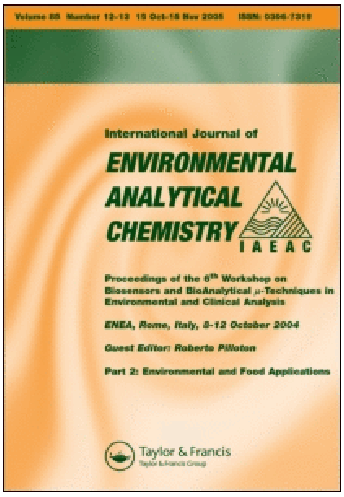

International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

Chemical Characterization of Respirable Coal-Oil-Mixture Fly Ash

Wesley R. Harris[a]; Otto G. Raabe[a]; David Silberman[a]; Stephen V. Teague[a]
[a] Laboratory for Energy-Related Health Research, University of California Davis, Davis, CA

To cite this Article Harris, Wesley R. , Raabe, Otto G. , Silberman, David and Teague, Stephen V.(1984) 'Chemical Characterization of Respirable Coal-Oil-Mixture Fly Ash', International Journal of Environmental Analytical Chemistry, 18: 3, 167 — 182

To link to this Article: DOI: 10.1080/03067318408076999

URL: http://dx.doi.org/10.1080/03067318408076999

Intern. J. Environ. Anal. Chem., 1984, Vol. 18, pp. 167–182
0306-7319/84/1803-0167 $18.50/0

Printed in Great Britain

Chemical Characterization of Respirable Coal–Oil-Mixture Fly Ash

WESLEY R. HARRIS, OTTO G. RAABE, DAVID SILBERMAN and STEPHEN V. TEAGUE

Laboratory for Energy-Related Health Research, University of California, Davis, Davis, CA 95616

(*Received February 7, 1984*)

This paper reports the elemental analysis of respirable (VMD = 2.6 μm) baghouse collected fly ash from the combustion of a slurry of 60% oil and 40% coal. Compared to coal fly ash, this material has high concentrations of several trace elements, with the vanadium and nickel levels contributed by the oil being particularly high. Trace elements originating from the oil are highly enriched in the respirable ash. Leaching the coal–oil-mixture particles in HCl shows that the heavy metals are generally more soluble than is typical of coal fly ash.

KEY WORDS: Fly ash, trace elements, leaching.

INTRODUCTION

One of the environmental and public health concerns associated with fossil fuel combustion is the emission of large quantities of fly ash into the atmosphere. Even with very effective particle control technology, huge quantities of fly ash are still emitted annually from stationary sources.[1] The composition of coal fly ash has been studied by several investigators.[2-7] It consists largely of a relatively inert aluminosilicate core, which is coated with a variety of potentially toxic heavy metals. The concentration of many metals is a function of particle size,[2,3,5,7] with a strong enrichment of several heavy metals and other surface constituents in the smallest, respirable size range.

Since particle abatement equipment is designed to remove the larger particles, stationary sources may be releasing a relatively high percentage of the potentially more hazardous fine particles.[8] These smaller particles will travel farthest from the source before being removed from the air, thereby potentially exposing a larger population. The smallest particles (less than 5 μm in aerodynamic diameter) are respirable and undergo appreciable deposition in the pulmonary region of the human respiratory tract,[9] and may be retained for extended periods in the deep lung, allowing extensive mobilization of the potentially hazardous chemicals from the particle surfaces.

Oil combustion produces much less ash than does coal combustion.[10] However, where coal fly ash typically has heavy metal concentrations of a few hundred ppm,[2,4,5] oil fly ash may contain over 100000 ppm of elements such as nickel or vanadium.[10,11] Furthermore, since oil lacks any appreciable aluminosilicate core, the metal salts of oil ash are readily soluble in acidic solutions.[10,11] Nonetheless, oil is regarded as the cleaner fuel whose use is restricted by dwindling domestic supplies and higher costs. The use of finely pulverized coal suspended in petroleum oil as a fuel for power plants has been considered by the U.S. Department of Energy and commercial utilities. Such a fuel would take advantage of the native abundance of coal in the United States and might be utilized by existing oil-burning power plants with relatively inexpensive boiler or firebox modifications and minimal conversion time. However, the emissions of both particles of fly ash and sulfur oxides from such a mixture are likely to be substantially larger than for oil alone, and the physical and chemical properties of the fly ash particles produced from the combustion of a coal–oil-mixture (COM) may represent a new environmental problem with a potential health impact different from either coal fly ash or oil fly ash alone. This study was undertaken to evaluate chemical properties which might be related to the potential biological activity of respirable fly ash particles generated by the combustion of a coal–oil-mixture for power generation.

EXPERIMENTAL

Sampling

The samples of fly ash were collected during a test combustion of a mixture of 40% Illinois No. 6 coal and 60% No. 6 fuel oil in a 700 HP water tube industrial oil-designed boiler at the Department of Energy's Pittsburgh Energy Technology Center (PETC). Samples were taken from the baghouse collection hoppers and subsequently size classified into three fractions as previously described.[12] These fractions consisted of 2.3 kg of very coarse particles (VMD = 95 μm), 103 kg of coarse particles (VMD = 12.8 μm), and 7.7 kg of respirable particles (VMD = 2.6 μm).

This baghouse was outfitted with 120 teflon-coated fiberglass filter bags each 14 cm in diameter by 360 cm long designed to withstand operating temperatures in excess of 200°C. The bags were briefly coated with some previously collected COM ash injected into the flue line to create the needed base cake of ash prior to use in this study, but they had not been used in any prior tests. Each bag was pulsed with filtered air every 1.5 min in a 12 minute cycle. Ash collected during the first two hours of sampling was discarded. These precautions were taken to preclude contamination of the collected ash with other ash types or experimental test fuels from previous combustion tests.

Chemical analyses

Instrumentation Metals were analyzed by flame methods with a Perkin-Elmer model 306 atomic absorption spectrophotometer using the quadratic standardization function described by Limbeck *et al.*[13] Coal samples were high temperature ashed (HTA) in a muffle furnace at 500°C. Oil and COM residues were ashed in an L.F.E. model 504 low temperature asher. Metal concentrations in samples of coal–oil-mixture ashes were also determined by neutron activation analyses performed by Dr. Roy Filby at Washington State University according to published procedures.[14]

Reagents and glassware All water for washing, rinsing, and dilutions was first deionized and then glass distilled. Glass and plasticware were all soaked in a 1:20 nitric acid bath, rinsed with fresh acid solution and distilled water and dried at 105°C. Hydrofluoric acid (J. T. Baker, 49% w/w), nitric acid (J. T. Baker, 70% w/w), and hydrochloric acid (G. F. Smith Co., 20–22% w/w) were all analytical reagent grade. The boric acid (Aldrich, Gold Label) was 99.999% pure.

Total digestion of fly ash Replicate samples of 2–3.3 g COM ash were shaken for a few hours in 20 ml of 6 M redistilled HCl. Twenty-five ml of concentrated HF was added and the samples were shaken overnight. Individual solutions were filtered (47 mm, 0.2 μm nuclepore filters) into clear 250 ml polymethylpentene (PMP) volumetric flasks. The black residue remaining on the filter paper was washed with several small volumes of distilled water, and the rinsings were added to the volumetric flask. The residue and filter were then transferred to 60 mm glass petri dishes. Distilled water was added and the plates were sonicated in a 1 quart 25 watt Branson ultrasonic bath. The sonicated filter was then removed and the solution was evaporated to dryness at 90°C. The residue was ashed in the LTA overnight at 400 watts in a 0.5 torr oxygen atmosphere.

When ashing was complete, 5 ml of 6 M HCl was added and the solution was heated to 90°C. To avoid splattering and loss of part of the sample, the solution was not allowed to boil. The yellow solution and the insoluble siliceous residue were transferred to the volumetric flask containing the HF and shaken overnight. Ten grams of boric acid was added to the flask, and when the solution had cooled, the sample was brought up to volume with distilled water. After an additional 4–6 hr of shaking, the contents of the flask were vacuum-filtered through a tared 47 mm, 0.2 μm Nuclepore filter. The filtrate was then stored in a 250 ml plastic bottle for subsequent analyses by atomic absorption spectroscopy. The filter and insoluble residue were washed with several portions of distilled water, then dried and weighed. The residue was reported as the percent undissolved material.

Samples of NBS standard coal fly ash were digested and analyzed as described for the COM fly ash. The recovery factors for various elements were calculated as the ratio of our value for the NBS ash to the certified value.

Digestion of coal Four samples of Illinois coal No. 6 (6–7 g/sample) were high temperature ashed in a muffle furnace at 500°C for 63 hrs in glass weighing bottles. The weight loss for each sample was recorded, and the ashes were then pooled. Four samples of the pooled ash (0.2–0.8 g each) were weighed into 100 ml PMP volumetric flasks, and digested essentially as described for the COM fly ash, except that no low temperature ashing was necessary, as there was no visible residue in these samples. The samples were filtered as in the COM ash digestion prior to their analysis.

Digestion of oil Four 1 g samples of fuel oil No. 6 were mixed with equal weights of cornstarch to reduce foaming in 60 mm glass petri plates. The oil–cornstarch samples were dried at 110°C overnight, then transferred to the LTA. The sample chambers of the LTA had to be evacuated very carefully to avoid spattering. The chamber was evacuated until boiling began, then the vacuum was softened until the sample was quiet. This vacuum was then gradually hardened over several hours to remove the volatile oil components. The remaining oil was then ashed for 48 hours at 600 watts under 5–10 torr of a 50–50 volume % argon–oxygen atmosphere. The metal salts were then dissolved by warming the sample in 8.3 ml of 6 M HCl. This solution was transferred to a 100 ml PMP volumetric flask and diluted to volume with distilled water.

Four 1 g portions of cornstarch were also weighed into petri plates as reagent blanks. The cornstarch reagent blanks were ashed for a few hours at 400 watts under 0.5 torr of a 50–50 argon–oxygen atmosphere. The salts were then taken up as described for the oil–cornstarch samples.

HCl leachates Duplicate 2.7 g samples of the COM ash were shaken overnight with 200 ml of 0.5 M HCl. After 24 hrs all suspensions were vacuum filtered through plastic filter funnel assemblies fitted with 47 mm, 0.2 μm Nuclepore filters. The filtrates were stored in 250 ml plastic bottles for analysis by atomic absorption spectroscopy.

RESULTS

Chemical characterization

Bulk elemental concentrations have been determined for both the coarse and respirable ashes by a combination of atomic absorption spectroscopy and neutron activation analysis. Table I lists all elements which were detected at >10 ppm in the respirable ash. The carbon content was estimated from the weight loss from ashing. Samples of the unburned oil and coal which were used to prepare the COM fuel were also analyzed for selected elements, and the results are shown in Table II. The coal contains a higher concentration of every element considered except nickel and lead. In

TABLE I

Elemental composition of the respirable and coarse particles of coal–oil-mixture fly ash.[a]

Element	Respirable (2.6 μm VMD)	Coarse (12.8 μm VMD)	Method[b]	Recovery[c]
C (%)	20	14	ashing	
Si (%)	13.2 (4)[d]	19.2 (2)	AA	96
Al (%)	8.68 (2)	8.61 (2)	NA/AA	105
Fe (%)	8.06 (3)	9.90 (2)	NA/AA	
Ca (%)	1.7 (2)	2.8 (3)	NA	
Na (%)	1.53 (4)	0.513 (3)	AA	89
K (%)	1.6 (2)	1.44 (4)	AA	105
Mg (%)	1.2 (3)	1.1 (1)	NA	97
Ti	5,900 (500)	4,200 (200)	NA/AA	110
Pb	4,520 (130)	657 (14)	AA	95
Zn	4,280 (30)	730 (15)	AA	100
Ni	4,100 (150)	760 (20)	NA/AA	98
V	4,000 (10)	760 (20)	NA/AA	93
Ba	1,630 (110)	760 (40)	NA	
Hg	500 (160)	480 (120)	NA	
Zr	450 (50)	270 (30)	NA	
Cr	428 (5)	210 (3)	NA/AA	98
Mn	368 (5)	300 (10)	NA/AA	81
Cu	360 (1)	107 (3)	AA	93
Mo	252 (3)	53.4 (5)	AA	103
Co	228 (10)	52 (1)	NA/AA	101
Sr	222 (14)	167 (11)	AA	101
Rb	156 (11)	160 (10)	NA	
Ce	106 (7)	93 (2)	NA	
As	103 (1)	25.3 (6)	NA	
Ga	102 (5)	19.1 (3)	NA/AA	96
La	69 (2)	61 (3)	NA	
Se	31 (2)	19 (1)	NA	
U	30 (2)	17.7 (4)	NA	
Sc	24 (3)	19 (1)	NA	
Sb	23 (2)	4.0 (2)	NA	
Th	19 (1)	14.4 (4)	NA	
Cd	16.3 (1)	2.0 (1)	AA	
Sm	10 (2)	11 (2)	NA	
Cs	10.3 (5)	7.4 (3)	NA	

[a] Values in μg of metal per gram of ash unless otherwise noted.

[b] AA = atomic absorption spectroscopy, NA = instrumental neutron activation analysis.

[c] Percent recovery of individual elements based on an analysis of NBS certified coal fly ash.

[d] Numbers in parentheses indicate the uncertainty in the least significant digit.

TABLE II

Concentrations of selected elements in the native oil and coal fuels ($\mu g/g$).

Elements	Coal	Oil
Al	11,400 (300)[a]	<5
Cr	32.5 (7)	n.d.[b]
Cu	10.3 (2)	2.1 (1)
Mn	45 (2)	0.5 (2)
Ni	16 (1)	25 (2)
Fe	17,500 (90)	45 (4)
V	29 (1)	22 (2)
Zn	90 (2)	10 (1)
As	2.2 (1)	0.13 (1)
Mo	57 (3)	n.d.
Pb	5.0 (8)	10 (2)
Si	30,000 (100)	n.d.

[a] Numbers in parentheses indicate the uncertainty in the least significant digit.

[b] n.d. = not detected.

the case of iron, silicon and aluminum, the concentrations in coal are several orders of magnitude greater than those found in the oil, such that essentially all the aluminum found in the ash probably originates from the coal.

The ash content of the coal was determined by ashing both in a muffle furnace at 500°C and in a plasma low temperature asher. The results are 12.8 ± 0.3% ash from the muffle furnace and 15.6% from the low temperature asher. Part of this discrepancy may be due to the decomposition of carbonate in the furnace, while carbonate salts are more stable in the low temperature asher. The value reported by PETC was 11.5%.

Electron micrograms of both the coarse and respirable COM samples are shown in Figure 1. The coarse fraction (VMD = 12.8 μm) consists primarily of large spheres typical of aluminosilicates from coal. This fraction also contains some flakes and large irregular particles which based on the high carbon content of the ash may represent unburned coal. The respirable fraction (VMD = 2.6 μm) consists largely of two types of particles. One is the spherical particles typically found in coal fly ashes. These are mixed and

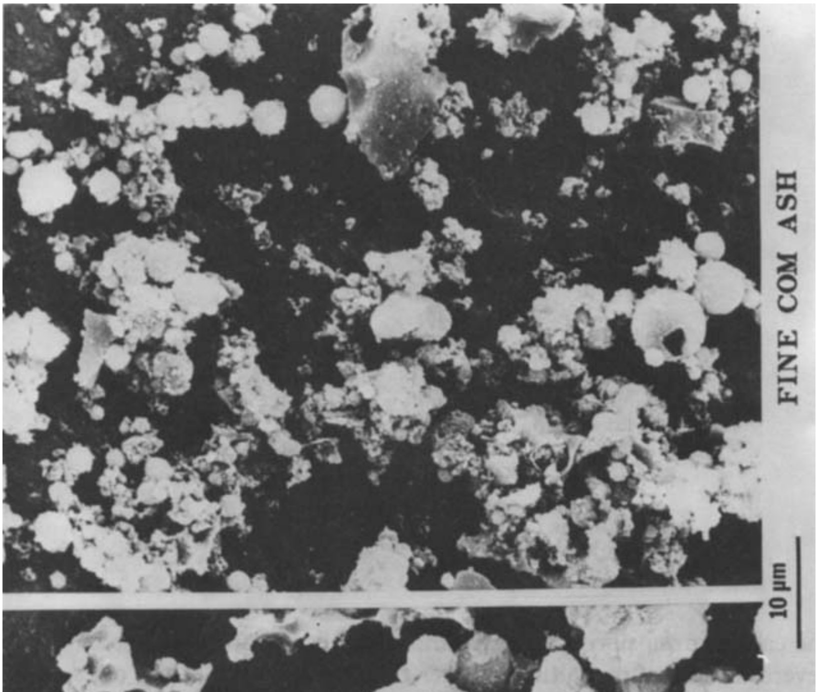

FIGURE 1 Scanning electron micrographs of the coarse coal–oil-mixture (COM) fly ash fraction (VMD = 12.8 μm) and the respirable-sized COM fly ash fraction (VMD = 2.6 μm) used in this study.

frequently coated with aggregates of very small particles that form clusters in the range of 1–5 μm in size. The respirable fraction also contains a small number of large irregular particles similar to those seen in the coarse ash.

Several individual particles of COM ash were analyzed using an SEM with an energy disperse X-ray microprobe system. The analyses included a series of small spheres and a series of the aggregates of very small particles, and the results are shown in Table III. The composition of the spheres is typical of coal fly ash. There is a preponderance of Al and Si, with low concentrations of sulfur and essentially undetectable concentrations of Ni and V. The composition of the aggregates is uniform, but distinct from that of the spheres. The aluminum and silicon content is 67 atom %, compared to 85 atom % in the spheres. The most significant change is in the sulfur concentration, which is ~14 atom % in the aggregate, compared to only ~2 atom % in the spheres. Other than iron, nickel and vanadium were the only trace elements detectable in the aggregates. However, even these elements were detected at less than 1 atom % and were found only in 3 of 10 particles for nickel and 7 of 10 particles for vanadium. A few of the large irregular particles were also analyzed. The composition was extremely variable, such that it is not possible to describe general features of such particles.

TABLE III

XRF microprobe analyses of individual particle types (atom %).

Element	Oil ash crystals	COM spheres	COM aggregates
S	61	1.7	14
Ni	18	n.d.[a]	<0.5
V	9.2	n.d.[a]	<0.8
Fe	4.1	3.1	6.9
Ca	3.7	3.3	3.8
Si	2.6	60	45
Al	1.1	25	22
K	0.8	4.9	4.3
Mg	0.5	0.2	n.d.[a]
Na	n.d.[a]	0.8	1.2

[a] Not detected.

Individual particles of a stack-collected oil fly ash were also chemically analyzed with the X-ray microprobe. The oil fly ash consisted primarily of aggregations of small microcrystals similar to the oil ash particles previously described by Henry and Knapp.[10] The average composition of four such particles is shown in Table III. These particles are characterized by a very high sulfur content and 10–20 atom % vanadium and nickel. In sharp contrast to coal and COM ash, the genuine oil ash particles contained only 2.6 atom % silicon and 1.1 atom % aluminum. The oil ash also contained a small number of spheres which visually resemble coal fly ash. These spheres contained 60–70 atom % of aluminum and silicon, with about 10 atom % sulfur and 1 atom % nickel and vanadium.

Enrichment factors

Previous studies have shown that the aluminum in coal fly ash is associated primarily with the aluminosilicate matrix in the core of the particles,[15] and that its concentration is largely independent of particle size, especially in particles $>1\,\mu$m. Therefore, we chose to define an enrichment factor for the respirable and coarse ash samples for an element X in terms of aluminum concentrations as

$$EF=\frac{[X]_A/[Al]_A}{[X]_C/[Al]_C} \qquad (1)$$

where the subscripts A and C refer to the ash and coal, respectively.

The enrichment factors for the two size fractions are listed in Table IV. The enrichment of Ni, Pb and V is very high, reflecting the contribution of large amounts of these elements from the oil. Smaller changes between the enrichment factors of the fine and coarse fractions are characteristic of those elements such as Cr, Mn, Si, and Fe, which originate principally from the coal. Higher and more variable enrichment factors are associated with elements originating in significant part from the fuel oil.

Leaching We have examined the solubility of the trace elements associated with the respirable (VMD $=2.6\,\mu$m) COM fly ash particles by leaching samples in 0.5 M HCl. The amounts of selected elements leached by this solvent are listed in Table V.

TABLE IV

Enrichment factors for selected transition elements in the two size fractions of coal–oil-mixture fly ash.

Element	Respirable (2.6 μm VMD)	Coarse (12.8 μm VMD)	Lit. range[a]
Cr	2.3	1.1	1.1–3
Cu	6.0	1.8	1.1–2.4
Mn	1.4	1.2	0.7–1.1
Ni	44.3	8.3	1.4–2.1
Fe	0.8	1.0	0.8–1.1
V	23.8	4.6	0.8–2.5
Zn	8.2	1.4	1.5–7.0
As	6.1	1.5	1.2–10.5
Mo	0.6	0.1	0.8–4.2
Pb	118	17	1.4–8.1
Si	0.6	0.8	—

[a] Literature values for 1–5 μm particle sizes from references 3 and 5.

TABLE V

Solubility of metal ions from respirable coal–oil-mixture fly ash.

Element	Mass removed by 0.5 M HCl (μg/g ash)	Mass removed by 0.5 M HCl (% of bulk)	f_n[a]
Al	27,500	32	17
Cd	14	85	54
Co	198	86	23
Cr	198	47	53
Cu	268	74	46
Fe	20,700	26	23
K	7,320	44	9
Mn	175	48	27
Mo	152	60	86
Na	12,100	79	19
Ni	2,580	66	40
Pb	3,720	82	13
Sr	178	80	48
Ti	2,000	34	19
V	3,470	93	75
Zn	2,730	64	78

[a] f_n = fraction of "non-matrix" or surface material from reference 15.

DISCUSSION

Chemical composition

Oil combustion typically generates a much smaller amount of ash than coal combustion. Thus, even though the fuel was 60% oil by weight, most of the mass of the fly ash probably originates from the coal. Therefore one might expect the ash to resemble conventional coal ash. However, even though relatively little ash is produced by oil combustion, oil fly ash is generally very rich in heavy metals,[10, 11] so that the much smaller mass of oil ash actually contributes disproportionately large amounts of many metals to the final COM ash mixture and especially to the respirable size fraction. The respirable COM fly ash (VMD 2.6 μm) is highly enriched in several trace elements compared to the levels found in typical coal fly ash samples. The levels of V (4000 ppm), Ni (4100 ppm), Zn (4300 ppm), and Pb (4500 ppm) are especially high. In addition to these elements, Co, Cr, and Mo appear to have higher concentrations in the respirable COM ash than usually found in coal fly ashes.

Normally most of the mass of coal fly ash is composed of an aluminosilicate core. In the respirable COM ash, the concentrations of aluminum and silicon are somewhat low. This is largely due to the anomalously high carbon content of 20%. Typical coal fly ash has very little unburned carbon. It is not clear whether the higher carbon content is representative of COM ash or whether further improvement in the combustion conditions could lower the amount of unburned carbon. If significant reductions in the carbon content are achieved, then the concentrations of V, Ni, Pb, and Zn would presumably approach 5000 ppm.

Previous workers have reported strong size dependences for elements such as As, Cd, Pb, Sb, Se, Zn, Tl, Ni, Cr, W, Ga, and Mo.[3] In general, these are relatively volatile elements. The concentrations of less volatile elements tend to display little, if any, dependence on particle size. Comparison of the composition of the respirable and coarse ash shows that the respirable ash has a greater than four-fold increase in the concentrations of Pb, Zn, Ni, V, Mo, As, Ga, Sb, and Cd. The enrichment of As, Ga, Sb, and Cd could be ascribed to a volatilization procedure. However, the extremely high concentrations of Pb, Zn, Ni, and V in the respirable ash may indicate that elements from the fuel oil are selectively concentrated in the smaller particles.

Because the particles were sized after their collection in the baghouse of the combustion facility, the larger particles are somewhat contaminated with adhering smaller particles. Thus the size-dependence can only be discussed in general terms. However, this type of contamination of the larger particles would tend to mask, rather than enhance, the relative enrichment of trace elements in the respirable fraction. Thus the relative enrichment of the respirable fly ash may be even higher than these data indicate.

The chemical analysis of individual COM particles failed to locate any particles which could be described as typical oil fly ash. The concentrations of sulfur, nickel, and vanadium, even in the aggregates, were too low to identify these particles as oil fly ash. The trace elements in oil fly ash are typically 1000 × concentrated in the ash. With over 20 ppm V and Ni in the oil used in the generation of the COM ash, one would expect concentrations of greater than 2 atom % in the ash, which would be readily detectable by the technique used. Furthermore, all the COM particles examined contained substantial concentrations of aluminum and silicon. Therefore, it appears that the enrichment of normally non-volatile elements in the smaller COM particles is due to the deposition of the metal salts from the oil onto the surfaces of the large number of particles generated from the combustion of the coal. By providing an abundance of nucleation sites, the coal ash appears to prevent the formation of the small, metal-rich crystals typical of oil fly ash.

Enrichment factors

Element enrichment factors for the COM ash are compared with the range of values for similar size coal fly ash samples in Table IV. There is good agreement between the coal and COM values for the elements Cr, Mn, Fe, As, and Zn. Inspection of Table II shows that for a 60% oil:40% coal mixture, more than 90% of the mass of these elements originates from the coal. Conversely, very large enrichment factors are observed for Pb, Ni, and V, and Table II suggests that at least 50% of the mass of these elements is supplied by the oil. About 25% of the copper appears to originate from the oil, and this element has an intermediate enrichment factor which is outside the range of normal coal fly ash, but is not as large as the Pb, Ni and V values. The enrichment factors for Pb, Ni and V also show large increases on going from the coarse to the respirable ash. Thus the elements derived in large part from the oil appear to be especially enriched in the finer, respirable size fly ash.

Leaching studies In addition to establishing the elemental composition of the COM ash, we are also interested in the enrichment of trace elements on the surface of the fly ash particles, since it is this surface material which will initially leach from the particles following inhalation. It has been shown that 0.5 M HCl will strip most of the trace elements from the surface of coal fly ash particles within 24 hrs, but will only slowly dissolve the more inert aluminosilicate matrix material in the core of the particle.[15] Thus the HCl leaching indicates the relative enrichment of specific concentrations of the metal ions on the surface of the particles.

Table V lists the solubility of several elements in 0.5 M HCl, expressed as a percentage of the bulk particle content of each element. Hansen and Fisher[15] have previously introduced the parameter f_n, which is defined as the fraction of an element associated with the "non-matrix" component, i.e. surface layer, of coal fly ash. Thus the HCl solubility values listed in Table V as a percent of the bulk analysis for the respirable particle size-fraction of the COM ash can be compared directly the reported f_n values for coal ash. There is a significant increase in the acid solubility of the elements Ni, Cu, Co, Pb, Sr, K, Ga, Na, Ti, Mn, and Cd in the COM ash. In some cases this increase is quite large; the respective values compared to coal ash f_n for Pb are 82% and 13%, for Na 79% and 19%, for Co 86% and 23%, for K 44% and 9%, and for Ni 66% and 40%. For the elements Pb, Cd, Co, Cu, Sr, V and Na, greater than 70% of the total COM particle content leaches into the HCl. Thus when compared to typical coal fly ash, the COM ash has higher levels of many trace elements, and these heavy metals are generally more soluble and/or more accessible to leaching agents. The substantial increase in the acid solubility of the trace elements in the fine COM ash compared to conventional coal fly ash is consistent with the deposition of the trace elements from the oil on the particle surfaces. The observed enrichment in the respirable fraction would presumably be due to the increased surface-to-mass ratio of the smaller particles.

Acknowledgement

The authors are indebted to K. D. McFarland for sampling assistance, light microscopy, and data analysis; to M. Brummer for preparation of the scanning electron micrographs; and C. Baty for the preparation of the manuscript. We are also indebted to the staff and scientists at the U.S. Department of Energy Pittsburgh Energy Technology Center, particularly Drs. Y. S. Pan and Gerst A. Gibbon and Mr. David Lunifeld, for their help, support and valuable suggestions.

This work was supported by the Office of Health and Environmental Research of the U.S. Department of Energy under contract No. DE-AM03-76SF00472 with the University of California.

References

1. P. Urone and M. A. Kenney, "Atmospheric pollution," in: *Coal Burning Issues* (A. E. S. Green, Ed.), University Presses of Florida, 1980, pp. 169–186.
2. R. L. Davison, D. F. S. Natusch. J. R. Wallace and C. A. Evans, "Trace elements in fly ash: Dependence of concentration on particle size," *Environ. Sci. Tech.* **8,** 1107 (1974).
3. G. L. Fisher and D. F. S. Natusch, "Size dependence of the physical and chemical properties of fly ash," in: *Analytical Methods for Coal and Coal Products* (C. Karr, Ed.), Academic Press, 1979, Vol. III, pp. 489–541.
4. J. A. Campbell, J. C. Laul, K. K. Nielson and R. D. Smith, "Separation and chemical characterization of finely-sized fly-ash particles," *Anal. Chem.* **50,** 1032 (1978).
5. D. G. Coles, R. C. Ragaini, J. M. Ondov, G. L. Fisher, D. Silberman and B. A. Prentice, "Chemical studies of stack fly ash from a coal-fired power plant," *Environ. Sci. Tech.* **13,** 455 (1979).
6. J. W. Kaakinen, R. M. Jordan, M. H. Lawasani and R. E. West, "Trace element behavior in coal-fired power plant," *Environ. Sci. Tech.* **9,** 862 (1975).
7. E. S. Gladney, J. A. Small, G. E. Gordon and W. H. Zoller, "Composition and size distribution of in-stack particulate material at a coal-fired power plant," *Atmosph. Environ.* **10,** 1071 (1976).
8. R. L. Carpenter, G. J. Newton, S. J. Rothenberg and P. B. DeNee, "Respirable aerosols from fluidized bed coal combustion. 2. Physical characteristics of fly ash," *Environ. Sci. Tech.* **14,** 854 (1980).
9. O. G. Raabe, "Deposition and clearance of inhaled aerosols," in: *Mechanisms in Respiratory Toxicology*, Vol. I (H. Witschi and P. Nettesheim, Eds.), CRC Press, Boca Raton, Florida, 1982, pp. 27–76.
10. W. M. Henry and K. T. Knapp, "Compound forms of fossil fuel fly ash emissions," *Environ. Sci. Tech.* **14,** 450 (1980).
11. O. G. Raabe and D. Silberman, "Chemical composition of oil fly ash," Laboratory for Energy-Related Health Research, 1980, unpublished results.
12. O. G. Raabe, K. D. McFarland and B. K. Tarkington, "Generation of respirable aerosols of power plant fly ash for inhalation studies with experimental animals," *Environ. Sci. Tech.* **13,** 836 (1979).

13. B. E. Limbeck, C. J. Rowe, J. Wilkinson and M. W. Routh, "A high-accuracy calibration technique in AA," *American Laboratory* **10,** 89 (1978).
14. F. S. Jacobs and R. H. Filby, "Solvent extraction of oil–sand components for determination of trace elements by neutron activation analysis," *Anal. Chem.* **55,** 74 (1983).
15. L. D. Hansen and G. L. Fisher, "Elemental distribution in coal fly ash particles," *Environ. Sci. Tech.* **14,** 1111 (1980).