Fundamental studies of the removal of contaminants from ground and waste waters via reaction with 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 soluble in water and mobile in the environment.

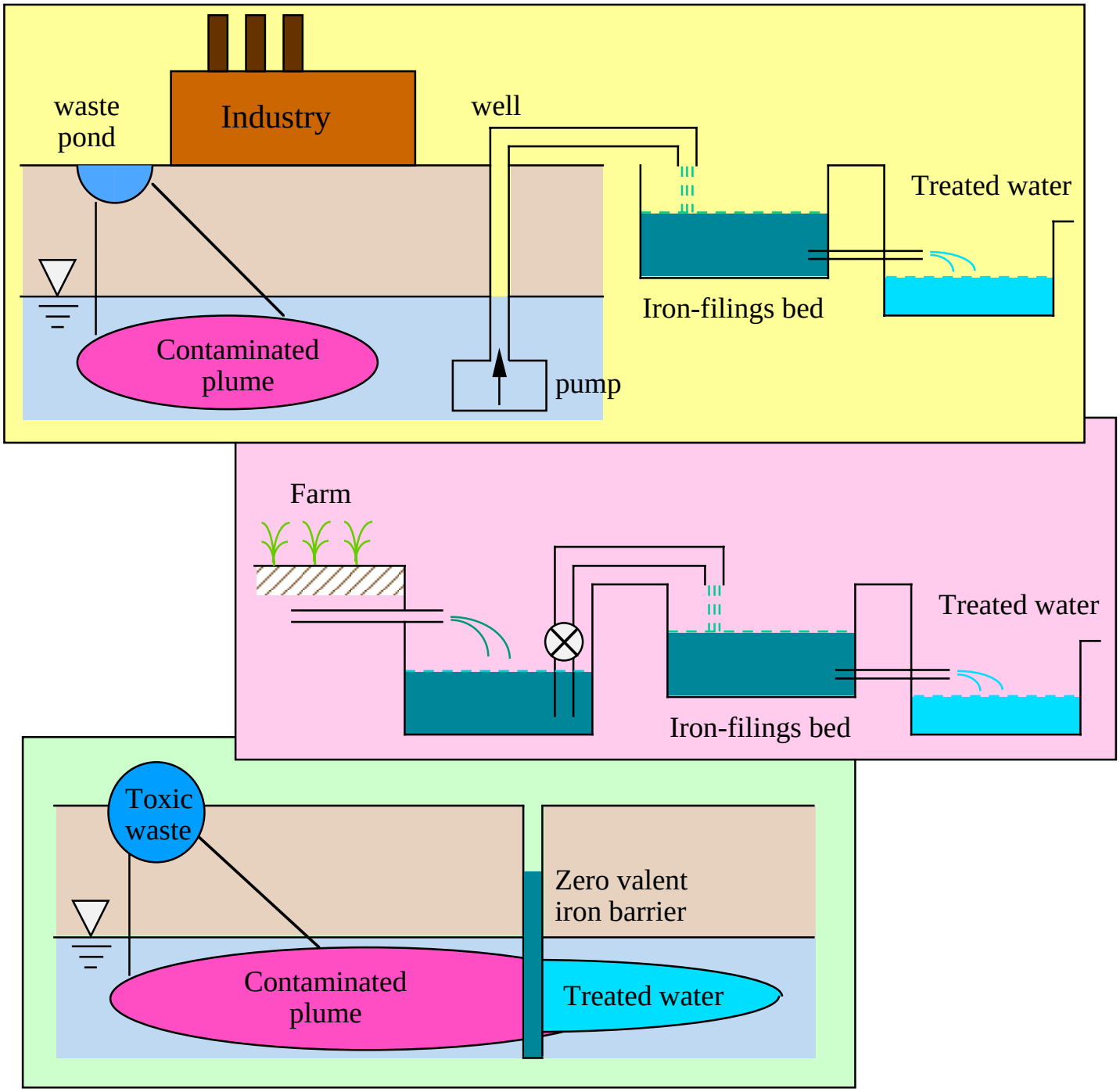
- These ions have contaminated groundwaters throughout the United States.

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

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

Zero-Valent Iron

- Zero valent iron (ZVI) can be used to reduce mobile forms of toxic elements in water to insoluble forms, presumably via a redox reaction.
- There are various ways in which to implement this process.



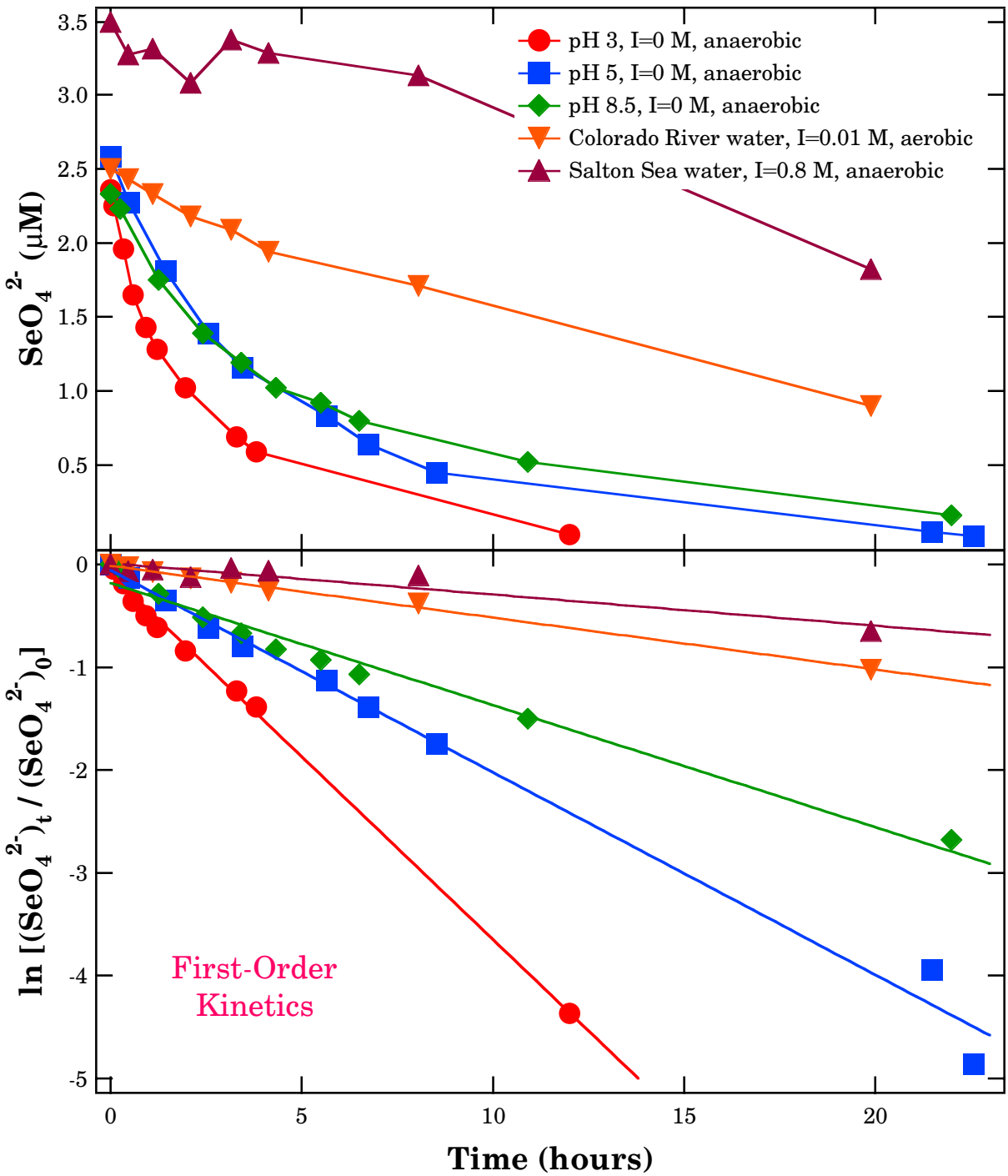
The Project

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

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

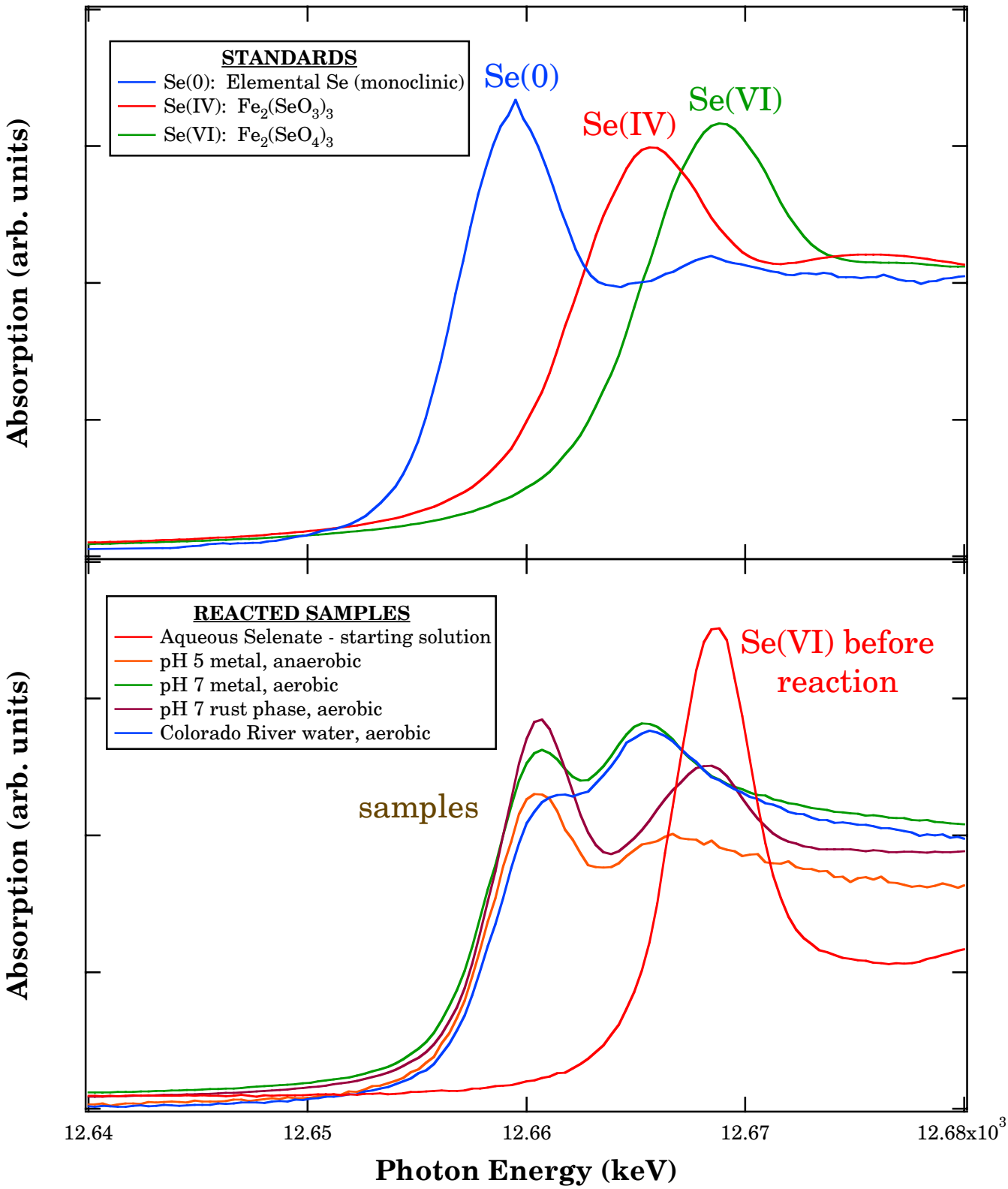
- Experiments
  - ⇒ Reaction of model gaseous compounds with iron foils in UHV
  - ⇒ STM and XPS analysis of iron foils reacted in solution
  - ⇒ XPS, XANES, XRD, RBS and SEM analysis of uranium oxide films formed by reaction with iron foil
  - ⇒ Rate measurements of reduction via iron filings
  - ⇒ SEM, XRD and XANES analysis of reacted filings

Aqueous Selenate Reduction with Zero Valent Iron



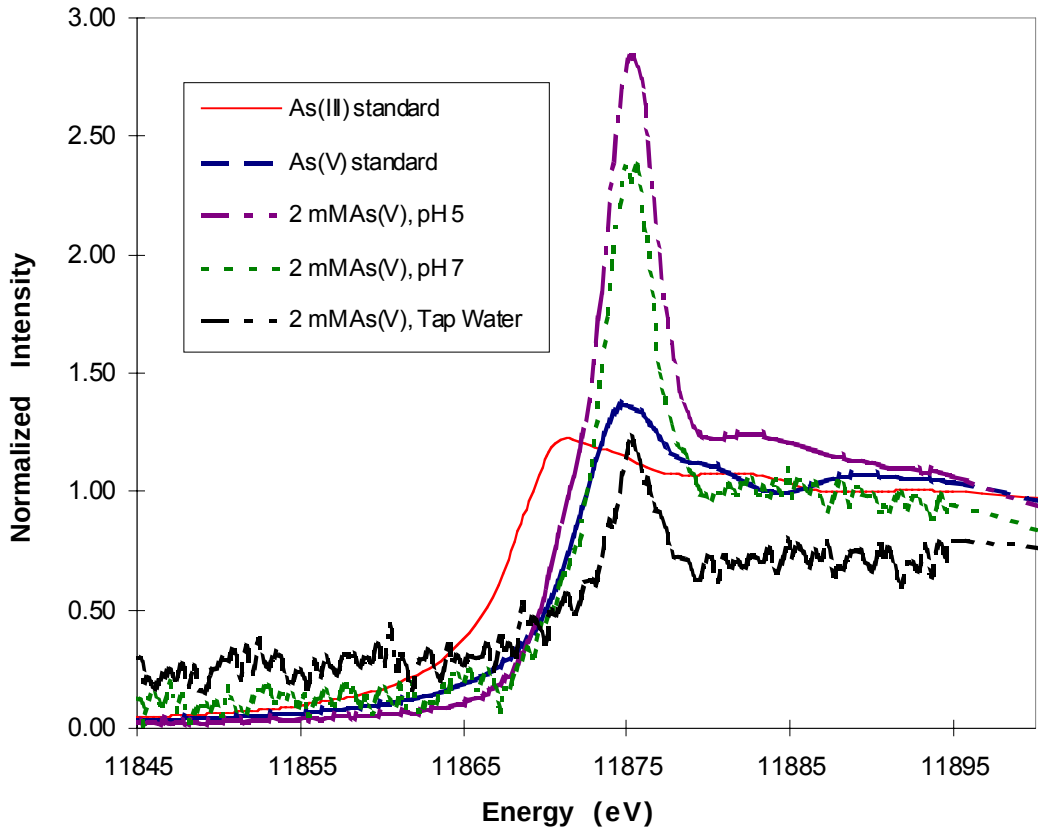
The reduction of aqueous selenate using zero-valent iron is affected by the solution's composition. Competing reduction reactions, ionic strength (I) and ratios of chloride, sulfate and bicarbonate also affect the rate. Reactions at low pH go faster due to the cathodic H^+ ion. Initially, reactions in which the solution is open to air have a faster reduction rate than N_2-purged reactions. However, when open to air, the rate decreases over time due to an oxide build up on the iron surface.

X-Ray Absorption Near-Edge Structure (XANES)



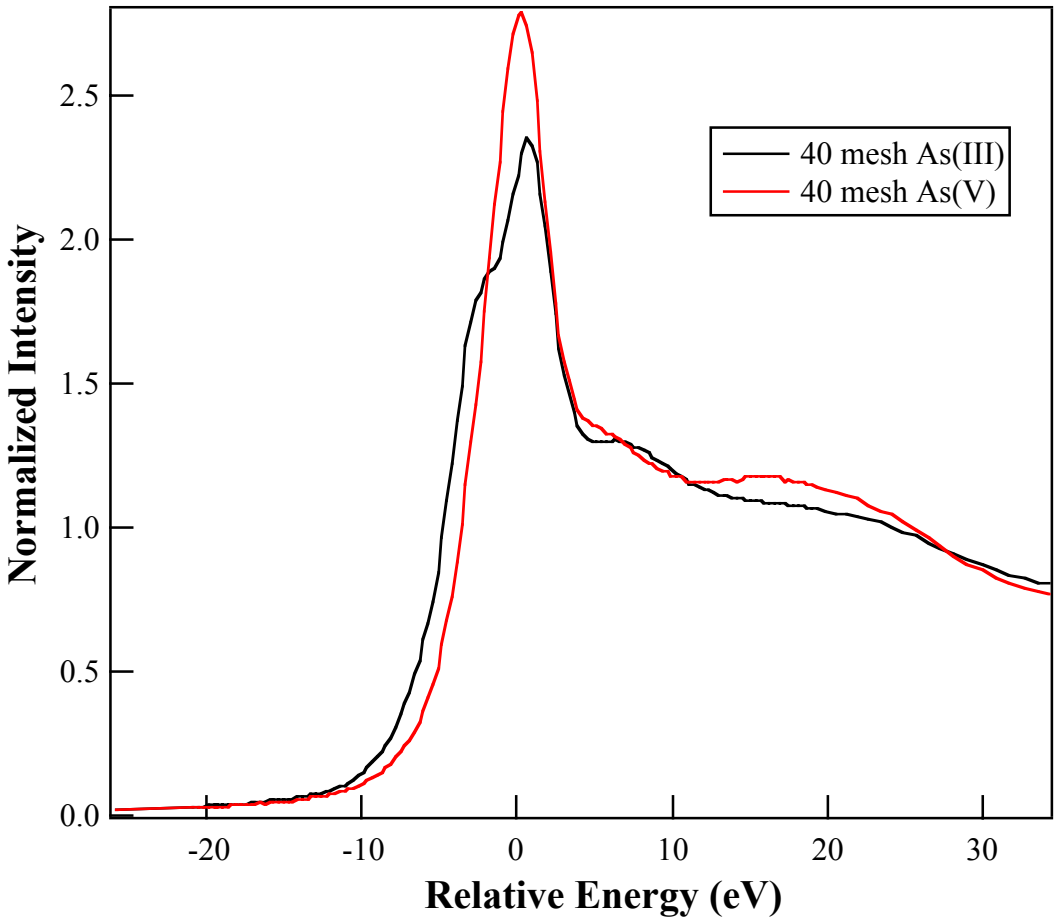
XANES spectra were collected from samples reacted under various reducing conditions. The spectra collected from metal samples all indicate a mixture of Se(0) and Se(IV). The spectra collected from the rust phase products of the reaction also show some Se(VI).

NEXAFS Spectra of As(V) Removal from Solution via Zero-Valent Iron



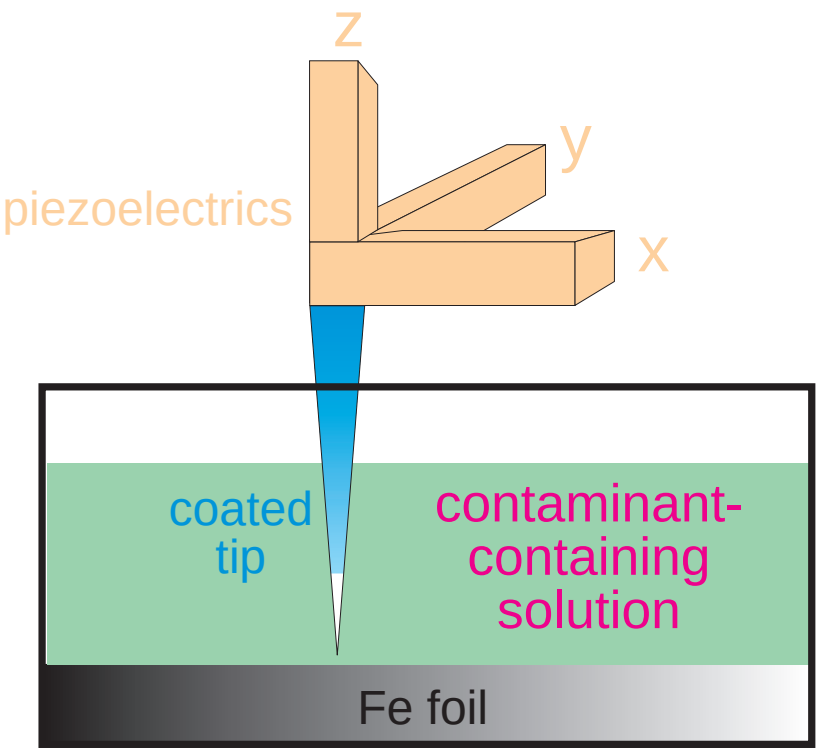
- **NEXAFS spectra of As(III) and As(V) standards and iron samples reacted with arsenate (AsO_4^{3-}) were collected.**
- **Unlike the reactions with selenate, chromate, and uranyl, arsenate shows no reduction to lower oxidation states.**

NEXAFS Spectra of As(III) and As(V) Reacted with Zero-Valent Iron



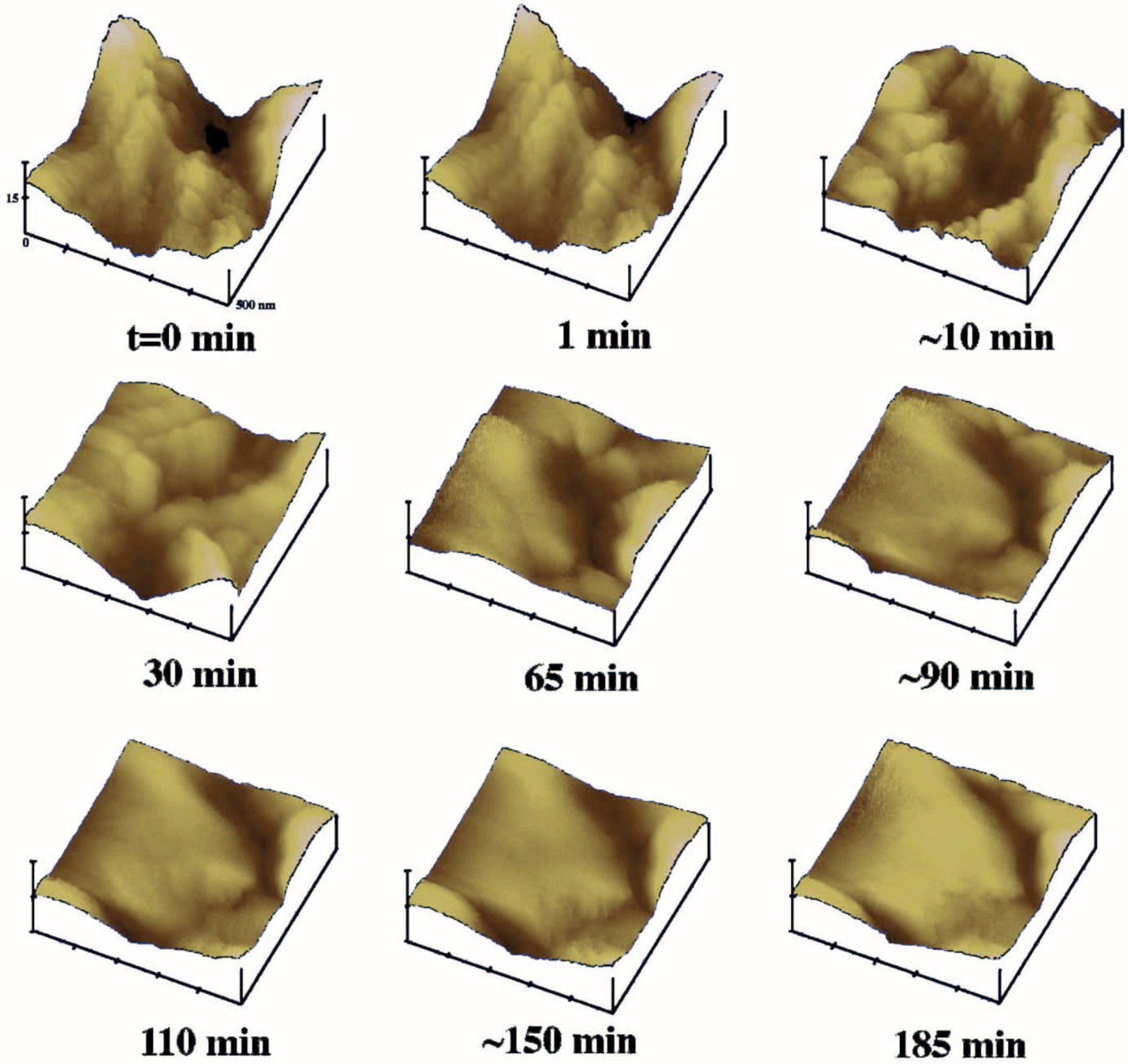
- **Both As(III) and As(V) were removed from solution with >99% efficiency by 40-mesh zero-valent iron (ZVI).**
- **There was no reduction of the adsorbed As(V).**
- **After 24 hours, >65% of the adsorbed As(III) had been <u>oxidized</u> to As(V) by the ZVI. Experiments with pure ferric hydroxides and ferric oxides showed that lepidocrocite, magnetite, and hematite could oxidize As(III).**

Scanning Tunneling Microscopy (STM) in solution



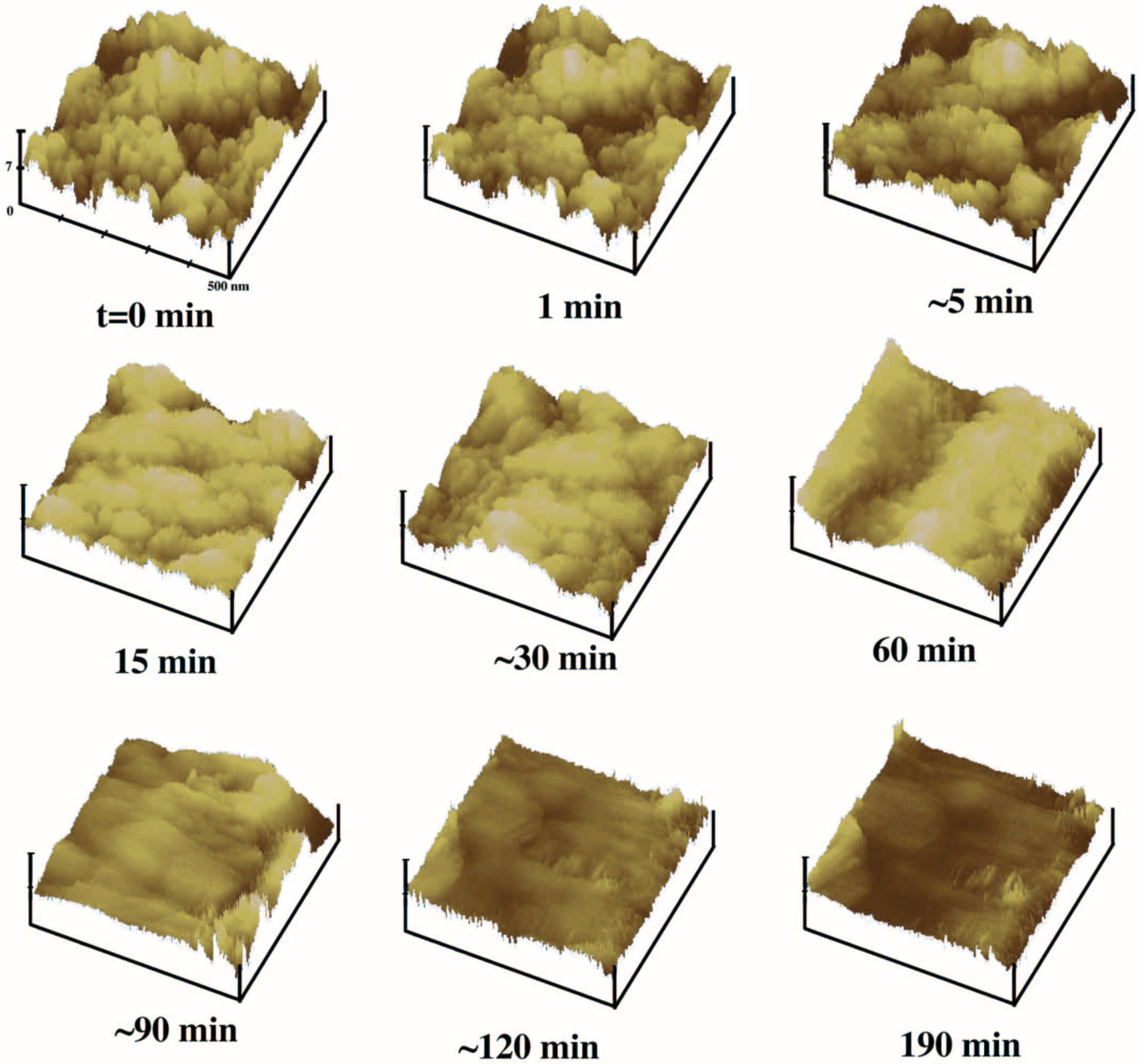
- Iron foil was monitored *in situ* with STM during the reaction with trace-element containing solutions
- The same spot on the surface could be imaged over a long period of time
- A blank solution showed no reaction

Iron foil in a Sodium Selenate Solution



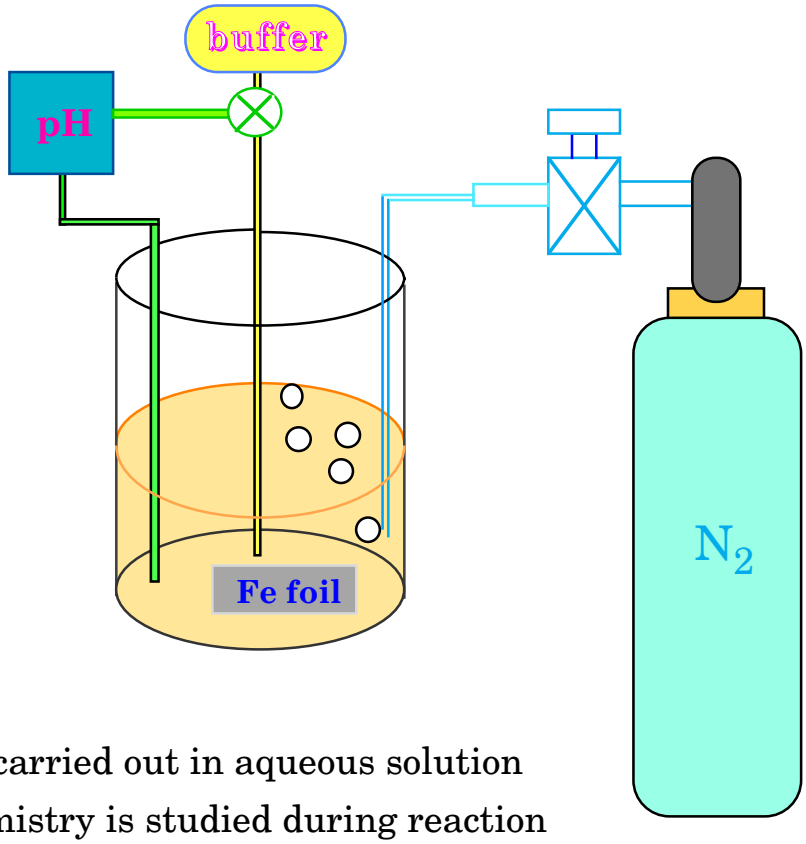
Iron foil was monitored *in situ* with STM during the reduction of selenate in solution. The 500 x 500 nm images show the rough surface, characteristic of a native iron oxide, becoming smoother as the reaction proceeds. Comparison between XPS and STM results suggests that surface smoothing is due to both the deposition of the reduced Se and etching of the substrate.

Iron foil in a Uranyl Nitrate Solution

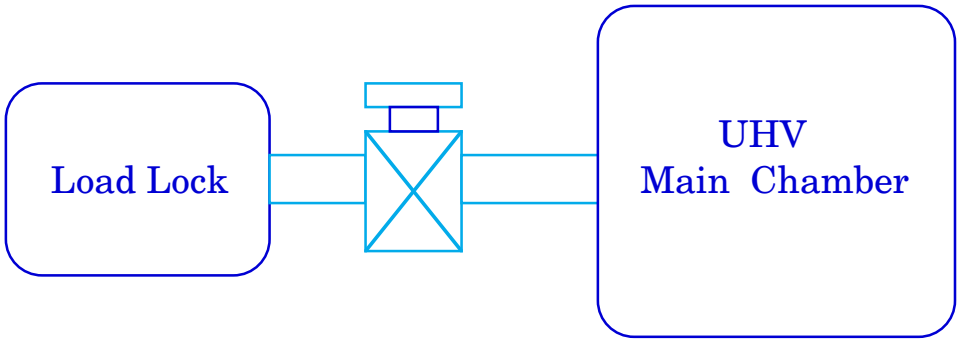


The surface of an iron foil was monitored with *in situ* STM in a solution containing uranyl nitrate. The 500 x 500 nm images show the rough surface, characteristic of a native iron oxide, becoming smoother as the reaction proceeds. XPS analysis showed that the smooth morphology is due to the deposition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

Experimental Set-up



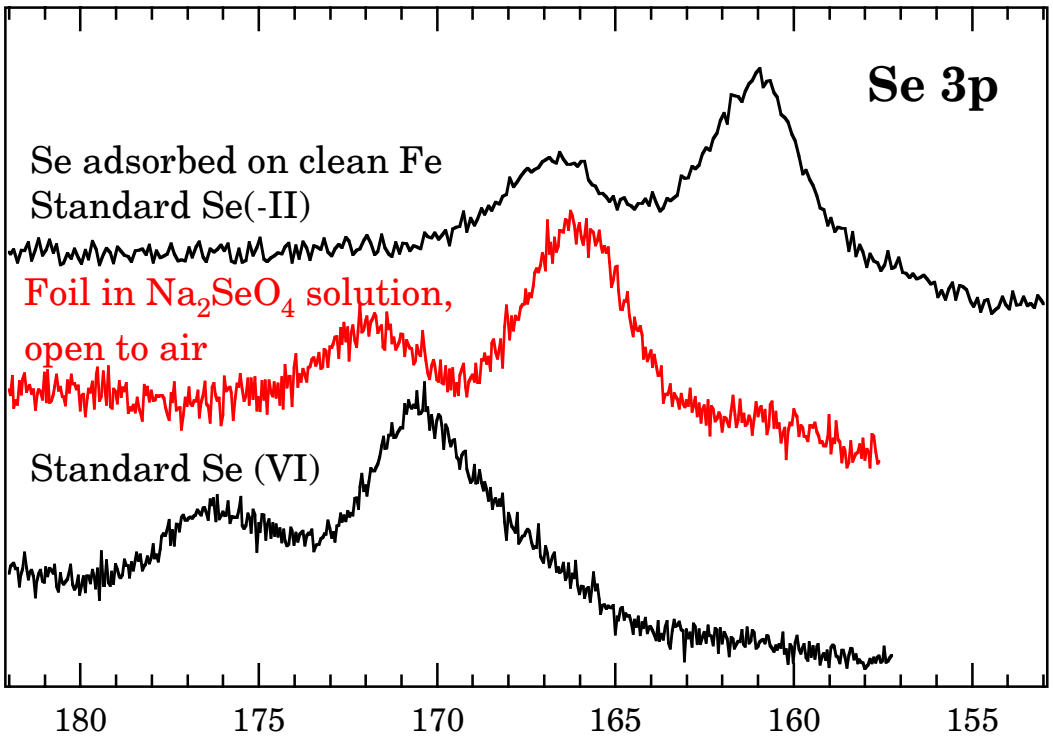
- Reaction carried out in aqueous solution
- Bulk chemistry is studied during reaction
- pH is monitored during reaction and can be controlled
- Ar or N_2 is bubbled to remove dissolved O_2 and CO_2



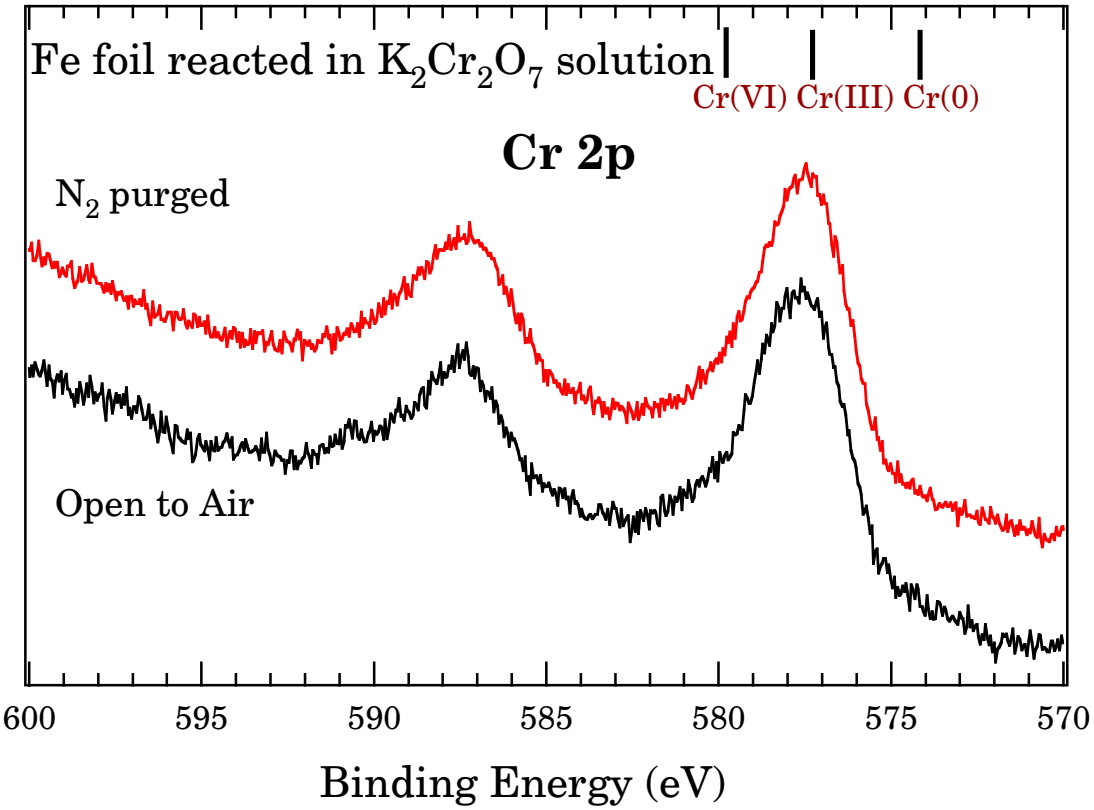
Following reaction:

- Samples are dried with N_2
- Samples are transfered to UHV in order to collect XPS data
- Transfer is either through an inert environment or through air for a short time (5 min.)

Reduction of Selenate and Chromate

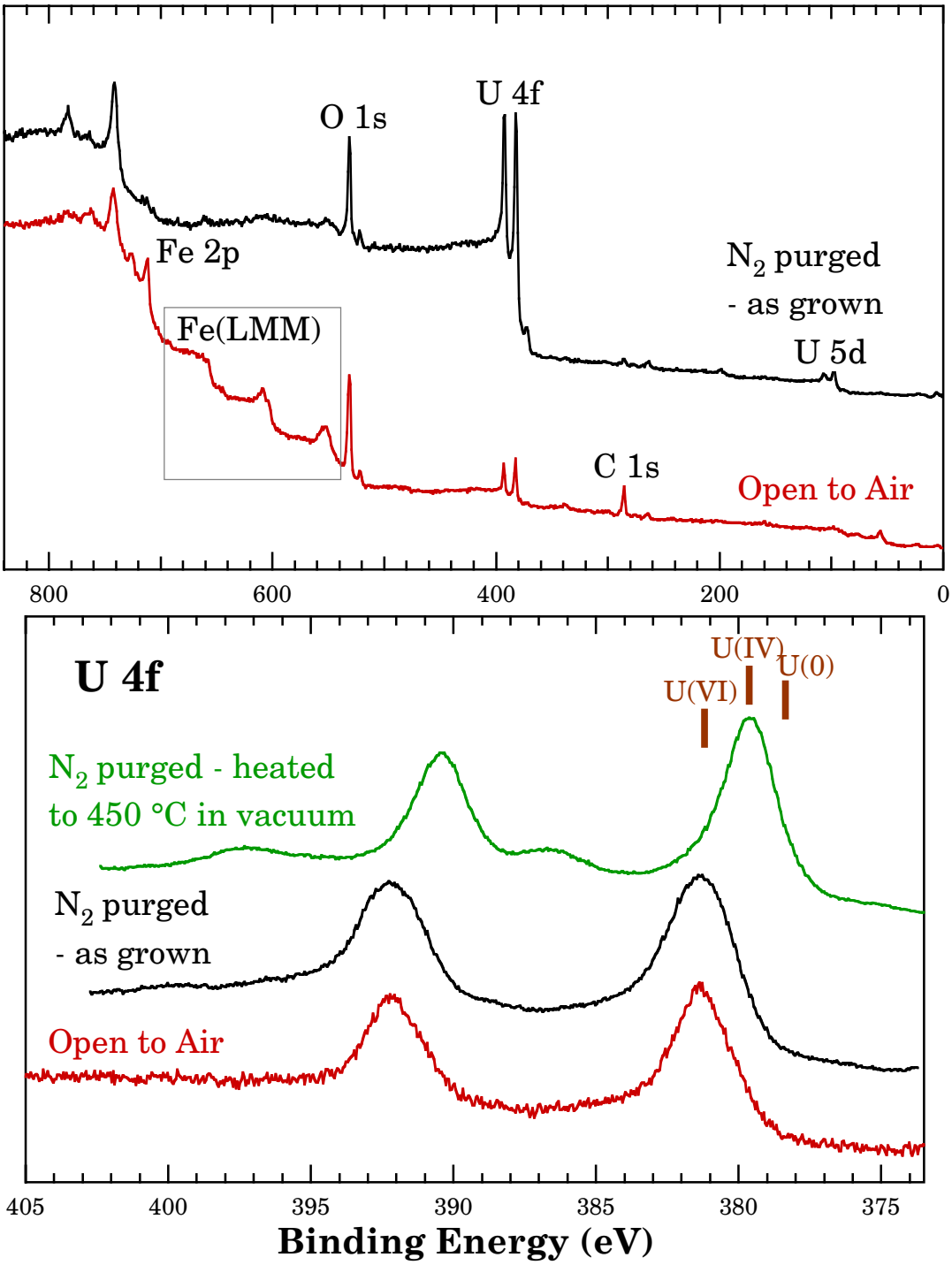


Selenate is partially reduced on the surface, and deposited into a single state as Se(VI)



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

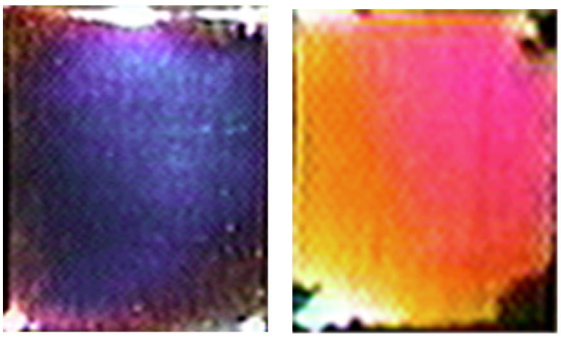
X-ray Photoelectron Spectroscopy (XPS)



- Films of U(VI) oxide grow under both conditions.
- Much more U is deposited with N_2 purging, as no Fe is visible
  - this is due to carbonate formation from dissolved CO_2 when open to air
- When heated in vacuum, surface of films reduce to UO_2

Growth of UO_3 films

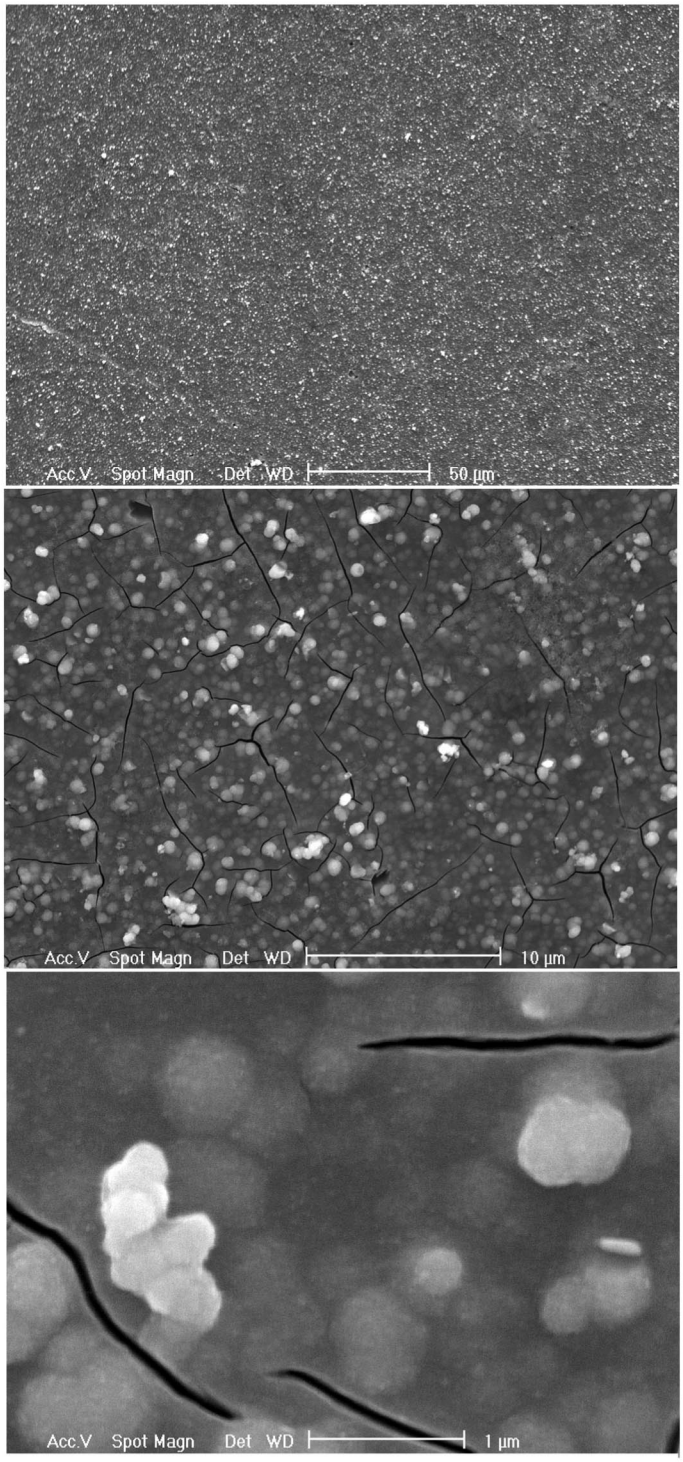
Film surface before reaction



Foil surfaces after reaction in an Ar or N_2 purged solution

- Films are grown by immersing Fe foil in a 1 mM $UO_2(NO_3)_2$ solution at pH 5
- If left open to air, only ~1 ML of U is deposited
- To remove atmospheric gases, such as O_2 and CO_2, Ar or N_2 is bubbled into the solution
  - Following such a reaction, the sample surface appears iridescent, as shown above
- Spectroscopy shows that:
  - An approximately 1 µm thick film grows
  - The film is composed of amorphous UO_3, with incorporated water
- When heated in vacuum to ~450°C, the film is reduced and crystallizes to UO_2
- When exposed to air, the film surface reoxidizes to UO_3, but the bulk remains UO_2

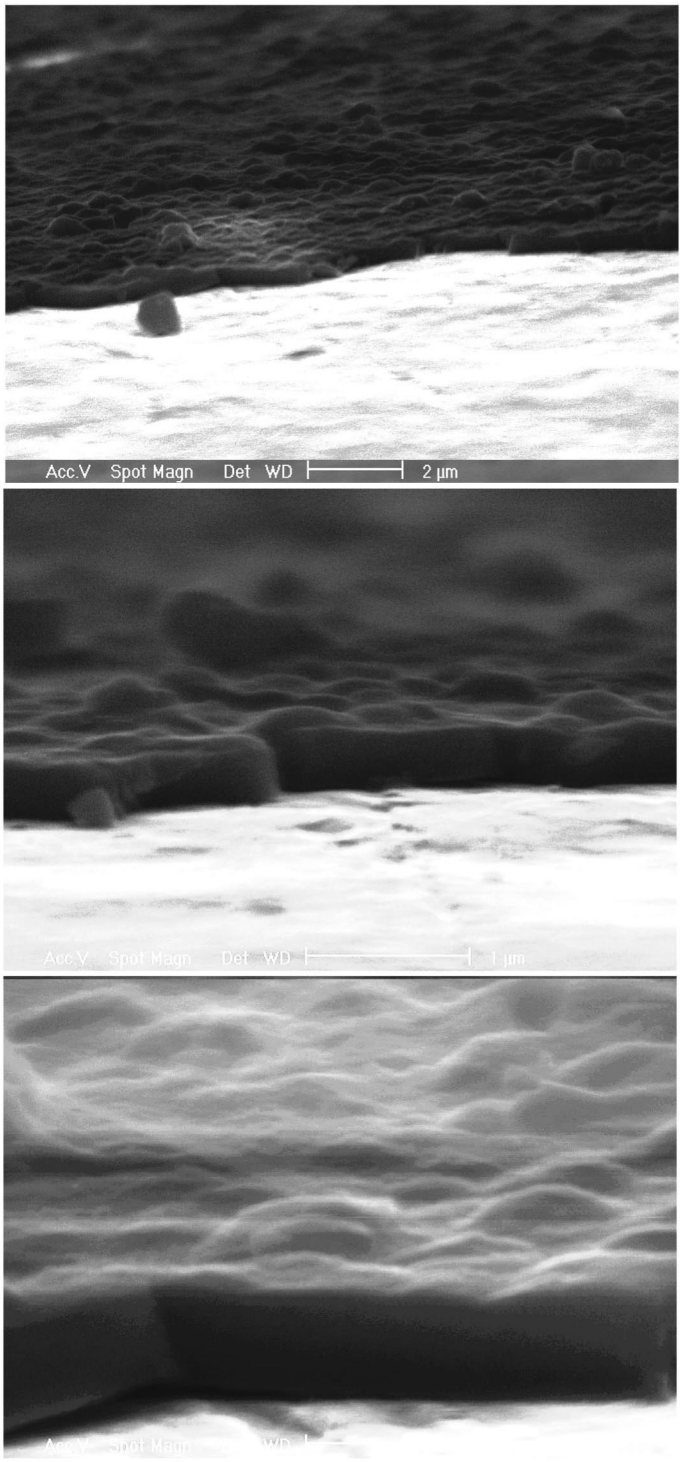
Scanning Electron Microscope Images of UO_3 film



The surface of the film is fairly smooth, with small bumps and cracks that expose the Fe substrate. EDX shows only U, O, and Fe.

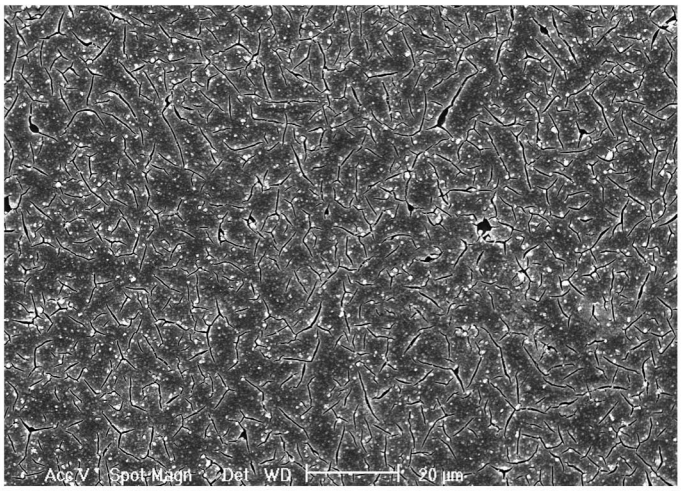
Scanning Electron Microscope Images of UO_3 Films

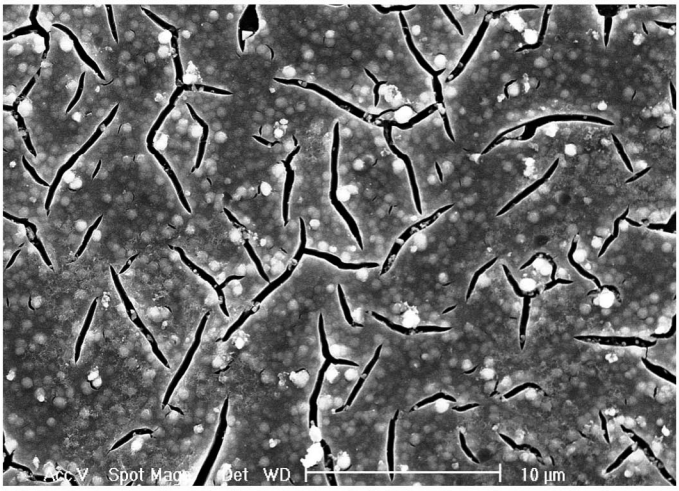
Edge view

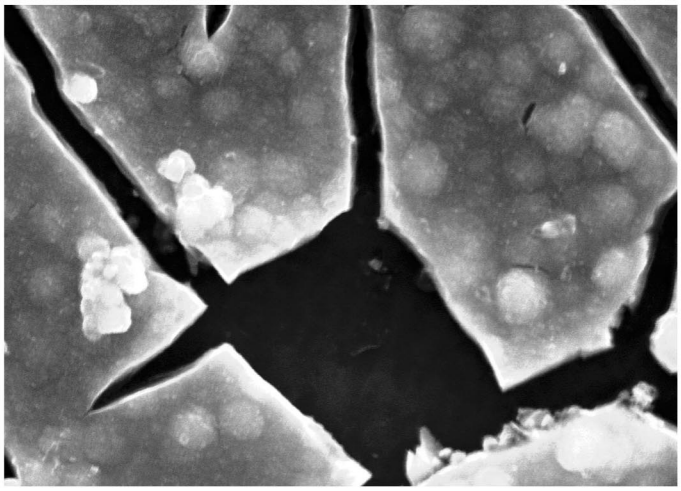


The thickness of the film can be measured *in situ* where the film has flaked off. The measurement is consistent with the RBS results.

Scanning Electron Microscope Images from Heated Films





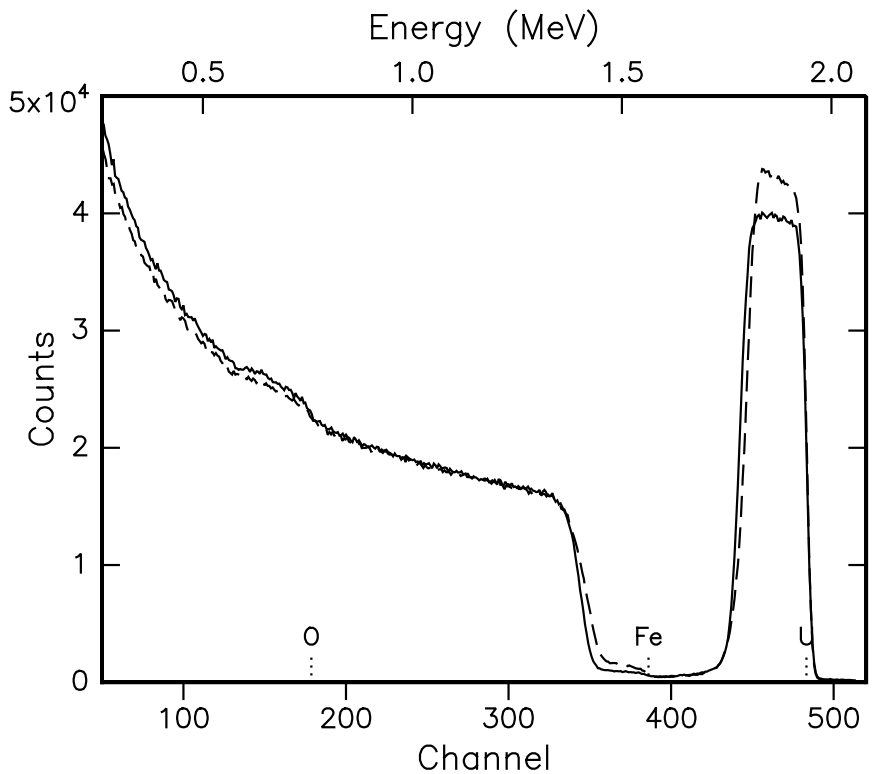


The crack density increases as the film is heated

Rutherford Backscattering Spectroscopy (RBS)

- 2.06 MeV He^+ is scattered from the films

- The backscattered energy is related to the mass of the target atoms and to the depth penetrated within the material



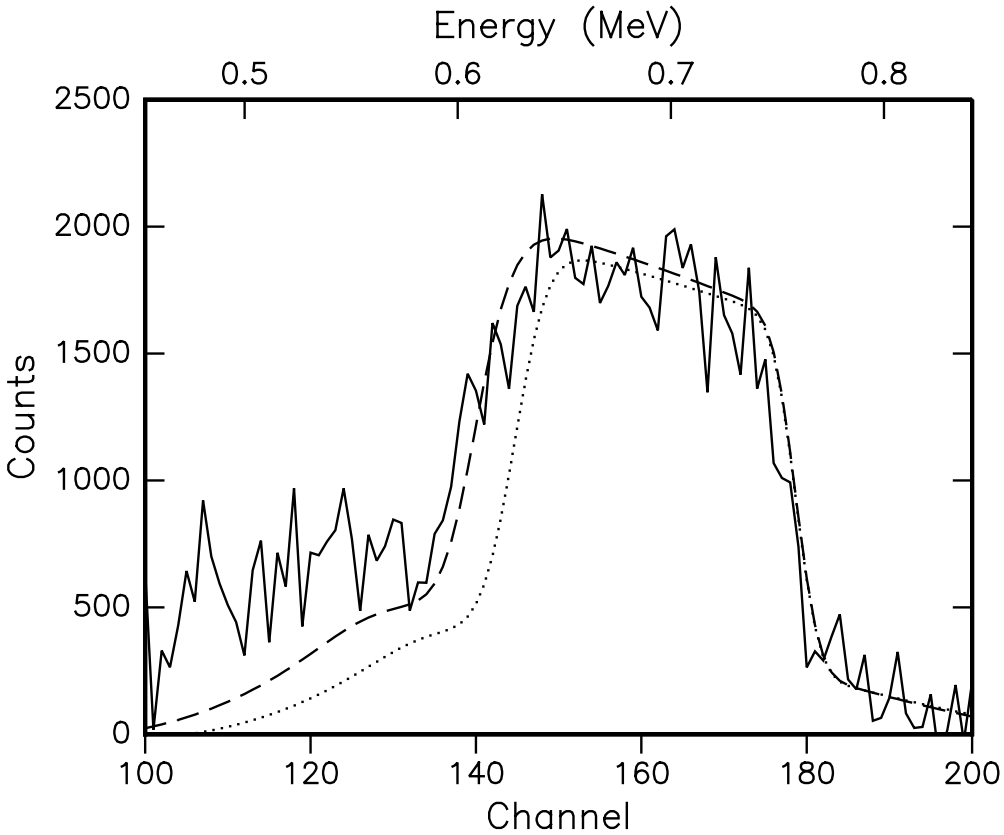
- The film has the stoichiometry of UO_3 with water incorporated throughout

- If the water were removed, the thickness would be 0.65 µm

- There is 400 Å of iron oxide below the uranium oxide film

- Either there are holes in the film, or Fe is incorporated

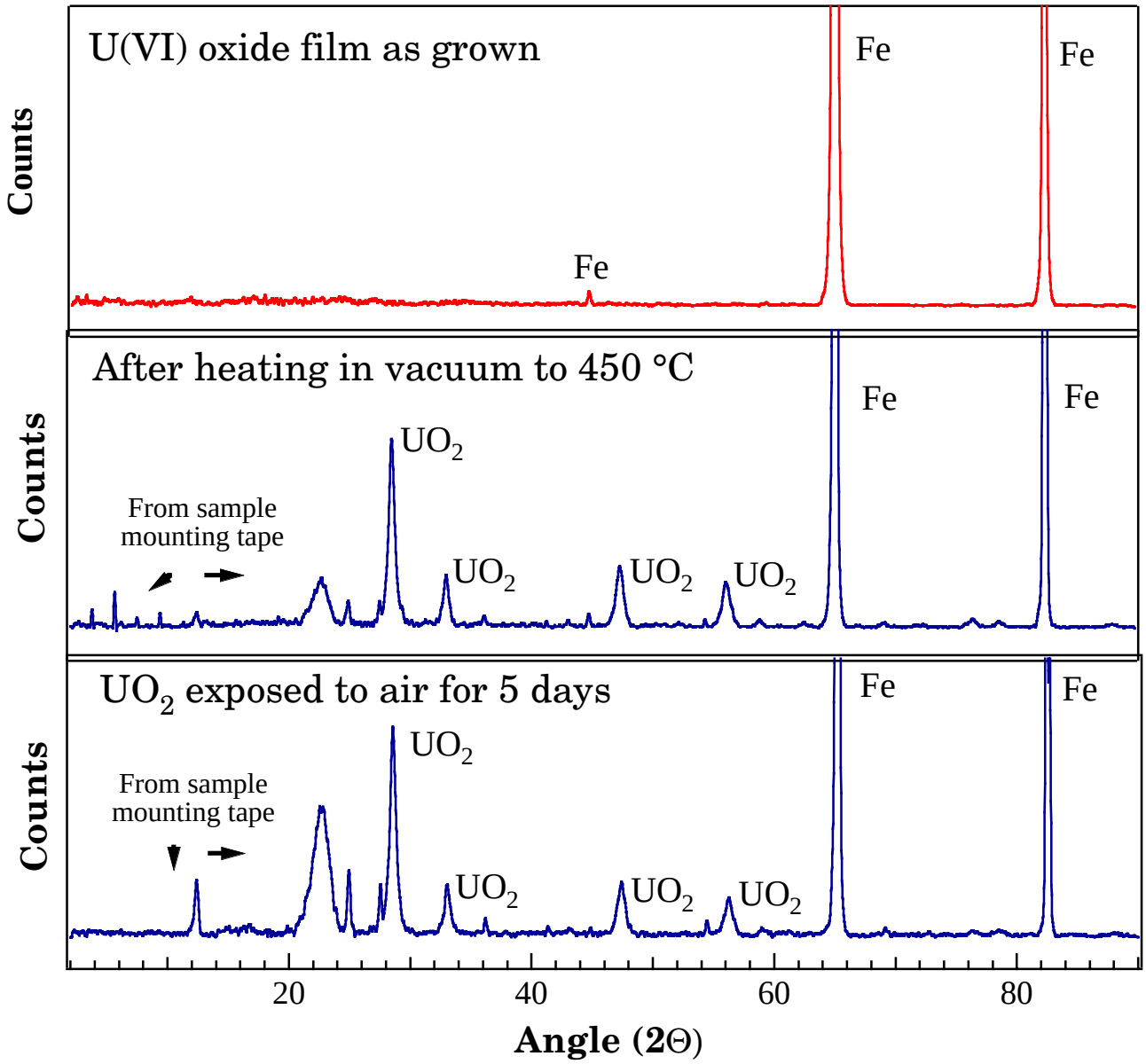
Rutherford Backscattering Spectroscopy (RBS)



- Blow-up of O edge is fit by two models:
  1) UO_x / Fe metal
  2) UO_x / FeO_y layer / Fe metal

- Analysis indicates that:
  1) Stoichiometry of uranium oxide is 1:3, i.e., UO_3
  2) ~400 Å of FeO_y is present

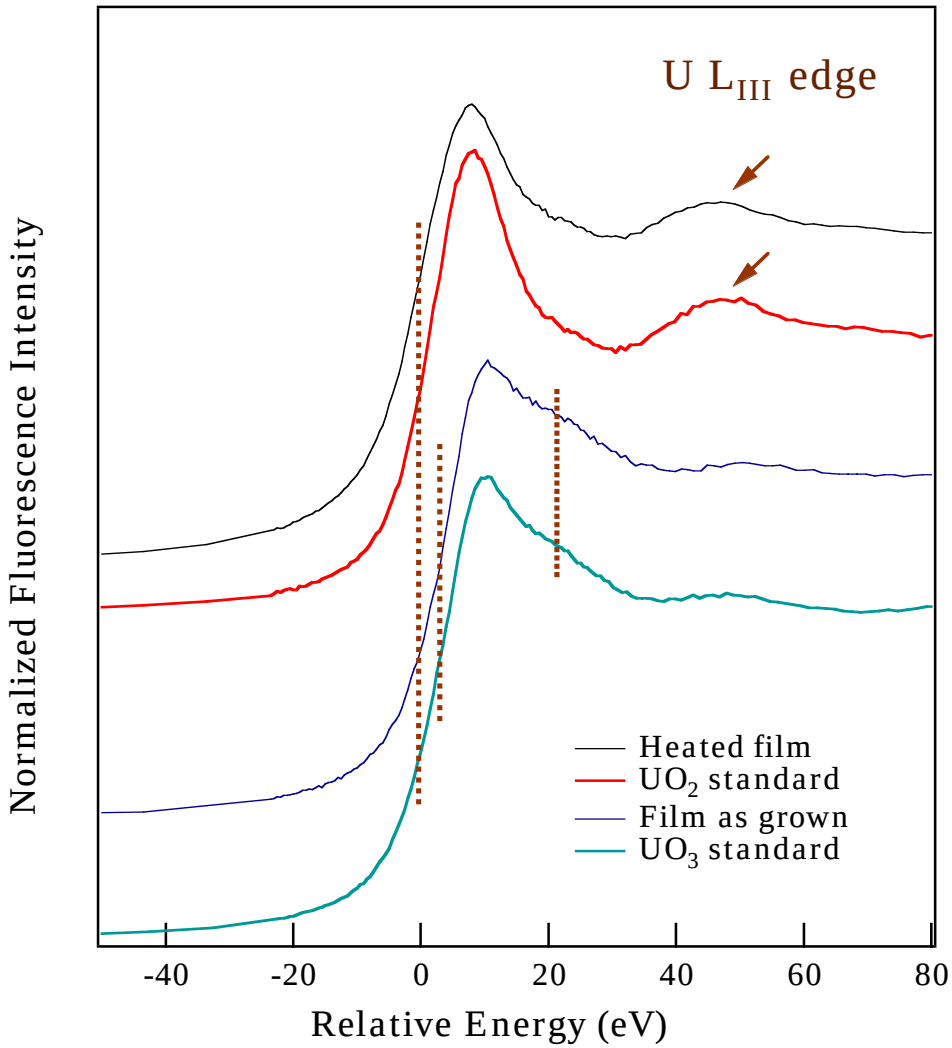
X-Ray Diffraction (XRD)



- The U(VI) oxide film as grown is amorphous
- When heated in vacuum, a crystal form of UO_2 is produced
- When exposed to air, the bulk UO_2 is unchanged

Near-Edge X-ray Absorption Fine Structure (NEXAFS)

SSRL Beamline 4-1

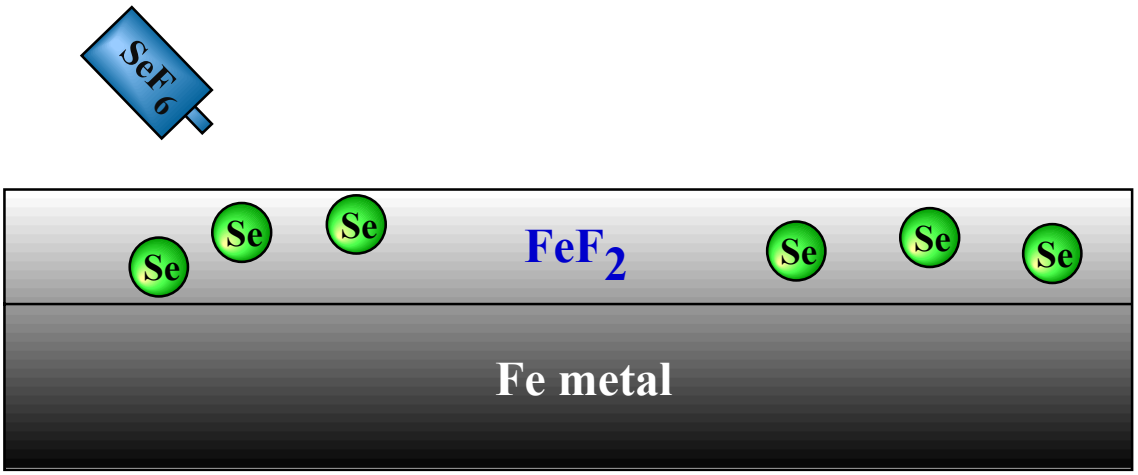


- U in the bulk of the film as grown is U(VI).
- It reduces to U(IV) when heated.

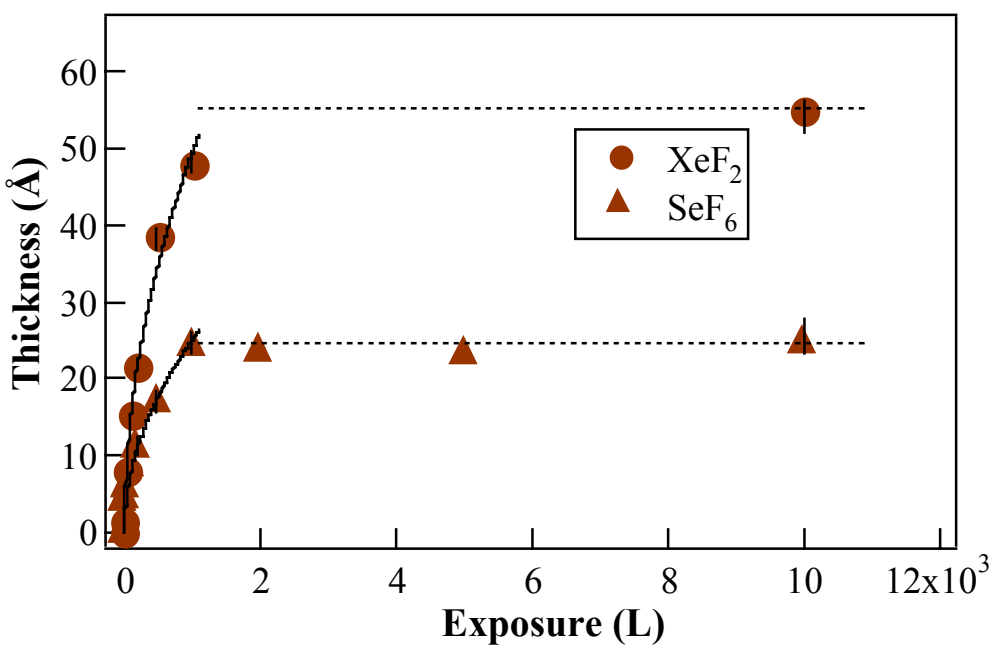
Model system for studying the reduction of selenate

SeF_6 is reacted with an Fe surface in ultra-high vacuum (UHV)

- 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

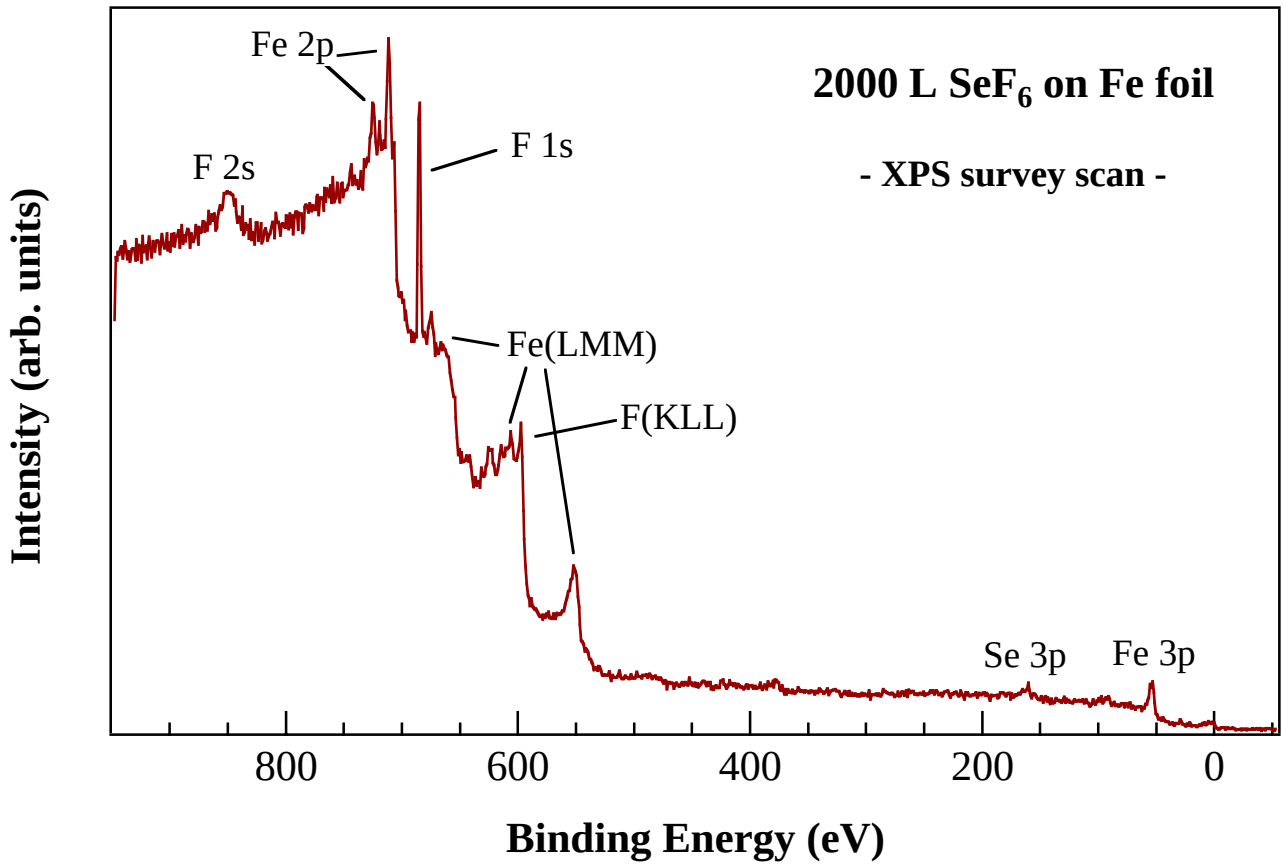


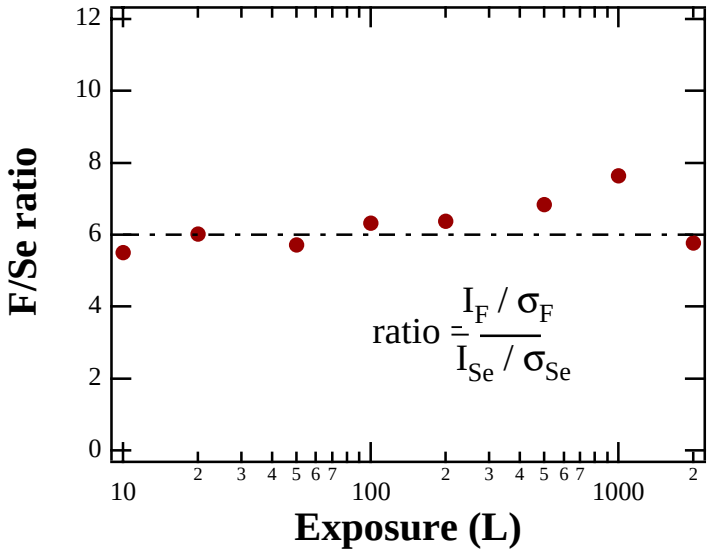
- **SeF_6 is completely reduced by reaction with iron**
- **An FeF_2 film is grown by the reaction**
- **Fe oxide inhibits the reaction**



- **Film growth initially follows a Mott-Cabrera mechanism**
- **The growth abruptly stops when a limiting thickness is obtained due to the inability of electrons to tunnel from the substrate and induce dissociation**

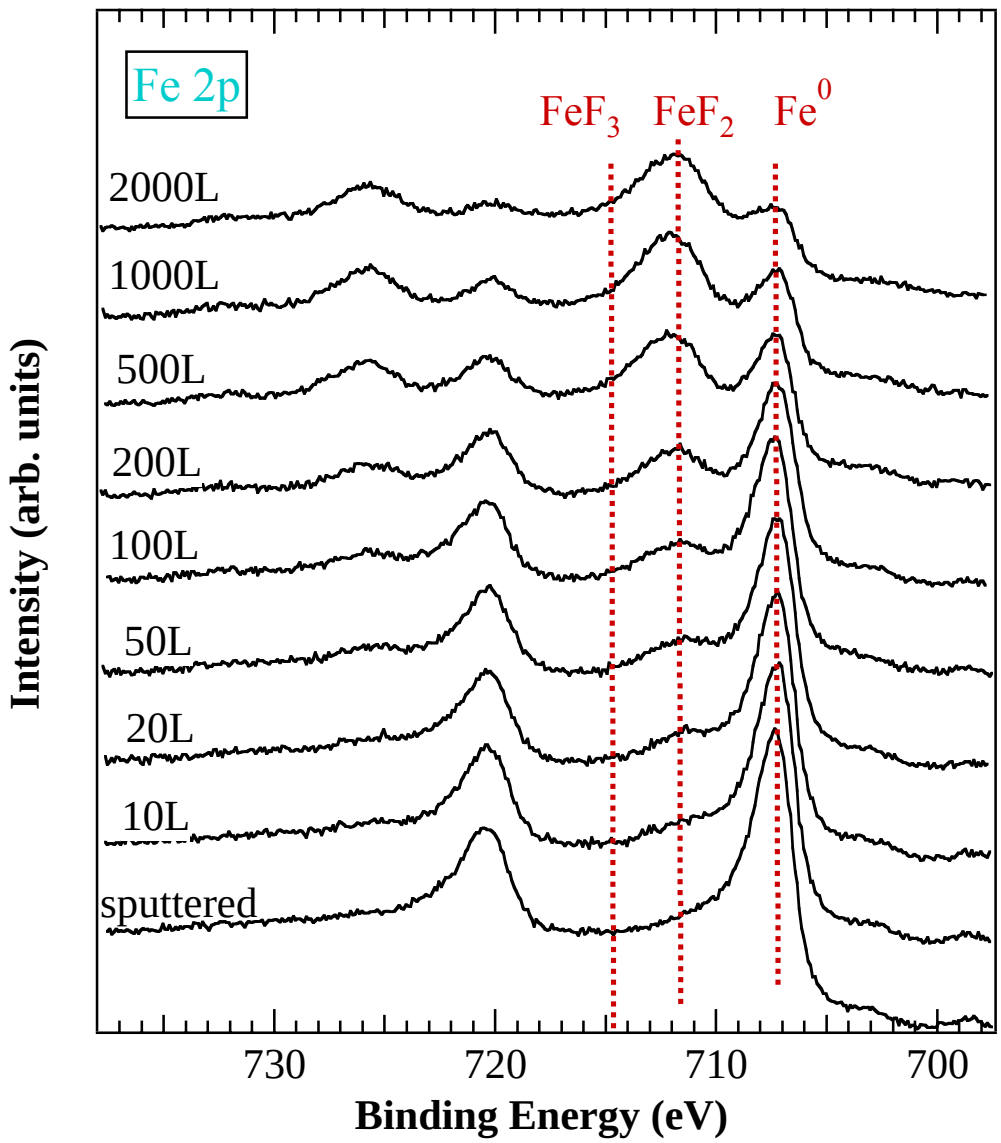
SeF_6 reacted with Fe foil





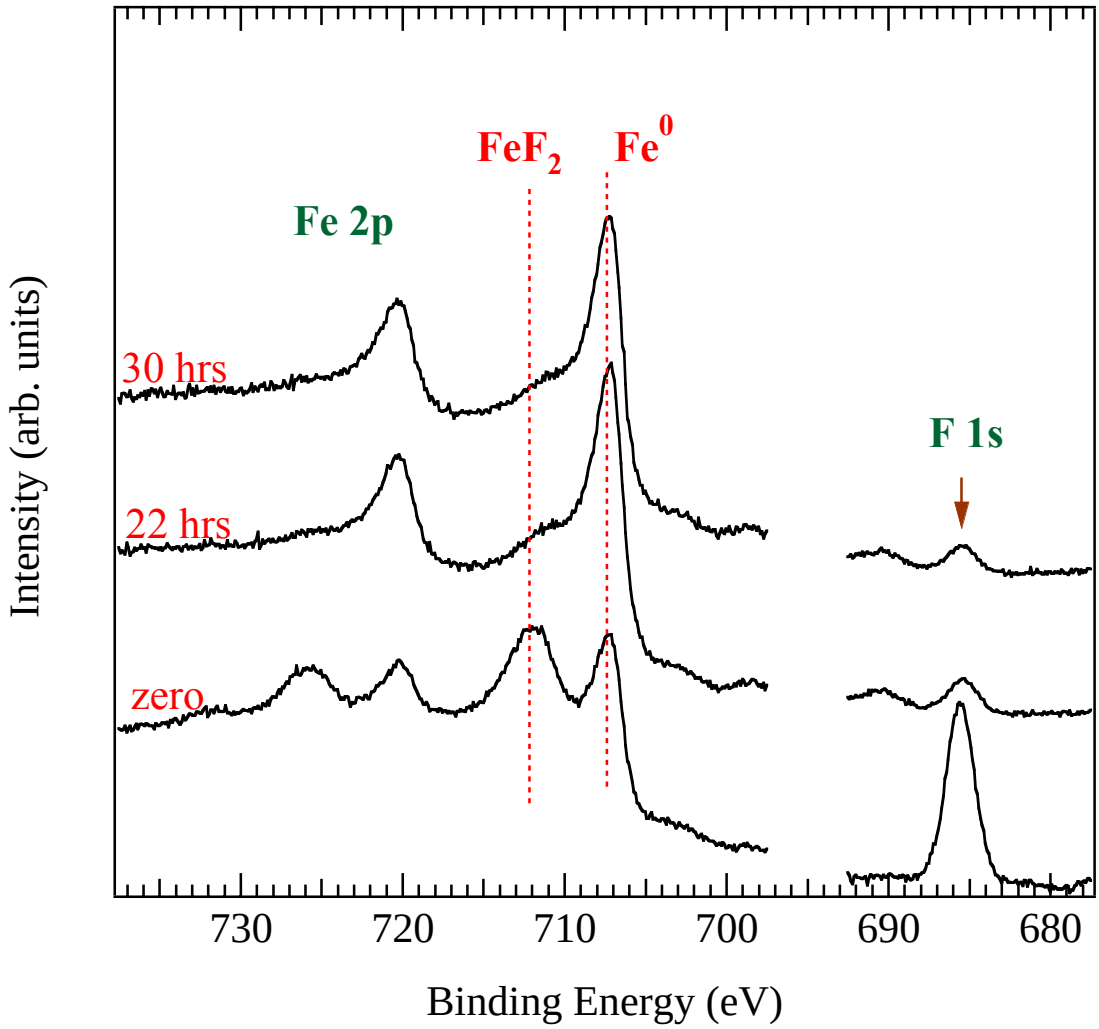
- XPS shows only Se, F and Fe
- The F to Se ratio is approximately 6 following each exposure
- This implies that all of the Se and F remain on the surface

SeF_6 / Fe foil



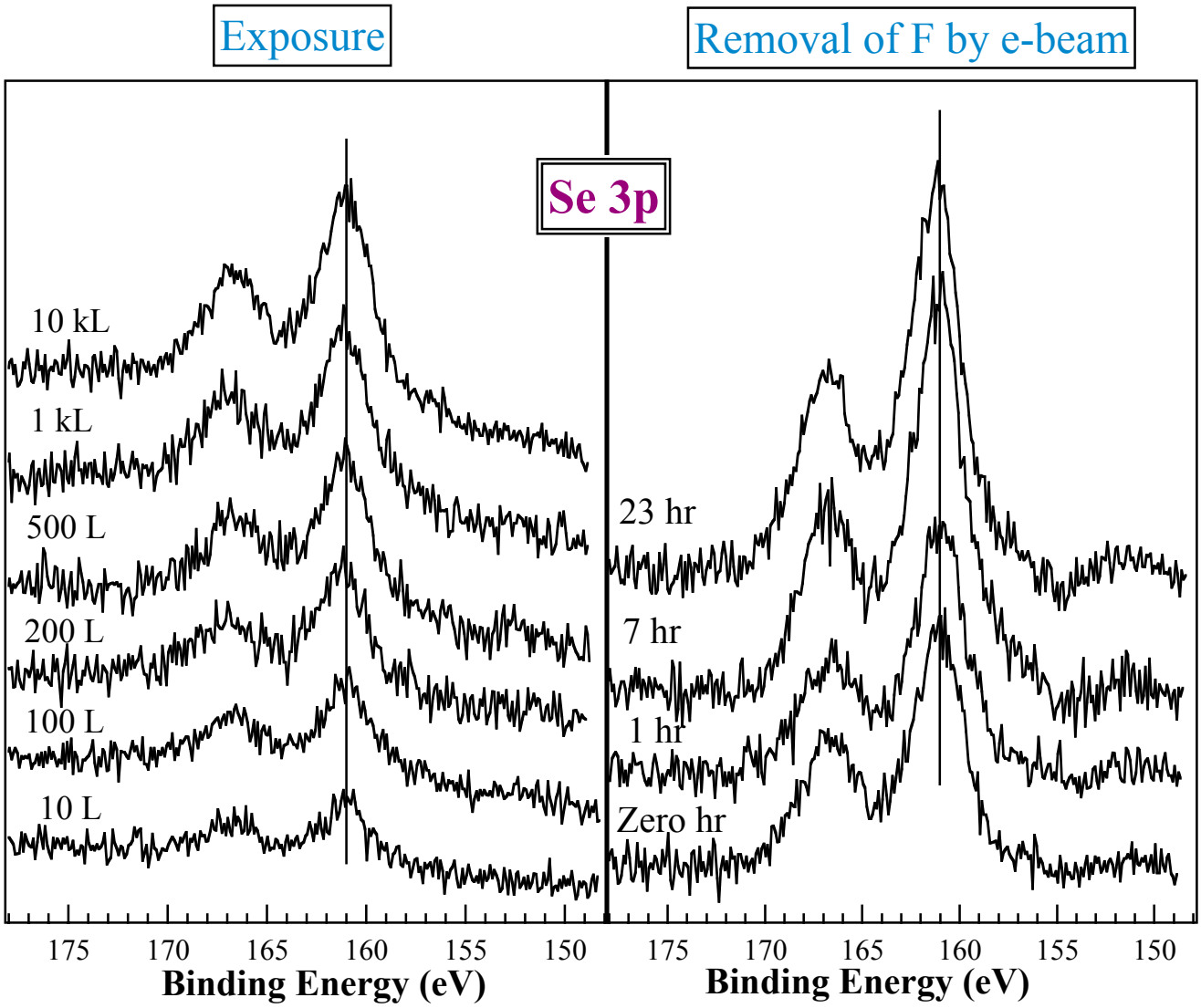
- An FeF_2 film is grown by the reaction

500L SeF_6 on Fe foil followed by e^- beam bombardment



- The amount of F decreases with e-beam exposure.

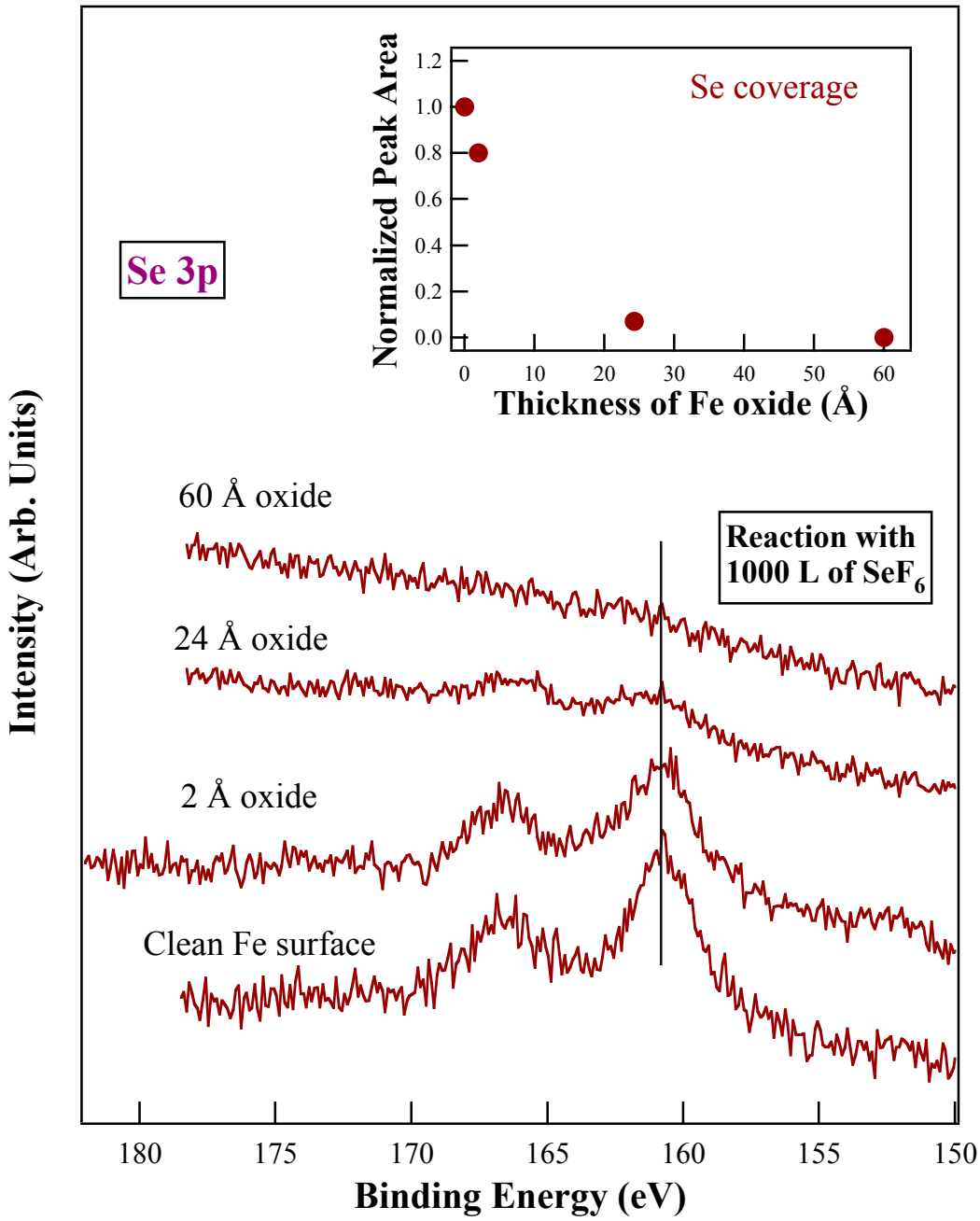
Reaction of SeF_6 with Fe



- **Se attaches to the surface in a single oxidation state**
- **Removal of F does not alter the state**

→ Following the reaction, Se is not bonded to F, i.e., SeF_6 is completely reduced

Reaction of SeF_6 with oxidized Fe surfaces



- **Oxygen inhibits the reaction of SeF_6 due to the inability of electrons to travel through the oxide layer and induce dissociation**

Summary

- Zero-valent iron provides a means for the remediation of ground and waste waters via reduction or 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.

  - Surface oxide significantly affects the reactions
    - ⇒ For SeF_6 reaction with Fe, surface oxide impedes the adsorption.
    - ⇒ For bulk reactions with Ar or N_2 purging, the contaminant reduction rate is initially high, but slows due to oxide build-up.
    - ⇒ Surface oxide films quench the reaction by inhibiting the transport of electrons that are needed for the reduction reaction.

  - For many dissolved species, partial reduction accompanies contaminant removal
    - ⇒ Adsorbed selenate and chromate were partially reduced.
    - ⇒ Dissolved oxygen reduces the amount of deposition.

  - 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 our previous studies on anaerobic sediments, in which 75% of the solid-phase U was U(VI) and 25% was U(IV).
    - ⇒ Dissolved CO_2 inhibits the adsorption of U(VI).

Future Directions

- We will continue to characterize uranium oxide films grown from solution under various conditions in order to determine the film growth mechanism.

- Surface studies will be performed of the reactions of Fe with other gaseous compounds.
  ⇒ Uranium hexafluoride (UF_6)
  ⇒ Selenic, selenous acids (H_2SeO_4, H_2SeO_3)

- Studies of modified iron surfaces, 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.

- Single crystal Fe surfaces will be reacted with model gaseous compounds in UHV to determine adsorption sites and the role of atomic structure.

- A wet-cell has been constructed which will allow reactions of iron in aqueous solution under very well-controlled conditions with direct transfer to UHV for surface sensitive measurements.

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