

Arsenic in Coal

Sources of Arsenic

Arsenic is a persistent toxin that occurs naturally in trace amounts in rocks, sediments, and coal. Small amounts of arsenic may be present in ground water or, less commonly, surface waters, especially where there is a nearby source of arsenic. The most widespread natural source of arsenic is pyrite, a common mineral composed of iron and sulfur, which can contain a small amount of arsenic in its structure in place of sulfur.

Arsenic occurs in some ground-water aquifers due to chemical oxidation of pyrite or to reduction (the opposite of oxidation) of iron oxide minerals in the aquifer. Other sources of arsenic include past industrial activities, application of arsenic as a pesticide, and drainage from abandoned mine lands that contain pyrite. Prolonged consumption of drinking water from wells that greatly exceed arsenic health standards is the most serious arsenic-related health hazard in the United States and throughout the world.

Arsenic in bituminous coal occurs primarily in pyrite and, to a lesser extent, in organic portions of the coal. A small fraction of this arsenic is emitted during coal combustion. This Fact Sheet provides information on the arsenic content of U.S. coals, how arsenic occurs, and its behavior during mining, coal preparation, and coal combustion and in postcombustion beneficial uses.

Arsenic in U.S. Coal

All coals contain some arsenic. The U.S. Geological Survey (USGS) maintains an extensive database of over 7,000 analyses of U.S. coals. Data from this compilation indicate that the average arsenic concentration for U.S. coal is about 24 parts per million (ppm; Bragg and others, 1998; fig. 1). There is considerable variation by coal basin, ranging from an average low of 1.4 ppm in the Raton Mesa Basin of Colorado and New Mexico to a high of 71 ppm in the southern (Alabama-Tennessee) portion of the Appalachian Basin (table 1).

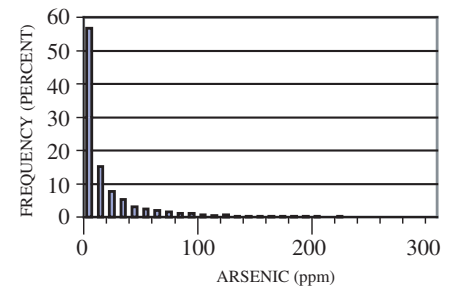


Figure 1. Histogram showing arsenic distribution in U.S. coal samples (data from Bragg and others, 1998). Arsenic (in parts per million, ppm) is expressed on a remnant moisture whole coal basis. Forty samples having arsenic values exceeding 300 ppm are excluded to make the sample distribution easier to view but are included in statistics given in table 1.

Many Eastern U.S. coals are subjected to a cleaning process prior to use in coal-burning power stations. Coal cleaning is primarily intended to reduce the sulfur content of these coals, but in many cases arsenic contents are reduced as well. As a result, for coals that are cleaned, the arsenic concentration is, on average, lower than equivalent in-ground arsenic contents.

Table 1. Comparison of average arsenic content in U.S. coals by basin and calculated average powerplant input loadings of arsenic.

[Data from Bragg and others, 1998. ppm, parts per million; Btu, British thermal unit; lb, pound]

Coal basin	Arsenic (ppm)			Calorific value (Btu/lb)			Arsenic input loadings (in 10 ³ lbs per 10 ¹² Btu)		
	Median	Mean	Number of samples	Median	Mean	Number of samples	Median	Mean	Number of samples
Appalachian, Northern	16	28	1,607	12,570	12,440	1,500	1.3	2.3	1,500
Appalachian, Central	7.8	22	1,742	13,360	13,210	1,643	0.6	1.7	1,643
Appalachian, Southern	29	71	974	12,850	12,760	968	2.2	5.8	968
Eastern Interior	10	19	289	11,510	11,450	255	0.92	1.7	255
Fort Union	4.2	8.5	280	6,340	6,410	257	0.7	1.4	257
Green River	1.2	4.8	391	9,950	9,560	264	0.13	0.44	264
Gulf Coast	2.2	3.2	141	6,440	6,470	110	0.34	0.54	110
Pennsylvania Anthracite	3.2	8.1	51	12,860	12,530	39	0.25	0.79	39
Powder River	1.6	4.2	602	8,050	8,080	486	0.2	0.5	486
Raton Mesa	0.99	1.4	40	12,500	12,300	34	0.073	0.1	34
San Juan River	0.92	2.5	185	9,380	9,640	169	0.095	0.26	169
Uinta	0.7	1.5	249	11,290	10,820	222	0.074	0.14	222
Western Interior	14	21	286	11,320	11,420	261	1.2	1.9	261
Wind River	2.4	7	41	9,630	9,570	41	0.25	0.75	41

Mode of Occurrence

The mode of occurrence of arsenic is important in determining its relative mobility during mining, combustion, and storage of coal for electric power generation; disposal or use of coal combustion byproducts; and leaching of coal beds in contact with ground water. Iron sulfides such as pyrite and marcasite are common inorganic constituents of coal, composing anywhere from a negligible amount to about 5 percent by weight. Other than iron and sulfur, arsenic is generally the most abundant element in pyrite and marcasite, but its concentration is highly variable (fig. 2).

In bituminous coals, pyrite generally accounts for the single largest fraction of arsenic, with lesser fractions in the organic portion of the coal and in other inorganic forms (fig. 3). Lower rank coals (lignite and subbituminous) generally have a larger proportion of their arsenic in the organic portion. Some coals have unusually high levels of arsenic, independent of coal rank. This enrichment is thought to result from past geologic interaction of coal beds with metal-enriched fluids, similar to the process

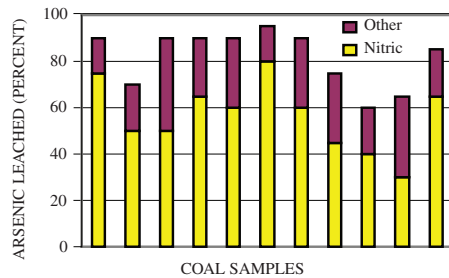


Figure 3. Selective leaching results for 11 U.S. bituminous coal samples. Plot shows that arsenic leached by nitric acid (yellow sub-bars) is the dominant form in these samples. Nitric acid is known to dissolve pyrite. The fraction of arsenic not leached (100 percent minus total bar height) represents organic-associated arsenic not removed by the leaching process. Arsenic present in all other forms is shown as "other." Modified from Palmer and others, 1998.

by which metallic ore deposits are formed (Goldhaber and others, 2003).

Arsenic in Waste from Coal Mining, Processing, and Storage

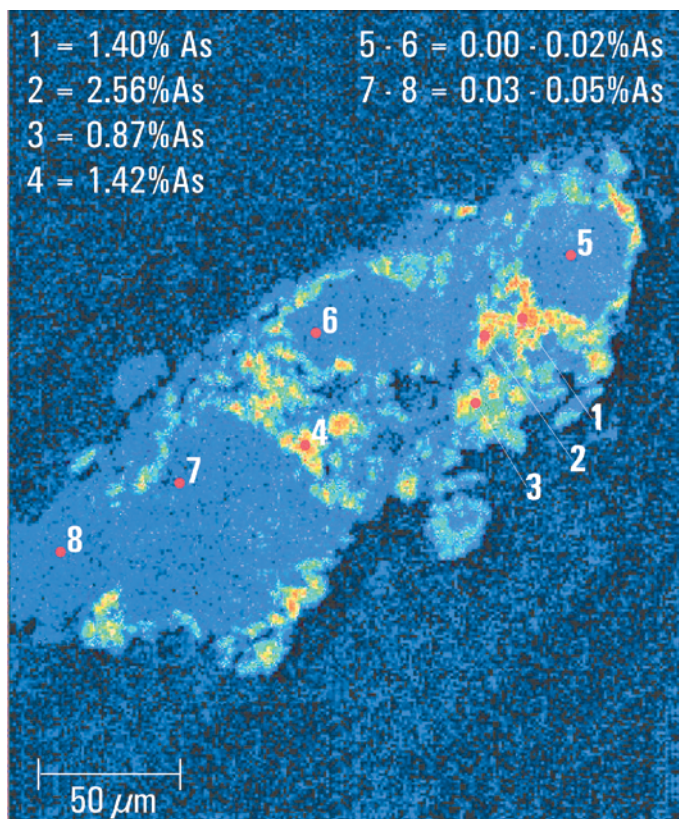
Mining operations in the United States generally must meet water-quality standards for discharge of mine water. In some

abandoned mines or undisturbed pyrite-rich strata, however, decomposition of pyrite in coal and rock can lead to dispersal of arsenic to the environment. For example, in the Warrior Coal Field of Alabama, stream sediments in areas that have been mined have higher arsenic concentrations than stream sediments outside the coal-mining areas (Goldhaber and others, 2001).

With exposure to moisture and atmospheric oxygen, arsenic in pyrite is rapidly converted to an oxidized form known as arsenate that is readily leached by precipitation and ground water (Huggins and others, 2002). The presence of arsenic in pyrite is thought to destabilize it, possibly hastening its decomposition to iron oxyhydroxide minerals. Because pyrite in coal oxidizes rapidly, coal storage facilities and waste materials from coal washing operations are potential sources of arsenic mobilization.

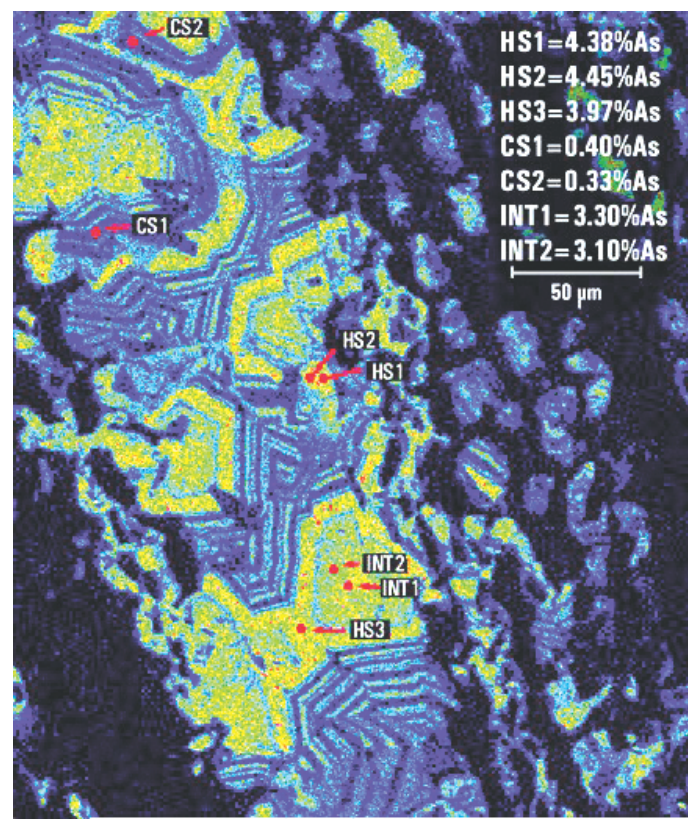
Arsenic in Coal Combustion Products

USGS studies indicate that, during coal combustion in modern coal-fired utilities, 90–100 percent of arsenic is



A

Figure 2. Elemental maps and microprobe analysis points showing distribution of arsenic (As) in pyrite in two Alabama coal samples. Maps are false-color images using a "thermal" intensity scale. A, Pyrite from a bituminous coal sampled in Cullman County, Alabama. Arsenic concentration at the points shown ranges from less than the detection limit (0.01 weight percent) to 2.6 weight percent. Image by Allan Kolker, USGS. B, Pyrite collected from a fracture in bituminous coal from Walker County, Alabama. Image shows zoning of arsenic content ranging up to nearly 4.5 weight percent. Image by Rob Koeppen, USGS; from Goldhaber and others (2003).



B

captured in coal combustion byproducts (Brownfield and others, 1999). Coal combustion byproducts such as fly ash and bottom ash likely contain multiple forms of arsenic. Some researchers have concluded that arsenic in coal ash is incorporated into iron-rich glass and crystalline silicate minerals that constitute the bulk of the solid ash. A more widely held view is that arsenic in flue gases combines with calcium oxide in the hot gases to form calcium arsenate ($\text{Ca}_3(\text{AsO}_4)_2$) that is concentrated on the surfaces of coal ash particles.

Coal combustion byproducts are widely used in a variety of commercial applications. These include cement and concrete, aggregates, structural fill, and even reclamation of abandoned coal mines. Such uses for coal ash are permitted by its designation as nonhazardous waste under the Resource Conservation and Recovery Act. Standardized tests, including the U.S. Environmental Protection Agency's (USEPA) Toxicity Characteristic Leaching Procedure, show that harmful substances such as arsenic are not readily leached from these materials under simulated environmental conditions. Additional information on coal combustion products is given in Kalyoncu and Olson (2001).

Technological Impact

Coal-fired utilities have been required to reduce emissions of nitrous oxides (NO_x) to meet air quality standards. To comply with these new emissions regulations, many existing coal-fired powerplants and new installations are equipped with selective catalytic reduction (SCR) technology. SCR works by injecting ammonia into the flue gas stream. The ammonia passes over a catalyst that reduces the nitrous oxides (NO_x) in the flue gas to elemental nitrogen and water. Although SCR is very effective in controlling NO_x emissions, the effectiveness of the catalyst is greatly reduced if there are elevated concentrations of arsenic and selenium present in the flue gas stream. As a result, the amounts of these two elements in utility feed coal are a potential concern to utilities (Rigby and others, 2000) and may be monitored closely.

Health Impact

In the United States, human exposure to arsenic primarily occurs in rural areas, through consumption of water from wells that greatly exceed the arsenic drinking water standard (10 micrograms per liter) specified by the USEPA. In the vast majority of cases, this exposure is unrelated to coal or emissions from coal-burning power-

plants. More direct exposure to arsenic from coal occurs where coal is used for domestic purposes. In the United States, such exposure is very limited. Domestic coal use is far more common in countries such as China, India, and South Africa. Health effects from arsenic have been documented where extraordinarily arsenic-rich coals were used to dry foods that were later consumed (Finkelman and others, 2002; fig. 4).



Figure 4. Interior view of residence in southwestern Guizhou Province, China, where arsenic-rich coal and coal briquettes are used to dry crops (chili peppers) that are later consumed, resulting in arsenic toxicity. Note the lack of ventilation in this dwelling. Photograph by Harvey Belkin, USGS.

Summary

Arsenic in bituminous coals is present primarily within the mineral pyrite. Pyrite occurs in small amounts in many rock types and sediments and coal. Pyrite and its weathering products are potential sources of arsenic in ground water and, more locally, in surface water. During coal combustion in modern coal-fired utilities, most of the arsenic is captured in coal combustion byproducts, which are considered nonhazardous waste, on the basis of acceptable performance in standardized leaching tests. Arsenic exposure in the United States primarily results from consumption of drinking water from private wells that exceed drinking water standards. Documented health effects from arsenic in coal are known elsewhere in the world in cases where unusually arsenic-rich coal is used domestically.

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