Multisolute metal ion sorption at the γ-Al$_2$O$_3$/water interface

E. Boyle-Wight   University of Maine, Orono, ME, USA

L. E. Katz   University of Texas, Austin, TX, USA

G. A. Waychunas   Lawrence Berkley Laboratory, Berkeley, CA, USA

K. F. Hayes   University of Michigan, Ann Arbor, MI, USA

Many environmental problems associated with raw material production and past waste management practices require reliable quantitative prediction of the fate and transport of metal ion contaminants in surface and groundwaters. Sorption reactions at the mineral/water interface typically reduce solute mobility and often control the fate and transport of metal ions. Therefore, determination of specific sorption mechanisms has been a primary focus of research aimed at understanding metal ion transport, mineral growth and the development of catalyst materials. Typically, reactions at the mineral/water interface have been studied with a combined macroscopic/microscopic approach. Sorption experiments conducted in batch reactors describe specific ion sorption to oxide and clay materials as a function of pH, background electrolyte, surface coverage and competing adions. Select samples are then studied using various spectroscopy and microscopy methods including XAS, IR, XPS, AFM, SEM and TEM to determine the structure of sorbed species relative to macroscopic observations.

Spectroscopic investigations have focused primarily on single solute systems. XAS data has been used to differentiate between innersphere and outersphere complexes and reveal the formation of polymeric species at high surface coverages. The variability in structure of many transition metal ion surface complexes as a function of surface coverage indicates that competing adions may have an impact on surface complexation and speciation. The goal of this study is to determine the effect of various adions including Co^{2+}, Fe^{2+}, SeO_3^{2-} and SeO_4^{2-} on the sorption mechanism of cobalt at different surface coverages and to evaluate the types of surface complexes formed in multisolute systems using XAS techniques.

Materials and methods. Batch equilibrium studies were conducted using γ-Al$_2$O$_3$ (Buehler Alumina), 82 g/m^2, and metal basis grade nitrate or chloride salts Co(NO$_3$)$_2$, FeCl$_2$, Na$_2$SeO$_3$, Na$_2$SeO$_4$ and NaNO$_3$ (Johnson Matthey Co.). Metal stock solutions

were prepared using double deionized boiled water (Nanopure^{TM}) with a 0.01 M HNO$_3$ storage matrix and stored in a nitrogen atmosphere. Samples were prepared in a nitrogen glovebox by adding the required quantities of Nanopure^{TM} water, γ-Al$_2$O$_3$ slurry, NaNO$_3$ and metal stock solutions to centrifuge tubes or bottles. The pH was adjusted incrementally starting below the sorption edge and using small aliquots such that the initial pH never exceeded the metal hydroxide solubilities. Base additions of carbonate free 0.1 M NaOH (Dilut-IT, J.T. Baker) were made a minimum of 2 hours apart with the final addition equilibrating for at least 12 hours. Samples were centrifuged after pH measurement at 12,000 RPM for 40 minutes. Solute analysis on the supernatant was conducted using flame atomic absorption. Samples for XAS were prepared by aspirating the supernatant from centrifuged samples and mounting the wet paste in aluminum cryostat samples cells while in the nitrogen glove box. Samples were then immediately frozen in liquid nitrogen.

Specific samples for EXAFS analysis were chosen from macroscopic adsorption data such that the surface coverages would be the same for both the single and multisolute samples. X-ray absorption spectra were collected at the Stanford Synchrotron Radiation Laboratory (SSRL) using wiggler beam lines 4-3 and 7-3. Fluorescence spectra were collected at the Co, Fe and Se k-edge using a Si(220) monochromator, 13 element Ge array detector and liquid helium cryostat cooled to approximately 15 K. Data analysis using the EXAFSPAK (George *et al.*, 1995) suite of programs consists of background subtraction with a linear or gaussian function through the pre-edge region, quadratic three segment spine fit normalized with a Victoreen polynomial and tabulated McMaster atomic absorption fall off coefficients. The EXAFS spectra were Fourier filtered over a k-range of 3 to 13 and individual shell contributions were back transformed. Spectra were fit using phase and
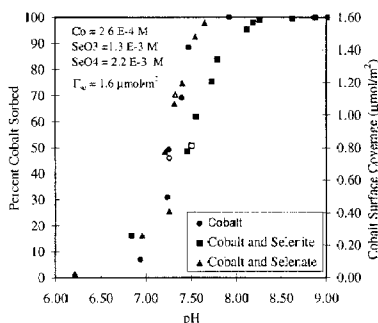
FIG. 1. Cobalt/selenium sorption data on 2 g/L γ-Al$_2$O$_3$.

FIG. 2. Radial structure functions for cobalt and cobalt/selenium at Co-Kα.

amplitude functions derived from FEFF 7 (Zabinsky et al., 1995) and Debye-Waller factors determined from fitting experimental models with ab initio calculations. Fit parameters for each shell were then combined to fit the entire EXAFS spectra..

Results. Macroscopic adsorption data for the cobalt-selenium bisolute systems show a decrease in cobalt sorption in the presence of selenite but no effect in the presence of selenate at cobalt surface coverages greater than 0.5 μmol/m^2 (Fig. 1). Selenite has been shown to be more strongly sorbing than selenate (Hayes et al., 1987) and may be more competitive with cobalt for surface sites. Furthermore, cobalt has been shown to form polynuclear surface complexes on γ-Al$_2$O$_3$ at surface coverages greater than 0.5 μmol/m^2 (Chisholm-Brause et al., 1990). X-ray absorption data for cobalt (Fig. 2) show a decrease in cobalt second shell coordination in the presence of selenite but no effect with selenate. This suggests that selenite is preventing the formation of polynuclear surface complexes, resulting in reduced cobalt sorption.

Macroscopic adsorption data for the Co(II)/Fe(II) bisolute system show a slight decrease in cobalt sorption in the presence of iron. These results are consistent with previous findings with Co(II)/Se(IV), however, bisolute EXAFS data for both cobalt and iron show an increase in second shell coordination at elemental surface coverages equal to single solute controls (Single-solute Γ_{Co} = Bi-solute Γ_{Co}). Comparing single- and bi-solute samples having equal coverages on a total coverage basis (Γ_{Fe} + Γ_{Co}) and fit with only a Co backscatterer component reveal a coordination of similar magnitude at approximately 3.1 Å. These results contrast the cobalt/selenite data which showed a greater decrease in Co-Co interactions with increasing total coverage
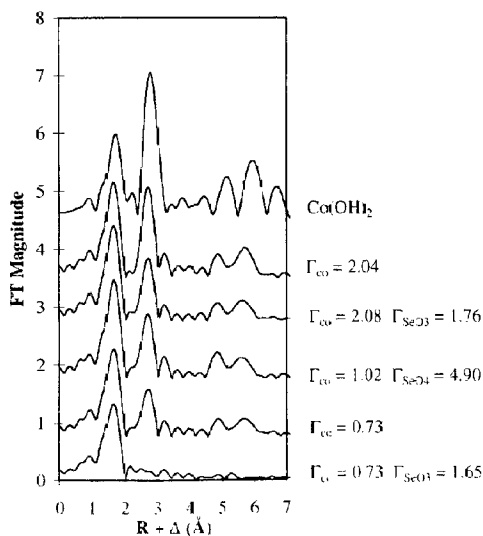
as represented by Γ_{Se} + Γ_{Co}. The reduction in cobalt sorption, increase in polynuclear species formation and similar coordination on a total coverage basis indicate that Co(II) and Fe(II) could be forming a mixed cation polynuclear surface complex..

Conclusion. The structure of surface complexes which form at high metal ion surface coverage is a function of the type of competing adions present in the system. Both selenite and Fe(II) reduce cobalt sorption at high coverage but selenite decreases polynuclear species and iron increases polynuclear species. Thus, macroscopic data alone may not be indicative of the nature of competive interactions which greatly influence the structure of surface complexes forming at high surface coverage.

References

Sabinsky, S.I., Rehr, J.J., Ankudinov, A., Albers, R.C. and Eller, M.J. (1995) *Phys. Rev. B.*, **52**, 2995.

George, G.N. and Pickering, I.J. (1995) Stanford Synchrotron Radiation Laboratory, Menlo Park, Ca.

Chisholm-Brause, C.J., Hayes, K.F., Roe, A.L., Brown, G.E. Jr., Parks, G.A. and Leckie, J.O. (1990) *Geochim. Cosmochim. Acta*, **54**, 1897–909.

Hayes, K.F., Roe, L.A., Brown, G.E., Jr., Hodgson, K.O., Leckie, J.O. and Parks, G.A. (1987) *Science*, **238**, 783–6.