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

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Project Summary/Progress Report

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CONTAMINANTS FROM GROUND AND WASTE WATERS
VIA REDUCTION BY ZERO-VALENT METALS

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I. 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 chemical 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 (including radioisotopes) that are soluble and mobile in soils and aquifers. Oxyanions of uranium, selenium, chromium, arsenic, technetium, and chlorine (as perchlorate) are frequently found as contaminants on many DOE sites. Uranium is a particularly widespread contaminant at most DOE sites including Oak Ridge, Rocky Flats, Hanford, Idaho (INEEL), and Fernald. The uranium contamination is associated with mining and milling of uranium ore (UMTRA sites), isotope separation and enrichment, and mixed waste and TRU waste burial. In addition, the careless disposal of halogenated solvents, such as carbon tetrachloride and trichloroethylene, has further contaminated many groundwaters at these sites.

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 at many DOE sites. 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. 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.

II. RESEARCH PROGRESS AND IMPLICATIONS

As of June 1999, we have performed bulk chemical measurements of the reduction reactions and surface science studies of model chemical systems. Initially, we focused primarily on the reaction of selenate and arsenate with elemental iron. More recently, we have been concentrating on the uranyl (uranium VI) reaction. We also performed work with chromate, perchlorate, and carbon tetrachloride. Our studies of trace-element removal from aqueous solution with zero-valent iron have led to a new understanding of the surface adsorption and precipitation of these contaminants in reactive-barrier walls. In the following sections, some highlights of our research are described.

A. Bulk chemical studies

We studied the factors affecting the reaction of selenate, arsenate, chromate, uranyl, perchlorate, nitrate, and carbon tetrachloride with zero-valent iron to determine the optimum conditions for the remediation of contaminated shallow groundwater. We characterized the effects of pH, O_2 concentration, ionic strength and solution composition, degree of agitation, and iron surface pretreatment on the removal of UO_2^{2+}, $As(OH)_3^{o}$, AsO_4^{3-} SeO_4^{2-}, CrO_4^{2-}, ClO_4^{-}, NO_3^{-}, and CCl_4 in synthetic and natural groundwater solutions. In the absence of oxygen, the reduction and removal of trace elements was found to be first-order with respect to both contaminant concentration and the ratio of the iron surface area to solution volume. Increases in the pH, ionic strength, or bicarbonate concentration decreased the rate of trace element reduction, with pH being the most important variable. Under aerobic conditions, the rate of reduction was 2 to 3 times faster but rapidly decreased due to the passivation of the surface by iron oxyhydroxide precipitates. The fact that the reduction reaction was faster at high electrode potentials, E_h, indicates that the oxidation of the iron, and not the reduction of the contaminant, was the rate-limiting step.

A palladium coating on the iron metal tripled the rate of trace element reduction. However, there was no reduction of perchlorate by either iron or Pd-coated iron. Carbon tetrachloride reduction was significantly faster in oxygenated, as compared to O_2-free, water and was not inhibited by competitive adsorption of toluene or humic acid.

Near edge x-ray absorption fine structure (NEXAFS) spectroscopy of the reacted iron was carried out at the Stanford Synchrotron Radiation Laboratory (SSRL). One of the more interesting findings of our NEXAFS experiments was that As(V) (arsenate) was not reduced to As(III) by zero-valent iron. There was some concern that the more toxic and mobile form of arsenic, As(III), might form in a reactive barrier wall. The discovery that As (III) is oxidized and coprecipitated by iron was an unexpected result that expands the applicability of zero-valent iron reactive barrier walls. NEXAFS analysis of the iron and corrosion products from the selenate reactions showed mixtures of elemental Se and selenite, Se(IV). Under aerobic conditions, elemental selenium was found in the highest percentage. This was unexpected because the reactions performed in the absence of oxygen had a much lower E_h, which should have favored the lower oxidation state. Studies carried out with chromate revealed that it passivated the surface of the iron and this passivation slowed down the sorption and reduction of other trace elements.

X-ray diffraction (XRD) was used to determine the species of iron oxyhydroxides formed as a result of the reactions with zero-valent iron. The dominant product was lepidocrocite (γ-FeOOH) with minor amounts of maghemite (γ-Fe_2O_3) and "green rust".

The mechanism and kinetics of trace element reactions with zero-valent iron were dramatically different than expected. In the presence of oxygen, all the reactions were accelerated. However, the formation of Fe(III) oxyhydroxide precipitates led to passivation of the iron and, in the field, barrier plugging has been observed. On the other hand, reactions without oxygen were slower, but long-term performance of the iron was improved in many cases. Thus, additives that help to deplete oxygen from groundwater prior to a reactive barrier need to be further investigated.

B. Surface studies of reactions in aqueous solution

The evolution of the surface morphology during reaction in aqueous solution was investigated with scanning tunneling microscopy (STM). Figure 1 shows how the surface morphology of the Fe foils was altered by the reactions. With this *in situ* STM method, we can continuously monitor the same spot on a sample as the reaction proceeds. The surfaces were smoothed by the reactions, while a blank run using only water showed no changes. STM cannot, however, distinguish between erosion of the substrate or film deposition as being the cause of the smoothing.

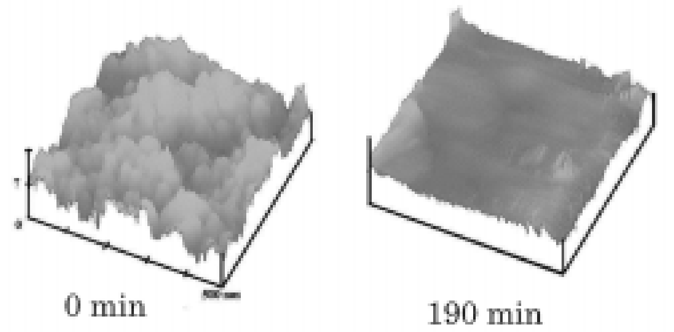

Figure 1. STM images collected *in situ* from Fe foil under a 1 mM Uranyl solution. Images were collected continuously from the same spot, and are shown following reaction for the indicated time. The image sizes are 500x500 nm^2.

The chemical composition and oxidation states of the surface products were determined with x-ray photoelectron spectroscopy (XPS). It was found that selenate deposits onto Fe surfaces by reduction to Se(IV), i.e., selenite. The amount of Se deposited is slightly increased if the atmospheric gasses are removed with an N_2 purge. We attribute this to a thickening of the

Fe oxide layer when O_2 is in solution. We obtained the same basic results for the removal of chromate. Uranium, however, was deposited as U(VI), i.e., it was not reduced. It has generally been assumed that zero-valent iron removes contaminants from solution by a surface redox process, but these results indicate that this is not the mechanism operative for uranium removal.

The removal of uranium had an additional surprising result. When the dissolved atmospheric gases were removed, an extremely thick film of uranium oxide was deposited. The film was thick enough to be seen by eye, and XPS showed no emission from the Fe substrate. Further experiments, described below, show that the films grown under these conditions are actually more than 0.5 µm thick. If the atmospheric gases are allowed to remain in solution, only a thin film (12 Å) was deposited. We hypothesize that this difference is due to the presence of CO_2 in the atmosphere-containing solutions. Aqueous CO_2 reacts with the uranium in solution to form uranyl-carbonate complexes, which are stable in solution. Thus, we believe that the concentrations of dissolved CO_2 and bicarbonate play important roles in determining the amount of uranium that can be effectively removed from solution by zero-valent iron. Since anaerobic conditions are beneficial in minimizing Fe-oxyhydroxide formation, it might be desirable to modify the chemistry of the groundwater prior to reaction with iron. However, the use of organic matter to remove oxygen will greatly increase the CO_2 concentration in the water.

Since we discovered how to grow thick uranium oxide films by reacting iron under an N_2 purge, we have performed a number of measurements on the films in order to characterize them. Scanning electron microscopy (SEM) indicates that the film surfaces are fairly smooth, but they contain microscopic cracks. X-ray diffraction (XRD) did not show any peaks, suggesting that the films are amorphous. Rutherford backscattering spectroscopy (RBS) indicated that the O:U ratio is approximately 3:1, suggesting that the film is composed of UO_3. If it is assumed that the film is composed solely of UO_3, then the thickness of film would be 6,500 Å. However, a more detailed analysis of the RBS data also suggests that there is water incorporated in the layer, perhaps as much as 1.5 molecules per U atom. Thus, the actual film is even thicker.

Because of the uniqueness of these films, we have had requests from research groups in the U.S. and in Europe for samples to be used in other experiments. It is often difficult to work with bulk uranium oxide samples, due to the inherent radiation. Even if one employs depleted uranium, as we did, there is still measurable radioactivity from large samples. However, these films are thin enough that the level of radiation emitted is very small. Also, it is relatively easy to prepare either UO_3 or UO_2 from these samples.

C. Surface studies of model reduction systems

In order to probe the reduction reaction mechanisms on an atomic scale, we have begun investigations of the reactions of model gas-phase molecules with atomically clean iron in UHV. We began with the reaction of SeF_6 with iron and iron oxide surfaces, since Se in SeF_6 is in the +6 oxidation state just as in selenate, and SeF_6 is easy to employ in vacuum. We prepared atomically clean polycrystalline Fe foils, Fe foils with controlled coverages of oxygen, as well as surfaces of fully oxidized Fe_2O_3. We exposed the surfaces to controlled amounts of SeF_6, and used XPS to monitor the coverage and oxidation states of the adsorbed Se and the changes to the chemical states of the Fe surfaces. We found that the major reaction pathway involves the reduction of Se by dissociative adsorption. In the presence of minute amounts of adsorbed oxygen, some Se sticks to the surface by attachment to O. If the surface is completely oxidized, however, the adsorption of SeF_6 is completely suppressed. These fundamental surface chemical studies show that the reduction process itself is inherent to surface reactions with iron metal, and that the reaction is severely perturbed by the presence of oxygen.

III. PLANNED ACTIVITIES

The bulk and surface studies described above will be continued employing different materials. For example, we will use Fe single crystals for reaction of SeF_6 in order to obtain detailed information on the adsorption sites. We will also perform similar measurements for the adsorption of UF_6, and for other volatile oxyanion reactants that can be reduced by iron, such as selenic acid and various chlorohydrocarbons.

New work to be done involves having better control of the starting surfaces. We have nearly completed the design of a unique reaction cell that will allow samples to be prepared with UHV techniques, and to then be reacted under solution without any exposure to the atmosphere. In this way, we can probe the reaction with absolutely clean Fe, or with Fe covered with controlled amounts of oxide, hydroxide or a metal coating. This wet cell will be attached to our XPS/STM chamber so that we can immediately analyze the reacted surfaces.

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