Analysis of anion adsorption and its effects on alumina nanoparticles stability

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Nanoparticles may enhance contaminant transport in groundwater provided the contaminant is irreversibly adsorbed onto their surface and they are stable and mobile. Colloid-driven contaminant transport is an issue of concern associated to hazardous waste repositories, because many uncertainties still exists.

The chemistry of the groundwater mainly determines the size and charge of the particles and has a large impact on particles stability and mobility but the colloidal properties can also be affected by the contaminant adsorption itself. This is a point potentially very relevant on the overall colloid-driven transport, but scarcely considered.

The stability of colloidal systems is generally evaluated by studying the aggregation kinetic after the change of a specific chemical condition, generally pH or ionic strength of the aqueous solution. Often, the effects of divalent cations, especially Ca^{2+}, are evaluated. On the other hand, the effect of anion adsorption on colloid stability is mostly neglected.

In this work, the effects of Se(IV) (selenite) adsorption on alumina (Al_2O_3) nanoparticles were analysed. Selenite adsorption was studied in a wide range of pH (2-12) and ionic strengths ($5\cdot10^{-4}$ - $1\cdot10^{-1}$ M in $NaClO_4$) and the effect of the adsorption on the main properties of the colloids (size and charge) were analysed. Similarly, the effects of SO_4^{2-} competitive adsorption were studied.

Adsorption on Al_2O_3 was almost independent of the ionic strength and decreased with increasing pH, as expected for anions. The set of adsorption data was successfully fit by surface complexation modeling.

It was clearly shown that the anion adsorption (at medium-high surface occupancies) affected alumina nanoparticle stability. A clear shift of the isoelectric point towards more acid pH and enhancement of colloid aggregation, even at low ionic strength, were observed.

The presence of anions in the chemical composition of natural water, frequently not accounted for in stability studies, will be discussed, as well as the implications on possible colloid-driven contaminant transport in the environment.

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Coupled μ-XAFS-FISH technique for direct observation of the microbe-metal-mineral interaction

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Many geochemical important redox reactions are largely associated with microbial activity and are energy sources for microorganisms. For instance, recent studies suggest a significant relationship between Fe(II)-oxidizing bacteria and ancient Banded Iron Formation, one of the large geochemical events [1]. However, the detailed mechanisms of environmental biogenic reactions are largely unknown, because there are few adequate analytical techniques to observe it in high spatial resolution.

Here, we directly coupled synchrotron microprobe (μ-XAFS) with *in situ* phylogenetic analysis, fluorescence *in situ* hybridization (FISH), to determine simultaniously the chemical species and distributions of microbial community at micrometer scale (Fig. 1), which leads to better understanding the microbial reaction in the environment. We applied the coupled μ-XAFS-FISH to one of the most ubiquitous environmental biomineralizations, Fe mineral deposition by Fe(II)-oxidizing bacteria (FeOB).

In situ visualization of microbes by FISH revealed that *Betaproteobacteria* (presumably revealed to FeOB, *Gallionella spp.*) were localized within 10 μm of the Fe mat surface. Furthermore, *in situ* mineralogical characterization by μ-XAFS suggested that Fe local structure at the FeOB accumulating parts was dominantly composed of secondary short-ordered Fe-O_6 linkage, which is normally not observed in synthetic Fe oxyhydroxides [2]. The present study indicates that the coupled XAFS-FISH technique could be a potential technique to provide direct information on specific biogenic reaction mediated by specific microbe.

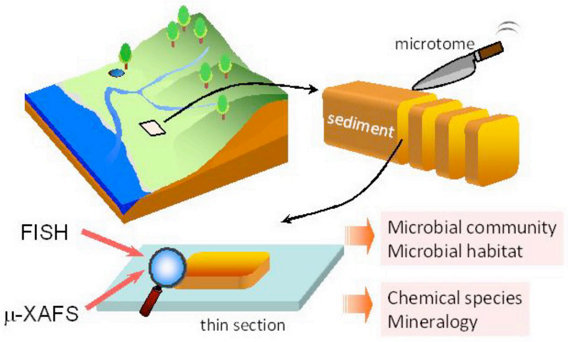

Fig. 1 Schematic figure showing coupled μ-XAFS-FISH technique.

[1] Kappler *et al*. (2005) *Geology* **33**, 865. [2] Mitsunobu *et al*. (2012) *Environ. Sci. Technol*. **46**, 3304.

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