Products of Chromate Bioremediation in Alluvial Sediments from Thun, Switzerland

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Chromium Contamination

- Hexavalent chromium, Cr(VI), linked to cancer, and kidney and liver damage
- Estimated to impact the quality of life of 13 – 17 million people worldwide (US HHS, 2008)
- **Biores Remediation** – stimulating indigenous aquifer microbes to reduce and thus immobilize chromium
Reductive immobilization of heavy metals

**DIRECT REDUCTION PATHWAY**

- **Cr(VI)**: Soluble, mobile
- **Cr(III)**: Insoluble, immobilized

- Reduced organics
- Oxidized organics

Electrons
Reductive immobilization of heavy metals

Reduced organics ➔ Microbes ➔ Oxidized organics

Fe(III) ➔ Fe(II)

Cr(VI) Soluble, mobile

Cr(III) Insoluble, immobilized

INDIRECT REDUCTION PATHWAY

What are these products under varying aquifer (geo)chemistry?
Field Site

- *Thun, Canton Bern*
  - Oxic aquifer
  - Former chromium plating facility
  - Extensive current remediation effort by two Swiss remediation firms
  - Reactive zero-valent iron pillars have not succeeded in immobilizing all of the Cr(VI) in groundwater – looking for a novel solution to immobilize the contamination
Typical wellbore geologic material
Site aerial view
The problem – chromium contamination
Site temperature gradient in winter
Cross-section through source region
Thun groundwater chemistry analysis

<table>
<thead>
<tr>
<th>Component</th>
<th>Concentration (µM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na</td>
<td>102</td>
</tr>
<tr>
<td>Ca</td>
<td>1140</td>
</tr>
<tr>
<td>Mg</td>
<td>203</td>
</tr>
<tr>
<td>K</td>
<td>27</td>
</tr>
<tr>
<td>NO₃</td>
<td>25</td>
</tr>
<tr>
<td>SO₄</td>
<td>343</td>
</tr>
<tr>
<td>Cl</td>
<td>42</td>
</tr>
<tr>
<td>Si</td>
<td>12</td>
</tr>
<tr>
<td>HCO₃</td>
<td>2040</td>
</tr>
<tr>
<td>pH</td>
<td>7.8</td>
</tr>
</tbody>
</table>

*Potential electron acceptors for bioremediation*

Oxygen – very high (near saturation)  
Nitrate – very low  
Iron – in the solid phase (sediments)  
Sulfate – low, but significant
## Thun sediment analysis

**Complete digestion (HF) results**

<table>
<thead>
<tr>
<th>Element (unit)</th>
<th>Amount</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al ( ppm)</td>
<td>9108.28</td>
</tr>
<tr>
<td>Ca (%)</td>
<td>27.37</td>
</tr>
<tr>
<td>Cr (%)</td>
<td>0</td>
</tr>
<tr>
<td>Fe (%)</td>
<td>0.71</td>
</tr>
<tr>
<td>K ( ppm)</td>
<td>4509</td>
</tr>
<tr>
<td>Mg ( ppm)</td>
<td>3573</td>
</tr>
<tr>
<td>Mn ( ppm)</td>
<td>346</td>
</tr>
<tr>
<td>Si (%)</td>
<td>9.46</td>
</tr>
</tbody>
</table>

**XRD analysis**

- Mainly comprised of SiO$_2$ and CaCO$_3$
- Secondary phases include NaAlSi$_3$O$_8$ (albite) and Al$_4$(OH)$_4$Si$_4$O$_{10}$ (kaolinite)
Experimental setup

14°C laboratory
Three types of column experiments

Electron Donors Tested:
- Acetate
- Lactate
- Molasses
Cr(VI) added from the beginning ($t_0$)
Cr(VI) added during Fe reduction

![Graph showing the relationship between Fe(II) and Cr(VI) over time.](image)

- **Fe(II) (μM)** on the y-axis
- **Cr(VI) (μM)** on the x-axis
- **Time (d)** on the x-axis

Legend:
- **Fe 1**
- **Fe 2**
- **Cr 1**
- **Cr 2**
Cr(VI) added during sulfate reduction

The graph shows the relationship between time (d) and the concentrations of Fe(II) and Cr(VI). The x-axis represents the time in days, ranging from 0 to 300. The y-axis on the left shows the concentration of Fe(II) in uM, ranging from 0 to 450. The y-axis on the right shows the concentration of Cr(VI) in uM, ranging from 0 to 140.

The data points are color-coded as follows:
- Fe 1 (squares)
- Fe 2 (circles)
- Cr 1 (squares)
- Cr 2 (circles)
Sediment chemistry results in 3 column types

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Condition</th>
<th>Total Run Time (days)</th>
<th>Day Cr(VI) added</th>
<th>Fe sediment concentration at end of expt. (ppm)</th>
<th>Cr sediment concentration at end of expt. (ppm)</th>
<th>Estimated % Cr removed</th>
</tr>
</thead>
<tbody>
<tr>
<td>t₀</td>
<td>Full AGW-Cr(VI) added from beginning</td>
<td>213</td>
<td>0</td>
<td>3,406</td>
<td>75</td>
<td>26</td>
</tr>
<tr>
<td>Fe</td>
<td>No sulfate in AGW-Cr(VI) added when Fe(II) detected</td>
<td>221</td>
<td>88</td>
<td>3,604</td>
<td>350</td>
<td>39-88</td>
</tr>
<tr>
<td>SO₄</td>
<td>Full AGW-Cr(VI) added when S(-II) detected</td>
<td>247</td>
<td>143</td>
<td>7,687</td>
<td>317</td>
<td>86-96</td>
</tr>
<tr>
<td>TBS</td>
<td>Thun background sediment</td>
<td>NA</td>
<td>NA</td>
<td>7,106</td>
<td>18</td>
<td>NA</td>
</tr>
</tbody>
</table>

Experimental parameters for laboratory columns. Bioavailable Fe in TBS is 4,949 ppm. NA means not applicable. Fe and Cr content in TBS represents initial values prior to any amendment.
X-ray maps

Blue = Ca
Red = Fe
Green = Cr

Sulfate reducing conditions
Cr and Fe speciation

Fe XANES

A

Cr(VI) standard
Cr(III) standard
Sulfate column
Ferrihydrite
Fe(II)-chloride

Fe column

Energy (eV)

7080 7100 7120 7140 7160 7180 7200

Cr XANES

B

Fe column

Sulfate column
Cr(VI) standard
Cr(III) standard

Energy (eV)

5970 5990 6010 6030 6050 6070
Sulfate reduction - electron microscopy

Up to 11.2% Cr (EDS)

y = 2.263x + 0.3589
R² = 0.95735

y = 0.9805x + 0.1244
R² = 0.8617
Microbial community analysis

OTUs taxonomic affiliation

- Actinobacteria
- Alphaproteobacteria
- Bacteroidetes
- Betaproteobacteria
- Firmicutes
- Gammaproteobacteria
- Unassigned
- Verrucomicrobia

OTU proportion (%)

- 0
- 20
- 40
- 60

Samples

- TBS
- t-zero
- Fe no Cr
- Fe with Cr
- SO4 no Cr
- SO4 with Cr

Microbial taxonomic affiliation

- Opitutus – OTU14
- Lysobacter – OTU101
- Pseudomonas – OTU11
- Paenibacillus – OTU2
- Clostridium – OTU35
- Paenibacillus – OTU3
- Pelosinus – OTU12
- Thermancola – OTU9
- Pelosinus – OTU15
- Paenibacillus – OTU5
- Lutispora – OTU22
- Paenibacillus – OTU8
- Paenibacillus – OTU10
- Paenibacillus – OTU19
- Comamonadaceae – OTU1
- Comamonadaceae – OTU7
- Oxalobacteraceae – OTU96
- Massilia – OTU60
- Massilia – OTU21
- Comamonadaceae – OTU87
- Paenibacillus – OTU83
- Rhizobacter – OTU89
- Sphingobacteriales – OTU4
- Pedobacter – OTU6
- Sphingobacteriales – OTU31
- Chitinophagaceae – OTU17
- Arcticibacter – OTU23
- Sediminibacterium – OTU53
- Flavobacterium – OTU32
- Phreatobacter – OTU104
- Mesorhizobium – OTU82
- Micrococcaceae – OTU100
- Unassigned OTUs
Conclusions and future plans

• Electron microscopy, X-ray microprobe, and XAS work indicate formation of Fe(III)/Cr(III) grain coatings during both iron and sulfate reduction

• Mixed, amorphous Fe(III)/Cr(III) precipitates seem to dominate immobilized Cr pool in all three conditions (t₀, Fe, and SO₄²⁻), suggesting that the indirect Cr reduction pathway dominates

• Ongoing field experiments will assess:
  • Solid speciation of in situ Cr products, and their remobilization potential
  • Actual field injection of molasses (to begin this Spring)
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