TRACE METAL CONTENT OF COAL AND ASH AS DETERMINED USING SCANNING ELECTRON MICROSCOPY WITH WAVELENGTH-DISPERSIVE SPECTROMETRY

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ABSTRACT

Scanning electron microscopy with wavelength-dispersive spectrometry has been used to measure trace metals in coal and ash. Hg, As, Ni, and Se have been detected in individual pyrite grains in Illinois #6 coal at levels up to 2680 ppm, 410 ppm, 320 ppm, and 880 ppm, respectively. These elements were present in fewer than half the grains analyzed. Cr has been detected at up to 950 ppm in half of clay mineral grains analyzed in Illinois #6 coal. The same trace metals were detected in pyrite and clay grains from Pittsburgh #8 coal.

Ash samples show a similarly heterogeneous distribution of trace metals. Hg has been detected at up to 700 ppm in 24% of aluminosilicate particles analyzed in ash from Absaloka coal, a subbituminous Montana fuel.

These data confirm that coal cleaning processes which remove pyrite are likely to be suitable for trace metal emissions control. In addition, back-end control devices which target specific types of ash particles may be helpful for control of air toxics emissions.

INTRODUCTION

Scanning electron microscopy (SEM) is one of the analytical tools available for determining the abundance of trace metals in coal and ash samples. This information is important in predicting and evaluating the behavior of these substances in combustion processes, a topic which is of increased importance in recent years as stricter regulation of trace metal emissions from coal-fired power plants is under consideration. Although scanning electron microscopy is not routinely applied to detection of trace quantities of metals, the use of a wavelength-dispersive spectrometer attachment makes such analyses possible.

Scanning electron microscope techniques differ from traditional trace metal analysis techniques in that SEM provides information with high spatial resolution, compared with the bulk compositions obtained through atomic absorption and other widely-used methods. High-spatial-resolution data concerning trace metal distribution in coal and ash is important for two reasons. First, ash behavior in fossil fuel combustion systems is best understood in terms of the behavior of individual particles. Knowledge of the bulk composition of an ash deposit frequently is not sufficient in determining what caused that deposit to have its particular physical characteristics such as size, friability, crystallinity, and density. Information concerning the chemical and mineralogical composition of individual ash particles can provide insight into how particles interact and transform to produce a deposit. Methods for obtaining this information using SEM with energy-dispersive x-ray spectrometry (EDS) have become widely available (1-3). The SEM-EDS technique provides data for major elements only, with detection limits of approximately 0.1 wt%. In order to obtain similar information concerning trace elements, SEM with wavelength-dispersive spectrometry (SEM-WDS) must be used. The SEM-WDS technique has detection limits of approximately 100 ppm (0.01 wt%) for most metals. Although it is time-consuming, the SEM-WDS method is valuable because it provides a means for acquiring single-particle trace element data for coal and ash particles, information that is essential in understanding how best to control the emission of trace elements from combustion sources. Trace metal emissions from coal-fired power plants may be subject to increased regulation; thus knowledge of how best to control them is vital.

A second reason for investigating the distribution of trace metals at high spatial resolution is that this information is helpful in understanding potential health effects of these substances. Trace metals can occur as coatings on airborne particles, and frequently are found in particles in the respirable size range (4,5); in these instances, the toxicity of the trace metals is greater than if those elements were distributed evenly throughout a particle, or were present in larger, non-respirable particles. For the purposes of assessing potential health impacts of trace metal emissions, it is important to know whether these elements are distributed homogeneously throughout an ash sample, or whether their distribution varies on an individual-particle basis.

METHODS

Samples were mounted in epoxy, cross-sectioned, polished, and coated with carbon to improve conductivity. Analyses were conducted on a JEOL 35C scanning electron microscope equipped with two JEOL wavelength-dispersive spectrometers with xenon-filled proportional counters, and a Noran Instruments energy-dispersive spectrometer. The analytical capabilities of the microscope are controlled by a Noran Instruments Voyager 2 computer system, which can coordinate simultaneous EDS and WDS.

The microscope was operated at an accelerating voltage of 25 kV with a beam current of 8 nA. Wavelength-dispersive spectral peaks were counted for 100 s; the total energy-dispersive live time per spectrum was 3 s. Certified standards were used for calibration. The data were subjected to ZAF corrections following collection.

Individual coal mineral grains and ash particles as small as 5 µm in diameter were analyzed. Under the more commonly used SEM-EDS analysis conditions, it is possible to analyze volumes as little as 1 µm in diameter, but the more intensely energetic conditions required of SEM-WDS make it impossible to analyze these smaller quantities without exciting the surrounding area (6).

RESULTS AND DISCUSSION

Coal and ash samples were analyzed for trace metal content using SEM-WDS. EDS was also used to determine the major element composition of each coal mineral grain or ash particle.

Ash Analyses. A sample of Absaloka ash was inspected for Hg content using SEM-WDS. Iodated activated carbon sorbent had been added to this Montana subbituminous coal. Ash particles analyzed ranged from 5 to 20 µm in diameter. As shown in Table 1, Hg was detected in six particles (21% of the total analyzed), in amounts ranging from 100 to 700 ppm (0.01 to 0.07 wt%). These Hg-bearing particles are mostly Ca- and Al-bearing silicates, with some S present.

Results for the 22 non-Hg-bearing particles analyzed in the same ash sample are shown in Table 2. The major element composition of these particles is similar to that of the Hg-bearing particles listed in Table 1, suggesting that the occurrence of Hg in these ash particles is not related to any compositional parameter.

Another sample of Absaloka ash, produced from coal to which a non-iodated activated carbon sorbent had been added, did not have any detectable Hg in individual particles. The ash particles in this sample were predominantly Ca- and Al-bearing silicates, as in the sample produced using iodated carbon sorbent, but with little S present.

Coal Analyses. In a sample of Illinois #6 bituminous coal, individual mineral grains were selected for trace metal analysis. Table 3 shows results for pyrite grains in Illinois #6 coal. Hg, As, Ni, and Se are present in individual grains at levels up to 2680 ppm, 410 ppm, 320 ppm, and 880 ppm, respectively. These trace metals were present in fewer than half of the pyrite grains analyzed. Clay mineral grains from the Illinois #6 coal sample were examined for Cr content; this element was detected at up to 950 ppm in half of the grains analyzed. These results show the heterogeneous distribution of these trace metals in coal mineral grains.

Similar results are evident for Pittsburgh #8 bituminous coal. Table 4 shows the distribution of trace metals in pyrite grains. As and Hg values for individual grains range up to close to 3000 ppm; Cd was detected in amounts less than 100 ppm only; Ni ranges up to approximately 1300 ppm; and Se values are as high as almost 2000 ppm. In clay mineral grains from Pittsburgh #8 coal, Cr ranges up to 377 ppm in 27 individual grains, including six grains with Cr not detected. The average value for Cr in the Pittsburgh #8 clay mineral grains is 75 ppm.

CONCLUSIONS

This study has shown the varied distribution of trace metals in coal and ash samples. The relative abundance of Hg and other trace metals in pyrite grains suggests the effectiveness of coal-cleaning processes in helping to reduce toxic emissions from power plants. Further investigation of the distribution of trace elements in ash particles of different compositions may lead to the development of emissions control devices tailored for removal of specific metals.

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Table 1. Composition of Hg-Bearing Particles in Absaloka Ash
(With Iodated Activated Carbon Sorbent Added)

Particle number	Normalized composition (wt%, C- and O-free basis)									
	Hg	Na	Mg	Al	Si	S	K	Ca	Ti	Fe
1	0.04	0.0	11.0	25.4	10.1	1.8	0.0	49.0	1.7	1.1
2	0.02	0.0	0.0	10.7	12.0	0.0	0.5	1.0	0.0	76.2
3	0.01	0.0	7.4	14.7	25.6	0.0	0.0	52.4	0.0	0.0
4	0.03	0.0	4.2	26.7	28.1	4.3	0.0	36.7	0.0	0.0
5	0.03	0.0	10.5	17.0	12.5	6.5	0.0	52.0	0.8	0.7
6	0.07	0.0	6.1	11.9	37.8	0.0	0.0	44.1	0.0	0.0
Avg.	0.03	0.0	6.5	17.7	21.0	2.1	0.1	39.2	0.4	13.0

Table 2. Composition of Non-Hg-Bearing Particles in Absaloka Ash
(With Iodated Activated Carbon Sorbent Added)

Particle number	Normalized composition (wt%, C- and O-free basis)								
	Na	Mg	Al	Si	S	K	Ca	Ti	Fe
1	0.0	0.0	10.6	26.7	0.0	0.0	62.7	0.0	0.0
2	0.0	0.0	20.4	41.9	0.0	0.0	37.8	0.0	0.0
3	0.0	10.5	9.4	19.3	0.0	0.0	58.5	1.1	1.2
4	2.2	3.4	19.0	42.6	0.4	0.7	29.5	1.3	0.9
5	0.0	6.8	12.4	27.7	1.8	0.0	49.6	1.8	0.0
6	0.0	5.7	20.7	21.8	2.6	0.0	46.0	0.7	2.5
7	1.7	1.6	27.6	42.2	0.0	1.8	23.1	1.0	1.0
8	4.0	2.9	18.7	40.7	0.0	0.8	21.4	0.0	11.4
9	0.0	4.3	13.5	15.0	0.0	0.0	64.9	1.6	0.8
10	0.0	1.2	22.3	31.6	8.2	2.6	29.4	0.0	4.7
11	0.0	6.2	20.6	12.1	10.6	0.0	50.4	0.0	0.0
12	0.0	4.2	18.9	37.9	0.0	0.0	35.5	1.7	1.9
13	0.0	0.0	33.9	57.2	0.0	1.6	5.9	1.5	0.0
14	0.0	0.0	31.9	59.8	0.0	1.4	4.7	1.0	1.2
15	0.0	0.0	0.0	100.0	0.0	0.0	0.0	0.0	0.0
16	0.0	7.5	27.8	18.3	0.0	0.0	43.3	1.6	1.5
17	0.0	6.2	14.9	29.5	2.3	1.2	41.5	2.6	1.8
18	0.0	6.9	14.8	17.3	4.5	0.0	54.4	0.0	2.1
19	0.0	10.1	18.2	17.2	6.4	0.0	48.1	0.0	0.0
20	4.4	2.9	21.7	43.1	2.2	1.3	22.0	2.4	0.0
21	0.0	9.7	11.1	10.3	7.6	0.0	61.4	0.0	0.0
22	0.0	11.7	14.7	10.1	0.0	0.0	63.6	0.0	0.0
Avg.	0.6	4.6	18.3	32.8	2.1	0.5	38.8	0.8	1.4

Table 3. Trace Element Content of Pyrite Grains in Illinois #6 Coal

Element	Values in ppm	
	Mean	Range
As	310	210-410
Cd	ND	---
Hg	2680*	2680*
Ni	210	140-320
Se	760	530-880

ND = not detected
• Hg values are for a single pyrite grain

Table 4. Trace Element Content of Pyrite Grains in Pittsburgh #8 Coal

Particle number	Values in ppm				
	As	Cd	Hg	Ni	Se
1	273	ND	2660	459	ND
2	ND	ND	103	797	ND
3	ND	ND	ND	1330	1810
4	2030	77	1240	149	730
5	123	ND	1870	285	13
6	532	ND	974	ND	1220
7	2900	13	ND	ND	1280
8	ND	ND	ND	90	1950
9	575	ND	1040	ND	1120
10	146	ND	ND	ND	1650

ND = not detected