Fundamental studies of the removal of contaminants from ground and waste waters via reduction by zero-valent metals

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Environmental Problem

- Oxidized forms of several toxic trace elements (e.g., SeO_4^{2-}, CrO_4^{2-}, UO_2^{2+}) are mobile in the environment.

- These ions have contaminated groundwaters throughout the United States.

- In many areas, the discharge of shallow groundwater has resulted in the death or birth-deformaties of wildlife, e.g., Kesterson reservoir in the Central Valley of California and the Salton Sea.

- Groundwater contamination at many DOE sites is becoming a critical cleanup issue, e.g., Hanford, Rocky Flats, Oak Ridge, Idaho Falls, etc.

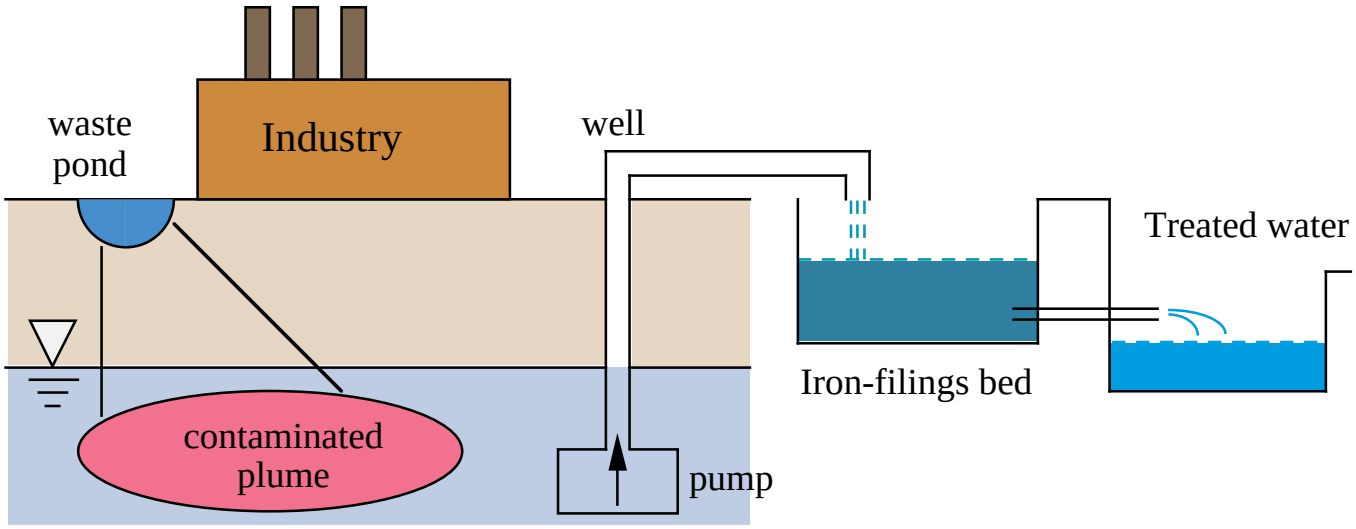
Possible Solution

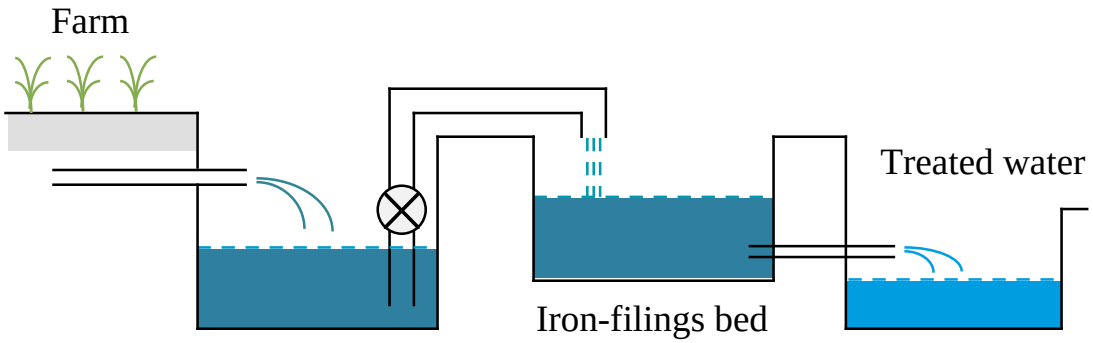
- Iron filings can be used to reduce mobile forms of toxic elements in water to insoluble forms.

- The insoluble compounds can then be easily removed.

- Example:

selenate (SeO_4^{2-})	soluble
selenite (SeO_3^{2-})	slightly soluble
selenide (Se^{2-})	insoluble
elemental Se^0	





This Project

- Objectives
  - fi Determine the best working conditions for treatment with zero-valent iron
  - fi Determine the microscopic mechanisms of the reduction of contaminants via reaction with iron
  - fi Determine the basic physics and chemistry of electron transfer reactions at metal surfaces

- Approach
  - fi Bulk chemical studies of model systems
  - fi Ultra-high vacuum surface science techniques

- Experiments
  - ® Rate measurements of reduction via iron filings
  - ® SEM, XRD and XANES analysis of reacted filings
  - ® STM, XPS and SEM analysis of iron foils reacted in solution
  - ® Reaction of model gaseous compounds with iron foils in UHV

Aqueous Contaminant Reduction with Zero Valent Iron

Iron Corrosion

Fe^{0} Æ $Fe^{2+} + 2e^{-}$ (anaerobic)

Fe^{2+} ´ $Fe^{3+} + e^{-}$ (aerobic)

$Fe^{2+} + 2OH^{-}$ ´ $Fe(OH)_2^{0}$

$Fe^{3+} + 3H_20$ ´ $Fe(OH)_3 + 3H^{+}$

$2H^{+} + 2e^{-}$ ´ H_2

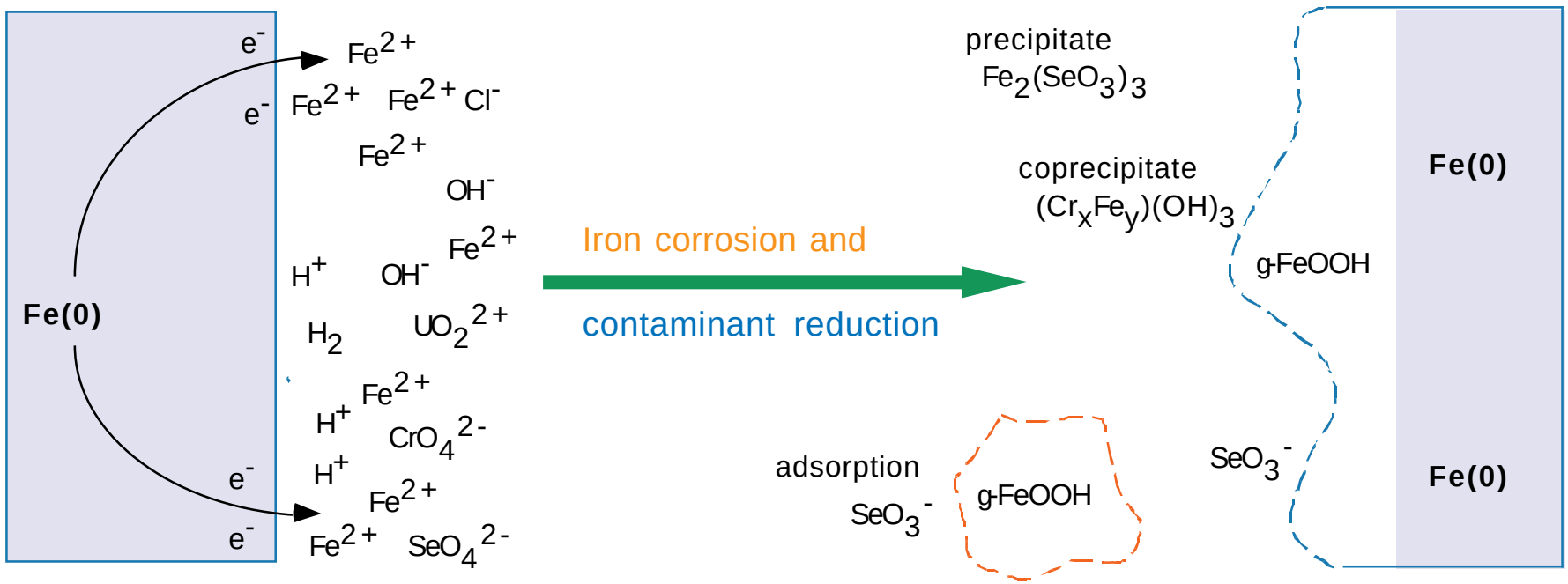
Contaminant Reduction

$SeO_4^{2-} + 2e^{-} + 2H^{+}$ ´ $SeO_3^{2-} + H_2O$

$CrO_4^{2-} + 3e^{-} + 4H_2O$ ´ $Cr(OH)_3 + 5OH^{-}$

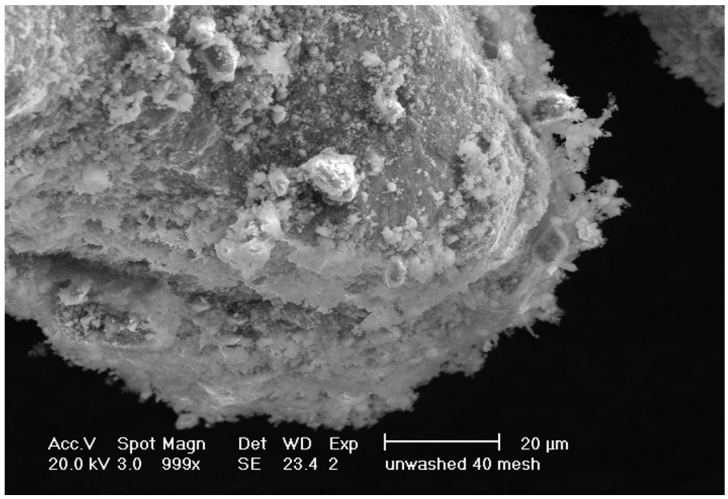
$UO_2^{2+} + 4H^{+} + 2e^{-}$ ´ $U^{4+} + 2H_2O$

$CCl_4 + 8e^{-} + 4H^{+}$ ´ CH_4 (g) $+ 4Cl^{-}$

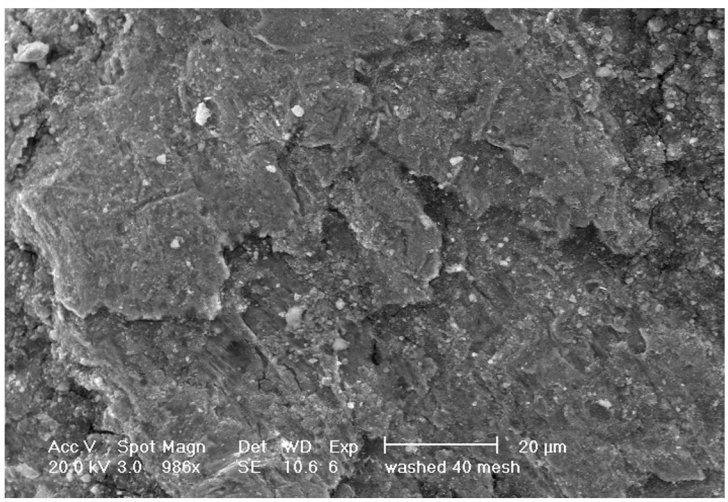


The equations that govern the chemistry of iron corrosion are listed on the left and the proposed equations for the reduction of contaminants are on the right. During aqueous corrosion, the iron metal serves as the anode and ferrous iron is released to solution. On the cathodic side oxidized contaminants, protons, and dissolved oxygen are available for reduction. The combination of these processes results in various corrosion products as well as iron surface modification.

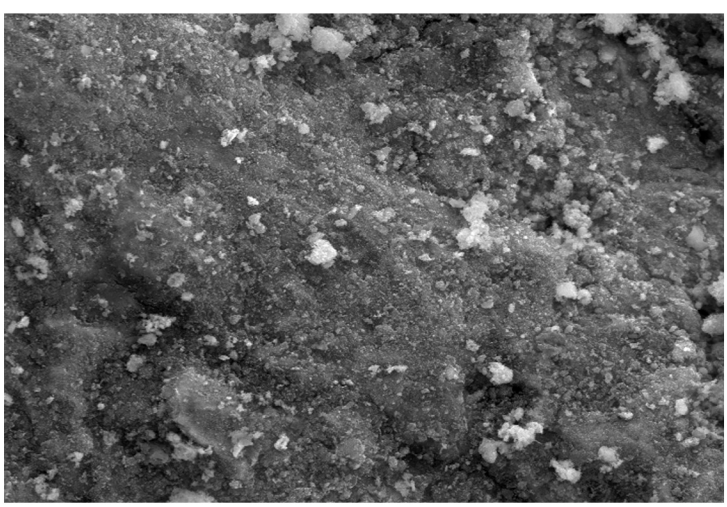
SEM Images of 40 Mesh Iron Filings



Unwashed



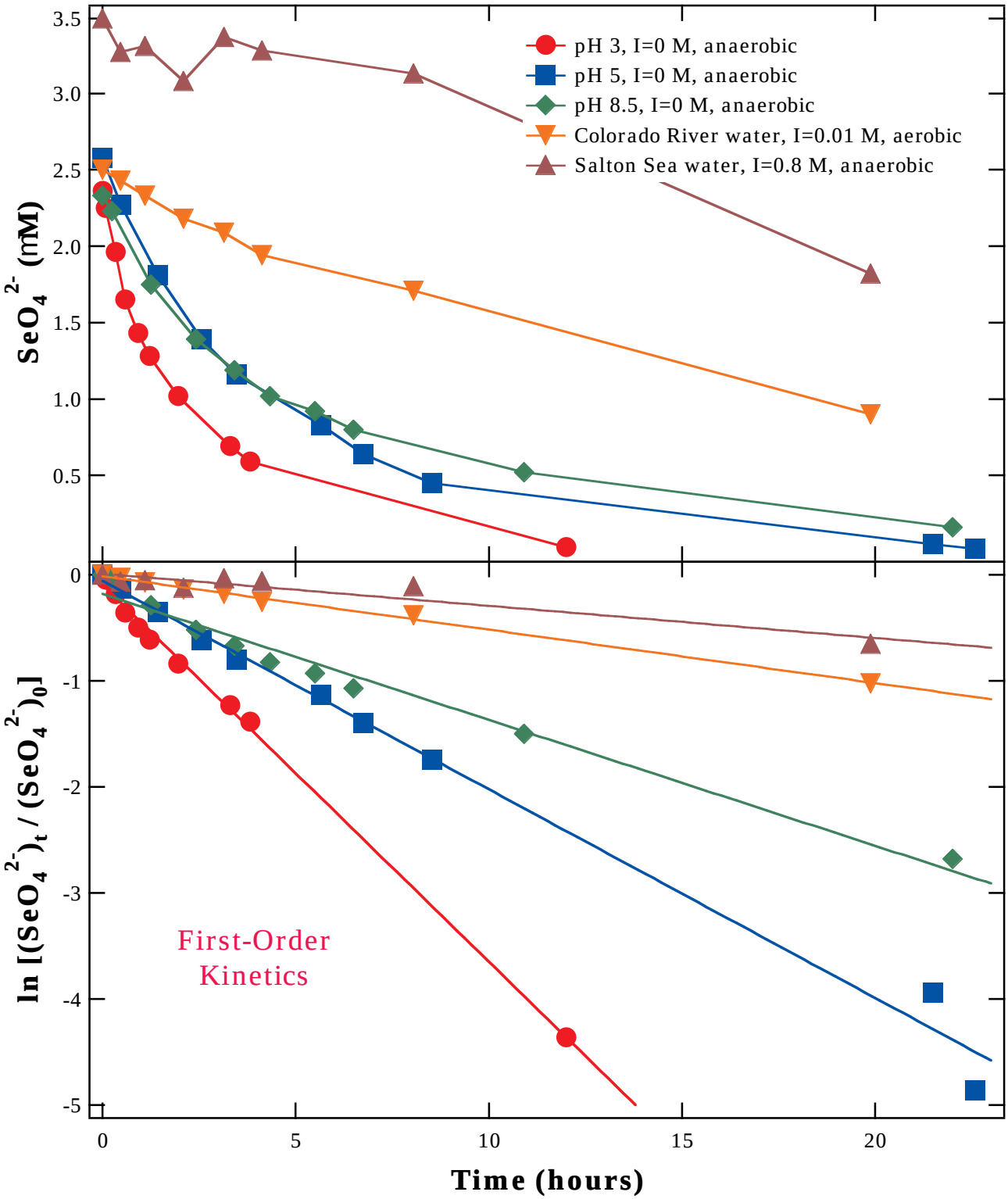
Washed



Se reacted

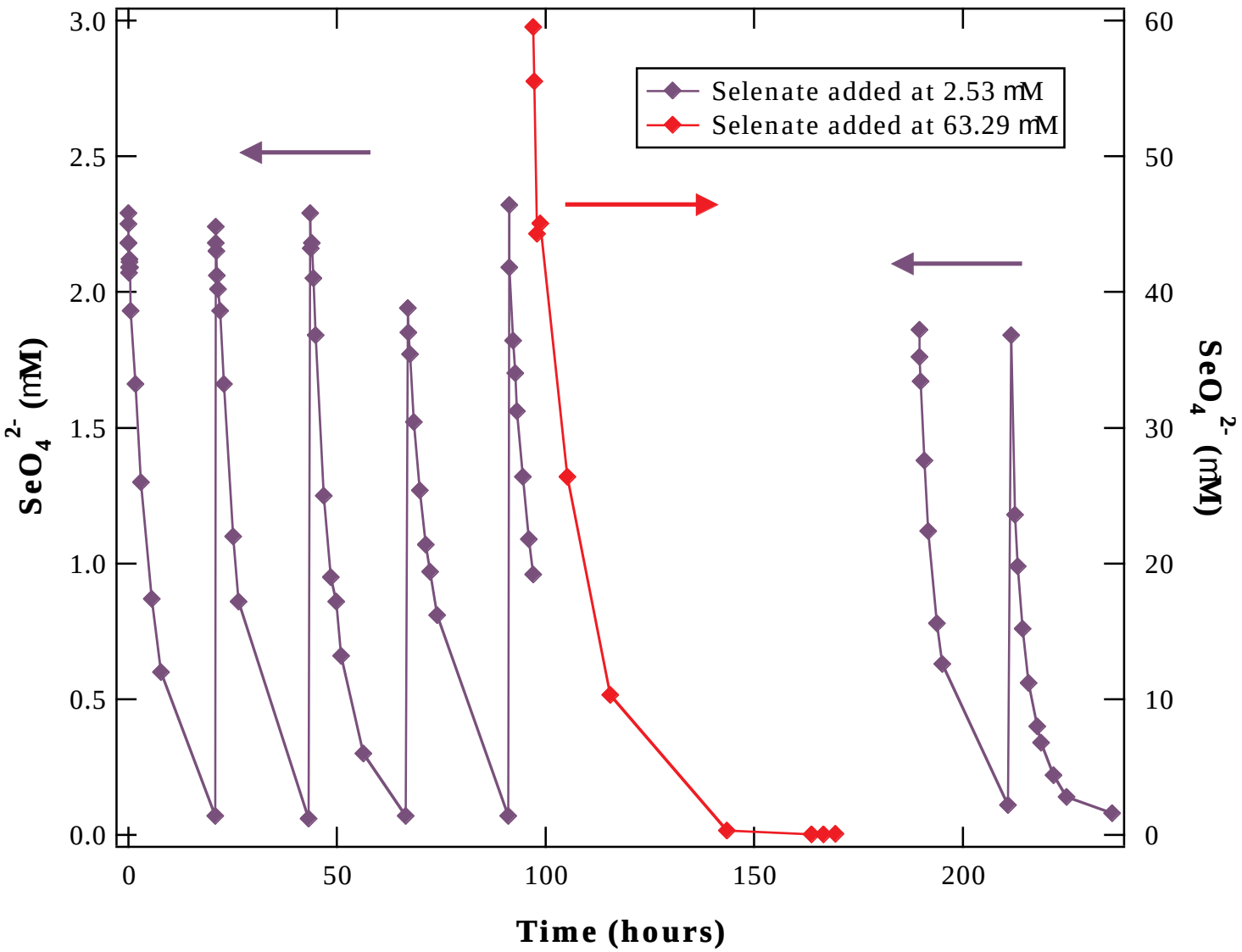
Scanning electron microscopy was used to observe gross surface morphologies. The physical condition of the zero-valent iron affects its reactivity. Unwashed iron shows a heavy oxide buildup that prevents access to the metal surface. Washed iron shows a surface with most of the oxide build up removed. Zero-valent iron reacted under aerobic conditions shows a surface with a moderate amount of oxide.

Aqueous Selenate Reduction with Zero Valent Iron



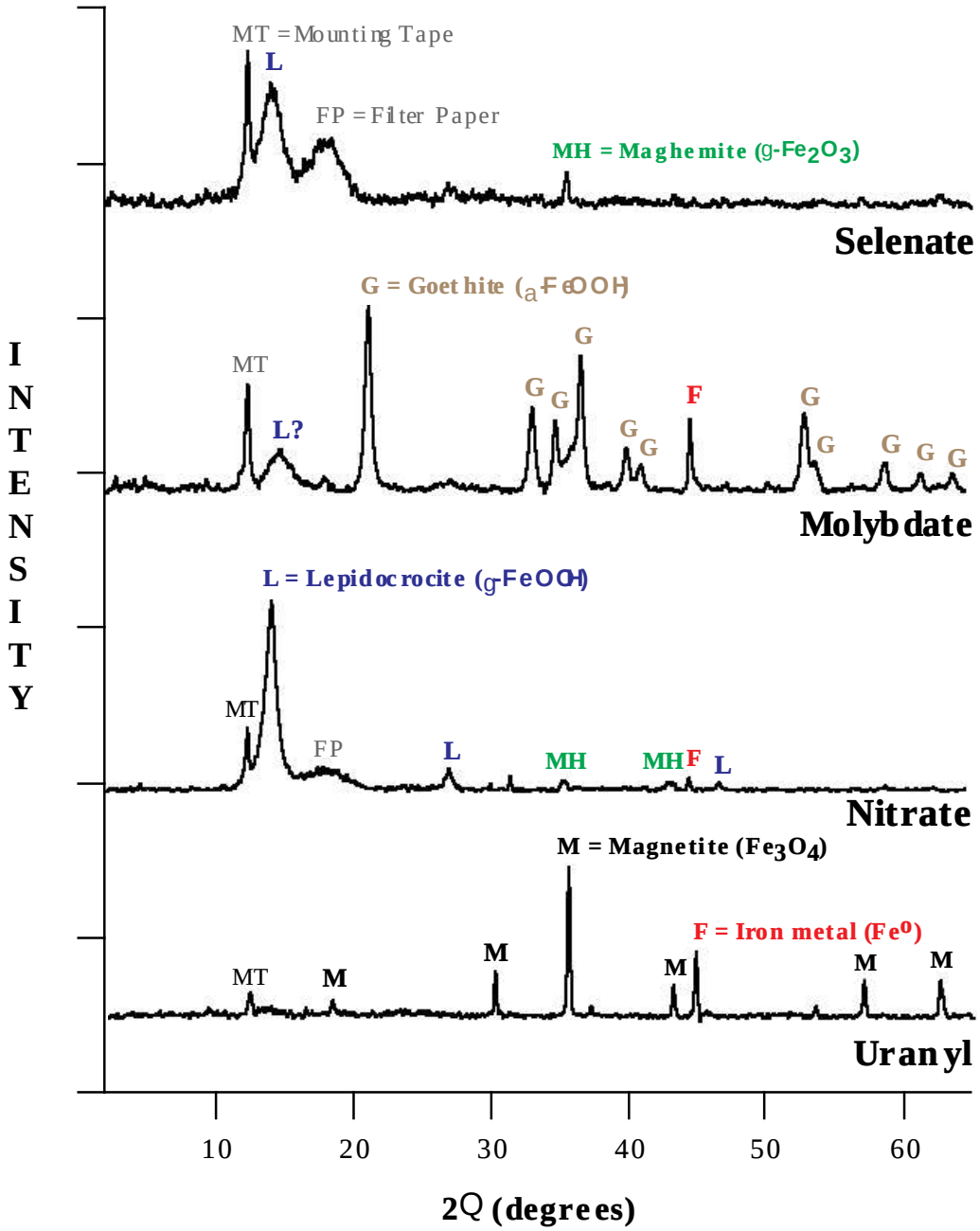
The reduction of aqueous selenate using zero-valent iron is affected by the solution's composition. Competing reduction reactions, ionic strength (I) and ratios of chloride, sulfate and bicarbonate also affect the rate. Reactions at low pH go faster due to the cathodic H^+ ion. Initially, aerobic reactions have a faster reduction rate than anaerobic reactions. However, under aerobic conditions the rate decreases over time due to an oxide build up on the iron surface.

Reaction Under Anaerobic Conditions



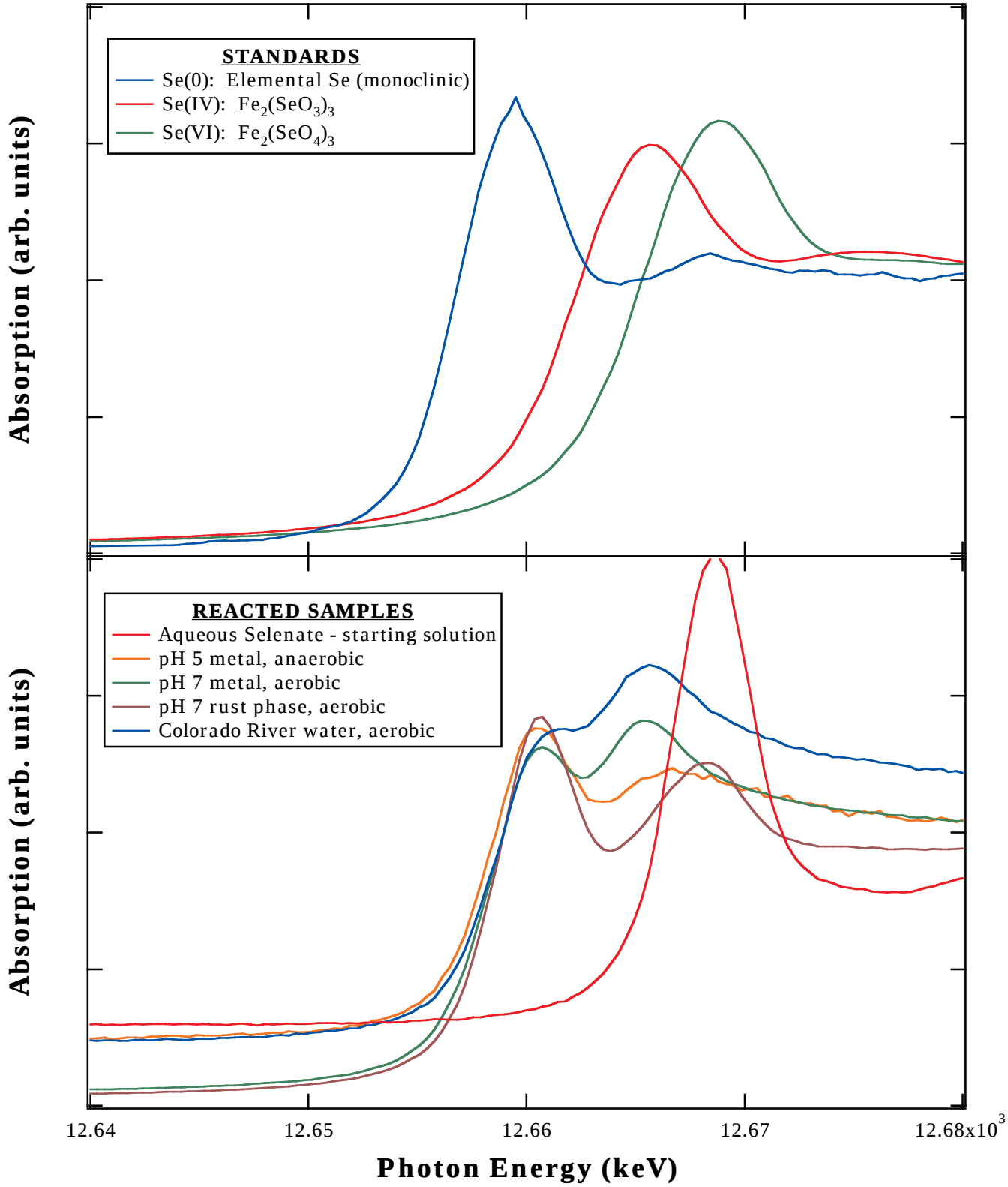
Under anaerobic conditions there is little build up of oxides on the surface of the zero-valent iron. The lack of an oxide build up prevents metal passivation and allows the metal to continuously corrode. For this experiment zero-valent iron was aged in solution for 4 days prior to the addition of selenate. Selenate was added daily for ten days with no loss in reduction rate.

X-Ray Diffraction Patterns of Secondary Iron Precipitates



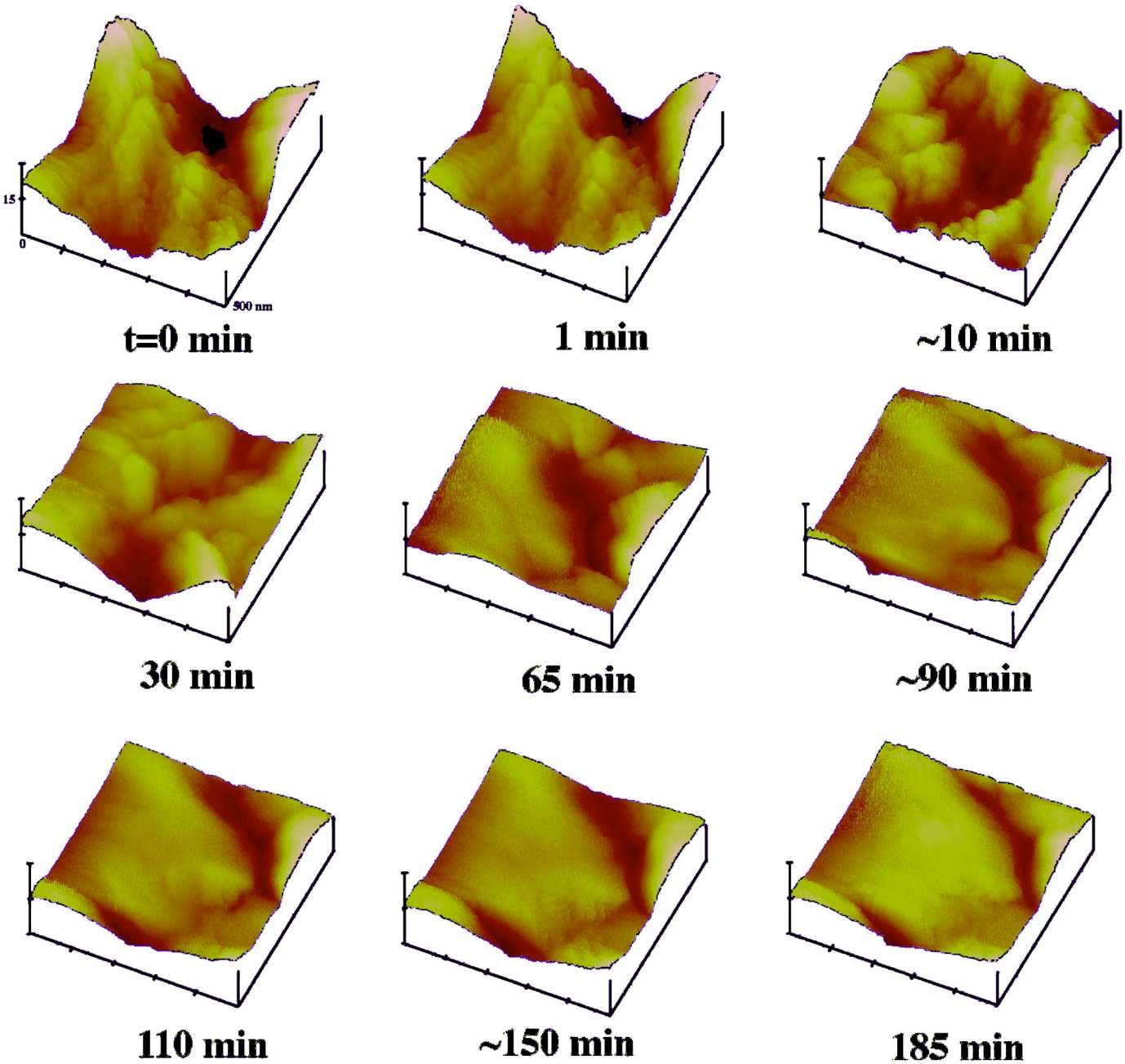
XRD patterns are used to identify corrosion products formed from the reactions with iron metal. Secondary precipitates cause cementation within the reactors, reduction in hydraulic conductivity, and reactor failure. The mineralogy of the products is a function of pH, ionic strength, bicarbonate and oxygen concentrations, and the type of contaminant. Research is ongoing to charaterize the conditions required to form each mineral phase.

X-Ray Absorption Near-Edge Structure (XANES)



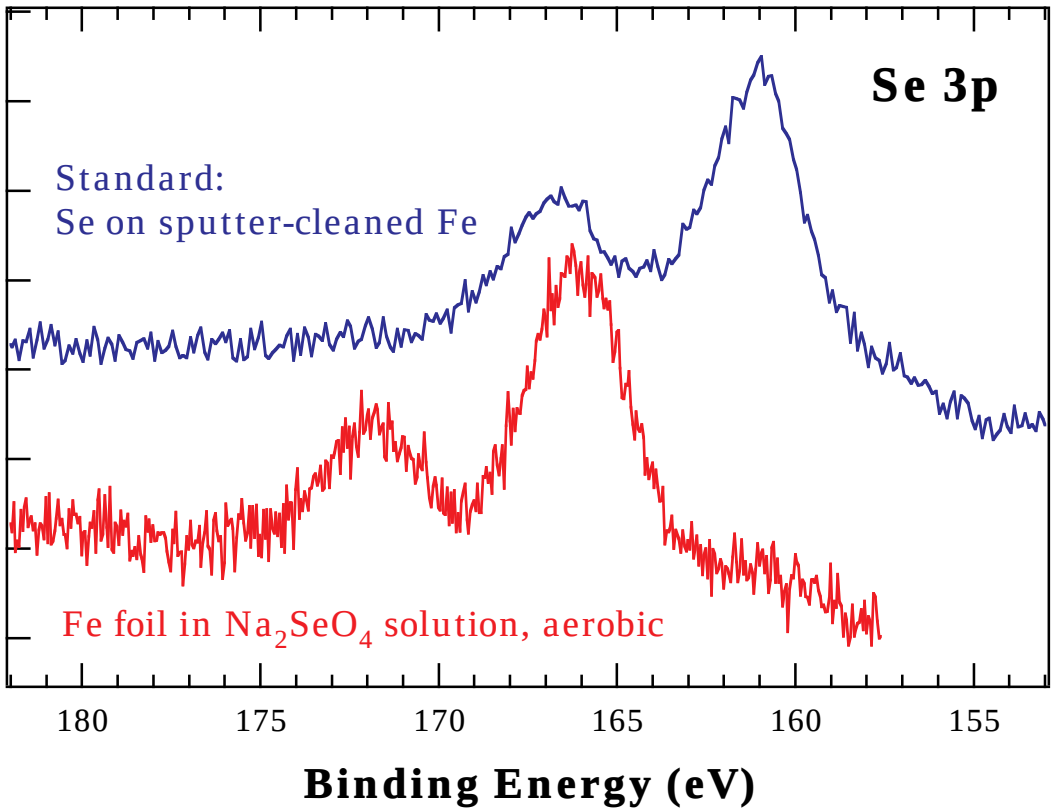
XANES spectra were collected from samples reacted under various reducing conditions. The spectra collected from metal samples all indicate a mixture of Se(0) and Se(IV). The spectra collected from the rust phase products of the reaction also show some Se(VI).

Iron foil in a Sodium Selenate Solution

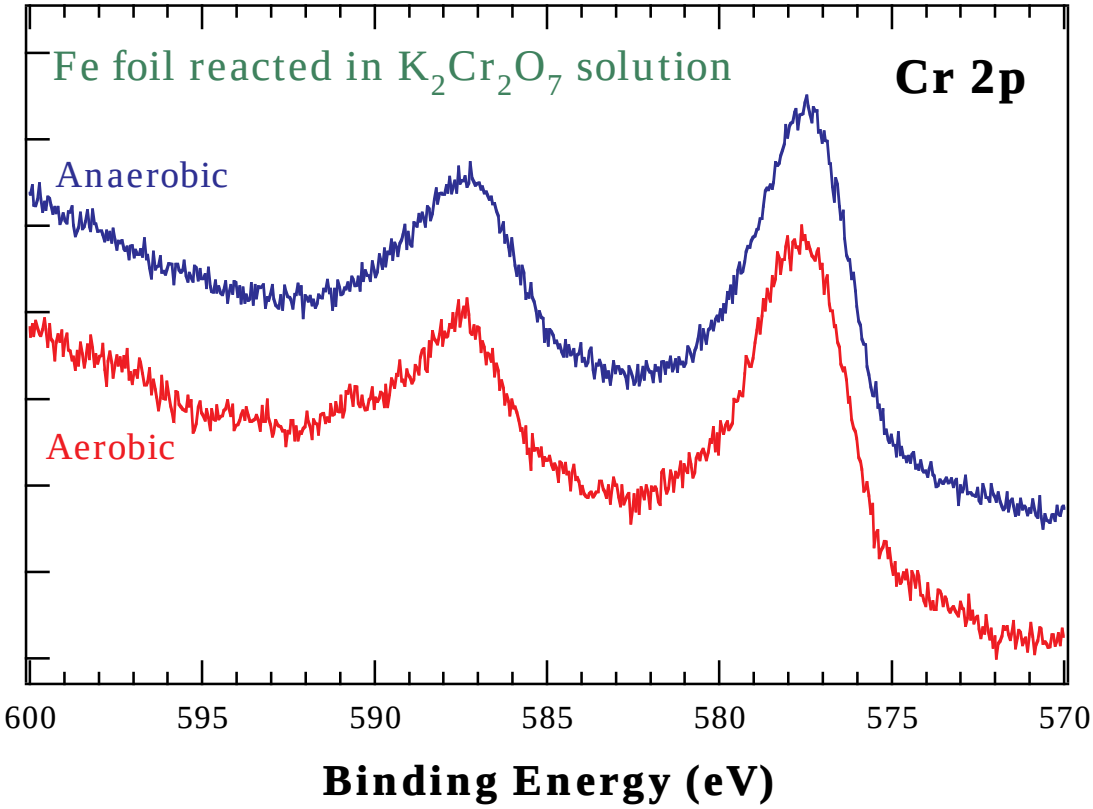


Iron foil was monitored *in situ* with STM during the reduction of selenate in solution. The 500 x 500 nm images show the rough surface, characteristic of a native iron oxide, becoming smoother as the reaction proceeds. XPS showed that the smooth morphology is due to the deposition of selenite.

Reduction of Selenate and Chromate

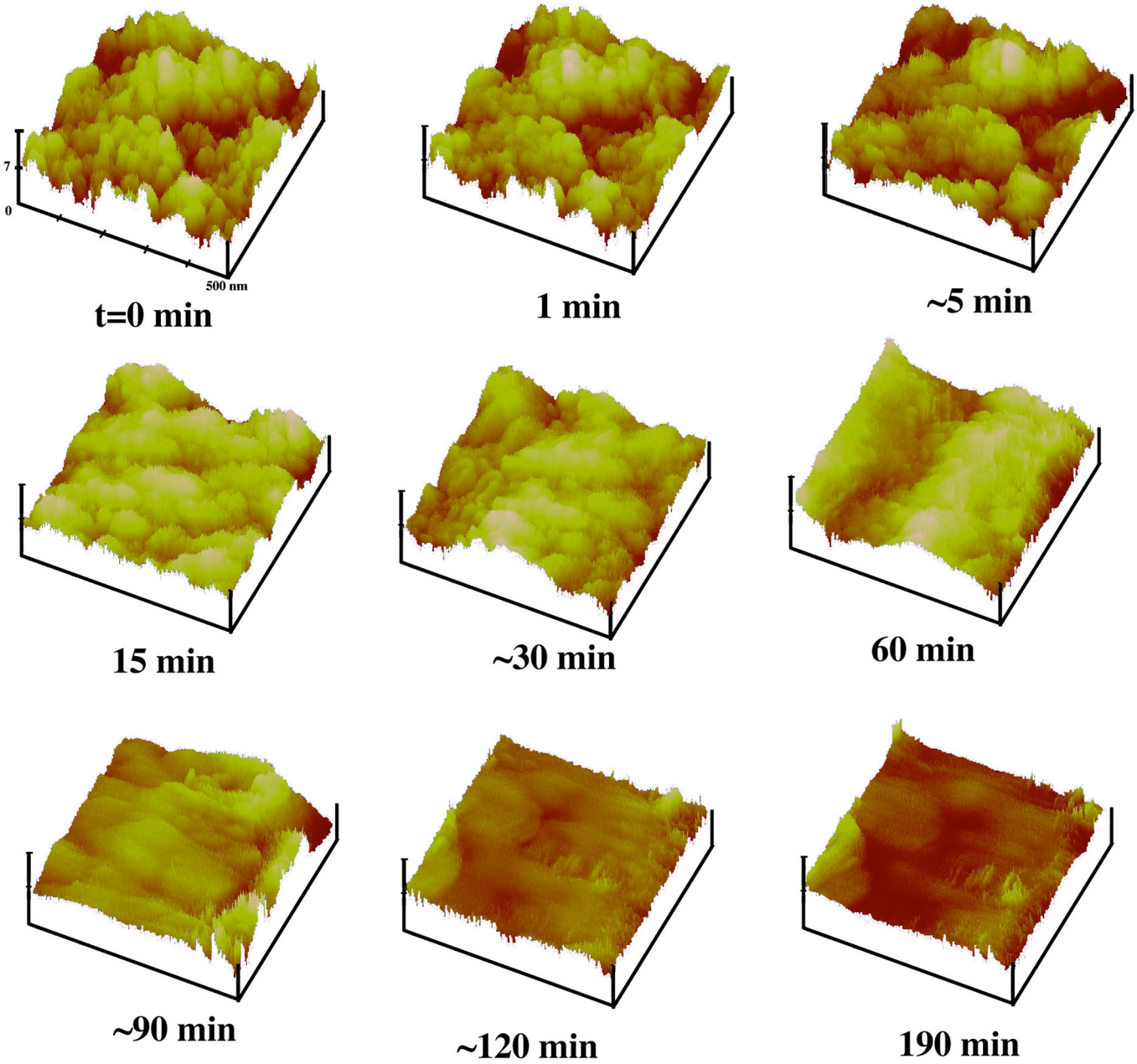


Selenate is partially reduced on the surface, consistent with Se(IV)



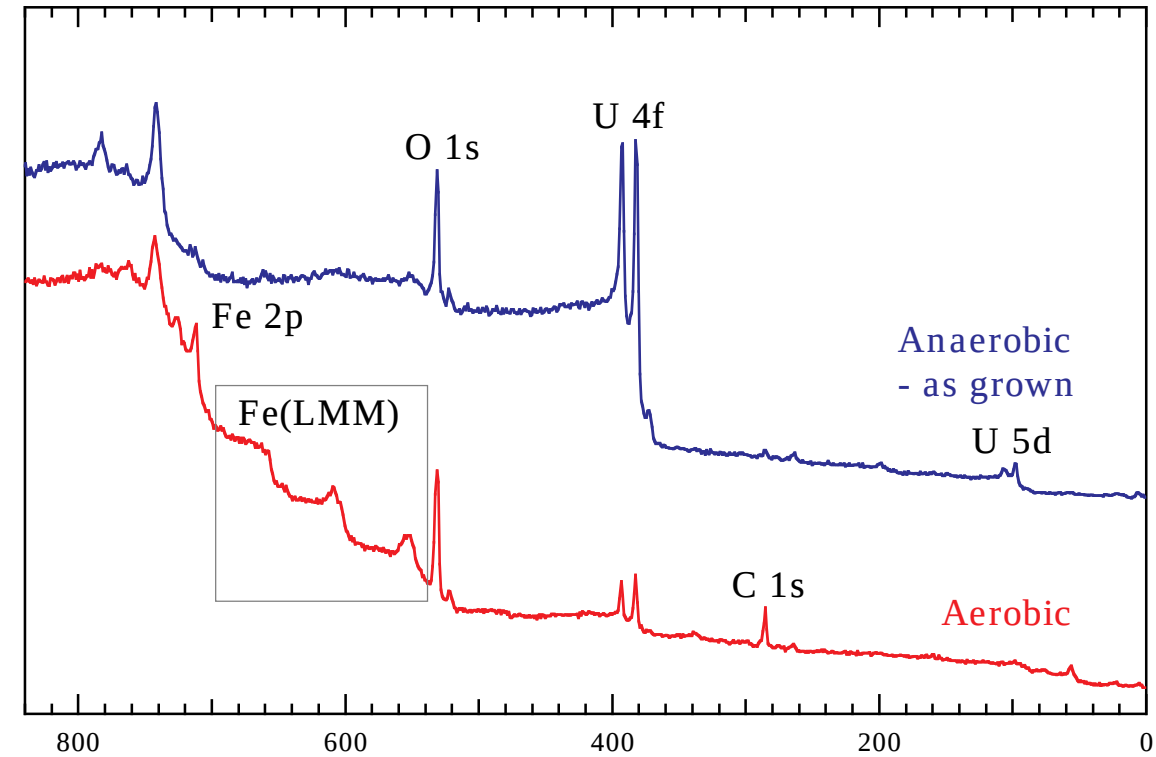
Chromate is partially reduced on the surface, consistent with Cr(III)

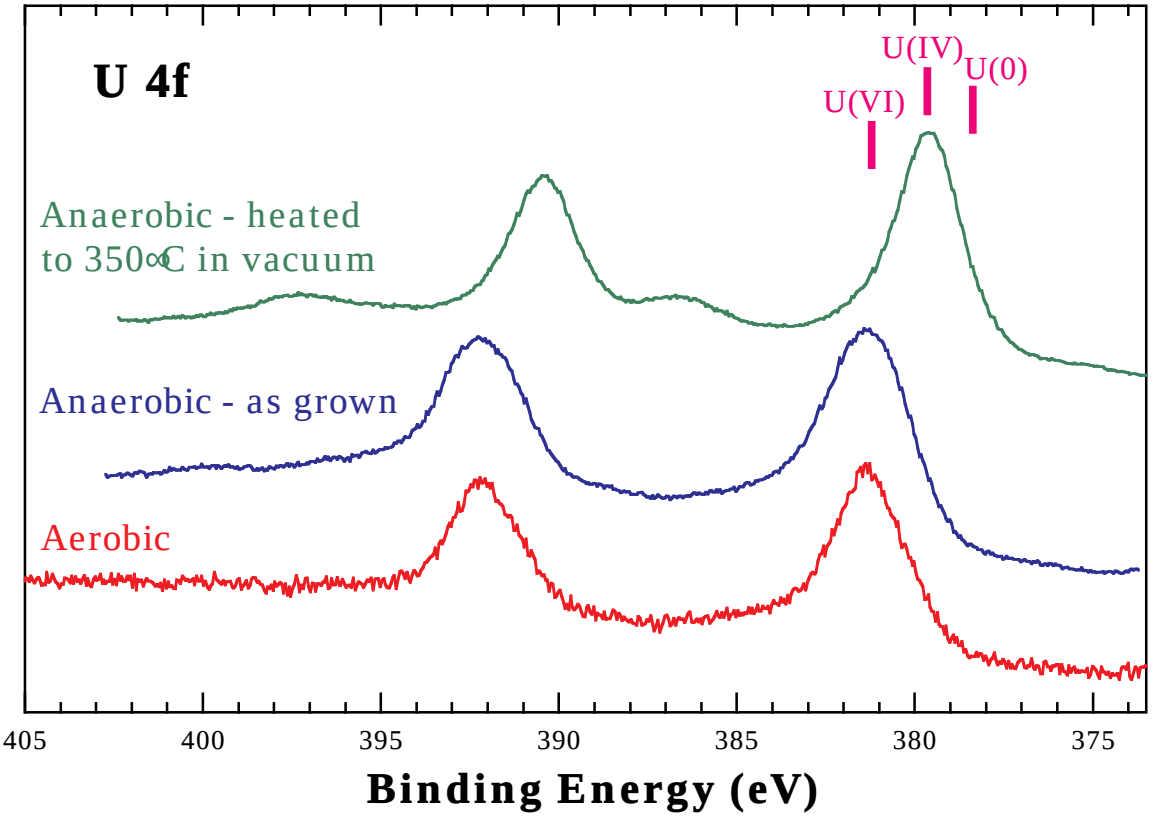
Iron foil in a Uranyl Nitrate Solution



The surface of an iron foil was monitored with *in situ* STM in a solution containing uranyl nitrate. The 500 x 500 nm images show the rough surface, characteristic of a native iron oxide, becoming smoother as the reaction proceeds. XPS analysis showed that the smooth morphology is due to the deposition of UO_3.

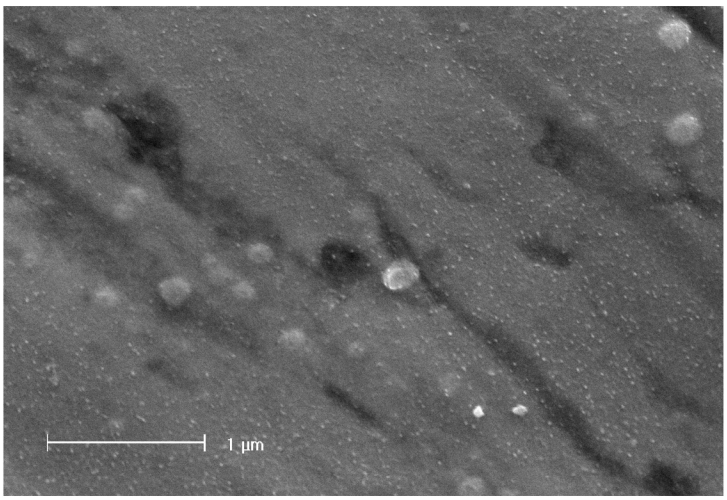
Fe foil reacted in $UO_2(NO_3)_2$ solution



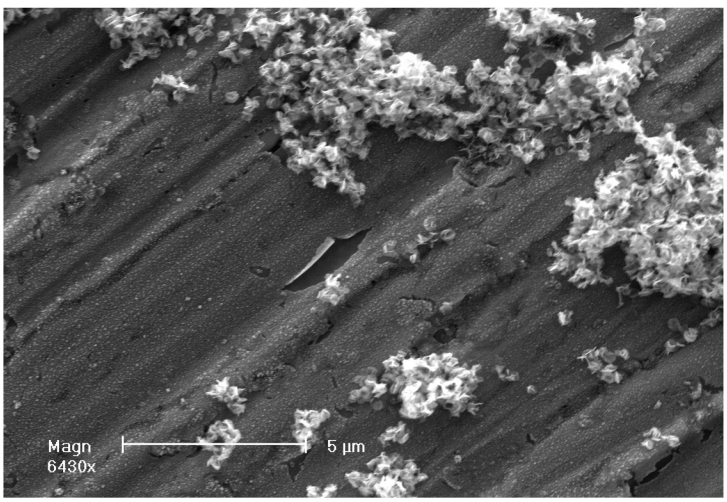


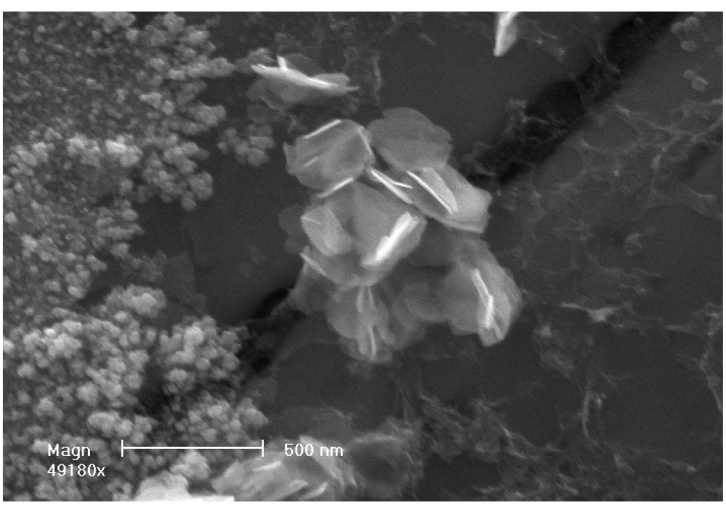
- Films of UO_3 grow under both conditions
- Under anaerobic conditions: much more U is deposited, no Fe is visible, sample appears dark blue
- When heated in vacuum, films reduce to UO_2

SEM Images of Uranium Oxide Films grown on Iron



As grown





After Heating in Vacuum and Exposure in Air

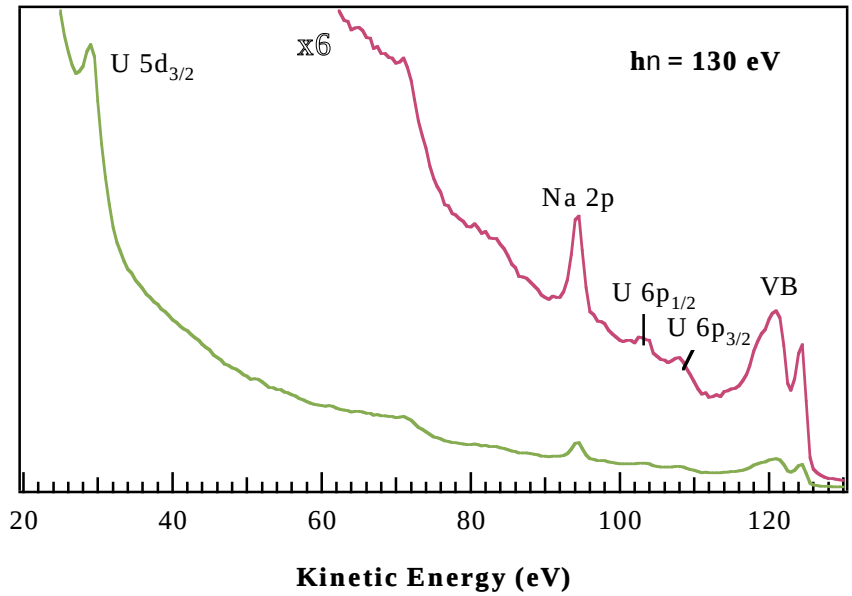
The films grown in anaerobic conditions are fairly smooth. EDX confirms their stoichiometry as UO_3. After heating, the films are converted to UO_2, but reaction with air rapidly forms uranyl carbonate. The precipitates shown are the carbonate, while the film below is oxide.

Synchrotron Radiation Studies of Uranium Oxide films

- Heated in vacuum to form UO_2

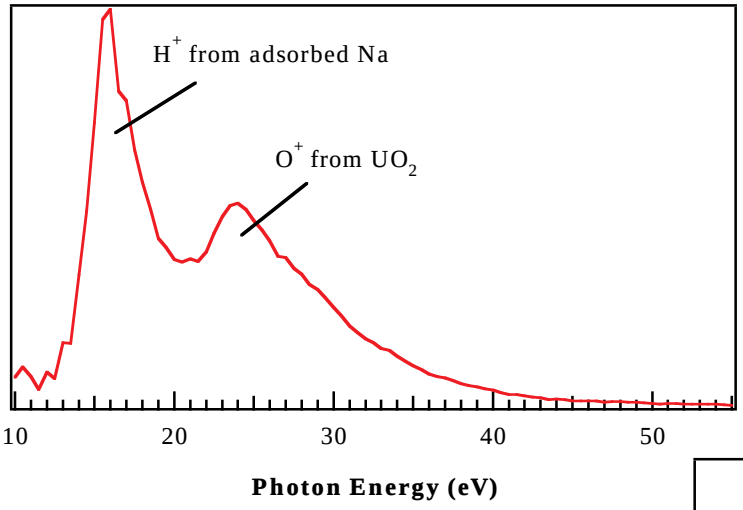
Soft X-Ray Photoelectron Spectroscopy

Photoelectron spectrum shows VB with sharp state at E_F, some U levels and possibly adsorbed Na.



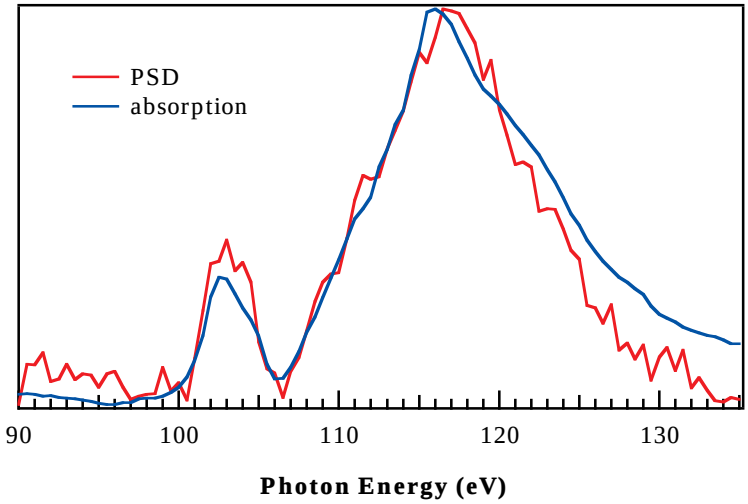
Photon Stimulated Desorption (PSD)

- monitor ion yield vs. excitation energy



- First peak at too low an energy to be from O^+
- Likely to be H^+ associated with Na adsorbate

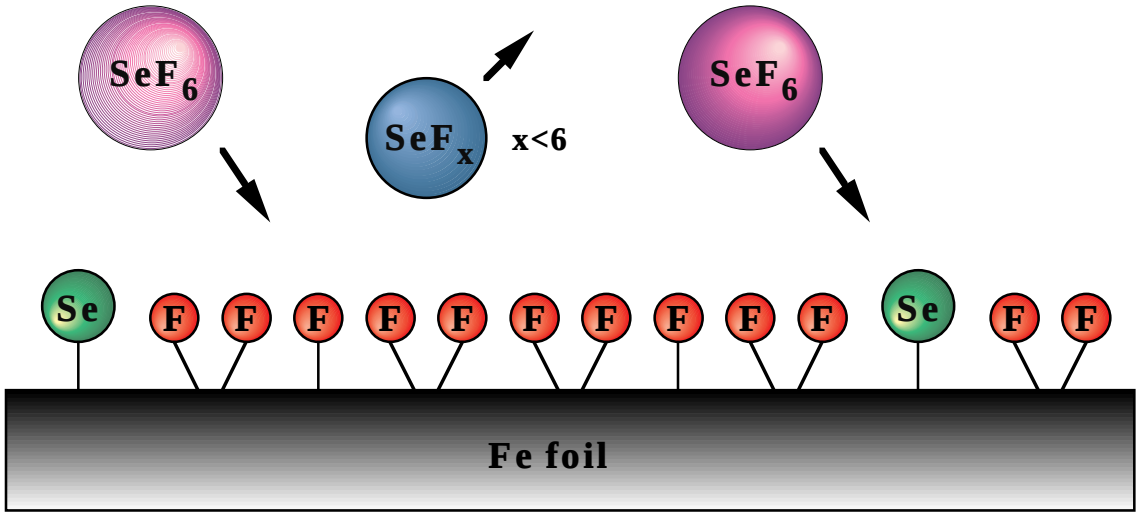
- PSD matches absorption
- O^+ likely formed by Knotek-Feibelman process



Reaction of SeF_6 with Iron and Iron Oxides

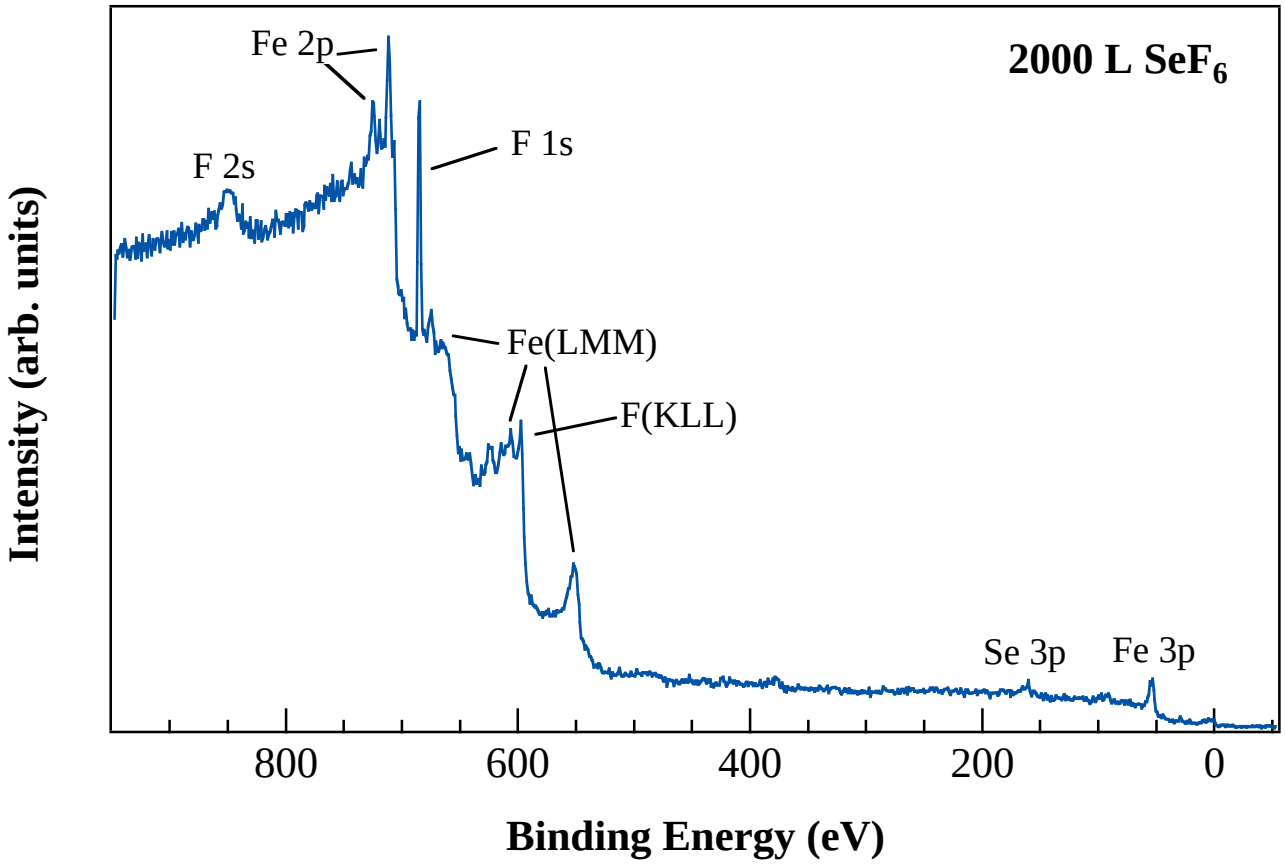
- SeF_6 is a model of the selenate reduction reaction
- Se in SeF_6 is in the same oxidation state as in selenate
- SeF_6 is a gas that can be precisely controlled in UHV
- XPS core-level shifts due to fluorine bonding are easily discernable
- It is found that SeF_6 is reduced by reaction with iron
- Pre-exposure to oxygen reduces sticking, while no SeF_6 reacts with fully oxidized surface

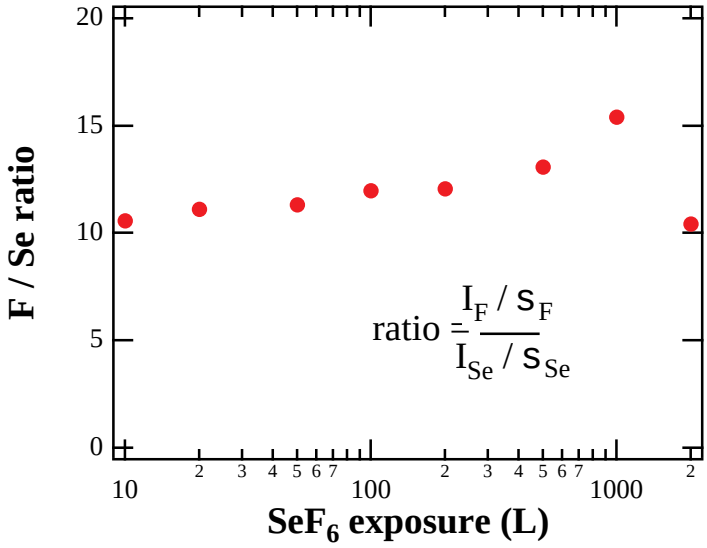
Two reduction pathways:



1) Some SeF_6 is (partially) reduced by the surface, but does not stick
2) The Se that does stick is completely reduced

SeF_6 reacted with Fe foil

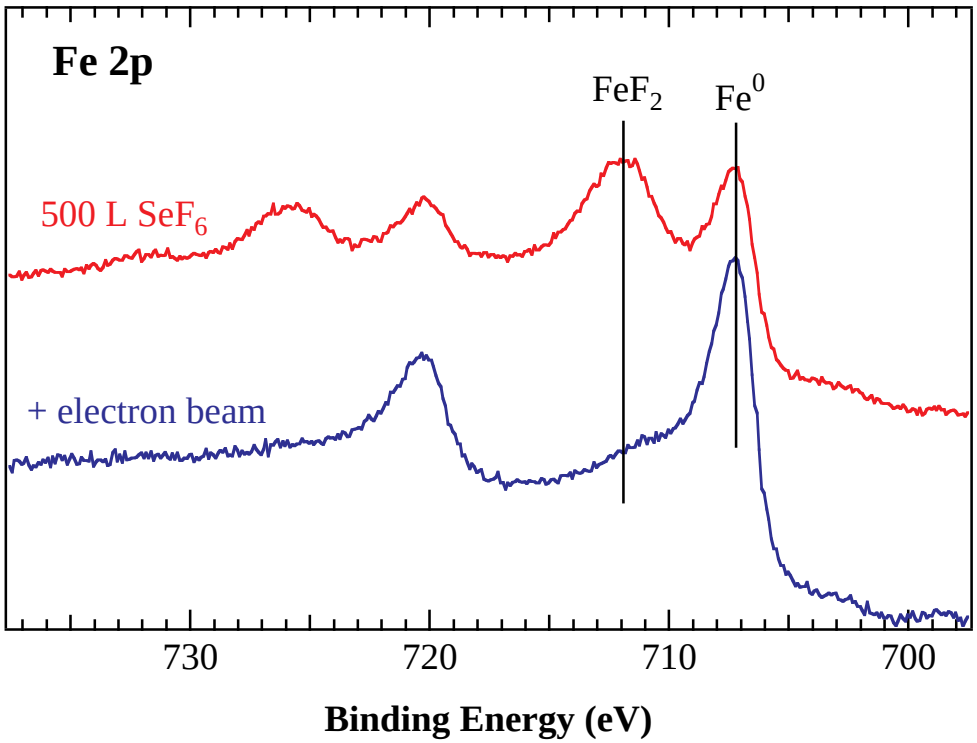




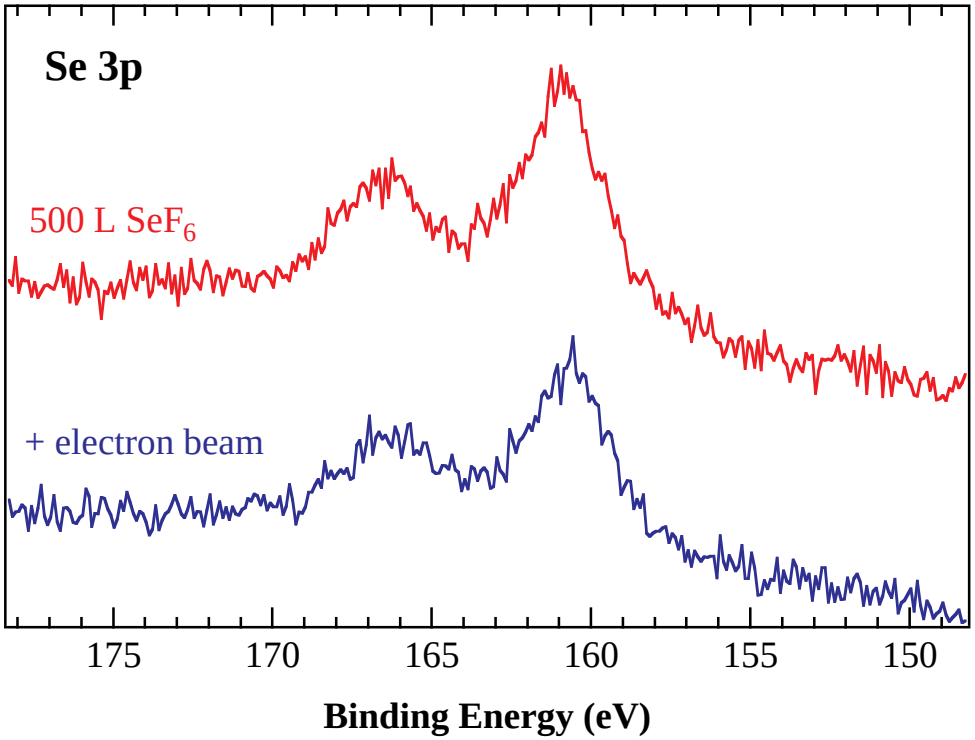
- The F to Se ratio is greater than 10 for each exposure
- This implies that not all the reacted Se remains on surface
- Some Se may be liberated as SeF_x

Reaction of SeF_6 with Iron Foil

- XPS shows the chemical state of the adsorbed species
- An electron beam is used to remove fluorine in order to determine how it was bound

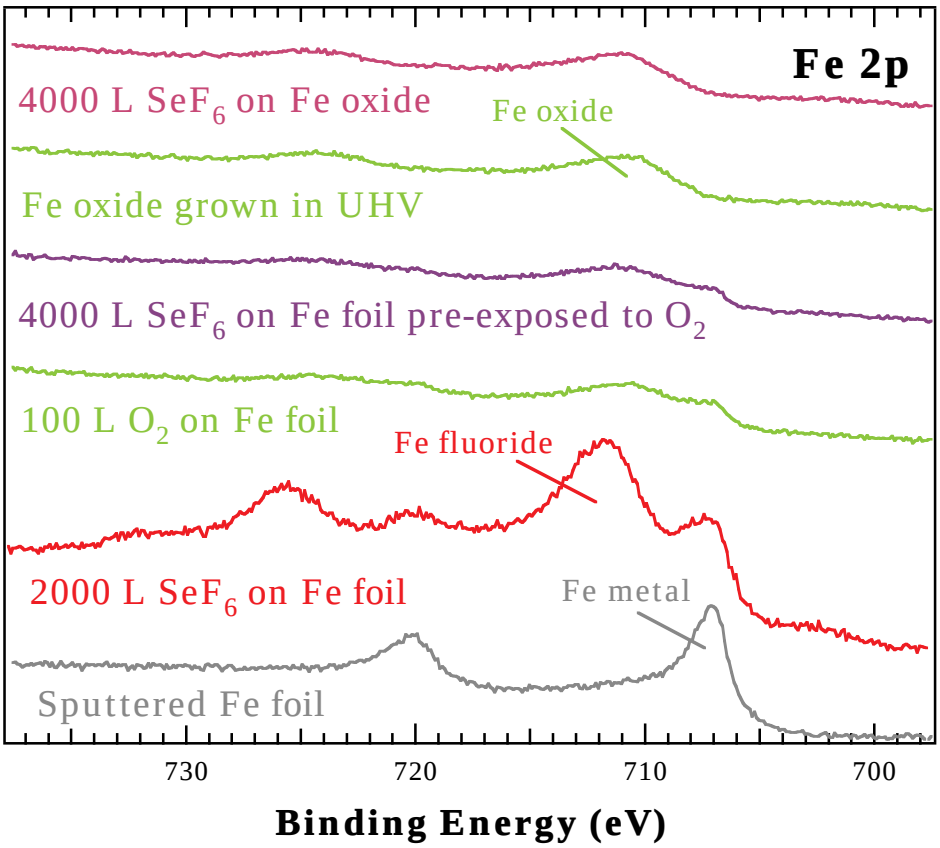


- The reaction forms FeF_2



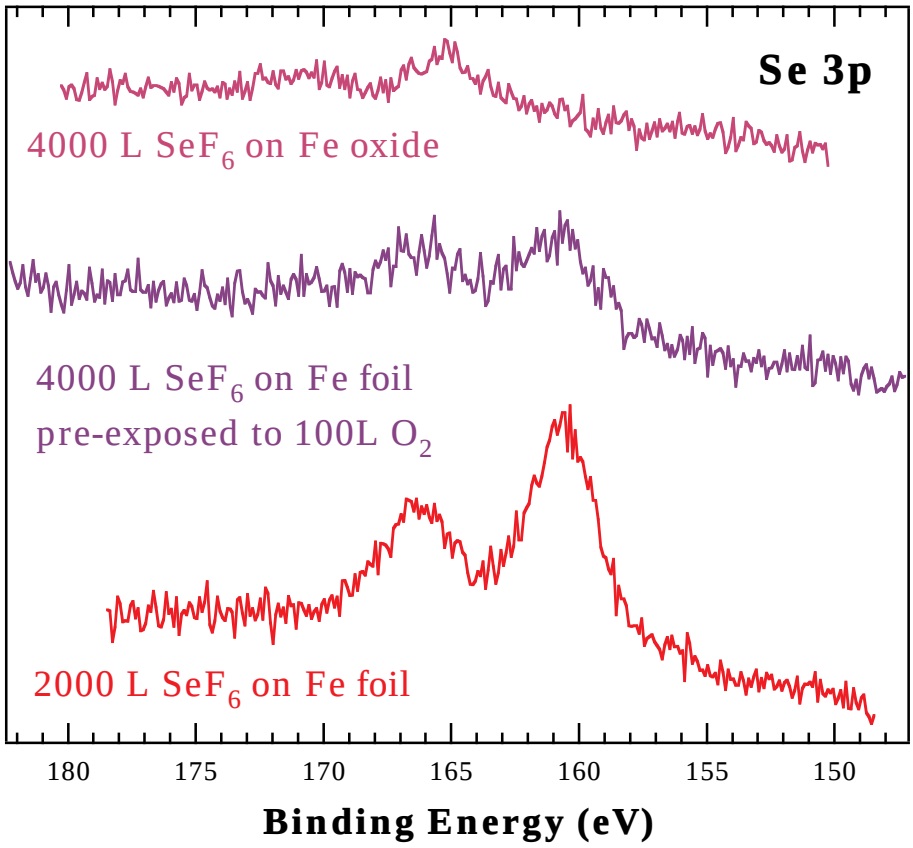
- The adsorbed Se is not bound to F

SeF_6 reacted with oxidized Iron foil



- Iron oxides inhibit the sticking of SeF_6
- On the fully oxidized Fe_2O_3 surface, no SeF_6 sticks

- Adsorbed Se on partial oxide is in same environment as on clean Fe
  - It is likely on patches of clean Fe
- On full oxide, the small amount of Se that sticks is partially oxidized



Summary

- Zero-valent iron provides a means for remediation of ground and waste waters via reduction, adsorption, and precipitation of dissolved contaminants.

- Fundamental studies that combine bulk chemical and surface-sensitive techniques have been successfully used to characterize the mechanism of contaminant binding on iron surfaces.

  - For many dissolved species, partial reduction accompanies contaminant removal.

    - Adsorbed selenate and chromate were partially reduced.

  - Surprisingly, much of the contaminant loss from solution may not involve reduction.

    - Adsorption and coprecipitation of U(VI) was found to be significant, and UO_2 formed only after heating the U(VI) films in vacuum.

    - This is in agreement with previous studies we performed on anaerobic sediments, in which 75% of the solid-phase U was U(VI) and 25% was U(IV).

  - Surface oxide significantly affects the reactions.

    - Under aerobic conditions the contaminant reduction rate is initially high, but slows due to oxide build-up.

    - Under anaerobic conditions the rate is slower, but remains more constant since Fe(III)-precipitates do not form.

    - For model compounds in UHV, surface oxide inhibits reduction and modifies the adsorbed species.

Future Directions

- Studies will continue to characterize the reaction of iron with many contaminants, such as arsenate, molybdate, vanadate, perchlorate, nitrate, chromate, uranyl, and carbon tetrachloride. Extensive work is ongoing to identify the mineralogy of the secondary products that affect both surface reactivity and the hydraulic properties of barrier walls and reactive iron beds.

- Studies of modified iron surfaces are underway, e.g., palladium-coated iron and iron alloys. We are also interested in the effects of impurities in the iron, such as carbon, sulfur, manganese, and silicon.

- Surface studies using a single crystal of iron will investigate reactions with model gaseous compounds. In addition to SeF_6 and SF_6, selenic acid (H_2SeO_4) and selenous acid (H_2SeO_3), both volatile acids of selenium with oxidation states of +6 and +4, will be used.

- A wet cell is being constructed to allow reaction of iron under very well-controlled conditions with direct transfer to UHV for surface sensitive measurements.

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Siping "Roger" Qiu - *Physics*
Mark J. Roberson - *Environmental Sciences*

STM Images Collected by
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