# NOTES

# Scanning Electron Microscopy and Energy-Dispersive X-ray Spectroscopy Analysis of Submicrometer Coal Fly Ash Particles

# **David Lichtman\***

Physics Department and Surface Studies Laboratory, University of Wisconsin-Mllwaukee, Milwaukee, Wisconsin 53201

# Susan Mroczkowski

Midwest Research Microscopy Inc., Milwaukee, Wisconsin 53218

■ Scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDX) were used to analyze two groups of submicrometer coal fly ash particles from eastern and western power plants. The composition of the particles was related to the composition of the regional coal used. No sulfur was detected in the ash from the plant using low-sulfur western coal. The power plant using the higher sulfur concentration eastern coal produced ash containing 1.5% SO<sub>2</sub> equivalent. Similar correlations were found for other elements. While essentially all of the particles were spherical, the topography of the two groups was different. The particles from the Bull Run, TN (eastern), collection had a variable topography ranging from smooth to a few surface nodules. These surface nodules had a slightly elevated sulfur concentration. The particles from the Mojave, NV (western), collection were covered with surface nodules of varying size; none were glass smooth.

#### Introduction

As energy sources that are alternatives to oil continue to be investigated, a logical choice, at least for the near future, lies in the use of domestically available coal resources. The potential environmental and physiological effects have been discussed, but definitive studies have not yet been completed on the effect of coal fly ash on biological systems.

One of the possible sources of danger from coal-burning plant emissions lies in the interaction of submicrometer particles with living systems (1). For example, submicrometer particles can penetrate the deep lung regions of humans. In this study, submicrometer particles from two power plants were compared by using scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDX) to determine their basic morphology and composition and if there were any significant differences between the two sets of particles. Previous studies (2) reported on similar measurements taken on micrometer size particles and compared them to some submicrometer particle data.

#### Collection

One set of particles was collected on Aug 30, 1982, from the Bull Run Steam Plant of TVA near Oak Ridge, TN. Kentucky coal was burned in the plant. The stack gas temperature was 280 °F at collection. Stack gas velocity was about 60 ft/s, and the samples were collected isokinetically at a rate of about 0.8 atmospheric cubic feet (ACF)/min. According to Anderson, Inc., for each stage of the collector, the average effective aerodynamic diameter

Table I.	Distribution	of Particles	from	the Col	lection at
<b>Bull Rur</b>	n Steam Plan	t, Oak Ridge,	$\mathbf{TN}^{\mathfrak{a}}$		

plate no.	$D'_{p}, \ \mu m$	$D^{\prime\prime}{}_{\rm p}$ , $\mu{ m m}$	g	%
1	11	7.6	0.0003	3.8
2	7	4.8	0.0012	15.2
3	4.5	3.1	0.0014	17.7
4	3	2.0	0.0018	22.8
5	2	1.4	0.0013	16.5
6	1	0.7	0.0007	8.9
7	0.6	0.5		
8	0.4	0.2	0.0001	1.3
filter			0.0011	13. <del>9</del>

 ${}^{a}D'_{p}$  = effective aerodynamic diameter of a spherical, unit density particle.  ${}^{b}D''_{p}$  = effective aerodynamic diameter, corrected for density = 2.5 and 280 °F.

of spherical particles, corrected to a density of 1 and 2.5 and the prevailing temperature, is shown in Table I, together with the amounts collected.

The later stages which collect the submicrometer particles were used dry to allow for future surface analysis. To minimize particle bounce-off, the first three stages which collect the micrometer particles were lightly greased. This approach apparently worked well since SEM observations indicated that the distribution of particles on each stage was close to that predicted.

The second set of particles was collected at the Mojave Generating Station of the Southern California Edison Co. located at Laughlin, NV, on the Colorado River. The plant burns pulverized Black Mesa (AZ) coal, which is transported from the mine to the plant as a slurry, dewatered, pulverized, and burned in a double boiler installation rated at 800 MW per boiler. Both boilers vent into a common stack after passage through a set of electrostatic precipitators which has a rated efficiency of about 98.5%.

Sampling was performed on Sept 22, 1983, at the outlet of the electrostatic precipitators, just before entering the stack. Approximately 5 ACF of gas was sampled. The collection disks were equilibrated at 70 °F and about 40% relative humidity before each weighing. Table II gives the weight distribution. The total particle loading averages about 0.02 g/ACF, but there is considerable variability. The distribution appears to be bimodal, with maxima of 6 and 0.7  $\mu$ m. Almost 20% of the particles are smaller than 0.4  $\mu$ m, and about 3.5% are larger than 30  $\mu$ m.

#### **Results and Discussion**

**Topography Studies.** SEM was used to investigate the morphology of the fly ash particles in the  $0.3-1.0-\mu m$  range.

Table II. Particulate Distribution from the Mojave Station at Laughlin,  $NV^a$ 

plate no.	$D'_{\rm p},\ \mu{ m m}$	average of 3 runs, %
1	32	3.6
2	16	4.6
3	6	18.0
4	3	11.6
5	1.5	14.0
6	0.7	23.0
7	0.4	6.3
filter		18.9
total		100.0

 ${}^{a}D'_{p}$  = accordynamic diameter for particle of unit density.



Figure 1. Typical coal fly ash particles from Mojave collection.

The SEM used in this study was a JEOL JSM-35C with a resolution of 60 Å. The samples were taken from plates 6 and 8 of the Bull Run collection and plates 6 and 7 from the Mojave collection. The particles were examined on the stainless steel substrate used during collection; a section of the assembly was coated with vapor-deposited 60/40 gold/palladium to provide conductivity.

In both cases, essentially all of the particles were spherical. Approximately one quarter of the particles from the Bull Run Steam Plant were glassy smooth; the remaining particles had a few irregularly spaced but regularly sized nodules. Contrastingly, none of the particles from the Mojave Plant were smooth; nodules of varying diameter covered the surface of the particles. For typical examples, see Figures 1 and 2.

**Composition Studies.** Energy dispersive X-ray analysis (EDX) was used to analyze the composition of the samples (above atomic number 10). The SEM was equipped with an Ortec Model 7965T Si (Li) X-ray detector. The X-ray spectra generated were analyzed with



Figure 2. Typical coal fly ash particles from Bull Run collection.

a Tracor-Northern NS880 data handling system. Quantitative information was obtained by comparing the areas of the peaks in the spectra with the area of single element standard peaks; the ratio obtained was corrected with a standard ZAF computer program. The error inherent in this type of analysis is generally less than 5%. The particles were prepared for analysis by transferring them from the stainless steel substrates to graphite substrates followed by subsequent carbon vapor deposition to provide conductivity. EDX analysis of submicrometer particles has many limitations. Under the conditions used during analysis, X-rays are emitted from a volume of approximately 1-4  $\mu$ m<sup>3</sup>; therefore, the EDX analysis of submicrometer particles will include significant background levels. Since the particles were on a graphite substrate, and because EDX will not detect carbon X-rays, the high background level manifests itself as a low total concentration. Because the particles are emitted from a coalburning power plant, it will be assumed that all the com

 Table III. EDS Composition of Fly Ash Samples in Normalized Weight Percent of Assumed Oxides (A) and Weight Percent

 of Elements above Atomic Number 10 Detected in Coal Mined in Western and Eastern United States (B)<sup>a</sup>

	Bull Run ash						
	Mojave ash, general	general	rough areas	smooth areas		coal	
						western	eastern
$Na_2O$	$4.4 \pm 1.9$	$0.5 \pm 1.3$	0.5	0.4	Na	0.14	0.04
MgO	$2.8 \pm 2.6$				Mg	0.14	0.06
$Al_2O_3$	$20.5 \pm 3.9$	$28.1 \pm 3.0$	25.5	24.8	Al	1.0	1.7
SiO <sub>2</sub>	$56.2 \pm 8.7$	$56.7 \pm 3.3$	59.7	61.3	Si	1.7	2.8
$P_2O_5$	$2.9 \pm 3.0$	$4.8 \pm 2.9$	4.3	4.6	Р	130 ppm	150 ppm
$SO_2$		$1.5 \pm 1.1$	2.1	0.9	S	0.4	0.9
Cl				0.1	Cl	0.03	0.17
K <sub>2</sub> O	$1.0 \pm 0.8$	$2.9 \pm 0.7$	2.5	2.8	K	0.05	0.25
CaO	$5.8 \pm 7.1$	$0.8 \pm 0.7$	0.9	0.7	Ca	1.7	0.47
$TiO_2$	$1.5 \pm 1.2$	$1.4 \pm 1.1$	0.5	0.8	Ti	0.05	0.09
$V_2O_5$					V	14 ppm	38 ppm
Cr <sub>2</sub> O <sub>3</sub>		$0.4 \pm 0.4$	0.5		Cr	9 ppm	20 ppm
MnŐ		$0.1 \pm 0.1$			Mn	49 ppm	18 ppm
FeO	$4.7 \pm 1.5$	$3.5 \pm 1.2$	3.4	3.5	Fe	0.53	1.5
NiO					Ní	5 ppm	15 ppm
m ref 3.							

ponents are in their most stable oxidized form. The EDX will be reported as normalized, assumed oxide concentrations. Some precautions must be taken when the normalized concentrations are used. The detectable limit with EDX is approximately 0.1 wt %; if only 5% of the total mass is detected due to a small particle diameter and a high concentration of oxygen, components which make up less than 2% of the bulk of a single particle would routinely not be detected. The data reported have been signal averaged over many particles in an attempt to approach the 0.1% detectability limit.

Thirteen particles from the Bull Run Steam Plant were analyzed; the analyses included surface nodules, smooth areas, and a general analysis of the entire particle. From the 13 particles, 15 nodules and 19 smooth areas were analyzed. The spectra from the nodules, smooth areas, and general areas were signal averaged and compared. The only significant difference between the nodules and their background was the sulfur concentration. The smooth areas averaged 0.9 wt % sulfur (as SO<sub>2</sub>) while the nodules averaged 2.1% SO<sub>2</sub>. All other elemental compositions were within expected statistical variations. The average composition for the entire particle, the nodules, and the smooth areas is given in Table IIIA. Despite a rough topography, no sulfur was detected in any of the 17 particles analyzed from the Mojave Plant.

In both cases, the total nonnormalized weight percent detected increased with increasing particle size, indicating a uniform particle density and thus implying the absence of hollow spheres. No correlation could be found between particle size and composition.

When the general compositions of particles from the Bull Run Steam Plant and the Mojave Plant are compared, obvious differences are noticeable. The Mojave ash contains magnesium not found in the Bull Run ash; the Bull Run ash contains sulfur not found in the Mojave ash. The ash from the Bull Run plant has significantly higher levels of aluminum, phosphorus, and potassium, while the ash from the Mojave plant has significantly higher levels of calcium, sodium, and iron. The chemistry of the coal was investigated to determine if any trends in coal composition could be related to the composition of the ash.

Table IIIB lists the composition of some elements in the range Z = 11-28 found in eastern and western coal as tabulated by Valković (3). When these compositions are compared to the ash analyses done here, a good degree of

correlation is evident. In general, the element with the higher concentration in the coal also has the higher concentration in the ash. The only exceptions in those elements detected were titanium and iron. The coal compositions listed are regional compositions only and not the specific coal used in the power plant, so a few variations are not unreasonable. With the exception of phosphorus, elements which exist in the ppm level in coal are not detectable in the ash with EDX. The reason for the high phosphorus concentration (3–5%) has not been determined at this time. Valković (3) has reported from 0.14% to 1% phosphorus in ash from Nebraska and Utah coal.

Diamond and Lopez-Flores (4) found that high-calcium fly ashes (30% CaO) have substantial sulfate content; the opposite was determined in this case. The mean particle diameter in their study ranged between 12 and 13.5  $\mu$ m.

Rahn and Lowenthal (5) described a method whereby a seven-element tracer system was used to determine the sources of pollution aerosol in Northeastern United States, Scandinavia, and the Arctic. The elements involved were As, Sb, Se, Zn, In, Mn, and V. Their study demonstrated that pollution aerosols could more often than not be correlated to a distant regional pollutant.

#### Conclusions

SEM and EDX analysis of two groups of submicrometer coal fly ash particles from two different power plants leads to a number of general conclusions. Although the total number of particles analyzed was small, as the analysis proceeded it was quite clear that fairly accurate average values could be specified. Thus, we are confident that the average values indicated for these samples are quite representative of the submicrometer fly ash as a whole.

The particles appear to be solid. They are quite similar to micrometer size fly ash particles in that they are basically an aluminosilicate matrix with small amounts of impurities. Differences in impurity content at the several percent level could generally be correlated to differences in the coal used, i.e., eastern vs. western coal. At the sensitivity limit of the instrumentation, that is, no better than 0.1%, there is no evidence of significant accumulation of trace metals. The collection from Tennessee using higher sulfur content eastern coal showed considerably more sulfur content than the collection from the Mojave Plant which burned low sulfur content western coal. Although the ash from the Mojave Plant showed more surface morphology, there was no evidence that the surface nodules were composed of any special, unique element. These particles from these particular collections seem to be quite similar to the micrometer size particles emitted in the ash (2). It is not clear, therefore, why the collected ash shows a bimodal distribution of micrometer size particles centered around 5  $\mu$ m and submicrometer size particles centered around 0.5  $\mu$ m. X-ray photoelectron spectroscopy (XPS) and depth profile XPS have been applied to these samples to determine surface composition. Results of these analyses will be presented in the near future.

### Literature Cited

(1) "Planning Studies for Measurements of Chemical Emissions in Stack Gases of Coal-Fired Power Plants". Report prepared for EPRI, Palo Alto, CA, by Southern Research Institute, Birmingham, AL, Battelle Columbus Laboratory, Columbus, OH, and Roth Associates, Inc., Rockville, MD (EA-2892, Research Project 1776-1), March 1983.

- (2) Kaufherr, N.; Lichtman, D. Environ. Sci. Technol. 1984, 18, 544.
- (3) Valković, V. "Trace Elements in Coal"; CRC Press: Boca Raton, FL 1983; Vol. I, pp 83-177.
- (4) Diamond, S.; Lopez-Flores, F. Proc. Symp. N. Mater. Res. Soc. 1981, 34.
- (5) Rahn, K. A.; Lowenthal, D. H. Science (Washington, D.C.) 1984, 223, 132.

Received for review April 23, 1984. Revised manuscript received September 4, 1984. Accepted October 30, 1984. This work was supported by Electric Power Research Institute Contract RP 1625-1.

# Anaerobic Degradation of Trichloroethylene in Soil

#### Robert D. Kleopfer,\* Diane M. Easley, Bernard B. Haas, Jr., and Trudy G. Deihl

Region VII Laboratory, U.S. Environmental Protection Agency, Kansas City, Kansas 66115

#### David E. Jackson<sup>†</sup>

Ecology and Environment, Inc., Kansas City, Kansas 66101

#### **Charles J. Wurrey**

Department of Chemistry, University of Missouri, Kansas City, Missouri 64110

■ When trichloroethylene (TCE) isotopically labeled with one <sup>13</sup>C atom is used and gas chromatography/mass spectrometry is employed to monitor the production of 1,2-dichloroethylene-<sup>13</sup>C<sub>1</sub> (DCE), it has been demonstrated that reductive dechlorination of TCE takes place in the soil. Microbial involvement in this process is indicated since unsterilized soil samples yielded up to 78 ppb of labeled DCE while sterilized soil samples produced none. Isomer specificity was also found; only 1,2-DCE was produced—no 1,1-DCE was observed.

# Introduction

Since trichloroethylene (TCE) is a major industrial solvent (234000 metric tons produced annually, worldwide (1)) used for degreasing and cleaning metal parts and electronic components, it is perhaps not surprising that TCE has found its way into the environment. In fact, TCE appears to be widely distributed in the aquatic environment (1).

However, the environmental fate of TCE has not been well documented, and considerable controversy still exists concerning its behavior in environmental matrices. Early literature references have concluded that  $C_1$  and  $C_2$  halogenated hydrocarbons are not metabolized by microorganisms (2, 3). More recent studies, however, are split on the issue of whether TCE is biodegraded (4–7), with one research group reporting both "no appreciable anaerobic degradation" and 40% degradation of TCE in similar methanogenic cultures (8, 9).

In a very recent publication, Parsons et al. have demonstrated that tetrachloroethylene (herein referred to as perchloroethylene, PCE) is reductively dechlorinated to TCE, dichloroethylene (DCE), and vinyl chloride in Florida muck/surface water microcosms (10). Whether TCE, which was present as a 1.6% impurity in the PCE study, was similarly biotransformed was not directly investigated but was implied by the results for PCE (10).

Therefore, in order to determine whether TCE itself undergoes biodegradation, we have undertaken a study using TCE with single atom <sup>13</sup>C isotopic labeling, soil from a TCE spill site in Des Moines (11), and very sensitive gas chromatography/mass spectrometry (GC/MS) analytical techniques. Since DCE-<sup>13</sup>C<sub>1</sub> could only arise via a soil or soil-microbe-induced reductive dechlorination of TCE-<sup>13</sup>C<sub>1</sub>, this experimental method should provide concrete evidence in support of such a pathway. The results of our investigation of this problem are reported herein.

# Experimental Section

Materials. Since any microbes present had probably adapted to TCE, soil samples were collected at the Des Moines site, at depths of 1–2 ("A" samples), 6–8 ("B" samples), and 15–17 ft ("C" samples), by using an 18 in. long by 2 in. o.d. split barrel sampler (11). These soil samples were analyzed by GC/MS for the presence of TCE and DCE. In spite of the TCE sludge application having been discontinued in 1979 (11), all soil samples contained 6 ppb of "native" (unlabeled) TCE. No DCE's were found in any soil sample. (An analysis of the Des Moines TCE sludge itself by this laboratory and by an independent testing laboratory showed very high levels of TCE (3000 ppm), but no DCE was detected.)

TCE-<sup>13</sup> $C_1$  was purchased from Merck Sharp & Dohme Isotopes. Single <sup>13</sup>C labeling was used to produce molecular and fragment ion peaks which did not have the same m/z values as the <sup>35</sup>Cl/<sup>37</sup>Cl natural isotopic mixtures. GC/MS analysis showed the TCE-<sup>13</sup> $C_1$  to be 97% isotopically pure and free of any DCE (labeled or unlabeled)

<sup>&</sup>lt;sup>†</sup>Present address: Department of Civil Engineering, University of Illinois, Urbana, IL 61801.