

CHROMIUM VALENCE FORMS OF COAL FLY ASH IN THE SOLID STATE AND LEACHATES

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INTRODUCTION. Speciation of chromium in fly ash is a significant and complicated issue. Huggins et al. [1] used a synchrotron X-ray method to show that most of the chromium in coal fly ash is Cr(III), an important finding that should be evaluated further. Also, questions pertaining to the bioavailability of Cr and its phase distribution in fly ash, whose determination is subject to the redox chemistry of fly ash, will need to be answered for risk assessment purpose.

METHODOLOGY. Cr(VI) in leachates was determined by cathodic stripping voltammetry (CSV), and Cr(III), Cr(total) as Cr(VI) after H₂O₂ treatment [2,3]. Independent analysis of Cr(III) and Cr(VI) was achieved by either separating Cr(III,VI) on Chelex 100 [4] prior to CSV or by using a diphenylcarbazide (DPCI)-modified carbon paste electrode (CPE) in cyclic voltammetry of the mixture [5]. By doping CPE with fly ash and/or standard and using it in a DPCI-containing electrolyte, the Cr valence forms in the solid state were quantitated. Fe(II,III) speciation was carried out spectrophotometrically [6]. The Tessler procedure modified for phase separation and digestion of Ni in fly ash [7] was adapted for Cr speciation. SRM 1633b was obtained from NIST and CFF ash samples from Dr. Huggins of the Univ. of Kentucky.

RESULTS AND DISCUSSION. Table 1 shows Cr(VI) to be 72-82% of total Cr in the 50% HF digest of 4 coal fly ash samples, contradicting the X-ray solid analysis by Huggins et al. [1]. The SRM ash was extracted sequentially and compared with total digestion for valence form and mass balance. As shown in Table 2, the water-soluble and bioavailable Cr (Step 1) is only Cr(III). No Cr was detected in the iron oxide matrix (Step 2). The electromagnetic Cr phase (Step 3) may be Ni-Cr alloy or CrO₂. In acid extractions, Cr(III) was 1.8 times of Cr(VI) in HCl, but Cr(VI) was 2.6 times of Cr(III) in HF. The summation of Cr(III) in extracts 1-5 was 41% vs. 27% in the total digest. Starting with the residue of Step 3 where the water-soluble, iron oxide, and magnetic phases were removed, Table 3 showed that the 2-step acid extraction yielded 35% of total remaining Cr as Cr(III) vs. 29% from the single step treatment. In all these extractions, the Cr mass balance was 99-100%. It seems likely that redox chemistry in different leachates may have effected these varying ratios of Cr valence forms.

To understand redox chemistry in Cr speciation, the Fe(II,III) species in the 5 sequential extracts of 1633b are shown in Table 4. The absence of Fe(II) in leachate 1 is indicative of the true origin of Cr(III) identified therein. Table 5 validates the reducing power of Fe(II) and FeS₂ in 3 extractants. For comparison, arsenite did not reduce Cr(VI) at pH 5 but gave partial reduction in acid (cf. Table 6). In leachates 4 and 5, there was no Fe(II) detected and Cr(VI) was observed. In Table 6 is shown the partial oxidation of Cr(III) by MnO₂ at pH5 and complete oxidation in acid. The latter may be responsible for generating Cr(VI) in the acid leachates of the coal fly ash.

Solid state voltammetric peaks of Cr(III) at 600 mV (Fig. 1A) and Cr(VI) at -600 mV (Fig. 1B) are diagnostic of Cr valence forms. Direct Cr speciation of 2 coal fly ash, Fig. 2 for SRM 1633b and Fig. 3 for LS102, revealed Cr(III) only, whose oxidation peak was enhanced by spiking with Cr₂O₃ (Fig. 4,5). The quantitation of Cr(III) shown in Table 7 agrees to within 5% of the total Cr found in the HF-digested samples. In Fig. 6 is shown the emergence of the Cr(VI) peak at -600 mV in the residue of 1633b heated in 2N HCl for 2 h, which disappeared after heating it for 4 h. A similar phenomenon is seen in Fig. 7 for 1633b heated in 50% HF but the Cr peaks were broadened due to more extensive leaching. The Cr species in the solids and leachates of 1633b were determined to obtain closure. As shown in Table 8, Cr(III) in 1633b was either oxidized to Cr(VI) and detectable on the residue surface or dissolved and then partly oxidized in solution.

REFERENCES

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Table 1. Voltammetric analysis of chromium valence states of HF digests of coal fly ash

Samples ^a	Cr(VI) ug/g	Cr Total ug/g	Cr(VI) Cr Total %Total
CFF-LS100	116.3	155.1	75.0
CFF-LS102	112.1	137.4	81.6
CFF-LS100/FLT	108.8	140.8	77.3
SRM 1633b	142.0	196.4	72.3

^a CFF samples were obtained from Dr. F.E. Huggins, Univ. of Kentucky, who showed Cr(III) to be the predominant species by XAFS spectroscopy.

Table 2. Chromium speciation of SRM 1633b by phase separation

Sequential Extraction	Cr(III)		Cr(VI)		Cr(ttl)	
	ug/g	%	ug/g	%	ug/g	% certified ^a
1. NaOAc, pH5	13.0	100.0	0.0	0.0	12.7	6.7
2. Na2S2O4-Citrate pH5	0.0	0.0	0.0	0.0	0.0	0.0
3. Electromagnet	-	-	-	-	5.9	3.0
4. 2N HCl, heat	30.2	64.9	16.4	35.1	46.8	24.0
5. 50% HF, heat	35.6	28.1	91.1	71.9	129.4	66.4
Extracts 1 to 5	78.8	41.0	107.5	59.0	194.8	100.1
50% HF (total digest)	53.5	26.9	145.4	73.1	196.4	99.1

^a Cr certified 198.2 ug/g

Table 3. Comparison of chromium valence state of SRM 1633b by 2 extractions

A: Electromagnet residue ----- 2N HCl ----- 50% HF

B: Electromagnet residue ----- 50% HF

Sequential Extractions	A			B		
	Cr(III) ug / g	Cr(VI) ug / g	Cr(Tot) ug / g	Cr(III) ug / g	Cr(VI) ug / g	Cr(Tot) ug / g
2N HCl	30.7	16.5	46.6			
CV%	4.0	3.1	2.6			
50% HF	30.9	97.7	127.8	50.3	123.8	175.3
CV%	4.8	2.9	2.3	3.0	2.8	4.6
Subtotal	61.6	114.2	174.4	50.3	123.8	175.3
% Valence	35.0	65.0		28.9	71.1	

Table 4. Mass balance of Fe determination in 5-step extraction of SRM 1633b

Extraction step	Fe ²⁺ found (ug/g)	Fe ³⁺ found (ug/g)	Fe(T) found (ug/g)	% Certified
1. NaOAc, pH 5	0.0	2076.8	2076.8	2.7
2. Na ₂ S ₂ O ₄ -citrate, pH 5	6367.0	0.0	6367.0	8.2
3. electromagnet	5447.7	9990.2	15437.9	19.9
4. 2 N HCl, heat	0.0	8144.4	8144.4	10.5
5. 50 % HF, heat	0.0	45462.6	45462.6	58.7
Total	11814.7	65674.0	77488.7	100.0

Fe Certified in 1633b: 77800 ug/g

Table 5. Fate of Cr(VI) in the presence of Fe(II) and FeS₂ in extractions

Extractant	A, Cr Recovered		B, Cr Recovered			
	Cr(III)		Cr(III)		Cr(VI)	
	ug	%	ug	%	ug	%
NaOAc, pH5 Bransonic	4.72	94.4	0.00	0.0	0.96	96.0
2N HCl, heat	4.91	98.2	0.96	96.0	0.00	0.0
50% HF, heat	4.88	97.6	1.05	105.0	0.00	0.0

A: 5 ug Cr(VI) + 50 ug Fe(II)

B: 1 ug Cr(VI) + 10 mg FeS₂

Table 6. Fate of Cr(III) and Cr(VI) in the presence of arsenite and MnO₂

Extractant	A, Cr Recovered				B, Cr Recovered			
	Cr(III)		Cr(VI)		Cr(III)		Cr(VI)	
	ug	%	ug	%	ug	%	ug	%
NaOAc, pH5 Bransonic	0	0	4.77	95.4	2.30	46.0	2.80	56.0
2N HCl, heat	2.35	4.7	2.47	49.4	0.00	0.0	4.76	95.2
50% HF, heat	2.31	46.2	2.44	48.8	0.00	0.0	4.80	96.0

A: 5 ug Cr(VI) + 5 ug As(III)

B: 5 ug Cr(III) + 10 mg As(V)

Table 7. Solid state Cr speciation of fly ash by CPE^a

Fly Ash	Peak Current uA	Cr(III) found ug/g	CV %	Cr(total) ^b ug/g
SRM 1633b ^c	8.46	205.5	2.5	195
CFE-LS102	5.60	135.4	4.9	137

^a Carbon paste electrode: fly ash-CPE in electrolyte: 0.002M H₂SO₄+0.5M KNO₃+10⁻⁴M DPCI; single peak from anodic scan, no Cr(VI) peak in cathodic scan; CV from 3 separate analysis

^b Cr determined after digestion of fly ash in 50% HF

^c Certified Cr 198.2 ug/g

Table 8. Chromium speciation of SRM 1633b in solids and leachates

Treatment	Cr in solids ^a (ug/g)		Cr in leachates ^b (ug/g)		Cr(sum) Cr certified %
	Cr(III)	Cr(VI)	Cr(III)	Cr(VI)	
(None) before extraction	205.5	0	0	0	105.4
2N HCl, heat 2h	146.1	9.65	29.4	11.5	99.1
2N HCl, heat 4h	135.4	0	39.4	22.7	99.5
50% HF, heat 4h	0	0	53.9	149.2	102.2

^a 100 mg 1633b--1 g carbon as CPE in electrolyte 0.002M H₂SO₄+0.5M KNO₃+10⁻⁴M DPCI

^b DPCI--MCPE in electrolyte 0.002M H₂SO₄+0.5M KNO₃

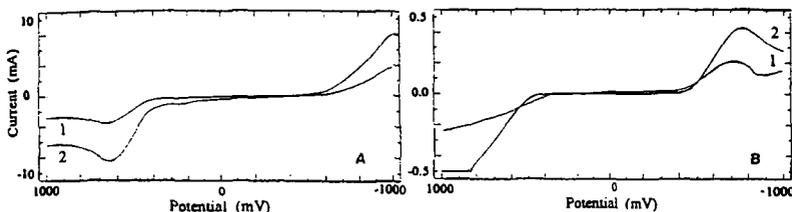


Fig. 1A Oxidation voltammograms of Cr(III) in carbon paste electrode in electrolyte: 2×10^{-3} M H₂SO₄+0.5 M KNO₃+10⁻⁴ M DPCI
1-- 100 mg KCr(SO₄)₂/g carbon
2-- 100 mg Cr₂O₃/g carbon

Fig. 1B Reduction voltammograms of Cr(VI) in carbon paste electrode in the above electrolyte.
1-- 100 mg PbCrO₄/g carbon
2-- 100 mg BaCrO₄/g carbon

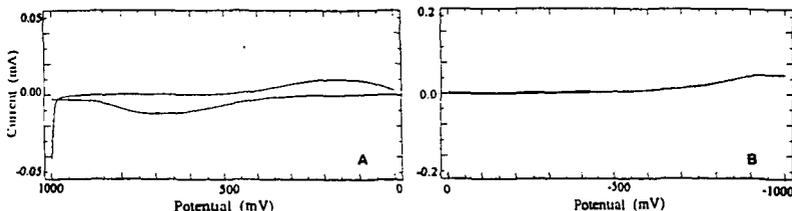


Fig. 2 Cyclic voltammograms of SRM 1633b in carbon paste electrode (100 mg/g) in the above electrolyte.
A--plotted 1000 mV--0 mV at $\pm 50 \mu\text{A}$ B-- plotted -1000 mV--0 mV at $\pm 200 \mu\text{A}$.

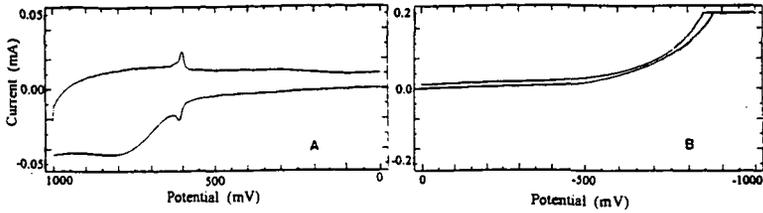


Fig. 3 Cyclic voltammograms of CFF-LS102 in carbon paste electrode (100 mg/g) in the above electrolyte. A—plotted 1000 mV–0 mV at $\pm 50 \mu\text{A}$ B—plotted -1000 mV–0 mV at $\pm 200 \mu\text{A}$.

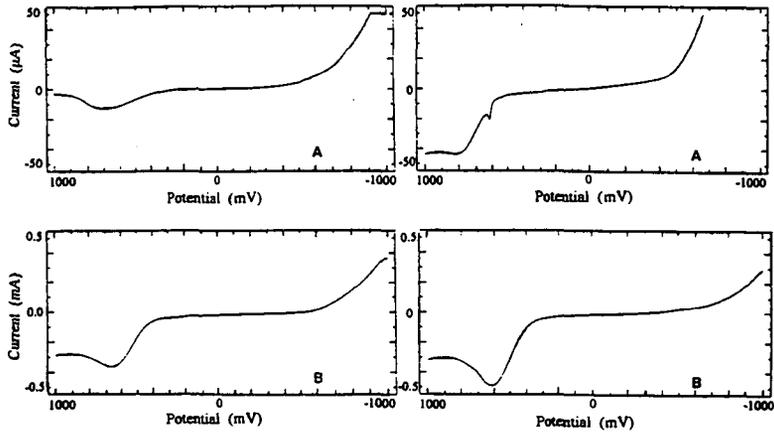


Fig. 4 Oxidation voltammograms of SRM 1633b spiked with Cr_2O_3 in carbon paste electrode in the above electrolyte
A—100 mg 1633b/g carbon
B—0.5 mg Cr_2O_3 added

Fig. 5 Oxidation voltammograms of CFF-LS102 spiked with Cr_2O_3 in carbon paste electrode in the above electrolyte
A—100 mg CFF-LS102 /g carbon
B—0.5 mg Cr_2O_3 added

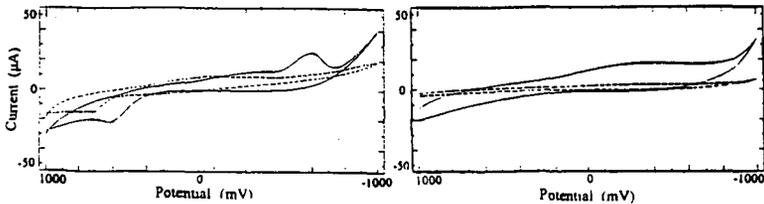


Fig. 6 Cyclic voltammograms of SRM 1633b residue of 2N HCl treatment in carbon paste electrode in the above electrolyte
(—)—140°C. 2 h.
(---)—140°C. 4 h.

Fig. 7 Cyclic voltammograms of SRM 1633b residue of 50% HF treatment in carbon paste electrode in the above electrolyte
(—)—140°C 2 h.
(---)—140°C 4 h.