Reductive Immobilization of Toxic Metals and Radionuclides by Hydrogen Sulfide

Baolin Deng (PI) and Silvia Jurisson
University of Missouri-Columbia, Missouri

E.C. Thornton
Pacific Northwest National Laboratory (PNNL)

Jeff Terry
[3]Illinois Institute of Technology (IIT), Chicago, IL

Acknowledgments:

Financial support - DOE Environmental Remediation Science Program/EMSP

Reductive Immobilization

$HCrO_4^- + 3e^- + 4H^+ = Cr(OH)_3(s) + H_2O$

$UO_2^{2+} + 2e^- = UO_2(s)$

$TcO_4^- + 3e^- + 4H^+ = TcO_2(s) + 2H_2O$

Reductants for groundwater remediation

Dithionite, sulfide

Fe^{2+}, Fe^0, FeS

Organic compounds

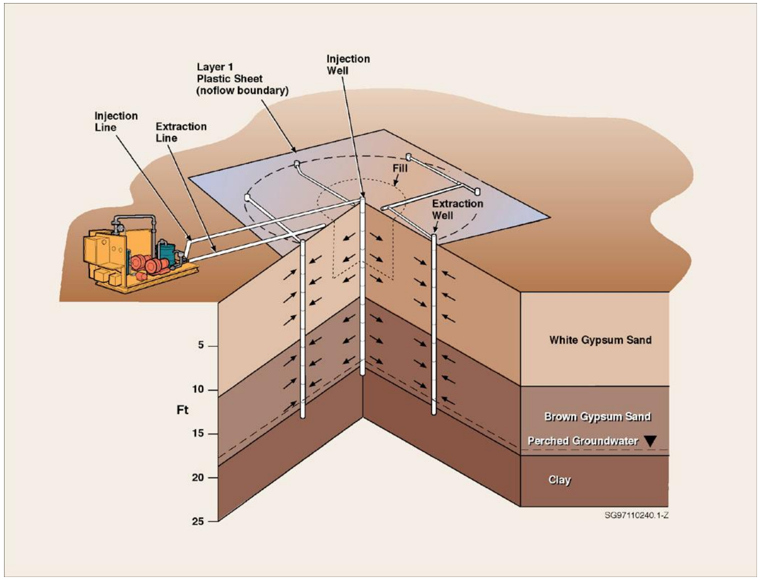
Biotic vs abiotic processes

Gaseous Reductant for soil remediation

Hydrogen Sulfide

In Situ Gaseous Reduction with H_2S

- >70% of Cr(VI) at the demonstration site was immobilized
- ISGR technology can be safely deployed



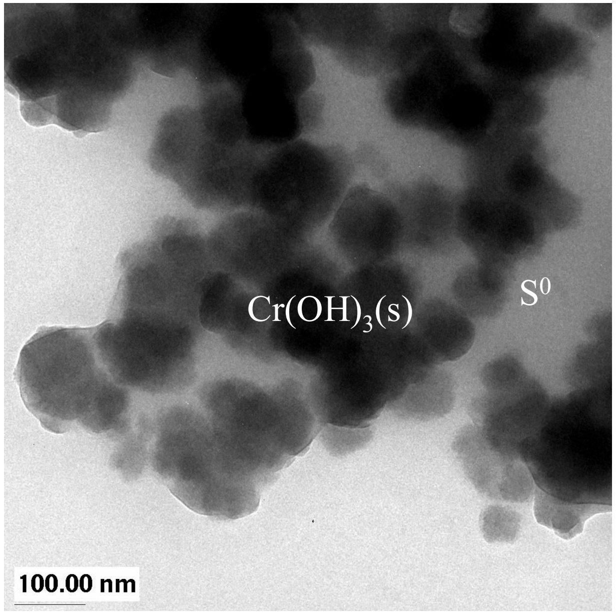
Reductive Immobilization of Existing Contaminants

Creation of Reductive Barriers for Contaminant Interception

Aqueous Chromate Reduction by Sulfide in Anoxic Systems

Molar ratios of the consumption of S(-II) vs. Cr(VI)

Temp. (ºC)	$[S^{II-}]_{t=0}$ (μM)	$[Cr^{VI}]_{t=0}$ (μM)	S^{II-} oxidized v.s. Cr^{VI} reduced	R^2
15	100	40	Y = 1.49 x - 0.28	0.9625
15	100	200	Y = 1.60 x + 0.38	0.9968
25	100	200	Y = 1.54 x + 0.72	0.9972
25	100	40	Y = 1.53 x + 2.74	0.9894
25	200	40	Y = 1.44 x + 0.42	0.9769



HRTEM Image

Reaction Stoichiometry:

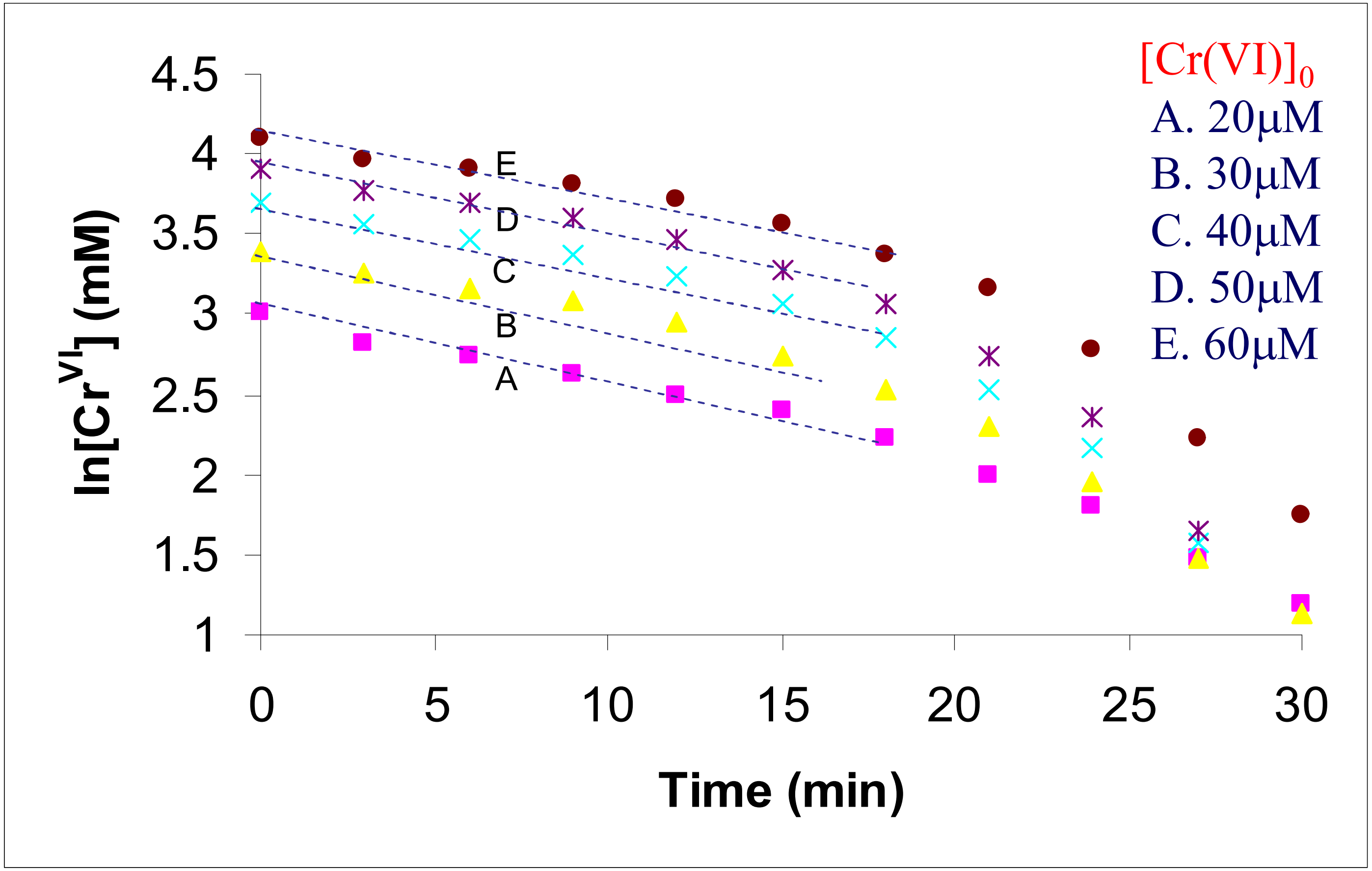
$$2CrO_4^{2-} + 3HS^- + 7H^+ = 2Cr(OH)_3(s) + 3S(s) + 2H_2O$$

NOT as previously reported

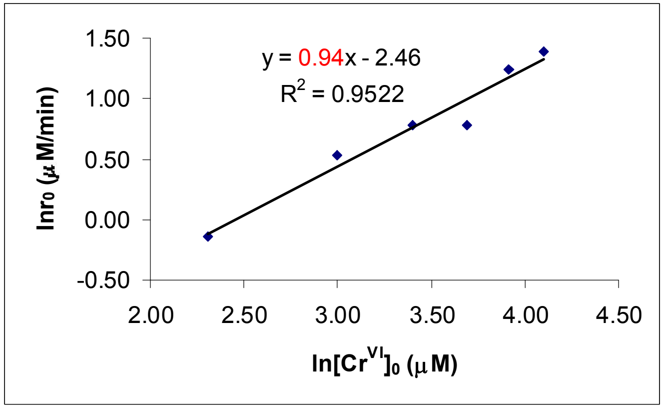
$(8CrO_4^{2-} + 3H_2S + 10H^+ + 4H_2O \rightarrow 8Cr(OH)_3(s) + 3SO_4^{2-})$

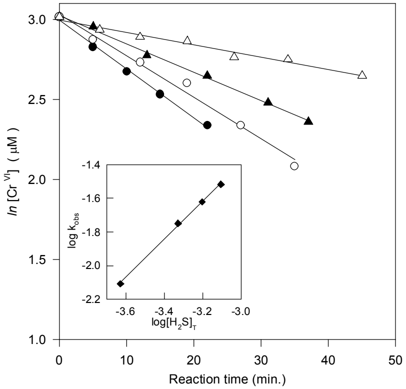
Kinetics of Chromate Reduction by Sulfide in Anoxic Systems

(pH=7.80, 25°C, $[S^{II-}]_0$ = 800 μM)



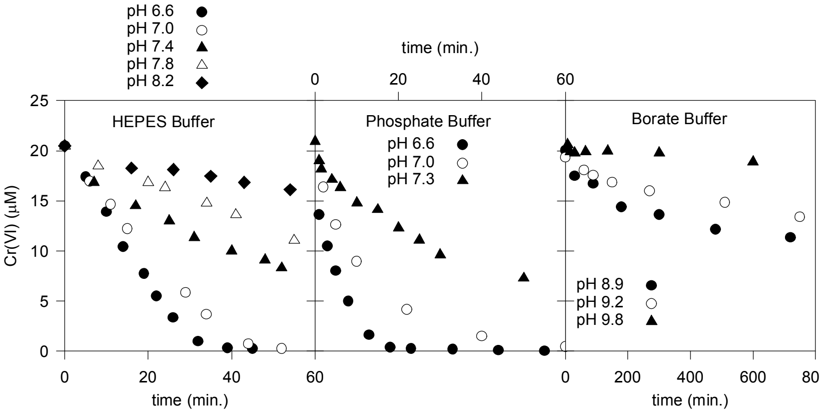
Kinetics Determined by the Initial Rate Method

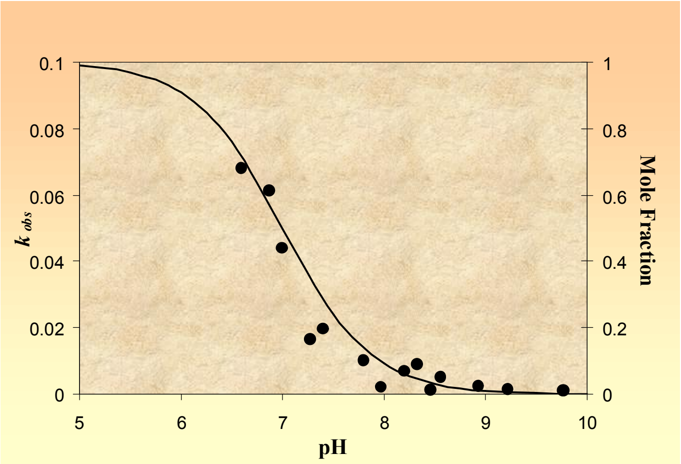




Reaction order with respect to $[Cr^{VI}] = 0.94$

Reaction order with respect to $[H_2S]_0 = 1.1$





Reaction rate increases as pH is decreased

Proposed Reaction Mechanism

Step 1. Precursor Formation

$$CrO_4^{2-} + H_2S \underset{k_{-1}}{\overset{k_1}{\longleftrightarrow}} \{HS\cdots(CrO_3)\cdots OH\}^{2-}$$

Step 2. Electron Transfer

$$\{HS\cdots(CrO_3)\cdots OH\}^{2-} \xrightarrow{k_2} S_0 + Cr^{IV}O_3^{2-} + H_2O$$

Step 3. Fast reactions involving Cr(IV) and Cr(V)

$$Cr^{IV} + Cr^{VI} \overset{k_3}{\longleftrightarrow} 2Cr^{V}$$

$$2Cr^{IV} \overset{k_4}{\longleftrightarrow} Cr^{III} + Cr^{V}$$

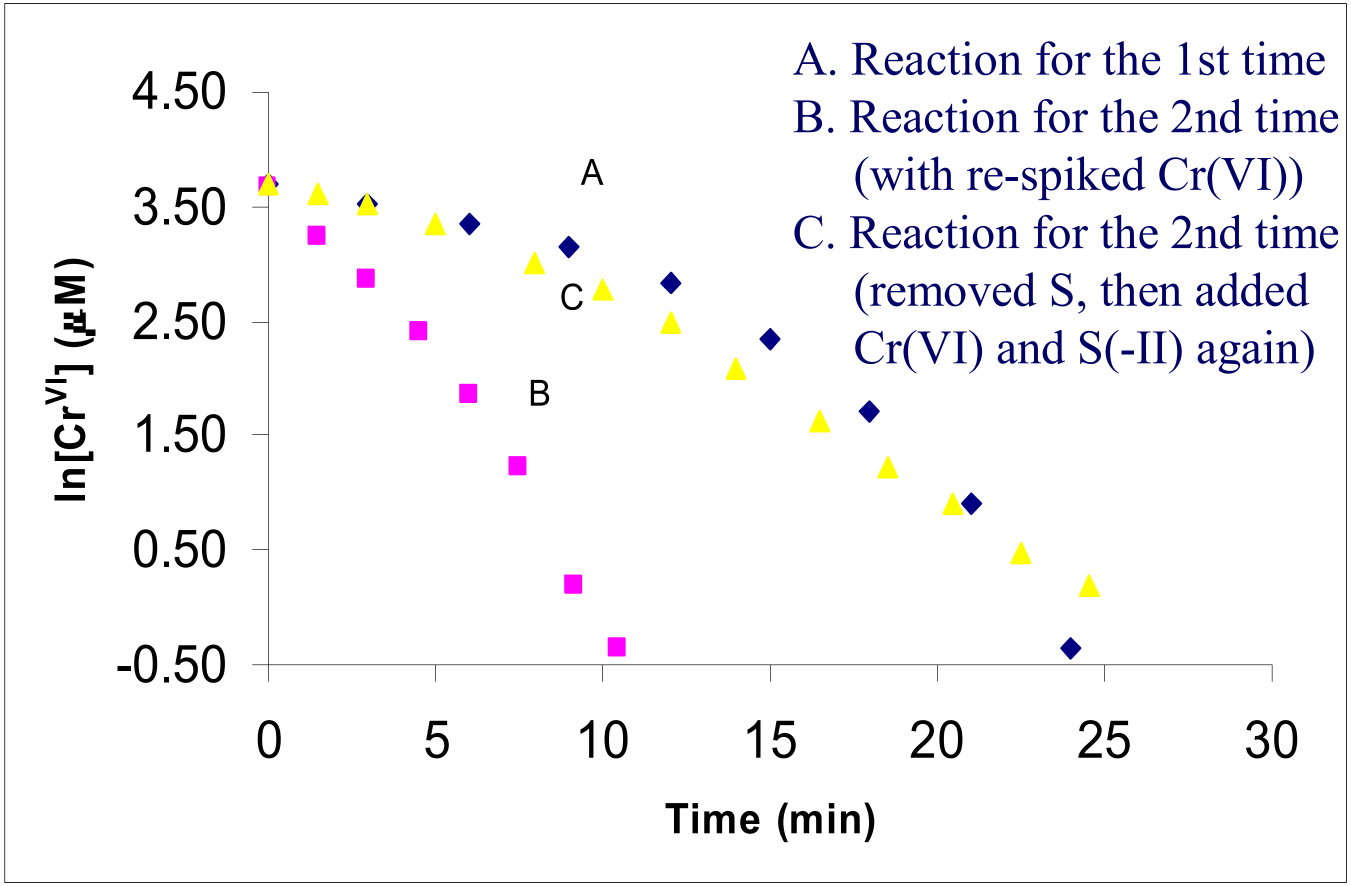
$$Cr^{V} + S^{II-} \overset{k_5}{\longleftrightarrow} 2Cr^{III} + S^{0}$$

The following derived kinetic equation explains all experimental observations

$$\frac{d[Cr(VI)]}{dt} = \frac{-k_1 k_2 [CrO_4^{2-}][H_2S]_T}{k_{-1} + k_2} \left\{ \frac{[H^+]^2}{[H^+]^2 + [H^+]K_1 + K_1 K_2} \right\}$$

Reduction of Re-spiked Cr(VI)

(pH=7.80, 25°C, $[Cr(VI)]_0$ =40μM, $[S(-II)]_0$=800 μM)



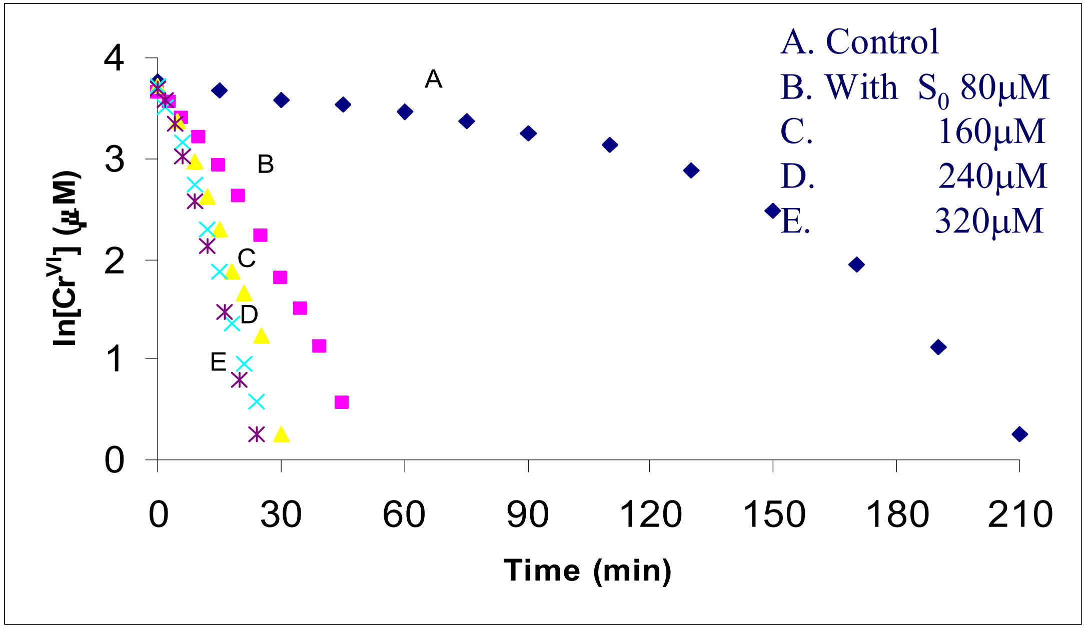
A. Reaction for the 1st time

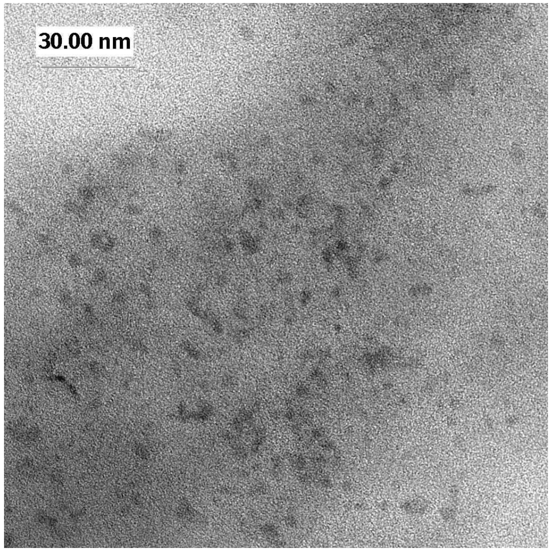
B. Reaction for the 2nd time (with re-spiked Cr(VI))

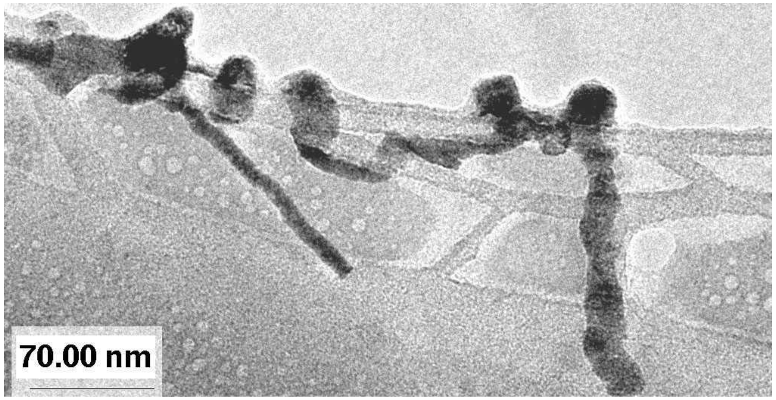
C. Reaction for the 2nd time (removed S, then added Cr(VI) and S(-II) again)

Effect of externally added elemental S

(pH=8.30, 25°C, [H_2S]=800mM)





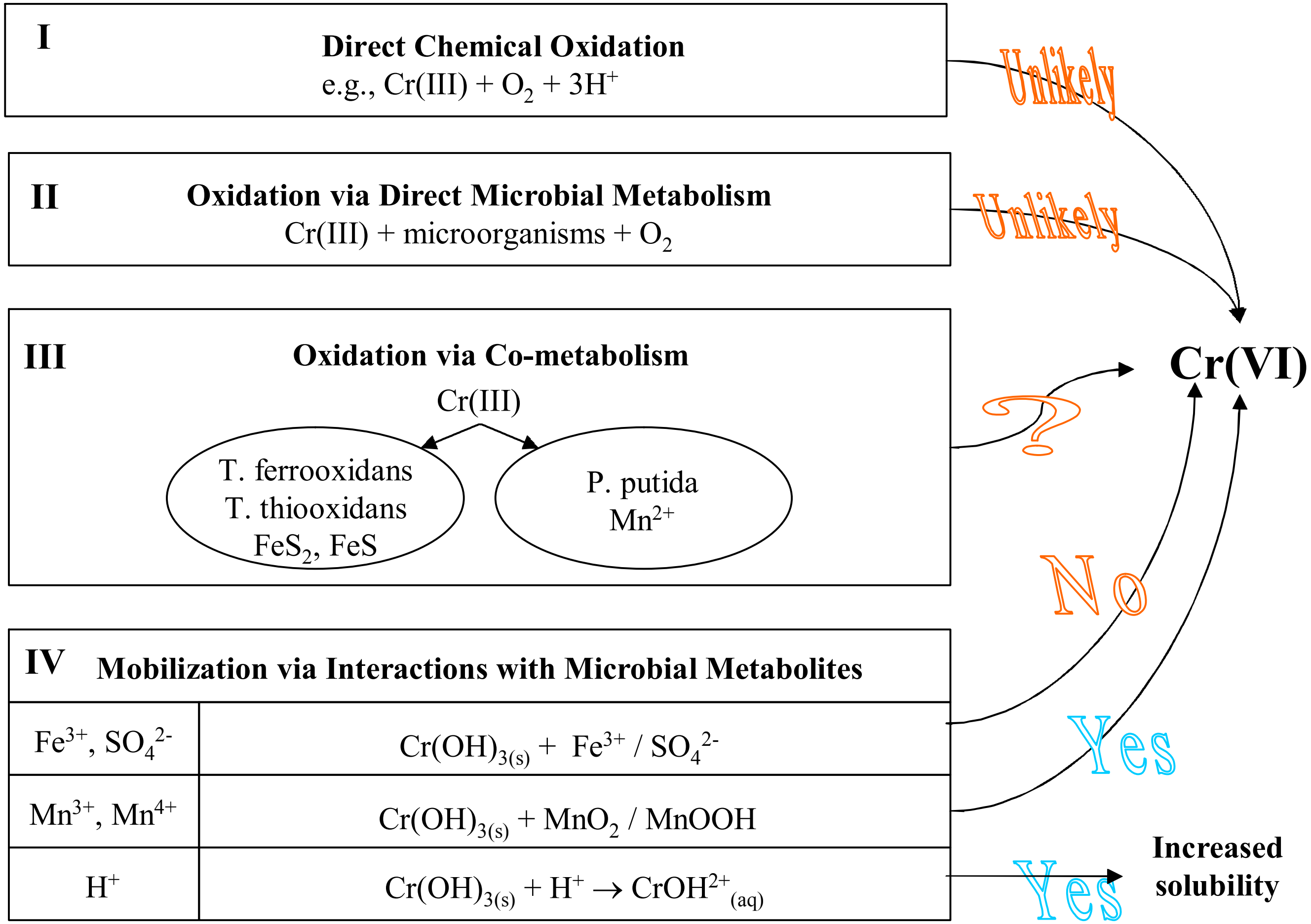


Elemental sulfur nanoparticles catalyze Cr(VI) reduction by sulfide

Environ. Sci. Technol. 39, 2087 – 2094 (2005)

Cr(III) Reoxidation and Remobilization

Possible Mechanisms



I **Direct Chemical Oxidation**
e.g., $Cr(III) + O_2 + 3H^+$

II **Oxidation via Direct Microbial Metabolism**
$Cr(III)$ + microorganisms + O_2

III **Oxidation via Co-metabolism**
$Cr(III)$

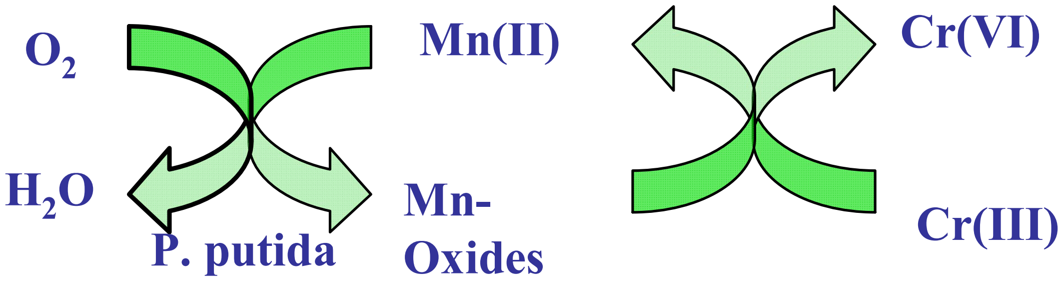
T. ferrooxidans
T. thiooxidans
FeS_2, FeS

P. putida
Mn^{2+}

IV **Mobilization via Interactions with Microbial Metabolites**

Fe^{3+}, SO_4^{2-}	$Cr(OH)_{3(s)} + Fe^{3+} / SO_4^{2-}$
Mn^{3+}, Mn^{4+}	$Cr(OH)_{3(s)} + MnO_2 / MnOOH$
H^+	$Cr(OH)_{3(s)} + H^+ \rightarrow CrOH^{2+}_{(aq)}$

Coupled Biotic/Abiotic Processes for Cr(III) Oxidation



O_2

Mn(II)

Cr(VI)

H_2O

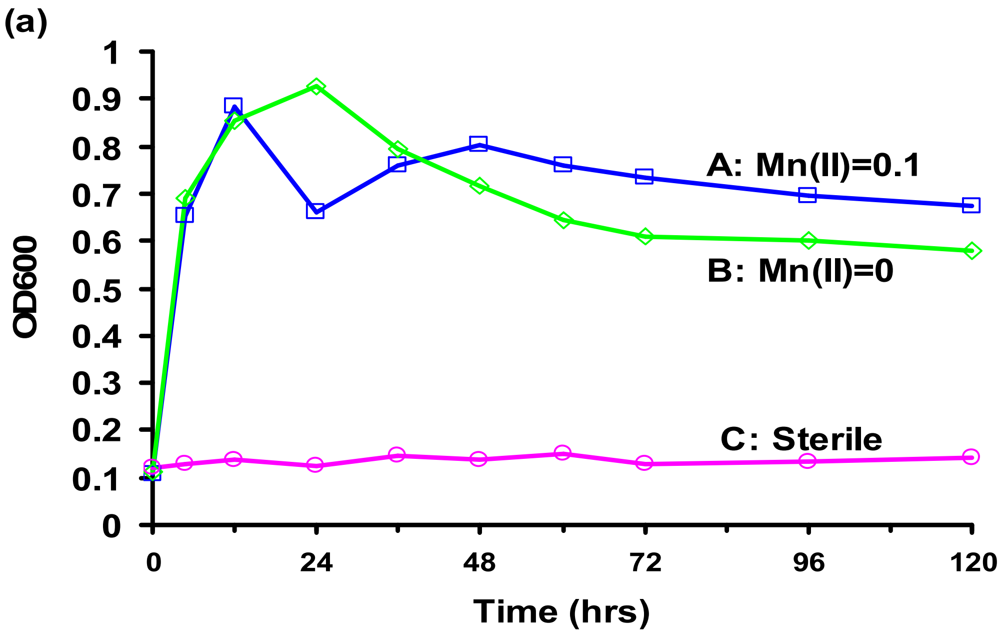
P. putida

Mn-Oxides

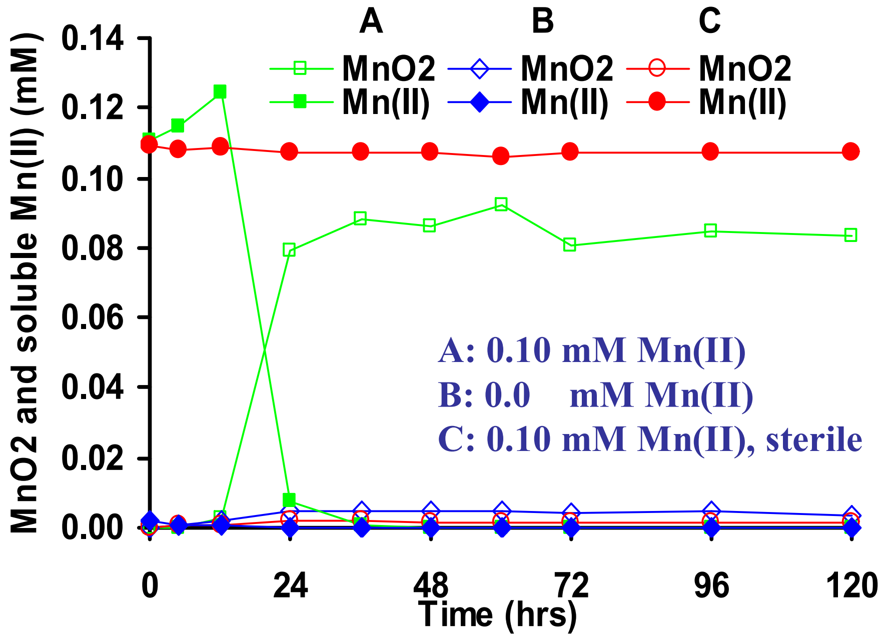
Cr(III)

- *Pseudomonas putida* was obtained from ATCC
- Microbial experiments were conducted in modified LEP medium with 10mM HEPES buffer (pH 7) in a shaker at 150 rpm at 26°C
- **Cell density (OD600):** using spectrophotometric method at 600 nm
- **Mn oxides:** modified LBB assay (Boogerd and de Vrind, 1987)
- **Cr(VI):** measured using diphenyl carbazide colorimetric method after filtration through 0.2 μm membrane filters.
- **Total soluble Mn and Cr:** measured with ICP.

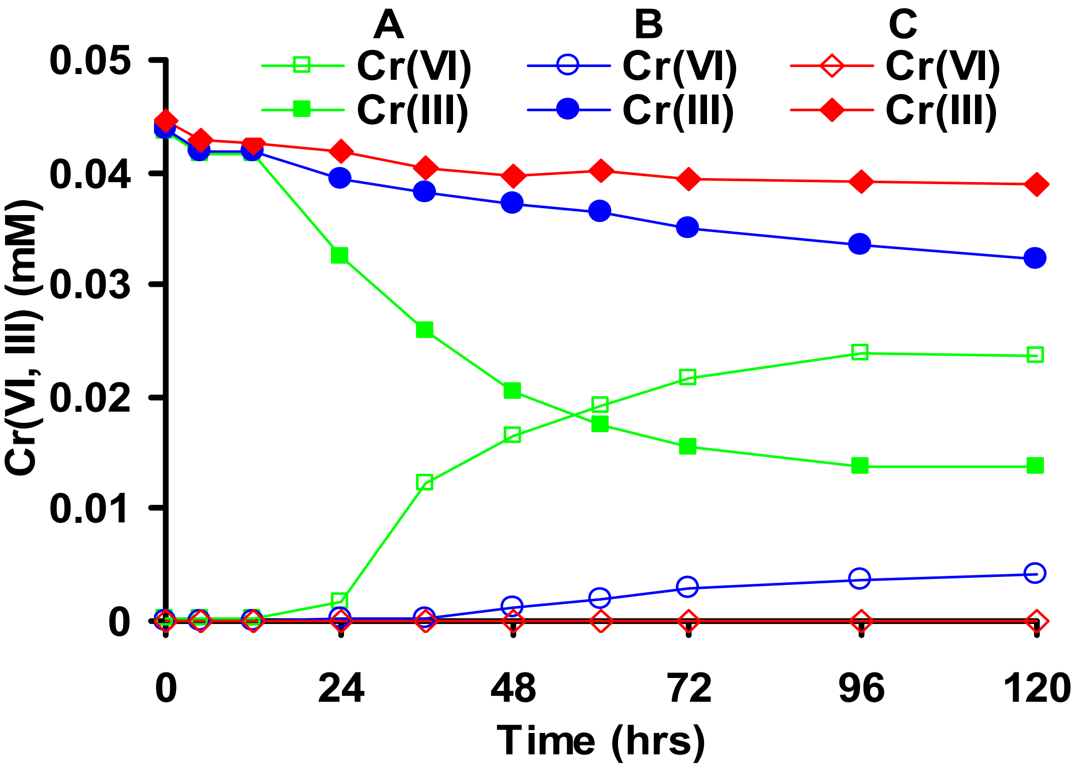
Microbial Growth



Mn(II) Oxidation



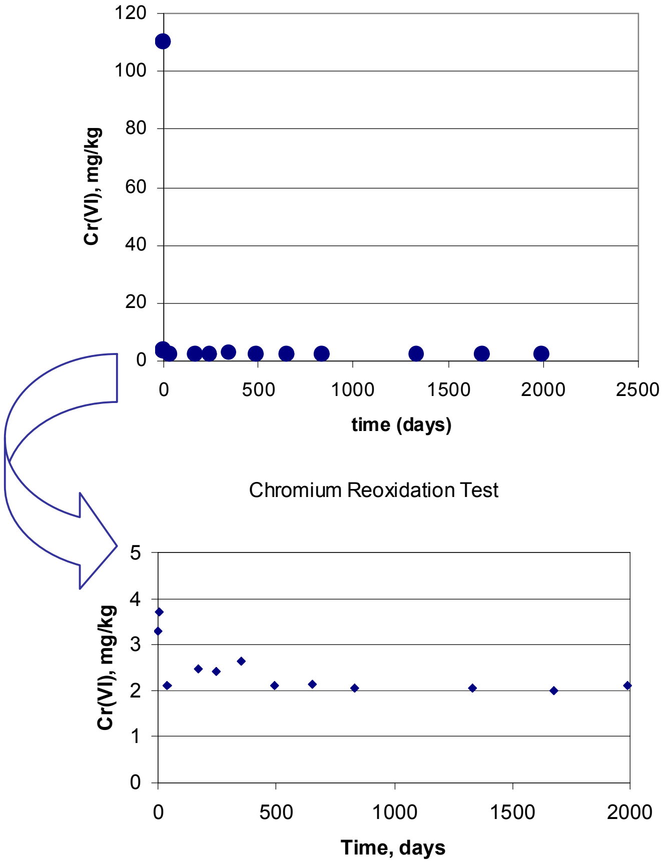
Cr(III) Oxidation Coupled with Microbially-mediated Mn-Oxides Production



A: 0.10 mM Mn(II)
B: 0.0 mM Mn(II)
C: 0.10 mM Mn(II), sterile

Geomicrobiology Journal, 22:161-170, 2005

Long term stability of Cr in soils following H_2S treatment



Contaminated soil sample from the 100K Area at the Hanford Site was treated with diluted hydrogen sulfide gas.

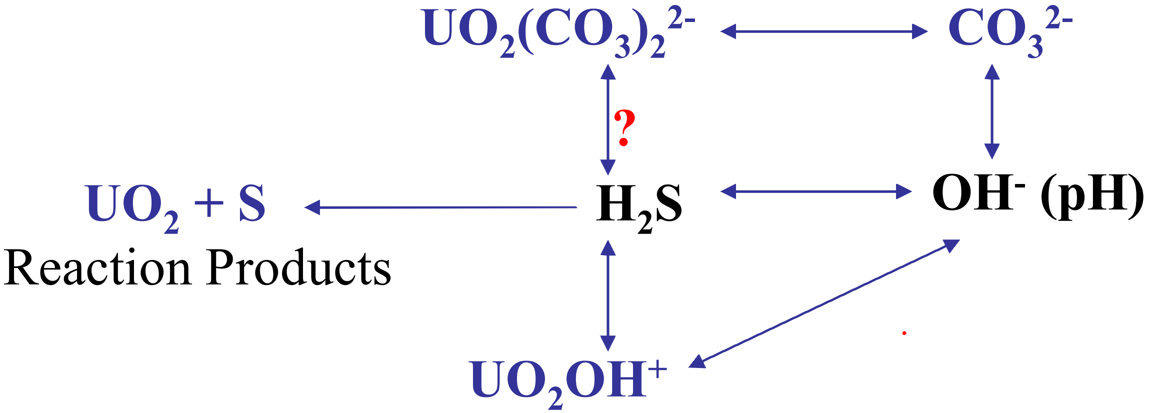
Original Cr(VI) concentration: 110 mg/kg

How Important Is U(VI) Reduction by Hydrogen Sulfide in the Aqueous Phase??? --- UNCLEAR ---

- U(VI) could coexist with high concentration of sulfide (400mM) in anoxic see water (Anderson et al., 1989)
- U(VI) was not reduced by sulfide in bicarbonate (30 mM) buffered solution (Lovley et al., 1991).

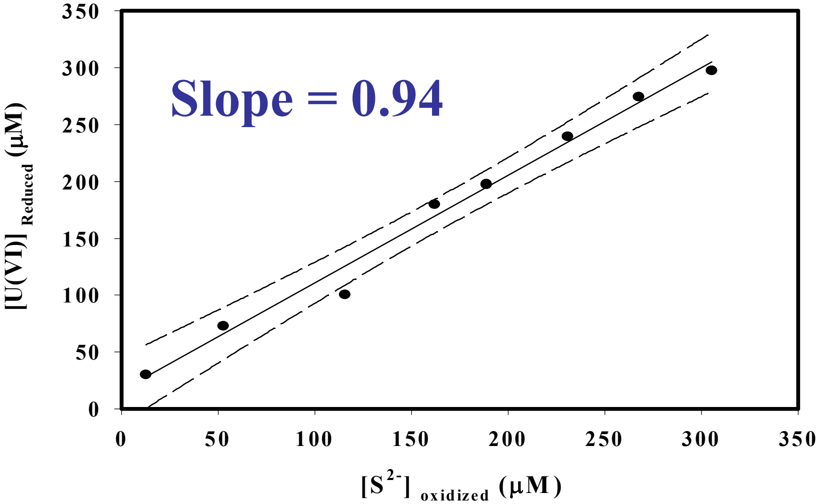
- Uranyl (CO_2-free) was precipitated by 800 mg/L H_2S at pH 6.0-6.5 (Kochenov et al., 1977).
- Uranyl was reduced to uraninite by 500 mM sulfide in the anoxic system with P_{CO2} = 0.15 atm (Beyenal et al., 2004).

A better understanding of the effect of carbonate on U(VI) reduction by sulfide is needed.



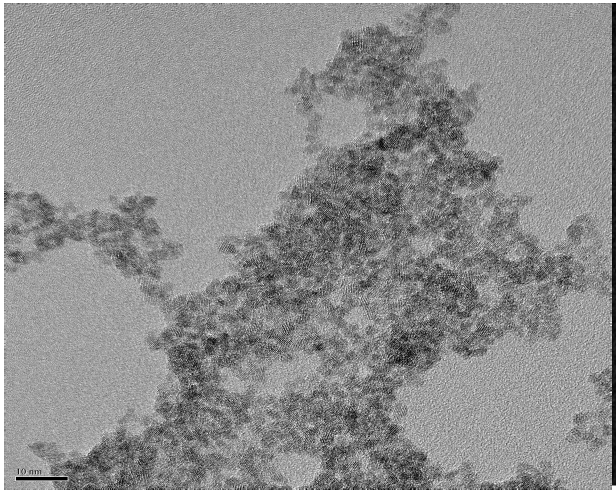
Molar ratio of $[U(VI)]_{reduced}$ to $[S^{2-}]_{oxidized}$

(pH = 6.89; $[CO_3^{2-}]_T$ = 4.0 mM)

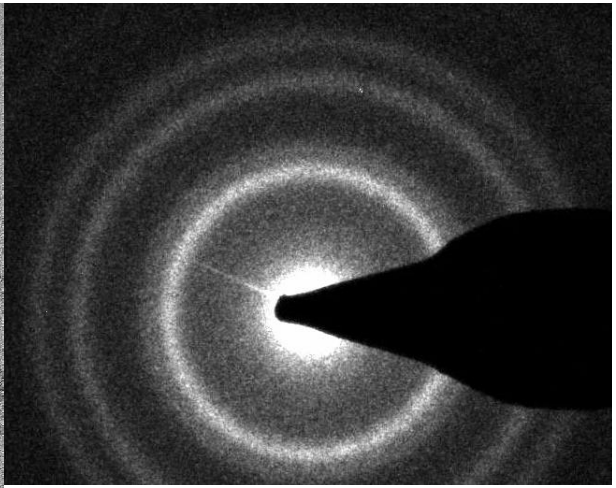


Reaction Stoichiometry

$$UO_2^{2+} + H_2S = UO_2 + S^0 + 2H^+$$

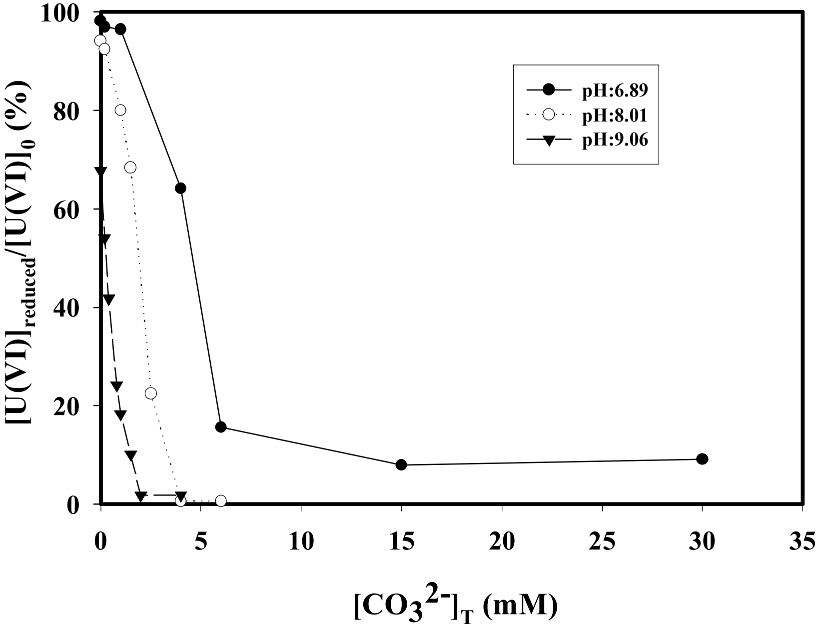


HRTEM Micrograph

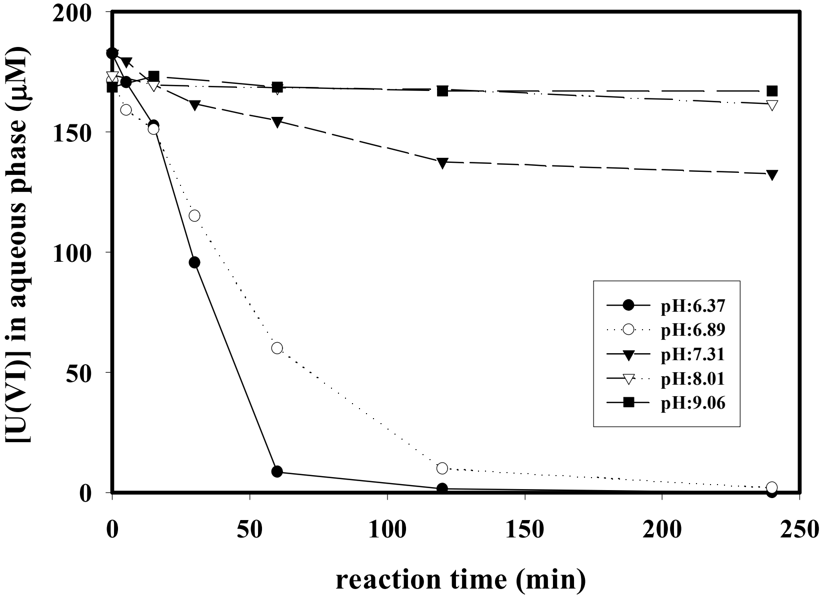


Electron Diffraction Pattern

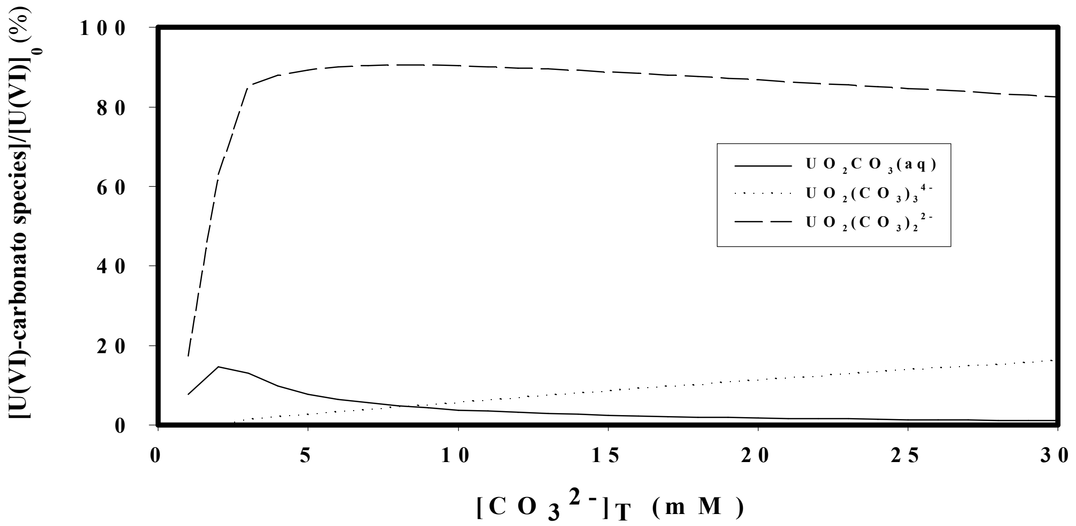
Effects of $[CO_3^{2-}]_T$ on $[U(VI)]_{reduced}/[U(VI)]_0$ (%)
$([S^{2-}]_0 = 2.0$ mM; $[U(VI)]_0 = 168$mM;
<u>reaction time = 60 min</u>)



Effects of pH on U(VI) reduction
$([CO_3^{2-}]_T = 4.0$mM; $[S^{2-}]_0 = 2.0$ mM)



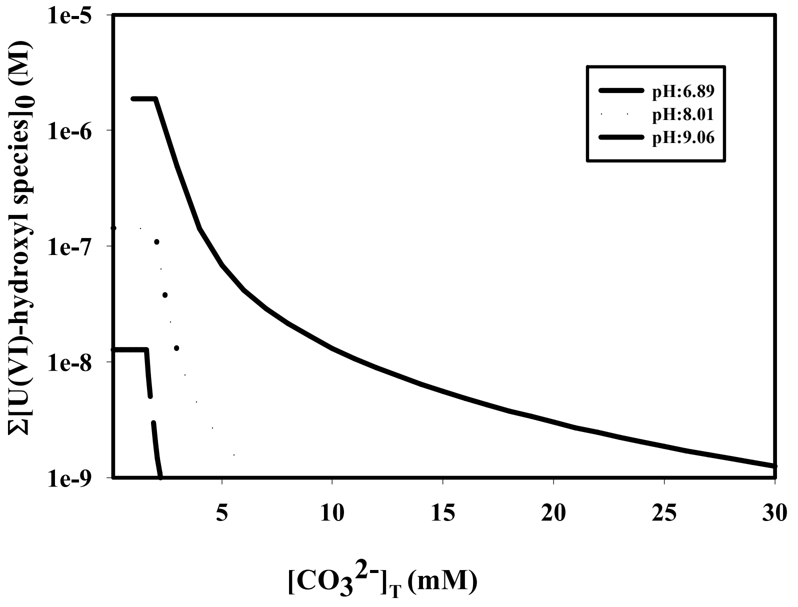
Impact of carbonate on U(VI) speciation and reduction (calculated with MINEQL+, 1998)

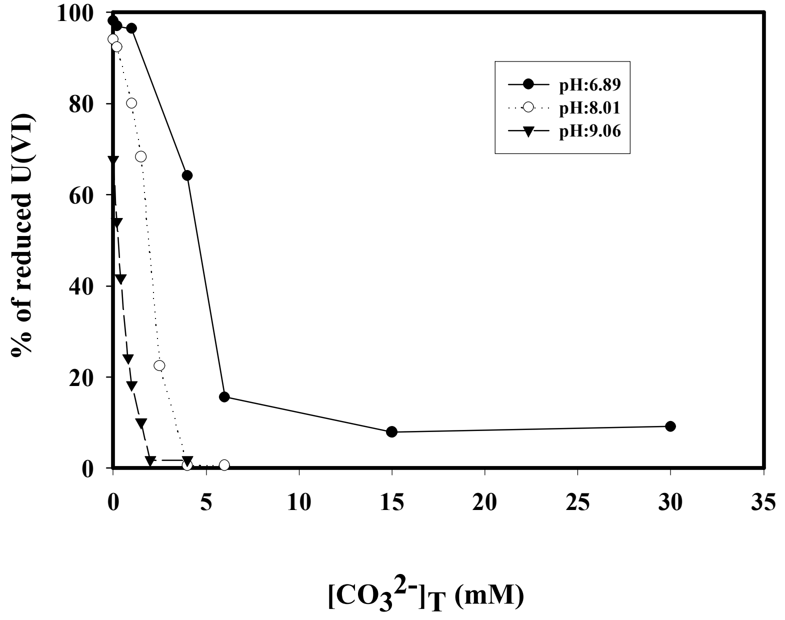


$$-\frac{d[U(VI)]}{dt} = (k_1[UO_2^{2+}] + k_2[UO_2OH^+] + k_3[(UO_2)_2(OH)_2^{2+}]^2 + k_4[(UO_2)_3(OH)_5^{2+}]^3$$

$$+ k_5[UO_2CO_3] + k_6[UO_2(CO_3)_2^{2-}] + k_7[UO_2(CO_3)_3^{4-}])[H_2S]_{total}$$

Effects of [CO$_3^{2-}$]$_T$ on Σ[U(VI)-hydroxyl species]$_0$

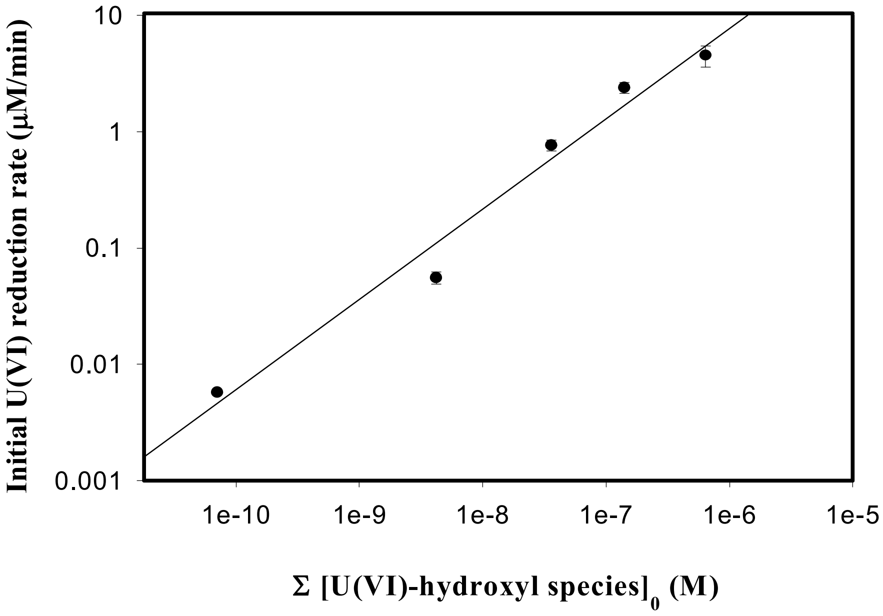


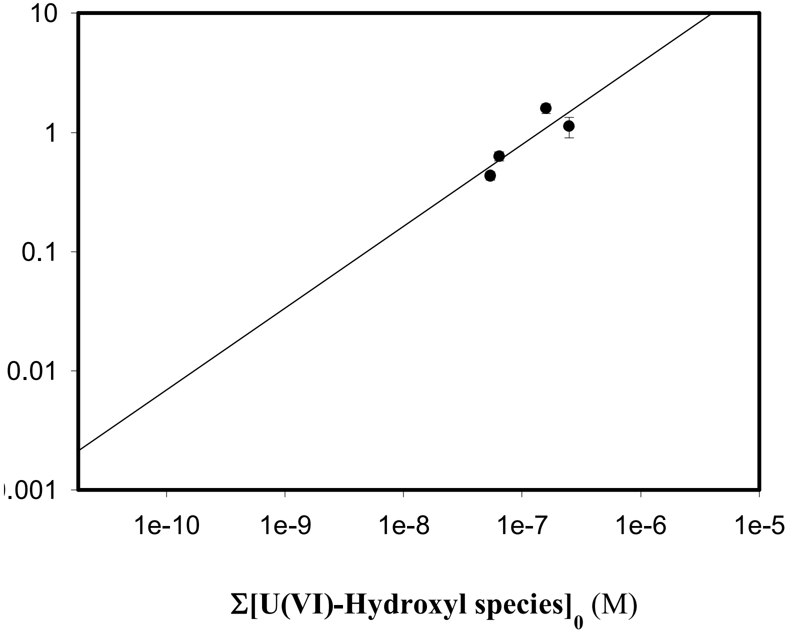


$$-\frac{d[U(VI)]}{dt} = (k_1[UO_2^{2+}] + k_2[UO_2OH^{+}] + k_2[(UO_2)_2(OH)_2^{2+}]^2$$

$$+ k_3[(UO_2)_3(OH)_5^{2+}]^3)[H_2S]_{total}$$

Measured initial rate is directly proportional to the calculated Σ[U(VI)-hydroxyl species]$_0$





U(VI) Reduction on FeS - A Two-step Process

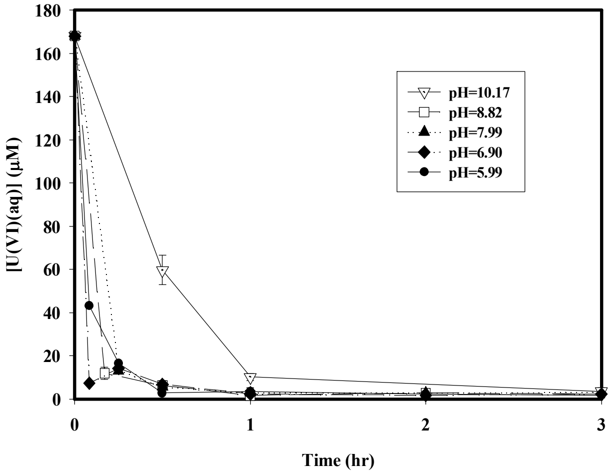


FIG 1. Rapidly U(VI) uptake by iron sulfide ([U(VI)]$_0$ = 168.0 μM; [FeS] = 0.18 g/L

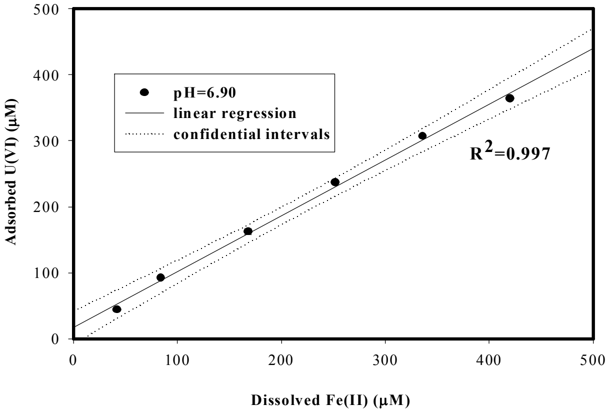


FIG. 2 Release of Fe(II) is proportional to the amount of U(VI) uptake (pH 6.90. ([U(VI)]$_0$ = 168.0 μM)

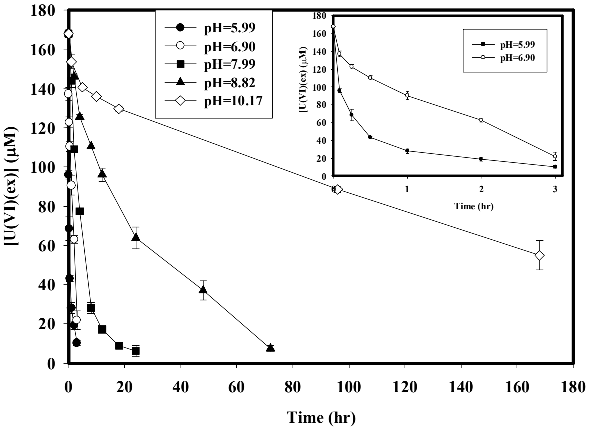


FIG. 3. Reduction of [U(VI)] on the FeS surfaces measured by carbonate extraction of U(VI).

Technetium Sulfide Chemistry

- **Investigation the pertechnetate-sulfide chemistry in aqueous solution**
  - **Controlled pH, O_2, ionic strength**
  - **Product determination**
  - **Tc immobilization (precipitation/colloid formation)**
  - **Reaction kinetics and stoichiometry determination**

Pertechnetate-sulfide chemistry in aqueous media

In acidic solution:

$$2\ TcO_4^- + 7\ H_2S + 2\ H^+ \longrightarrow Tc_2S_7 + 8\ H_2O \qquad \text{(Equation 1)}$$

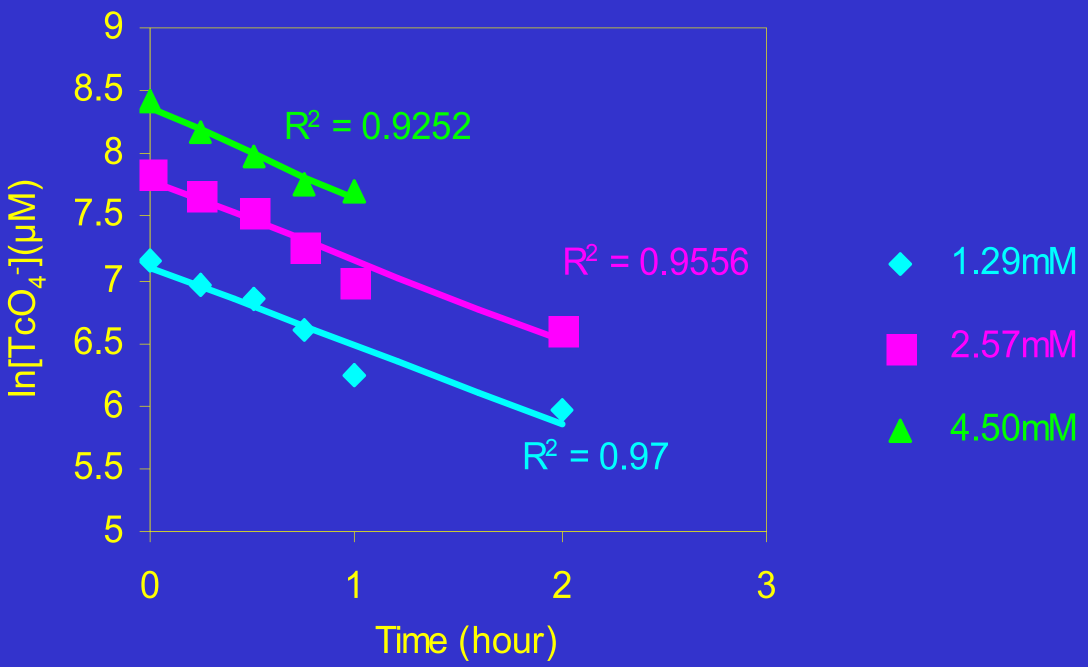
In basic solution:

$$TcO_4^- + S^{2-} \longrightarrow Tc(S)O_3^-/TcS_4^- \qquad \text{(Equation 2)}$$

$$2\ TcO_4^- + 7\ HS^- + H_2O \longrightarrow Tc_2S_7 + 9\ OH^- \qquad \text{(Equation 3)}$$

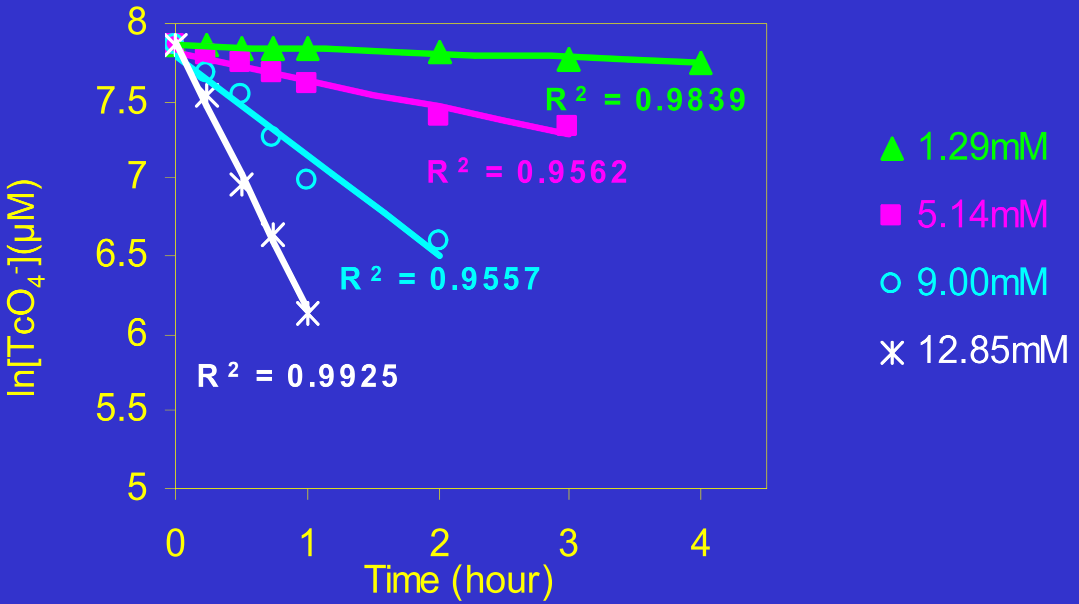
$$2\ TcO_4^- + 7\ S^{2-} + 8\ H_2O \longrightarrow Tc_2S_7 + 16\ OH^- \qquad \text{(Equation 4)}$$

Kinetics studies under pH 9 anaerobic conditions



With respect

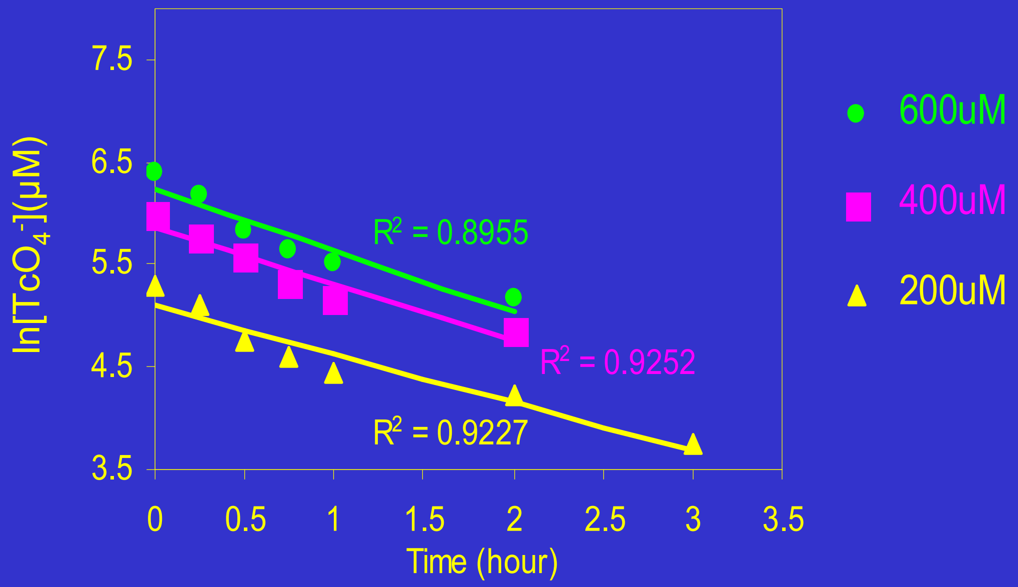
to [TcO$_4^-$]



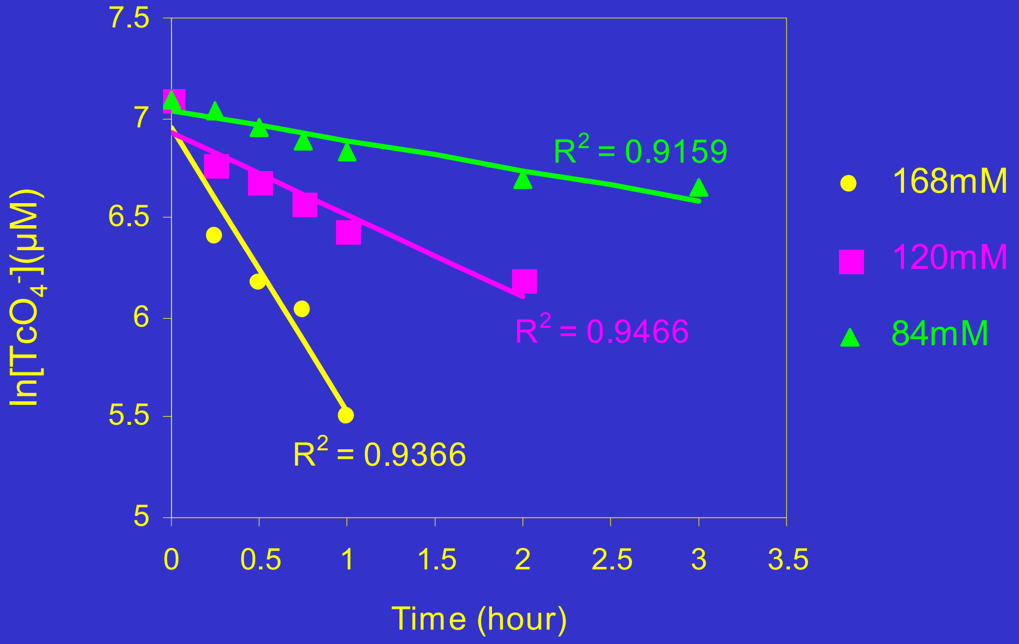
With regard

to sulfide

Kinetics studies under pH 4 aerobic conditions



With respect to $[TcO_4^-]$



With regard to sulfide

Sample characterization

- XANES & EXAFS
- Elemental analysis

Sample	S (%)	Tc (%)	Mole ratio of S/Tc	Suggested formula
Product from pH 4 aerobic solution	45.585	39.95	3.53	Tc_2S_7
Product from pH 9 anaerobic solution	45.88	40.5	3.54	Tc_2S_7

$\boxed{TcO_4^- + 3e^- + 4H^+ \quad = TcO_2\,(s) + 2H_2O}$???

SUMMARY

- Reductive Cr(VI) immobilization could be achieved by ISGR treatment. Reoxidation of Cr(III) is possible by biogenic Mn-oxides. A thorough evaluation under a wide variety of environmental conditions is needed.

- Reductive immobilization of U(VI) takes place by H_2S under anoxic environments, and the rate depends on pH and $[CO_3^{2-}]_{total}$. It is Σ [U(VI)-hydroxyl complex], not total [U(VI)], that determines the rate of U(VI) reduction at various pH and $[CO_3^{2-}]_{total}$. Reduction rates could be predicted through speciation calculation. U(VI) reduction on FeS surfaces takes place through a two-step process.

- Tc(VII) could be immobilized by H_2S treatment, with Tc_2S_7 being the product. Research is under way to understand the reaction mechanism.

Thank you!

QUESTIONS?