

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

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Chromite Ore Processing Residue (COPR)



High Lime Process

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

$4FeCr_2O_4 + 8Na_2CO_3 + 7O_2 \longrightarrow 8Na_2CrO_4 + 2Fe_2O_3 + 8CO_2$



water leach

China Japan UK India Pakistan USA New Jersey

Maryland



Burke et al. (1991) Environmental Health Perspectives

Common Minerals in COPR

Chromite	(Fe,Mg)Cr ₂ O ₄	Major host of Cr(III)	
Brownmillerite	Ca ₂ (Fe, AI) ₂ O ₁₀	Can host Cr(III) [Cr(VI)?]	
Periclase	MgO		
Larnite	Ca ₂ SiO ₄		
Brucite	Mg(OH) ₂		
Calcite/Aragonite	CaCO ₃		
Calcium silicate hydrate	CaH ₂ SiO ₄		
Hydrogarnet	$Ca_3Al_2((Si/H_4)O_4)_3$	Can host Cr(VI)	
Hydrocalumite	$Ca_4AI_2(OH)_{12}(OH)_2 \cdot 6H_2O$	Can host Cr(VI)	
Hydrotalcite	$Mg_{6}Al_{2}(CO_{3})(OH)_{16} \cdot 4H_{2}O$	Can host Cr(VI)	
Ettringite	$Ca_{6}AI_{2}(OH)_{12}(SO_{4})_{3} \cdot 26H_{2}O$	Can host Cr(VI)	

Geelhoed et *al*. (2002) *GCA* Hillier et *al*. (2003) *STOTEN* Mahlerbe et *al*. (2011) *ES&T*



Layered Double Hydroxides (anionic clays)

 $[M^{2+}_{1-x}M^{3+}_{x}(OH)_{2}]^{b+}[A^{n-}_{b/n}] \bullet mH_{2}O$ 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) Ca₄Al₂ (OH)₁₂SO₄ • 6H₂O

 $\frac{\text{Cr(VI) Hydrocalumite}}{\text{Ca}_4\text{Al}_2(\text{OH})_{12}\text{CrO}_4 \cdot 6\text{H}_2\text{O}}$



Kuang et al. (2010) Materials

Acidic Extraction is Not Possible



USGS

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:

- Extracting solution must solubilize all forms of Cr(VI)
- Conditions of the extraction must not induce reduction of native Cr(VI) to Cr(III)
- 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 $MgCl_2$ precipitates as $Mg(OH)_2$ or $MgCO_3$
 - 0.5 mmoles K_3PO_4 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

<u>Analysis</u>

- 7196A Visible Spectrophotometry of diphenyl carbazide complex
- 7199 Ion Chromatography with diphenyl carbazide detection
- 6800 Speciated Isotope Dilution Mass Spectrometry (SIDMS) add ⁵³CrO₄ and ⁵⁴Cr(III) spikes



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

Method	7196A ¹	7199 ¹	6800 ¹	XANES
Median Cr(VI) Concentration (mg kg ⁻¹)	365	390	551	2300-2600 ³ 3000-3400 ²
Standard Deviation	74	72	16	

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.)

NIST Certificate revised 13 Sept 2013
Mahlerbe et al. 2011 ES&T
USGS and NIST data



Approaches

Particle Size

- Mahlerbe et al. (2011, ES&T) indicated that increased grinding of NIST SRM 2701 did not change extraction efficiency
- Others found that intensive grinding resulted in increased extraction efficiency and more Cr(VI) reduced by various remediation treatments^{1,2}
- We investigated the effect of several different grinding regimes

Liquid to Solid Ratio

- EPA3060A specifies 2.5 g field moist sample and 50 mL extraction solution
 - liquid to solid ratio = 20 mL g⁻¹
- Large sample amount may have advantages for detection limit and sample heterogeneity.
- Low liquid to solid ratio for COPR may prevent mineral dissolution or may affect exchange equilibrium

Extraction Time

- EPA 3060A specifies extraction time of at least 1 hour.
- Dissolution of mineral phases and exchange processes may be kinetically limited.
- We investigated a range of extraction times up to 72 hours.

Extraction Vessel

- We found that borosilicate glass is dissolved by the high pH extraction fluid which affects efficiency of Cr(VI) extraction from sample.
- We compared glass with Teflon extraction vessels
 - 1. Moon et al. (2008) STOTEN
 - 2. Jagupilla et al. (2009) J. Haz. Mat.



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 (liquid to solid ratio 380 mL g⁻¹)
- 190 mL of 0.5 M NaOH & 0.28 M Na₂CO₃ (pH=13.4)
- Shake in heated water bath at 90 °C for 2 hours (+15 min warm up)
- Cool 1 hour on orbital shaker
- Filter (0.22 micron) recover residual solid for analyses
- 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





Effect of Micronization on Particle Size – 2701





NIST 2701 Particle Size – Extraction Results



Glass extraction vessel

Effect of Micronization on Particle Size – 2B





2B Particle Size – Extraction Results



- Extraction time 2 hours
- Liquid to Solid ratio = 380
- Glass extraction vessel

Liquid:Solid Ratio & Teflon Versus Glass - Results





Extraction time 2 hours

Liquid:Solid Ratio & Teflon Versus Glass - Results



Elements from glass dissolution





Particle Size & Teflon Versus Glass - Results













Mineralogy (XRD preliminary results)



Weight %



Conclusions

Particle Size (micronizing)

- Change in NIST 2701 particle size distribution from ~0.5 to 500 microns to ~0.1 to 50 microns resulted in up to 65% increase in Cr(VI) extracted.
- Water and methanol lubricants resulted in similar particle size distributions, but less Cr(VI) was extracted from water ground samples. Cr(VI) likely lost during grinding with water.

Liquid to Solid Ratio

- We observed an approximately 50% increase in Cr(VI) extracted when a liquid to solid ratio of 900 mL g⁻¹ or greater was used versus a liquid solid ratio close to that prescribed by EPA 3060A.
- A range of 370 to 620 mg Cr(VI) kg⁻¹ was extracted (2 hour Teflon) from NIST 2701 unground over a liquid to solid ratio of 47 to 2800 mL g⁻¹.
- A range of 620 to 950 mg Cr(VI) kg⁻¹ was extracted (2 hour Teflon) from NIST 2701 10 min methanol grind over a liquid to solid ratio of 95 to 4500 mL g⁻¹
- Liquid to solid ratios >~900 mL g⁻¹ did not increase Cr(VI) extraction

Extraction Time

- 48 hour extraction time appeared to be optimal and resulted in:
 - 100% more Cr(VI) extracted from NIST 2701 unground than 1 hour extraction.
 - 50% more Cr(VI) extracted from NIST 2701 10 min MeOH grind than 1 hour extraction

Extraction Vessel

- Extractions performed in Teflon flasks typically yielded 20-25% more Cr(VI) than extractions performed in glass flasks.
- Aluminum, boron, silicon, and iron were abundant in blank extracts performed in glass flasks indicating substantial dissolution of the glass.



Spectroscopic Studies - Two Goals

Direct determination of Cr(VI) in solids

Bulk XANES spectroscopy



Bulk Raman spectroscopy



Synchrotron lightsource



Raman Spectrometer



Identification of Cr(VI) mineral residence

 μ -XANES, μ -XRF



μ-Raman spectroscopy

Cr(VI) has a single, intense pre-edge XANES feature that allows detection at low concentration



Empirical approach needed to fit XANES spectrum of complex mixtures like SRM 2701

norm. absorption [a.u.]

- Position, intensity, and even width of Cr3+ and Cr6+ peaks change with speciation*
- Analysis of pre-edge peaks based on theory (number and position of known peaks for each species would overdetermine the system
 - Fit non-convergence
 - Highly-correlated fit parameters
- Empirical rather than theoretical approach needed (5 peaks + background function)
- Peak parameters need constraints to obtain realistic and consistent fits

*Farges (2009); Dubrail and Farges (2009)



photon energy [keV]



Only partial agreement between solid phase and aqueous phase Cr(VI) post-extraction



XANES and solution chemistry results *in glass* are NOT consistent with continuous dissolution of Cr(VI) from solid

Newer extractions in Teflon do show continuous increase Cr(VI) up to 48 hrs

New XANES data (just collected) may support this



Future Directions

- Continue validation work on EPA Method 3060A changes
 - Including isotope dilution studies to evaluate possible oxidation of Cr(III) during extractions
 - Publish suggested method changes
 - Work with Kim Kirkland's group at EPA to initiate round robin study on proposed Method 3060A changes
- Finalize calculations on collected XANES data consulting with Julien Malherbe and NIST for data comparisons with 2011 study
- Synthesize model compounds for microRaman and collect reference spectra
- Evaluate detection levels possible with microRaman
- Investigate reports of WDXRF to determine Cr(VI)



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