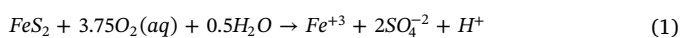
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be excavated during the entire operating period of a future geological repository facility. This excavated geological material is generally piled onto the soil surface where it forms a technosol (Scholtus et al., 2015). Although the excavated COx material (currently stored on the surface as tailings) serves no specific function, several options are being considered: for example, the suitability of the COx argillite as a raw material for the production of alkali-activated binders has been investigated (Gharzouni et al., 2017), and some of this material is also considered for use in the completion of the waste deposit operations to fill in the excavated galleries. The COx tailings to be stored on the surface for several decades to a century will be subject to weathering that could modify the COx properties from both chemical (goal of this study) and permeability perspectives. The main weathering effects are expected to be mechanical disintegration of the rock and chemical oxidation of the sulfide and reduced iron-bearing minerals. COx oxidation mainly results in pyrite weathering (Belcourt, 2009; Bildstein and Claret, 2015; De Windt et al., 2014; Vinsot et al., 2014): as it oxidizes with exposure to oxygen and water, pyrite releases sulphate and proton. The overall reaction under oxic conditions is expressed as:



The release of ferric ions causes precipitation of iron (oxy)hydroxides (e.g. ferrihydrite, goethite). If carbonates are absent, oxidation of pyrite present in mine tailings produces acid conditions that increase the rate of weathering of other primary minerals, possibly ultimately resulting in acid mine drainage (AMD) with high concentrations of contaminants such as As, Cu, Zn, Pb and Cd (Akcil and Koldas, 2006; Alakangas et al., 2012; Chandra and Gerson, 2010; Johnson and Hallberg, 2005). However, if carbonates are present, as in the COx tailings, the protons released are buffered and the resulting pore water should have a near-neutral pH (e.g. Akcil and Koldas, 2006; Alakangas et al., 2012). Since the COx tailings are being considered as sealing/backfill material after the nuclear waste disposal site has operated for approximately a century (Tang et al., 2010; Zhang, 2014), the transformation of the material (e.g. clay alteration) has to be assessed and quantified in order to assess potential impacts on future uses of the material. Moreover, several radioactive elements potentially released from waste packages are redox-sensitive (e.g. Altmann, 2008) and knowledge of the oxidation state of the sealing/backfill material is therefore crucial to make accurate prediction for the speciation of these elements.

A previous work published by Marty et al. (2015a) put forward a selection of kinetic data for primary minerals of the COx clay-rocks. The authors showed excellent consistency between modelling predictions and the experimental data obtained by Suzuki-Muresan et al. (2011) at various temperatures (25, 50 and 90 °C). However, the kinetic data were only validated for a few parameters (i.e. final pH and Si concentrations), so that additional comparisons of the full chemistry (e.g. Ca, Mg and Al concentrations) was required to improve confidence in the data selection proposed. Flow-through experiments were then carried out and the chemistry of the outlet solutions was monitored over time, with a particular focus on sulphates. The reacting materials were carefully examined before and after the experiments in order to detect potential mineralogical transformations, and the experimental results were simulated with a reactive transport model.

2. Materials and methods

2.1. Materials

2.1.1. Claystone samples

Claystone samples were taken in February 2016 from tailings at the surface site of the Andra Underground Research Laboratory (URL) in Meuse/Haute-Marne, France. The material in the tailings originated from the excavation of tunnels in the URL in 2013. Since the

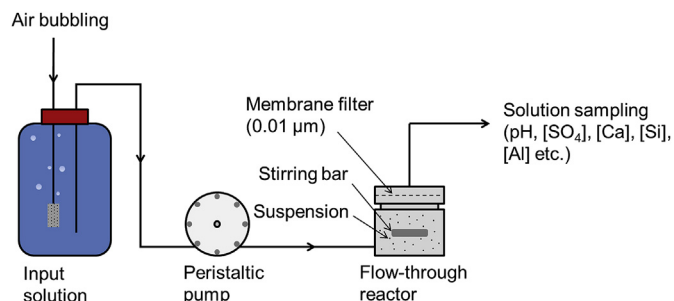


Fig. 1. The experimental apparatus, modified from Marty et al. (2015b). COx tailing samples were weathered using ultra-pure water brought into equilibrium with atmospheric conditions. Alkalinity, pH, SO_4 , Cl, Al, Fe, Ca, Si, Sr, Na, K and Mg concentrations as well as flow rates were monitored as a function of time.

excavation, the COx claystone has been exposed to weathering. Samples were taken from the first twenty centimeters of the upper part of the tailings. Samples were kept in sealed boxes to minimize evaporation of pore water and exposure to the atmosphere. An initial water content of 14% was measured by water mass loss after sample freeze-drying. Flow-through experiments were started within a month following the sampling.

2.1.2. Input solutions

Deionized water was bubbled with atmospheric air for two days prior to the experiments in order to bring the water into equilibrium with atmospheric O_2 and CO_2 partial pressures ($\log p\text{O}_2 \sim -0.67$ and $\log p\text{CO}_2 \sim -3.45$ in bar).

2.2. Flow-through experiments

2.2.1. Experimental setup

Weathering experiments were carried out on COx tailings using a flow-through reactor (Fig. 1) at room temperature ($20\text{ °C} \pm 2\text{ °C}$). The total volume of the reactor was 84 mL. The input solution was continuously bubbled under an air flux in order to maintain atmospheric CO_2 and O_2 partial pressures during the experiments. The solution was injected into the reactor with a peristaltic pump (Watson Marlow, 205U). A magnetic stirrer rotating on an axle kept the solid material in suspension and prevented any grinding of the mineral grains between the bar and the bottom of the reactor (Metz and Ganor, 2001). A $0.01\text{ }\mu\text{m}$ membrane filter (Sartorius cellulose nitrate filter) at the outlet of the reactor prevented the loss of solid material during the experiments. Outlet solutions (exposed to atmosphere, Fig. 1) were sampled as a function of time to measure their chemical composition (pH, alkalinity, SO_4 , Cl, Al, Fe, Ca, Si, Sr, Na, K and Mg concentrations) and to monitor the flow rate. Flow-through experiments were conducted at various solid concentrations in two stages (Table 1). In stage 1, a high flow rate of $\sim 1\text{ mL}\cdot\text{min}^{-1}$ was set in order to rapidly leach the species

Table 1

Experimental conditions of flow through experiments.

Experiment	Initial dry mass (g)	Flow rate ($\text{mL}\cdot\text{min}^{-1}$)		Duration (h)	
		Stage 1	Stage 2	Stage 1	Stage 2
F-1	6.82	1.05 to 0.28	0.024 ± 0.001	53	451
F-2	3.44	1.22 to 0.91	0.025 ± 0.002	53	618
F-3	6.98	1.22 to 0.39	0.025 ± 0.001	53	618
F-4	10.3	0.96 to 0.55	0.025 ± 0.002	52	621

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