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Donald C. Haney, State Geologist and Director
University of Kentucky, Lexington

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TRACE ELEMENTS IN COAL: THE NEXT CHALLENGE

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The occurrence of trace elements in coal is an important topic currently being discussed by coal and electric-power-industry personnel, and by environmental regulators and government officials. The high level of interest in trace elements is demonstrated by the many conferences currently being held on the subject, and also by the increased activity in trace-element research. The Environmental Protection Agency (EPA) is currently involved in a federally mandated investigation to determine whether further regulation of trace-element emissions is necessary for coal-fired utilities.

Trace elements are chemical elements such as lead and mercury that generally occur in very small amounts in coal. Coal is composed not only of the elements normally considered to be components of coal (carbon, oxygen, hydrogen, sulfur, and nitrogen), but also of other elements that combine with the organic molecules that comprise the coal, and minerals that are associated with the coal. The present concern is that the combustion of coal in power plants causes the release of these trace elements into the environment. While coal contains only tiny amounts of these elements (usually measured in parts per million), the large volumes of coal burned each year have the potential to emplace large amounts of these elements into the environment.

The following hypothetical example might help explain the importance of trace elements in coal. If a trace element exists in coal in the concentration of 50 parts per million, then the combustion of 1 million tons of coal would produce 50 tons of this trace element. Considering that some power plants burn 2 to 3 million tons of coal per year, substantial amounts of this trace element could be emitted. This is only a hypothetical example, and many factors not considered here might moderate the actual amount of trace elements emitted into the environment. For instance, not all trace elements are volatilized upon combustion and escape into the atmosphere with flue gases. In fact, many are trapped in the bottom or fly ash byproduct of coal combustion. Others become incorporated into flue-gas-desulfurization (scrubber) residue.

Industries other than electric utilities that are deemed to be "significant emitters" (i.e., those that emit 10 tons per year of any one trace element, or 25 tons or more of any combination of elements) will automatically be required by the EPA to implement pollution-reduction technologies. These control strategies must use the maximum achievable technology. If a public-health risk remains after control strategies are adopted, then further controls may be required. Presently, coal-burning electric utilities are not classified as significant emitters, although EPA is in the process of determining the status of coal and other fossil-fuel-burning power plants.

Title III of the Clean Air Act Amendments of 1990 concerns *Hazardous Air Pollutants* (HAP's). Of the nearly 200 substances listed in the act as hazardous air pollutants, 11 are trace elements commonly found in coal. These 11 are, in alphabetical order, antimony, arsenic, beryllium, cadmium, cobalt, chromium, mercury, manganese, nickel, lead, and selenium (Table 1). Electric utilities will be required to monitor the levels of these elements in their emissions and perhaps in the feed stock. Testing for trace elements in coal by coal companies will become a much more common practice. This testing requires very specialized and sophisticated equipment, which translates into increased cost.

Trace elements in coal can be divided into two broad groups: those that occur as part of the coal molecule (organic) such as beryllium and selenium, and those that occur as part of the mineral fraction of coal (inorganic) such as arsenic and lead (Swaine, 1990). This distinction is important because some trace elements linked to the minerals in coal may be removed by coal cleaning prior to combustion. Some of the 11 HAP's in coal, however, may occur in both the organic and inorganic fractions of coal, thus making accurate washability predictions difficult. When coal is burned, some trace elements are concentrated in the incombustible portion of coal that either is collected as bottom ash (slag) or fly ash by particulate control systems (e.g., electrostatic precipitators). some very volatile elements, notably mercury and selenium, may escape with flue gas.

The subject of trace elements in Kentucky coals is not new to coal scientists and geologists. Sampling of Kentucky coal to characterize the trace-element content began almost 20 years ago. The Kentucky Geological Survey, aware of the potential concerns about trace elements in coal, has worked closely with the U.S. Geological Survey to collect and analyze more than 1,000

Table 1.—The Periodic Table of Elements. The 11 Trace Elements in Coal that the EPA has Listed as Hazardous Air Pollutants (HAP's) are Highlighted.

H 1 Hydrogen																	He 2 Helium
Li 3 Lithium	**Be 4 Beryllium**											B 5 Boron	C 6 Carbon	N 7 Nitrogen	O 8 Oxygen	F 9 Fluorine	Ne 10 Neon
Na 11 Sodium	Mg 12 Magnesium											Al 13 Aluminum	Si 14 Silicon	P 15 Phosphorus	S 16 Sulfur	Cl 17 Chlorine	Ar 18 Argon
K 19 Potassium	Ca 20 Calcium	Sc 21 Scandium	Ti 22 Titanium	V 23 Vanadium	**Cr 24 Chromium**	**Mn 25 Manganese**	Fe 26 Iron	**Co 27 Cobalt**	**Ni 28 Nickel**	Cu 29 Copper	Zn 30 Zinc	Ga 31 Gallium	Ge 32 Germanium	**As 33 Arsenic**	**Se 34 Selenium**	Br 35 Bromine	Kr 36 Krypton
Rb 37 Rubidium	Sr 38 Strontium	Y 39 Yttrium	Zr 40 Zirconium	Nb 41 Nobelium	Mo 42 Molybdenum	Tc 43 Technetium	Ru 44 Ruthenium	Rh 45 Rhodium	Pd 46 Palladium	Ag 47 Silver	**Cd 48 Cadmium**	In 49 Indium	Sn 50 Tin	**Sb 51 Antimony**	Te 52 Tellurium	I 53 Iodine	Xe 54 Xenon
Cs 55 Cesium	Ba 56 Barium	La 57 Lanthanum	Hf 72 Hafnium	Ta 73 Tantalum	W 74 Tungston	Re 75 Rhenium	Os 76 Osmium	Ir 77 Iridium	Pt 78 Platinum	Au 79 Gold	**Hg 80 Mercury**	Tl 81 Thallium	**Pb 82 Lead**	Bi 83 Bismuth	Po 84 Polonium	At 85 Astatine	Rn 86 Radon
Fr 87 Francium	Ra 88 Radium	Ac 89 Actinium															

channel samples. The Kentucky Geological Survey has both coal-quality and trace-element data available to the public, both in the form of publications and computer disks. Data from these samples give a general pictures about the trace elements in Kentucky coal (Figs. 1–2), but because of the variations (sometimes very large) in quality between coal beds and even within coal beds, these gneeral characteristics should not be construed to represent any specific coal.

Trace elements in coal exist in a variety of forms. The following list, based on an article by Finkelman (in press), gives a brief description of some of these forms.

1. Antimony (Sb)—Antimony many be present in solid solution in pyrite and as an accessory sulfide (e.g., stibnite, Sb_2S_3). Some may be organically bound. There is a wide range of behavior in coal cleaning; it is probable that less than 50 percent can be removed by conventional coal cleaning. There is a positive correlation between antimony and pyritic sulfur for bituminous coals, but no correlation for low-rank western United States coals.

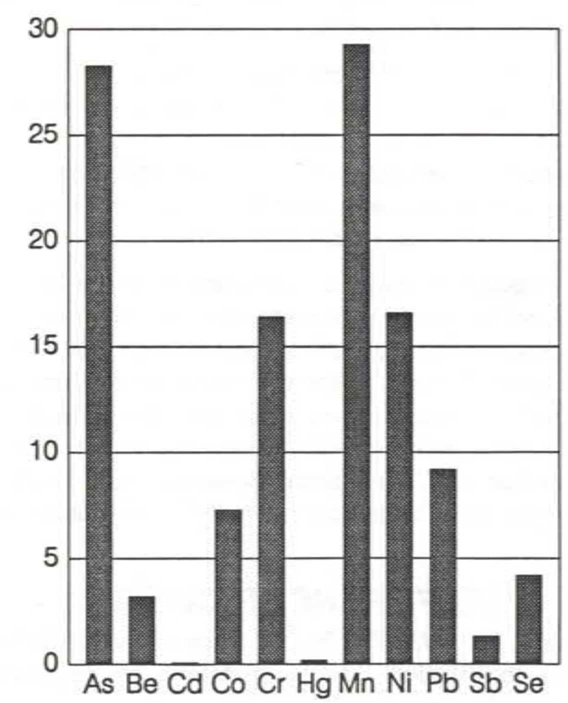

Figure 1. The distribution of 11 trace elements in eastern Kentucky coal beds. Note the relatively high concentration of arsenic, chromium, manganese, and nickel and the relatively low concentrations of beryllium, cadmium, mercury, antimony, and selenium.

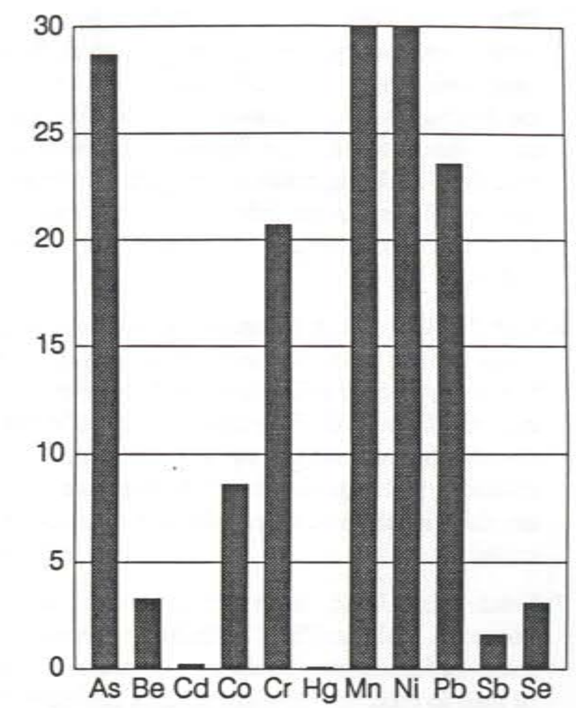

Figure 2. The distribution of the same 11 trace elements shown in Figure 1 in western Kentucky coal beds. Note the higher concentrations of manganese, nickel, and lead compared to eastern Kentucky coals.

2. Arsenic (As)—Arsenic is mainly associated with pyrite, primarily epigenetic forms. Fifty to 75 percent should be removable by conventional coal cleaning. A strong positive correlation exists between arsenic and pyritic sulfur. Highest arsenic concentrations are found in high-sulfur coals in basins that have been subjected to extensive late-stage sulfide mineralization (e.g., Eastern and Western Interior and Warrior Basins).
3. Beryllium (Be)—Beryllium is hard to detect because of its low atomic number (4). It is mainly associated with the organic fraction of coal (varies inversely with ash yield), but can replace aluminum in clays and can occur in quartz. Beryllium is difficult to remove using coal-cleaning techniques.
4. Cadmium (Cd)—Cadmium primarily occurs in solid solution in sphalerite (ZnS) in Illinois Basin coals. It exhibits a wide range of behavior in coal cleaning. Eastern Interior (Eastern Kentucky, Illinois, and Indiana) and Western Interior (Kansas, Missouri, Oklahoma, and Iowa) Basin coals have a high potential for cadmium enrichment.

5. Chromium (Cr)—Much chromium is apparently organically bound, as indicated from float-sink data, but information as to its association is inconclusive. Chromite ($FeCrO_4$) is an inorganic source. Potential removal by standard coal preparation procedures is inconclusive. There is no information on the distribution of chromium in coals in the United States.

6. Cobalt (Co)—Cobalt probably is associated with sulfide minerals in coal, mainly pyrite. Some may occur with clays, and some may be organically bound. Fifty to 75 percent of cobalt should be removable by conventional coal-cleaning techniques. There is no information on the distribution of cobalt in United States coals.

7. Lead (Pb)—Lead is associated with sulfide minerals. Galena (PbS), both fine-grained and massive forms, may be the most common form of lead in coal. Much of the lead in coal should be removable by conventional coal-cleaning techniques. Areas that have high concentrations of cadmium and zinc may also have high lead concentrations.

8. Manganese (Mn)—Manganese in bituminous coal occurs mainly in solid solution in the carbonate minerals siderite ($FeCO_3$) and ankerite ($Ca(Fe, Mg, Mn)(CO_3)_2$). In low-rank coals, some manganese may be organically bound. At least a 50 percent reduction of manganese should be expected using conventional coal-cleaning techniques.

9. Mercury (Hg)—Mercury is extremely volatile, and is present in very low concentrations (generally less than 0.5 ppm). Much of the mercury in coal is in solid-solution pyrite, especially epigenetic (late-stage) pyrite. Mercury and arsenic have similar occurrences in raw coal and behave similarly in coal cleaning. Coals with low levels of mercury will also tend to be low in mercury. Twenty-five to 50 percent of mercury in coal should be removable by preparation procedures, but the data are somewhat anomalous.

10. Nickel (Ni)—Nickel may have both an inorganic (primarily with sulfides) and organic association in coal. Removal by coal-cleaning techniques will depend on this association. There is virtually no information on the distribution of nickel in United States coals.

11. Selenium (Se)—Selenium is mostly organically bound. A small portion is associated with pyrite and some other sulfide minerals (e.g., galena). As most selenium appears to be organic, coal-cleaning practices will not remove much. The highest concentrations of selenium in United States coals are in Gulf Coast lignites.

Most coal-fired power plants employ electrostatic precipitators or fabric filters (e.g., baghouses) for the collection of very fine particulate matter in flue gases. As most of the trace elements are associated with these particulates, some concern exists as to the fate of trace elements, and their potential interaction with ground waters, when fly ash is buried or introduced into a settling pond.

While coal itself is a primary source of trace elements, some elements may actually come from sorbents, additives, or fluxes. Clarke (1993) referred to two studies in Europe where the crushed limestone used in flue-gas-desulfurization systems provided a significant source (more than 90 percent) of certain trace elements, especially arsenic, cadmium, lead, and zinc. Furthermore, although flue-gas-desulfurization systems effectively prevent trace elements from gaining access to the atmosphere, they do concentrate elements in scrubber residue and waste water (Clarke, 1993).

In an experimental atmospheric fluidized bed combustion unit, the addition of limestone to the bed to control SO_2 emissions was found to increase the levels of some trace-element emissions, notably lead, cadmium, and manganese, four to six times the levels when tests were run without the sorbent (Clarke, 1993).

The concentration of certain trace elements in Kentucky coal is a growing concern, and certainly warrants further study. We need to better define the variability of these trace elements in the coal we mine and use. We also need to be concerned about the fate of these elements in coal-ash byproduct and desulfurization residue so that we can continue to use coal as a primary power source in an environmentally sound manner.

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