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Dissolution of montmorillonite in groundwater simulants (MOPO)

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Introduction

The behaviour of bentonite in alternating groundwater conditions is an important part of safety assessment of nuclear waste repository. The favourable properties of bentonite for nuclear waste disposal, like high swelling capacity and high cation exchange capacity are greatly based on the properties of bentonite's main mineral component montmorillonite. However, most of the studies done so far, have concentrated on bentonite, which contains also accessory minerals complicating also the interpretation of analysed data.

Aim of this study is to gain better understanding on the behaviour of montmorillonite in different groundwaters, alteration of montmorillonite and formation of secondary minerals.

The results of the experiments are compared to the modelled results and the models are then hopefully advanced further.

Materials and methods

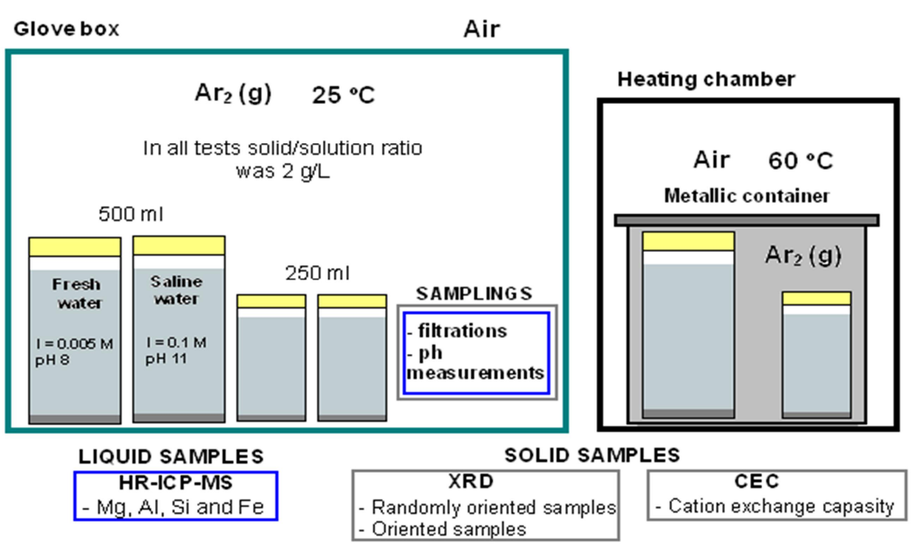
The experiments were planned based on the literature review and pre-models of montmorillonite dissolution.

$(Ca_{0.06}Na_{0.16}K_{0.025})(Al_{1.51}Fe_{0.205}Mn_{0.005}Mg_{0.28}Ti_{0.01})(Si_{3.99}Al_{0.01})O_{10}(OH)_2$

The thermodynamic equilibria of groundwater simulants were calculated by using geochemical equilibrium model EQ3/6. Calculations ensured (at least theoretically) that nothing precipitates from water itself.

	Fresh water (mmol/L)	Saline water (mmol/L)
Na^+	3.23	40.38
Ca^{2+}	0.36	20.41
K^+	0.28	0.17
Cl^-	3.66	79.70
SO_4^{2-}	0.28	-
Br^-	-	0.24
pH	8	11
Ion strength	0.005	0.1

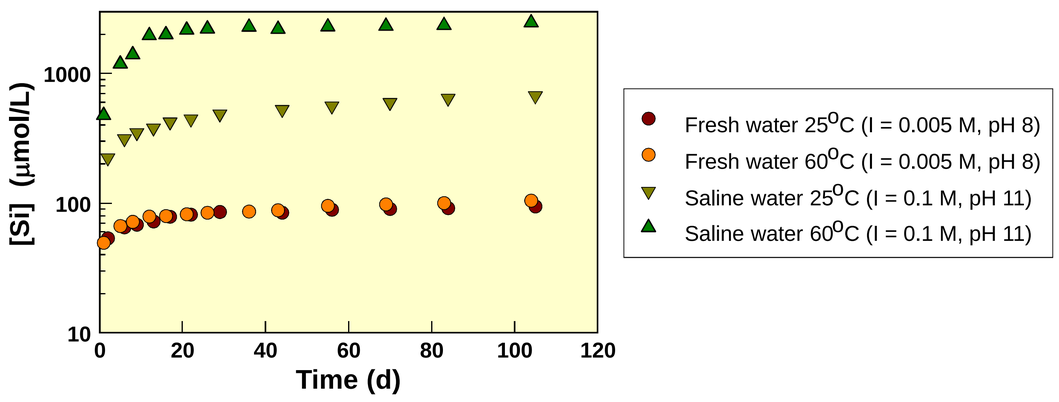
The batch experiments were conducted with purified Swy-2 montmorillonite in two types of water at 25 and 60 ºC in anaerobic conditions.



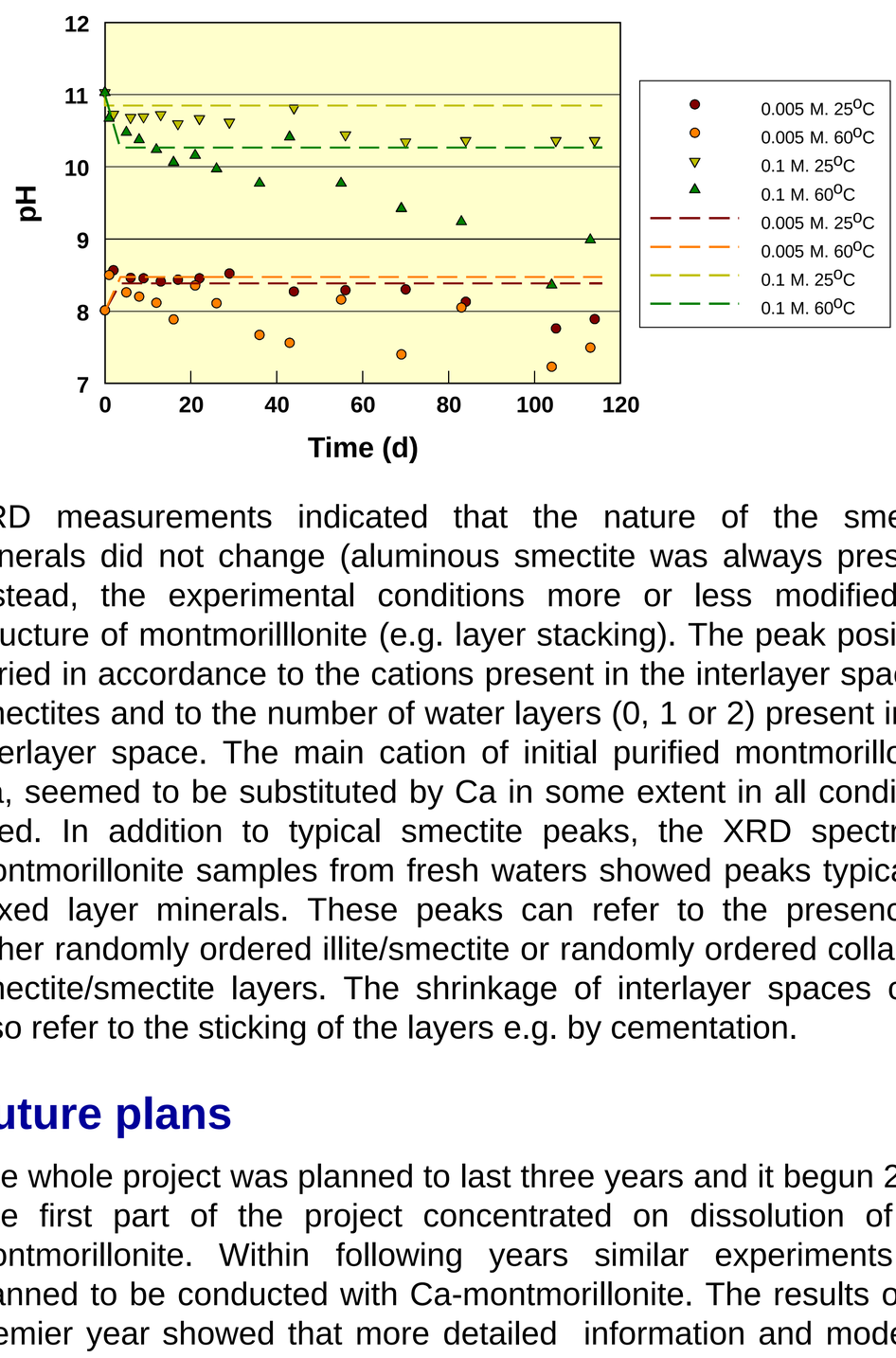
The elemental concentrations of ultra filtrated solution samples were analysed with high resolution inter coupled plasma mass spectrometer (HR-ICP-MS). The purified montmorillonite and the solid material gained from experiments were analysed with XRD (X-ray diffraction) at ERM (Etudes Recherches Matériaux) in Poitiers, France.

Results and discussion

The analysed concentrations of Al, Mg and Fe were between 0.01 and 2 µmol/L and no clear increase in these concentrations was detected. Al and Fe concentrations fluctuated in most cases, which agreed with the observation from the literature, that especially Al and Fe take part of precipitation or sorb on developing secondary minerals. Mg concentrations were usually higher at the beginning of the experiment than at the end, expect in the case of moderately saline solution in 60 ºC, in which concentration first decreased and then started to increase. The concentrations of Si were much higher than concentrations for other elements in multielemental analysis. Prelimariny results for Si are presented below.



The dissolution of montmorillonite was modelled with TOUGHREACT, so that the salinity of waters was taken into account. Modelling results were compared with the experimental result. The comparison of pH results (see below) reveals the need for development of the models.



XRD measurements indicated that the nature of the smectite minerals did not change (aluminous smectite was always present). Instead, the experimental conditions more or less modified the structure of montmorilllonite (e.g. layer stacking). The peak positions varied in accordance to the cations present in the interlayer space of smectites and to the number of water layers (0, 1 or 2) present in the interlayer space. The main cation of initial purified montmorillonite, Na, seemed to be substituted by Ca in some extent in all conditions used. In addition to typical smectite peaks, the XRD spectra of montmorillonite samples from fresh waters showed peaks typical for mixed layer minerals. These peaks can refer to the presence of either randomly ordered illite/smectite or randomly ordered collapsed smectite/smectite layers. The shrinkage of interlayer spaces could also refer to the sticking of the layers e.g. by cementation.

Future plans

The whole project was planned to last three years and it begun 2010. The first part of the project concentrated on dissolution of Na-montmorillonite. Within following years similar experiments are planned to be conducted with Ca-montmorillonite. The results of the premier year showed that more detailed information and modelling are needed to broaden the understanding behaviour of montmorillonite in different kinds of groundwaters.