1. Cover Sheet

Final Report
U.S. Department of Energy

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

Principal Investigator: Jory A. Yarmoff
Institution: Department of Physics
University of California, Riverside
Riverside, CA 92521
(909) 787-5336
yarmoff@ucr.edu

Co-Investigator: Christopher Amrhein
Institution: Department of Environmental Science
University of California, Riverside
Riverside, CA 92521
(909) 787-5196
chrisa@mail.ucr.edu

Project Number: 55061
DOE Award Number: DE-FG07-96ER14707
Grant Project Officer: Dr. Roland Hirsch
Project Duration: September 1, 1996 to September 14, 2000

2. Table of Contents

3. Executive Summary

Oxyanions of uranium, selenium, chromium, arsenic, technetium, and chlorine (as perchlorate) are frequently found as contaminants on many DOE sites, and in other areas of the U.S.. A potential remediation method is to react the contaminated water with zero-valent iron (ZVI). 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 physical and chemical understanding that is necessary for the development of cleanup techniques and procedures.

We performed bulk chemical measurements of the reduction reactions and surface science studies of model chemical systems. It is important to understand the bulk chemistry, but since this is essentially a surface chemical reaction that is being utilized, model surface science studies are the only way in which to assess the fundamental chemical mechanisms involved. Surface studies included reactions carried out in solution as well as model systems studies under ultra-high vacuum (UHV). 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.

Bulk chemical studies were performed of 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 various oxyanions in synthetic and natural groundwater solutions. Overall, the kinetics of trace element reactions with ZVI were dramatically different than expected. In addition, long-term studies are ongoing to determine the potential for resolubilization of uranium from the ZVI surface. The initial findings suggest that the abandonment of reactive barrier walls is not a good idea because the reoxidation and remobilization of U by bicarbonate-rich, aerobic groundwater is likely.

The evolution of the Fe surface morphology during reaction was investigated with scanning tunneling microscopy (STM) performed under aqueous solution. These images showed a smoothing of the surface that is associated with contaminant removal. The chemical composition and oxidation states of the surface products were measured with x-ray photoelectron spectroscopy (XPS). We found that both selenate and chromate deposit onto Fe surfaces by reduction. The amount of Se or Cr deposited is slightly increased if the atmospheric gasses are removed by N_2 purging, which is attributed to a thickening of the Fe oxide layer when O_2 is in solution. Uranium, however, was deposited as U(VI), i.e., it was not reduced. It had 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 only 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. We have concluded that the as-grown films produced in absence of atmospheric gasses are a amorphous U(VI) oxide with incorporated water, most likely a dehydrated schoepite. After annealing in vacuum, the films reduce to U(IV).

In order to probe the reduction reaction mechanisms on an atomic scale, we investigated the reactions of SeF_6 with iron and iron oxide surfaces in UHV. 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 showed 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. In the course of the above studies, we also found that thin Fe fluoride films grow from the spontaneous reaction of SeF_6 with Fe surfaces. Such insulating films may have numerous applications. We performed additional studies of fluoride film growth, and found that the growth initially follows the Mott-Cabrera parabolic rate law, but that the growth abruptly stops and a self-limiting thickness is attained. The sudden stop in film growth is attributed to the inability of the precursor molecules to dissociate at the surface when the insulator film becomes too thick for electrons from the substrate to transport through. This work suggests the use of molecular precursors to grow thin films via a self-limiting chemical process.

4. Research Objectives

Oxyanions of uranium, selenium, chromium, arsenic, technetium, and chlorine (as perchlorate) are frequently found as contaminants on many DOE sites, and in other areas of the U.S.. 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.

5. Methods and Results

We performed bulk chemical measurements of the reduction reactions and surface science studies of model chemical systems. It is important to understand the bulk chemistry, but since this is essentially a surface chemical reaction that is being utilized, model surface science are the only way in which to assess the fundamental chemical mechanisms involved. 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”.

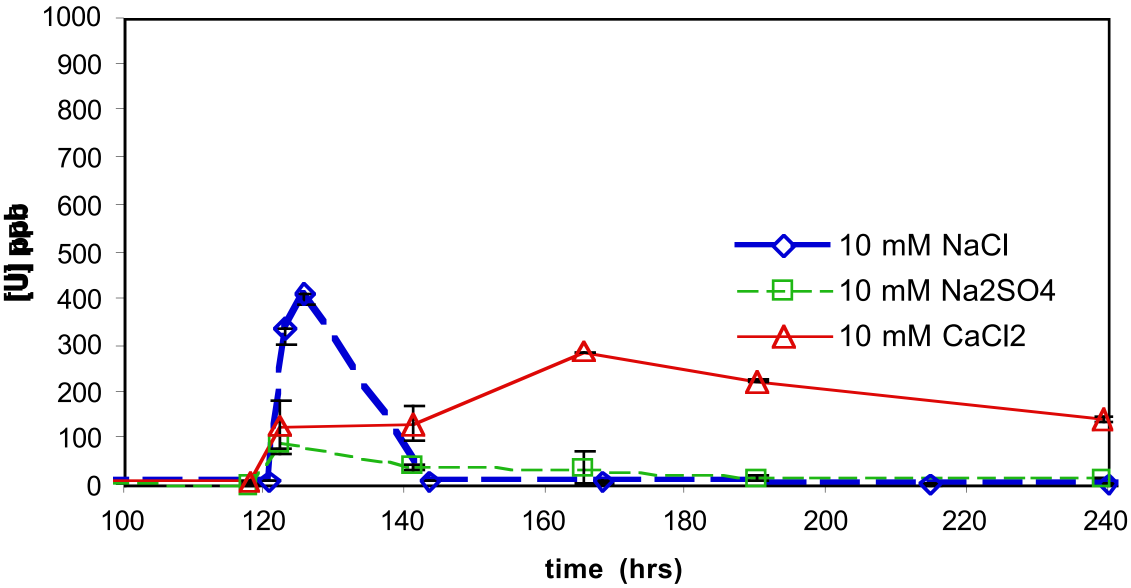

Figure 1. The release of uranium from solids under different electrolyte conditions following modification of purging gas at 120 hours.

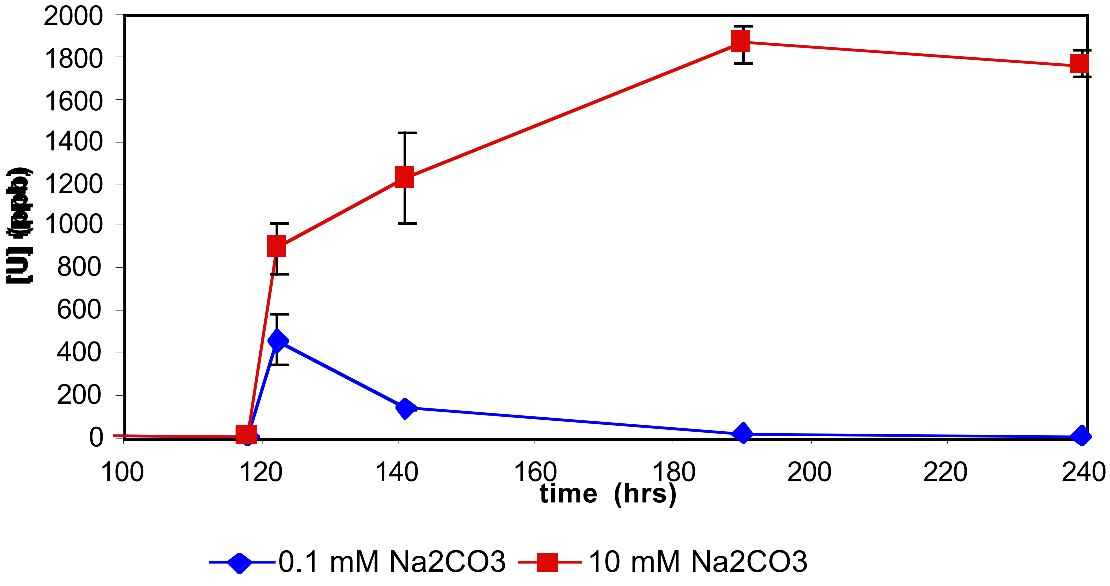

Figure 2. The release of uranium from solids with different bicarbonate concentrations following modification of purging gas at 120 hours.

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 up to 6 months to determine if the precipitated uranium can be redissolved, after all of the iron material has been oxidized. Results have shown that a "pulse" of U goes into solution when the chloride-based solutions are switched from anaerobic to aerobic conditions (Fig. 1). If the solutions contained bicarbonate or carbonate, substantially more U was solubilized under aerobic conditions from the exhausted ZVI. The amount of U resolubilized was dependent on the alkalinity and pH of the solutions. Under high alkalinity and pH, substantial amounts of U can be remobilized (Fig. 2). These findings suggest that the abandonment of reactive barrier walls is not a good idea because the reoxidation and remobilization of U by bicarbonate-rich, aerobic groundwater is likely.

B. Surface studies of reactions in aqueous solution

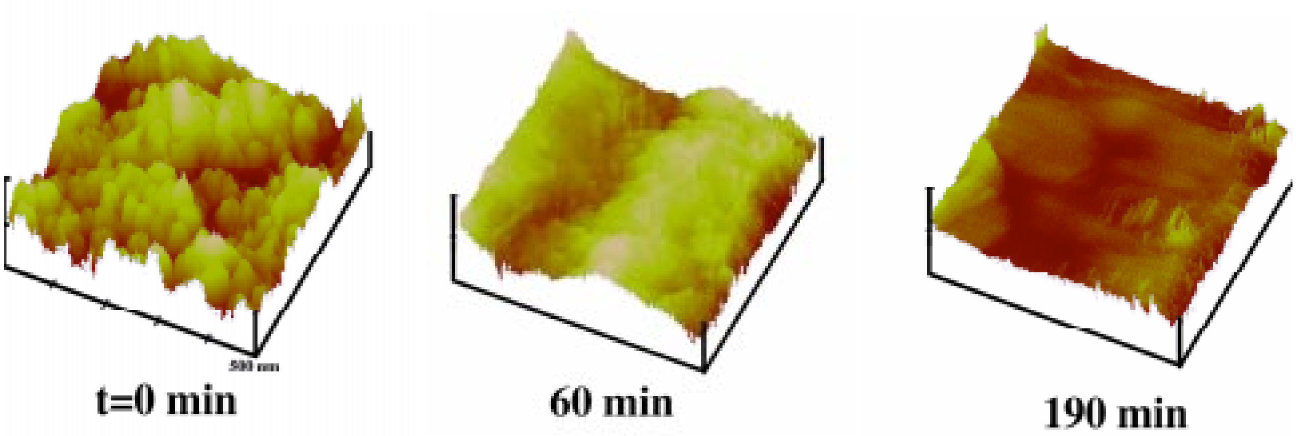

Figure 3. STM images collected *in situ* from Fe foil under a 1 mM uranyl solution. Images were collected continuously from the same spot, and are shown following reaction for the indicated time. The image sizes are 500x500 nm^2.

The evolution of the Fe surface morphology during reaction was investigated with scanning tunneling microscopy (STM) performed under aqueous solution. An *in situ* STM method, which continuously monitored the same spot as the reaction proceeded, showed that Fe surfaces are smoothed by reactions of selenate, chromate and uranyl with untreated Fe foils [3]. Note that the solutions were purged of atmospheric gasses prior to reaction, but some dissolution may have occurred while the images were collected. Figure 3 shows representative images collected during the reaction of uranyl nitrate with Fe foil. It is seen that the film was considerably smoothed after three hours of reaction. A similar smoothing was observed for reactions of selenate and chromate with Fe foil.

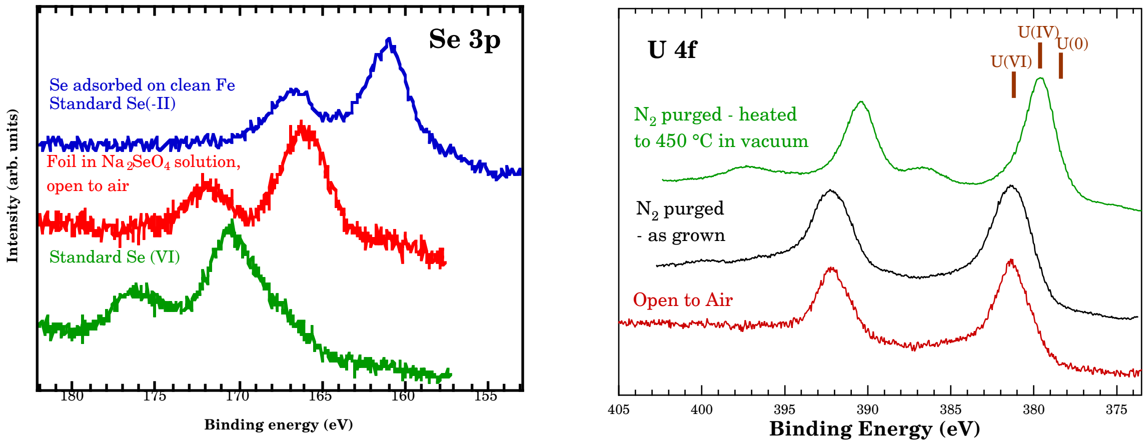

Figure 4. Left: XPS spectra of the Se 3p level collected from Fe foil following reaction with sodium selenate, and from Se standards. The data shows that selenate was reduced to selenite by the surface redox reaction in solution. Right. XPS spectra of the U 4f level collected from Fe foil following reaction with uranyl nitrate with and without purging of the atmospheric gasses, and following annealing in vacuum.

The chemical composition and oxidation states of the surface products were measured with x-ray photoelectron spectroscopy (XPS). For these measurements, the pH and atmospheric gasses were very carefully controlled during reaction, but the sample was removed from solution following reaction and then transferred to an ultra-high vacuum (UHV) chamber for analysis. We performed experiments both by transferring in air and by reacting and transferring inside an Ar-filled glove bag, and concluded that no measurable atmospheric contamination occurred between the time of reaction and insertion into the UHV chamber. As shown in the left side of Fig. 4, we 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, as seen in the right side of the figure. It had 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 only 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. We employed a variety of techniques to characterize the films [7]. Scanning electron microscopy (SEM) indicated that the surfaces of the films are fairly smooth. Figure 5 shows a side-view SEM image in which the edge of a film can be clearly seen. Such an image also allows for an estimate of the film thickness. The film surfaces contain microscopic cracks, however, that expose the underlying Fe substrate. The cracks enlarge if the sample is heated in vacuum. X-ray diffraction (XRD) data did not show any peaks associated with the as-grown films, suggesting that they are amorphous. After heating in vacuum, however, the films crystallize into a U(IV) oxide. Rutherford backscattering spectroscopy (RBS) allowed us to make more accurate measurements of the film thickness, and also indicated that the film is composed of UO_3 with water incorporated.

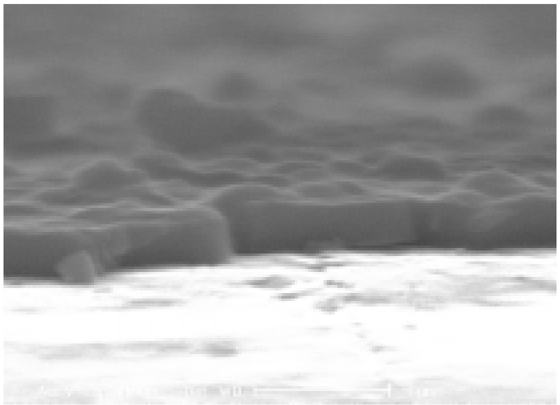

Figure 5. Scanning Electron Microscope (SEM) image of an approximately 1 µm thick uranium oxide film grown atop an iron substrate by immersion under controlled conditions into a solution containing uranyl ions. This illustrates how iron can be used for the remediation of uranium dissolved in groundwater.

We have thus concluded that the as-grown films produced in absence of atmospheric gasses are a amorphous U(VI) oxide with incorporated water, most likely a dehydrated schoepite [7]. After annealing in vacuum, the films reduce to U(IV). Although the surface of one of these U(IV) films will oxidize in air to U(VI), the bulk of the U(IV) films are inert to re-oxidation. These methods provide a unique way to make quality films of U(VI) or U(IV) in a safe, economical manner. The chemical compositions of films are very similar to those of spent nuclear fuel materials. The success of this work has great promise for producing materials that will enable various fundamental and applied studies of uranium oxide surfaces.

If the atmospheric gases remain in solution, however, 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

i. Reduction of SeF_6

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 reactions 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 deploy in vacuum [6]. We prepared atomically clean polycrystalline Fe foils by sputtering with Ar^+, and also 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.

ii. Fluoride film growth from molecular precursors

In the course of the above studies, we found that thin Fe fluoride films grow from the spontaneous reaction of SeF_6 with Fe surfaces. Such insulating films may have applications in numerous areas, so we spent some time investigating the growth mechanism for these films. The reactions of XeF_2 and SeF_6 with polycrystalline iron, vanadium, and copper surfaces at room temperature were investigated [4,5]. X-ray photoelectron spectroscopy was used to ascertain that films of FeF_2, VF_3, and CuF_2 form on the respective substrates. The film growth initially follows the Mott-Cabrera parabolic rate law, indicating that the process is initially diffusion limited. At a certain film thickness, however, the growth abruptly stops and a self-limiting thickness is attained. The sudden stop in film growth is attributed to the inability of the precursor molecules to dissociate at the surface when the insulator film becomes too thick for electrons from the substrate to transport through. The thickness using XeF_2 is nearly double that obtained with SeF_6, which suggests that SeF_6 must approach the surface more closely then XeF_2 in order to dissociate. Thicker films grow on iron and vanadium than on copper, which is due to different densities of states at the Fermi level. This work suggests the use of molecular precursors to grow thin films via a self-limiting chemical process.

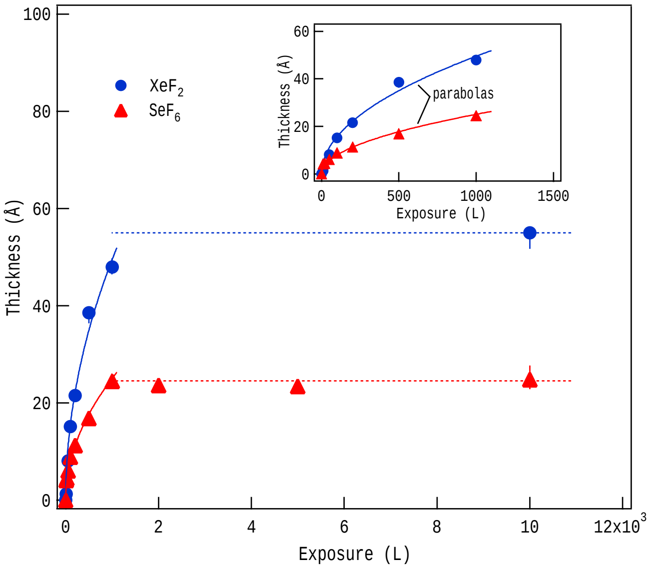

Figure 6. The thickness of the FeF_2 films grown on Fe foils as a function of exposure to both XeF_2 and SeF_6. The inset shows a blowup of the initial exposure region.

6. Relevance, Impact and Technology Transfer

The use of zero-valent iron has become the treatment option of choice in many DOE UMTRA sites and groundwater-contamination sites throughout the US. As engineering solutions are developed to solve field-scale problems of treatment technology, fundamental surface chemistry studies can identify reaction mechanisms and potential problems not yet seen in the field. Of particular interest in these studies is the identification of chemical conditions under which zero-valent iron reactors are likely to perform best. Up until now, there has been very little attention paid to the specific chemical conditions of the groundwater to be remediated. In particular, the oxygen content, alkalinity, pH, PCO_2, and ionic strength can have dramatic effects on reaction rate and long-term viability of a reactor. Before ZVI reactor barrier walls are installed, detailed chemical analysis of the groundwater is needed to identify potential problems. In these studies we have shown that exhausted ZVI reactors used to treat U plumes can be a source of further groundwater contamination if aerobic, bicarbonate-rich water continues to pass through the rusted-out reactor. Engineering options should include the reexcavation of emplaced barrier walls to recover the precipitated uranium before reoxidation can occur. Thus, systems in which the zero-valent iron is isolated in tanks are particularly attractive because of the ease of recovering the spent iron. Installations such as this are being tested at various sites, including one at an UMTRA site near Durango, CO.

We have worked with Stan Morrison in Colorado on the Durango UMTRA sites where ZVI reactors have been emplaced. We collected NEXAFS data on the actual reactor material from this site to characterize the oxidation state of U on the ZVI. We concluded that our laboratory reactions were good representations of the actual site in Durango and the precipitate that had formed was a mixed oxidation state uranium oxide that had the potential for rapid reoxidation upon exposure to oxygen.

Our work on ZVI treatment of arsenic-contaminated water is being used to support development of well-head treatment systems for shallow groundwater pumps in Bangladesh, where As contamination is widespread problem. Our work has been shared with Prof. James Farrell at the University of Arizona, Tucson, who has been working on this kind of reactor.

Collaborations with surface scientists and environmental chemists have been strengthened at UC Riverside and Columbia University. Additional research is being considered on the application of surface science techniques to the oxidation of sulfide minerals, a potential problem in mine tailings throughout the west.

7. Project Productivity

The project accomplished the goals of the proposal and had some unexpected spin-offs, including the uranium thin-film discovery. The list of publications from this work demonstrates the productivity of this project and papers are still being written from the theses of Matthew Hunt, Mark Roberson, Siping Qiu, and Logan Raub (students supported on this grant).

8. Personnel Supported

Faculty:
Jory A. Yarmoff
Chris Amrhein

Graduate Students:
Siping “Roger” Qiu
Hsu-Feng Lai
Mark Roberson
Mathew Hunt
Bryan Corbitt
Ha Trong Than
Logan Raub

9. Publications

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. **85**, 1492-1495 (2000).
5. S.R. Qiu, and J.A. Yarmoff, “Self-limiting growth of transition metal fluoride films from the reaction with XeF_2”, Phys. Rev. B **63**, 115409-115415 (2001).
6. 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”, Surf. Sci. **468**, 17-26 (2000).
7. S.R. Qiu, C. Amrhein, M.L. Hunt, R. Pfeffer, B. Yakshinskiy, L. Zhang, T.E. Madey and J.A. Yarmoff, “Characterization of uranium oxide thin films grown from solution onto Fe surfaces”, Appl. Surf. Sci. **181**, 211-224 (2001).
8. 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).
9. M.J. Roberson. “Removal of selenate from irrigation drainage water using zero-valent iron” (Ph.D. Dissertation, University of California, Riverside, 1999).
10. 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).
11. 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).
12. 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).
13. 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).
14. L.B. Raub, “Zero-valent iron for the cleanup of uranium-contaminated water” (M.S. Thesis, University of California, Riverside, 2001).

10. Interactions

The following presentations of this work were made:

National Meeting of the Soil Science Society of America, Anaheim, CA, October 26-31, 1997. Presentation given by M.J. Roberson entitled “The Use of Iron Metal for the Removal of Selenate in Irrigation Drainage Water” by M.J. Roberson, C. Amrhein, J.A. Yarmoff and M. Hunt.

American Physical Society, Los Angeles, CA, March 16-20, 1998. Talk given by S.R. Qiu entitled “Reduction of trace element contaminants in aqueous solution using iron foil” by S.R. Qiu, H.-F. Lai, J.A. Yarmoff, C. Amrhein, M.J. Roberson, M. Hunt, L.C. Giancarlo and G.W. Flynn. Talk given by H.-F. Lai entitled “The reduction of SeF_6 by Fe and Fe oxides” by H.-F. Lai, S.R. Qiu, J.A. Yarmoff and C. Amrhein.

16th World Congress of Soil Science. Montpellier, France. August 20-26, 1998. Poster presented by C. Amrhein entitled “X-ray absorption near edge spectroscopy for the identification of selenium species on zero-valent iron” by M.J. Roberson, C. Amrhein, and M. Hunt.

V.M. Goldschmidt Conference, Toulouse, France. August 30-September 3, 1998. Poster presented by C. Amrhein entitled “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” by C. Amrhein, M.L. Hunt, M.J. Roberson, J.A. Yarmoff, and S.R. Qiu.

A**merican Vacuum Society National Symposium, Baltimore, MD, November 2-6, 1998.** Talk given by S.R. Qiu entitled “Reduction of trace element contaminants in aqueous solution by iron and iron oxides” by S.R. Qiu, H.-F. Lai, J.A. Yarmoff, C. Amrhein, M.J. Roberson, and M. Hunt.

Gordon Conference on Chemical Reactions at Surfaces, February 28-March 5, 1999, Ventura, CA. Poster presented by S.R. Qiu entitled “The removal of trace-element contaminants from aqueous solution by reaction with iron surfaces” by S.R. Qiu, H.-F Lai, M.J. Roberson, M.L. Hunt, C. Amrhein and J.A. Yarmoff.

American Chemical Society, New Orleans, LA, August 22-26, 1999. Talk given by J.A. Yarmoff entitled “Fundamental Investigations of the Remediation of Trace Element Contaminants in Aqueous Solution by Zero-Valent Iron” by J.A. Yarmoff, S.R. Qiu, H.-F. Lai, C. Amrhein, M.J. Roberson and M. Hunt. Talk given by B.V. Yakshinskiy entitled “Interaction of water vapor with uranium oxide surfaces” by M.N. Hedhili, B.V. Yakshinskiy, R. Dobrozemsky, S.R. Qiu, J.A. Yarmoff and T.E. Madey.

American Vacuum Society National Symposium, Seattle, WA, October 25-29, 1999. Talk given by S.R. Qiu entitled “Reaction of SeF_6 with iron and iron oxides” by S.R. Qiu, H.-F. Lai, H.T. Than, C. Amrhein and J.A. Yarmoff.

Soil Science Society of America Annual Meeting, 1999, Salt Lake City, UT. Two invited talks with published abstracts given: (1) “Oxyanion adsorption and reduction on zero-valent iron and iron oxides” by C. Amrhein, M.J. Roberson, M.L. Hunt, S.R. Qiu, and J.A. Yarmoff; (2) “Sorption and oxidation of arsenic(III) on zero-valent iron” by M.L. Hunt, B.A. Manning, S.R. Qiu, M.J. Roberson, J.A. Yarmoff, and C. Amrhein.

Gordon Conference on Chemical Reactions at Surfaces, February 18-22, 2001, Ventura, CA. Poster presented by J.A. Yarmoff entitled “Self-limiting growth of transition metal fluoride films from the reactions of XeF_2 and SeF_6 with polycrystalline metal surfaces” by S.R. Qiu and J.A. Yarmoff

State University of Moldova, Department of Chemistry, March 20, 2001. Talk given by C. Amrhein entitled "The chemistry of uranium, selenium, arsenic, and chromium in soils and groundwaters."

12. Patents

None.

13. Future work

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.