Environmental Management Science Program

Project ID Number 55061

Fundamental Studies of the Removal of Contaminants from Ground and Waste Waters via Reduction by Zero-Valent Metals

J. A. Yarmoff
University of California at Riverside
Riverside, California 92521
Phone: 909-787-5336
E-mail: yarmoff@ucr.edu

C. Amrhein
University of California at Riverside
Riverside, California 92521
Phone: 909-787-5196
E-mail: chrisa@mail.ucr.edu

June 1, 1998
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J. A. Yarmoff, University of California at Riverside

C. Amrhein, University of California at Riverside

**Research Objective**

Contaminated groundwater and surface waters are a problem throughout the United States and the world. In many instances, the types of contamination can be directly attributed to man’s actions. For instance, the burial of wastes, casual disposal of solvents in unlined pits, and the development of irrigated agriculture have all contributed to groundwater and surface water contamination. The kinds of contaminants include chlorinated solvents and toxic trace elements that are soluble and mobile in soils and aquifers. Oxyanions of selenium, chromium, uranium, arsenic, and chlorine (as perchlorate) are frequently found as contaminants on many DOE sites. In addition, the careless disposal of cleaning solvents, such as carbon tetrachloride and trichloroethylene, has further contaminated many groundwaters at these sites. Oxyanions of selenium, nitrogen, arsenic, vanadium, uranium, chromium, and molybdenum are contaminants in agricultural areas of the Western U.S.

The management of these waters requires treatment to remove the contaminants before reuse or surface water disposal. In one instance in the Central Valley of California, the discharge of selenate-contaminated shallow groundwater to a wildlife refuge caused catastrophic bird deaths and deformities of embryos.

A potential remediation method for many of these oxyanions and chlorinated-solvents is to react the contaminated water with zero-valent iron. In this reaction, the iron serves as both an electron source and as a catalyst. Elemental iron is already being used on an experimental basis. Both in-situ reactive barriers and above-ground reactors are being developed for this purpose. However, the design and operation of these treatment systems requires a detailed process-level understanding of the interactions between the contaminants and the iron surfaces. Only limited success has been achieved in the field, partly because the basic surface chemical reactions are not well understood. We are performing fundamental investigations of the interactions of the relevant chlorinated solvents, and trace element-containing compounds with single- and poly-crystalline Fe surfaces. The aim of this work is to develop the fundamental physical and chemical understanding that is necessary for the development of cleanup techniques and procedures.

**Research Progress and Implications**

As of May 1998, we have performed both bulk chemical measurements of the reduction reactions and surface science studies of model chemical systems. During these first two years of funding, we have made significant progress in both areas. Initially, we focused primarily on the reduction of selenate by elemental iron. We also performed some work with chromate, perchlorate, uranyl, and carbon tetrachloride. In the following sections some of our progress is described.

We studied the factors affecting the selenate reduction reaction to determine the optimum conditions for the remediation of wastewater. We characterized the effects of pH, O₂ concentrations, ionic strength and solution composition, degree of agitation, and iron surface pretreatment in solutions contaminated with 0.20 mg L⁻¹ selenate (+VI oxidation state). The reaction was found to be first-order with respect to selenate concentration. Increases in either the pH or ionic strength decreased the rate of selenate reduction, with pH being the more important variable. The reaction was also sensitive to changes in the preparation of the iron and type of iron. Washing with 0.01N HCl and rinsing with O₂-free water
resulted in the most reproducible surface for use in these measurements. Agitation of the iron/water suspension increased the rate of reaction. Palladium coated iron metal tripled the rate of selenate reduction. There was little or no reduction of perchlorate by either iron or Pd-coated iron. Carbon tetrachloride reduction was significantly faster in oxygenated water compared to O$_2$-free and was not inhibited by competitive adsorption of toluene or humic acid.

In order to probe the solid species formed by the reduction of selenate with iron filings, near edge x-ray adsorption fine structure (NEXAFS) analysis of reacted iron was carried out at the Stanford Synchrotron Radiation Laboratory (SSRL). Se was found on all of the surfaces in mixtures of the (0) and (+IV) oxidation states. Samples prepared under O$_2$ produced a greater amount of the (0) species, while samples prepared under N$_2$ produced a greater portion of (+IV). Samples prepared at low pH had greater amounts of (0) than samples prepared at higher pH values.

X-ray diffraction (XRD) was used to determine the species of iron rust formed as a result of the reactions with zero-valent iron. The dominant product is lepidocrocite (g-FeOOH) with minor amounts of maghemite (g-Fe$_2$O$_3$). These are insoluble mineral forms of oxidized iron (+III oxidation state) that are suspended in the reaction solutions.

Bulk solution studies carried out with uranium and chromium have revealed that both can passivate the surface of iron. Depending on solution concentration, the reaction of uranium and chromium with iron can occur with no rust formation. This is important because of the implications of possible shutdown of the sorption and/or reduction reactions. Additionally, this passivation slows down the sorption and reduction of other trace elements. Chromium (as chromate) slowed down both the loss from solution and reduction of selenium (as selenate) by a factor of about 15. NEXAFS analysis indicated that uranium coprecipitated with selenium on the iron surface. However, the selenium was in the +VI oxidation state. This hasn’t been observed in any other reactions with selenium and iron. Also, uranium seems to buffer the pH of the reaction solution, whereas other target oxyanions are associated with an increase in pH (> 9.0).

Previous studies have often overlooked the formation and reaction of green rust, which is a mixed +II/+III oxidation-state iron hydroxide mineral. It has a pyroaurite mineral structure with the anions substituting in the place of hydroxyl ions. Chloride, nitrate, sulfate, carbonate, and selenate have been reported to be in the structure of green rust. We’ve confirmed the presence of green rust formation in our reactions visually and chemically.

Studies of iron foils were carried out in order to utilize surface-sensitive techniques that can better characterize the surfaces. We used scanning tunneling microscopy (STM) to look at polycrystalline iron foils during the reduction of selenate, chromate and uranyl. This was done in-situ, using an STM that is designed for operating under solution. We found that, for all three reactions, the surface morphology changed from the roughened surface characteristic of iron oxides to a smooth surface. Note that a blank run using only water showed no changes. X-ray photoelectron spectroscopy (XPS) was used to measure Fe foils following the reduction of selenate, chromate and uranyl in aqueous solution. For all three species, films composed of partially reduced oxides were found. The reduction of U was found to be very sensitive to dissolved oxygen, while the reductions of Se and Cr are not. No changes to the native iron oxides were observed with XPS, due to the inherent surface sensitivity of the technique.

In order to probe the reaction mechanism on an atomic scale, we have begun investigations of the reduction reactions of model gas-phase molecules with atomically clean iron in ultra-high vacuum (UHV). We began with the reaction of SeF$_6$ with iron and iron oxide surfaces, as Se in SeF$_6$ is in the (+VI) oxidation state just as in selenate. Polycrystalline iron foils were cleaned in vacuum by sputtering with Ar$^+$ ions. The foils were then reacted with SeF$_6$ gas in a special UHV reaction chamber, and XPS was used to measure the iron foils following reaction. The spectra showed a large excess of fluorine, which indicates that the major reaction pathway involves the reduction of Se and its subsequent ejection from the surface. A small amount of adsorbed selenium does remain on the surface, which was found to be in a completely reduced form. An iron oxide was grown in-situ, and it was found to be largely unreactive to SeF$_6$.

In summary, we have begun our program with a number of detailed investigations of the reduction of selenate, chromate and uranyl by reaction with Fe surfaces. Excellent collaboration between the
Physics Department and the Department of Environmental Sciences has stimulated a wealth of new ideas for this and other environmentally-relevant projects.

**Planned Activities**

More bulk studies will be performed to determine the optimal operating conditions for reaction. This information will help determine which solutions will be later used for the surface science experiments. More NEXAFS will be done with other species, as the initial data collected following Se reduction was very useful. More STM and XPS will be performed using iron foils, but we will be first cleaning the foils with Ar⁺ bombardment and then transferring the samples to the solution under an inert atmosphere. This will allow us to probe the actual reaction with zero-valent iron, rather than just measuring the native oxide overlayer. More detailed UHV work will also be performed in order to clarify the reaction mechanism. For example, we will repeat the SeF₆ experiments using Fe single crystals, which will eliminate grain boundary effects. We will also employ other volatile oxyanion reactants that can be reduced by iron, such as selenic acid and various chlorohydrocarbons.