Improvement of a Cr(VI) Extraction Method for Chromite Ore Processing Residue (COPR)-Contaminated Materials

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Toxicity and carcinogenesis of chromium

\[
\text{Cr(VI)} (\text{HCrO}_4^-) \rightarrow \text{anion transporter} \\
\text{Reduction - Detoxification} \\
\text{Cr(VI)} \rightarrow \{
\text{Cr(V)} \\
\text{Reduction by Vitamin C}
\} \rightarrow \text{Cr(IV)} \\
\text{Cr(IV)} + \text{H}_2\text{O}_2 \rightarrow \text{DNA adducts} \\
\text{Cr(III)} \rightarrow \text{DNA adducts} \\
\text{Oxidative DNA breakage} \\
\text{Cr(III)} - \text{ligand}
\]

National Toxicology Program
Chromium Redox Cycle

Oxidation

Mn Oxides

Cr(III)

e.g. Cr(OH)$_3$, CrOH$^{2+}$

Cr(VI)

e.g. HCrO$_4^-$, CrO$_4^{2-}$

Reduction

- Fe$^{2+}$
- Organic Carbon
- Sulfides
Chromite Ore Processing Residue (COPR)

High Lime Process

Chromite ore, CaO, & Na₂CO₃ are heated at ~1100°C in a rotating kiln

\[ 4\text{FeCr}_2\text{O}_4 + 8\text{Na}_2\text{CO}_3 + 7\text{O}_2 \rightarrow 8\text{Na}_2\text{CrO}_4 + 2\text{Fe}_2\text{O}_3 + 8\text{CO}_2 \]

Water leach

China
Japan
UK

India
Pakistan
USA
New Jersey
Maryland

Burke et al. (1991) *Environmental Health Perspectives*
## Common Minerals in COPR

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Formula</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chromite</td>
<td>(Fe,Mg)Cr$_2$O$_4$</td>
<td>Major host of Cr(III)</td>
</tr>
<tr>
<td>Brownmillerite</td>
<td>Ca$_2$(Fe, Al)$<em>2$O$</em>{10}$</td>
<td>Can host Cr(III) [Cr(VI)?]</td>
</tr>
<tr>
<td>Periclase</td>
<td>MgO</td>
<td></td>
</tr>
<tr>
<td>Larnite</td>
<td>Ca$_2$SiO$_4$</td>
<td></td>
</tr>
<tr>
<td>Brucite</td>
<td>Mg(OH)$_2$</td>
<td></td>
</tr>
<tr>
<td>Calcite/Aragonite</td>
<td>CaCO$_3$</td>
<td></td>
</tr>
<tr>
<td>Calcium silicate hydrate</td>
<td>CaH$_2$SiO$_4$</td>
<td></td>
</tr>
<tr>
<td>Hydrogarnet</td>
<td>Ca$_3$Al$_2$((Si/H$_4$)O$_4$)$_3$</td>
<td>Can host Cr(VI)</td>
</tr>
<tr>
<td>Hydrocalumite</td>
<td>Ca$_4$Al$<em>2$(OH)$</em>{12}$(OH)$_2$ • 6H$_2$O</td>
<td>Can host Cr(VI)</td>
</tr>
<tr>
<td>Hydrotalcite</td>
<td>Mg$_6$Al$_2$(CO$<em>3$)(OH)$</em>{16}$ • 4H$_2$O</td>
<td>Can host Cr(VI)</td>
</tr>
<tr>
<td>Ettringite</td>
<td>Ca$_6$Al$<em>2$(OH)$</em>{12}$(SO$_4$)$_3$ • 26H$_2$O</td>
<td>Can host Cr(VI)</td>
</tr>
</tbody>
</table>

Geelhoed et al. (2002) *GCA*

Hillier et al. (2003) *STOTEN*

Mahlerbe et al. (2011) *ES&T*
Layered Double Hydroxides (anionic clays)

\[ [M^{2+}_{1-x}M^{3+}_x(OH)_2]^{b+} [A^{n-}_{b/n}] \cdot mH_2O \]

x usually between 0.2 and 0.33

Hydrotalcite
\[ Mg_6Al_2(OH)_{16}(CO_3) \cdot 4H_2O \]

Hydroxy Hydrocalumite
\[ Ca_4Al_2(OH)_{12}(OH)_2 \cdot 6H_2O \]

Sulfate Hydrocalumite (monosulfate)
\[ Ca_4Al_2(OH)_{12}SO_4 \cdot 6H_2O \]

Cr(VI) Hydrocalumite
\[ Ca_4Al_2(OH)_{12}CrO_4 \cdot 6H_2O \]

Kuang et al. (2010) *Materials*
Acidic Extraction is Not Possible

Bradl (2004) *Journal of Colloid and Interface Science*
EPA Method 3060A

Objective
To quantify total Cr(VI) in a solid matrix, three criteria must be satisfied:
• the extracting solution must solubilize all forms of Cr(VI)
• the conditions of the extraction must not induce reduction of native Cr(VI) to Cr(III)
• the method must not cause oxidation of native Cr(III) contained in the sample to Cr(VI)

Extraction Procedure
• 2.5 g field-moist sample
• 50 mL digestion solution (0.5 M NaOH; 0.28 M Na₂CO₃; pH=13.4) (20 liquid:solid ratio)
• Optional if isotope dilution is used to correct for oxidation/reduction
  • 4 mmoles MgCl₂ – precipitates as Mg(OH)₂ or MgCO₃
  • 0.5 mmoles K₃PO₄ – interferes with HPLC separation
• Stir samples at 90-95°C for 1 hour
• Filter (0.45 micron)
• Adjust pH to 7.5 with nitric acid
• Dilute to 100 mL

Analysis
• 7196A Visible Spectrophotometry of diphenyl carbazide complex
• 7199 Ion Chromatography with diphenyl carbazide detection
• 6800 Speciated Isotope Dilution Mass Spectrometry (SIDMS) – add ⁵³CrO₄²⁻ and ⁵⁴Cr(III) spikes

USGS
Initial Approach – Sample Grinding

• Mahlerbe et al. (2011, ES&T) indicated that increased grinding of NIST SRM 2701 did not change extraction efficiency

• Others found that intensive grinding did result in increased extraction efficiency and more Cr(VI) reduced by various remediation treatments\(^1,2\)

• We investigated the effect of several different grinding regimes

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1. Moon et al. (2008) *STOTEN*
Our Sample Preparation, Extraction, and Analysis

- Micronize several grams of sample
  - Dry (10 min)
  - Water (10 min)
  - Methanol (10, 20, & 40 min)
- 500 mg subsample
- 190 mL of 0.5 M NaOH & 0.28 M Na$_2$CO$_3$ (pH=13.4)
- Shake in heated water bath at 95°C for 2 hours
- Cool 1 hour on orbital shaker
- Filter (0.22 micron)
- Adjust to pH 7.5 with nitric acid
- Dilute to 250 mL
- 2 different analyses for Cr(VI)
  - Colorimetric (EPA 7196A)
  - HPLC – Dynamic Reaction Cell ICPMS
**NIST SRM 2701**

- Soil heavily contaminated with chromite ore processing residue (COPR)
- Collected from Liberty State Park, Jersey City, NJ
- Prepared by Steve Wilson (USGS), Ball mill ground
- Total Cr 4.26% (42,600 mg kg\(^{-1}\)), pH = 9.6

<table>
<thead>
<tr>
<th>Method</th>
<th>7196A(^1)</th>
<th>7199(^1)</th>
<th>6800(^1)</th>
<th>XANES(^2)</th>
<th>XANES(^3) preliminary</th>
</tr>
</thead>
<tbody>
<tr>
<td>Median Cr(VI) Concentration (mg kg(^{-1}))</td>
<td>365</td>
<td>390</td>
<td>551</td>
<td>3000-3400</td>
<td>1891-1973 3028-3339</td>
</tr>
<tr>
<td>Standard Deviation</td>
<td>74</td>
<td>72</td>
<td>16</td>
<td></td>
<td>2.3 (RSD) 4.8 (RSD)</td>
</tr>
</tbody>
</table>

Other studies show Method 3060A results in incomplete extraction of Cr(VI) from other COPR contaminated soils

- Ratio of Cr(VI) determined by XANES to 3060A = 1.5 to 3.9 (Dermatas et al., 2006, ES&T)
- XANES 7600 mg kg\(^{-1}\) and 3060A 4600 mg kg\(^{-1}\) (Wazne et al., 2007 J. Haz. Mat.)
- XANES 19,500 mg kg\(^{-1}\) and 3060 A 9,200 mg kg\(^{-1}\) (Yu et al., 2012 J. Haz. Mat.)

1. NIST Certificate revised 13 Sept 2013
2. Mahlerbe et al. 2011 ES&T
3. This study – performed at SLAC
Effect of Micronization on Particle Size – 2701

The graph illustrates the effect of micronization on particle size distribution. The x-axis represents the particle size in microns, while the y-axis shows the volume percent. Different processes are represented by distinct lines:

- **Unground**
- **Dry, 10 min**
- **MeOH, 10 min**
- **MeOH, 20 min**
- **MeOH, 40 min**
- **H2O, 10 min**

The graph shows how micronization affects the particle size distribution, with different methods altering the particle size distribution compared to the ungrounded state.
Extraction Results for NIST SRM 2701

Grind Time & Lubricant

<table>
<thead>
<tr>
<th>Grind Time &amp; Lubricant</th>
<th>Extraction</th>
<th>Extracted Cr(VI) (mg kg$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>None</td>
<td>2 Hour</td>
<td>13</td>
</tr>
<tr>
<td>10 Minute Dry</td>
<td>2 Hour</td>
<td>10</td>
</tr>
<tr>
<td>10 Minute Water</td>
<td>2 Hour</td>
<td>4</td>
</tr>
<tr>
<td></td>
<td>6 Hour</td>
<td>25</td>
</tr>
<tr>
<td>10 Minute Methanol</td>
<td>24 Hour</td>
<td>6</td>
</tr>
<tr>
<td></td>
<td>70 Hour</td>
<td>6</td>
</tr>
<tr>
<td>20 Minute Methanol</td>
<td>2 Hour</td>
<td>4</td>
</tr>
<tr>
<td>40 Minute Methanol</td>
<td>2 Hour</td>
<td>4</td>
</tr>
</tbody>
</table>

Certified value = 551 mg kg$^{-1}$

Max. extracted = 829 mg kg$^{-1}$
Extraction Results for 2B

<table>
<thead>
<tr>
<th>Grind Time &amp; Lubricant</th>
<th>Extraction</th>
<th>Extracted Cr(VI) (mg kg⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>None (&lt;2 mm)</td>
<td>2 Hour</td>
<td>4</td>
</tr>
<tr>
<td>Shatterboxed</td>
<td>2 Hour</td>
<td>4</td>
</tr>
<tr>
<td>10 Minute Water</td>
<td>2 Hour</td>
<td>4</td>
</tr>
<tr>
<td>10 Minute Methanol</td>
<td>2 Hour</td>
<td>4</td>
</tr>
</tbody>
</table>
2701 Mineralogy (XRD preliminary results)

<table>
<thead>
<tr>
<th>Grind Time &amp; Lubricant</th>
<th>Extraction</th>
<th>Quartz</th>
<th>Calcite</th>
<th>Layered Double Hydroxides</th>
<th>Brownmillerite</th>
</tr>
</thead>
<tbody>
<tr>
<td>None</td>
<td>None</td>
<td>[6]</td>
<td>[10]</td>
<td>[8]</td>
<td>[10]</td>
</tr>
<tr>
<td>2 Hour</td>
<td></td>
<td>[6]</td>
<td>[20]</td>
<td>[8]</td>
<td>[10]</td>
</tr>
<tr>
<td>10 Minute Methanol</td>
<td>None</td>
<td>[6]</td>
<td>[30]</td>
<td>[8]</td>
<td>[10]</td>
</tr>
<tr>
<td>2 Hour</td>
<td></td>
<td>[6]</td>
<td>[40]</td>
<td>[8]</td>
<td>[10]</td>
</tr>
</tbody>
</table>

Weight %
Direct Analysis - Chromium X-ray Absorption Near-Edge Spectra are sensitive to oxidation state

- Tetrahedral Cr(VI) has a diagnostic pre-edge feature
- Cr XANES line shape is related to molecular speciation
Extracted Cr(VI) versus Residual Cr(VI) by XANES

**Extracted Cr(VI) (mg kg\(^{-1}\))**

- 10 min MeOH - 2 hour
- 10 min MeOH - 6 hour
- 10 min MeOH - 24 hour
- 10 min MeOH - 70 hour
- 20 min MeOH - 2 hour
- 40 min MeOH - 2 hour
- 10 min H\(_2\)O - 2 hour
- 10 min dry - 2 hour
- Unground - 2 hour

**XANES Cr(VI) Peak Area (Solid Phase)**

- 0.09
- 0.10
- 0.11
- 0.12
- 0.13

**Unextracted Samples**

- Unground
- 10 min Dry
- 10 min MeOH
- 20 min MeOH
- 10 min H\(_2\)O

**Grind**

- 0.025
- 0.050
- 0.075
- 0.100
- 0.125
- 0.150
Alternative Techniques Employed

Direct determination of Cr(VI) in solids

Identification of Cr(VI) mineral residence

Synchrotron lightsource

Bulk XANES spectroscopy

μ-XANES Mapping

μ-XRF Mapping

Bulk Raman spectroscopy

μ-Raman

Laboratory instrument
Micro-X-ray Fluorescence Mapping – 2 Types of Info

Sample 2B (unground, unextracted)

Single-energy map (6009 eV)

Multiple-energy map

Normalized Absorbance

Energy (eV)
μ-Raman sensitive to Cr(VI)-rich grain in COPR

μ-XRF Map

μ-Raman

unknown

crocoite PbCrO₄

USGS
Conclusions

• Micronization of NIST 2701 results in more Cr(VI) extracted than ever before reported for the standard

• Still getting <30% of total Cr(VI) as determined by XANES as reported by Malherbe

• USGS XANES results for NIST 2701 vary depending on how constrained the peak fitting routines are used to perform quantitative analysis by XANES

• Substantial dissolution of layered double hydroxides does not appear to occur during extraction - principal mineralogical residence of Cr(VI) is maintained
Acknowledgements

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EPA

Stephen Long
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