Reductive Immobilization of Toxic Metals and Radionuclides by Hydrogen Sulfide

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Reductive Immobilization

\[ \text{HCrO}_4^- + 3e^- + 4\text{H}^+ = \text{Cr(OH)}_3(\text{s}) + \text{H}_2\text{O} \]
\[ \text{UO}_2^{2+} + 2e^- = \text{UO}_2(\text{s}) \]
\[ \text{TcO}_4^- + 3e^- + 4\text{H}^+ = \text{TcO}_2(\text{s}) + 2\text{H}_2\text{O} \]

**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$_2$S

- >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**

**Reaction Stoichiometry:**

\[2\text{CrO}_4^{2-} + 3\text{HS}^- + 7\text{H}^+ = 2\text{Cr(OH)}_3(s) + 3\text{S(s)} + 2\text{H}_2\text{O}\]

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

<table>
<thead>
<tr>
<th>Temp. (°C)</th>
<th>([\text{S}^{\text{II-}}]_{t=0}) (µM)</th>
<th>([\text{Cr}^{\text{VI}}]_{t=0}) (µM)</th>
<th>(\text{S}^{\text{II-}}) oxidized v.s. (\text{Cr}^{\text{VI}}) reduced</th>
<th>(R^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>15</td>
<td>100</td>
<td>40</td>
<td>(Y = 1.49 x - 0.28)</td>
<td>0.9625</td>
</tr>
<tr>
<td>15</td>
<td>100</td>
<td>200</td>
<td>(Y = 1.60 x + 0.38)</td>
<td>0.9968</td>
</tr>
<tr>
<td>25</td>
<td>100</td>
<td>200</td>
<td>(Y = 1.54 x + 0.72)</td>
<td>0.9972</td>
</tr>
<tr>
<td>25</td>
<td>100</td>
<td>40</td>
<td>(Y = 1.53 x + 2.74)</td>
<td>0.9894</td>
</tr>
<tr>
<td>25</td>
<td>200</td>
<td>40</td>
<td>(Y = 1.44 x + 0.42)</td>
<td>0.9769</td>
</tr>
</tbody>
</table>

**NOT as previously reported**

\((8\text{CrO}_4^{2-} + 3\text{H}_2\text{S} + 10\text{H}^+ + 4\text{H}_2\text{O} \rightarrow 8\text{Cr(OH)}_3(s) + 3\text{SO}_4^{2-})\)
Kinetics of Chromate Reduction by Sulfide in Anoxic Systems
(pH=7.80, 25ºC, [S^{II-}]_0 = 800 µM)
Kinetics Determined by the Initial Rate Method

Reaction order with respect to [Cr\textsuperscript{VI}] = 0.94

Reaction order with respect to [H\textsubscript{2}S\textsubscript{0}] = 1.1

Reaction rate increases as pH is decreased
Proposed Reaction Mechanism

Step 1. Precursor Formation

\[ \text{CrO}_4^{2-} + \text{H}_2\text{S} \xrightleftharpoons[k_1]{k_{-1}} \{\text{HS}\cdots(\text{CrO}_3)\cdots\text{OH}\}^{2-} \]

Step 2. Electron Transfer

\[ \{\text{HS}\cdots(\text{CrO}_3)\cdots\text{OH}\}^{2-} \xrightarrow[k_2]{\text{S}_0 + \text{CrIVO}_3^{2-} + \text{H}_2\text{O}} \]

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

\[ \text{CrIV} + \text{CrVI} \xrightleftharpoons[k_2]{k_4} 2\text{CrV} \]

\[ 2\text{CrIV} \xrightleftharpoons[k_5]{\text{CrIII} + \text{CrV}} \]

\[ \text{CrV} + \text{S}^{II-} \xrightleftharpoons[k_5]{\text{2CrIII} + \text{S}^0} \]

The following derived kinetic equation explains all experimental observations

\[
\frac{d[\text{Cr(VI)}]}{dt} = \frac{-k_1 k_2 [\text{CrO}_4^{2-}] [\text{H}_2\text{S}]_T}{k_{-1} + k_2} \left\{ \frac{[\text{H}^+]^2}{[\text{H}^+] K_1 + K_1 K_2} \right\}
\]
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, [H₂S]=800mM)

Elemental sulfur nanoparticles catalyze Cr(VI) reduction by sulfide

Cr(III) Reoxidation and Remobilization

Possible Mechanisms

I Direct Chemical Oxidation
e.g., Cr(III) + O₂ + 3H⁺

II Oxidation via Direct Microbial Metabolism
Cr(III) + microorganisms + O₂

III Oxidation via Co-metabolism
Cr(III)

T. ferrooxidans
T. thiooxidans
FeS₂, FeS

P. putida
Mn²⁺

IV Mobilization via Interactions with Microbial Metabolites

<table>
<thead>
<tr>
<th>Species</th>
<th>Reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe³⁺, SO₄²⁻</td>
<td>Cr(OH)₃(s) + Fe³⁺ / SO₄²⁻</td>
</tr>
<tr>
<td>Mn³⁺, Mn⁴⁺</td>
<td>Cr(OH)₃(s) + MnO₂ / MnOOH</td>
</tr>
<tr>
<td>H⁺</td>
<td>Cr(OH)₃(s) + H⁺ → CrOH²⁺ₐq</td>
</tr>
</tbody>
</table>

Increased solubility
Coupled Biotic/Abiotic Processes for Cr(III) Oxidation

- *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

- A: 0.10 mM Mn(II)
- B: 0.00 mM Mn(II)
- C: 0.10 mM Mn(II), sterile
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
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???

- U(VI) could coexist with high concentration of sulfide (400 mM) 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 (CO₂-free) was precipitated by 800 mg/L H₂S 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.

\[
\begin{align*}
\text{UO}_2\text{(CO}_3\text{)}_2^{2-} & \quad \leftrightarrow \quad \text{CO}_3^{2-} \\
\text{UO}_2 + \text{S} & \quad \leftrightarrow \quad \text{H}_2\text{S} \\
\text{H}_2\text{S} & \quad \leftrightarrow \quad \text{OH}^- \text{ (pH)} \\
\text{UO}_2\text{OH}^+ & \quad \leftrightarrow \quad ?
\end{align*}
\]
Molar ratio of $[\text{U(VI)}]_{\text{reduced}}$ to $[\text{S}^{2-}]_{\text{oxidized}}$ (pH = 6.89; $[\text{CO}_3^{2-}]_T = 4.0$ mM)

Slope = 0.94

**Reaction Stoichiometry**

$\text{UO}_2^{2+} + \text{H}_2\text{S} = \text{UO}_2 + \text{S}^0 + 2\text{H}^+$

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HRTEM Micrograph

Electron Diffraction Pattern
Effects of $[\text{CO}_3^{2-}]_T$ on $\left[ \frac{\text{U(VI)}\text{reduced}}{\text{U(VI)}_0} \right]$ (%) ($[\text{S}^2^-]_0 = 2.0 \text{ mM}; [\text{U(VI)}]_0 = 168 \text{ mM};$ reaction time = 60 min)

Effects of pH on U(VI) reduction ($[\text{CO}_3^{2-}]_T = 4.0 \text{ mM}; [\text{S}^2^-]_0 = 2.0 \text{ mM}$)
Impact of carbonate on U(VI) speciation and reduction (calculated with MINEQL+, 1998)

\[
- \frac{d[U(\text{VI})]}{dt} = (k_1[UO_2^{2+}] + k_2[UO_2OH^+] + k_3[(UO_2)_2(OH)^{2+}]^2 + k_4[(UO_2)_3(OH)^{2+}]^3 + k_5[UO_2CO_3] + k_6[UO_2(CO_3)^{2-}] + k_7[UO_2(CO_3)^{4-}])[H_2S]_{\text{total}}
\]
Effects of $[\text{CO}_3^{2-}]_T$ on $\Sigma[\text{U(VI)}$-hydroxyl species]$_0$

\[- \frac{d[U\text{(VI)}]}{dt} = (k_1[U\text{O}_2^{2+}] + k_2[U\text{O}_2\text{OH}^+] + k_2[(U\text{O}_2)_2(\text{OH})^{2+}])^2 \\
+ k_3[(U\text{O}_2)_3(\text{OH})^{2+}]^3[H_2\text{S}]_{\text{total}}\]
Measured initial rate is directly proportional to the calculated $\Sigma [\text{U(VI)-hydroxyl species}]_0$.
**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:

\[ 2 \text{TcO}_4^- + 7 \text{H}_2\text{S} + 2 \text{H}^+ \rightarrow \text{Tc}_2\text{S}_7 + 8 \text{H}_2\text{O} \quad \text{(Equation 1)} \]

In basic solution:

\[ \text{TcO}_4^- + \text{S}^2^- \rightarrow \text{Tc(S)O}_3^-/\text{TcS}_4^- \quad \text{(Equation 2)} \]

\[ 2 \text{TcO}_4^- + 7 \text{HS}^- + \text{H}_2\text{O} \rightarrow \text{Tc}_2\text{S}_7 + 9 \text{OH}^- \quad \text{(Equation 3)} \]

\[ 2 \text{TcO}_4^- + 7 \text{S}^2^- + 8 \text{H}_2\text{O} \rightarrow \text{Tc}_2\text{S}_7 + 16 \text{OH}^- \quad \text{(Equation 4)} \]
Kinetics studies under **pH 9 anaerobic conditions**

With respect to $[\text{TcO}_4^-]$:

- $R^2 = 0.9252$
- $R^2 = 0.9556$
- $R^2 = 0.97$

With regard to sulfide:

- $R^2 = 0.9839$
- $R^2 = 0.9562$
- $R^2 = 0.9557$
- $R^2 = 0.9925$
Kinetics studies under pH 4 aerobic conditions

With respect to $[\text{TcO}_4^-]$

With regard to sulfide
Sample characterization

- XANES & EXAFS
- Elemental analysis

<table>
<thead>
<tr>
<th>Sample</th>
<th>S (%)</th>
<th>Tc (%)</th>
<th>Mole ratio of S/Tc</th>
<th>Suggested formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>Product from pH 4 aerobic solution</td>
<td>45.585</td>
<td>39.95</td>
<td>3.53</td>
<td>Tc_2S_7</td>
</tr>
<tr>
<td>Product from pH 9 anaerobic solution</td>
<td>45.88</td>
<td>40.5</td>
<td>3.54</td>
<td>Tc_2S_7</td>
</tr>
</tbody>
</table>

\[
\text{TcO}_4^- + 3e^- + 4\text{H}^+ = \text{TcO}_2 (s) + 2\text{H}_2\text{O} \quad \text{???}
\]
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$_2$S under anoxic environments, and the rate depends on pH and [CO$_3^{2-}$]$_{total}$. It is $\Sigma$[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$_2$S treatment, with Tc$_2$S$_7$ being the product. Research is under way to understand the reaction mechanism.
Thank you!

QUESTIONS?