

## Coprecipitation: Mechanisms and quantitative models

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Coprecipitation is referred to as the simultaneous removal of a trace with host constituent in the aquatic environment. Solid-solution aqueous-solution (SSAS) equilibrium models have been developed to close the often huge solubility gap in the continuum between surface complexation and single-component precipitation of trace elements [1]. These models were originally developed to explain incongruent dissolution and secondary mineral formation in weathering reaction path modeling including carbonates and clay minerals [2,3]. They became of major interest, however, in long-term environmental assessment of radionuclide repositories, in particular for evaluation of near-field geochemical barrier performance. Such barrier concepts include radionuclide coprecipitation with more or less long-term stable minerals like sulfates [4], carbonates [5], and silicate hydrates [6]. More recently, the SSAS modeling concept became also of interest to manage enhanced geogenic radium leaching [7], which may occur during deep geothermal resource exploitation or hydraulic fracturing for shale gas recovery. This keynote contribution will give an overview on the most promising applications in geochemical engineering, as well as model concepts spanning from the classical Lippmann equation approach for drawing aqueous solubility diagrams of binary solid solutions [8] to the most advanced non-ideal multi-site sublattice concept [9,10].

[1] Kersten & Kulik (2005) In: Cornelis *et al.* (eds.) *Handbook of Elemental Speciation*, Vol. 2. Wiley, Chichester, pp. 651-689. [2] Glynn *et al.* (1990) *Geochim. Cosmochim. Acta* **54**, 267-282. [3] Zhu *et al.* (2010) *Geochim. Cosmochim. Acta* **74**, 3963-3983. [4] Aimo *et al.* (2012) *Appl. Geochem.* **27**, 2117-2129. [5] Kulik *et al.* (2010) *Phys. Chem. Earth* **35**, 217-232. [6] Gaona *et al.* (2012) *Appl. Geochem.* **27**, 81-95. [7] Fernández-González *et al.* (2013) *Geochim. Cosmochim. Acta* **105**, 31-43. [8] Kersten (1996) *Environ. Sci. Technol.* **36**, 2919-2925. [9] Rozov *et al.* (2011) *Clays Clay Min.* **59**, 215-232. [10] Kulik (2011) *Cem. Concr. Res.* **41**, 477-495.

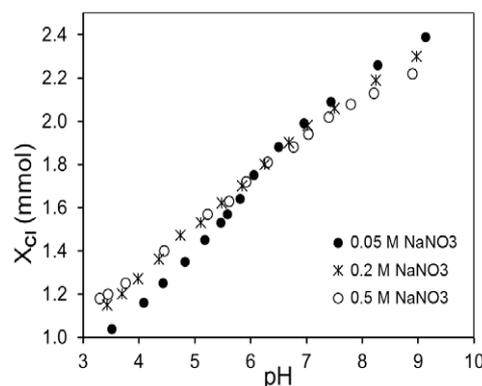
## Arsenate adsorption by akaganéite

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The  $\beta$ -type is the last among the FeOOH polymorphs for which there is yet no multi-site surface complexation (MUSIC) model, which requires information about the proton affinity of the various types of surface groups. Enigmatic behavior during acid-base titrations where protons are co-released from tunnel sites renders interpretation a challenge for akaganéite. In batch experiments, our akaganéite sample show a CIP at pH 7.7. However, the apparent surface charge is not equal to zero at this CIP but shows an offset by  $-0.25$  C/m<sup>2</sup>, obviously due to the excess tunnel site protons. We propose to monitor the chloride exchange with at least two days batch equilibration time (Fig. 1). The chloride is not significantly re-adsorbed on outer surfaces and may be used to monitor and quantify the excess tunnel HCl release. The thus corrected  $\sigma_0$  vs. pH curves become sigmoidal and can be fitted to parameterize a reliable surface complexation model based on recently published site densities for singly and triply coordinated hydroxyl surface groups [1]. This provides a sound basis to set up CD-MUSIC adsorption models for arsenate and competing oxyanions. Furtheron, breakthrough curves of akaganéite based GFH fixed-bed adsorber column units can be calculated for different groundwater chemistry using a homogeneous surface diffusion model and Langmuir adsorption isotherms predicted by the surface complexation model.



**Figure 1:** Tunnel chloride ion release vs. pH at different NaNO<sub>3</sub> electrolyte concentrations

[1] Kozin & Boily (2013) *J. Phys. Chem.* C117 (Article ASAP, DOI: 10.1021/jp3101046).