2.3.P07

Experiments to identify the molecular properties of Step-Pinning Adsorbates on KDP

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We explore the molecular properties of adsorbates that dramatically affect the growth kinetics and morphology of the $\{100\}$ face of Archerite, or KDP (KH_2PO_4). Using *in situ* atomic force microscopy (AFM), we measured changes in the growth rates of the $\{100\}$ face of KDP with supersaturation in the presence of trace amounts of $Co(NH_3)_6^{3+}$, $Fe(CN)_6^{3-}$, η^1-$Co(NH_3)_5HPO_4^+$, η^2-$Co(NH_3)_4HPO_4^+$, η^2-$Co(NH_3)_4P_2O_7H_2^+$, and $Rh(H_2PO_4)_2(H_2O)_4^+$. Unlike most experiments using trivalent-metal dopants to alter KDP growth, these complexes do not change stoichiometry or structure on the timescale of step motion, so that the actual molecular interactions between the adsorbate and the step edge that affect growth can be identified. Step velocity and morphology on the $\{100\}$ face is unaffected by the presence of outer-sphere coordination complexes of either charge. Surprisingly, inner-sphere phosphatoammine complexes do not affect growth rates regardless of how the phosphate group is coordinated to the metal within the complex. However, doping the growth solution with $Rh(H_2PO_4)_2(H_2O)_4^+$ results in profound step pinning, matching the behavior of KDP surfaces grown in the presence of Rh(III) after an equilibration period.

2.3.P08

Colloidal particle release from porous media—an inner-sphere complexation approach

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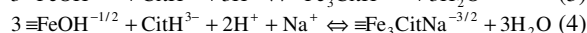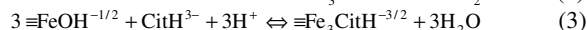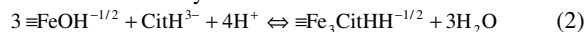[1] Cardiff School of Engineering, Cardiff University, PO Box 925, Cardiff CF24 0YF, UK (liang@cardiff.ac.uk)
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The release of ferrihydrite colloids from a porous medium as influenced by citrate ion adsorption was modeled with an inner sphere complexation approach. A triple plane-1pK-surface complexation model was applied, including surface ion pair formation and charge distribution of the surface-ligand complexes among the d0, d1 and d2 planes of the triple layer as described in CD-MUSIC [1]. Unlike goethite, no clear crystal surfaces are available on ferrihydrite, thus only singly coordinated sites were considered:
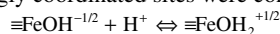
$$\equiv FeOH^{-1/2} + H^+ \Leftrightarrow \equiv FeOH_2^{+1/2}$$
(1)

Citrate ions form inner-sphere complexes with the iron oxide surface. From the five complexes that have been described previously [2] for goethite, three were sufficient to fit our data for ferrihydrite:

$$3 \equiv FeOH^{-1/2} + CitH^{3-} + 4H^+ \Leftrightarrow \equiv Fe_3CitHH^{-1/2} + 3H_2O \quad (2)$$
$$3 \equiv FeOH^{-1/2} + CitH^{3-} + 3H^+ \Leftrightarrow \equiv Fe_3CitH^{-3/2} + 3H_2O \quad (3)$$
$$3 \equiv FeOH^{-1/2} + CitH^{3-} + 2H^+ + Na^+ \Leftrightarrow \equiv Fe_3CitNa^{-3/2} + 3H_2O \quad (4)$$

The modeled logK values for reaction 2-4 were within 1.5 units of those determined for the goethite surface [2], which is within the range of variability expected for different iron-oxides. At low pH, the dominant surface species are $\equiv Fe_3CitH^{-3/2}$ and $\equiv Fe_3CitHH^{-1/2}$. The electric potential, ψ_2 at plane-2, modeled as a function of pH, closely approximated the measured ζ-potentials. To simulate colloid mobilization, a reactive 1-dimensional transport model with chemical equilibrium was implemented using ORCHESTRA [3] as a mathematical framework. Using $\equiv Fe_3CitHH^{-1/2}$ as an effective species during ferrihydrite dissolution, the model showed that both dissolution induced bond breaking and interfacial repulsion maintain a low yet observable colloid release at steady state citrate elution. During citrate breakthrough the colloid release, which was maximal, correlated with the repulsive surface energy due to ligand sorption. The modeled curves produced the main features of pH and colloid breakthrough as shown by the experimental data.

References
(1) Hiemstra, T.; Van Riemsdijk, W. H. (1991) *Coll. Surf.* **59**, 7-25.
(2) Filius, J. D.; Hiemstra, T.; Van Riemsdijk, W. H. (1997) *J. Col. Interf. Sci.*, **195**, 368-380.
(3) Meeussen, J. C. L. (2003) *Environ. Sci. Technol* **37,** 1175-1182.