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# Project Summary

# Correlation of Coal Properties with Environmental Control Technology Needs for Sulfur and Trace Elements

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This report reviews existing reports and data on the occurrence of sulfur and trace elements in U.S. coals and on the effect of coal properties on trace element partitioning during coal utilization. Areas of emphasis include 1) the effect of depositional conditions on the formation and composition of mineral matter in coal, 2) the elemental concentration of major and trace elements in U.S. coals as a function of rank and geographic location, 3) analytical methods used for evaluating the modes of occurrence of these elements in coal, 4) conceptual models for predicting sulfur and trace element occurrence as a function of depositional conditions and chemical equilibrium, and 5) the fate of major and trace elements during coal cleaning, combustion, gasification, and waste disposal.

Coal washability data for 44 U.S. coal samples were used to statistically estimate the trace element reduction potential for a coal as a function of sulfur and ash reduction. Data fits were especially good for elements associated with the clay minerals, and to a lesser extent with the sulfides. Coal combustion data from 15 previous studies at commercial power plants were also analyzed; but, due to differences in technological processes at various plants, possible analytical errors, and limited data, statistical correlations are uncertain. Areas identified for future research into elemental partitioning as a function of coal properties include

development of further information on the effect of depositional conditions on coal quality, extension of the coal washability data base to additional coals (including analysis of mineral forms in these coals), and collection and analysis of additional data on the partitioning of trace elements during combustion.

This Project Summary was developed by EPA's Industrial Environmental Research Laboratory, Research Triangle Park, NC, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

## Introduction

Of the 92 naturally occurring elements, all but 16 have been detected in coal. Except for the elements which form the organic structure of coal (H, C, O, S, and N) and the associated major minerals (Al, Ca, Fe, Mg, K, Si, Na, and Ti), the concentrations of other elements are almost universally less than 0.1 percent Eight of the trace elements—Sb, As, B, Cd, Ge, Hg, Mo, and Se—are frequently found in concentrations greater than typically found in the earth's crust. For certain locations and ranks of coal, Pb and Zn are also found in concentrations greater than the earth's crustal average All other trace elements are found in smaller amounts than in typical crustal rocks Table 1 summarizes the average enrichment factors for U.S coals.

**Table 1.** *Enrichment Factors of Trace Elements in Coal Relative to the Average Composition of the Earth's Crust*[a]

| Limited Enrichment (1-3) | | Moderate Enrichment (3-10) | | Significant Enrichment (>10) | |
|---|---|---|---|---|---|
| Element | Enrichment | Element | Enrichment | Element | Enrichment |
| Pb | 1.04 | Sb | 5.80 | As | 10.2 |
| Hg | 2.38 | B | 4.30 | Se | 61.4 |
| Mo | 2.15 | Cd | 4.35 | | |
| Zn | 1.11 | Ge | 4.23 | | |

[a]*Average enrichment factor = average element concentration in coal ÷ average element concentration in earth's crust.*

During coal mining, preparation, transportation, and utilization, trace elements may be released into the environment and potentially affect occupational and public health. The exact pathways and magnitudes of human exposure to coal-related trace element releases are not known. The National Research Council has identified seven trace elements (As, B, Cd, Pb, Hg, Mo, and Se) plus compounds of C, N, and S as being of greatest concern.

## Minerals in Coal

### Origin and Characteristics

Over 125 separate minerals have been identified in coal. General pathways for accumulation of mineral matter in coal include:

1. Accumulation in the plant during its growth.
2. Detrital materials washed or blown into the peat-forming environment (including volcanic sources).
3. Sorption of soluble ions from associated water sources on the surface of peat particles.
4. Precipitation by chemical and/or biochemical processes during peat accumulation.
5. Precipitation by chemical processes during subsequent stages of coalification.

Minerals resulting from materials introduced into the bog or swamp at the time of peat accumulation are generally referred to as "syngenetic" minerals and include the first four processes of mineral matter origin discussed above. Minerals precipitated in cracks, fissures, and other voids in the coal matrix after peat burial are identified as "epigenetic" minerals. The syngenetic minerals are further subdivided into two groups: "authigenic" minerals formed from materials originally in the peat or formed in-place by precipitation or other chemical/biological processes, and "detrital" minerals consisting of solids transported into the peat by water and wind. An alternative method of differentiating minerals is to distinguish minerals easily separated from the organic structure of coal ("extraneous" or "adventitious" minerals) from those too closely associated with the organic matrix to be readily separated ("inherent" minerals). While epigenetic minerals are generally large and thus readily separable (i.e., extraneous), precise and unequivocal distinctions between authigenic and detrital, or between extraneous and inherent—although potentially of substantial scientific and technological importance—are not always possible.

### Major Mineral Groups

The four major mineral groups are clays, carbonates, sulfides, and silicates. Lesser mineral groups include sulfates, phosphates, oxides, hydroxides, and salts. The associations of trace elements with the various mineral groups are identified in Table 2.

The clay minerals (also referred to as "aluminosilicates") constitute the largest single mineral group in most coals, ranging from 40 to 80 percent of the total inorganic fraction. The most common clays are illite, kaolinite, found as finely divided grains (grain diameters are generally less than several microns) mixed with the coal and as horizontally banded kaolinite-rich claystones interbedded with the coal. Illite and montmorillonite are important in coal preparation processes because of their swelling tendencies in the presence of water (and thus the lowering of their specific gravity). Clay minerals are important to trace element analyses because of their cation exchange capacity, particularly in lignite and subbituminous coal.

The second largest mineral group in most coals is the carbonates. Siderite and dolomite formation are associated with peatification: siderite forms in peats of fresh-water origin and dolomite forms in marine-influenced environments. Calcite and ankerite are commonly found in cracks and fissures and are therefore considered to be primarily associated with second-stage coalification.

Sulfide minerals are of major environmental importance because of their conversion to $SO_2$ during combustion and to $H_2S$ during reduction processes. Principal among the sulfide minerals are the two polymorphs of iron disulfide ($FeS_2$): pyrite and marcasite. Sphalerite (ZnS), galena (PbS), and chalcopyrite ($CuFeS_2$) are also common. As and Hg are found in coal primarily in association with pyrite, while Cd is associated with sphalerite. Fine-grained sulfides are usually formed by syngenetic processes associated with the bacterial conversion of sulfates to sulfur. Coarse-grained sulfide complexes of pyrite, sphalerite, galena, and sometimes chalcopyrite are associated with both syngenetic and epigenetic precipitation processes. Reaction of siderite [iron carbonate ($FeCO_3$)] with $H_2S$ can also produce pyrites.

Quartz ($SiO_2$) is the dominant silicate mineral in coal. Quartz grains found in coal can result both from authigenic precipitation of pore fluids and from fine-grained detritus carried by water and wind. Detrital quartz is a significant constituent of clay tonsteins. With the possible exception of feldspars, the other silicates found in coal are generally too rare to be of significance.

## Occurrence of Trace Elements in U.S. Coals

### Elemental Concentrations

Trace element statistics were tabulated by rank province for the 4,402 channel samples in the National Coal Resource Data System (NCRDS) as of November 1982. Statistics were also prepared for bituminous coals from the Pottsville, Monongahela, and Allegheny units of the Appalachian Region, the eastern and western regions of the Interior Province, and the Rocky Mountain Province. Significant variations are present in the trace element contents of U.S. coals, both by rank and by geographic area. The variation in composition by rank is given in Table 3 which shows the average value of each element in the earth's crust (known as "clarkes") in the far right column.

Several trends in these data are noteworthy. First, Ca, Mg, Na, B, Ge, and Sr occur at increased concentrations in low-rank coals; these elements are believed to occur as exchangeable cations bound to the organic matter and clays in low-rank coals. Second, the average concentration of several chalcophiles (Fe, As, Cd, Ni, and Zn) and S are greater in the Interior Province and the

**Table 2.** Principal Minerals Found in Coal and Trace Constituents

| Mineral Phases | Major Constituents | Abundance[a] | Trace Constituents[b] |
|---|---|---|---|
| **Clay minerals** | | | |
| Kaolinite | Al, Si | 5-30% | Ti, Mg, Fe, and others |
| Illite | Al, Si, K | 30->60% | Fe, Mg, Ca, Na, K, Ti, |
| Montmorillonite | Al, Si, Mg, Fe | 1-10% | Rb, Cs, Ga, Be, Zn, Se, F, |
| Chlorite | Al, Si, Mg | 1-5% | La, Ba, Sr, Co, and others |
| **Sulfides** | | | |
| Pyrite, Marcasite | Fe, S | 1-10% | As, Cd, Hg, Ag, Pb, |
| Sphalerite | Zn, S | 1-5% | Fe, Zn, Cu, Co, Sn, |
| Galena | Pb, S | 1-5% | Ni, Mo, Se, Ga |
| Chalcopyrite | Cu, Fe, S | <1% | |
| **Carbonates** | | | |
| Calcite | Ca | 5-30% | Ba, Sr, Pb, Mn, Ca |
| Siderite | Fe | 5-30% | Fe, Mg |
| Ankerite | Ca, Fe | 5-30% | |
| Dolomite | Ca, Mg | 1-10% | |
| **Silicates** | | | |
| Quartz | Si | 1-10% | |
| Zircon | Si, Zr | 1-5% | Hf, Th, P |
| Tourmaline | Ca, Mg, Fe, B, Al, Si | <1% | Li, F |
| Plagioclase feldspar | Ca, Na, Al, Si | NC[c] | Ba, Sr, Mn, Ti, Fe, Mg |
| Alkali feldspar | K, Na, Al, Si | ND[c] | Rb, Ba, Sr, Fe, Mg, Ti, Li |
| Muscovite | K, Na, Al, Si | ND[c] | F, Rb, Cs, Ba, Mg, Fe |
| **Sulfates** | | | |
| Barite | Ba, S | 1-5% | Sr, Pb, Ca |
| Gypsum | Ca, S | 1-5% | |
| **Phosphates** | | | |
| Apatite | Ca, P, F | 1-5% | Rare earths, U, Ce, Mn, Cl, Mg |
| **Oxides and Hydroxides** | | | |
| Limonite, Goethite | Fe | 1-10% | ND[c] |
| Diaspore | Al | 1-5% | ND[c] |
| Hematite, Magnetite | Fe | <1-5% | ND[c] |
| Rutile | Ti | <1% | ND[c] |
| **Salts** | | | |
| Halite | Na, Cl | <1-10% | ND[c] |
| Sylvite | K, Cl | <1-10% | ND[c] |
| Bischofite | Mg, Cl | <1-10% | ND[c] |

[a]Percentage of the mineral matter.
[b]List of mineral/trace elements is representative; it does not preclude other possible associations.
[c]No data provided in reviewed publications.

Monongahela and Allegheny Formations of the Appalachian Province than elsewhere in the country. In some instances, enrichment may be at least partially attributable to regional geochemical conditions; e.g., Zn enrichment in coals of the Interior Province may be related to Zn-rich mineral deposits in that area. A third apparent trend is the increased levels of several elements (Ga, La, Sc, Se, Th, V, Yb, Y, and Zr) in Gulf Coast lignites.

## Modes of Occurrence

While knowledge of the amounts of sulfur and trace elements in a given coal is useful, additional scientific and technological information could be obtained if the modes in which these elements occur are understood. For example, the importance of a given trace element as a catalyst in a synthetic fuels process or the potential for separation of selected trace elements during physical coal cleaning may depend on whether the element is organically bound, occurs as a cation bound to an aluminosilicate, or is present as a sulfide. Several methods are available to aid in determining the mode of trace element occurrence. These methods include gravity separation to determine the "organic affinity" of an element, photomicrograph studies using scanning electron microscopy (SEM) to observe maceral/mineral relationships and mineral textures, and chemical analysis of elemental ratios of various major and trace elements.

Much of the work done on sulfur and trace elements in coal has sought to quantify the various elemental associations with respect to the organic versus the inorganic materials in coal. The most common method used in this research has been to physically separate particles of crushed coal by conventional gravity separation techniques. To a lesser extent, but in the same line of research, leaching of coal samples by selected acids has been used to chemically dissolve the inorganic matter in the coal matrix.

Gravity separations indicate only the physical association of sulfur and trace elements with extraneous minerals in the organic coal matrix. A frequent misconception is that an element with a high organic affinity is in some way chemically bound to the organic structure of the coal. While chemical bonding does occur with some trace elements, trace elements with high organic affinity can also occur in association with fine-grained minerals encapsulated in the lighter organic matrix. In these instances, gravity

**Table 3.** Sulfur, Ash, and Trace Elements in U.S. Coals by Rank[a]

| | Units | Anthracite | Bituminous | Subbituminous | Lignite | Clarkes[b] |
|---|---|---|---|---|---|---|
| Number of samples | | 52 | 3527 | 640 | 183 | |
| Total S | % | 0.86 ± 0.80 | 2.31 ± 2.08 | 0.59 ± 0.67 | 1.08 ± 1.01 | 0.026 |
| Sulfate S | % | 0.02 ± 0.02 | 0.14 ± 0.27 | 0.05 ± 0.10 | 0.22 ± 0.67 | — |
| Pyritic S | % | 0.37 ± 0.78 | 1.50 ± 1.82 | 0.19 ± 0.41 | 0.36 ± 0.64 | — |
| Organic S | % | 0.49 ± 0.16 | 0.92 ± 0.63 | 0.37 ± 0.30 | 0.57 ± 0.38 | — |
| Ash | % | 15.0 ± 8.94 | 12.6 ± 9.26 | 14.0 ± 23.7 | 21.5 ± 22.9 | — |
| Si | % | 6.56 ± 1.41 | 5.25 ± 1.51 | 5.21 ± 2.11 | 6.73 ± 4.62 | 28.15 |
| Al | % | 4.73 ± 0.77 | 2.87 ± 0.92 | 2.47 ± 0.85 | 2.77 ± 1.46 | 8.23 |
| Ca | % | 0.20 ± 0.24 | 0.42 ± 0.59 | 1.72 ± 1.16 | 3.31 ± 2.28 | 4.15 |
| Mg | % | 0.15 ± 0.21 | 0.11 ± 0.10 | 0.42 ± 0.33 | 1.01 ± 0.74 | 2.33 |
| Na | % | 0.07 ± 0.13 | 0.06 ± 0.07 | 0.25 ± 0.33 | 0.37 ± 0.53 | 2.36 |
| K | % | 0.30 ± 0.13 | 0.22 ± 0.09 | 0.10 ± 0.09 | 0.19 ± 0.24 | 2.09 |
| Fe | % | 0.87 ± 0.85 | 2.37 ± 1.86 | 0.95 ± 0.92 | 1.51 ± 1.41 | 5.63 |
| Mn | % | 0.01 ± 0.02 | 0.01 ± 0.01 | 0.01 ± 0.02 | 0.03 ± 0.02 | 0 10 |
| Ti | % | 0.29 ± 0.11 | 0.14 ± 0.07 | 0.13 ± 0.06 | 0.20 ± 0.12 | 0.57 |
| P | % | 0.07 ± 0.10 | 0.05 ± 0.09 | 0.13 ± 0.14 | 0.18 ± 0.28 | 0.11 |
| Sb | ppm | 1.12 ± 1.84 | 1.22 ± 2.27 | 0.85 ± 1.40 | 1.01 ± 2.23 | 0 2 |
| As | ppm | 7.67 ± 19.6 | 20.3 ± 41.8 | 6.17 ± 15.5 | 22.8 ± 138 | 1.8 |
| Ba | ppm | 102 ± 61.7 | 84.4 ± 132 | 447 ± 924 | 415 ± 531 | 425 |
| Be | ppm | 1.32 ± 0.85 | 2.22 ± 1.66 | 1.30 ± 1.77 | 1.98 ± 2.71 | 2.8 |
| B | ppm | 11.8 ± 10.5 | 37.6 ± 41.7 | 52.6 ± 38.5 | 114 ± 75.2 | 10 |
| Cd | ppm | 0.22 ± 0.30 | 0.91 ± 7.30 | 0.38 ± 0.47 | 0.55 ± 0.61 | 0.2 |
| Cr | ppm | 47.2 ± 60.9 | 20.5 ± 27.5 | 14.9 ± 25.6 | 13.5 ± 18.2 | 100 |
| Cu | ppm | 18.9 ± 16.4 | 17.8 ± 17.8 | 14.1 ± 14.3 | 17.2 ± 21.2 | 55 |
| Ge | ppm | 1.71 ± 2.17 | 6.33 ± 10.2 | 5.93 ± 6.55 | 10.7 ± 11.1 | 1.5 |
| Pb | ppm | 7.32 ± 6.92 | 14.3 ± 27.5 | 6.35 ± 5.47 | 6.90 ± 7.88 | 12.5 |
| Hg | ppm | 0.23 ± 0.27 | 0.21 ± 0.42 | 0.10 ± 0.11 | 0.15 ± 0.14 | 0.08 |
| Mo | ppm | 2.68 ± 2.44 | 3.28 ± 4.13 | 2.19 ± 2.82 | 5.99 ± 26.3 | 1.5 |
| Ni | ppm | 28.5 ± 32.0 | 16.9 ± 19.2 | 7.02 ± 8.44 | 8.35 ± 19.7 | 75 |
| Se | ppm | 3.11 ± 2.58 | 3.39 ± 4.00 | 1.44 ± 1.42 | 2.70 ± 3.67 | 0.05 |
| Sr | ppm | 73.7 ± 77.0 | 88.1 ± 95.0 | 171 ± 184 | 309 ± 258 | 375 |
| Th | ppm | 6.09 ± 2.92 | 3.03 ± 3.15 | 5.13 ± 4.64 | 7.13 ± 5.70 | 9.6 |
| U | ppm | 1.94 ± 3.38 | 1.85 ± 2.71 | 2.13 ± 3.84 | 3.39 ± 10.3 | 2.7 |
| V | ppm | 37.8 ± 33.1 | 22.3 ± 19.7 | 23.9 ± 30.6 | 29.1 ± 37.3 | 135 |
| Zn | ppm | 12.6 ± 14.5 | 92.4 ± 689 | 17.4 ± 21.1 | 22.5 ± 79.8 | 70 |

[a]Whole-coal basis; mean ± standard deviation.
[b]Average elemental concentration in crystal rocks.

separation of fine-grained minerals depends on both the actual modes of elemental occurrence and the size to which the sample is ground.

The initial efforts to examine the distribution of trace elements in coal by use of organic affinity methods were those of L. Horton and K.V. Aubrey, and of P. Zubovic and co-workers at the U.S. Geological Survey (USGS). During the 1970s, studies conducted by the Illinois State Geologial Survey (ISGS), U.S. Department of Energy (DOE), and Bituminous Coal Research, Inc. (BCR) provided additional information concerning the mineral and organic associations of sulfur and trace elements in coal.

The ISGS work consisted of a series of interrelated studies on the modes of sulfur and trace element occurrence. The three major components of this work addressed the level and variability of trace elements in various coals, statistical correlations between various trace elements and the cause of such relationships, and the organic affinity of individual trace elements. To express an element's organic affinity, ISGS developed an index to estimate the distribution of a specific trace element relative to the organic and inorganic fractions of an individual coal. To determine the index value, washability tests are conducted at several specific gravities and trace element contents of each specific gravity fraction are measured. For a trace element predominantly associated with the inorganic fraction of the coal, the organic affinity index will be near zero. For a trace element found predominantly in the organic fraction, the index value can be greater than 1.00.

Gravity separation studies conducted by DOE and BCR focused primarily on the potential for sulfur and trace element removal during coal cleaning. J.A. Cavallaro, M.T. Johnston, and A.W. Deurbrouck tested 455 coal channel samples to determine the potential for ash and sulfur reduction from coal cleaning. More recent studies of the ash and sulfur reduction potential of Pennsylvania, Ohio, West Virginia, and the wes-

tern U.S. have been initiated. Cavallaro, G.A. Gibbon, and Deurbrouck conducted gravity separation tests on 10 coals to determine the potential for removal of eight trace elements. Sulfur and trace element removal studies conducted by BCR analyzed 26 different coal samples. While significant variations in trace element reduction potential exist among the coals tested in the studies, general agreement exists between these values and the ISGS organic affinity index.

As indicated above, gravity separation methods provide only circumstantial evidence as to the mode of trace element occurrence in coal. To directly investigate modes of occurrence and organic/inorganic associations, photomicrographic methods, using optical and scanning electron microscopes and microprobes, are extremely valuable. The findings of such studies are of specific importance to understanding the environmental fate of trace elements in coal, particularly as they relate to trace element partitioning during coal cleaning. For example, a

number of trace elements were found in micronsized minerals throughout the organic matrix: Zn and Cd in sphalerite, Cu in chalcopyrite, Zr and Hf in zircon, and rare earth elements Y and Th in phosphates. Because of their small grain size and close association with the organic matrix, these elements may have a high apparent organic affinity based on float/sink tests. On the other hand, As and Hg were found to be in solid solution in coarser-grained pyrites: they are, therefore, more likely to be removed with the sink material. In most coals, Pb was found as a sulfide and as a substitute for Ba in various barium-bearing minerals. In some of the Appalachian Basin coal samples, lead selenide was found more frequently than lead sulfide. Significant amounts of Se, Br, Be, B, Ge, Ti, and U have also been found in association with organic matter.

Conceptual models for predicting the modes of occurrence for various trace elements and sulfur in coal have been developed by several different researchers. The initial model, developed by P. Zubovic et al. at the USGS during the 1960s, focused on chemical bonding of trace elements to coal's organic matrix. Models developed by C.B. Cecil, R.W. Stanton, and F.T. Dulong and by R.B. Finkelman, both at the USGS, have deemphasized the importance of organic bonding for most trace elements, and have focused on the modes of occurrence and origin of inorganic minerals in coal. The model of Cecil et al. attributes the mineral matter in most coals to authigenic materials found in coal-forming plants, while the Finkelman model postulates that detrital materials washed or blown into the ancient swamp system account for many of the minerals present in coal. Cecil et al. and Finkelman used some of the same coal samples for obtaining support for these two models, but drew different interpretations on the origin of minerals found in these common samples.

## Relationships Between Coal Properties and Utilization Technologies

### Coal Preparation

Several distinct processes can be used to clean raw coal. The most commonly used approach is mechanical separation of inorganic minerals based on the difference in specific gravity of various minerals (s.g.=2.0-4.0) and pyrite (s.g.=5.0) versus the organic coal fraction (s.g.= .15-1.5). The raw coal is divided into a 'float" fraction (primarily containing the

lighter organic materials and fine-grained "inherent ash" in coal) and a "sink" fraction (consisting mainly of clays, shales, pyrites, and other "extraneous" minerals).

## Sulfur and Ash Removal

DOE has analyzed the removal of sulfur from roughly 750 raw coal samples from throughout the U.S. The DOE study, published in 1976, analyzed 455 samples, roughly half of which were from producing mines in the Northern Appalachian Region, and the balance from the other major U.S. coal regions. More detailed studies on the coals of Pennsylvania have also been completed, and studies of Ohio, West Virginia, and western U.S. coal are underway. These studies have included standard washability tests to determine sulfur and ash removal potential for various coals as a function of the specific gravity of separation and size of the raw coal feed.

The general conclusion of these studies is that ash and sulfur contents can be reduced for almost all coals by physical coal cleaning (PCC). Figure 1 shows significant similarities in coal washability for coal from the same seams and regions. For example, excluding the Allegheny Formation coals, most eastern and midwestern coals show a greater improvement in cleanability by grinding from 3/8-in. (9.5 mm) to 14 mesh (1.18 mm) than from 1-1/2 in. (38.1 mm) to 3/8-in. (9.5 mm). The high sulfur reduction potential for the Allegheny coals may be explained in part by the higher percentage of pyritic sulfur found in the Allegheny coals, and may also indicate that the size of pyrites in these coals is larger—and thus more readily separable than in other coals. Genetically, this suggests that the Allegheny coals may have formed under geologic conditions which resulted in relatively low levels of syngenetic sulfur fixation, followed by precipitation of significant amounts of coarse-grained epigenetic pyrite.

## Trace Element Removal

The removal of trace elements from coal during coal cleaning has been examined both in laboratory washability studies and in analyses of operating preparation plants. A total of 45 coal samples have been evaluated in three separate studies—23 from Appalachia, 13 from the Illinois Basin, and 9 from the western U.S.

Element removal data for major and trace species from these coals are

summarized in Table 4. The table is divided into six regions—the Monongahela, Allegheny, and Pottsville units of the Appalachia Region, the Illinois Basin, the Northern Great Plains, and the Rocky Mountains. Dividing the Appalachian Province into three units is based on the differences in depositional conditions believed to have existed during each of these geologic periods and the resulting impact on the coals. These geologic units are also roughly equivalent to dividing the Appalachian Province into a southern region consisting of southern West Virginia and states to the south (which produce coals from the Pottsville Group) and a northern region consisting of the remainder of the province (which produce primarily from the Monongahela and Allegheny Formations).

These data indicate that Allegheny Formation coals have the greatest removal potential for most trace elements and that Rocky Mountain coals have the least potential. Due to the limited number of samples available from each region (especially from the Northern Great Plains Province), the validity of the computed values is subject to considerable statistical uncertainty. However, the favorable comparison of these results with the sulfur reduction data obtained by others suggests that the computed values for trace element removal may reasonably reflect the regional values.

The data on gravity separation of trace elements from these earlier studies were analyzed by Radian Corporation during this study, using several statistical techniques, including linear correlations, cluster analysis, discriminant analysis, principal components, step-wise regression, and regression of the logit transform* of the data. Mineral suites identified from correlation analysis of the feed coal (i.e., elements with correlation coefficients ≥0.70) were the trace element sulfides (As, Cd, Pb, Sb, and Zn), the clays (Al, K, Si, Ti, plus the trace elements Co, Cr, and V), and pyrite (Fe and S). Flourine correlated with elements in several mineral suites—the clays (Al, K, Si, Ti, and Cr), the chalcophiles (Cu and Ni), and Be.

Correlation tests of the trace element removal data found that every element examined (except sulfur and the chalcophiles As, Cd, Hg, and Sb) correlated strongly with total ash removal. The chalcophiles As, Hg, and Fe, were moderately correlated with pyritic sulfur, while As, Co, Hg, Pb, Se, and Fe correlated with total sulfur. Efforts to
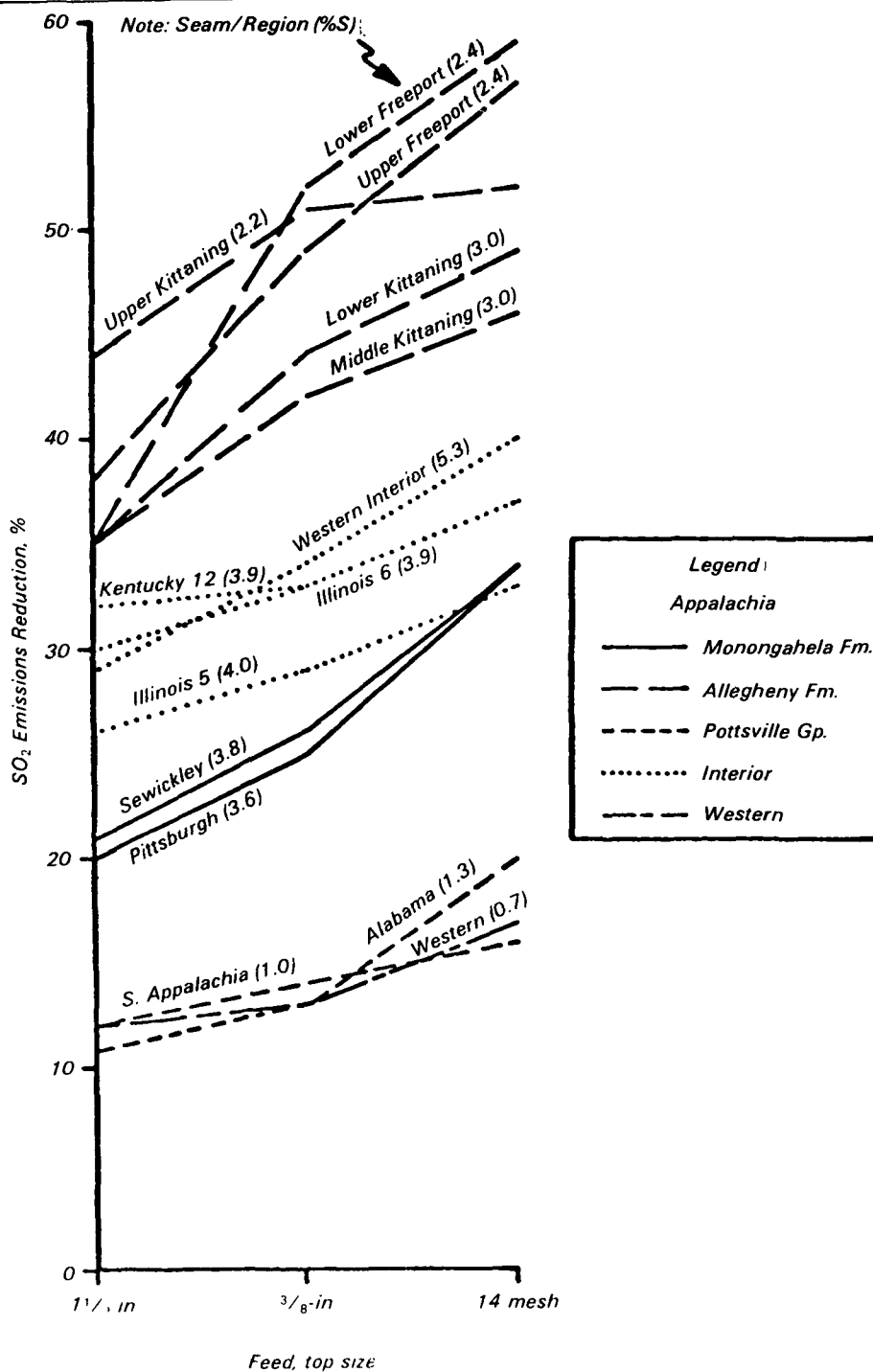
*logit (p) = ln [p/(100-p)].

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Figure 1. Coal cleaning $SO_2$ emissions reduction percentages for selected coals and feed sizes.

variable and ash removal and sulfur removal as the independent variables.[*] Ash and sulfur removal are parameters commonly obtained during standard coal washability tests and, therefore, are attractive as independent variables for predicting trace element partitioning. The strong statistical correlation of trace element removal with ash and sulfur removal in the existing data also supports use of these two independent variables.

Table 5 gives results of regressions obtained for trace element removal versus ash removal alone. Corresponding to the results obtained using simple linear correlation analysis, R-square values for a number of elements are relatively good. As expected, the data for Al, Si, V, and other clay-associated elements fit the predicted value line well. For As and other elements more closely associated with the sulfides in the coal than with the total ash content, the scatter of data and the size of the confidence intervals are large.

For the elements which exhibited relatively strong correlations with sulfur removal as well as for selected other elements, fits of the element removal were made as a function of both ash and sulfur removal. These results are shown in Table 6. The R-square values for Pb, Co, As, Fe, Se, and Hg are significantly improved. This result is to be expected, given the mode of occurrence of these elements in association with pyrite. Also as expected, the R-square for the chalcophiles Cd, Cu, and Zn — occurring as fine-grained sphalerite and chalcopyrite distributed throughout the coal matrix— is only slightly influenced by the addition of sulfur reduction as a variable. This also reflects the fact that, although these three trace elements occur in coal as sulfides, only a small percentage of the total sulfur in the coal is present as trace element sulfides.

## Combustion

Direct combustion is currently the primary use of coal in the U.S. Most coal is pulverized and fired in large boilers, although a significant percentage is also stoker-fired in smaller industrial and commercial burners. During combustion, trace elements undergo a variety of transformations. Some are melted and included in the aluminosilicate matrix which forms the major structure of coal fly ash; others fall to the base of the boiler as bottom ash or slag; and still others are

correlate percent removal of an element with the quantity of that element in the feed coal found that, except for elements occurring in the clays, no strong correlations existed. A logical interpretation of this finding is that the abundance of clays, rather than the abundance of the trace element itself, determines the extent of removal possible.

Regressions using the logit transformation were run on the data using element removal as the dependent variable.

*logit (ER) = A + (B x logit (AE)) + (Cxlogit (SR)) where ER= percent element removal, AR = percent ash removal, SR = percent sulfur removal, and A, B, and C = fitted regress coefficients

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**Table 4.** Regional Summary for Removal of Major and Trace Element Species by Gravity Separation of 44 U.S. Coals[a]

| | Appalachian Province | | | Interior Province | N. Great Plains Province | Rocky Mountain Province |
|---|---|---|---|---|---|---|
| | Monongahela | Allegheny | Pottsville | | | |
| Number of samples | 9 | 5 | 9 | 13 | 2 | 6 |
| Total S | 29 ±15 | 53 ±17 | 27 ±18 | 38 ± 9 | 50 ± 8 | 11 ± 8 |
| Pyritic S | 40 ±20 | 66 ±15 | 52 ±22 | 57 ±15 | 53 ± 9 | 32 ±23 |
| Organic S | 4 ± 4 | 14 ± 9 | 9 ± 8 | 0 ± 5 | 15 ± 3 | -9 ±13 |
| Ash | 52 ±23 | 73 ±12 | 74 ±20 | 48 ±15 | 41 ± 8 | 35 ±23 |
| Si | 57 ±27 | 78 ±12 | 79 ±15 | 47 ±22 | 52 ± 4 | 22 ±30 |
| Al | 52 ±28 | 72 ±13 | 71 ±21 | 42 ±21 | 36 ± 2 | 14 ±20 |
| Ca | 55 ±26 | 51 ±14 | 56 ±26 | 55 ±34 | 13 ± 7 | 8 ±20 |
| Mg | 57 ±29 | 80 ±11 | 79 ±17 | 53 ±25 | 16 ± 1 | 12 ±20 |
| Na | 48 ±29 | 72 ±11 | 70 ±25 | 44 ±28 | 18 ± 9 | 12 ±19 |
| K | 62 ±27 | 82 ±12 | 81 ±19 | 47 ±27 | 59 ±10 | 34 ±46 |
| Fe | 45 ±20 | 76 ± 5 | 65 ±24 | 61 ±19 | 68 ±15 | 28 ±23 |
| Mn | 54 ±24 | 78 ±13 | 75 ±24 | 57 ±25 | 31 ±16 | 37 ±38 |
| Ti | 58 ±25 | 71 ±14 | 70 ±23 | 42 ±24 | 42 ± 6 | 15 ±23 |
| P[b] | 56 ±23 | 57 ±25 | 64 ±25 | 67 ±44 | 24 ± 6 | 11 ± 8 |
| Sb[b] | 34 ±19 | 32 ± 2 | 28 ±13 | 17 ±16 | 43 ±22 | 24 ±27 |
| As[b] | 53 ±22 | 77 ±11 | 75 ±10 | 61 ±20 | 69 ±11 | 32 ±23 |
| Be[b] | 37 ±23 | 44 ±12 | 43 ±20 | 22 ±10 | 12 ± 6 | -5 ±31 |
| B[b] | 20 ±21 | 62 ±- | 30 ± 6 | 10 ± 6 | — | 1 ±- |
| Cd | 43 ± 20 | 48 ±12 | 54 ±20 | 71 ±22 | 33 ±13 | 35 ±26 |
| Cr | 41 ±24 | 57 ±17 | 65 ±23 | 37 ±18 | 34 ±13 | 24 ±15 |
| Co[b] | 46 ±30 | 69 ±15 | 39 ±25 | 39 ±20 | — | 3 ±- |
| Cu | 46 ±22 | 61 ±14 | 48 ±20 | 35 ±20 | 28 ± 3 | 14 ±11 |
| F[b] | 51 ±25 | 66 ±16 | 80 ±12 | 46 ±20 | 28 ±11 | 24 ±15 |
| Pb | 49 ±25 | 74 ±10 | 60 ±23 | 48 ±19 | 41 ± 4 | 34 ±18 |
| Hg | 36 ±14 | 58 ± 8 | 51 ±20 | 34 ±22 | 36 ±21 | 25 ±20 |
| Ni | 43 ±20 | 52 ± 7 | 46 ±23 | 31 ±18 | 5 ± 2 | 15 ±15 |
| Se[b] | 39 ±18 | 65 ±13 | 43 ±17 | 35 ±16 | 46 ±13 | 15 ±15 |
| V[b] | 41 ±23 | 59 ±16 | 60 ±28 | 29 ±15 | 16 ±13 | 8 ±21 |
| Zn[b] | 50 ±28 | 65 ±10 | 69 ±24 | 57 ±27 | 47 ±22 | 34 ±30 |

[a]Whole-coal basis; mean ± standard deviation.
[b]Mean and standard deviation based on less than total number of samples due to lack of data.

**Table 5.** Estimated Trace Element Removal During Coal Washing Based on Regression of Logit Transform of Ash Removal Data

| Element | N | 100% x $R^2$ | Coefficients | |
|---|---|---|---|---|
| | | | Intercept[a] | % Ash Removed[a] |
| Al | 33 | 95 | -0.2107 (0.054) | 1.0451 (0.042) |
| Si | 31 | 94 | 0.2585 (0.056) | 0.9285 (0.045) |
| V | 33 | 91 | -0.9691 (0.077) | 1.1124 (0.063) |
| K | 33 | 90 | 0.3398 (0.087) | 1.1668 (0.068) |
| Na | 34 | 86 | -0.5754 (0.116) | 1.3246 (0.092) |
| Ti | 31 | 85 | -0.0357 (0.089) | 0.9040 (0.071) |
| Cr | 43 | 84 | -0.6115 (0.077) | 1.0051 (0.069) |
| Be | 33 | 75 | -1.3232 (0.106) | 0.8508 (0.087) |
| Pb[b] | 43 | 74 | -0.2583 (0.095) | 0.9227 (0.085) |
| Mn | 44 | 74 | -0.0376 (0.150) | 1.4249 (0.130) |
| Cu | 42 | 70 | -0.6770 (0.092) | 0.7979 (0.082) |
| Co[b] | 25 | 68 | -0.8937 (0.168) | 0.8703 (0.126) |
| Ni | 42 | 67 | -0.9964 (0.110) | 0.8805 (0.097) |
| Zn | 34 | 66 | -0.0250 (0.145) | 0.9127 (0.115) |
| P | 33 | 56 | -0.3041 (0 215) | 1.0525 (0.169) |
| Ca | 33 | 49 | -0.4688 (0.227) | 1.0123 (0 185) |
| Fe[b] | 34 | 48 | 0.1355 (0.157) | 0.6725 (0.124) |
| Se[b] | 34 | 47 | -0.6969 (0.133) | 0.5590 (0.105) |
| As[b] | 33 | 42 | 0.3095 (0.135) | 0.4992 (0.105) |
| Hg[b] | 44 | 38 | -0.7126 (0.134) | 0.5796 (0.115) |
| Cd | 43 | 20 | -0.0358 (0.183) | 0.5024 (0.156) |

N=The number of coal samples used in the regression.
$R^2$ x 100 = R-square expressed as a percentage. This is the percent of total variation around a horizontal (average) line that is reduced by tilting the line to the indicated regression line ($R^2$ is computed in the transformed scale).
[a]Coefficients are for the logit equation (see previous footnotes); the standard error for each coefficient (a measure of the goodness of fit) is shown in parentheses.
[b]Elements showing significant improvement in $R^2$ when fit includes both ash and sulfur removal; see Table 6.

vaporized and oxidized. The volatile elements may subsequently condense onto the available surfaces (mostly fly ash particles) or be vented as vapors. Nearly all trace elements become enriched in the ash since most of the mass (i.e., the carbon) has burned away. For sulfur and most trace elements, the nature of the combustion and cooling processes (i.e., temperature profiles, residence time, amount of excess oxygen) is more important in determining the final form of the element than its structure or form in the original coal.

Table 7 presents the elemental distribution patterns for the more common major and trace elements based on data from 15 studies where a mass balance for trace elements was calculated. The *Emissions* column refers to measurements of the flue gas/fly ash mixture exiting the plant via atmospheric (stack) emissions. All the plants included in the averages controlled particulate emissions with at least 98 percent control efficiency.

The mass flow of the major ash-forming elements, which generally are not enriched or depleted in any waste stream, give an idea of the total mass partitioning. For example, for Al, Ca, Fe, Mg, and Ti, the percentage into the bottom ash averaged

**Table 6.** *Estimated Trace Element Removal During Coal Washing Based on Regression of Logit Transform of Ash and Sulfur Removal Data*

| Element | N | 100% x $R^2$ | Estimated Coefficients | | |
|---|---|---|---|---|---|
| | | | Intercept[a] | Ash Removal[a] | Sulfur Removal[a] |
| Pb | 43 | 74 | -0.2583 (0.95) | 0.9227 (0.085) | — |
| | | 51 | 0.7117 (0.166) | — | 0.7978 (0.123) |
| | | 88 | 0.2024 (0.096) | 0.7268 (0.067) | 0.4615 (0.069) |
| Co | 25 | 68 | -0.8937 (0.168) | 0.8703 (0.126) | — |
| | | 52 | 0.2525 (0.247) | — | 0.8294 (0.166) |
| | | 79 | -0.3696 (0.202) | 0.6491 (0.120) | 0.4615 (0.131) |
| As | 33 | 42 | 0.3095 (0.135) | 0.4992 (0.105) | — |
| | | 58 | 1.0303 (0.147) | — | 0.6870 (0.107) |
| | | 70 | 0 7483 (0.147) | 0.3145 (0.090) | 0.4922 (0.107) |
| Fe | 34 | 48 | 0.1355 (0.157) | 0.6725 (0.124) | — |
| | | 53 | 1.0441 (0.187) | — | 0.7810 (0.131) |
| | | 67 | 0.7004 (0.183) | 0.4273 (0.115) | 0.5444 (0.128) |
| Se | 34 | 47 | -0.6969 (0.133) | 0.5590 (0.105) | — |
| | | 47 | 0.0280 (0.167) | — | 0.6155 (0.116) |
| | | 63 | -0.2741 (0.164) | 0.3755 (0 103) | 0.408 (0.115) |
| Hg | 44 | 38 | -0.7126 (0.134) | 0.5796 (0.115) | — |
| | | 36 | -0.0126 (0.175) | — | 0.6192 (0.126) |
| | | 50 | -0.2954 (0.179) | 0.3958 (0.120) | 0.4111 (0.130) |
| Cd | 43 | 20 | -0.0358 (0.183) | 0.5024 (0.156) | — |
| | | 17 | 0.5608 (0.245) | — | 0.5024 (0.175) |
| | | 25 | 0.2798 (0.273) | 0.3633 (0.179) | 0.2999 (0.196) |
| Cu | 42 | 70 | -0.6770 (0.092) | 0.7979 (0.082) | — |
| | | 19 | -0.0397 (0.196) | — | 0.4826 (0.159) |
| | | 72 | -0.5295 (0 129) | 0.7477 (0.086) | 0.1615 (0 102) |
| Zn | 34 | 66 | -0.0250 (0.145) | 0.9127 (0.115) | — |
| | | 24 | 0.8042 (0.273) | — | 0.6110 (0.191) |
| | | 67 | 0.1211 (0.211) | 0.8493 (0.132) | 0.1407 (0.147) |

N = The number of coal samples used in the regression.

$R^2$ x 100 = R-square expressed as a percentage. This is the percent of total variation around a horizontal (average) line that is reduced by tilting the line to the indicated regression line ($R^2$ is computed in the transformed scale).

a = Standard error in parentheses.

18.0 ± 0.8 and the hopper ash averaged 80.5 ± 0.8; this would leave about 1.5 percent for the emissions. Using these values as indicative of total mass flow, the enrichment/depletion of an element in a particular output stream can be assessed.

These data reveal:

- Ag, As, Cd, Cl, F, Hg, Pb, S, Sb, Se and Zn are depleted in the bottom ash. Only U appears to be enriched at all, and the standard deviation for U is large.
- Elements significantly depleted in the hopper ash are Cl, F, Hg, Mo, and S. Only Ag appears to be significantly enriched in the hopper ash.
- Elements enriched in the fly ash/flue gas emissions are As, B, Cd, Cl, Cr, F, Hg, Mo, Ni, Pb, S, Sb, and Se.
- Note should be taken of the standard deviation of each number; a large

deviation indicates a very broad range of values or that one data point was far from the average.

- Closure of from 70 to 130 percent is within the expected limits of sampling and analytical procedures. For values outside this range, the partitioning data are uncertain.
- Low closure values indicate that some of the element was escaping detection in the waste streams (e.g., Hg, F). High closure indicates that either coal analysis was low or the waste stream samples are easily contaminated (e.g., Cl, Cr). Elements with poor closure (or large uncertainty) are Ba, Cl, Cr, Cu, F, Hg, Mo, Pb, S, Sb, Se, U, and Zn.

Further analyses of these data were carried out, but the results are uncertain. For example, analysis of partitioning and enrichment as a function of coal rank

indicated that several chalcophile elements (As, Fe, Pb, Zn) may be enriched in the emissions stream of subbituminous coals, but may be erroneous due to the limited amount of data available.

Evidence, while sparse, suggests that partitioning of the elements is largely independent of the properties of the coal and that elemental partitioning during combustion is determined by the process conditions (e.g., temperature and combustor design). However, data are insufficient to detail these relationships in any well-defined manner.

## Synfuels

A survey of published synfuel characterization studies shows that most of the sulfur originally in the coal is found in the product gas and tar/oil by-products. Roughly 90 percent of the sulfur found in the gas phase is usually in the form of hydrogen sulfide, with the remainder consisting of carbonyl sulfide, methyl and ethyl mercaptan, carbon disulfide, and other organic sulfur species. Most of the trace elements appear to remain in the gasifier ash/slag and solids removed from the product gas. General exceptions are F, Hg, Se, Zn, and Pb. However, closure on the trace element mass balances is generally poor due to problems inherent in analyzing for species present in low concentrations and in the collection efficiency of the sampling methods, especially for gas-phase trace elements.

The available data on sulfur and trace element partitioning in coal gasification systems have not generally been correlated with coal properties. However, as would be expected, coals with higher concentrations of sulfur and various trace elements produce higher concentrations of these species in the process streams.

## Leaching of Coal Wastes

Coal utilization by the electric power industry generates more than 70 million tons of solid waste per year. These wastes include refuse from coal preparation plants, bottom ash and fly ash from coal combustion, and flue gas desulfurization wastes. Most of these utility wastes are nonhazardous and are disposed of in landfills. However, because of their large volumes, constituents released from coal-fired utility wastes through leaching may constitute a potential hazard.

A substantial amount of work has been performed on the leaching of coal wastes. However, the relationship of coal properties to the leachate from coal wastes, the principal point of this study, is not directly addressed in the open literature. Although

**Table 7.** Average Elemental Distribution of Fly Ash

| Element | No. of Points | Percent Distribution of Element[a] Bottom Ash | Hopper Ash | Emissions | Closure Percent |
|---------|------|------|------|------|------|
| Ag | 3 | 5.4 ± 3.5 | 91.8 ± 5.2 | 2.8 ± 1.7 | 112 ± 4 |
| Al | 8 | 17.1 ± 5.4 | 81.6 ± 5.4 | 1.2 ± 1.6 | 96 ± 12 |
| As | 10 | 5.8 ± 8.0 | 84.4 ± 16.4 | 9.7 ± 14.0 | 114 ± 32 |
| B | 7 | 11.2 ± 8.8 | 81.3 ± 11.8 | 7.6 ± 9.5 | 106 ± 36 |
| Ba | 7 | 15.8 ± 5.0 | 82.8 ± 6.4 | 1.4 ± 3.0 | 128 ± 35 |
| Be | 9 | 15.3 ± 6.0 | 82.5 ± 8.6 | 2.2 ± 3.9 | 92 ± 22 |
| Ca | 6 | 17.8 ± 5.3 | 80.6 ± 5.2 | 1.6 ± 2.0 | 99 ± 16 |
| Cd | 7 | 9.1 ± 5.4 | 76.3 ± 20.9 | 14.6 ± 17.6 | 102 ± 34 |
| Cl | 4 | 6.9 ± 7.0 | 7.8 ± 7.4 | 85.3 ± 10.8 | 167 ± 140 |
| Co | 6 | 15.4 ± 3.7 | 82.3 ± 2.5 | 2.3 ± 1.6 | 98 ± 17 |
| Cr | 9 | 12.7 ± 5.2 | 80.5 ± 9.6 | 6.8 ± 8.8 | 121 ± 65 |
| Cu | 7 | 11.9 ± 3.2 | 83.4 ± 8.0 | 4.7 ± 7.3 | 83 ± 32 |
| F | 8 | 2.5 ± 2.6 | 60.2 ± 37.3 | 37.4 ± 38.2 | 73 ± 37 |
| Fe | 8 | 19.5 ± 4.9 | 79.3 ± 5.0 | 1.3 ± 1.5 | 115 ± 10 |
| Hg | 10 | 2.7 ± 3.9 | 31.3 ± 35.2 | 66.0 ± 38 | 62 ± 51 |
| K | 3 | 19.9 ± 1.2 | 79.1 ± 2.8 | 1.0 ± 1.7 | 104 ± 24 |
| Mg | 7 | 18.0 ± 4.3 | 79.9 ± 5.4 | 2.1 ± 2.4 | 103 ± 16 |
| Mn | 7 | 16.8 ± 6.1 | 80.8 ± 8.9 | 2.4 ± 4.4 | 122 ± 16 |
| Mo | 7 | 12.9 ± 14.9 | 63.9 ± 29.8 | 23.2 ± 34.0 | 141 ± 85 |
| Na | 3 | 15.5 ± 5.7 | 83.4 ± 3.9 | 1.1 ± 1.8 | 98 ± 23 |
| Ni | 9 | 14.4 ± 6.4 | 74.3 ± 13.9 | 11.2 ± 15.4 | 113 ± 32 |
| Pb | 10 | 7.0 ± 4.8 | 83.5 ± 18.0 | 9.5 ± 18.1 | 100 ± 60 |
| S | 5 | 3.1 ± 5.2 | 28.2 ± 36.4 | 68.6 ± 40.9 | 77 ± 50 |
| Sb | 8 | 7.1 ± 6.7 | 85.6 ± 13.9 | 7.3 ± 12.9 | 115 ± 83 |
| Se | 11 | 3.0 ± 3.9 | 71.1 ± 22.4 | 25.9 ± 22.1 | 64 ± 30 |
| Ti | 5 | 17.6 ± 5.6 | 81.2 ± 5.2 | 1.2 ± 1.3 | 92 ± 23 |
| U | 4 | 26.2 ± 16.0 | 71.8 ± 16.0 | 2.0 ± 1.9 | 65 ± 25 |
| V | 8 | 12.5 ± 6.5 | 83.8 ± 7.9 | 3.7 ± 3.5 | 100 ± 41 |
| Zn | 8 | 10.0 ± 8.7 | 85.1 ± 10.7 | 4.9 ± 5.4 | 127 ± 70 |

[a]Normalized to 100 percent by dividing measured values by closure value. Measured values equal normalized distribution times closure value.

general ranges of coal ash leachate quality can be approximated from information on what was originally in the coal, specific or quantitative correlations between coal properties and those of coal ash leachate are not available. The most useful correlation of coal properties to leachate properties may be accomplished for coal preparation wastes which are not affected by the combustion process.

Coal preparation wastes are produced when mineral matter is removed from coal prior to combustion, conversion to synthetic fuels or coke, or other final uses. The resultant waste contains a variety of inorganic materials ranging from fine-grained clays to sands, shales, and macroscopic mineral nodules. Elements generally found in coal refuse at or above the 1 percent level include Fe, S, Al, Si, K, Ca, Mg, Ti, and Na. As, B, Cd, Cr, Pb, Mn, Hg, Ni, Se, and Zn may also be present in significant amounts.

Boiler fly ash is generally removed from the flue gas by electrostatic precipitators or fabric filters. The alkali, alkaline earth, and rare-earth elements plus As, Se, Cd, Pb, Hg, and U are concentrated in the glass phase of fly ash, while Cr, V, and Ga appear to concentrate in the crystalline mullite phase. Due to their silicate structure these materials are only moderately leachable. Of greater concern are the elements found in the more leachable spinel oxide—V, Cr, Mn, Co, Ni, Cu, and Zn.

Boiler bottom ash is a vitrified, relatively inert residue which generally contains lower concentrations of volatile trace elements (As, Se, Cd, F, Mo, Pb, S, and Zn) than fly ashes. While solid-phase fly ash and bottom ash contain similar major constituents, significant variations occur in trace element composition. Leachates from fly ash and bottom ash ponds in general are also markedly different with respect to trace element concentrations.

Flue gas desulfurization (FGD) can involve several gas scrubbing processes. The scrubber waste will contain small amounts of entrained fly ash and volatile trace elements absorbed from the flue gas. Laboratory column leaching studies of Ca-based FGD sludges have shown that the first few pore volumes of leachate contain elevated concentrations from the entrained scrubber liquor. Subsequent leachates level off to a dissolved solids concentration controlled by the solubility of the calcium sulfite, sulfate, or carbonate.

## Recommendations

### Coal Quality

● Extension of Depositional Models to Include Coal Quality. Depositional models have been developed to interpret the relationship between ancient peat-forming environments and coal deposit geometry. These models can aid coal geologists in interpreting the lateral continuity, thickness, and overall tonnages in a seam; and the association of coals with other sedimentary facies. Correlations have also been made between depositional environments and the ash and sulfur contents of coals. The next logical step is the extension of these models to help predict additional coal quality information based on depositional chemistry and other relevant parameters.

● Additional Study of the Origin of Mineral Matter in Coal. Knowledge of the origin of mineral matter in coal is potentially of significant technological and environmental benefit by assisting in prediction of coal quality variations and in process selection and optimization. Significant disagreements still exist among coal geoscientists over the origin of various minerals in coal. Currently two significantly different models exist. One model assumes that detrital materials account for much of the mineral matter in most coals. The other model assumes that detrital minerals are of minor importance. Using existing analytical methods, support for both models has been demonstrated using the same coal samples. These models need to be refined, and existing data need to be reevaluated in order to reconcile these differences. Where appropriate, additional analytical procedures and coal samples should also be examined.

● Factors Influencing the Distribution of Mineral Matter in Coal. Directly related to the above recommendations is the analysis of genetic factors which influence the extraneous versus inherent nature of ash found in coal. Extraneous minerals can be readily removed from coals by conventional washing, while inherent ash cannot be removed. Coals such as those from the Allegheny Formation have good washability, while those from the Monongahela are more difficult to clean. Determination of the major difference in the coals as a function of mineralogy, depositional

environments, and other related factors could be beneficial in evaluating the use of future coal resources.

● Additional Analysis of the Mode of Trace Element Occurrence. Existing trace element data bases, such as the USCHEM file currently maintained by the USGS, are focused on providing information on the quantity of trace elements in U.S. coals, but do not provide information on the modes of occurrence for these elements. Before compiling extensive data on mineralogy or other characteristics, however, standardized procedures for evaluating samples need to be developed. Existing methods are expensive and imprecise.

## Coal Utilization

● Analysis of Coal Washability for Additional Coals. The 44 coals included in this study include samples from the major coal provinces in the U.S., but provide little or no information on a number of the major coal-producing seams and regions in the U.S. By comparison, sulfur removal data is available for over 750 samples. Specific attention in the additional studies should be given to major coal seams and regions which are presently washing coals or for which coal washing is likely in the future.

● Impact of Mineralogy on Cleanability. During this study the potential for trace element removal from coals was examined relative to the major ash-forming elements and as a function of the level of ash and sulfur removable from the coal. Neither approach directly evaluates the minerals in the coals. Cleanability needs to be examined as a function of the minerals in the coals and the modes of trace element occurrence.

● Additional Analysis of Existing Data on Partitioning During Combustion. The current study limited analysis of the partitioning of trace elements during combustion to studies for which material balances were also accomplished. Many additional studies (30-50) have been completed which give elemental concentrations in various combustion waste streams without measuring flow rates. While estimation of absolute elemental distributions between process streams is not possible for these studies, it is possible to estimate enrichment ratios. Using these studies, the data base on partitioning of trace elements during combustion could be expanded

significantly. Such a data base should be large enough to allow a more detailed analysis of statistical relationships associated with combustion partitioning.

● Catalytic Effects of Trace Elements on Sulfur Retention. Va, Fe, and certain other elements can serve as a catalyst for the conversion of $SO_2$ to $SO_3$. Because of the increased efficiency by which $SO_3$ is absorbed onto the surface of fly ash particles, this catalytic effect may be important, but has not been extensively investigated.

● Correlation of Leaching Characteristics with Coal Properties. Little research has been done on the effects of coal properties on the composition of combustion ashes and their associated leachabilities. The leaching potential of fly ash is related to the abundance and composition of spinel (ferrite oxide) versus aluminosilicates in the ash which in turn is believed to be associated with the composition of the coal. However, these relationships have not been well defined. When sampling coal and coal ash in the same time periods and under well known operating conditions, the coal and the leachability of the ash need to be analyzed in in detail, and correlations between analyses examined.