

Modes of Occurrence of Selected Trace Elements  
in  
Several Appalachian Coals

Robert B. Finkelman, Ronald W. Stanton,  
C. Blaine Cecil and Jean A. Minkin

U.S. Geological Survey, National Center, Reston, VA 22092

Most coal-cleaning processes are predicated on differences in physical properties between the coal and the included mineral matter believed to contain the undesirable elements. However, as the mode of occurrence of most elements in coal (particularly the trace elements) is not clearly understood, the effectiveness of the coal-cleaning procedures in removing these trace elements is uncertain. By combining detailed chemical, mineralogical, and petrographic techniques we have determined how various trace elements, particularly those of environmental interest occur in several Appalachian bituminous coals.

This study was conducted primarily on polished blocks of coal using a scanning electron microscope (SEM) with an energy dispersive X-ray detector. With this system individual *in situ* mineral grains as small as 0.5  $\mu\text{m}$  can be observed and analyzed for all elements of atomic number 11 (Na) and greater that are present in concentrations as low as about 0.5 weight percent [Finkelman (1), and Finkelman and Stanton (2)].

On the basis of the abundance of the accessory minerals in the Waynesbury coal, Finkelman (1) calculated the concentrations for 10-15 trace elements. The calculated values for many of these elements, including Zn and Cu, correlated well with their analytical values. These data suggest that the trace elements occur in this coal predominantly as specific accessory minerals. For example, zinc occurs as zinc sulfide (sphalerite; Figure 1) and copper as copper iron sulfide (chalcopyrite; Figure 2). SEM analysis of other coals from the Appalachian Basin appears to substantiate this conclusion. Preliminary estimates based on the new data suggest that most of the selenium in these coals and much of the lead occur as 1 to 3  $\mu\text{m}$  particles of lead selenide (clausthalite?), which are often associated with cadmium-bearing sphalerite and chalcopyrite, (Figure 3). These fine-grained mineral intergrowths occur exclusively within the organic constituents and in all probability formed in place. Experiments by Bethke and Barton (3) on the chemical partitioning of selenium between sphalerite, galena (PbS) and chalcopyrite suggest that the sphalerite-chalcopyrite-clausthalite assemblage would be the expected assemblage at low temperature (300°C).

If all the selenium in these coals occurred as lead selenide this would tie up about half the available lead. Although galena is not found associated with sphalerite or chalcopyrite it does occur as micrometer-sized particles on the edges of pyrite grains (Figure 4). This mode of occurrence may account for the lead in excess of that tied up by the selenium.

Because substantial amounts of Zn, Cu, Pb, Cd, and Se occur as finely dispersed mineral grains in the organic matrix, considerable amounts of these elements can be retained in the lighter specific gravity fractions of cleaned coal (4).

Figure 5 illustrates the concentration of Zn in a size-gravity separation of the Upper Freeport coal. Similar results have been obtained for Cd, Cu, and Pb on six samples of this coal. The divergence of these curves in the high specific gravity range is consistent with the observation that these elements occur as fine-grained minerals which are increasingly released from their organic matrix with fine grinding.

It is evident from Figure 5 that the concentrations, on a whole coal basis, of Zn (this would apply to Cu, Cd, and Pb as well) are much greater for the higher specific gravity (Sp. G.) fractions. However, the bulk of the coal generally floats at the lower Sp. G. levels. Recalculating these data to show the proportion of each element in each Sp. G. fraction reveals that substantial amounts of these

elements are retained in the lighter (<1.50) fractions (Table 1). Similar results were obtained in a washability study of these coals by Cavallaro and others (5). Not all the Upper Freeport samples demonstrated this type of behavior. In several samples more than 50 weight percent of the coal sank in Sp. G. 1.60 liquids, carrying with it as much as 85 percent of these trace elements.

Figure 6 illustrates the concentration of Zn in the high-temperature ash of one of the size-gravity fractions. Similar results have been obtained for Cd, Cu, and Zn in many of the Upper Freeport samples. The highest concentrations of these elements commonly occur in the ash of the lightest fraction of the coal. This reflects the association of fine-grained sphalerite, chalcopyrite, and clausthalite (?) with the organic matrix. The high concentrations in the sink 1.8 fractions are probably due to the release of some of these minerals during grinding.

Many of the trace elements of environmental interest (e.g. As, Cd, Cu, Hg, Pb, Tl, Se, Zn) occur as sulfides. In coal the most prominent sulfide mineral is pyrite (FeS<sub>2</sub>). The crystal chemistry of pyrite allows for only a small amount of solid solution with most of the above mentioned elements (6). Indeed, preliminary electron microprobe and ion microprobe analyses of pyrite and its dimorph marcasite from several coals suggest that most pyrite is free of trace constituents to concentrations as low as 100 ppm.

Arsenic is one chalcophile element whose mode of occurrence and behavior differs from that of Zn, Cd, Pb, Cu, and Se. Although arsenic sulfide has been observed in coals, the bulk of the As in the Upper Freeport coal appears to be associated with pyrite. The distribution of As in the Upper Freeport coal appears to be controlled, to a large extent, by the fractures within the coal and within the pyrite. Thus far, arsenic has been found only in pyrite horizons that are associated with fractured coal, although not all such pyrite occurrences had detectable arsenic. Within these favorable sites As was found only along the outer rims of pyrite grains or along fractures within the pyrite. Optically, the As-bearing pyrite always appears "dirty" due to abundant microfractures, perhaps caused by reactions with epigenetic As-bearing solutions. Pyrite without microfractures did not have detectable arsenic (>0.01 weight percent).

In the size-gravity separations, As was found to concentrate in the sink 1.8 fraction along with pyrite.

Correlation coefficients based on statistical analyses of analytical data from 96 Upper Freeport coal samples indicate that As and pyrite correlate well with each other (7). Mercury, the only other element with which arsenic and pyrite have a strong positive correlation, behaves similarly to arsenic in the size-gravity separations (Table 1). In all probability the mode of occurrence of mercury is similar to that of arsenic.

With this type of information on mode of occurrence, coal-cleaning procedures can be devised to effectively remove the undesirable trace elements.

#### References

- (1) R. B. Finkelman, Scanning Electron Microscopy/1978/vol. 1, 143, (1978).
- (2) R. B. Finkelman and R. W. Stanton, Identification and significance of accessory minerals from a bituminous coal. Fuel (in press).
- (3) P. M. Bethke and P. B. Barton, Jr. Econ. Geol., 66, 140, (1971).
- (4) C. B. Cecil, R. W. Stanton, S. D. Allshouse and R. B. Finkelman, Preparation characteristics of the Upper Freeport coal, Homer City, PA. R & D Program Report (in press).
- (5) J. A. Cavallaro, A. W. Deurbrouck, H. Schults, G. A. Gibbon, and E. A. Hattman. A washability and analytical evaluation of potential pollution from trace elements in coal. EPA interagency Energy/ Environmental R & D Program Report EPA-60017-78-038, (1978).
- (6) W. A. Deer, R. A. Howie and J. Zussman; Rock Forming Minerals, vol. 5, non-silicates, 1962, J. Wiley and Sons Inc.
- (7) C. B. Cecil, R. W. Stanton, S. D. Allshouse, R. B. Finkelman and L. P. Greenland. Mineral matter in the Upper Freeport Coal Bed, Homer City, Pa., EPA, Inter-agency Energy/Environmental R & D Program Report (in press).

Table 1. Trace element concentrations in size-gravity splits of two Appalachian coals. Values are in percentages of the element in each Sp. G. fraction of a size split.

Upper Freeport (H2-42P-1.1)

Mesh size	Cd		Cu		Pb		Zn		Hg		As	
	+1/4"	8x100	+1/4"	8x100	+1/4"	8x100	+1/4"	8x100	+1/4"	8x100	+1/4"	8x100
Float 1.275	36	9	20	10	19	13	5	28	21	0.5	8	tr
1.300	17	16.5	33	30	18	9	12.5	27	13	3.5	10.5	6
1.325	10	0.5	18	12	16	2	11	4	2	3.5	7	1
1.400	6	6.5	13	12	18	9	7.5	4.5	4	5	8	2.5
Cumulative percent	(69)	(42.5)	(67)	(45)	(71)	(33)	(35)	(63.5)	(40)	(12.5)	(33.5)	(15.5)
1.600	9	4	11	8.5	14	10	5	7	10	4	4	6
1.80	9	14.5	32	5	5	4	65	9	15	10	4	2.5
Sink 1.80	12.5	49.5	10	42	10	53	21	40	75	46.5	75	99
												69.5
												75

Waynesburg

Mesh size	Cu		Pb		Zn		As*	
	>10	10-20	>10	10-20	>10	10-20	>10	10-20
Sp. G.								
Float 1.30	33	18	34	15.5	27	15	34.5	<150
1.50	65.5	79	60.5	41.5	59.5	62.5	33	<150
Cumulative percent	(98.5)	(97)	(94.5)	(85)	(70)	(86.5)	(77.5)	(67.5)
1.70	0.5	1.5	1.5	4.5	9	2.5	6	<150
Sink 1.70	0.5	1.5	4	10	21	11	17	25
								1500
								990
								610

\*ppm

tr = trace

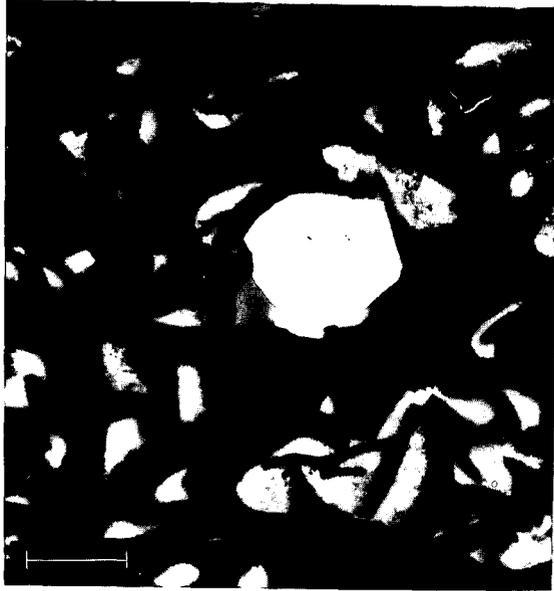


Figure 1. SEM photomicrograph of a sphalerite crystal in semifusinite.  
Scale bar = 10  $\mu\text{m}$ .



Figure 2. SEM photomicrograph of a chalcopyrite grain.  
Scale bar = 10  $\mu\text{m}$ .



Figure 3. SEM photomicrograph of a grain consisting of sphalerite (right rim), chalcopyrite (left rim), and lead selenide (bright cap).  
Scale bar = 10  $\mu\text{m}$ .



Figure 4. SEM photomicrograph of galena (light gray) on pyrite (medium gray). Backscattered electron image.  
Scale bar = 1  $\mu\text{m}$ .

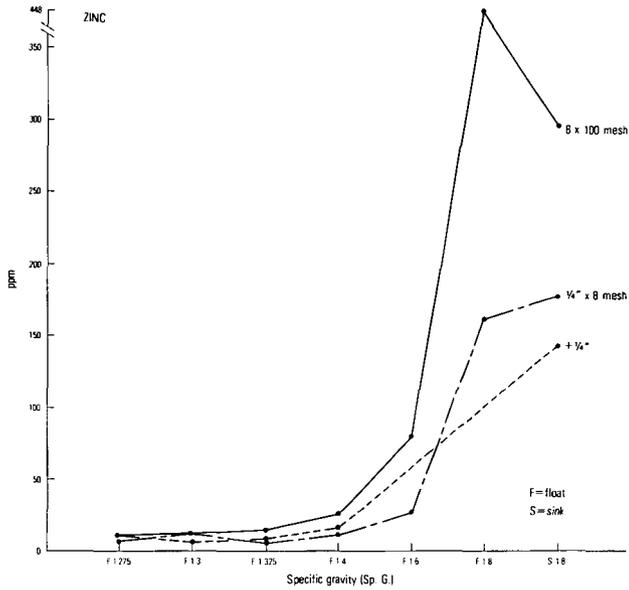


Figure 5. Concentration of zinc (whole-coal basis) in size-gravity separates of the Upper Freeport coal sample H2-42P-1.1.

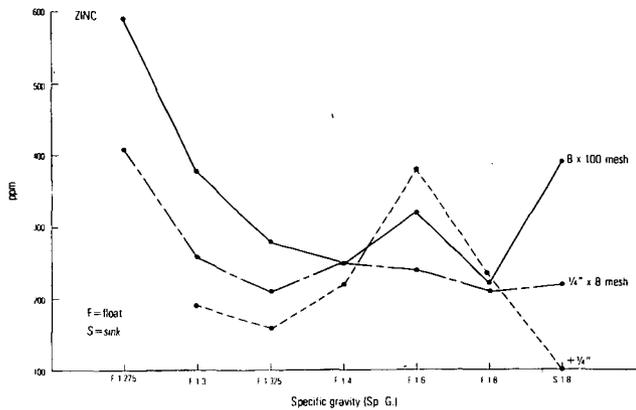


Figure 6. Concentration of zinc in the ash of size-gravity separates of Upper Freeport coal sample H2-53L-1.0.