

# Trace Element Chemistry of Fly Ashes from Co-combusted Petroleum Coke and Coal

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## ABSTRACT

Because of economics, petroleum coke sometimes replaces or supplements coal as a fuel in power plant combustors. Fly ashes were recovered from the combustion of petroleum coke with moderate- to high-sulfur Illinois Basin bituminous coal in a western Kentucky power plant. The fly ashes primarily consist of glass, quartz, mullite and spinels. When compared with ordinary fly ashes from Illinois Basin coals, the petroleum coke-coal fly ashes are relatively enriched in nickel, vanadium, and other metals. Associations between trace elements and compounds within the ashes were identified through the use of distilled, deionized water batch leaching, magnetic separations, and other laboratory techniques.

## INTRODUCTION

Petroleum coke is a byproduct of heavy oil refining (Wang *et al.*, 2004, p. 1341). Because it is a high-carbon fuel that is often cheaper than coal, petroleum coke use in power plants has increased in recent years. According to a 2002 survey, petroleum coke represents more than 10% of the fuel in some Kentucky power plants (Hower *et al.*, 2005). At the same time, there are environmental issues associated with the utilization of petroleum coke. For example, the combustion of petroleum coke may release high emissions of SO<sub>2</sub>, CO<sub>2</sub> and NO<sub>x</sub> (Wang *et al.*, 2004, p. 1341). Additionally, its combustion byproducts are usually enriched in vanadium, nickel, and other potentially harmful metals (Hower *et al.*, 2005).

Although there are environmental and health concerns associated with nickel and vanadium, vanadium and nickel compounds are usually not as toxic to humans as mercury, cadmium, lead, or other "heavy metals." Specifically, vanadium and nickel are not included on the list of National Primary Drinking Water Standards (40 Code of Federal Regulations [CFR] 141.62) or monitored with the Toxicity Characteristic Leaching Procedure (TCLP) (40 CFR 261.30).

Most health problems related to nickel deal with skin and respiratory exposure. If nickel compounds come into contact with human skin, they may cause severe dermatitis

(Nielsen, 1977, p. 134). Inhalation of nickel carbonyl, nickel subsulfide, and nickel oxide may cause cancer (Nielsen, 1977, p. 136), although these compounds may not occur in oil and petroleum coke combustion byproducts. Although the oral toxicity of most nickel compounds is low, their ingestion may cause some gastrointestinal irritation (Nielsen, 1977, p. 129).

The most common health problems associated with vanadium exposure result from inhalation (Waters, 1977, p. 148, 160). Air emissions and ashes from petroleum coke or oil combustion facilities may cause respiratory problems in humans, especially if  $V_2O_5$  is present (Ress *et al.*, 2003; Waters, 1977, p. 149). Common symptoms from respiratory exposure to vanadium include coughing, bronchitis, and eyes, nose and throat irritation (Waters, 1977, p. 160-161).

## ASH PRODUCTION

Fly ashes were collected from electrostatic precipitator (ESP) hoppers at a 444 megawatt power plant in western Kentucky (Hower *et al.*, 2005). The pulverized fuel that produced the ashes consisted of at least 58 volume percent (v%) petroleum coke from an unknown source blended with moderate- to high-sulfur Illinois Basin bituminous coal from western Kentucky (Hower *et al.*, 2005). The coal-petroleum coke feed had a moderate ash content of 10.68% and a high concentration of sulfur (3.88%) (Hower *et al.*, 2005). The coal-coke blend also contained 520 ppm of vanadium and 82 ppm of nickel (Hower *et al.*, 2005). The compositions of the coal and petroleum coke prior to blending are unknown.

Hower *et al.* (2005) discusses the chemistry and “mineralogy” of different size fractions of the ashes. In my study, the nickel, vanadium, and major element chemistry of two of the fly ashes (identification numbers: 93067 and 93068) were characterized in detail. Fly ash 93067 was collected in ESP Row 1 and Bin 1E, whereas fly ash 93068 was from Row 2 and Bin 5E. Because flue gases pass first through the ESPs in Row 1 and then proceed on to the second row, first row fly ash 93067 is expected to have more ash with coarser particles than sample 93068 (Hower *et al.*, 2005).

## ASH CHEMISTRY

The ash contents of the two bulk (as received) fly ashes were measured with ASTM Method D3174-97, which involves heating the samples to 750°C. Afterwards, the major, minor and trace element chemistry of the uncombusted residues were determined with a Philips PW2404 X-ray fluorescence (XRF) spectrometer using ASTM Method D4326-97. The XRF and ash results are listed in Tables 1-2. Analysis #1 is from Hower *et al.* (2005). Two sets of duplicate ash and XRF analyses were performed and are listed in Tables 1-2 along with averages and  $2\sigma$  standard deviations. Overall, the major element analyses for each ash are reasonably consistent (Table 1).

However, the standard deviations of many of the trace elements are rather high (Table 2).

Table 1: Major element chemistry of fly ashes 93067 and 93068 after ashing to remove moisture and organic residues.

Fly ash 93067

Wt% Oxide	Analysis #1	Analysis #2	Analysis #3	Mean	Std. Dev. ( $2\sigma$ )
SiO <sub>2</sub>	43.31	46.07	44.38	44.59	2.78
Al <sub>2</sub> O <sub>3</sub>	20.16	20.86	20.83	20.62	0.79
Fe <sub>2</sub> O <sub>3</sub>	21.20	20.22	20.38	20.60	1.05
CaO	2.50	2.55	2.60	2.55	0.10
MgO	0.88	0.85	0.97	0.90	0.12
K <sub>2</sub> O	2.54	2.57	2.52	2.54	0.05
Na <sub>2</sub> O	0.24	0.22	0.25	0.24	0.03
P <sub>2</sub> O <sub>5</sub>	0.20	0.20	0.20	0.20	<0.01
TiO <sub>2</sub>	1.08	1.18	1.34	1.20	0.26
SO <sub>3</sub>	1.83	1.77	2.25	1.95	0.52
Ash	64.13	64.01	64.44	64.19	0.44

Fly ash 93068.

Wt% Oxide	Analysis #1	Analysis #2	Analysis #3	Mean	Std. Dev. ( $2\sigma$ )
SiO <sub>2</sub>	43.31	45.04	45.03	44.46	1.99
Al <sub>2</sub> O <sub>3</sub>	20.29	20.65	21.12	20.69	0.83
Fe <sub>2</sub> O <sub>3</sub>	21.17	20.11	20.48	20.59	1.08
CaO	2.56	2.58	2.62	2.59	0.06
MgO	0.91	0.84	0.98	0.91	0.14
K <sub>2</sub> O	2.51	2.54	2.52	2.52	0.03
Na <sub>2</sub> O	0.25	0.20	0.24	0.23	0.05
P <sub>2</sub> O <sub>5</sub>	0.20	0.21	0.21	0.21	0.01
TiO <sub>2</sub>	1.07	1.15	1.34	1.19	0.28
SO <sub>3</sub>	1.79	1.97	2.30	2.02	0.52
Ash	60.44	60.61	60.70	60.58	0.26

Table 2: Minor and trace element chemistry of fly ashes 93067 and 93068 after ashing to remove moisture and organic residues.

Fly ash 93067

Element, ppm	Analysis #1	Analysis #2	Analysis #3	Mean	Std. Dev. ( $2\sigma$ )
Ni	1006	1263	1182	1150	263
V	6558	7893	7606	7352	1405
As	158	65	73	99	103
Ba	723	1329	972	1008	609
Cr	85	635	1079	600	996
Co	69	62	72	68	10
Cu	95	64	80	80	31
Pb	72	54	52	60	23
Mn	429	673	512	538	248
Hg	0.006	---	---	0.006	---
Mo	53	54	33	47	24
Sr	379	396	381	385	19
Zn	237	312	319	289	91

Fly ash 93068

Element, ppm	Analysis #1	Analysis #2	Analysis #3	Mean	Std. Dev. ( $2\sigma$ )
Ni	976	1268	1171	1138	297
V	6585	7808	7627	7340	1320
As	170	80	86	112	101
Ba	766	1323	1003	1031	559
Cr	68	631	1087	595	1021
Co	69	62	72	68	10
Cu	96	67	70	78	32
Pb	79	56	55	63	27
Mn	384	671	518	524	287
Hg	0.006	---	---	0.006	---
Mo	56	36	54	49	22
Sr	377	394	403	391	26
Zn	243	330	317	297	94

Besides fuel chemistry and combustion conditions, the inorganic chemistry of fly ashes is dependent on several other factors, including: the surface area of the ash, flue gas temperature, and the type and amount of carbon in the fly ash (Hower *et al.*, 2005). Overall, the average chemistries of the two ashes are nearly identical (Tables 1-2). Their major element chemistry is consistent with  $\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3 \geq 70\%$  “Class F” fly ashes, which typically result from the combustion of eastern US bituminous coals (ASTM Method C618). The ash contents of the ashes are only 64.19% and 60.58% (Table 1), where carbon dominates the combustible fraction (Hower *et al.*, 2005). Because these and other ashes produced from petroleum coke are relatively rich in carbon (Hower *et al.*, 2005), they are usually unsuitable for cement and concrete utilization.

Nickel and vanadium concentrations in Kentucky coal fly ashes (without the addition of petroleum coke, tires or other fuels) rarely exceed 1000 ppm (Hower *et al.*, 2005). As shown in Table 2, petroleum coke has clearly enriched the 93067 and 93068 fly ashes with vanadium and nickel.

#### ASH “MINERALOGY”

Powder X-ray diffraction (XRD) analyses were performed on the fly ashes with a Philips diffractometer. The XRD scans detected amorphous materials (including glass), quartz, mullite, spinels (“magnetite”), and hematite. Additionally, distilled and deionized (D&D) water leachates of the ashes (see below) are commonly saturated with gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ), which suggests the presence of anhydrite ( $\text{CaSO}_4$ ) and/or other calcium sulfates in the ashes.

#### BATCH LEACHING TESTS

Batch leaching tests are laboratory procedures that provide some estimations of the types and concentrations of potentially toxic contaminants that might be released from a solid combustion byproduct if it comes into contact with groundwater or surface water. The most common batch leaching test in the United States is the U.S. Environmental Protection Agency’s Toxicity Characteristic Leaching Procedure (TCLP), which is used to determine toxic hazardousness (40 CFR 261, Appendix II). Because the TCLP uses sodium acetate or acetic acid to simulate leaching conditions in municipal landfills, the test has been widely criticized as inappropriate for evaluating the leaching properties of ashes and other combustion byproducts that would never be codisposed with municipal waste. As an alternative, Kosson *et al.* (2002) present a protocol that is more appropriate for evaluating the leaching properties of fly ashes.

## D&D Batch Leaching Tests

Samples of fly ashes 93067 and 93068 were leached with D&D water. The leaching procedure consisted of placing a known mass of ash (Table 3) into a borosilicate glass jar and then filling the jar with a known mass of D&D water (Table 3). The liquid-to-solid (L/S) ratios of the batch leachates varied from 1.71 to 10.4 to simulate relatively wet or dry leaching conditions. The jars were then sealed with Teflon®-lined lids.

Table 3: Batch leaching results (mg/L) on bulk (as received) fly ashes 93067 and 93068.

Fly ash 93067

Leaching Solution	D&D water	D&D water	0.1% HCl	0.1% HCl Blank
g of ash	200.1	40.0	40.2	0
g of liquid	349.4	415.5	421.6	----
Liquid/solid (L/S)	1.75	10.4	10.5	0
Post-filter pH	9.21	9.13	3.82	1.86
Al	9.88	8.90	96.2	0.67
Ca	689	351	602	0.80
Chloride	0.39	---	---	---
Fe	0.52	0.10	3.70	0.11
Fluoride	2.57	---	---	---
K	138	32.5	35.3	0.17
Mg	63.5	6.13	15.6	0.07
Na	105	17.3	19.5	0.02
Sulfate	1870	---	---	---
Zn	0.07	0.01	1.85	<0.01
Ni	<0.01	<0.01	6.74	<0.01
V	8.80	16.8	1.62	0.06

Fly ash 93068.

Leaching Solution	D&D water	D&D water	0.1% HCl	0.1% HCl Blank
g of ash	200.1	40.0	40.0	0
g of liquid	342.5	406.3	431.5	----
Liquid/solid	1.71	10.2	10.8	0
Post-filter pH	9.07	8.97	3.74	1.84
Al	9.15	6.10	110	0.90
Ca	689	376	564	0.84
Chloride	0.34	---	---	---
Fe	0.47	0.07	7.70	0.15
Fluoride	2.91	---	---	---
K	154	31.7	36.8	0.14
Mg	67.5	7.16	15.2	0.09
Na	109	18.6	19.4	0.01
Sulfate	2020	---	---	---
Zn	0.07	0.05	2.11	<0.01
Ni	<0.01	<0.01	7.23	<0.01
V	7.80	14.0	1.38	0.07

The D&D leachates were tumbled on a TCLP end-over-end stirrer for 48 hours. Afterwards, the mixtures were filtered at 0.45 microns. The pH values of the filtrates were determined with a ThermoOrion model 410+ meter using Fisher pH 4, 7 and 10 buffers. For anion analyses, aliquots of the filtrates were refrigerated at zero headspace and analyzed within 48 hours. The remaining filtrates were preserved with 1-2% ultrapure nitric acid, refrigerated, and analyzed for metals.

University of Kentucky Center for Applied Energy Research (CAER) personnel performed the anion and metal analyses on the batch leachates. The metals were analyzed with a PlasmaQuad 3 Inductively Coupled Argon Plasma Mass Spectrometer (ICPMS) using EPA Method 200.8 (US EPA, 1994) and a Spectrometrics Inc. Inductively Coupled Argon Plasma-Atomic Absorption Spectrometer (ICP-AA) using EPA Method 200.7 (US EPA, 1994). Chloride, fluoride, and sulfate concentrations were measured on a Dionex LC-20 ion chromatograph using EPA Method 300.0 (US EPA, 1993).

As shown in Table 3, the D&D leachates are moderately alkaline. The concentrations of aluminum, iron, and other species in the D&D leachates (Table 3) are consistent with alkaline conditions. That is, iron, nickel, and zinc are essentially insoluble (Drever, 1997, chapter 9). Because aluminum is amphoteric, it is probably more soluble at pH 9

than under neutral conditions (Faure, 1998, p. 192). The computer model MINTEQA2 (HydroGeoLogic, Inc. and Allison Geoscience Consultants, Inc., 1999) indicates that the L/S = 1.75 and 1.71 leachates are saturated with gypsum. The concentrations of magnesium, sodium, and potassium become significantly diluted at L/S = 10. When the magnesium, potassium and sodium concentrations of the D&D leachates are compared with XRF data in Table 1 that have been corrected for ashing with ASTM Method D 3174-97, D&D leaching dissolves about 16-18% of the sodium, 1-3% of the magnesium and only about 2-3% of the potassium in the ashes. The majority of these alkalis may be encapsulated in essentially water-insoluble silicate glass. Magnesium concentrations may also be controlled by hydroxide and carbonate precipitation.

Although the D&D leachates contain up to 17 ppm vanadium, comparisons with the vanadium concentrations in the ashes (Table 2) indicate that only about 0.3% of the vanadium is water soluble in the L/S= 1.7 leachates and about 3% in the L/S =10 leachates. Unlike most other elements, vanadium concentrations in the D&D water leachates are higher in the more dilute L/S = 10 samples. MINTEQA2 calculations suggest that the water-soluble vanadium exists as  $V(OH)_3^+$ ,  $H_2V_2O_4^{2+}$ , and perhaps  $VOOHCO_3^-$ . However, MINTEQA2 provides no insight on why the vanadium concentrations are higher in the L/S = 10 leachates.

### HCl Batch Leaching Tests

Batch leaching tests using 0.1% HCl were performed on various components of the 93067 and 93068 fly ashes. The 93067 samples used a 0.1% HCl solution with a pH of 1.86, whereas the 0.1% HCl leaching solution for the 93068 specimens had a pH of 1.84 (Table 4). Except for the addition of acid, the HCl leaching experiments used the same procedures as the D&D leaching tests. The L/S ratios of all of the HCl batch leachates ranged from 10 to 11 (Tables 3-4), which allowed for comparisons with the L/S = 10 D&D water leachates (Table 3). The HCl-leached samples included bulk ashes (Tables 3 and 4), air dried residues from the L/S=1.7 D&D batch leaching tests (Table 4), and ashes that had been water-washed with most of their magnetic materials removed (Table 4; also see discussions on magnetic separation below). Duplicate HCl leaching tests were performed on the water-washed ashes (Table 4).

The water-washed and magnetically depleted water-washed samples were air dried at room temperature for at least four weeks prior to HCl batch leaching. Water washing and air drying, no doubt, resulted in the oxidation and hydration of some components in the ashes. In particular, any anhydrite might have been hydrated and spinels may have been oxidized. Some carbonates may also have formed through reactions with carbon dioxide in the air.

The pH values of the HCl leachates indicate that the fly ashes were unable to neutralize all of the acidity (Tables 3-4). As expected, the presence of HCl in L/S= 10 bulk ash leachates substantially increased the solubility of most metals, including: nickel (9-10% of the metal dissolved from the bulk ash), zinc (10-11%) and iron (0.04-0.10%) (Table

3). Acidic conditions would also hinder the precipitation of any calcium or magnesium as hydroxides or carbonates, which explain the increases in calcium and magnesium concentrations. In contrast, lower pH conditions had little effect on the solubility of potassium and sodium probably because of the inability of hydrochloric acid to substantially break down silicate glasses and release the remaining alkalis. Unlike other elements, vanadium concentrations dramatically decreased in the presence of HCl (Table 3). MINTEQ calculations were again unable to explain this behavior.

Table 4 compares the HCl leaching results for the bulk, water-washed, and water-washed/magnetically depleted ashes. For both fly ashes, the duplicate leaching results on the water-washed samples are generally very consistent with the originals. A comparison between the bulk and water-washed HCl leachates shows that the water-washed samples generally have less sodium and potassium. This trend is explained by the significant removal of alkalis through water-washing. Calcium and magnesium concentrations were only slightly affected by water-washing, which may be due to the presence of only partially water-soluble salts (such as calcium sulfates or magnesium carbonates) in the ashes. Comparisons between the bulk and water-washed HCl leachates also indicate that water-washing had no appreciable effect on the aluminum, nickel, and zinc concentrations of the leachates. Like the leaching results in Table 3, the leaching properties of vanadium in the samples of Table 4 are not easily explained.

Table 4: HCl (0.1%) batch leaching results (mg/L) on different fly ash components.

Fly ash 93067

Ash type	Bulk	Water washed (Duplicate leachate)	Water washed and magnetically depleted	Acid Blank
g of ash	40.2	41.9 (42.4)	40.8	0
g of liquid	421.6	416.3 (424.1)	420.8	----
Liquid/solid	10.5	9.94 (10.0)	10.3	0
pH	3.82	3.78 (3.77)	3.39	1.86
Al	96.2	101 (100)	558	0.67
Ca	602	554 (566)	554	0.80
Fe	3.70	1.88 (1.96)	7.88	0.11
K	35.3	14.9 (14.9)	5.86	0.17
Mg	15.6	12.3 (12.9)	9.74	0.07
Na	19.5	6.44 (6.28)	12.3	0.02
Zn	1.85	1.85 (1.86)	2.63	<0.01
Ni	6.74	7.06 (5.93)	5.26	<0.01
V	1.62	6.48 (6.25)	4.83	0.06

## Fly ash 93068

Ash type	Bulk	Water washed (plus Duplicate)	Water washed and magnetically depleted	Acid Blank
g of ash	40.0	40.0 (40.0)	37.0	0
g of liquid	431.5	415.1 (414.2)	403.9	---
Liquid/solid	10.8	10.4 (10.4)	10.9	0
pH	3.74	3.63 (3.66)	3.15	1.84
Al	110	113 (107)	13.1	0.9
Ca	564	548 (539)	173	0.84
Fe	7.70	3.05 (2.74)	13.1	0.15
K	36.8	19.1 (11.7)	5.72	0.14
Mg	15.2	12.8 (10.9)	10.9	0.09
Na	19.4	9.00 (5.09)	1.19	0.01
Zn	2.11	2.03 (2.04)	2.27	<0.01
Ni	7.23	6.66 (6.04)	5.89	<0.01
V	1.38	4.81 (4.70)	7.00	0.07

For unknown reasons, the HCl leachates of the water-washed/magnetically depleted 93067 and 93068 samples show large discrepancies, especially in their aluminum and calcium concentrations (Table 4). These discrepancies may be due to differences in how thoroughly 93067 and 93068 were water washed. Furthermore, variations in humidity, room temperature, the particle sizes of the drying ashes, and other conditions during air drying could profoundly affect the formation of carbonates, oxides, hydrates, and other species, which would influence the leaching properties of the ashes.

## MAGNETIC SEPARATIONS

Magnetic separations were utilized to determine whether nickel and vanadium are preferentially associated with magnetic spinels or the non-magnetic portions of the ashes. Runs with an Eriez magnetic separator suggested that bulk sample 93067 contains about 5 wt% magnetic spinel. However, even after several runs through the separator, the separation was not very effective because the “non-magnetic” portion of the ash still contained large amounts of magnetic materials that could be easily recovered with a magnetic stir bar.

Effective recovery of the magnetic materials was finally achieved by using Teflon®-coated magnetic stir bars. Each stir bar agitated 10.2-12.7 grams (Table 5) of fly ash in about 1.5 liters of distilled and deionized water for several days. Periodically, the stir bars were removed. Loose material on the bars was rinsed back into the suspension, whereas the firmly bonded material was collected onto a preweighed filter. After several days, very little magnetic material was recovered. The recovered magnetic materials were air dried over several days. In some cases, the air dried magnetic samples were placed overnight in an oven at about 110°C. As shown in Table 5, oven drying did not significantly lower the mass of the air dried materials. The separations indicate that both ashes contain about 8 wt% magnetic materials (Table 5).

Table 5: Weight percentages of magnetic materials in fly ashes 93067 and 93068.

Fly ash #	g of ash	g of magnetic material extracted	Wt% magnetic material
93067			
	10.5089	0.7886	7.50
	10.1697	0.8036	7.90
	10.1691	0.8487	8.35 (8.34 <sup>*</sup> )
		Average (air dried only)	7.92
		Std. dev. 2σ	0.84
93068			
	10.9377	0.9098	8.32 (8.31 <sup>*</sup> )
	12.7157	1.0898	8.57 (8.55 <sup>*</sup> )
	10.5254	0.8705	8.27 (8.26 <sup>*</sup> )
		Average (air dried only)	8.39
		Std. dev. 2σ	0.32

\*Masses after oven drying at about 110°C.

The magnetic and magnetically depleted materials for both ashes were analyzed by XRF and XRD. Table 6 shows the XRF results for the samples. For comparisons, the average results for the ashed bulk samples (Tables 1 and 2) are also listed. XRD analyses detected no spinels or other magnetic materials in the magnetically depleted samples. Although XRD analyses of the magnetic materials only detected spinel and hematite and not any non-magnetic impurities, some quartz grains and glass cenospheres were visible in the samples under a microscope and XRF analyses of the separations still indicate that SiO<sub>2</sub> is present.

Nickel, zinc and vanadium are known to occur in spinels. For example, the general formula for vanadium spinels is  $[(\text{Fe},\text{Mg},\text{Mn},\text{Zn},\text{Ni})\text{V}_2\text{O}_4]$ .  $\text{Ni}^{2+}$  and  $\text{Zn}^{2+}$  are also known to substitute for  $\text{Fe}^{2+}$  in magnetite and other magnetic spinels. Nevertheless, the results in Tables 3-4 and 6 suggest that essentially all of the zinc within the bulk ashes is located in water-insoluble non-magnetic materials.

The XRF results in Table 6 show substantial  $\text{SiO}_2$  in the magnetic samples. Because magnetite and other magnetic spinels typically lack silicon, the  $\text{SiO}_2$  is probably located in glass surrounding some of the magnetite grains. The XRF data in Table 6 when corrected with the information from Table 5 indicate that no more than 3% of the nickel and 7% of the vanadium in the two ashes are associated with magnetic materials.

Table 6: Chemistry of ashed bulk, magnetic, and magnetically depleted portions of fly ashes 93067 and 93068.

Fly ash 93067

Wt% Oxide or ppm	Average Bulk (after ashing with ASTM Method D 3174-97)	Magnetic Component	Water washed and magnetically depleted
$\text{SiO}_2$	44.59	19.42	51.86
$\text{Al}_2\text{O}_3$	20.62	8.07	23.94
$\text{Fe}_2\text{O}_3$	20.60	61.91	13.39
CaO	2.55	1.16	1.70
MgO	0.90	0.49	0.92
$\text{K}_2\text{O}$	2.54	0.72	2.85
$\text{Na}_2\text{O}$	0.24	0.02	0.22
$\text{P}_2\text{O}_5$	0.20	0.12	0.23
$\text{TiO}_2$	1.20	0.59	1.30
$\text{SO}_3$	1.95	0.24	1.02
Ni	1150	390	1612
V	7352	6159	8188
Zn	289	<1	460

## Fly ash 93068

Wt% Oxide or ppm	Average Bulk (after ashing with Method D 3174-97)	Magnetic Component	Water washed and magnetically depleted
SiO <sub>2</sub>	44.46	21.59	50.11
Al <sub>2</sub> O <sub>3</sub>	20.69	8.77	23.06
Fe <sub>2</sub> O <sub>3</sub>	20.59	59.00	14.34
CaO	2.59	1.20	1.55
MgO	0.91	0.51	0.90
K <sub>2</sub> O	2.52	0.83	2.79
Na <sub>2</sub> O	0.23	0.02	0.20
P <sub>2</sub> O <sub>5</sub>	0.21	0.11	0.23
TiO <sub>2</sub>	1.19	0.64	1.29
SO <sub>3</sub>	2.02	0.23	1.00
Ni	1138	378	1656
V	7340	5635	8079
Zn	297	<1	496

## CONCLUSIONS

Leaching studies and chemical analyses of bulk, magnetic, and magnetically depleted samples of two petroleum coke-bituminous coal fly ashes indicate that vanadium and nickel are largely associated with non-magnetic and water-insoluble materials. Therefore, magnetic extractions of these ashes for the economic recovery or environmental treatment of these metals would probably be ineffective. Currently no primary drinking water standards exist for nickel and vanadium. Nevertheless, batch studies indicate that significant leaching of nickel and vanadium is not expected.

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