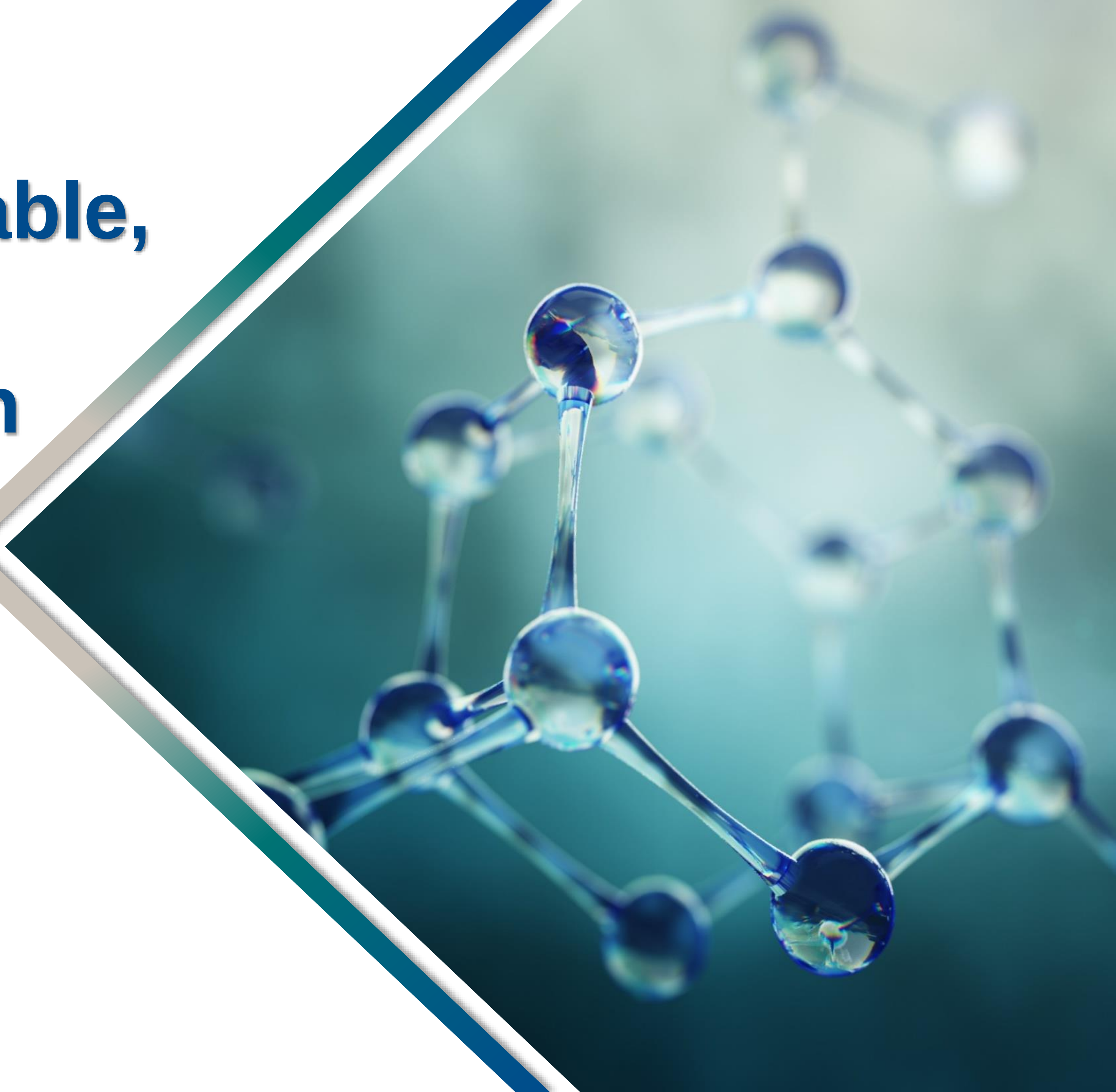
Cr(VI):

Soluble, Exchangeable, Total in Slag with XANES Comparison



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July 31, 2023

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Agenda

- Study Objectives
  - Is there Cr(VI) in Iron and Steel Slag ?
  - Do conventional methods provide accurate and unbiased measurements?
- Study Design & Results
  - Three leaching methods followed by conventional analysis (SW-846 7199)
  - Unconventional analysis - XANES
- Questions

Strategies
- Define the question, evaluate existing information, evaluate data quality, identify lines of evidence, identify data gaps and gather needed data

Type and Quantity of Data
- Tiers
  - Conventional with enhanced spikes and replicates
  - XANES

Data Analysis
- Comparison across conventional leaching techniques and with XANES results

Iron and Steel Slag

- Non-metallic co-product of manufacturing process
  - Limestone and dolomite added in furnace
- Slag type is function of furnace employed and cooling process
  - Basic Oxygen Converter Furnace (BOF)
  - Electric Arc Furnace (EAF), recycled steel
  - Blast Furnace (BF), including Air Cooled (ACBF)
  - Ladle Metallurgical Furnace (LMF)
- Annual world production of iron slag is ~350 million tons, with steel slag approximately 200 million tons (USGS).

Photos: https://www.epa.gov/smm/electric-arc-furnace-eaf-slag

Slag Uses & Components

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

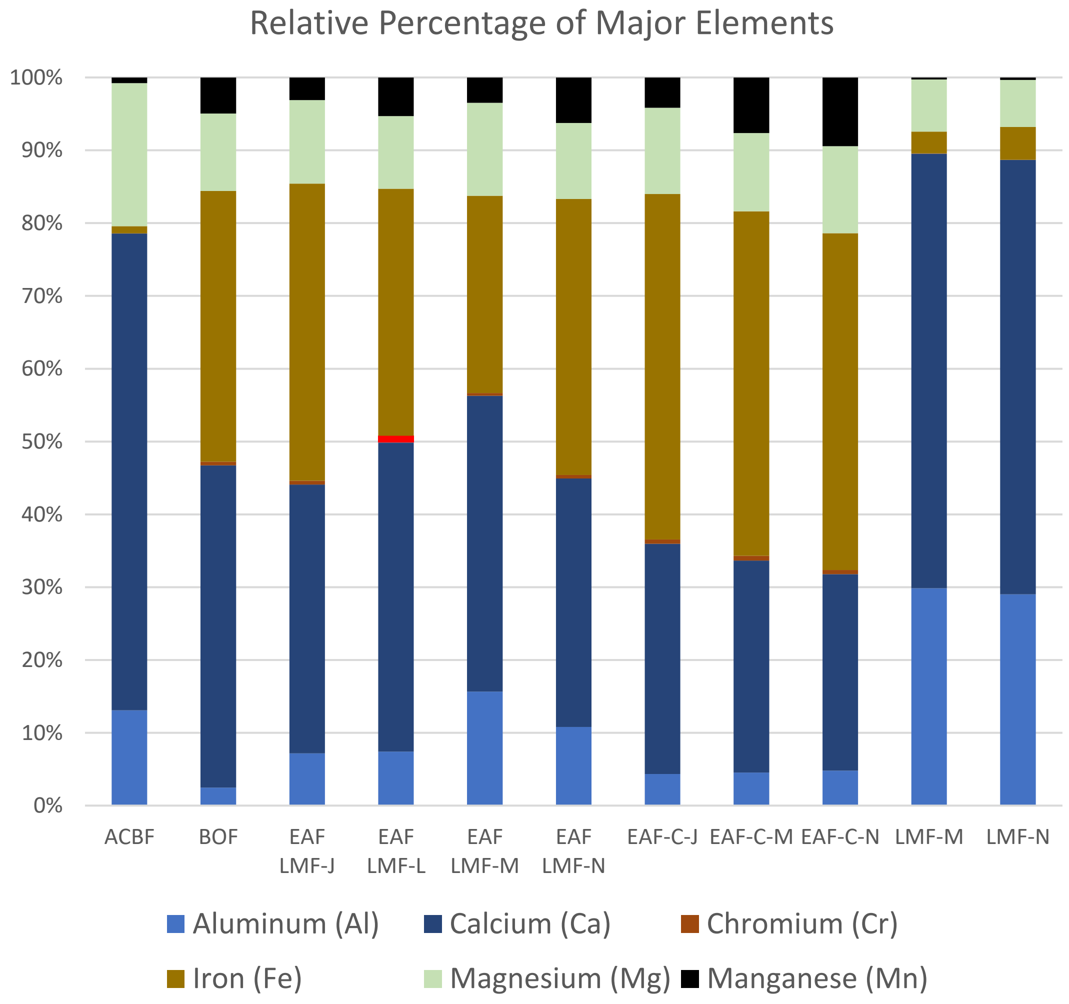
- Aggregate Material
  - Residential Ground Cover.
  - Road construction applications.
  - Added to Concrete.
- Major Component
  - Iron oxide may be a mix of FeO and Fe_2O_3 as a mixture of ferric and ferrous iron.
- Cr in steel slag associated with calcium silica minerals, as sparingly soluble Cr_2O_3, and as iron and magnesium chromite, all are forms of Cr(III).

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

Slag Test Samples

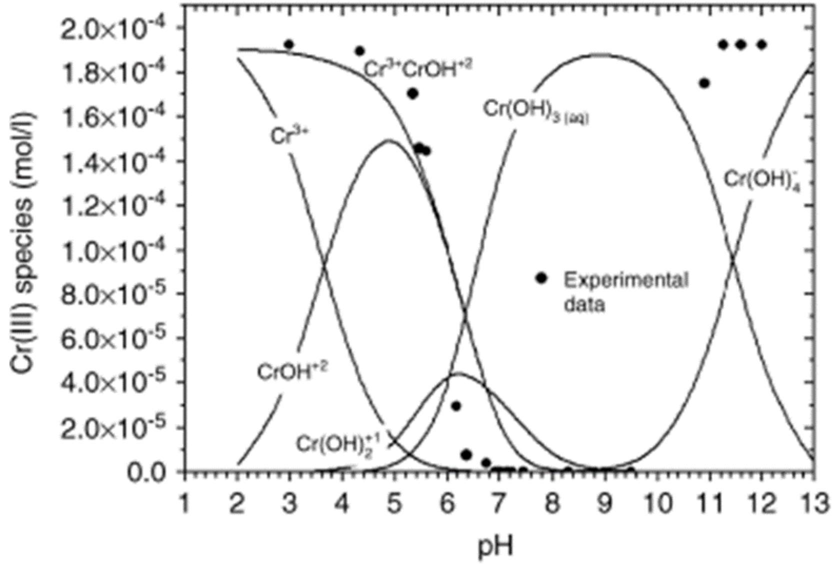
- 11 Source Materials with focus on EAF type.
- Also tested in 2019 study.

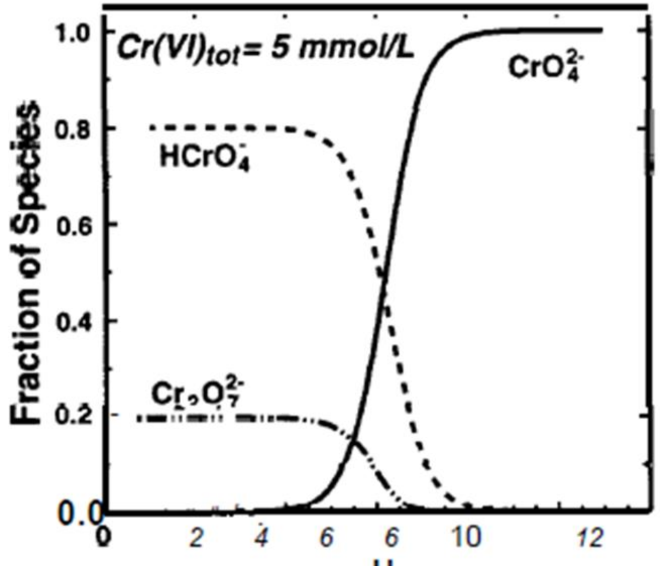
Material Type	Raw Materials and Mill Type	2019 Total Cr (mg/kg)
ACBF	Integrated Mill	21
BOF	Integrated Mill	2900
EAF LMF	Sheet Mill and Beam Mill, Scrap and DRI	2700
EAF LMF	Bar Mill, Scrap and DRI	4500
EAF LMF	Hot Rolled Bands, Scrap	1900
EAF LMF	Flat Roll, Scrap and Hot Liquid Iron	2500
EAF-C	Sheet Mill and Beam Mill, Scrap and DRI	3000
EAF-C	Hot Rolled Bands, Scrap	3700
EAF-C	Flat Roll, Scrap and Hot Liquid Iron	2900
LMF	Hot Rolled Bands, Scrap	150
LMF	Flat Roll, Scrap and Hot Liquid Iron	170



Geochemistry - Cr

- Cr(III) is strongly hydrolyzed in aqueous solutions and the predominant species in the pH range 6.5–10.5 is $Cr(OH)_3$.
- Most species of Cr(III) have a very low solubility and a strong tendency to adsorb to surfaces.
- Cr(VI) forms oxyanion compounds that also have an adsorption affinity for certain proton-specific mineral surfaces.



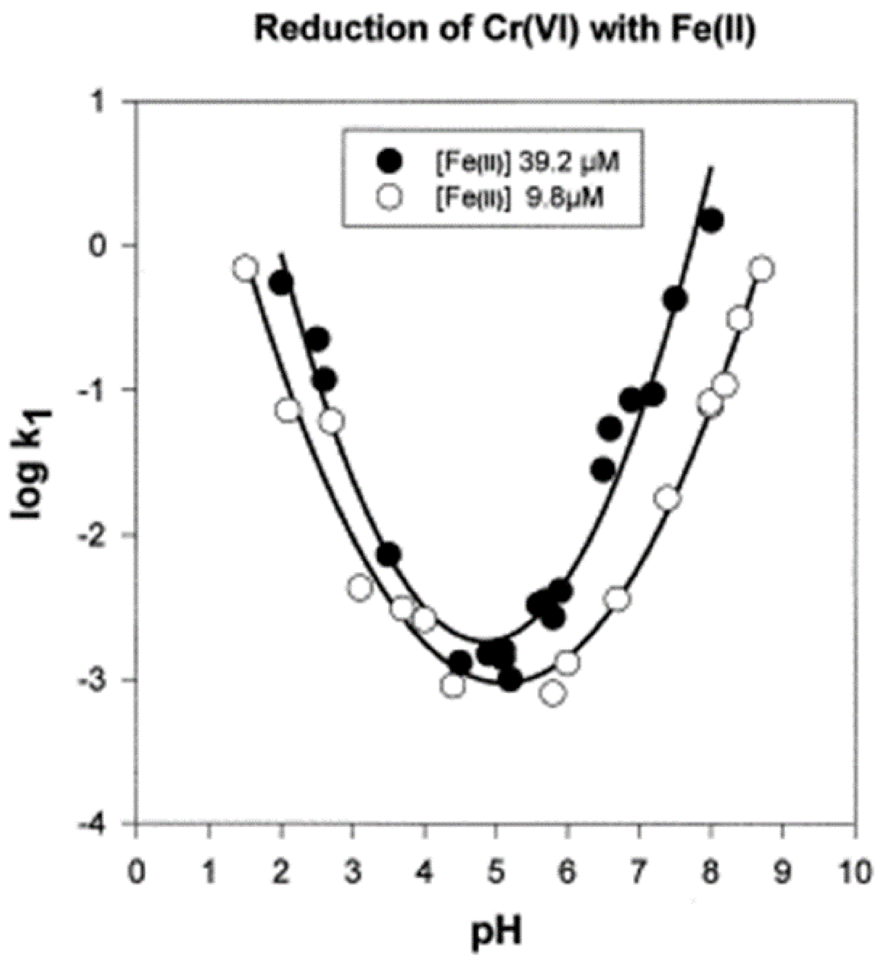


References: (Baes and Mesmer 1976, Murray et al 1983, Sass and Rai 1987)

Chromium Reaction - Fe

Iron:

- Reduction of Cr(VI) in solution in the presence of Fe(II) and (co-) precipitation of Cr(III) in the presence of Fe(III) noted by Palmer et al., (Palmer 1994).
- Wide use of Fe(II) for the precipitative reduction of Cr(VI).
- Reduction in solution is increased with increasing pH above 7, also shown with iron-clay surfaces ->Cr(III) OH.



Chromium Reaction - Mn

- As noted, Cr(III) limited solubility, but studies have shown oxidation of Cr(III) – Cr(VI) via MnO_2 reduction [Mn(IV) – Mn(II)]
  - Rate of reaction greatest at lower pH
  - Some indication oxygen enhances Cr(VI) oxidation when in combination with Mn

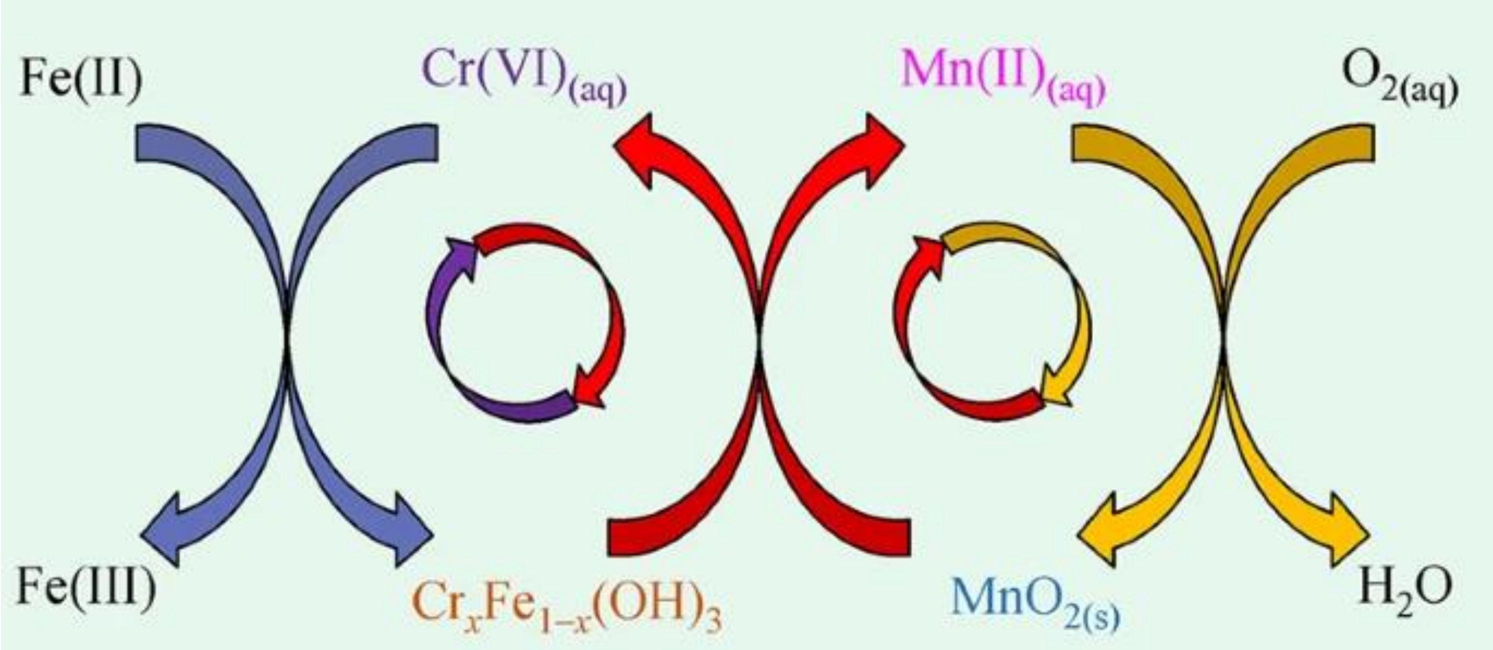
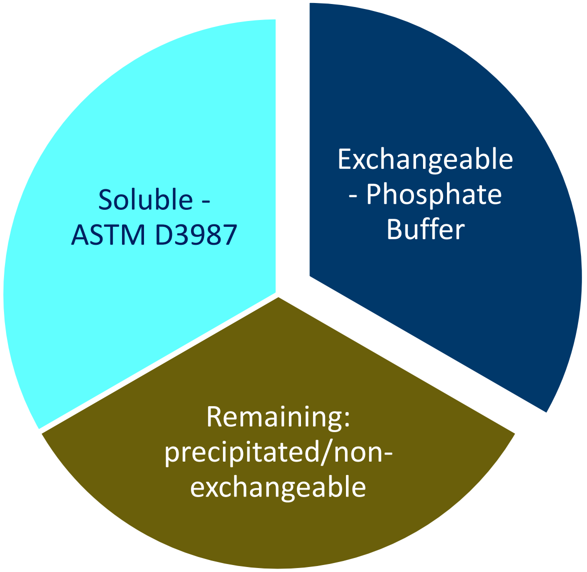


Figure source: Interplay of transport processes and interfacial chemistry affecting chromium reduction and reoxidation with iron and manganese | SpringerLink

Cr(VI) Conventional Analysis



- James and Vitale
- Operationally Defined Soluble, Exchangeable, Total Chromium
  - ASTM D3987-12 *Standard Practice for Shake Extraction of Solid Waste with Water* – **Soluble** Cr(VI)
    - Deionized water agitated for 18 hours at 21°C, 0.45-µm filter
  - Phosphate Buffer – **Exchangeable** Cr(VI)
    - 10 mM K-phosphate buffer prepared at pH 7.0, agitate for 10 min at 21°C, 0.45-µm filter
  - US EPA Method 3060A – **Total** Cr(VI)
    - Environmentally relevant, codified method for Cr(VI) in solid materials for waste characterization
    - pH > 11.5 solutions designed to prevent both reduction of Cr(VI) and adsorption of CrO_4^{2-} onto mineral surfaces
    - 90-95°C for 1-hour continuous stirring, 0.45-µm filter

Experimental Design

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

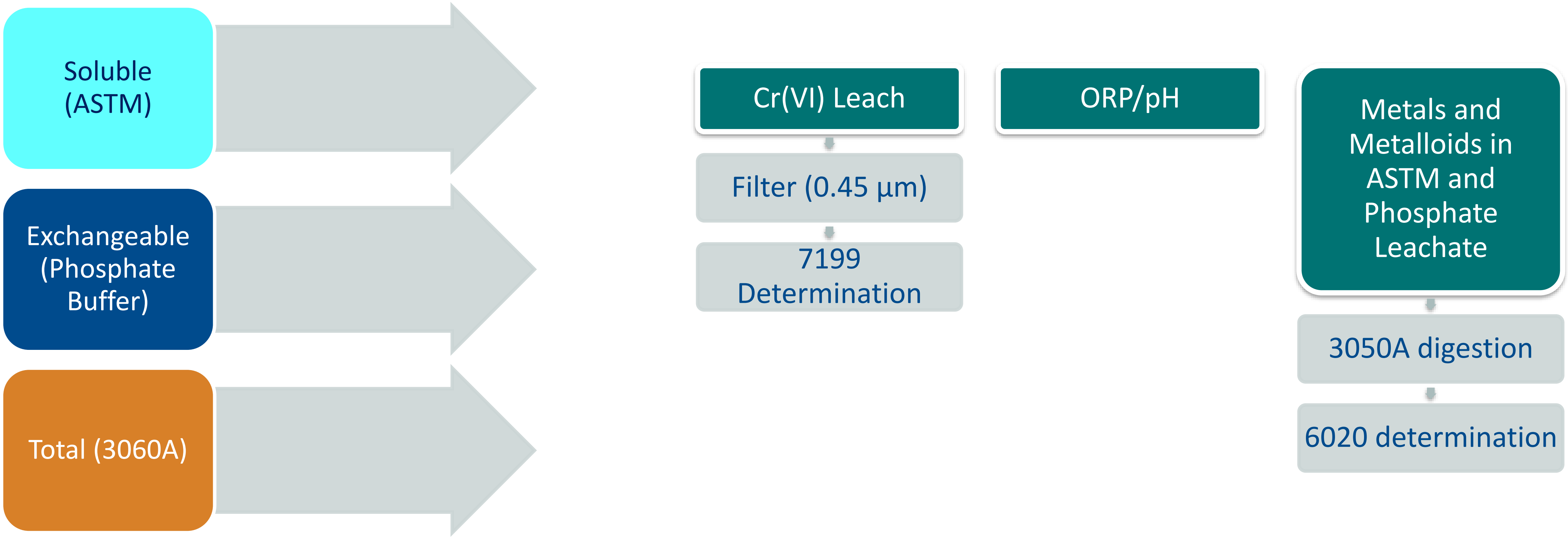
- One set fine ground to ASTM 60 Mesh (0.25mm),
- One set of coarse aggregate (½ inch * 0)

Pre-Sizing – Two Different Sets

- Coarse-Aggregate Set (<~½ inch × 0)
  - First measured size range of each sample
  - Screening into > 3/8”; > #4 (4.75mm); > #20 (0.841 mm); and < #20 sizes
  - Sample mass increased for Phosphate Buffer and US EPA 3060A (25 g) to match leachate:sample ratio in publication/method. Same also done for fine-ground for comparison, requiring larger vessels and heating units (3060A).
- Fine-Ground Set (0.25 mm × 0)
  - Fine-ground with ring and puck

Percentage of total sample			
> 3/8” sample	#4 sample	#20 sample	<#20 sample
10%	32%	35%	24%
Ideal Fractional Mass (25g total)			
2.501	7.909	8.629	5.961

Experimental Design



- One set “Fine Ground” - ASTM size 60 Mesh (0.25mm),
- One set “Coarse Aggregate” (½ inch X 0)

Quality Controls

- Soil CRM – ERA Associates 921 employed with both 3060A and Phosphate Buffer.
  - Reference Value 19.9 mg/kg
- All samples (coarse-aggregate and fine-ground) for all three leaching procedures included duplicates. Five of 11 samples also had triplicate analyses.
- Spiking employed both soluble ($K_2Cr_2O_7$) and insoluble ($PbCrO_4$) Cr(VI) for Method 3060A procedure. ASTM and Phosphate Buffer only employed soluble Cr(VI).
- Considered spiking with soluble forms of Cr(III) [$Cr(NO_3)_3$] but prior experience noted this will form an insoluble multi-element conglomerate.

ORP (Eh) and pH

Material Type	ID#	pH - FINE	pH - COARSE	Eh-FINE (mV)	Eh-COARSE (mV)
ACBF	83191245-01	11.5	10.8	-93	+120
BOF	83191244-01	12.2	12.2	-22	+160
EAF LMF	83191158-01	12.2	12.2	-112, -173 (dup)	+140
EAF LMF	83191175-01	11.9	11.7	-12	+180
EAF LMF	83191210-01	11.8	11.6	16	+190
EAF LMF	83191217-01	11.8	11.8	-28, -9 (dup)	+100
EAF-C	83191159-01	11.8	11.8	14	+210
EAF-C	83191209-01	11.5	11.3	-4	+280
EAF-C	83200095-01	11.6	11.4	0	+260
LMF	83191211-01	11.9	11.2	-92	+210
LMF	83191216-01	11.9	12.2	-52	+150

ASTM D3987-12 (pH 10.5-11.5) – Cr(VI) via 7199

Material Type	Fine (mg/kg)			Coarse (mg/kg)		
	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 (pH 7-8) – Cr(VI) via 7199

Material Type	Fine (mg/kg)			Coarse (mg/kg)		
	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)		**.16J**	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)	

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US EPA 3060A (pH ~11.5) – Cr(VI) via 7199

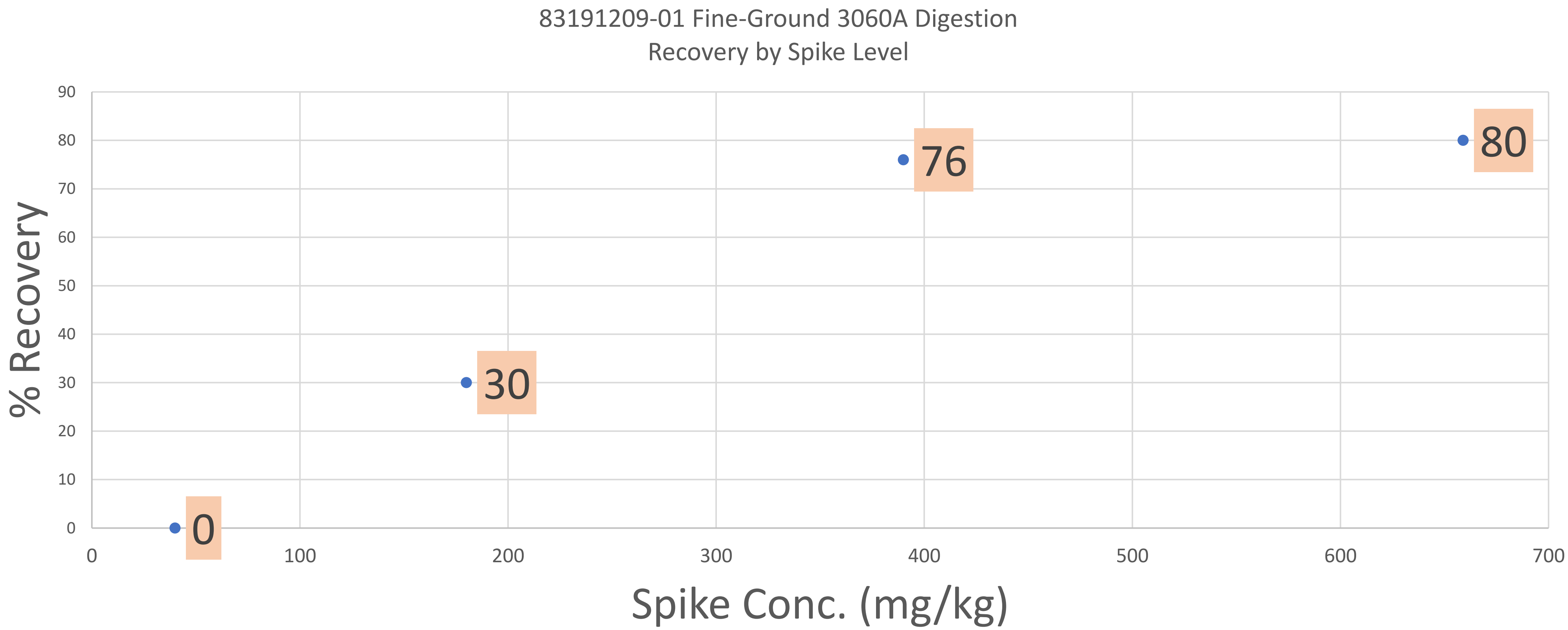
Material Type	Fine (mg/kg)			Coarse (mg/kg)		
	Primary	Duplicate	Triplicate	Primary	Duplicate	Triplicate
ACBF	ND (0.4)	ND		**0.46**	**0.44**	
BOF	**4.7**	**10.5**	**ND (0.4)**	**11**	**10.5**	**10.4**
EAF LMF	**.33J**	**0.48**		**1.2**	**0.78**	
EAF LMF	ND (0.4)	ND	ND (0.4)	**12**	**11.2**	**10.3**
EAF 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**	

Spike Recoveries – Influenced by Redox

	US EPA 3060A Fine		US EPA 3060A Coarse	
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%

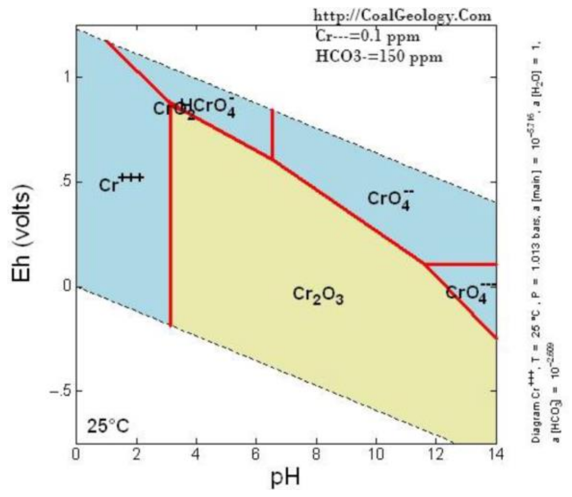
Peaks on chromatograms look specific to Cr(VI)

Adding soluble Cr(VI) spike level to overcome reductive capacity of fine-ground sample



Chromium Solubility

Dotted lines identify areas of Cr(III) precipitation



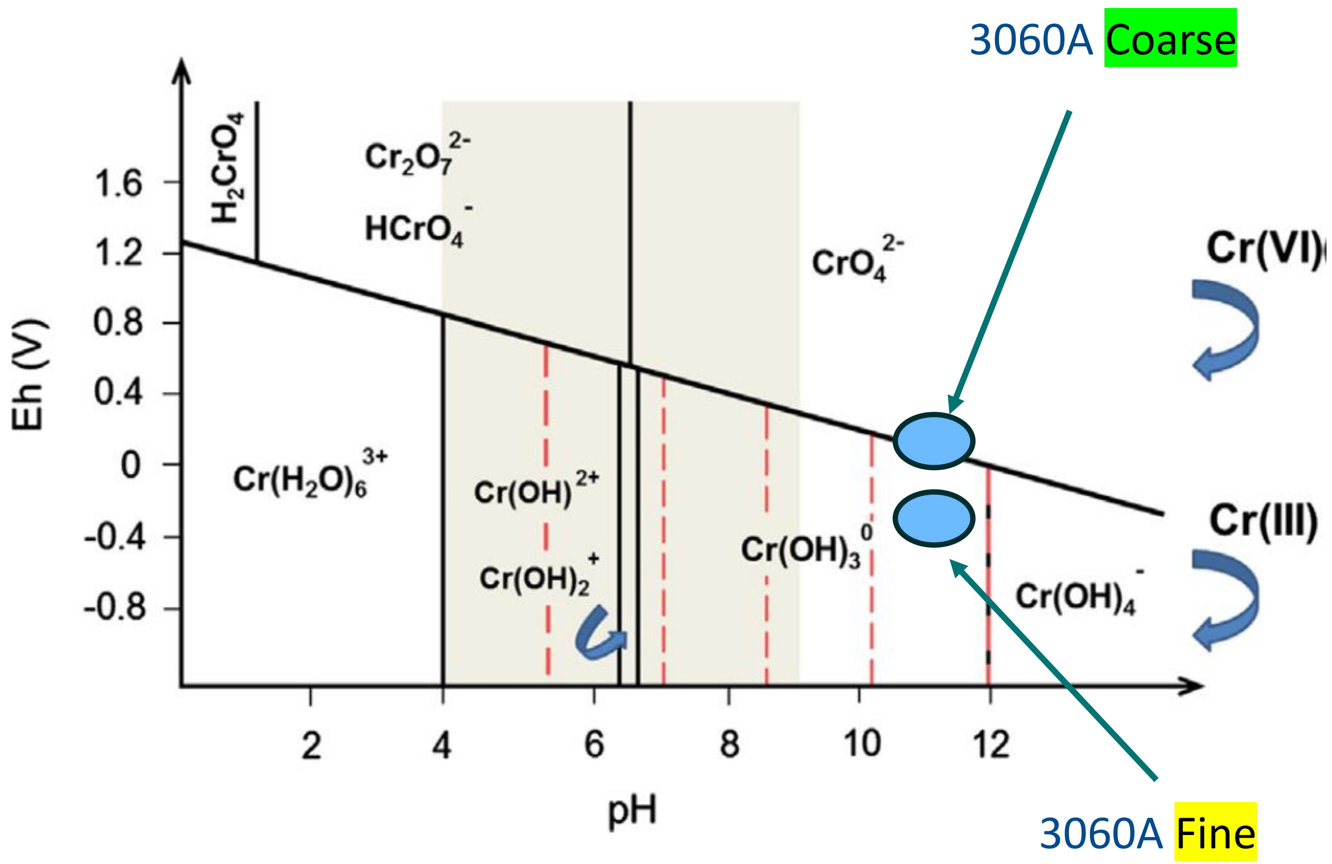


Figure source: DOI: 10.1016/j.talanta.2014.10.002 · Source: PubMed

Fe and Mn in Leachates

ASTM (Soluble) – ND
  -Solubility

Phosphate (Exchangeable):

Fe highly variable across material types.

Mn greater in the fine-ground than coarse aggregate.

Leachate	Fine	Coarse
Fe in ASTM (pH~11)	ND (200 µg/L)	ND (200 µg/L)
Fe in Phosphate (pH ~7.5)	4600 – 2.0E6 (highly variable)	4600 – 28000 µg/L
Mn in ASTM (pH~11)	ND (10 µg/L)	ND (10 µg/L)
Mn in Phosphate (pH ~7.5)	10× coarse aggregate	3500 – 35000 µg/L

Conventional Analysis – Data Summary

- All sample slurries produce alkaline conditions with DI water, as expected.
- Fine-ground slurries show reducing conditions: ~200-400mV less than coarse aggregate.
  - Likely due to Mn and Fe reductants.
- Course-aggregate slurries show oxidizing conditions:
  - Likely due to the much less solubilized Mn and Fe reductants.
- Cr(VI) levels are primarily observed in the coarse-aggregate, even with significant surface area difference. Single digit, up to 12 mg/kg.
- Cr(VI) levels in the fine-ground is ND or sub-ppm (0.2-0.4)mg/kg in all forms (Soluble, Exchangeable, Total).
- Spiking illustrates reducing nature of fine-ground material, some cases no recovery at 300-600 Cr(VI) mg/kg levels. Clearly demonstrating the strong reducing power from the crushed, solubilized reductants in the fine-ground material.

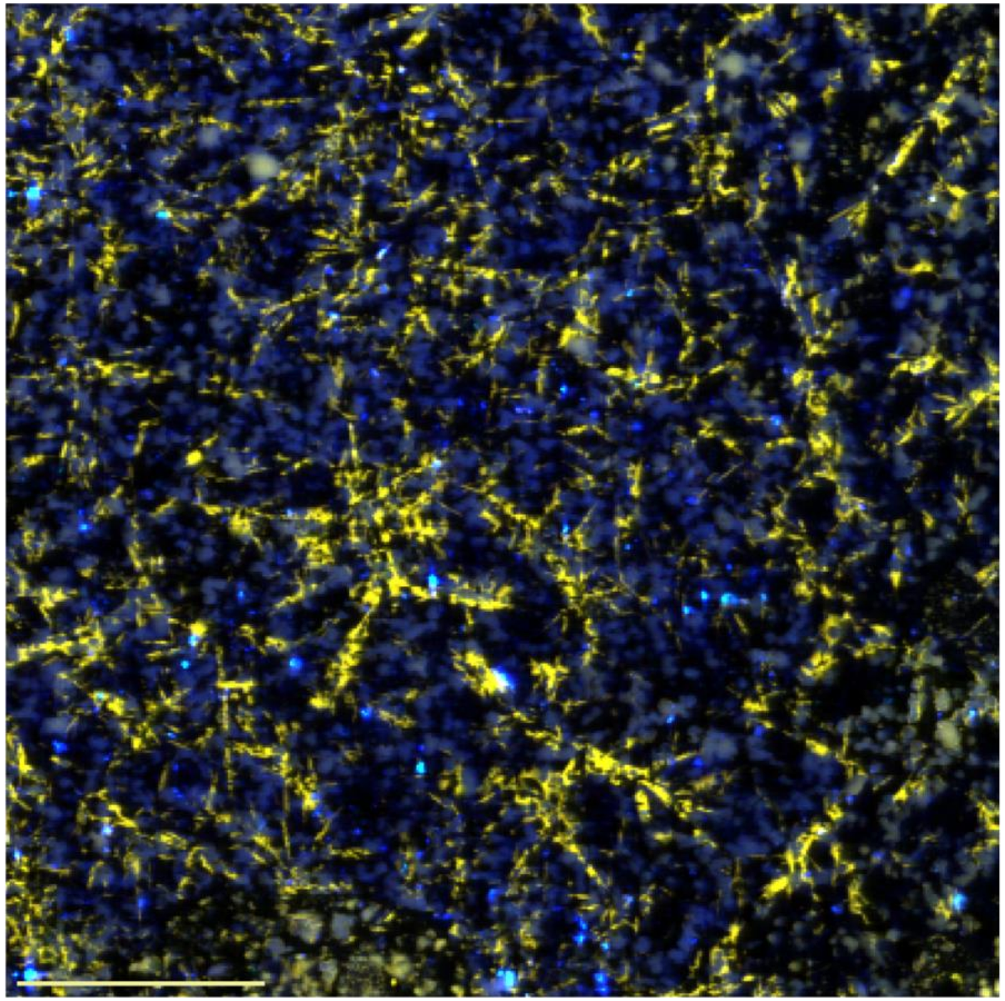
XANES Testing

- X-ray fluorescence microprobe. Beamline 4-BM - National Synchrotron Radiation Lightsource-II – Brookhaven National Laboratory.
- Three Slag Samples – 30-µm thin sections (low oxygen conditions) mounted on low-element quartz slides.
  - Samples selected based on 2019 testing with detectable Cr(VI) results from 3060A/7199 analysis.
- X-ray energy was tuned to 15 keV, scanned in *x*-*y* direction using step sizes ranging from 2-10 microns. Element fluorescence signals were collected using a germanium detector.
- A minimum of 18 points were selected based on apparent Cr intensities; points were chosen across a range of Cr intensities for representative analysis.

XANES Testing

- Non-destructive.
- Non-reactive, method does not impact chemistry.
- Considered definitive.

XANES Testing

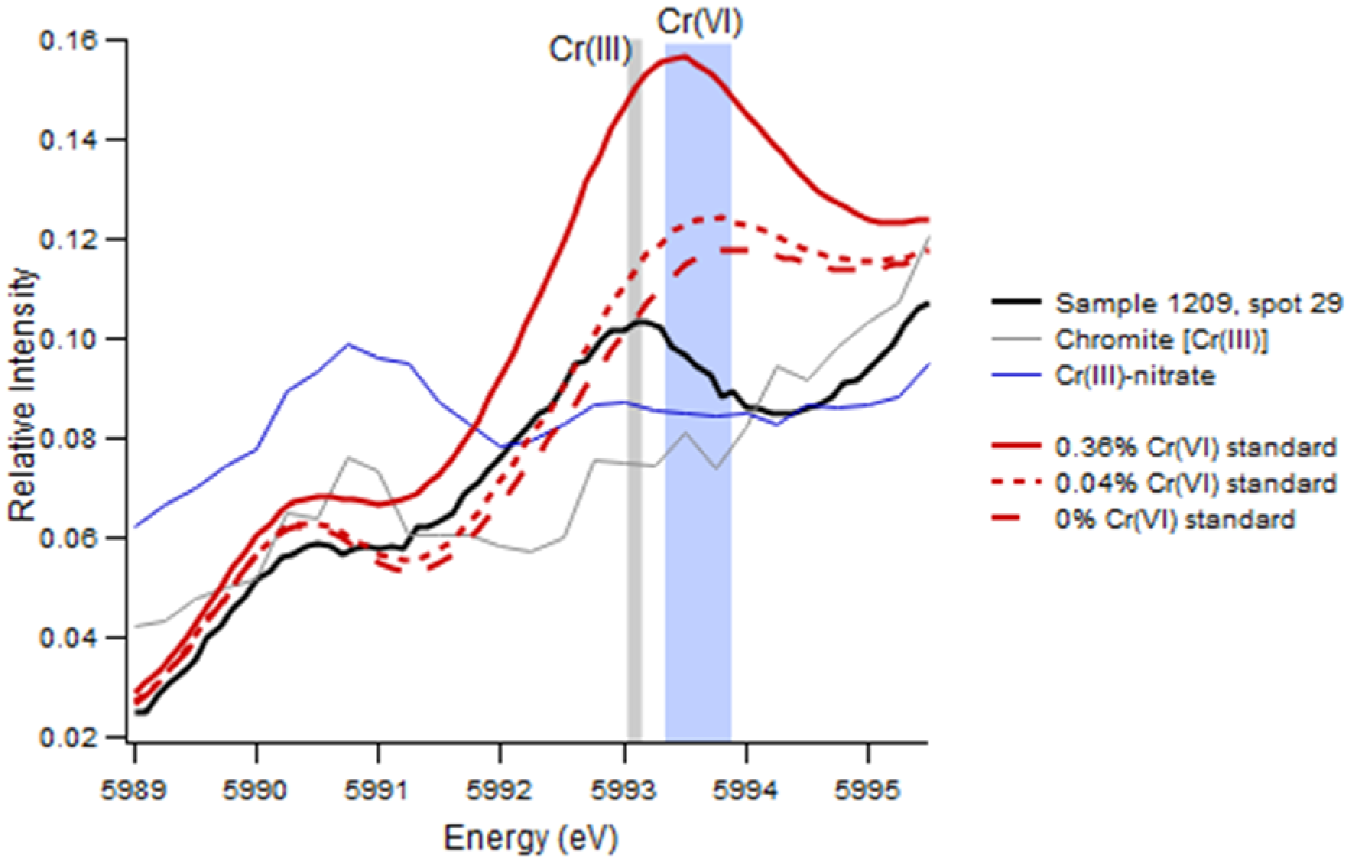


- Mapping revealed a heterogeneous distribution of Cr, Mn, and Fe.
- Tricolor plot of chromium, manganese, and iron for slag sample 83191244-01 (Cr Mn Fe). Scale bar in lower left corner represents 1 millimeter.

Red = Chromium
Green = Manganese
Blue = Iron

Cr K-edge X-ray Adsorption Near-Edge Structure (XANES)

- Location of Cr species and standard ratios



- Gaussian peak height of Cr pre-edge used to quantify Cr(VI) within samples.
- Lowest observable change in pre-edge peak height represented nominal LOD.
- ≥ 18 data points selected across range of Cr intensities -> micro-XAD.

Note energy resolution – new beamline at Brookhaven National Laboratory - March 2022

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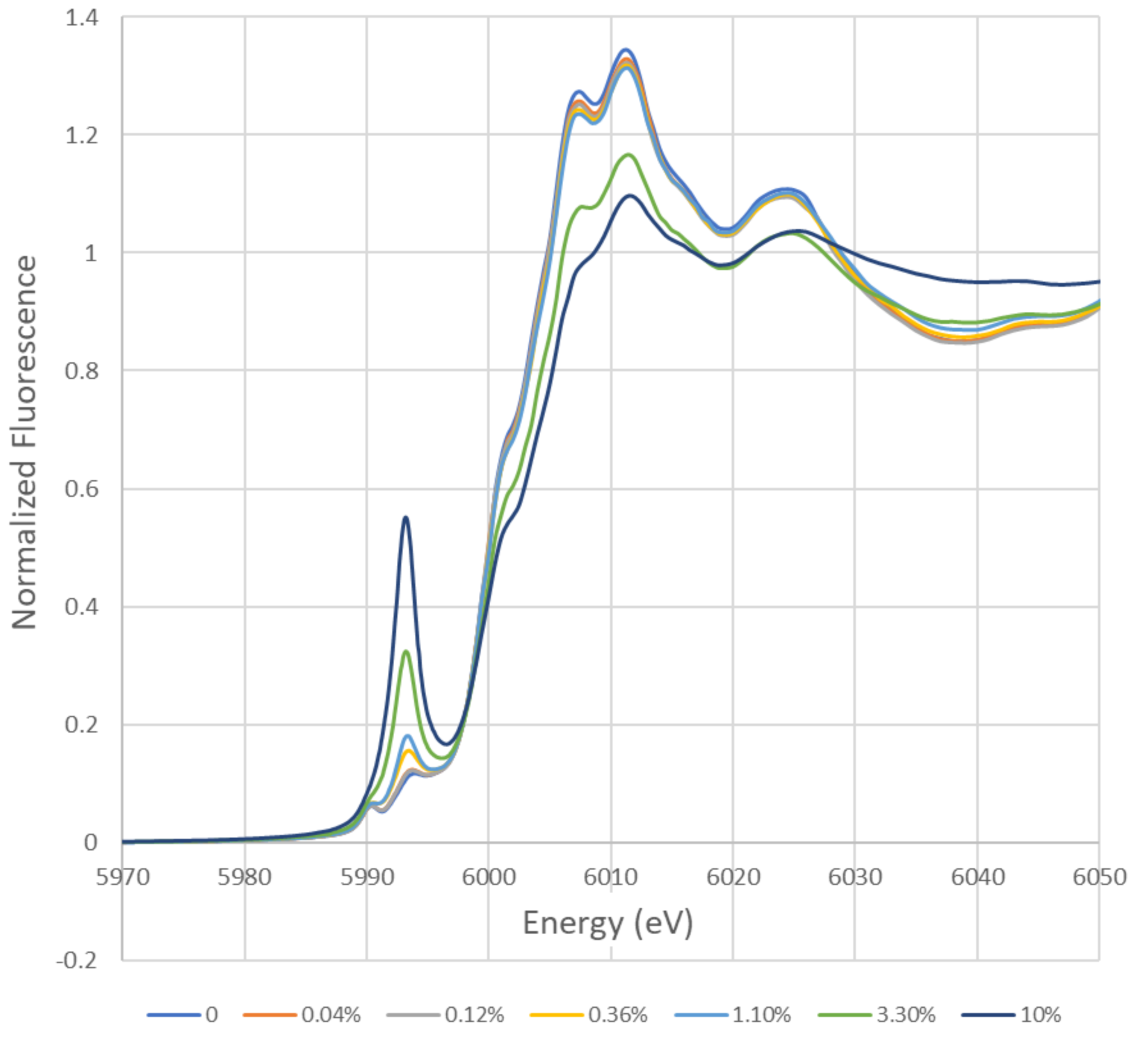
XANES

"Calibration"



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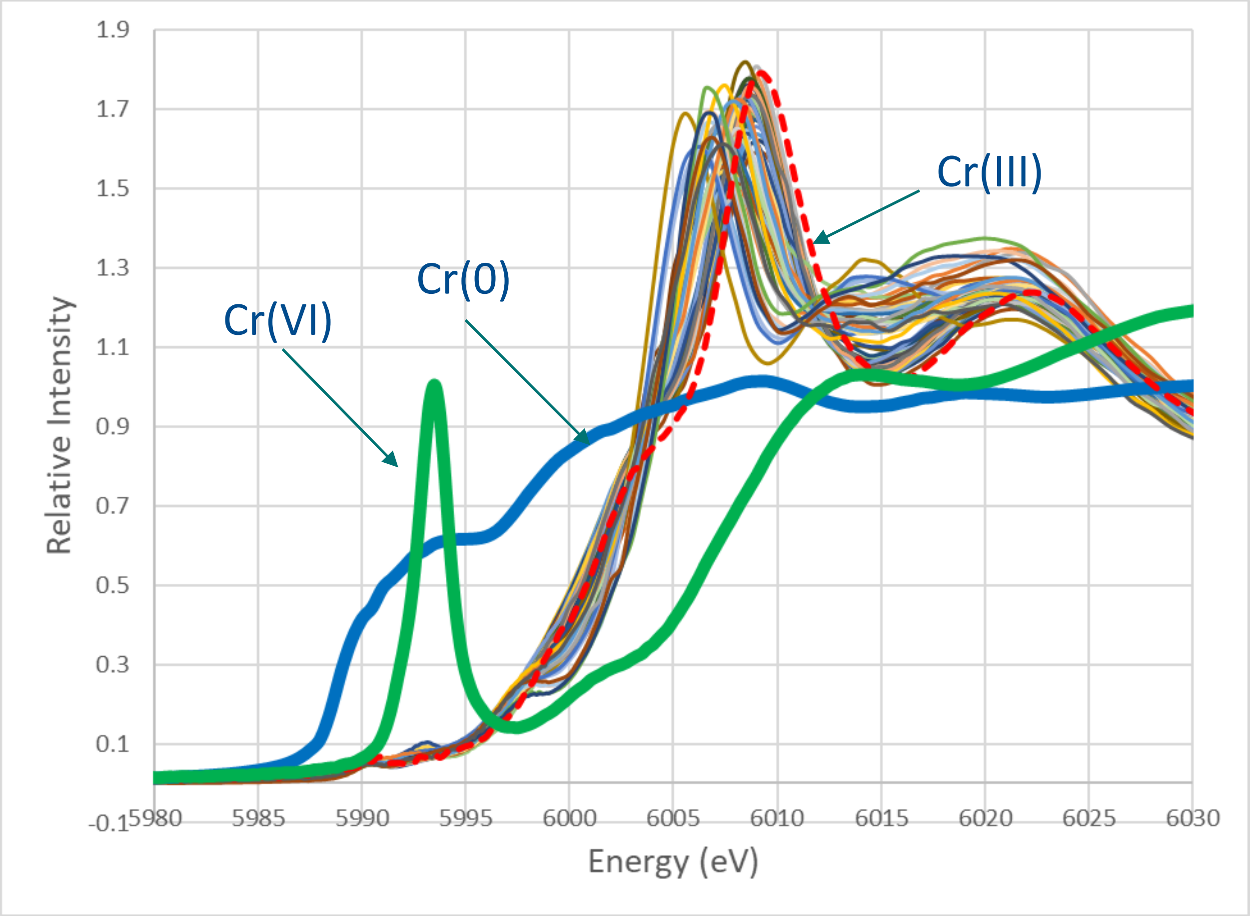
XANES vs. Conventional



Sample ID and Type	XANES	2023 Cr(VI) (fine) 3060A/ 7199	2023 Cr(VI) (coarse) 3060A/ 7199	2019 Total Cr	2023 Total Cr
1175-01 EAF LMF	<1.8	ND (0.4)	12, 11, 10	4500	awaiting
1209-01 EAF-C	<1.5	ND (0.4)	3.2, 3.1, 1.9	3700	awaiting
1244-01 BOF	<1.2	4.7, 10, ND (0.4)	11, 10, 10	2900	awaiting

All units are mg/kg.

XANES indicates no Cr(VI) above 1.8 mg/kg.

XANES

- A relatively small pre-edge feature was observed in some XAS spectra but was below the peak height observed for the lowest concentration standard of 0.04% Cr(VI).
- No XAS spectra collected on slag samples displayed a prominent Cr(VI) pre-edge feature, and instead, XAS spectra closely resembled the Cr(III) standard (chromite).
  - 1175-01: Micro-XAS spectra collected on various points (28 spectra, total) exhibited an absent pre-edge feature (5993.0 eV) indicative of reduced Cr(VI) [or Cr(III) coordinated with O], and the white line position of all samples was indicative of Cr(III). There was, therefore, no evidence of Cr(VI) within this sample.
  - 1209-1: Nine of 28 micro-XAS spectra collected on various points within the analyzed area exhibited a small pre-edge feature. Pre-edge feature yielded peak-heights that were near or less than the lowest Cr(VI) standard, and the white line position of all samples was indicative of Cr(III).
  - 1244-01: All 18 micro-XAS spectra collected on various points within the analyzed area exhibited a small pre-edge feature. Pre-edge feature yielded peak-heights near or less than the lowest Cr(VI) standard [0.12% Cr(VI) within a sample], and the white line position of all samples was indicative of Cr(III). XAS spectra only indicate the presence of relatively oxidized Cr(III) species.
- Although the presence of Cr(VI) cannot be ruled out, the white line position of all XAS spectra collected on slag samples was indicative of Cr(III).

XANES *vs.* Conventional

- XANES is considered least susceptible to interference, misidentification.
- Conventional analysis designed to minimize redox reactions of Cr, but not validated with Iron & Steel Slag.

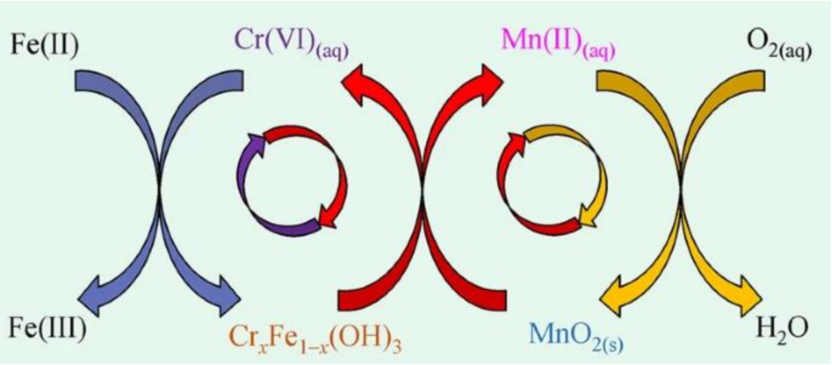
Material Type and Sample ID	XANES	Conventional 2023 Cr(VI) (Coarse) 3060A/ 7199
BOF 1244-01	< 1.2	11, 10, 10
EAF LMF 1175-01	< 1.8	12, 11, 10
EAF-C 1209-01	< 1.5	3.2, 3.1, 1.9

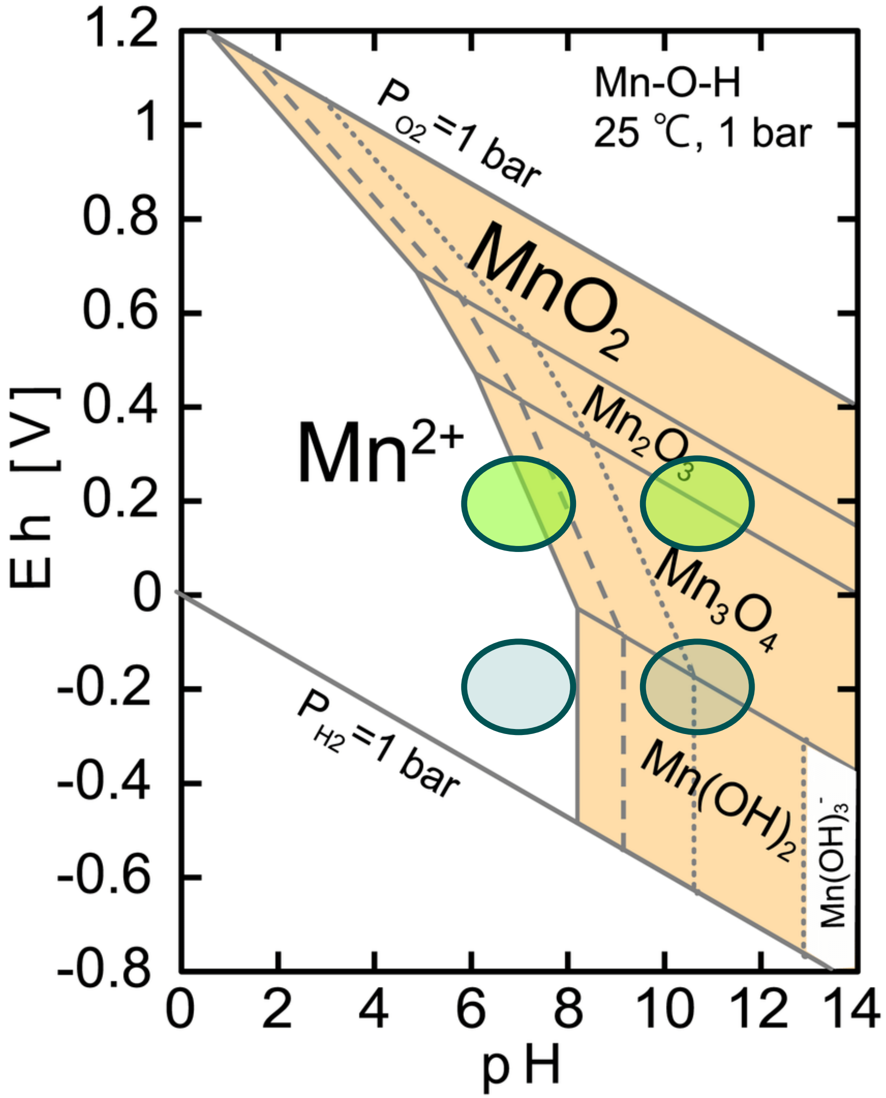
Units are mg/kg

Cr(III) Oxidation Pathway

- Differences point to oxidation of Cr(III) – Cr(VI) which is known where dissolved Mn(IV) and **solid-phase** MnO_2 are present.
- Mn in leachate:

Leachate	Coarse (oxidizing)	Fine (reducing)
Phosphate (pH ~7.5)	3500 – 35000 µg/L	10× coarse aggregate





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 (3060A -> 7199) identified levels 2-12 mg/kg in the Coarse Aggregate.
- Does conventional analysis bias results?
  - Mn and Fe forms are present at significant concentrations in slag.
  - Fe(II) can reduce Cr(VI) to Cr(III), esp. in alkaline solutions.
  - MnO_2 can oxidize Cr(III) to Cr(VI) with potential to occur under alkaline conditions of method 3060A.

Thank You

QUESTIONS?

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Coarse

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Fine