Chromium Chemistry with Focus on Measurement in Slag Material

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Agenda

- Overview of Chromium Chemistry
- Prior Studies of Cr(VI) Measurement
- Current Cr(VI) in Slag Study
  - Research Objectives
  - Scope
- X-Ray Adsorption Near Edge Structure (XANES) Study
- Questions

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Chromium

- Chromium was named after the Greek word "chroma" meaning “color because of the many colorful compounds derived from it.
- Chromium was first isolated in 1797.
- Atomic Number 24 on Periodic Table.
- One of Earth’s most abundant elements and transition metals.
- Many uses throughout history and today.

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Chromium Chemistry

- Highly Variable Properties
  - The form of chromium, trivalent [Cr(III)], or hexavalent [Cr(VI)], control its properties.
- Cr(III) *vs* Cr(VI) - significantly different
  - Physical and Chemical Properties
  - Human and Ecological Toxicity
  - Environmental Fate and Transport

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Chromium Properties

- Cr(VI) is a Human Inhalation Carcinogen.
- Cr(VI) not really an issue by ingestion.
  - Effectively Reduced to Cr(III) following Ingestion at Low Levels by Stomach Acids.
  - After massive inadvertent ingestion orange juice is an effective reductant.
- Cr(III) is Considered an Essential Element and Dietary Supplement .
- Most Forms of Cr(VI) are Soluble & Mobile.
- Most Forms of Cr(III) are Insoluble & Immobile.
- Inter-valence Conversions – Predictable.

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Chromium Chemistry

- Environmental Media Transformation
- Cr(VI) ←→Cr(III) possible in both directions
  - Reduction to Cr(III) in reducing conditions, presence of ferrous iron, sulfur, and oxidizable organic matter. Generally irreversible under static environmental conditions.
  - Oxidation of Cr(III) to Cr(VI) is limited in the environment, requires oxygen (slow) or Mn(VI) (low pH increases rate).
  - Both Redox conditions (ORP) and pH impact transformation, pH generally more important since reduction is dominant.

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Chromium Chemistry in Slag Materials

- Chromium varies with slag type and facility. Formation of slag entails reducing conditions that greatly favor a stable form of Cr(III).

	Mean (mg/kg)			Minimum (mg/kg)			Maximum (mg/kg)		
Slag Type	BF	BOF	EAF	BF	BOF	EAF	BF	BOF	EAF
Cr (Total)	132	1271	3046	10	440	320	740	2000	6200
Cr(VI)	ND	ND	1.3	ND	ND	1.0	ND	ND	9.1

Proctor, et al., *Env. Sci Tech* 2000, 34, 1576-1582 using USEPA Methods 3050B/6010 and 3060A/7197

- Others have reported up to 3.4% (34,000 mg/kg) total chromium in slag.

BF, blast furnace; BOF, basic oxygen furnace; EAF, electric arc furnace

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Chromium Chemistry in Slag Materials

- Primary mineral forms as Cr_2O_3, iron and magnesium chromite = Cr(III).
- Chromium associated with spinel mineral family [including ($MgAl_2O_4$)], wüstite
  - (FeO = iron(II) oxide).
- Wüstite, and spinel forms are considered resistant to significant chromium aqueous leaching.
- Spinel is reported to provide stability to chromium as Cr(III) and potentially inhibits the oxidation of chromium to Cr(VI).

Kaja, A. M. *Effects of carbonation on the retention of heavy metals in chemically activated BOF slag* pastes. Cement and Concrete Research, 2021.

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Conventional Chromium Measurement

- Environmental media (US EPA Methods)
  - Total *vs* Speciation [Cr(III) vs Cr(VI)]
  - Total – acid digestion followed by spectroscopy (ICP, ICP-MS)
    - Acid digestion for environmentally available elements (US EPA Method 3050).
    - ICP and ICP-MS via US EPA 6010 and 6020. As a total analysis this cannot be used to differentiate chromium forms. Both US EPA methods employed at different times.
  - Cr(VI) measurement requires removing only that form, keeping it in that form, and then selective measurement.
    - Not trivial, reduction to Cr(III) is favored under at low pH conditions needed for analysis.
    - US EPA Method 3060 developed, high pH digestion steps to minimize oxidation or reduction while selectively extracting Cr(VI) from solid matrices.
    - US EPA Methods 7196, 7199, and rarely used, 6800 for analytical finish.

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Specialized Chromium Measurement

- X-ray adsorption near edge structure (XANES)
  - *In-situ* measurement, no extraction or significant sample handling.
  - Slag requires cutting to form thin sections.
  - Requires a synchrotron light source (~70 total world-wide)
- XANES ability
  - Local electronic structure of atom via adsorption of photon. The structures are used to identify and quantify Cr(III) *vs.* Cr(VI)
  - Microprobe allows the pointing at fine structures after bulk spectroscopy identifies the areas of interest

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Examples of Cr Speciation using XANES for Speciation

- Reduced Chromite Ore Processing Residues (rCOPR) Liu et al., 2020.
  - Treat COPR materials to reduce Cr(VI) to Cr(III).
- Can Mn(II) oxidize Cr(III) to Cr(VI) in natural systems? Fandeur et al., 2009
  - Ultramafic Rocks
- Cr(VI) Extraction using US EPA Method 3060A for Soils. Malherbe et al., 2011.
- Modifications of US EPA Method 3060A. Mills et al., 2017.

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A Comprehensive Study of the Chromium - Objectives

- Evaluate conventional total and Cr(VI) test methods for applicability to slag materials.
- Quantify the soluble, exchangeable, and environmentally available levels of Cr(VI) in slag.
  - ASTM D3987, Phosphate Buffer, US EPA 3060A.
- Evaluate sample preparation impact and potential for bias of Cr(VI) measurement.
  - Coarse versus fine grain sample preparation.
- Evaluate potential for chemical matrix interferences with Cr(VI) measurement in slag.
  - Matrix spiking.
- Edw. C. Levy commissioned to perform the study.
  - Environmental Standards consulting chemists were retained to support the effort.

Planned Study Chromium in Slag Materials (2022)

- Elemental, mineralogical, Cr(VI) conventional and XANES characterization of 11 slag materials.

Material Type	Mill Type	Raw Materials Used	Sample Type
ACBF	None Provided	Integrated Mill	Stockpile
BOF	None Provided	Integrated Mill	Stockpile
EAF LMF	Sheet Mill and Beam Mill	Scrap and DRI	Stockpile
EAF LMF	Bar Mill	Scrap and DRI	Stockpile
EAF LMF	Hot Rolled Bands	Scrap	Stockpile
EAF LMF	Flat Roll	Scrap and Hot Liquid Iron	Stockpile
EAF-C	Sheet Mill and Beam Mill	Scrap and DRI	Production
EAF-C	Hot Rolled Bands	Scrap	Stockpile
EAF-C	Flat Roll	Scrap and Hot Liquid Iron	Stockpile
LMF	Hot Rolled Bands	Scrap	Stockpile
LMF	Flat Roll	Scrap and Hot Liquid Iron	Stockpile

Conventions Test Parameters (2022)

Test Parameter/Method	Bulk Size and Matrix
Total Moisture (AASHTO T255), pH (USEPA Method 9045D), Alkalinity (Titration to pH 4.0), Loss on Ignition (ASTM C25), XRF (ASTM E1031-96) Lithium Tetraborate Fusion, XRD Quantitative Analysis (Rietveld Method)	ASTM minus 60 mesh
Total Available Elements (USEPA 3050B/6020B)	ASTM minus 60 mesh
Hexavalent Chromium Speciation after 3 Digestion/Leaching Procedures [USEPA 3060A, ASTM D3987 – 12, Phosphate Buffer (B. R. James 1983)] Includes pH and ORP measurements	ASTM minus 60 mesh AND course (1/2” x 0) size (mimics use and exposure)
Total Available Elements (USEPA 3050B/6020B)	Digestion of Leachate Solutions

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Cr(VI) - Digestion/Leachate Operational Definitions

- ASTM D3987 – Deionized Reagent Water, 18 hours leach at 21°C.
  - "Soluble Fraction."
- Phosphate Buffer Extraction (James et al., 1983).
  - "Exchangeable Fraction."
- USEPA Method 3060A – Alkaline Digestion.
  - "Soluble, adsorbed, and precipitated forms."
  - High pH and addition of carbonate (0.28 M) are designed to aid in the dissolution of otherwise insoluble chromate salts.
- Analytical finish by USEPA Method 7199.

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Leaching Quality Control Measures

- Numerous replicates and soluble and insoluble forms of Cr(VI) matrix spikes.
- Leachates from phosphate and ASTM methods were analyzed for metals/metalloid suite including V, Tl, Se.
  - USEPA Method 3060A digestate is not amenable to normal acid digestion and metals analysis.
- Standard Reference Materials were also included in the quality control regimen.

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Overall Leaching Design (2022)

Study Design Parameters	Number per Parameter	Other
Number of Solid Sample Types	11	With replicates of individual sample types
Number of Particle Sizes (each as separate batch to the laboratory)	2	Fine ground and course, using 25-g sample size or 70-g (ASTM)
Number of Leaching Procedures for each sample type at each particle size	3	Method USEPA 3060A, ASTM D3987, Phosphate Buffer
Soluble and Insoluble Cr(VI) Matrix Spiking in addition to routine batch quality control	Varies with sample type/leachate	Soluble Cr(VI) spiked with all three leaching procedures. Insoluble Cr(VI) only applicable for method 3060A, with two different concentrations planned

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Leaching Study Sample Numbers (2022)

Slag Type	ACBF	BOF	EAF LMF	EAF C	LMF
Number of Distinct Sources	1	1	4	3	2
Replicates and Spikes	1	4	12	11	2
Total with 3 Leaching Procedures	6	11	40	34	9

- 100 individual aliquots underwent analysis for Cr(VI) in two particle size batches [minus 60 mesh and course (1/2” X 0)].
- The study had a focus on the EAF type slags, therefore numerous replicates and matrix spikes.

X-ray Adsorption Near Edge Structure (XANES)

- Synchrotron-based X-ray fluorescence mapping and micro- X-ray spectroscopy of thin section (30 µm).

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XANES Characterization and Summary of Conventional Data

- Bulk samples from 3 slag sources were tested at Brookhaven National Synchrotron.
- Bulk scans of thin sections of sample, with individual microprobe analysis was performed.

Conventional Data from 2019:

Slag Type	Total Cr (3050A/6010) mg/kg	Cr (VI) USEPA 3060A/7199 mg/kg
EAF LMF (1175)	4500	13.8
EAF C (1209)	2900	3.3
BOF	2900	33.5

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XANES Data and Interpretation

- Well, it's complicated:
  - Compare intensity at different energy points to identify chromium species.
  - Intensity also associated with concentration that is calculated against reference standards that are run separately under the same instrument conditions.

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XANES Data and Interpretation (cont.)

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XANES Data and Interpretation

- Standards as low as 0.04% Cr(VI) used to measure individual spots that spanned the range of apparent Cr(total) intensities. At least 18 points were examined on each sample.

Slag Type	Total Cr (3050A/6010) mg/kg (2019)	Cr (VI) USEPA 3060A/7199 mg/kg (2019)	XANES Cr(VI) (2022)*
EAF LMF (1175)	4500	13.8	ND (<2 mg/kg)
EAF C (1209)	2900	3.3	ND (<2 mg/kg)
BOF	2900	33.5	ND (<2 mg/kg)

XANES Cr(VI) data suggests that the conventional Cr(VI) analysis is biased high/generates false positives and may be the result of method-induced oxidation of Cr(III).

*Nominal detection limit, analysis in draft.

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Current Study Status

- XANES characterization is complete for Cr(VI), but the data will also be reviewed to evaluate minerology and other elemental (Mg, Fe, Se, V, Tl) correlations.
  - Study data is being compiled and investigators are preparing manuscript(s) for publication.
- Conventional measurement study in progress with the focus on Cr(VI) but includes measurement of total Se, V, Tl in bulk samples and leachates.
  - Levels of total Cr and Cr(VI) in ASTM and phosphate leachates, Cr(VI) in USEPA 3060A digestate/leach across 11 slag sources including multiple EAF types. Includes sample slag that underwent XANES testing.

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Thank You
QUESTIONS?

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