Technical Progress Review

FUNDAMENTAL STUDIES OF THE REMOVAL OF CONTAMINANTS FROM GROUND AND WASTE WATERS VIA REDUCTION BY ZERO-VALENT METALS

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Contaminated groundwater is 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 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.

In agricultural areas of the western US, shallow groundwaters have become contaminated with high levels of selenate, chromate, and uranyl. 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. At sites where solid-propellant rocket motors were tested or disposed of, high concentrations of perchlorate and trichloroethylene are being found in the groundwater.

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, for the reductive dechlorination of solvents and the removal of toxic trace elements. 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, trace elements, 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.

We are performing both bulk chemical measurements of the reduction reactions and surface science studies of model chemical systems. During this first year of funding, we have already made significant progress in both areas. Initially, we have focused primarily on the reduction of selenate by elemental iron. We have also performed some work with chromate, perchlorate, uranyl, and carbon tetrachloride, as well. 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 200 $\mu\text{g L}^{-1}$ selenate (+VI oxidation state). The reaction was found to be first-order with respect to selenate concentration with a rate constant of 0.4 d^{-1} at pH 7, 20 mM NaCl, and an iron:water ratio of 19 M^2L^{-1} . 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 removed surface hydroxides and resulted in the most reproducible surface for use in these measurements. Agitation of the iron/water suspension increased the rate of reaction, presumably due to the removal of surface hydroxides and the generation of new surface area. Palladium coated iron metal tripled the rate of selenate reduction. There was no reduction of perchlorate by either iron or Pd-coated iron. Carbon tetrachloride reduction was significantly faster in oxygenated water compared to O₂-free and was not inhibited by competitive adsorption of toluene or humic acid.

The reacted iron metal and iron oxide precipitates were characterized using a scanning electron microscope (SEM) with energy dispersive x-ray (EDX) analysis. EDX analysis of 100 mesh, 99% electrolytically produced iron powder indicated 98.69% Fe(O). Surface area analysis using the BET-N₂ method gave a surface area of 0.3 m² g⁻¹ for unreacted 100 mesh iron. EDX analysis of 40 mesh-iron filings indicated 84.37% Fe(0), 8.09 O, 5.75% Si. Surface area analysis of the 40 mesh unreacted iron showed 3 m² g⁻¹. These results were used to identify starting materials and surface area changes due to oxide precipitates. EDX analysis of reacted iron showed no Se. This, however, may just be due to the insensitivity of the EDX for the level of Se present. Additionally, the EDX may probe too deep into the sample, diluting the Se signal.

Near edge x-ray adsorption fine structure (NEXAFS) analysis of reacted iron filings was carried out at the Stanford Synchrotron Radiation Laboratory (SSRL). Se was found on all of the surfaces, in mixtures of the (-II), (0) and (+IV) oxidation states. Samples prepared under O₂ conditions produced a greater amount of the (-II) species, while samples prepared under N₂ conditions produced a greater portion of (0) and (+IV). Samples prepared at low pH had greater amounts of (-II) and (0) than samples prepared at higher pH values.

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. XPS studies will help to determine whether a surface precipitate or a removal of surface roughness was the dominant mechanism.

X-ray photoelectron spectroscopy (XPS) and Auger electron spectroscopy (AES) were collected from Fe foils following the reduction of selenate, chromate and uranyl in aqueous solution. For selenate and uranyl, very little of the reduced species was found on the surface, indicating that the iron surface served as a catalyst for reduction, but that the reduction products did not remain adsorbed on the surface. Chromate, on the other hand, appeared to plate out on the surface. Further work is underway to determine the nature of this chromium overlayer.

The reactions of SeF₆ with iron and iron oxide surfaces provide a model system for the reduction of selenate. In both cases, Se starts in the (+VI) oxidation state. Polycrystalline iron foils were cleaned in ultra-high vacuum (UHV) by sputtering with Ar⁺ ions. The foils were then reacted with SeF₆ gas in a special UHV reaction chamber. XPS was used to measure the iron foils after 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 may result from reaction at grain boundaries. In order to clarify this reaction mechanism, we will repeat the experiment with Fe single crystals, which will eliminate grain boundary effects. Our next step will be to adsorb oxygen onto Fe foil prior to SeF₆ reaction in order to ascertain the role of oxygen in the reduction process. Also, SeF₆ will be reacted with iron oxide films grown *in situ*. We will also compare these results to those obtained by reacting with SF₆.

In summary, we have begun our program with a number of detailed investigations of the reduction of Se by reaction with Fe surfaces. Work has begun on most of the other oxyanions and a few chlorinated solvents. We have identified some of the important variables in the reaction, which have indicated the next steps to be taken. For example, the nature of the adsorbed Se and the factors that affect the different oxidation states need to be clarified. Also, the role of iron oxides in either promoting or retarding the reaction must be ascertained. Excellent collaboration between the Physics Department and the Department of Soil and Environmental Sciences has stimulated a wealth of new ideas for this project.