

Clay-organic Association Kinetics Monitored by C(1s) Spectromicroscopy

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Beamline(s): X1A

Introduction: The importance of colloid enhanced contaminant transport depends preliminary on the colloid chemistry, their stability in the geochemical environment and the reversibility of metal/colloid association. Numerous electrokinetic experiments have been performed to elucidate the effect of humic (HA) and fulvic (FA) acids sorption onto inorganic colloid (clay, iron oxide) surface charge and coagulation kinetics. The groundwater used in this study originates from the Gorleben aquifer (Lower Saxony, Germany) representing the far-field of a potential deep geological final storage site for radioactive waste in Germany. The aim of this study is to elucidate the FA/HA stabilization/association of inorganic colloids and the time dependent C(1s) functional group changes.

Methods and Materials: Details on spectra deconvolution are given in [1]. The Clay fraction $< 2 \mu\text{m}$ of Na-montmorillonite (Swy-2, Crook County, Wyoming, U.S.A.) was separated by centrifugation. Suspensions of 10 g/L montmorillonite in natural groundwater (GoHy-2227) were prepared for kinetic sorption experiments. For detailed description of the groundwater composition and the Gorleben site it is referred to the study of [2]. Samples were taken after 1h, 7d and 6 months Swy-2/DOC reaction time, centrifugated and the supernatant discarded. The centrifugate was resuspended with MilliQ water and 1 μL was taken immediately and squeezed between two SiN_3 windows of the wet cell assembly designed by [3] for spectromicroscopic analysis. Additionally to the untreated original groundwater isolated freeze dried HA and FA were characterized by X-Ray spectromicroscopy.

Results & Discussion: Spectra de-convolution of isolated Gorleben groundwater (GoHy-2227) fulvic acid (FA) shows a significant higher carboxyl group content compared to the humic acid (HA) isolate. Kinetic investigations on the GoHy-2227 DOC uptake of smectite particles display at short contact times a significant increase in carboxyl functional group, which could be localized by microscopic investigations preliminary concentrated at the particle broken edges silanol/aluminol groups (Fig. 1, B3). An explanation for this observation might be a specific sorption (surface complexation) via carboxyl groups and a diffusion related higher attachment probability of small FA molecules compared to larger HA molecules. With increasing reaction time (7d, 6months) the clay associated organic carbon increases as documented by the optical density increase (Fig. 1). Carbon functional groups on edge sites still remains, but significantly higher aromatic content associated with basal surfaces and also broken edge sites can be observed. The enhanced sorption of aromatic compounds with increasing reaction time can be related to an increase in mineral surface hydrophobicity of broken edge and isomorphous substitution sites by low polar organic acids as shown for anthracene adsorption enhancement in the presence of low polar benzene carboxylates [4].

References:

- [1] Schäfer, T., Hertkorn, N., Artinger, R., Claret, F., Bauer, A. *J. de Physique IV* (submitted)
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- [4] Angove, M.J., Fernandes, M.B., Ikhsan, J., *J. Coll. Interface Sci.* **247/2** (2002) 282-289.

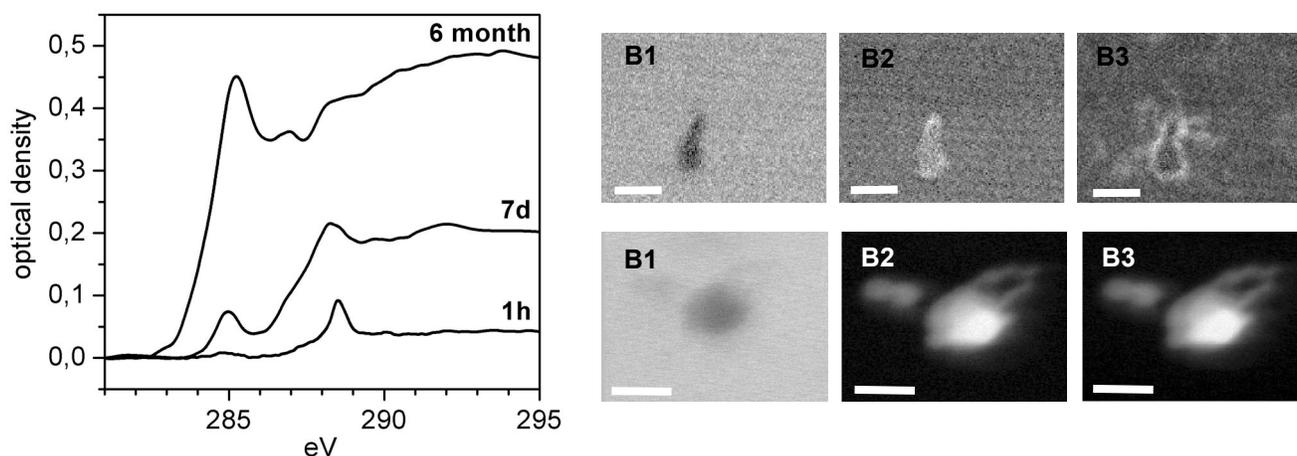


Figure 1: Left: Optical density and functional group changes with increasing Swy2 smectite/organic contact time. Spectra pre-edge optical density set to zero. Right: B1 pre-edge images taken at 280 eV. Ratio images $(-\log [I/I_0]; I_0 = \Sigma(280-283\text{eV}))$ of sample 1h contact time (upper row) and 6 months contact time (lower row); B2: aromatics, $I=285\text{eV}$; B3 carboxyl, $I=288.4\text{eV}$. (scale bar is equivalent to $1\mu\text{m}$).