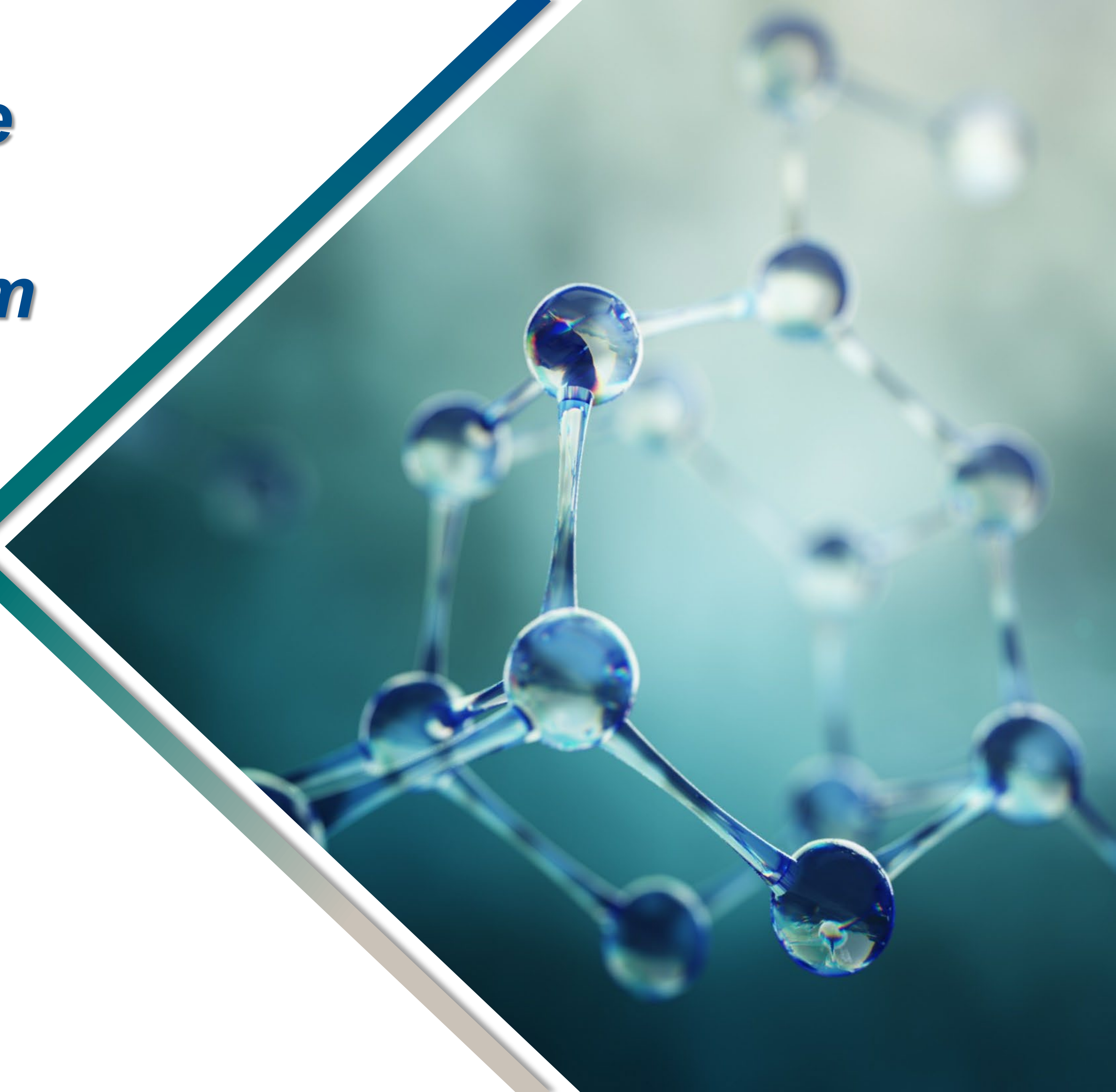
Testing Data from the Measurement of Hexavalent Chromium in Representative Steel Slags



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September 20, 2023

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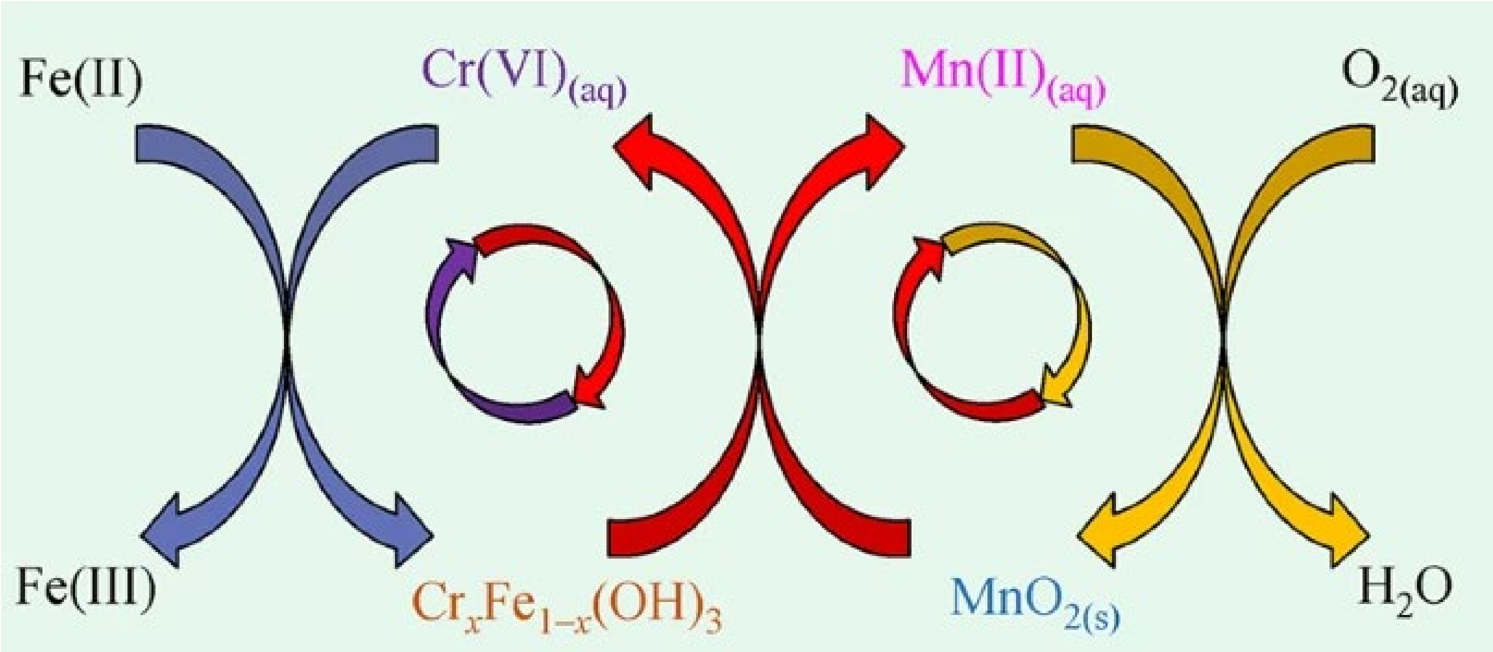
Agenda

- Chemistry 101 First - Total Chromium Exists in Two Forms
  - Hexavalent Cr [Cr(VI)] – considered harmful over time by inhalation
  - Trivalent Cr [Cr(III)] – considered an essential nutrient
  - Cr(VI) can be reduced to Cr(III) with reductant material (ferrous iron) - Fe(II)
  - Cr(III) can be oxidized to Cr(IV) with oxidizing material (manganese O_2) – MnO_2
- Slag Uses and Components
- Study Objectives
  - Is there Cr(VI) in Iron and Steel Slag?
  - Do conventional leaching methods represent accurate and true measurements given the amounts of *iron and manganese* in slag?
- Study Design & Results
  - Three conventional leaching methods, then Cr(VI) analysis of the leachates
  - Unconventional analysis - XANES
- Questions

Chromium Reaction – Redox Chemistry

- Cr(VI) can be reduced to Cr(III) with reducing material (ferrous iron) - Fe(II)
- Cr(III) can be oxidized to Cr(IV) with oxidizing material (manganese O_2) – MnO_2



Now --- back to the Agenda

Figure source: [Interplay of transport processes and interfacial chemistry affecting chromium reduction and reoxidation with iron and manganese | SpringerLink]

Slag Uses & Components

- Aggregate Material
  - Residential ground cover – Unconfined use
  - Road construction applications – Confined use
  - Added to concrete - Used as an ingredient
- Major Components
  - Iron and manganese (others, but…)
  - Just mix slag with various leaching liquids
    - Soluble Fe and Mn can react with and can then reduce or oxidize Cr
    - When Fe and/or Mn dissolve in solution it can change the pH and ORP
      - ***Positive ORP is OXIDIZING - Negative ORP is REDUCING***

Component	Iron & Steel Slags
Ca	20-52%
Si	10-30%
Fe	**10-40%**
Mn	**5-8%**
Mg	5-10%
Al	1-20%
Cr	<1% - 3.4%

References: (Yildirim 2011) (Menad 2021), (Sano 2004).
https://www.astm.org/d8021-20.htm

Slag Test Samples

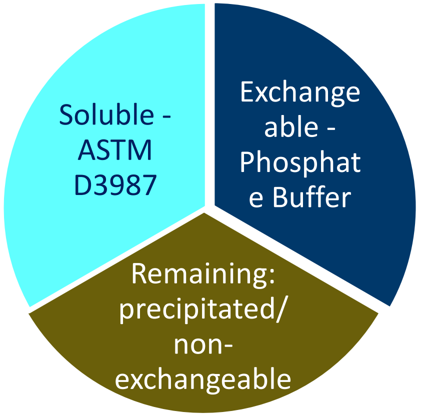
11 Source Materials with focus on EAF type

- Two Particle Sizes – Fine and Coarse
  - Fine ground to ASTM 60 Mesh (0.25 mm)
  - The coarse aggregate (everything that falls through ½ inch sieve)

Material Type	Raw Materials and Mill Type	Total Cr (mg/kg)
ACBF	Integrated Mill	28
BOF	Integrated Mill	3000
EAF LMF	Sheet Mill and Beam Mill, Scrap and DRI	3100
EAF LMF	Bar Mill, Scrap and DRI	5000
EAF LMF	Hot Rolled Bands, Scrap	2900
EAF LMF	Flat Roll, Scrap and Hot Liquid Iron	3000
EAF-C	Sheet Mill and Beam Mill, Scrap and DRI	3400
EAF-C	Hot Rolled Bands, Scrap	3800
EAF-C	Flat Roll, Scrap and Hot Liquid Iron	3000
LMF	Hot Rolled Bands, Scrap	200
LMF	Flat Roll, Scrap and Hot Liquid Iron	210

Conventional (Leaching Then) Cr(VI) Analysis

- Leaching Types – Soluble Cr(VI), Exchangeable Cr(VI) and Total Cr(VI)
  - ASTM D3987-12 – **Soluble** Cr(VI)
    - Deionized water agitated for 18 hours at 21°C, 0.45-µm filter
  - Phosphate Buffer – **Exchangeable** Cr(VI)
    - Phosphate buffer solution prepared at pH 7.0
  - US EPA Method 3060A – **Total** Cr(VI)
    - Environmentally relevant, US EPA method for Cr(VI) in solid samples
    - The solution pH (> 11.5) designed (*in theory*, for environmental media) to prevent both reduction [Cr(VI) to Cr(III)] and oxidation [Cr(III) to Cr(IV)]



Experimental Design

Quality Control Samples –

Replicates - show us how reproducible the leaching/analysis is

Matrix Spikes - show if we add 2 ppm of Cr(VI), what percentage do we get back?

We do soluble matrix spikes (easy) and insoluble matrix spikes (harder)

Certified Reference Materials (CRMs) – show us if we are close we are to a certified value

Soluble (ASTM)

Exchangeable (Phosphate Buffer)

Total (3060A)

Slag Type	Number of Material Types	Number of Replicates within a Type	Number of Soluble Cr(VI) Spikes included (all three procedures)	Number of Insoluble Cr(VI) Spikes (3060A only)	Number of Analyses with three leaching procedures
ACBF	1	1	0	0	6
BOF	1	1	1	2	11
EAF LMF	4	6	2	4	40
EAF-C	3	5	2	4	34
LMF	2	1	0	0	9
				Total	100
				Total at two particle sizes	**200**

Ground via ring and puck mill

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ORP and pH – Prepared in Deionized Water Slurries

Material Type	pH - FINE	pH – COARSE	ORP FINE (REDUCING)	ORP COARSE (OXIDIZING)
ACBF	11.5	10.8	-93	+120
BOF	12.2	12.2	-22	+160
EAF LMF	12.2	12.2	-112	+140
EAF LMF	11.9	11.7	-12	+180
EAF LMF	11.8	11.6	16	+190
EAF LMF	11.8	11.8	-28	+100
EAF-C	11.8	11.8	14	+210
EAF-C	11.5	11.3	-4	+280
EAF-C	11.6	11.4	0	+260
LMF	11.9	11.2	-92	+210
LMF	11.9	12.2	-52	+150

Unexpected Outcome – While the pH is similar, the ORP for Fine *vs.* Course is ***Substantially*** Different

So … the Fine can reduce Cr(VI) to Cr(III) and Course can oxidize Cr(III) to Cr(IV) - **except EAF-C**

ASTM D3987 – Soluble Cr(VI)

Material Type	Fine (mg/kg) (Reducing)			Coarse (mg/kg) (Oxidizing)		
	Primary	Duplicate	Triplicate	Primary	Duplicate	Triplicate
ACBF	ND (0.1)	ND (0.1)		ND (0.1)	ND (0.1)	
BOF	ND (0.1)	**0.15**	**0.13**	**0.34**	**0.42**	**0.50**
EAF LMF	ND (0.1)	ND (0.1)		ND(0.1)		
EAF LMF	ND (0.1)	ND (0.1)	ND (0.1)	**2.2**	**2.2**	**2.0**
EAF LMF	ND (0.1)	ND (0.1)		ND (0.1)	ND (0.1)	
EAF LMF	ND (0.1)	ND (0.1)	ND (0.1)	ND (0.1)	ND (0.1)	ND (0.1)
EAF-C	ND (0.1)	ND (0.1)	0.13	ND (0.1)	ND (0.1)	ND (0.1)
EAF-C	ND (0.1)	ND (0.1)	ND (0.1)	**0.74**	**0.70**	**0.73**
EAF-C	ND (0.1)	**0.11**		**0.44**	**0.50**	
LMF	ND (0.1)	ND (0.1)		ND (0.1)	0.25	
LMF	ND (0.1)	ND (0.1)		ND (0.1)	ND (0.1)	

Phosphate Buffer – Exchangeable Cr(VI)

Material Type	Fine (mg/kg) (Reducing)			Coarse (mg/kg) (Oxidizing)		
	Primary	Duplicate	Triplicate	Primary	Duplicate	Triplicate
ACBF	ND (0.2)	ND (0.2)		ND (0.2)	ND (0.2)	
BOF	ND (0.2)	ND (0.2)	ND (0.2)	**1.5**	**1.7**	**1.7**
EAF LMF	ND (0.2)	ND (0.2)		ND (0.2)	ND (0.2)	
EAF LMF	ND (0.2)	ND (0.2)	ND (0.2)	ND (0.2)	ND (0.2)	ND (0.20)
EAF LMF	ND (0.2)	ND (0.2)		ND (0.2)	ND (0.2)	
EAF LMF	ND (0.2)	ND (0.2)	ND (0.2)	ND (0.2)	ND (0.2)	ND (0.2)
EAF-C	ND (0.2)	ND (0.2)	ND (0.2)	ND (0.2)	ND (0.2)	ND (0.2)
EAF-C	ND (0.2)	ND (0.2)	ND (0.2)	**0.21**	**0.22**	**0.29**
EAF-C	ND (0.2)	ND (0.2)		**0.16**	ND (0.20)	
LMF	ND (0.2)	ND (0.2)		ND (0.2)	ND (0.2)	
LMF	ND (0.2)	ND (0.2)		ND (0.2)	ND (0.2)	

US EPA 3060A – Total Cr(VI)

Material Type	Fine (mg/kg) (Reducing)			Coarse (mg/kg) (Oxidizing)		
	Primary	Duplicate	Triplicate	Primary	Duplicate	Triplicate
ACBF	ND (0.4)	ND		**0.46**	**0.44**	
BOF	**4.7**	**10.5**	**ND (0.4)**	**11**	**10.5**	**10.4**
EAF LMF	**0.33J**	**0.48**		**1.2**	**0.78**	
EAF LMF	ND (0.4)	ND	ND (0.4)	**12**	**11.2**	**10.3**
EAF LMF	ND (0.4)	ND		**2.9**	**3.35**	
EAF LMF	ND (0.4)	ND	ND (0.4)	**1.5**	**1.4**	**1.2**
EAF-C	ND (0.4)	ND	ND (0.4)	ND	ND	ND
EAF-C	ND (0.4)	ND	ND (0.4)	**3.2**	**3.13**	**1.87**
EAF-C	**3.0**	**1.47**		**3.6**	**3.7**	
LMF	ND (0.4)	ND		**1.8**	**1.87**	
LMF	ND (0.4)	ND		**1.1**	**1.0**	

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Cr(VI) Matrix Spike Recoveries – Influenced by ORP

	US EPA 3060A Fine (Reducing)		US EPA 3060A Coarse (Oxidizing)	
Material Type	**Soluble Cr(VI) spike (~40 mg/kg or as cited)**	**Insol. Cr(VI) Spike (~600 - 1000 mg/kg)**	**Soluble Cr(VI) spike (~40 mg/kg)**	**Insol. Cr(VI) Spike (~600 -1000 mg/kg)**
BOF	68%, 118%	92%	87%	86%
EAF LMF	**0%** (40, 201, 383 mg/kg)	20%	87%	96%
EAF LMF	**0%** (40, 207, 398, 641 mg/kg)	**0%** (641 mg/kg)	91%	99%
EAF-C	**0%** (40 mg/kg), 10% (196 mg/kg), 58% (398 mg/kg), 60% (870 mg/kg)	61% (870 mg/kg)	110%	113%
EAF-C	**0%** (40 mg/kg), 30% (180 mg/kg), 76% (390 mg/kg), 80% (659 mg/kg)	82% (859 mg/kg)	88%	92%

Dissolved Fe in Fine reducing the Cr(VI) matrix spikes. The positive ORP in Coarse allows Cr(VI) spike to exist & recovered

Substantial dissolved manganese (the highest) in BOF is countering the Fe in Fine allows Cr(VI) spike to exist & recovered

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Conventional Analysis – Data Summary

- All sample slurries produced alkaline conditions with deionized water, as expected.
- Fine slurries yielded reducing conditions: ~200-400mV less than coarse aggregate.
  - Likely due to the solubilized Fe reductants.
- Coarse slurries show oxidizing conditions likely due to solubilized Mn oxidants.
- Cr(VI) levels are primarily observed in the (oxidizing) Coarse, single digit up to 12 mg/kg.
- Cr(VI) levels in the Fine is ND or sub-ppm (0.2-0.4) mg/kg. BOF is an exception.
- Matrix spiking illustrates reducing nature [Cr(VI) to Cr(III)] of the Fine material

All of these reactions seem to take place when we mix slag material with various types of solutions. So what if we analyze for Cr(VI) directly on the solid slags <u>without</u> the need to use leach solutions?

X-Ray Absorption Near Edge Structure (XANES)

X-ray fluorescence microprobe
Brookhaven National Laboratory.

- A non-destructive (and unreactive) technique
- Three Slag Samples – 30-µm thin sections mounted on low-element quartz slides.
- The slag samples were selected based on previous conventional leaching studies from 3060A Total Cr(VI) analysis.

XANES *vs.* Conventional

XANES is considered much less susceptible to interference, misidentification.

Material Type and Sample ID	XANES Cr+6 (mg/kg)	Conventional 2023 Total Cr(VI) (Coarse) mg/kg	Total Chromium (mg/kg)
BOF 1244-01	< 1.2	11, 10, 10	3000
EAF LMF 1175-01	< 1.8	12, 11, 10	5000
EAF-C 1209-01	< 1.5	3.2, 3.1, 1.9	3800

Conclusions

- Is Cr(VI) present in iron and steel slag?
  - XANES (nondestructive and unreactive technique) indicates no Cr(VI) down to < 2 mg/kg.
  - Conventional (Method 3060A) identified levels 2-12 mg/kg in the Coarse slag.
- Does the conventional analysis bias results?
  - YES – Data strongly suggest sample-specific redox reactions are complex.
  - Mn and Fe forms are present at significant concentrations in slag.
  - Fe(II) can reduce Cr(VI) to Cr(III).
  - MnO_2 can oxidize Cr(III) to Cr(VI)

Thank You

QUESTIONS?

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