

ADSORPTION MECHANISMS OF PB ON AMORPHOUS SILICA: AN XAS STUDY

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1. Introduction

To accurately predict the fate and mobility of heavy metals in soil and aquatic systems, fundamental knowledge of the mechanisms involved in the adsorption of heavy metals by soils and soil constituents is required. In this study we focused on characterizing the sorption behavior and mechanisms of Pb on amorphous silica using X-ray absorption spectroscopy (XAS). Amorphous silica is a commonly occurring natural sorbent, and Pb is a toxic and often encountered pollutant in the environment. XAS is a valuable tool in studying metal reactions on mineral surfaces, since it provides molecular scale information on the bonding environment of the sorbed metal.

2. Materials and Methods

Pb sorption on silica was studied as a function of pH. The pH range used was pH 3.4-6.5. The BET surface area of the silica used was $280 \text{ m}^2 \text{ g}^{-1}$. The studies were conducted in a 0.1M NaNO_3 background electrolyte. The solids concentration was 3 g L^{-1} , and the initial Pb concentration was 3 mM. All studies were carried out in a N_2 -purged glove box to prevent PbCO_3 precipitation. The silica was hydrated in background electrolyte for 24 hours prior to reaction with Pb. An appropriate amount of Pb stock solution was then added stepwise to achieve an initial Pb concentration of 3 mM. Different amounts of acid (1M HNO_3) or base (1M NaOH) were added to achieve the desired pH. The suspensions were allowed to react for 24 hours. The final pH was then measured in suspension, and the samples were centrifuged. The supernatants were passed through a 0.2 μm filter, acidified, and analyzed for Pb using AA spectrometry. The amount of Pb adsorbed was calculated from the difference between the initial and final Pb concentrations. The wet pastes of the samples with $\text{pH} > 4.89$ were analyzed by XAS.

XAS spectra were collected on beamline X-11A of the NSLS at BNL, Upton, NY. A Si(III) crystal was used to scan the samples at the Pb-L_{III}-edge (13055 eV). Four scans were taken per sample to increase the signal to noise ratio. The samples were cooled to liquid N_2 temperature to reduce the damping of the XAS signal due to thermal disorder. Data analysis was performed with the MacXAFS 4.0 package.

3. Results and Discussion

Figure 1 presents the Pb uptake on silica as a function of pH. A steep increase in Pb sorption is observed above $\text{pH} = 5.5$. The first derivative spectra of the XANES data of the samples with $\text{pH} > 4.89$ shown in Figure 1 are given in Figure 2, along with those of the reference compounds Pb^{2+} (aq) and $\text{Pb}_4(\text{OH})_4^{4+}$ (aq). Comparison of the XANES spectra of the Pb/silica samples to those of the reference compounds indicates that at low pH, the local chemical environment of Pb adsorbed onto silica resembles that of Pb^{2+} (aq) whereas with increasing pH, the Pb/silica XANES spectra increasingly resemble that of $\text{Pb}_4(\text{OH})_4^{4+}$ (aq). This indicates that at low pH, adsorbed Pb is

predominantly surrounded by water molecules. As pH increases, however, adsorbed Pb is increasingly coordinated to OH⁻ ligands. In terms of Pb adsorption mechanisms, this suggests that at low pH, Pb is mainly adsorbed in an outer-sphere fashion, whereas with increasing pH inner-sphere adsorption of Pb by coordination to surface OH⁻ ligands becomes increasingly important. Recent XAS studies by Strawn (1998) and Bargar *et al.* (1996), where Pb sorption was studied as a function of ionic strength and the type of surface sites respectively, have also shown the ability of Pb to form both inner-sphere and outer-sphere surface complexes at mineral interfaces.

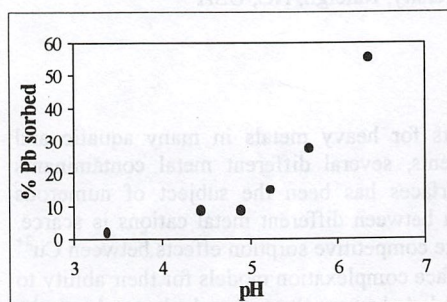


Figure 1. pH edge of Pb sorption on silica

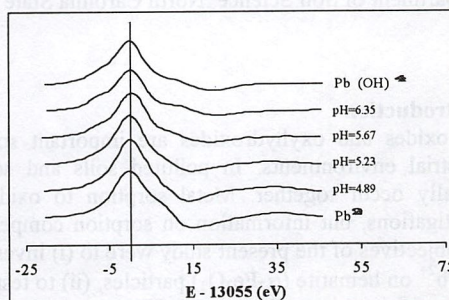


Figure 2. First derivative spectra of Pb/silica samples and Pb²⁺ and Pb₄(OH)₄⁴⁺ reference compounds

4. Conclusions

XAS can be used to distinguish between adsorption mechanisms of Pb adsorbed on silica. At low pH values, Pb adsorption is mainly outer-sphere, whereas inner-adsorption becomes dominant at high pH. At intermediate pH values, both inner-sphere and outer-sphere Pb adsorption complexes occur at the silica surface.

5. References

- BARGAR, J.R., TOWLE, S.N., BROWN, JR., G.E., AND PARKS, G.A. (1996) Outer-sphere lead adsorbed at specific surface sites on single crystal γ -Al₂O₃. *Geochimica et Cosmochimica Acta* 60, 3541-3547.
- STRAWN, D.G. (1998) *Kinetics and mechanisms of lead sorption and desorption on soils and soil materials*. PhD Dissertation, University of Delaware, Newark, Delaware.