Overcoming Barriers to the Remediation of Carbon Tetrachloride Through Manipulation of Competing Reaction Mechanisms

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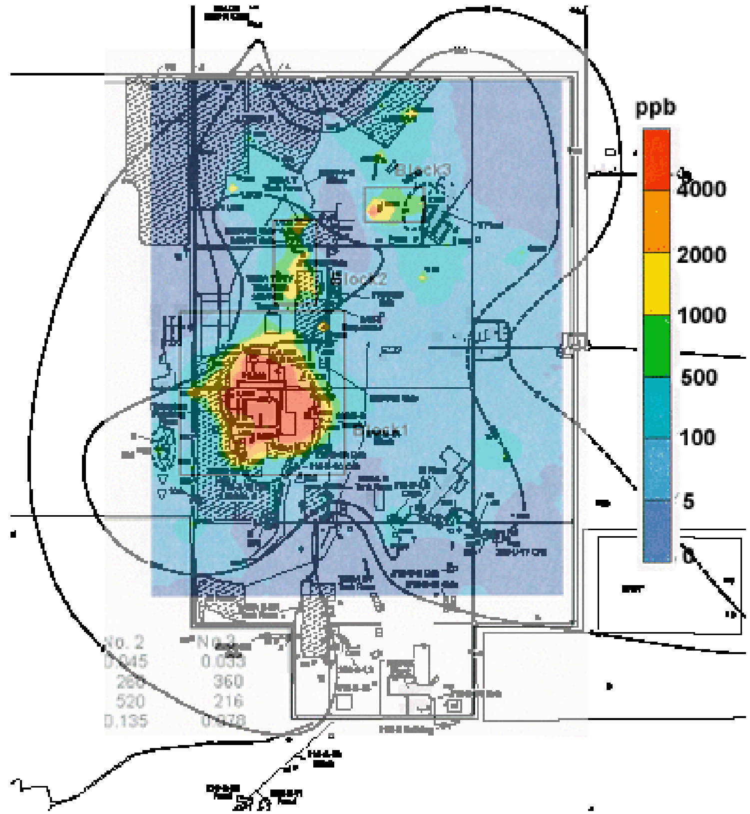
Subsurface Science Element
Project 86820

Carbon Tetrachloride at Hanford

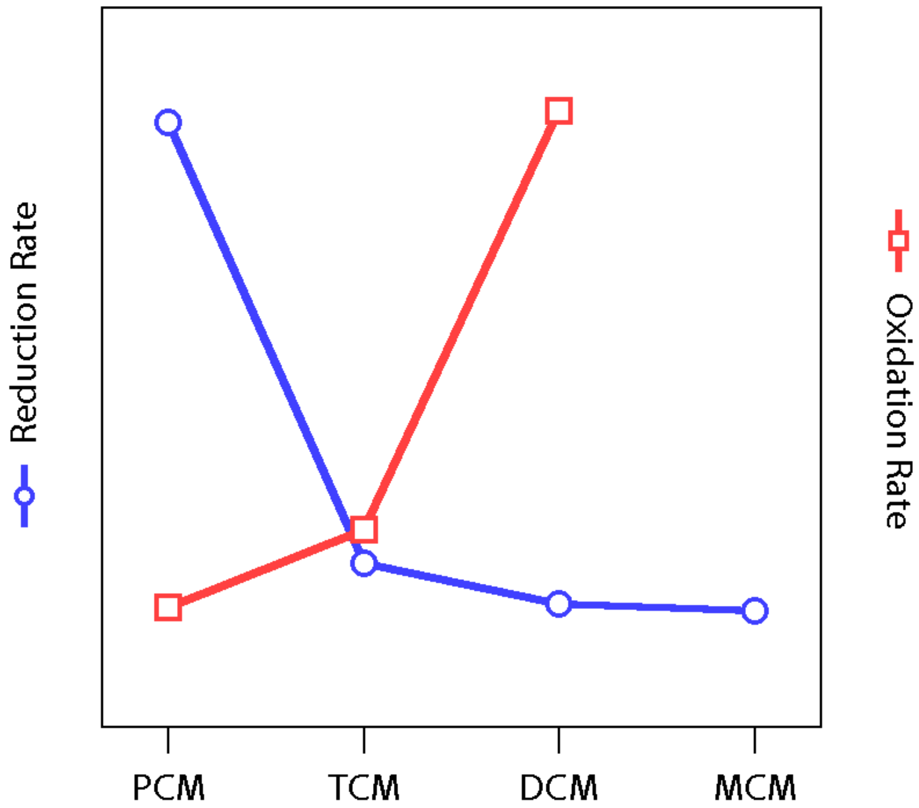
- 200 W Area of Hanford
  - 750,000 kg spilled
  - Vadose and GW zones
  - 11 km^2 plume
  - up to 7000 ug/L
- ITRD TAG since 1999
  - Completed PITT
  - Reviewed Natural Attenuation
  - Modeled Reactive-Transport
  - Reviewed Treatment Options



- Status
  - Active intervention probably needed
  - “Critical” Need for Remediation Technology (TIP No. 0006)

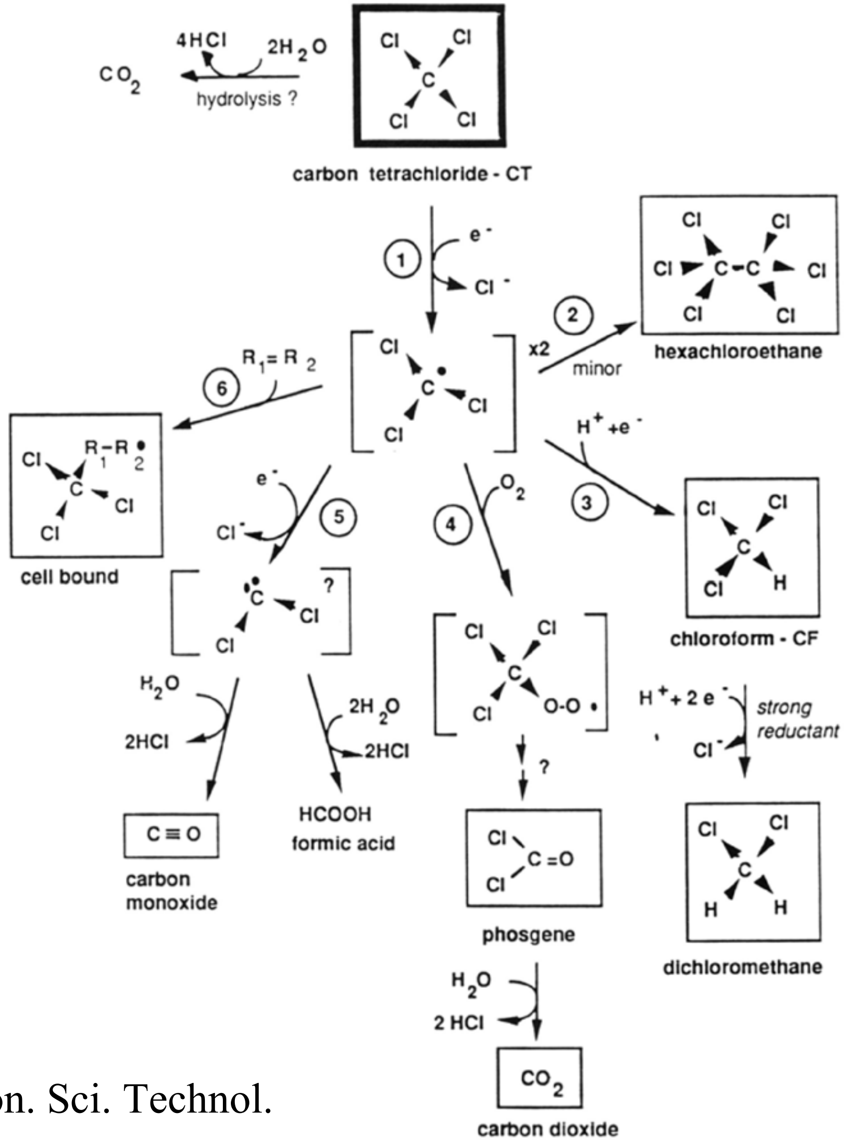
Treatment Options for Carbon Tetrachloride

- Extraction
  - Air sparging
  - Surfactant flushing
- Biodegradation
  - Aerobic
  - Anaerobic
- Chemical Oxidation
  - Permanganate
  - Fenton
- Chemical Reduction
  - Dithionite
  - Iron metal



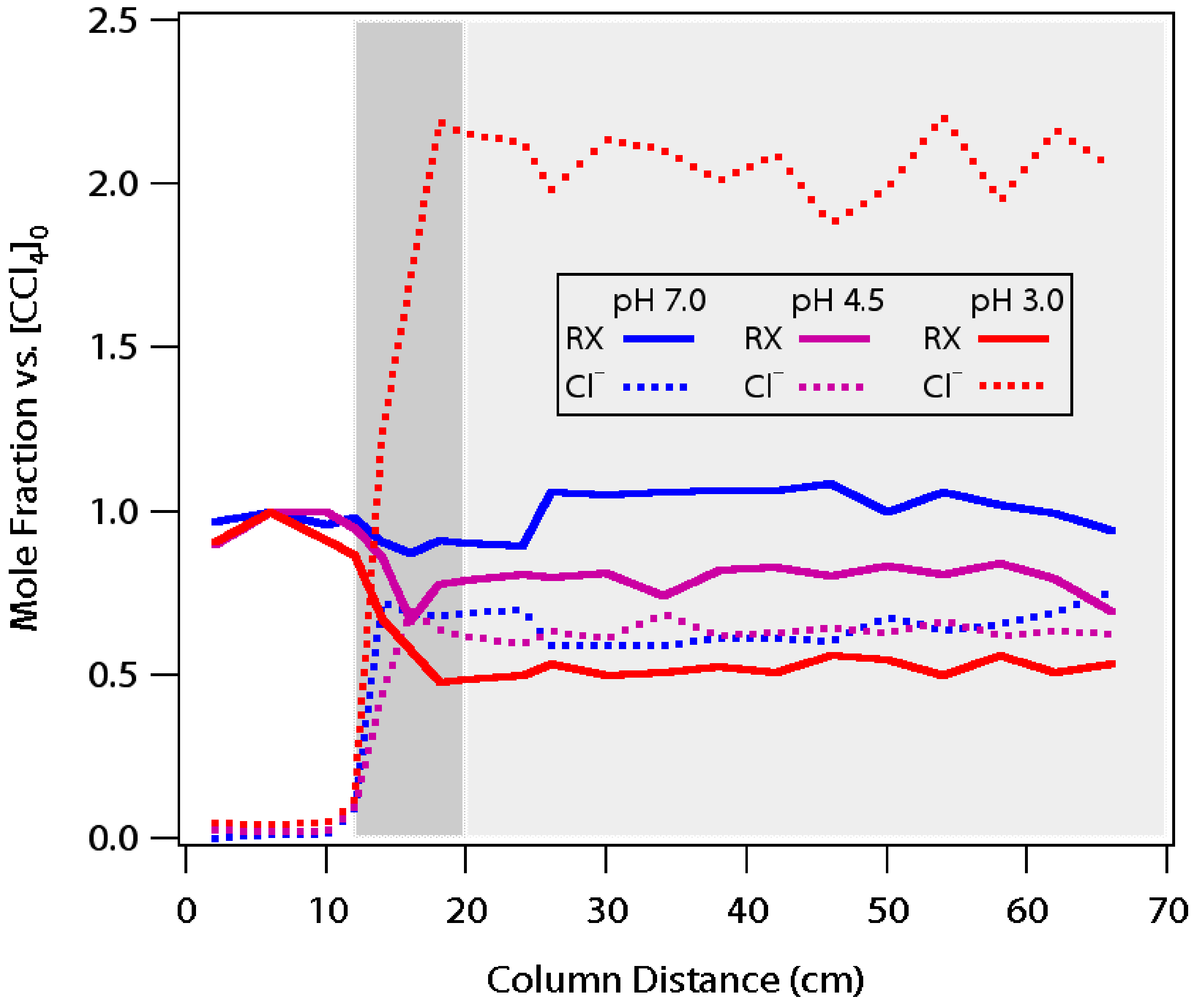
Byproducts from Carbon Tetrachloride

- Reduction
  - "1-electron" products:
    - $CHCl_3$
    - CH_2Cl_2
    - C_2Cl_6
    - C_2Cl_4
  - "2-electron" products:
    - CO
    - HCOOH
- Branching Ratios
  - 1- vs. 2-electron

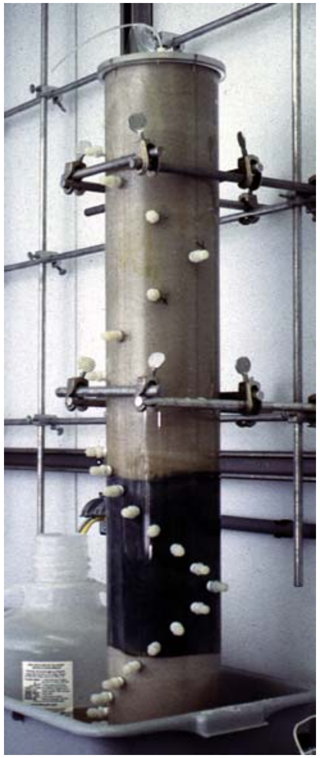


Criddle et al. (1991) Environ. Sci. Technol.

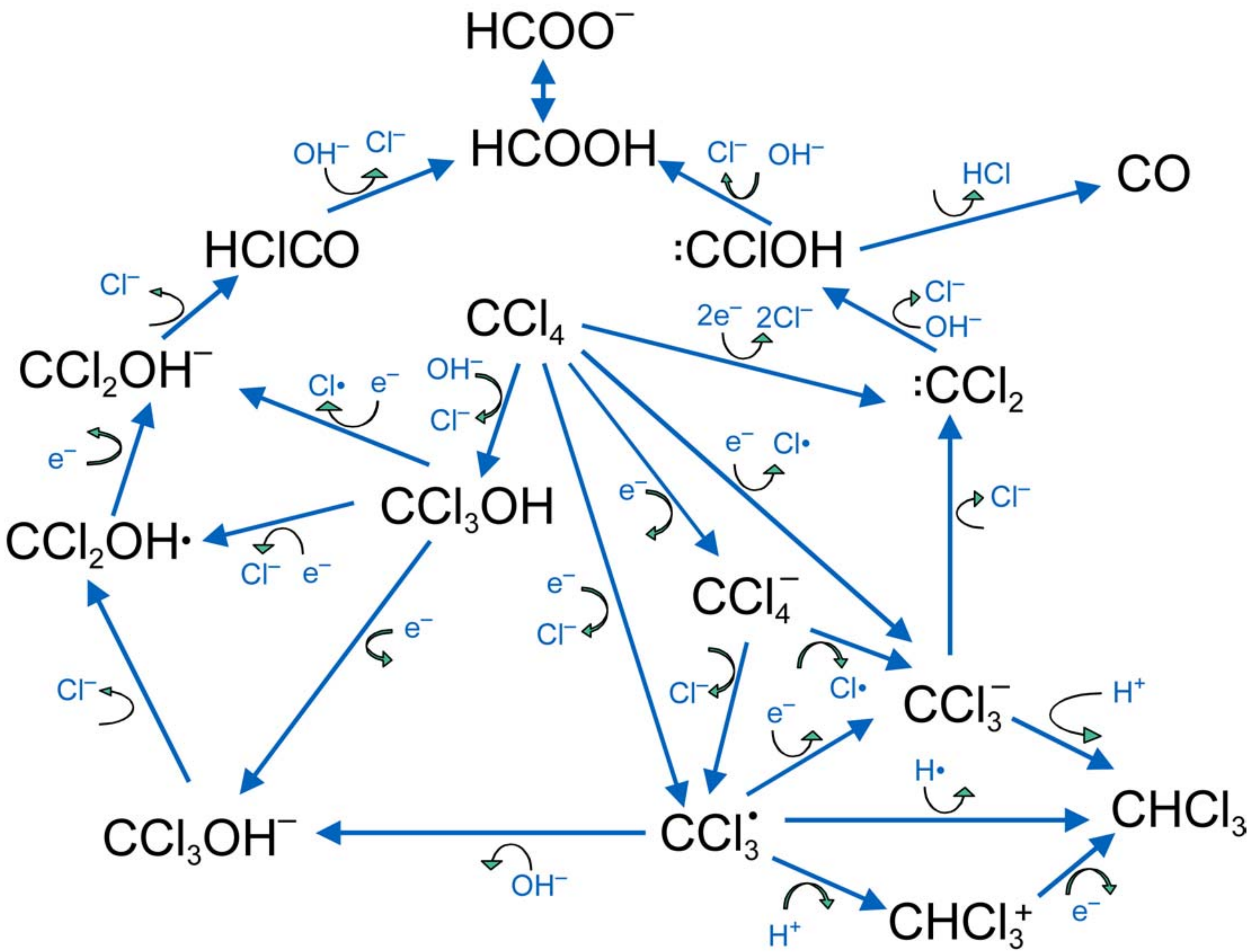
Affecting Branching Ratios—Fe(0)



Tratnyek et al.
(unpublished)



Controlling Branching Ratios

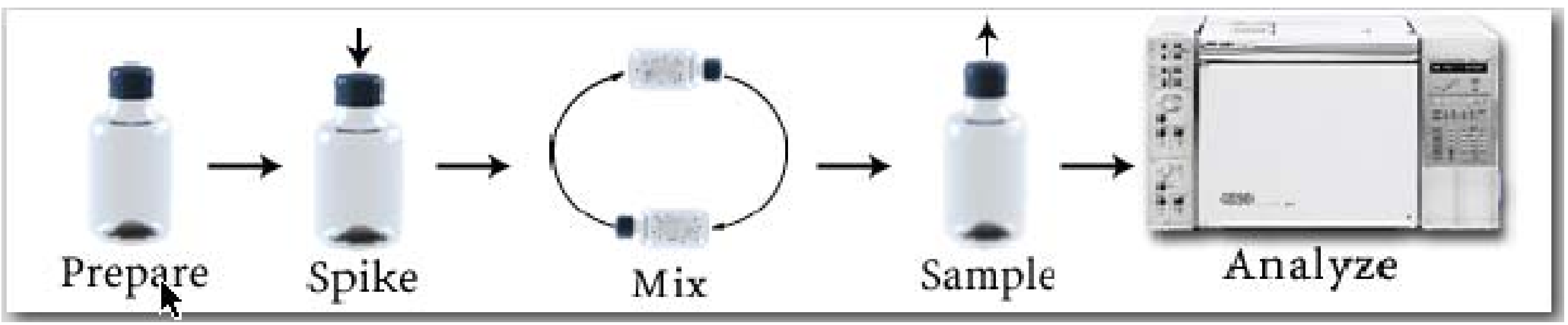


Project Outline

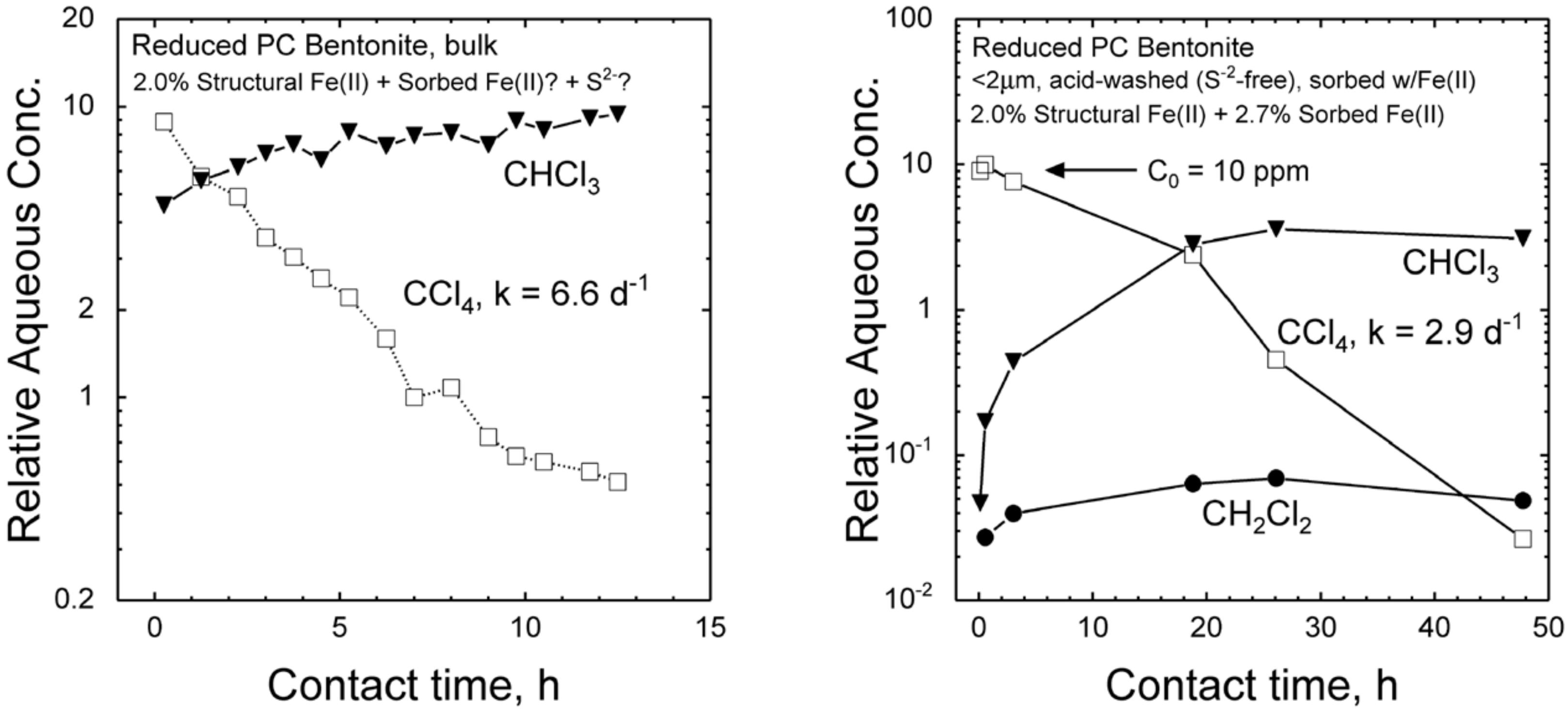
- Objective I. Characterize Mechanisms and Kinetics
  - Task 1. Batch Experiments
  - Task 2. Intermediates by Spectroscopy and Trapping
  - Task 3. Mechanistic Modeling
- Objective 2. Derive Control Strategies
  - Task 4. Batch Experiments
  - Task 5. Mechanistic Modeling
- Objective III. Test Control Strategies
  - Task 6. Column Experiments
  - Task 7. Reactive-Transport Modeling

Task 1. Batch Experiments

- Quantify the kinetics of all competing product-formation pathways, over a range of conditions relevant to groundwater remediation.
- Using well-mixed batch reactors and analysis primarily by chromatography.

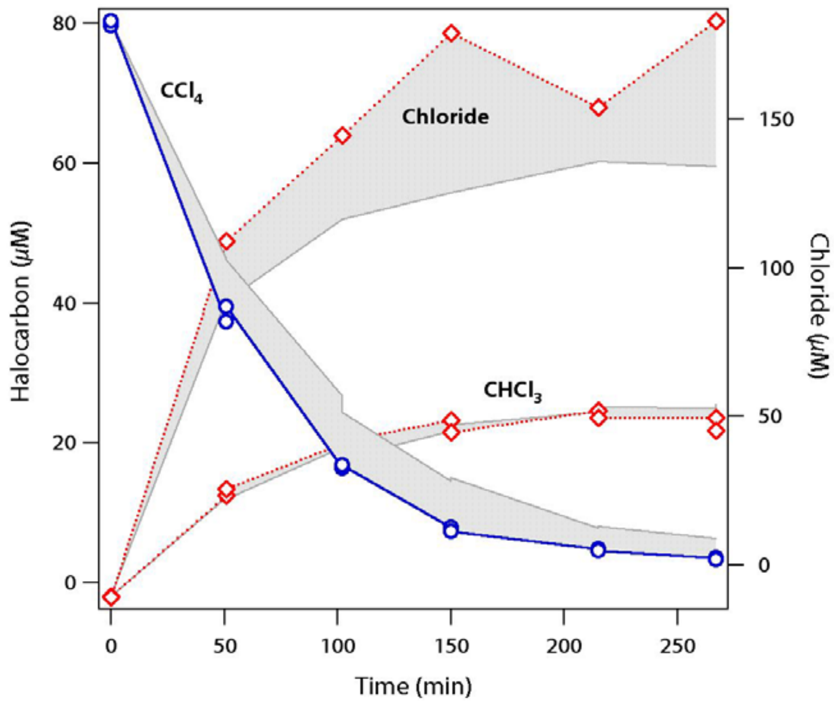


Task 1. Batch Experiments—Fe(II)

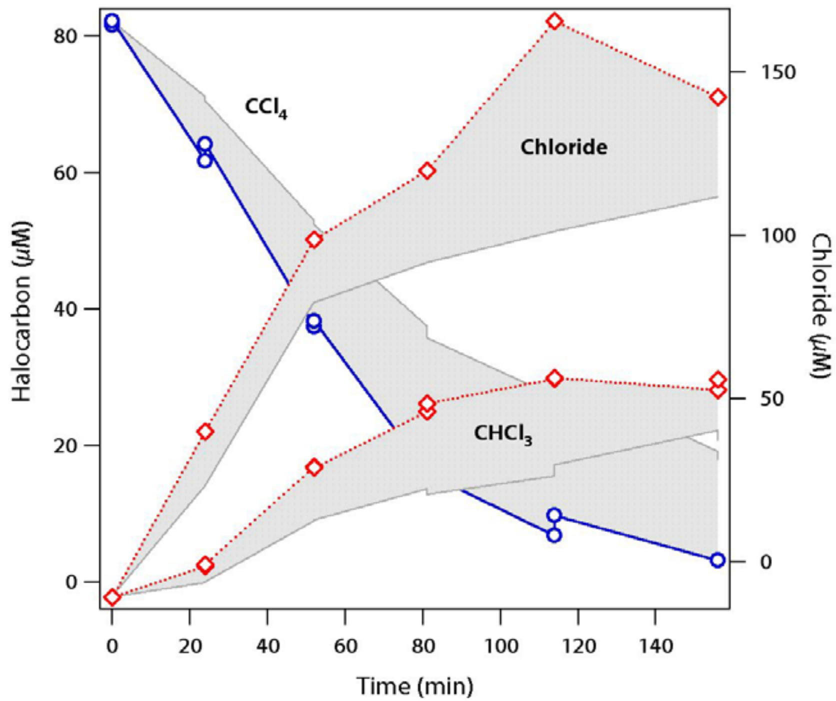


Amonette et al. (unpublished)

Task 1. Batch Experiments—Fe(0)



$Fe^0/CCl_4/H_2O$

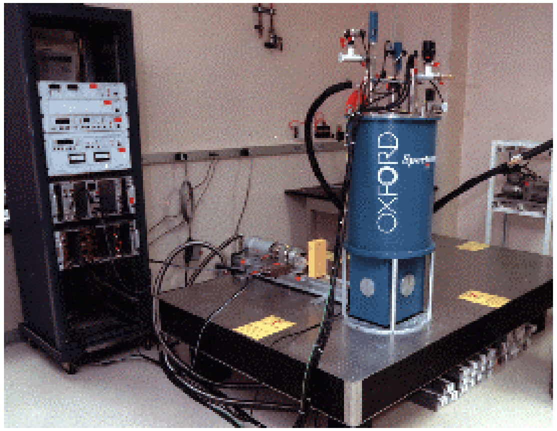


$Fe^0/CCl_4/H_2O/ROH$

Balko and Tratnyek (1998)

Task 2. Spectroscopy & Trapping Studies

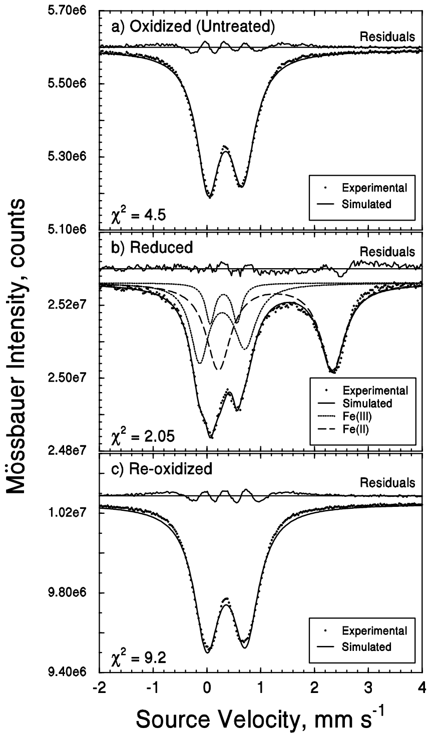
- Determine how the composition and structure of reactive surfaces, and the formation and fate of key reaction intermediates, control the distribution of reaction products formed.
- Use model systems similar to Task 1 but analyzed with complementary spectroscopic and molecular-trapping methods.



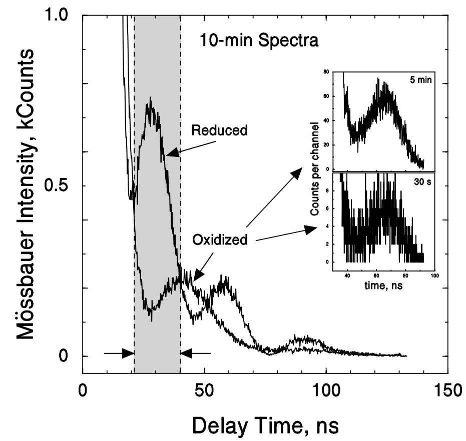
Conventional and synchrotron Mössbauer spectroscopy

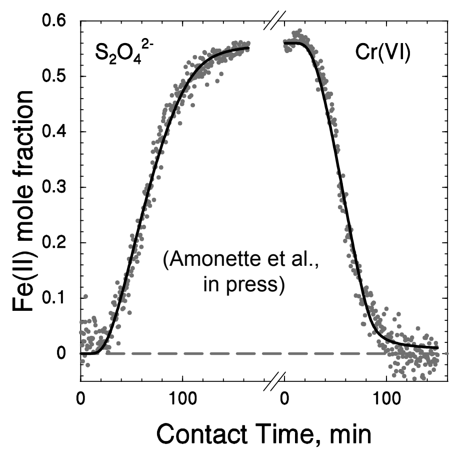
Electron paramagnetic resonance with stopped-flow apparatus

Task 2. Spectroscopy & Trapping

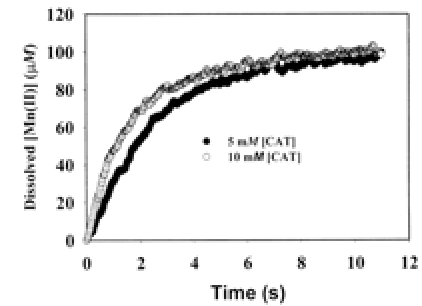


(Amonette et al., in press)





(Stoyanovsky and Cederbaum, 1999)



(Matocha et al., 2001)

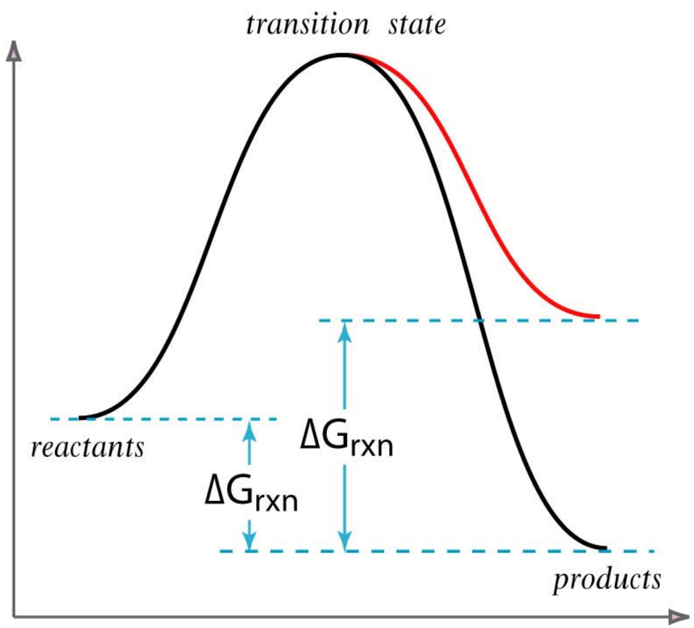
Fe valence and phase w/ conventional Mössbauer spectroscopy

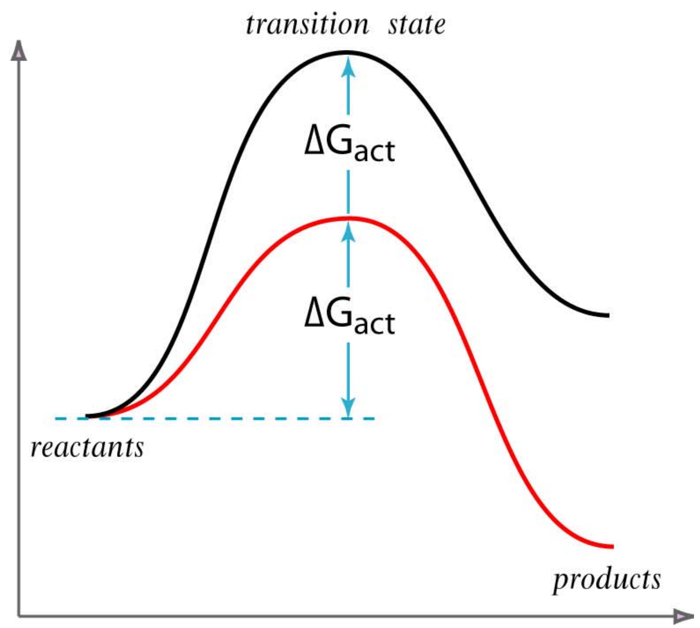
Fe transformation kinetics w/ synchrotron Mössbauer spectroscopy

Intermediate free radical trapping and stopped-flow kinetics w/ electron paramagnetic resonance spectroscopy

Task 3. Mechanistic Modeling

- Calculate the electronic structure and properties of all relevant contaminant species and intermediates using ab initio quantum mechanical models.
- Use these results to characterize the controls on branching among reaction products.





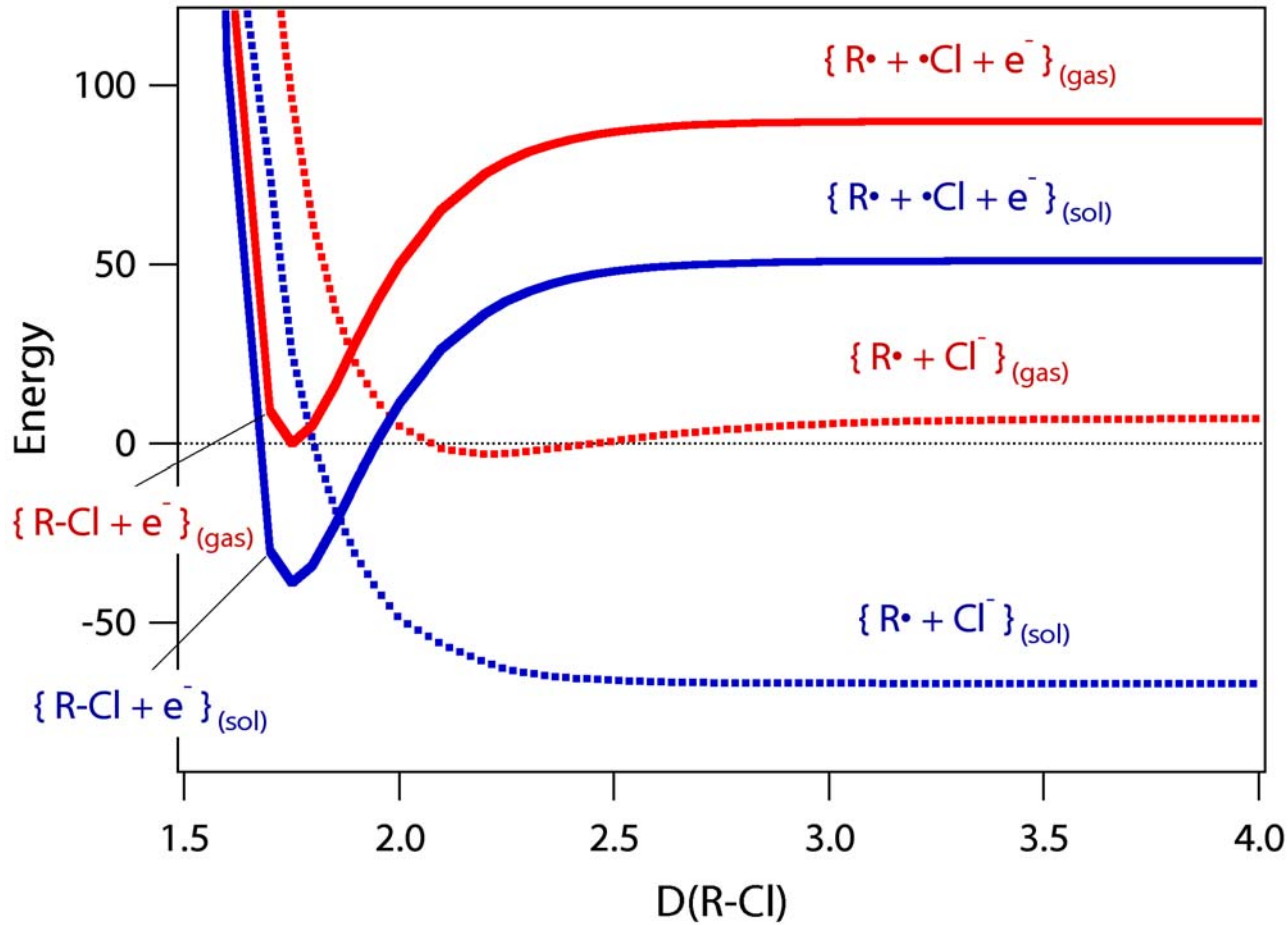
Task 3. Mechanistic Modeling—Energetics

- Thermochemical properties, $\Delta H^o_f(298.15K)$, $S^o(298.15K, 1\ bar)$, $\Delta G_S(298.15K, 1\ bar)$
- For the substituted chloromethyl radicals and anions: $CH_yCl_{2-y}L^{\bullet}$ and $CH_yCl_{2-y}L^-$, for y = 0,1,2 (with L^- = F^-, OH^-, SH^-, NO_3^-, HCO_3^- and x = 0,1,2,3).

$$CH_xCl_{3\text{-}x}L + 1e^- \rightarrow \begin{cases} CH_xCl_{2\text{-}x}L^{\bullet} + Cl^- & \text{(pathway 1)} \\ CH_xCl^{\bullet}_{3\text{-}x} + L^- & \text{(pathway 2)} \\ CH_xCl_{2\text{-}x}L^- + Cl^{\bullet} & \text{(pathway 3)} \\ CH_xCl^-_{3\text{-}x} + L^{\bullet} & \text{(pathway 4)} \end{cases}$$

where L^- = F^-, OH^-, SH^-, NO_3^-, HCO_3^- and x = 0, 1, 2.

Task 3. Mechanistic Modeling—Kinetics



Calculating barriers for outer-sphere dissociative electron transfer

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Anticipated Impact

- Make chemical reduction technologies useful for remediation of carbon tetrachloride by minimizing formation of undesirable byproducts.
  - Permeable Reactive Barriers: Fe(0), etc.
  - Injection of colloidal/nano size reductants: Fe(0)
  - In-Situ Redox Manipulation: Fe(II) from Dithionite, etc.
  - In-Situ Treatment Wells, etc.
- Provide chemical/mechanistic basis for improving bioremediation technologies for carbon tetrachloride.
- Provide improved fundamental understanding of how branching among dechlorination pathways is controlled.

Reduction of halogenated aliphatics, nitro compounds, azo dyes, nitrate, hypochlorite, cyanide.

$Fe^0 + RX + H^+ \rightarrow Fe^{II} + RH + X^-$

$Fe^0 + RNO_2 + H^+ \rightarrow Fe^{II} + RNH_2$

$Fe^0 + R\text{-}N\text{=}N\text{-}R + H^+ \rightarrow Fe^{II} + RNH_2$

Adsorption/coprecipitation of chromate, arsenate, selenate, uranyl, pertechnetate.

$Fe^0 + CrO_4^{2-} + H^+ \rightarrow Fe^{III} + Cr^{3+} + H_2O$

$Fe^{III} + Cr^{3+} + H_2O \rightarrow Fe_{(1-x)}Cr_{(x)}OOH + H^+$

(non-critical stoichiometry omitted)

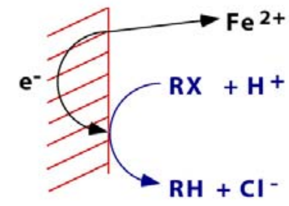
Corrosion Model

1. Reactions involving iron metal

$Fe^0 + 2H_2O \rightarrow Fe^{II} + H_2 + 2OH^-$

$Fe^0 + 1/2O_2 + H^+ \rightarrow Fe^{II} + OH^-$

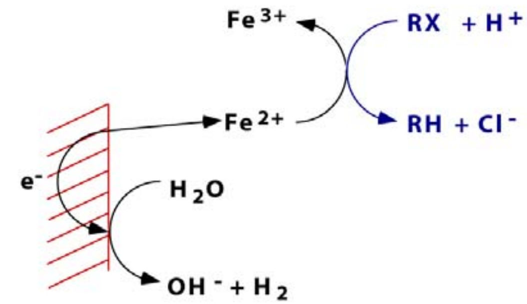
$Fe^0 + RX + H^+ \rightarrow Fe^{II} + RH + X^-$



2. Reactions involving ferrous iron

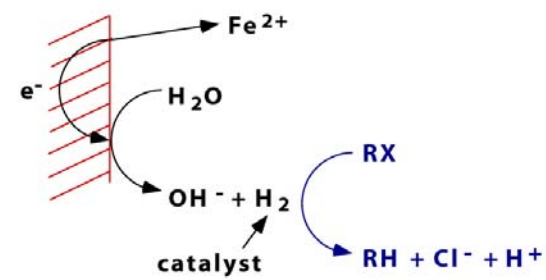
$2Fe^{II} + 1/2O_2 + H^+ \rightarrow 2Fe^{III} + OH^-$

$2Fe^{II} + RX + H^+ \rightarrow 2Fe^{III} + RH + X^-$



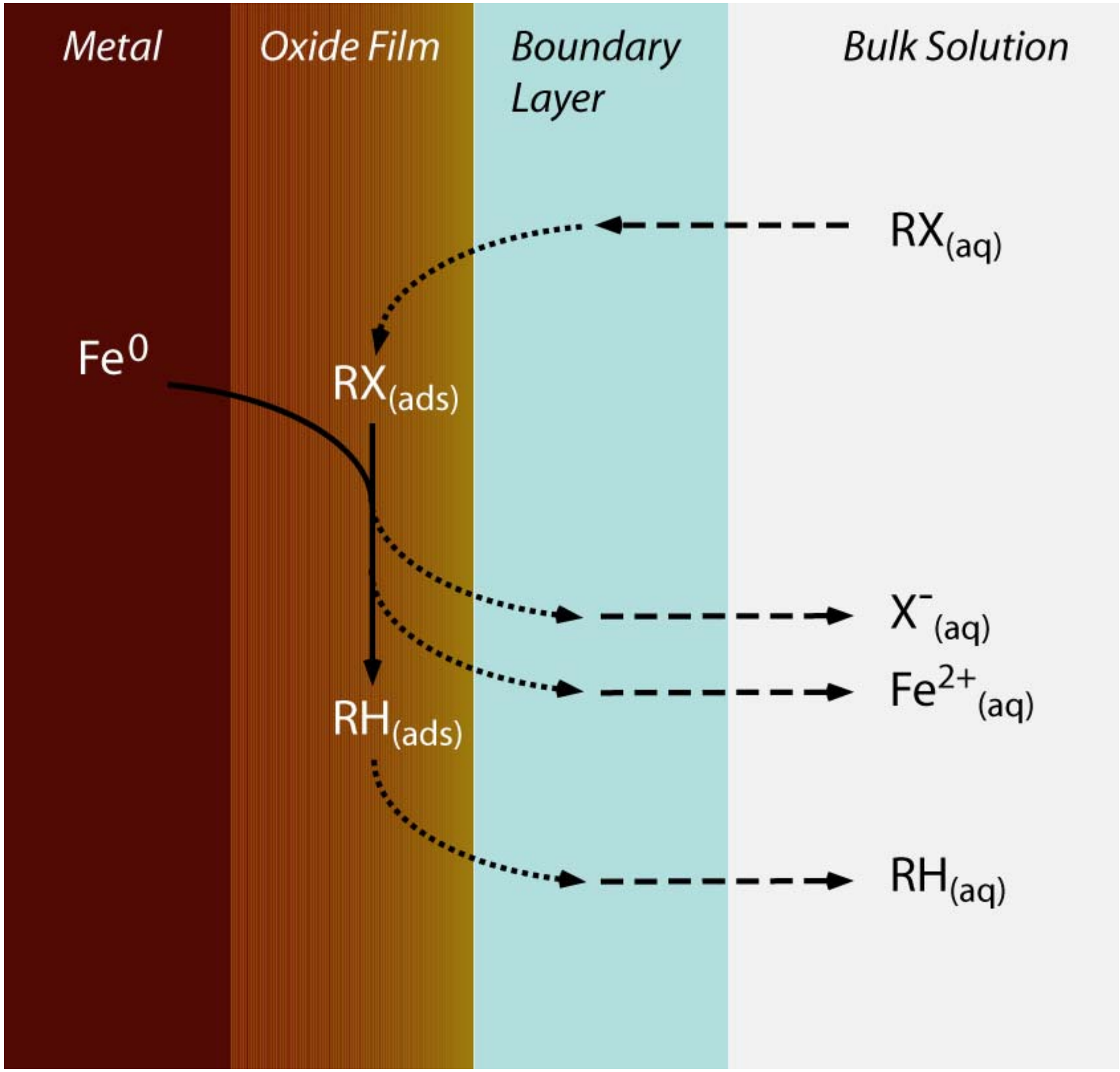
3. Other possible reactions

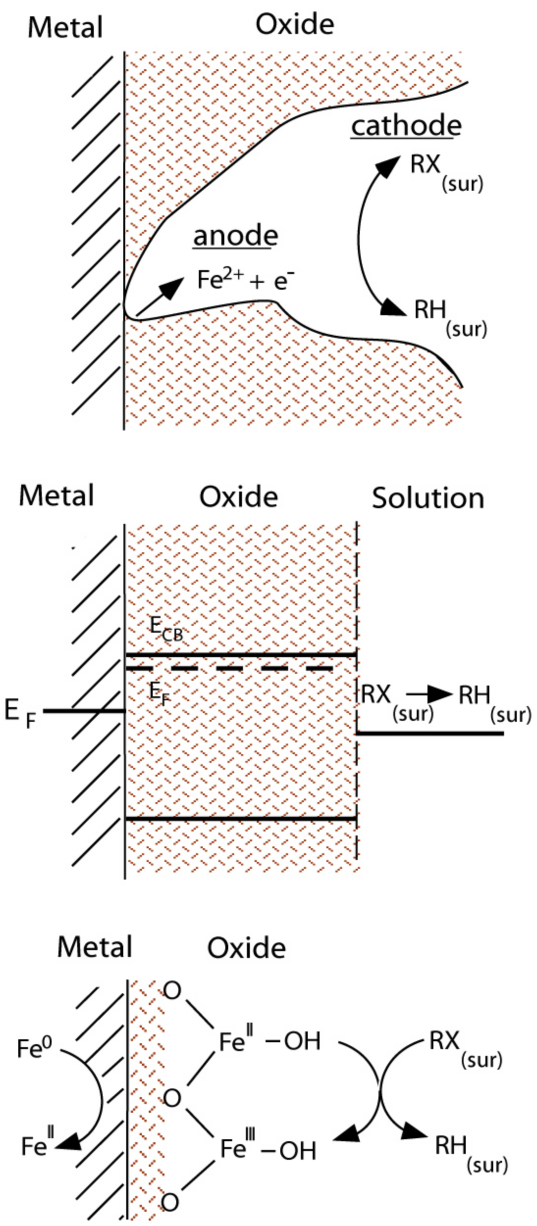
$H_2 + RX \rightarrow RH + H^+ + X^-$



Matheson & Tratnyek (1994) ES&T 28: 2045-2053

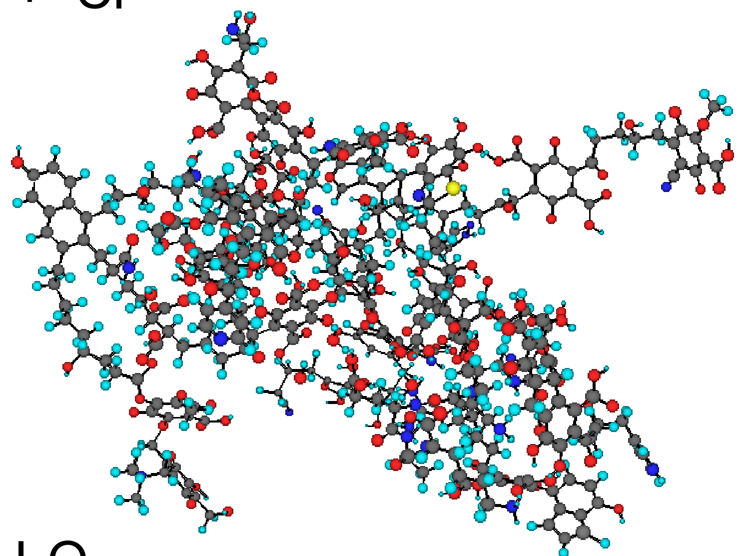
Oxide Film Model





Oxide Film Model > Photoeffects

CCl_4 + Fe^0 + H^+ –> $CHCl_3$ + Fe^{2+} + Cl^-



FeOOH + hυ –> e_{cb}^- + h^+

CCl_4 + e_{cb}^- –> •CCl_3 + Cl^-

•CCl_3 + e_{cb}^- –> :CCl_2 + Cl^-

h^+ + H_2O –> •OH

h^+ + RR'CHOH –> RR'(•C)OH + H^+

•OH + RR'CHOH –> RR'(•C)OH + H_2O

CCl_4 + RR'(•C)OH –> •CCl_3 + RR'CO + H^+ + Cl^-

•CCl_3 + RR'CHOH –> RR'(•C)OH + $CHCl_3$

•CCl_3 + RR'(•C)OH –> :CCl_2 + RR'CO + H^+ + Cl^-

:CCl_2 + H_2O –> CO + Cl^-

Project Plan

<table>
<tr><th rowspan="2">Objectives/Tasks</th><th colspan="4">Year I</th><th colspan="4">Year II</th><th colspan="4">Year III</th></tr>
<tr><th>1/4</th><th>2/4</th><th>3/4</th><th>4/4</th><th>1/4</th><th>2/4</th><th>3/4</th><th>4/4</th><th>1/4</th><th>2/4</th><th>3/4</th><th>4/4</th></tr>
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<tr><td>2. Reactive Surfaces & Intermediates</td><td colspan="8">Postdoc & Amonette</td><td></td><td></td><td></td><td></td></tr>
<tr><td>3. Theoretical calculations</td><td colspan="4">Bylaska</td><td colspan="4">Bylaska & Others</td><td></td><td></td><td></td><td></td></tr>
<tr><td>II. Derive Control Strategies</td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td></tr>
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<tr><td>7. Reactive-transport modeling</td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td colspan="4">Szecsody</td></tr>
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