Project Summary

Project Title:	FUNDAMENTAL STUDIES OF THE REMOVAL OF CONTAMINANTS FROM GROUND AND WASTE WATERS VIA REDUCTION BY ZERO-VALENT METALS
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I. RESEARCH OBJECTIVE

Oxyanions of uranium, selenium, chromium, arsenic, technetium, and chlorine (as perchlorate) are frequently found as contaminants on many DOE sites. A potential remediation method is to react the contaminated water with zero-valent iron (ZVI). 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 sites. Both *in situ* reactive barriers and above-ground reactors are being developed and field tested at this time. 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 compounds with Fe filings and single- and poly-crystalline 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 February 2000, we have performed bulk chemical measurements of the reduction reactions and surface science studies of model chemical systems. We have focused primarily on the reactions of uranyl, selenate, and arsenic with elemental iron. We also worked with chromate, perchlorate, and carbon tetrachloride. Our studies have led to a new understanding of the surface adsorption and precipitation of these contaminants in reactive-barrier walls.

A. Bulk chemical studies

We studied the reactions of various oxyanions with ZVI to determine the optimum conditions for remediation. 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. Overall, the kinetics of trace element reactions with ZVI were dramatically different than expected. In the absence of O_2, the reduction and removal of trace elements was 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 reduction, with pH being the most important variable. Under aerobic conditions, the reduction rate was 2 to 3 times faster but rapidly decreased due to passivation by iron oxyhydroxide precipitates. 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. Reactions without oxygen were slower, but long-term performance of the ZVI was improved in many cases. Thus, additives that help to deplete oxygen from groundwater prior to a reactive barrier need to be further investigated. The fact that the reduction reaction was faster at high electrode potentials indicates that oxidation of the iron, and not the reduction of the contaminant, is 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.

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 results was that As(V) (arsenate) was not reduced to As(III). There was some concern that the more toxic and mobile form of arsenic, As(III), might form in a reactive barrier wall. This unexpected result expands the applicability of ZVI reactive barrier walls. NEXAFS analysis of the iron and corrosion products from the selenate reactions showed mixtures of elemental Se and selenite, Se(IV). 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 reaction with ZVI. The dominant product was lepidocrocite (γ-FeOOH) with minor amounts of maghemite (γ-Fe_2O_3) and “green rust”.

Long term studies are ongoing to determine the potential for resolubilization of uranium from the ZVI surface. Solutions of varying ionic strength, pH, alkalinity, pCO_2, and pO_2 were reacted with ZVI for 6 months to determine if the precipitated uranium can be redissolved, after all of the material has been oxidized. Initial results have shown that a small “pulse” of U goes into solution when the solutions are switched from anaerobic to aerobic conditions. However, the amount of U resolubilized was <3% of the total precipitated U. These findings suggest that the long-term immobilization of U by ZVI does occur and permanent emplacement of iron reactive barrier walls is feasible.

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). An *in situ* STM method, which continuously monitored the same spot as the reaction proceeded, showed that Fe surfaces are smoothed by reaction. The chemical composition and oxidation states of the surface products were measured with x-ray photoelectron spectroscopy (XPS). It was found that selenate deposits onto Fe surfaces by reduction to Se(IV). The amount of Se deposited is slightly increased if the atmospheric gasses are removed by N_2 purging. This is attributed 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 (~1 μm) of uranium oxide was deposited. Note that 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. A number of measurements were used to characterize the films. Scanning electron microscopy (SEM) indicated that the surfaces are fairly smooth, but contain microscopic cracks. X-ray diffraction (XRD) did not show any peaks, suggesting that the films are amorphous. Rutherford backscattering spectroscopy (RBS) showed that the film is composed of UO_3 with water incorporated. If the atmospheric gases remain in solution, only a thin film (12 Å) is formed. This difference is likely due to the presence of aqueous CO_2, which reacts with uranium to form uranyl-carbonate complexes. Thus, dissolved CO_2 and bicarbonate play important roles in determining the amount of uranium that can be effectively removed by ZVI. 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. Further work is being conducted to determine the effects of pH, uranium concentration, alkalinity, and ionic strength on the film growth.

C. Surface studies of model reduction systems

In order to probe the reduction reaction mechanisms on an atomic scale, we have investigated 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, 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, and Fe foils with controlled coverages of oxygen. We exposed the surfaces to 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 complete dissociative adsorption. In the presence of minute amounts of adsorbed oxygen, the reaction of SeF_6 is dramatically 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 completed the design of a unique wet cell that allows 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 is attached to our XPS/STM chamber so that we can immediately analyze the reacted surfaces. Samples of ZVI from a reactor at Rocky Flats have been obtained and we are preparing to analyze them for total U content and oxidation state distribution using NEXAFS. We have beam time scheduled at the SSRL for April 26-30, 2000 for these measurements.

IV. INFORMATION ACCESS

1. A.S. Mutziger, “Factors affecting the reductive dechlorination of carbon tetrachloride by zero-valent iron” (M.S. Thesis, University of California, Riverside, 1997).
2. M.J. Roberson, M.L. Hunt, C. Amrhein, S.R. Qiu, and J.A. Yarmoff, “Removal of selenate from irrigation drainage water using zero-valent iron”, Environ. Sci. Technol., returned for revision.
3. S.R. Qiu, H.-F. Lai, M.J. Roberson, M.L. Hunt, C. Amrhein, L.C. Giancarlo, G.W. Flynn and J.A. Yarmoff, “The removal of contaminants from aqueous solution by reaction with iron surfaces”, Langmuir **16**, 2230 (2000).
4. S.R. Qiu, H.-F. Lai, and J.A. Yarmoff, “Self-limiting growth of metal fluoride thin films by oxidation reactions employing molecular precursors”, Phys. Rev. Lett., submitted.
5. S.R. Qiu, H.-F. Lai, H.T. Than, C. Amrhein, and J.A. Yarmoff, “Reaction of SeF_6 with iron and iron oxide surfaces: A model system for the study of selenate reduction”, in preparation.
6. S.R. Qiu, M.L. Hunt, C. Amrhein, R. Pfeffer, T.E. Madey and J.A. Yarmoff, “The characteristics of uranium oxide films grown by surface adsorption at solid-liquid interfaces”, in preparation.
7. M.L. Hunt, “Redox reactions and precipitation products of As(III) and As(V) on zero-valent iron” (M.S. Thesis, University of California, Riverside, 1999).
8. M.J. Roberson. “Removal of selenate from irrigation drainage water using zero-valent iron” (Ph.D. Dissertation, University of California, Riverside, 1999).
9. M.J. Roberson, C. Amrhein, and M. Hunt, “X-ray absorption near edge spectroscopy for the identification of selenium species on zero-valent iron” Presented at the 16th World Congress of Soil Science. Paper published on CD-ROM in Symposium 6, Paper #1942. pp. 1-3, (1998).
10. C. Amrhein, M.J. Roberson, M.L. Hunt, S.R. Qiu, and J.A. Yarmoff, “Oxyanion adsorption and reduction on zero-valent iron and iron oxides”, Agronomy Abstracts, p. 207 (1999).
11. M.L. Hunt, B.A. Manning, S.R. Qiu, M.J. Roberson, J.A. Yarmoff, and C. Amrhein, “Sorption and oxidation of arsenic (III) on zero-valent iron”, Agronomy Abstracts, p. 214 (1999).
12. C. Amrhein, M.L. Hunt, M.J. Roberson, J.A. Yarmoff, and S.R. Qiu, “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”, V.M. Goldschmidt Conference Extended Abstracts, Mineralogical Mag. 62A:51-52 (1998).