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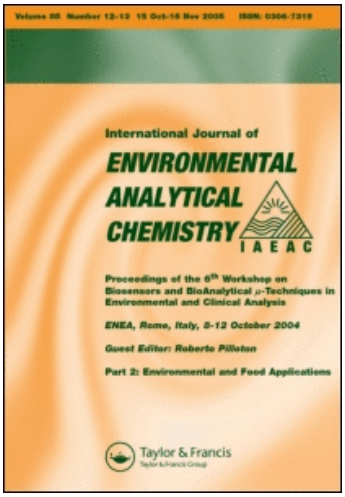

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Solubility of Trace Metals from Fly Ash from the Combustion of Lignite in an Atmospheric Fluidized Bed Combustor

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Fly ash has been collected from the baghouse of an experimental atmospheric fluidized bed combustor (AFBC) burning Beulah, N.D., lignite. The bulk ash has been size-separated after collection, and chemical analyses have been performed on the largest fraction, which had a mass median diameter of 2.0 μm. This lignite AFBC ash lacks the predominant aluminosilicate core characteristic of fly ash from the combustion of pulverised bituminous coal. Instead, it consists primarily of calcium carbonate. It appears that a large fraction of the ash is derived from the limestone bed material, rather than from the lignite fuel. The bulk concentrations of trace metals are within normal ranges, although the enrichment factors for Mn, Cr, Mg, Ni, K, and Ca are exceptionally large.

Although the concentrations of trace elements in this ash are unremarkable, these elements are exceptionally soluble in acidic solution. There is greater than 90% solubility for Al, As, Ca, Cu, K, Mn, V, and Zn. The solubilities of Fe, Ni, Pb, and Si are less than 90% but are significantly increased over those observed for fly ash from conventional combustion of pulverized coal.

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INTRODUCTION

The world-wide use of coal is expected to increase in the coming decades.[1] Although a number of processes are either available or under development for the conversion of coal to gaseous or liquid fuels, direct combustion is likely to continue as the primary energy utilization technology in the near term, especially for direct heat and electricity production.[2] Fluidized-bed combustion (FBC) offers a number of advantages over conventional combustion of pulverized coal (PCC). The addition of limestone or some similar calcium mineral to the bed eliminates a major fraction of SO_x emissions, while the lower combustion temperature compared to PCC reduces NO_x emissions.[3] Atmospheric fluidized bed combustion (AFBC) technology is nearing commercial viability, so the use of AFBC units is expected to increase rapidly.[4]

Advances in emission control technologies have drastically reduced the release of particulate matter (fly ash) from large-scale combustors. Nonetheless, the total mass of coal ash generated annually is so large that significant amounts of material are still released into the atmosphere.[5] In addition, the ash collected at the combustion site must still be disposed of, often by burial in strip pits, so that one must be concerned about the effect of fly ash leachates on water quality. This is particularly true for lignite ashes, since the original lignite and the ash which replaces it may be perfused by groundwater.

The elemental composition of a limited number of AFBC fly ashes has been measured and does not appear to differ markedly from that of fly ash from conventional combustion of similar coals.[6,7] One significant difference is that the concentrations of volatile trace elements in AFBC ash lack the strong particle-size dependence[6] which is characteristic of the respirable particles from PCC.[8–12] This lack of size dependence has been attributed to the lower combustion temperatures in AFBC units.[6]

One of the primary advantages of AFBC units is their ability to burn lower grades of coal,[4] which comprise a major fraction of the total U.S. coal reserves.[13] Thus a potential impact on atmospheric emissions may evolve not from combustor effects *per se*, but from a shift in the fuel composition. The concentrations of the bulk components of lignite ash have been well-characterized.[13–19] The ashes tend to be basic, with a large fraction of soluble calcium.[14,20] However, there are very few reports of the concentrations or solubilities of trace elements in lignite ash.[13,21] This paper reports bulk concentrations, enrichment factors and solubilities of selected trace metals in the fly ash from an AFBC unit burning North Dakota lignite. The results are compared to the limited data available on other lignite ashes, as well as the larger data base on fly ash from bituminous coals.

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EXPERIMENTAL

Collection and preparation of ash

The ash used in this study was initially collected from the baghouse hopper of the experimental AFBC unit at the Grand Forks Energy Technology Center (now the North Dakota Energy Research Center) which was burning Beulah, North Dakota lignite. The combustion test conditions have been described in detail.[22,23] After collection, the ash was size separated into five fractions, with volume median diameters of 20, 2.7, 2.0, 1.0, and 0.8 μm (Donaldson–Majac Co., Minneapolis, MN). The data reported here are primarily on the 2.0 μm ash, which represented the largest fraction of the total ash sample.

Chemical analyses

Fly ash samples for bulk elemental analyses were digested by sequential treatment with HCl and HF, and metal ion concentrations were determined by atomic absorption spectroscopy using a Perkin–Elmer model 306 as described previously.[24] A second series of samples was prepared by suspending one gram of ash in 100 mL of 0.50 M HCl and mechanically shaking the suspension for 24 hrs. The remaining ash particles were removed by filtration through 0.2 μm nuclepore filters, and the solution was analysed by atomic absorption spectroscopy.

Electron microscopy and X-ray fluorescence analyses of single particles were performed by the Department of Geology, University of California, Davis, CA, using a Hitachi S450 electron microscope with a Tracor Northern 2000 energy dispersive spectrometer for X-ray microanalysis.

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RESULTS

The bulk elemental analyses for the major components of the fly ash are listed in Table 1, along with a summary of the literature data on the composition of ashes from both lignite[13–19] and bituminous/sub-

Table 1 Concentrations of major components of AFBC lignite ash and literature values for lignite and coal ashes[a]

Element	*AFBC ash*	*Lignite ashes*			*Coal ashes*		
		n[b]	*Median*	*Range*	n[c]	*Median*	*Range*
Al	2.56	19	6.99	3.92–10.95	37	10.90	5.91 –21.00
Ca	20.90	19	13.8	3.86–30.14	33	3.95	0.40 –22.06
Fe	2.55	19	5.32	1.4 –13.37	37	6.90	2.71 –28.99
K	0.576	17	0.74	0.08– 2.16	36	1.42	0.13 – 5.00
Mg	7.69	18	1.80	0.66– 6.08	31	1.64	0.20 – 3.03
Na	7.14	17	2.37	0.15–14.0	33	0.35	0.05 – 2.30
Si	2.49	17	16.1	6.91–28.1	22	20.30	10.80 –35.0
Ti	0.18	17	0.66	0.36– 1.02	36	0.52	0.006– 1.2

[a]Concentrations expressed as percent by weight.
[b]n = number of individual ash samples. Data taken from references 13–19, 21.
[c]n = number of individual ash samples. Data taken from references 8–10, 14, 15, 17, 25–30.

bituminous coals.[8–10,14,15,17,21,25–30] Lignite ashes tend to have significantly higher concentrations of Ca and Na, with slightly lower concentrations of Al and Si. One of the most unusual features of the ash in this study is the extremely low content of aluminosilicate. The silicon content of the ash is only about 2.49%, whereas typical lignite and coal fly ash have median concentrations of Si of 16.1% and 20.3% ppm, respectively. The aluminum content of this ash is also low at only 2.56%, compared to median values of 6.99% and 10.9% for lignite and coal fly ashes, respectively. In addition, the Ti concentration of this AFBC ash is below the range for other lignite ashes.

Instead of an aluminosilicate core, the lignite ash used in this study has high levels of Ca and Mg, which together account for almost 30% of the weight of the ash. Lignite ashes have substantially higher concentrations of Ca than do coal ashes. Although the Ca content of this AFBC ash is high, it is within the range of other lignite ashes. However, this AFBC ash has 7.69% of Mg, which is well above the literature range for either coal or lignite.

Single particles of this ash were examined by scanning electron microscopy and analyzed by X-ray microprobe. The ash is highly agglomerated and consists primarily of clusters of irregular particles which contain very high calcium concentrations. There are a few angular aluminosilicate particles. The fused spherical particles characteristic of PCC ash are relatively rare. There are spherical particles, but they contain high concentrations of calcium as well as aluminum and silicon.

The bulk concentrations for trace elements in the AFBC lignite ash are given in Table 2 along with literature data on other lignite and coal ashes. There is general agreement between these values for the 2 μm size fraction of the AFBC ash and the values reported for the unfractionated hopper ash,[22,23] although there appears to be some enrichment of Cr, Mo, Ni, Pb and Zn in the 2 μm size fraction. In most cases the trace element concentrations for the AFBC ash and the PCC lignite ash described by Furr *et al.*[6] are within the literature range for coal ashes. The ash described by Henry and Knapp[21] is highly anomalous. The ash has extraordinarily high levels of Zn, Pb, Cd, Mo, and As. It appears that this lignite contained a vein of ZnS, which contained high concentrations of chemically similar metal ions such as Pb and Cd.

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Table 2 Concentrations of trace elements of AFBC lignite ash and literature values for lignite and coal fly ashes[a]

Element	*AFBC ash*	*Lignite PCC ash*		*Coal PCC ash*		
		Ref. 15	*Ref. 16*	*n*[b]	*Median*	*Range*
As	74	2,000	34	41	80	2.3– 1,200
Ba	4,990	200	6,917	32	1,020	465 – 7,800
Be	1.3	—	—	—	—	—
Cd	~1	2,200	0.3	34	1.2	0.1– 51
Co	~0	15	8.0	35	32	5 – 90
Cr	85	400	43	39	156	34 – 1,500
Cu	21	400	75	40	180	20 – 616
Ga	~30	—	—	—	—	—
Mn	1,270	100	543	36	200	58 – 1,100
Mo	33	500	19	34	29	4.2– 70
Ni	68	200	13	36	45	1.8– 900
Pb	96	7,400	12	40	44	3 – 1,500
Sr	3,600	200	3,855	—	—	—
V	26	300	73	36	256	31 – 1,180
Zn	45	73,000	15	40	120	14 –15,000

[a]Concentrations expressed as μg metal per g of ash.
[b]*n* = number of individual coal ash samples. Data taken from references 8–10, 14, 15, 21, 25–30.

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The composition of both the lignite and the limestone used in this study have been reported, along with the feed-rates of both materials during the combustion test.[22,23] Table 3 list the concentrations of several elements in the lignite and the limestone, as well as an estimate of the percentage of the total input of each element derived from the lignite. Only for aluminum, barium, and titanium does over 90% of an element originate from the lignite. Of course the percentages in Table 3 cannot be applied directly to the hopper ash. There are several other output streams from the combustor, and one would not expect an even distribution of each element among these streams.

Enrichment factors are often used to assess the increased concentrations of particular trace elements relative to the aluminosilicate matrix material which comprises the core of conventional coal fly ash. Since virtually all the input aluminum originates from the lignite, enrichment factors for this ash have been calculated based on aluminum, using the formula

Table 3 Feed sources of metal ions into the combustor[a]

Element	*Lignite*	*Limestone*	*% from lignite*
Al	6,460	3,098	92
As	4	<16	—
Ba	400	22.5	99
Ca	14,600	204,000	29
Cd	0.13	0.60	55
Co	1.7	10	50
Cr	2.1	10	55
Cu	2.0	1.5	88
Fe	5,910	15,780	68
K	376	2,820	43
Mg	3,980	115,400	17
Mn	25	1,601	8.2
Ni	1.2	4.8	58
Pb	<1	<8	—
Si	8,470	75,900	39
Ti	242	122	92
V	3.3	9.5	66
Zn	1.9	11.8	48

[a]Calculated from data in Reference 22 and expressed as μg metal per g of feed material (limestone plus lignite).

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$$EF_x = \frac{\text{ppm } X \text{ in ash}}{\text{ppm } X \text{ in coal}} \times \frac{\text{ppm Al in coal}}{\text{ppm Al in ash}} \quad (1)$$

The enrichment factors for selected elements are shown in Table 4 along with a range of literature values for PCC ashes.[8,27–29,31,32] The trace elements As, Cd, Co, Cu, Ti, V, and Zn show enrichment factors typical of PCC coal fly ash. However, the enrichment factors for Cr, Mn, and Ni are quite high and out of the range for conventional coal ashes. There is also a strong enrichment of Ca and Mg.

Often the smaller particles from PCC combustors are enriched in trace metals.[8–12] However, previous reports have indicated that the elemental composition of FBC ash shows little dependence on particle size, presumably due to the lower combustion temperature involved in FBC.[6] In this study analyses were also performed on

Table 4 Comparison of enrichment factors for AFBC lignite ash with literature values for PCC coal ash

Element	*EF*[a]	*PCC Lit. values*		
		n[b]	*Median*	*Range*
Al	1.0	9	1.0	0.8– 1.3
As	4.7	7	6.6	0.9–13.6
Ca	3.6	5	0.9	0.7– 1.0
Cd	1.9	4	—	2.0–15
Cr	10.2	7	2.2	0.9– 2.6
Cu	2.6	4	—	1.2– 2.4
Fe	1.1	7	1.1	0.9– 1.3
Mg	4.9	4	—	0.6– 1.1
Mn	12.8	5	1.1	0.7– 1.8
Ni	14.3	4	—	0.9– 2.1
K	3.9	5	1.0	0.7– 2.1
Si	0.76	1	—	1.0
Ti	1.9	3	1.4	1.4– 2.3
V	2.0	5	3.0	1.8– 5.7
Zn	5.9	9	2.7	1.1–17.6

[a]Defined in Eq. (1).
[b]Number of individual coal ash samples. Data taken from references 8, 27–29, 31, 32.

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size-separated fractions of this ash which had volume-median-diameters of 1 and 2.7 μm. The only consistent variations with particle size were for Na, Pb, Sr, and Ti. These results generally confirm earlier conclusions about a lack of strong dependence of composition on particle size, although the range of particle sizes used in this study was rather small.

Acid leaching has been used to estimate the fractions of individual elements which are on the surfaces of the fly ash particles, rather than inbedded in the aluminosilicate core. Table 5 lists the μg of metal leached per gram of AFBC ash and the fraction of total metal content removed from the particles by acid leaching. For comparison, Table 5 also contains values of f_n, the fraction of "non-matrix" material in a typical coal fly ash.[33] There are striking differences in the elemental solubilities between this lignite ash and the PCC ash studied by Hansen *et al.*[33] The PCC ash is characterized by a low acid solubility of Si, Al, K, and Pb. However, in the FBC ash 66% of the Si and Pb and essentially 100% of the K and Al are soluble.

Table 5 Comparison of acid solubility of metal ions from lignite AFBC and coal PCC fly ashes

Element	*AFBC lignite ash*		*Coal PCC ash*
	μg/g ash	*% of bulk conc.*	f_n[a]
Al	24,200	95	17
As	68	92	98
Ca	217,000	104	74
Cu	21	100	46
Fe	20,400	80	23
K	5,830	100	9
Mn	1,400	110	27
Ni	43	63	40
Pb	63	66	13
Si	16,900	66	4
V	42	165[b]	75
Zn	43	95	78

[a]Data from Reference 31. f_n refers to the fraction of "non-matrix", i.e. acid-soluble, material for each element.

[b]High value reflects the greater experimental errors resulting from low concentrations of V and the low sensitivity of V in atomic absorption spectroscopy.

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The lignite ash also shows large increases in the acid solubilities of Mn, Fe, Ni, and Cu and smaller increases for Zn, V and Ca. The only decrease was an insignificant change from 98% to 92% for As. Thus the increased solubility of metal ions from FBC ash is a very uniform feature, applying to almost every element examined.

The residual particles from the acid leaching studies were examined by scanning electron microscopy. The irregular, calcium-rich particles which comprise the bulk of the untreated ash are removed by the acid, so that other components are now visible. X-ray fluorescence of the leached sample identifies aluminum, silicon, iron, and chlorine as the major components. The treated ash consists primarily of angular aluminosilicate flakes and spheres. Some of the spheres appeared to be predominantly aluminosilicates. Others contained high levels of barium and sulfur, presumably as insoluble barium sulfate. The treated ash also showed fused regions which contained high levels of silicon, chloride, calcium, titanium, and iron. These areas probably consist of chloride salts deposited from the HCl solution as the original particles were dried after acid leaching.

DISCUSSION

Typical coal ash contains about 10% Al and about 20% Si, which comprise an aluminosilicate core to the particle. This composition appears to hold regardless of the combustor, since the Al and Si concentrations in an ash from coal combustion in a pressurized FBC unit fall within normal ranges.[7] There is a definite difference in particle morphometry between emissions from the two types of combustors. Conventional coal combustion generates temperatures high enough to fuse the aluminosilicate core into relatively uniform spheres.[34] The particles from an FBC are not fused, but are irregular in shape, with a large surface-to-volume ratio.[6]

One of the distinguishing characteristics of the AFBC lignite ash is the lack of a prominent aluminosilicate core. The lignite ash described by Henry and Knapp also contained very low levels of Si and Al.[21] However, that ash contained extraordinarily high concentrations of Zn and Cd and is regarded as an anomaly. The ash described here has an even lower Si content. Both the Si and Al concentrations are well below the normal range for either lignite or coal fly ash.

The major chemical components of this ash appear to be calcium salts, as indicated by a bulk Ca content of about 20%. The vigorous gas evolution observed upon acidification of this ash indicates a high carbonate content, and X-ray diffraction studies show calcite as the only major crystalline component in the bulk ash. The high carbonate content accounts for the basic nature of this and other lignite ashes.[13,14,20] If all the calcium and magnesium were present as the carbonates, it would account for almost 80% of the weight of the ash.

There are several indications that the large amounts of Ca and Mg in the AFBC ash are due to the introduction of limestone into the bed to reduce sulfur emissions. Another sample of Beulah lignite has been burned in a conventional pulverized coal combustor.[16] There are significant differences in the elemental composition of the ashes from the two types of combustors. The ash from the pulverized coal combustor has only 40% as much Ca and 22% as much Mg as the AFBC ash. Conversely, the PCC ash has three times the concentration of Al and almost seven times the concentration of Si. Although one cannot rule out variations in the lignite samples

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themselves, it certainly appears that substantial amounts of Ca and Mg are added to the ash during AFBC combustion.

A contribution to this ash from the bed material is also indicated by the enrichment factors for Ca and Mg (see Table 4). Since the enrichment factors are calculated relative to the Al concentrations as an internal standard, they are not subject to artifacts from variations in the composition of the lignite. The enrichmnt factor for Ca is 3.6, compared to a very narrow literature range of 0.7–1.0 for PCC ashes. Similarly, the Mg enrichment factor of 4.9 is well above the literature range of 0.6–1.1.

Thr limestone bed material may also be a significant source of trace element emissions. Over 90% of the manganese entering the combustor is associated with the limestone. The Mn content of the ash is very high, and the enrichment factor for Mn is 12.8, compared to a usual range of 0.7 to 1.1. High enrichment factors for Cr and Ni indicate that the bed material is supplying significant amounts of these elements as well. Elemental analyses of single particles show a large fraction of calcium rich particles that appear to be bed material, rather than typical fly ash. Thus it is not necessary to postulate volatilization of these trace elements to explain their enrichment in the ash.

A distinctive feature of the AFBC lignite ash is the high acid solubility of the metal ions. There is greater than 90% dissolution of Al, As, Ca, Cu, K, Mn, V, and Zn. The lack of a stable aluminosilicate core is readily evident from the dissolution studies. In the FBC ash, 95% of the Al and 66% of the silicon dissolve, compared to values of 17% and 4% for PCC coal fly ash. The Mn and K are largely associated with the aluminosilicate core of conventional coal fly ash particles, and acid leaching removed only 27% and 9% of Mn and K, respectively.[33] In the ash described here, 100% of each of these elements is acid-soluble.

It appears that the enhanced solubility is a function of both the type of coal and the combustor. Previous studies on lignite ash from PCC indicated a high solubility of Ca and Mg.[13,21] However, the solubilities for K, Al, and Si were intermediate between the very high values associated with the lignite AFBC ash described here and the low values reported for PCC coal ash.[33] It appears that the AFBC combustor may leave the aluminosilicate fraction of the ash more susceptible to acid leaching than does PCC combustion.

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There have been other studies on aqueous leaching of fly ashes.[13,15,20,21,25,35–37] The pH of the leachate is determined by the composition of the ash. For lignite ashes the pH tends to be quite basic, so that the concentrations of most elements in the leachate are determined by the solubility products of the hydroxide and carbonate salts. Thus it is difficult to compare these data directly to our results on leaching by acidic solutions.

CONCLUSIONS

Previous reports have emphasized the fact that there is little difference in the overall trace element content of FBC ash compared to PCC ash. Although this is generally true, there appear to be cases in which the bed material contributes significant amounts of individual trace elements, e.g. Mn in the ash used in this study.

In addition to bulk concentrations, one must also consider the solubility of the trace elements in an assessment of their potential health effects. It appears from this study that the trace elements from lignite ash, and especially lignite ash from AFBC units, are markedly more soluble than those from conventional coal fly ash, possibly due to the greater solubility of the aluminosilicate fraction of the ash. This result suggests that the trace elements will be much more readily removed from particles which are inhaled or buried in disposal sites.

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