2.8.P01

Interaction of aqueous aluminum species with pentel anions

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Introduction

Dissolved Al(III) forms polynuclear hydroxo complexes such as $AlO_4Al_{12}(OH)_{24}(H_2O)_{12}{}^{7+}$(aq) ($Al_{13}$, ε-Keggin) and $(AlO_4)_2Al_{28}(OH)_{56}(H_2O)_{26}{}^{18+}$(aq) ($Al_{30}$). Both nanoclusters are stable in acidic solutions due to their high positive charge. Their aqueous chemistry is of great interest in relation to many geochemical processes, including interactions with various environmentally significant anionic species like phosphates, arsenates and antimonates.

Experimental Procedure and Results

Batch experiments were performed for each anionic species as a function of anion concentration: Phosphate, arsenate and antimonate solutions of various concentrations were reacted separately with aqueous solutions of Al^{3+}, Al_{13}, Al_{30} and equimolar mixtures of these species. In experiments where precipitation occurred, the precipitates were separated by centrifugation, dried and analysed by solid-state NMR and XRD. The reacted solutions were subsequently analysed by ^{27}Al NMR spectroscopy. All Al species were stable in presence of all three anions and were precipitated as solids. For equimolar mixtures of Al_{13} and Al_{30}, it was observed that phosphate had a strong preference for the Al_{13} nanocluster, which was precipitated as a Al_{13}-phosphate salt while antimonate had a slight preference for the Al_{30} nanocluster. Arsenate showed preference for Al^{3+} and simultaneously precipitated both the nanoclusters. No kinetic effects were observed (as examined by NMR spectra or pH measurements of the solutions) in case of phosphate and antimonate. In case of arsenate, however, slower reactions continued after precipitation as evidenced by changes in solution pH over time.

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Diffusion-limited Sr sorption by hydrous ferric oxide aggregates: Influence of pore sizes

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Dense aggregates of hydrous ferric oxide (HFO) produced by freezing and thawing of freshly precipitated HFO [1] are composed of unit particles of 2 nm size. The pore volume is dominated by pores 2-6 nm in size (75 %). These pores are large enough to contain unbound water, but small enough that an electrical potential, caused by surface charge, develops across the pores. To predict ion diffusion in these pores, we developed a model that uses a Donnan electrostatic approach to calculate the pore solution chemistry. Ion diffusion in the pore water is calculated from the gradients in Donnan concentrations and is directly linked to pH and sorption dependent surface charge. The model was implemented with the software Orchestra [2]. To test the model, dense HFO aggregates were packed in a chromatographic column and equilibrated with an electrolyte solution of 10^{-2} M $NaNO_3$ to a given pH (pH 4 and 7). Then an identical solution, containing additionally 10^{-4} M Sr, was injected. To interpret the sorption behavior, Sr breakthrough curves were recorded and compared with the predictions of the Donnan-diffusion model. The good correspondence between model and experiment indicated that electrostatically constrained diffusion did influence sorption kinetics significantly. This result differs from sorption kinetic studies on freshly precipitated HFO [3], which indicated that surface diffusion was the sorption-limiting process at all internal sorption sites. Surface diffusion is only significant in pores smaller than approximately 2 nm, where pore diffusion is inhibited. Therefore the discrepancy between our results and those in [3] suggests that the physical aggregation, induced by freezing of HFO, generated pores slightly larger than those of freshly precipitated HFO. Diffusion kinetic studies appear useful to distinguish between these two categories of pores.

References

[1] Hofmann A. et al. (2004) *J. Coll. Interf. Sci.* **271** 163-173.
[2] Meeussen J.C.L. (2003) *Environ. Sci. Technol.* **37,** 1175-1182.
[3] Axe L. and P.R. Anderson (1995) *J. Coll. Interf. Sci.* **175**, 157-165.