The use of XANES, STM, and XPS to identify the precipitation products formed during the reaction of U, Cr, and Se with zero-valent iron

C. Amrhein
M. L. Hunt
M. J. Roberson
Department of Environmental Sciences, University of California, Riverside, Riverside, CA 92521, USA

J. A. Yarmoff
S. R. Qiu
H.-F. Lai
Department of Physics, University of California, Riverside, Riverside, CA 92521, USA

Shallow groundwaters in the western U.S. often contain elevated levels of trace oxyanions such as selenate, chromate, and uranyl. A potential remediation method is to react the water with zero-valent iron. Both in-situ permeable reactive barrier walls and pump-n-treat technologies are being used for to treat these contaminated waters (Wilson, 1995). In this reaction, the iron serves as both an electron source and as a catalyst. The objectives of this research were to determine the factors that affect the rate of reaction and the types of secondary products formed, including the iron hydroxide mineralogy and the fate of the trace elements. Variables that we studied included pH, ionic strength, O_2, competitive ions and forms of iron.

Materials and methods

Reactions between zero-valent iron metal and aqueous solutions were carried out in 1.3 L stirred batch reactors with controlled pH and gas composition (mixtures of N_2, CO_2, and O_2). Variable concentrations of selenate, chromate, and uranyl were reacted with coarse iron filings and iron foil. Reacting solutions were sampled every few hours and analysed for trace elements and soluble iron. Selenate and selenite were determined using hydride generation atomic absorption spectroscopy (AAS), chromate and chromite by the diphenylcarbazide colorimetric method and AAS, and total soluble uranium by ICP-MS. The solid phases were collected after 1 to 10 days and the iron hydroxide products separated from the metal by agitation and filtration.

X-ray diffraction of powder mounts was used for mineralogical identification of the secondary products.

X-ray absorption near edge spectroscopy (XANES) was conducted using the Beamline 4-2 at the Stanford Synchrotron Radiation Laboratory. Both fluorescence and X-ray transmission intensity were monitored at the Se and Fe absorption edges. Standard reference materials including iron oxides and selenium compounds were used to identify absorption edge shifts and fine-structure features for the different oxidation states and coordination environments (Pickering *et al.*, 1995).

X-ray photoelectron spectroscopy (XPS), Auger electron spectroscopy, and scanning tunneling microscopy (STM) were used to characterized the surface chemistry of iron foils reacted in aqueous solutions. The STM images were collected in aqueous solution periodically for several hours. The reacted foils were then rinsed with deionized water and dried under N_2 prior to being placed in the ultra-high vacuum chamber for XPS analysis.

Results

Reduction of selenate by zero-valent iron followed a pseudo first-order reaction. In addition, an increase in

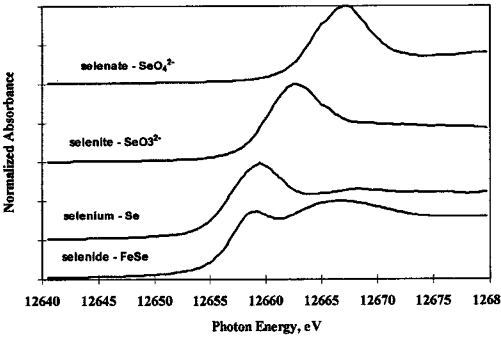

FIG. 1. Reference materials used for Se absorption edge identification.

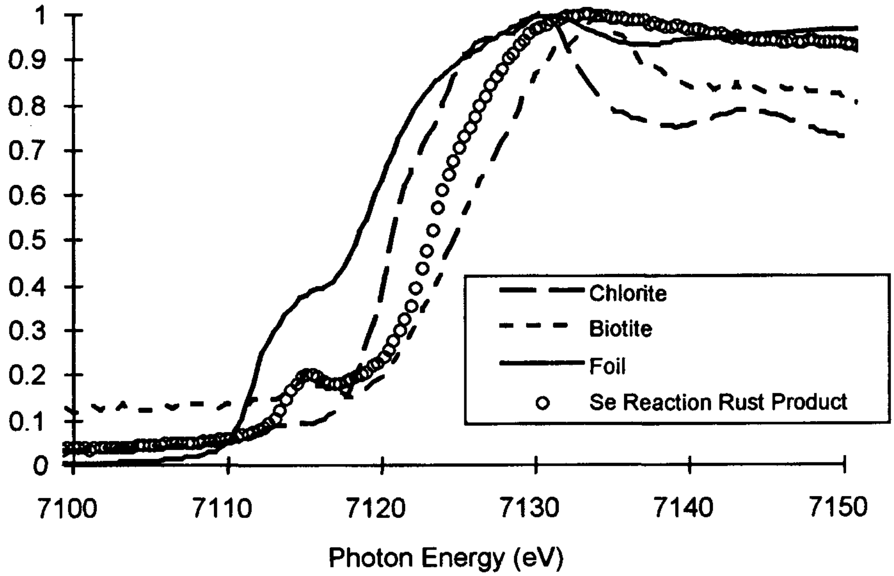

FIG. 2. Iron XANES spectra collected from secondary products and several natural iron-bearing minerals.

ionic strength, O_2 concentration or pH decreased the rate of selenate loss. Reactions carried out in Salton Sea water (44000 mg/L total dissolved salts) had a significantly lower rate of selenate reduction than samples of saline, shallow groundwater contaminated with Se.

The XANES spectra for the selenium standards are given in Fig. 1 and show that greater energy is required to eject core-level electrons as the oxidation state of the element increases. The oxidation states of Se in the iron hydroxide products and on the surface of the iron metal were determined using a least squares fit of the standard spectra to the sample spectra. Selenate (Se^{6+}) was absent in all precipitation products. Selenite was present in iron hydroxide phases from the reactions carried out with O_2. In the absence of oxygen, selenium was reduced to elemental Se. Initial data suggest that iron selenide (FeSe) formed on the surface of the iron metal. Decreasing ionic strength favoured lower oxidation states of Se.

The XANES spectra for iron in standard reference materials is given in Fig. 2. Based on the absorption edge position, we determined the proportion of Fe(II) and Fe(III) in the solid phases. Spectra from several natural iron-bearing minerals in addition to spectra collected taken from reaction products are shown in Fig. 2.

The STM pictures of the reacted iron foils showed a gradual decrease in surface roughness due to iron hydroxide precipitation and accumulation of reduced Cr and U on the surface. Using STM and XPS we identified a 400 nm thick surface layer of uranium oxide on the iron surface.

Conclusions

By combining surface science techniques with wet chemistry methods we have been able to characterize the atomic scale processes that occur on the surface of iron metal in contact with contaminated water. The reduction reactions of toxic trace elements continued even in the presence of 'thick' precipitation layers on the surfaces. Further work is ongoing to determine the effects of competitive ions, including phosphate and fluoride on these reactions.

References

Pickering, I., Brown, G.E. and Tokunaga, T. (1995) *Environ. Sci. Techn.*, **29**, 2456–9.

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