TRACE ELEMENT CONTENT OF CLEANED ILLINOIS BASIN COAL

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ABSTRACT

Illinois Basin coal samples treated to extract organic sulfur and selected hazardous air pollutants (HAPs) were examined for trace metal content using scanning electron microscopy with wavelength-dispersive spectrometry (SEM-WDS). The extraction process used subcritical water, defined as water held in the liquid state under sufficient pressure to remain liquid at temperatures greater than the normal boiling point, but below the supercritical point of water (218 atm and 374°C). The samples were sink-floated to remove pyrite prior to receiving the subcritical extraction treatment. Some mineral matter remains in the coal, including sulfates, aluminosilicates, and small amounts of pyrite. In individual mineral grains in the unextracted coal, mercury is found intermittently at levels up to 0.62 wt%, arsenic at up to 0.28 wt%, and selenium at up to 0.38 wt%. These occurrences appear to be localized concentrations.

INTRODUCTION

Scanning electron microscopy with wavelength-dispersive spectrometry (SEM-WDS) is useful for determining the trace metal content of materials in situations where high spatial resolution is desired. The technique is more time-consuming than atomic absorption or other methods used to determine bulk trace element content of materials, but the additional effort required provides information unobtainable through other means. For coal samples, use of SEM-WDS allows the associations of trace metals with particular minerals in coal to be determined. This approach is particularly important in gaining the information necessary to determine how coal-cleaning processes work.

METHODS

Samples were mounted in carnauba wax, cross-sectioned, polished, and carbon-coated to improve conductivity. Analyses were conducted on a JEOL 35C scanning electron microscope equipped with two JEOL wavelength-dispersive spectrometers with xenon-filler proportional counters and a Noran Instruments energy-dispersive spectrometer. The microscope is controlled by a Noran Instruments Voyager 2 computer system.

The microscope was operated at an accelerating voltage of 25 kV with a beam current of 100 nA. Wavelength-dispersive spectral peaks were counted for 100 s. Live time for each energy-dispersive spectrum used to obtain major-element chemistry was 30 s. Certified standards were used for calibration. The data were subjected to ZAF (atomic number, absorption, and fluorescence) corrections following collection. The detection limit for arsenic, selenium, and mercury using the SEM-WDS technique is approximately 0.01 wt%.

Four samples of Illinois Basin Coal were characterized: raw IBC-101, extracted IBC-101, raw IBC-102, and extracted IBC-102. The extracted coals were treated with subcritical water, defined as water held in the liquid state under sufficient pressure to remain liquid at temperatures greater than the normal boiling point, but below the supercritical point of water (218 atm and 374°C). The samples were sink-floated to remove pyrite prior to receiving the subcritical extraction treatment. Arsenic, selenium, and mercury were measured in individual mineral grains from each raw and extracted coal. Major element composition was also determined.

RESULTS AND DISCUSSION

Results show that trace metals are distributed irregularly throughout the mineral matter in the four samples. Data are presented in Tables 1 through 4 for the IBC-101 raw coal, IBC-101 extracted coal, IBC-102 raw coal, and IBC-102 extracted coal, respectively. The mineral grains analyzed represent a wide variety of compositions, including aluminosilicate, calcium sulfate, pyrite, and iron oxide. The copper-rich grains analyzed represent an additive used in the extraction process.

The most dramatic difference in major element composition between raw and extracted coal samples is for sulfur. Sulfur is abundant in both of the raw coal samples, but is almost entirely absent in the extracted samples, demonstrating that the extraction process is effective at removing this element. Iron is present at high levels in both raw and extracted samples.

Arsenic, selenium, and mercury occur in both raw and extracted samples, suggesting that the coal-cleaning process may not completely remove these trace metals. In the IBC-101 samples, mercury and selenium appear to have been reduced by the extraction process, but arsenic is more abundant in the extracted sample. In the case of the IBC-102 sample, the extraction process may have added mercury, as this element is present in a greater proportion of the mineral grains and in higher concentrations in the extracted sample than in the raw sample. Arsenic and selenium occur with roughly equivalent frequency and concentration in the raw and extracted IBC-102 samples. Most of the mineral grains analyzed contained one or more of these elements, although none of the grains contained all three of the trace metals measured.

CONCLUSIONS

Results presented here show that the distribution of trace metals in raw and extracted coals varies greatly. Arsenic, selenium, and mercury were found to be associated with a range of mineral compositions and are present even in low-pyrite cleaned coals. The extraction process appears to remove sulfur effectively, but some trace metals may remain in the coal after treatment.

TABLE 1

Elemental Composition of Individual Mineral Grains in IBC-101 Raw Coal

Point No.	Trace Metals, wt%			Major Elements, wt%						Total, wt%
	As	Se	Hg	Al	Si	P	S	Ca	Fe	
1	ND*	0.02	0.37	ND	ND	ND	36.11	ND	63.49	99.99
2	ND	0.38	0.13	ND	ND	ND	43.04	56.46	ND	100.01
3a	ND	0.01	0.04	ND	ND	2.12	40.05	57.79	ND	100.01
3b	ND	0.04	ND	ND	ND	ND	39.97	48.17	11.83	100.01
3c	ND	0.03	0.62	ND	ND	ND	42.24	57.12	ND	100.01
3d	ND	0.02	ND	ND	13.23	ND	40.92	45.83	ND	100.00
3e	0.02	0.01	ND	2.99	9.75	ND	34.51	34.01	18.71	100.00
3f	ND	0.03	ND	ND	ND	ND	44.34	55.64	ND	100.01
3g	ND	0.01	ND	ND	10.19	ND	32.72	17.58	39.51	100.01
3h	0.28	0.02	ND	8.73	28.70	ND	15.74	ND	44.35	100.00
3i	ND	0.01	ND	ND	ND	ND	44.03	55.97	ND	100.01
3j	ND	0.02	ND	6.41	20.19	ND	11.58	5.60	56.21	99.99
3k	0.01	0.02	ND	ND	ND	ND	12.43	ND	87.54	100.00
4a	ND	ND	ND	ND	ND	ND	20.25	ND	79.74	99.99
4b	ND	ND	ND	ND	ND	ND	20.43	ND	79.58	100.01
4c	0.01	ND	ND	ND	ND	ND	21.30	ND	78.68	99.99
4d	0.07	0.01	ND	7.73	14.45	ND	36.96	ND	40.77	99.99
4e	ND	ND	ND	17.01	21.42	ND	24.78	ND	36.80	100.01
4f	0.01	0.01	ND	35.45	64.53	ND	ND	ND	ND	100.00
4g	0.01	0.01	ND	ND	ND	ND	41.66	ND	58.33	100.01
4h	0.01	0.01	ND	34.62	65.37	ND	ND	ND	ND	100.01

* Not detected.

TABLE 2

Elemental Composition of Individual Mineral Grains in IBC-101 Extracted Coal

Point No.	Trace Metals, wt%			Major Elements, wt%								Total, wt%
	As	Se	Hg	Mg	Al	Si	S	Ca	Ti	Fe	Cu	
1	ND*	0.01	ND	ND	27.23	12.07	ND	ND	ND	60.68	ND	99.99
2	ND	ND	ND	ND	49.95	50.05	ND	ND	ND	ND	ND	100.00
3	ND	0.01	ND	ND	ND	ND	ND	ND	ND	99.99	ND	100.00
4	ND	ND	ND	ND	56.84	43.16	ND	ND	ND	ND	ND	100.00
5	0.03	0.02	ND	ND	ND	4.78	ND	ND	ND	ND	95.17	100.00
6	ND	0.03	ND	ND	ND	ND	ND	ND	ND	99.97	ND	100.00
7	ND	ND	ND	ND	ND	ND	ND	ND	ND	100.00	ND	100.00
8a	0.06	ND	ND	7.66	ND	26.11	ND	23.02	ND	43.15	ND	100.00
8b	0.14	ND	ND	3.78	ND	7.21	ND	24.47	ND	64.39	ND	99.99
8c	0.12	ND	ND	9.42	ND	32.32	ND	12.19	6.10	39.85	ND	100.00
8d	0.25	ND	ND	23.42	ND	51.39	ND	ND	ND	24.94	ND	100.00
8e	0.07	ND	ND	2.70	ND	26.98	ND	49.81	8.83	11.62	ND	100.01
8f	0.18	ND	ND	10.33	ND	24.13	ND	7.29	2.74	55.33	ND	100.00

* Not detected.

TABLE 3

Elemental Composition of Individual Mineral Grains in IBC-102 Raw Coal

Point No.	Trace Metals, wt% As	Se	Hg	Major Elements, wt% Al	Si	S	Ca	Ti	Fe	Zn	Total, wt%
1	ND*	0.03	ND	ND	ND	34.00	ND	ND	ND	65.96	99.99
2	ND	0.01	ND	ND	ND	37.94	ND	ND	62.05	ND	100.00
3	0.01	ND	ND	ND	ND	50.91	ND	ND	49.08	ND	99.99
4	ND	ND	ND	ND	ND	52.79	ND	ND	47.21	ND	100.00
5	ND	0.01	ND	ND	ND	46.74	ND	ND	53.25	ND	100.00
6	ND	ND	ND	ND	ND	50.66	ND	ND	49.33	ND	99.99
7	ND	ND	ND	ND	3.53	40.75	55.72	ND	ND	ND	100.00
8	ND	ND	ND	ND	ND	52.84	ND	ND	47.16	ND	100.00
9	ND	ND	ND	ND	0.93	55.84	ND	ND	43.23	ND	100.00
10	0.01	ND	ND	5.79	4.24	48.05	ND	ND	41.91	ND	100.00
11	0.02	ND	0.01	ND	ND	55.25	ND	ND	44.72	ND	100.00
12	ND	ND	ND	ND	ND	ND	100.00	ND	ND	ND	100.00
13	ND	ND	0.01	24.62	51.98	ND	ND	2.90	9.55	ND	100.01
14	0.03	ND	0.01	ND	ND	53.30	ND	ND	46.66	ND	100.00
15	0.01	ND	ND	16.69	40.93	19.90	ND	ND	12.62	ND	100.01
16	ND	ND	ND	ND	ND	53.25	ND	ND	46.75	ND	100.00
17	ND	ND	ND	ND	ND	54.71	ND	ND	45.29	ND	100.00

* Not detected.

TABLE 4

Elemental Composition of Individual Mineral Grains in IBC-102 Extracted Coal

Point No.	Trace Metals, wt% As	Se	Hg	Major Elements, wt% Al	Si	S	Mn	Fe	Cu	Total, wt%
1	0.01	0.01	ND*	ND	ND	ND	ND	99.98	ND	100.00
2	0.02	0.03	ND	ND	ND	ND	ND	99.94	ND	99.99
3	0.03	0.03	ND	ND	ND	ND	ND	99.93	ND	99.99
4	0.06	0.05	ND	ND	ND	ND	ND	99.89	ND	100.00
5	ND	ND	ND	ND	ND	ND	ND	ND	100.00	100.00
6	ND	ND	0.08	ND	ND	ND	ND	99.92	ND	100.00
7	ND	ND	0.01	ND	ND	ND	ND	99.99	ND	100.00
8	ND	ND	0.02	ND	ND	ND	ND	99.98	ND	100.00
9	ND	ND	ND	ND	ND	ND	ND	2.47	97.52	99.99
10	ND	ND	0.01	ND	ND	ND	ND	99.99	ND	100.00
11	ND	ND	ND	ND	ND	ND	ND	100.00	ND	100.00
12	ND	ND	0.08	ND	0.48	ND	0.60	98.84	ND	100.00
13	0.03	ND	0.06	ND	ND	0.52	ND	99.38	ND	99.99
14	ND	ND	0.05	ND	ND	ND	ND	99.95	ND	100.00
15	ND	ND	0.06	ND	ND	ND	ND	99.93	ND	100.00
16	ND	ND	ND	ND	ND	ND	ND	100.00	ND	100.00
17	ND	ND	0.05	ND	ND	ND	ND	99.95	ND	100.00
18	ND	ND	0.02	ND	ND	ND	ND	99.98	ND	100.00
19	ND	ND	0.03	ND	ND	ND	ND	99.97	ND	100.00
20	ND	ND	0.04	ND	ND	ND	ND	99.96	ND	100.00
21	ND	ND	0.01	ND	ND	ND	ND	99.99	ND	100.00

* Not detected.