Mineralogical and Chemical Composition of Inorganic Matter from Marketed Illinois Coals

Ilham Demir, Randall E. Hughes, Philip J. DeMaris,
and Rodney R. Ruch

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George H. Ryan, Governor

Department of Natural Resources
Brent Manning, Director

ILLINOIS STATE GEOLOGICAL SURVEY
William W. Shilts, Chief
Natural Resources Building
615 East Peabody Drive
Champaign, IL 61820-6964
(217) 333-4747

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ABSTRACT

The mineralogical and chemical compositions of marketed Illinois coals and coal combustion residues (CCRs) were investigated to obtain a better understanding of the relationship of these materials to air pollution and ash formation at coal-fired power plants. The coal samples were collected from 35 coal preparation plants in Illinois. The samples of CCRs (fly and bottom ashes), along with samples of feed coals, were collected from a fluidized bed combustion (FBC) plant, two cyclone combustion (CYC) plants, and a pulverized coal combustion (PC) plant. Average (mean ± standard deviation) abundances of minerals in the marketed coals were kaolinite, 2.07 ± 0.56%; quartz, 2.06 ± 0.78%; mixed-layered illite/smectite, 1.57 ± 0.70%; pyrite, 1.56 ± 0.50%; illite, 1.29 ± 0.46%; calcite, 0.84 ± 0.78%; chlorite, 0.18 ± 0.13%; marcasite, 0.13 ± 0.12%; plagioclase, 0.07± 0.05%; and K-feldspar, 0.01 ± 0.01%. Nineteen minor and trace elements positively correlated with some of the minerals. The correlations that involved elements of environmental concern were Mn-calcite, F-illite and F-illite/smectite, Th-illite and Th-illite/smectite, Th-kaolinite, Cr-illite/smectite, and Hg-pyrite. A comparison of the mineralogical composition of coals with CCRs suggested that combustion at the power plants partially converted quartz to silica glass. The clay minerals and feldspars were converted largely to aluminosilicate glass and, to a much lesser extent, to mullite. Pyrite and marcasite were converted to hematite, magnetite, and amorphous Fe oxides. Calcite was converted to anhydrite, gypsum, lime, and portlandite; some of the lime and portlandite was converted back to calcite through reaction with atmospheric CO_2. The minerals derived from calcite formed 30% and 71% of the FBC fly ash and bottom ash, respectively. The CCRs from the CYC and PC plants contained mostly amorphous material (78–98%). Other minerals in the CCRs from the four power plants were magnetite (0–4.95%), quartz (0.008–8.44%), mullite (0–5.09%), hematite (0–3.03%), and calcite (0–1.95%).

The combustion behaviors of 15 elements (As, Be, Cd, Co, Cr, F, Hg, Mn, Ni, P, Pb, Sb, Se, Th, and U) of environmental concern in coal were estimated by comparing the analytical data from the feed coals and CCRs from the power plants. These elements were partly retained in the CCRs and partly mobilized and airborne upon combustion. Fluorine and Mn mobilities were greatest (>50% of the original amounts in the feed lost) at the FBC plant, and F, Hg, and Se mobilities were greatest at the CYC and PC plants. The majority of the other elements were less mobile (<25%). The mobilized portions of the elements may not have been entirely emitted into the atmosphere; they may have been partially condensed on hardware at the cool side of the power plants. The concentrations of the 15 trace elements were greater in the fly ashes than in the bottom ashes, with a few exceptions. Some of the elements could be commercially produced from the CCRs.

Samples collected at four selected coal preparation plants at a 4-year interval showed some variations in the composition of the coals over time. These results give a general idea about the limited reliability of using outdated coal-quality data from a given mine for assessing the environmental and economic impacts of burning the coal currently produced from the mine.

INTRODUCTION

The industrial use of coal is greatly affected by the amount and variety of its inorganic content. The inorganic matter is the main source of pollutants emitted to the atmosphere during coal combustion or leached from wastes from various coal utilization processes. The inorganic matter in the coal, however, may also be a source of useful by-products.

Data on the mineralogical composition of coal and CCRs have broad applications in studies relating to commercial uses of Illinois coals and of the residues from cleaning, combustion, and conversion of these coals. Interpreting combined mineralogical and chemical data helps identify the modes of occurrence of toxic elements in coal; such information is essential for designing coal cleaning or post-combustion control methods to meet the requirements of current or future environmental regulations. Improved understanding of the fate of minerals in different types of boilers also increases the ability to design improved methods to predict slagging, fouling, and ash properties from the mineralogical and chemical composition of feed coal. Ash fusion temperatures, slagging, and fouling are strongly dependent on the mineralogical composition of coal and, therefore, cannot be accurately estimated from chemical analysis of coal or ash alone. The minerals in coals melt over a range of temperatures, which reflects the refractoriness of each type of mineral. The difference between the ash fusion temperature predicted from bulk chemistry and the actual or correct value increases as the partitioning of elements among different minerals increases. The CCR data can also help generate new ideas about increasing their commercial utilization.

RELATED RESEARCH

Inorganic Matter in Coal

The inorganic matter content of run-of-mine coal is highly variable and depends on geological conditions and the mining techniques used. Inorganic matter in coal is present mostly as discrete minerals with five different modes of occurrence: (1) microscopically disseminated inclusions within macerals; (2) layers or partings of variable thickness; (3) nodules, including lenticular and spherical concretions; (4) fissures, including cleat and other fracture and void fillings; and (5) megascopic rock fragments found within the coal bed because of faulting, slumping, or related disturbances and from intentional or accidental mining of the roof or floor strata (Harvey et al. 1983, Harvey and Ruch 1986). Physical coal-cleaning processes normally remove large, discrete grains and layers of inorganic matter more efficiently than they remove finely disseminated minerals. Mineralogical compositions of inorganic matter in channel and core samples of Illinois coals were investigated by Rao and Gluskoter (1973), Ward (1977), and Harvey et al. (1983). Minerals that commonly occurred in measurable quantities in these Illinois coal samples included illite, mixed-layered illite/smectite, kaolinite, pyrite, quartz, and calcite. Minerals with rare occurrences and trace abundances in the samples included chlorite, feldspars, zircon, sphalerite, dolomite (ankerite), siderite, barite, anhydrite, gypsum, rosenite, melanterite, coquimbite, jarosite, hematite, rutile, and apatite.

Inorganic minerals host the elements of environmental concern in coal. However, there are a few exceptions; for example, S can be part of the organic structure, and Cl can partly be adsorbed on the organic matter in exchangeable ionic form. Most elements of environmental concern in coal are categorized as trace elements (generally <200 mg/kg). Gluskoter et al. (1977) and Harvey et al. (1983) reported on the trace element contents of a large number of mostly channel and core samples of Illinois coals. Demir et al. (1998) used principal component analysis to determine the modes of occurrence of environmentally critical elements in channel samples of Illinois coals.

With respect to coal utilization, the National Committee for Geochemistry (National Research Council 1980) identified three categories of elements of environmental concern: (1) those of greatest concern—As, B, Cd, Pb, Hg, Mo, and Se; (2) those of moderate concern—V, Cr, Ni, Cu, Zn, and F; and (3) those of minor concern—Li, Na, Sr, Ba, Mn, Co, Ge, Cl, Br, Ra, Po, Rn, Th, and U. These categories were based upon known toxicity, levels of occurrence of each element in coal, and anticipated mobility upon combustion or upon disposal of ash. Sixteen elements in coal (As, Be, Cd, Cl, Co, Cr, F, Hg, Mn, Ni, P, Pb, Sb, Se, Th, U) are among the 189 hazardous air pollutants (HAPs) mentioned in the 1990 Clean Air Act amendments (U.S. Public Law 101-549, 1990). It should be pointed out that some of the elements in the National Research Council list were not considered HAPs by the amendments. Partitioning of HAPs and other elements among the CCRs and flue gas is highly variable (Swaine 1990, Clarke and Sloss 1992, Wesnor 1993, Davidson and Clarke 1996) because of the variation in the types and operational conditions of combustion units and in the chemical properties and modes of occurrences of the elements. Analytical errors and difficulties in obtaining representative samples also add to the variability of data on the retention or emission of potentially toxic elements from power plants. The HAP provisions of the 1990 amendments to the Clean Air Act focus on non-utility industries, including metals, petrochemicals, and papermaking (Moore 1994). A risk analysis by the U.S. Environmental Protection Agency (USEPA 1998) concluded that, for now, only Hg emission from the coal-fired electrical utilities is of potential health risk and thus requires further investigation; a final regulation on Hg will be issued by 2004.

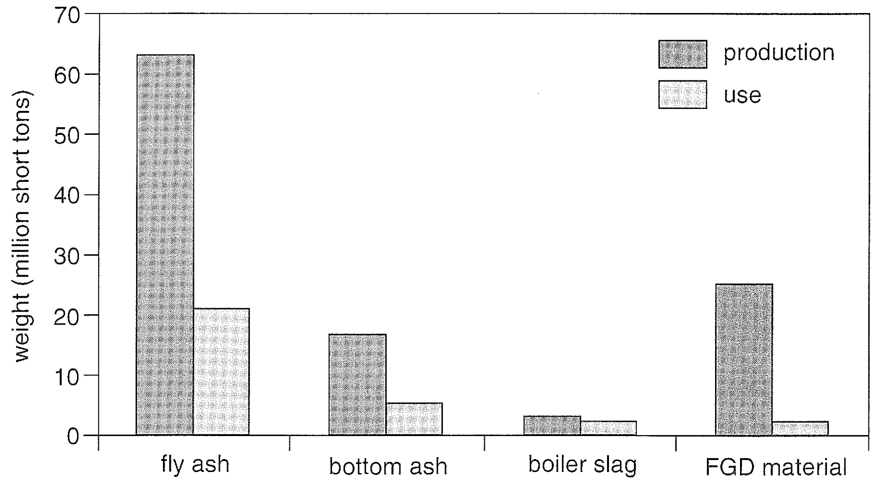

Figure 1 US production and use of CCRs for the year 1998 (plotted using data from ACAA 1999). FGD, flue gas desulfurization.

Coal Combustion Residues

Utilities in the U.S. annually generate108 million short tons of CCRs, 58% of which is fly ash (fig. 1). Current and potential commercial uses of CCRs include treatment of soil and of mine and industrial wastes; admixture in cement, concrete, and grout; making bricks and other ceramic products; mineral filler; fill materials in civil engineering projects including road base/subbase; blasting grit; roofing granules; making wallboards; snow/ice control; and extraction of valuable materials (Clarke 1992, DeBarr et al. 1996, Dreher et al. 1996, Hughes et al. 1996, Wirtz and Bukowski 1996, Roy et al. 1997, ACAA 1999, Barbieri et al. 1999, Dhir and Jones 1999, Niewiadomski et al. 1999, Sloan et al. 1999). However, only about 29% of the total CCR generated in the U.S. is used for commercial purposes (fig. 1); the rest is disposed of on land or in abandoned mines.

Chemical and Mineralogical Analyses of Coal and CCRs

Methods for determining the chemical composition of coal and CCRs have been well established at the Illinois State Geological Survey (Gluskoter et al. 1977, Harvey et al. 1983, Demir et al. 1994). Methods for mineralogical analysis of these same materials, however, vary greatly in their usefulness for solving various problems associated with coal use. Application of an improved x-ray diffraction (XRD) method for mineralogical analysis of coal and CCR samples was an important task of this study. Therefore, the mineralogical analysis methods are discussed in considerable detail.

The methods of analyzing minerals in coal are based on XRD analysis, chemical analysis, or a combination of the two. Methods based solely on conventional XRD analysis contain large errors, as do those based solely on chemical analysis (called normative methods). Errors in determining the mineralogy of a coal based solely on the chemical analysis generally result from assigning the chemical elements to the wrong normative minerals. Another shortcoming of normative methods is that they are costly and generally lack procedures for estimating errors (Slaughter 1989). As a result, most investigators have favored methods that combine XRD, chemical analysis, and sometimes other procedures such as scanning electron microscopy. An interlaboratory study of quantitative coal mineral analysis by computer-controlled scanning electron microscopy indicated that the mineralogical composition of coal cannot be determined precisely using this technique alone (Galbreath et al. 1996). Beginning in the 1970s, investigators at the Illinois State Geological Survey began to apply combined XRD and chemical methods for analysis of the non-clay mineral fraction of coals. It is important to note that the methods described in the literature generally lack provisions for the analysis of some important minerals, particularly marcasite, mixed-layered illite/smectite, and mixed-layered kaolinite/expandables.

There is extensive literature relating to the determination by XRD of mineral matter in coal. The following developments were especially relevant to this present study:

1. Development of a procedure for removing the combustible material from coal at low temperatures, called low-temperature ashing (Gluskoter 1965).
2. Development of an accurate and precise method for the determination of pyritic sulfur in coals (ASTM 1995).
3. Development of methods for the quantitative determination of minerals by XRD (Snyder and Bish 1989).
4. Development of NEWMOD® (Reynolds 1985) and its application to the quantitative analysis of clay minerals (Hughes and Warren 1989, Reynolds 1989, Hughes et al. 1994, Moore and Reynolds 1997).

The mineral concentrations in bulk coal samples often are too small to be accurately and precisely determined. Therefore, XRD of the low-temperature ashes (LTAs) of coals has been the principal method for mineralogical determinations for more than 30 years. The method yields a virtually certain identification of the minerals in a sample. In addition, variations in the relative intensity of XRD peaks for some minerals commonly can be used to estimate their chemical composition. The precision of different versions of XRD analysis varies widely, as do claims of their accuracy (Snyder and Bish 1989, Moore and Reynolds 1997). However, as a result of refinements during the 1980s, precise and accurate determination of non-clay minerals such as pyrite (and marcasite), quartz, dolomite, and calcite became possible (Harvey et al. 1983, Demir and Harvey 1990). A later study established analytical procedures that meet the requirements of most investigators for mineralogical analysis of inorganic matter in coal (Kruse et al. 1994). These procedures reduced or eliminated the following errors associated with historical XRD procedures:

1. *Preferred orientation error.* Two advances have been made that largely eliminate the error resulting from preferred orientation of mineral particles. The first is to grind the sample in a manner that creates a more random orientation of the crystallites. The McCrone micronizers® in our laboratory yield powders with crystallite sizes in the optimal 5-µm to 10-µm range. The second advance involves using side-loading powder holders and the capability to spin the samples during exposure to the x-ray beam to minimize preferred orientation effects. The typical practice of the past decade has been to use a random powder pack for non-clay mineral analysis and a bulk smear sample for analysis of clay minerals (Hughes et al. 1994). Historically, XRD analysis of clay minerals has been run on the segregated <2-µm fraction of a sample. This practice was developed partly because instruments at the time gave low peak intensities for most clay minerals and partly because clay minerals were thought to be essentially associated with the finest particle fractions, <2 µm by definition. In reality, the clay minerals in coal occur in a wide range of particle sizes. For example, illite/smectite crystallites commonly are <1 µm, while some kaolinite crystallites exceed 50 µm. As a result, errors in excess of an order of magnitude can occur from XRD analysis of samples prepared as <2-µm aggregates. This error has been eliminated by grinding the clay minerals to approximately the same size and by analyzing a bulk sample that includes all of the particles (Hughes and Warren 1989, Hughes et al. 1994).
2. *Standard mineral error.* The standard mineral error results from the measurement or calculation of a reference intensity for a "standard" mineral (Russell and Rimmer 1979, Hughes et al. 1994, Moore and Reynolds 1997). In the past, mineralogists analyzed standard samples with the highest purity possible and refined their procedure whenever a better standard was located. For clay minerals, Reynolds (1985) developed a computer program (NEWMOD®) that makes it possible to calculate a reference intensity ratio (RIR) for any clay mineral with a layer structure. This program makes it easy to calculate XRD peak ratios for the wide range of chemical variations observed in natural samples. Furthermore, NEWMOD® gives peak intensities relative to non-clay minerals. Therefore, the calculated intensities can be used to check the clay mineral

content, which is arrived at by proportioning the difference of 100% minus the non-clay mineral content. The net result of these improvements is to minimize the errors associated with the mismatch between reference standards and minerals in coal and thus eliminate the need for an almost infinite number of natural standard samples.

3. *X-ray absorption error.* The x-ray beam must pass through crystallite to be diffracted into the detector and recorded as a series of peaks. However, x-rays are absorbed in the crystallite in proportion to the atomic weight of its elements. Therefore, large grains of pyrite and marcasite will seem to be present at less than their true content because their diffracted x-rays are partially absorbed. In theory, highly precise and accurate analyses of these types of minerals require methods of sequential grinding to reduce errors to a minimum. In practice, it is possible to obtain adequate precision and accuracy with a single grinding in a McCrone® micronizer to produce 5-µm to 10-µm crystallites.
4. *Error in matching XRD peak intensities with mineral contents.* Attempts to calculate the content of all minerals directly from the XRD spectrum of a random bulk powder sample generally give erroneous results. This error was eliminated by applying a method that used chemical analysis of pyritic sulfur and XRD peak intensities from a random bulk pack to calculate the amount of pyrite, quartz, and calcite in LTA samples (Harvey et al. 1983, Demir and Harvey 1990). The bulk clay mineral fraction can then be calculated as 100% minus the non-clay mineral fraction. By extension, the amount of calcite (confirmed to be present in the sample by XRD) can be calculated also from CO_2 or CaO analyses by traditional chemical methods, providing that the concentration of other major Ca minerals in the samples is insignificant. For most coals, this calculation leaves only quartz among the major non-clay minerals in the sample to be determined solely with XRD.

OBJECTIVES

The objectives of this study were (1) to determine the mineralogical and chemical composition of the inorganic matter in marketed, conventionally cleaned Illinois coals from all operating mines and of CCRs from selected power plants; (2) to correlate the chemical composition with the mineralogical composition of the coals; (3) to investigate the fate of the inorganic constituents during combustion at the power plants; and (4) to determine the temporal variations in the mineralogical and chemical composition of marketed coals from selected mines.

EXPERIMENTAL PROCEDURES

Samples and Sample Preparation

Marketed coal samples were collected from each of 35 coal preparation plants that operated in the different regions of the Illinois coal field (fig. 2) between 1992 and 1996. In 1996, sets of fly ash, bottom ash, and feed coal samples were collected from a fluidized bed combustion (FBC) plant, two cyclone combustion (CYC) plants, and a pulverized coal combustion (PC) plant; a sample of the limestone used in the FBC plant was also collected. The coal sample from the FBC plant was a blend of coals from 17 different mines. Coal samples from the CYC and PC plants came from one of the 35 preparation plants that had been sampled four years earlier in 1992. In addition, three other preparation plants among the 35 were sampled again four years after the first

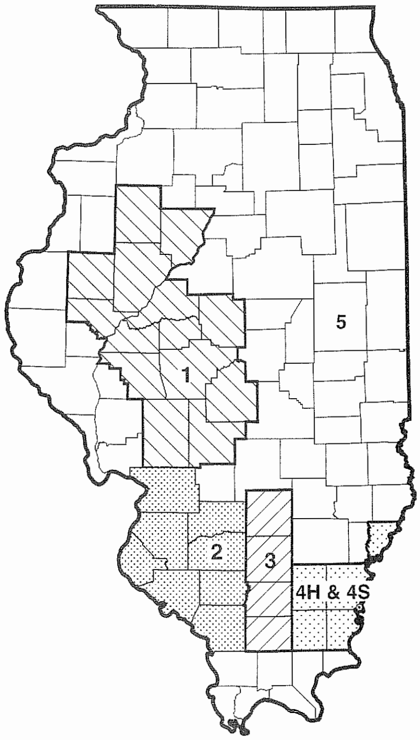

Figure 2 Coal regions of Illinois. Southeastern Illinois coal field is divided into Herrin (4H) and Springfield (4S) Coal seams.

sampling. Results for these three samples and for the coal samples from the PC and CYC plants were compared with results from samples collected at the same plants four years earlier to study the temporal variations in the mineralogical and chemical composition of marketed Illinois coals.

Details of location, collection, processing, and storage of the marketed coal samples from the coal preparation plants are described in Demir et al. (1998). As for sampling at the power plants, the company staffs at the PC and CYC plants used automatic samplers to collect the samples as part of their routine sampling. For the FBC plant, we used a sampling shovel to collect 15 increments of the coal from the belt carrying coal to the boiler. To sample the FBC fly ash, the ash stream was directed to a sampling bag for about 30 sec through an opening at the particulate collection system. We sampled the FBC bottom ash and crushed limestone by using a sampling shovel to collect 15 to 20 increments of the materials from widely spaced locations of their stock piles. The power plant samples were weighed and described after a visual inspection (table 1). Representative splits of the coal and coarse-grained bottom ash samples were separated by riffling, splitting, and then grinding to -60 mesh (<250 µm) particle size in a Holmes mill. The fly ash samples were already -60 mesh in particle size and did not need to be ground. Small splits of the ground coal and bottom ash samples and of fly ash samples were prepared for chemical, mineralogical, and microscopic analyses by riffling and splitting.

Table 1 Amounts and descriptions of samples of coal and CCRs from three types (FBC, CYC, PC) of power plants.

Plant type	Sample type	Amount (kg)	Sample description
FBC	coal	11.3	<0.95-cm (3/8 in) particle size
	fly ash	8.2	very fine particle size, light gray color
	bottom ash	10.9	<0.64-cm (<1/4 in) particle size, mostly yellowish and grayish particles, and small number of black particles
	limestone	11.3	crushed and off-white color
CYC1	coal	4.1	<4.76-cm (-4 mesh) particle size
	fly ash	3.6	fine particle size, dark gray color
	bottom ash	5.4	<0.95-cm (<3/8 in) particle size, black color, and high moisture content because of quenching in water
CYC2	coal	4.5	<4.76-cm (-4 mesh) particle size
	fly ash	3.2	fine particle size, dark gray color
	bottom ash	5.4	<0.95-cm (<3/8 in) particle size, black color, and high moisture content because of quenching in water
PC	coal	5.4	<4.76-cm (-4 mesh) particle size
	fly ash	3.6	fine particle size, light gray color
	bottom ash	6.8	<0.95-cm (<3/8 in) particle size, dark gray to black color, and high moisture content because of quenching in water

Chemical Analysis of Coal and CCR Samples

The samples of coals and CCRs were analyzed using the following methods:

x-ray fluorescence spectrometry: Al, Ba, Ca, Fe, Ge, K, Mg, Mn, Mo, Na, P, Si, Sn, Sr, Ti

energy-dispersive x-ray: Ba, Ge, Mo, Sn, Sr, Zr

instrumental neutron activation: As, Br, Ce, Co, Cr, Cs, Dy, Eu, Ga, Hf, La, Lu, Mn, Rb, Sb, Sc, Se, Sm, Ta, Tb, Th, U, W, Yb, Zn atomic absorption spectrometry: Cd, Cu, Li, Ni, Pb, Zn, Hg (by cold vapor atomic absorption)

optical emission spectrometry: Ag, B, Be, Ge, Mo, Pb, Sn, Tl, V

pyrohydrolysis-ion chromatography: F

inductively coupled plasma-mass spectrometry: Cd, Pb

ASTM methods: moisture, ash, volatile matter, C, H, N, O, total S and S forms, Cl, calorific value

Note that some of the elements were determined using more than one method. In such cases, the average or the most reliable value was used. Chemical analyses of the samples were performed following strict quality assurance and quality control rules to ensure reproducibility and accuracy of the data. The quality assurance and control plan (ISGS 1994) included standard operating procedures for sample preparation and for the analytical work. Blank, standard, and replicate samples were analyzed to ensure data reliability.

Low-temperature Ashing of Coal Samples

Generating the LTA of a coal sample was the first step for analysis of coal minerals. The LTAs were generated at about 150°C in an activated oxygen-plasma atmosphere that had been created by passing oxygen into a radiofrequency field (Gluskoter 1965). The minerals in the LTA were essentially unaltered from their original state in the coal. In the standard procedure, 10–20 g of the sample were spread evenly to a depth of 3 mm over the bottoms of Pyrex boats (12 × 4 cm in size). The boats with samples were put in a vacuum desiccator for a minimum of 24 hr for drying. The dry samples were then placed in the asher, and the pressure in the asher was reduced to about 1 torr. The radiofrequency field was then introduced at 37.5 W per chamber, and oxygen gas was introduced at a rate of 20 cm^3/min to produce the plasma. The ashing temperature was monitored occasionally with an infrared remote thermometer. The samples were stirred twice and weighed once each day. When the sample weight no longer changed, the ashing was complete.

Water Leaching of LTA Samples

Previous research indicated that the LTA samples contained some water-soluble, inorganic elements that reduced the accuracy of the mineralogical analysis (Kruse et al. 1994). To improve the accuracy of the mineralogical analyses, each LTA sample was washed with water to remove the water-soluble fraction. To accomplish the water extraction, each LTA sample was dispersed in demineralized water (1 g of LTA in 500 mL of water). After 12–16 hr, the LTA and water mixture was centrifuged, the clear supernatant was poured off, and the solid fraction was dried overnight at 70°C and weighed.

Mineralogical Analysis of LTA Samples

The water-extracted LTA samples were mineralogically analyzed by XRD. The data were then converted to whole-coal basis. For the XRD analysis, the LTA samples were micronized for 15 min with 10 mL of water buffered with a few drops of sodium dithionite in a McCrone® grinder. The samples were then transferred to 50-mL centrifuge tubes and centrifuged for 20 min at 2,000 rpm, which resulted in the separation of a clear supernatant. After the clear supernatant was discarded, the paste was mixed thoroughly, and some of it was smeared on glass XRD slides. The remaining paste was dried overnight at 70°C, mixed with a mortar and pestle, and then packed into an end-loading sample holder (a random bulk pack). The random bulk pack samples were x-rayed with a Scintag® diffractometer, and the peak areas were calculated with the DMS® software that is part of the instrument operating system. The smear slides were x-rayed after air-drying and after at least two days exposure to ethylene glycol, heating for 1 hr at 350°C, and then heating to 550°C, which produced the strong 14 Å XRD peak for detection of small amounts of chlorite. The results of XRD analysis of bulk packs and smear slides were fairly comparable. The bulk pack XRD analysis was the preferred method for determination of non-clay minerals. The XRD analysis of smear slides was used for clay mineral analysis. The detection limit of calcite determination with XRD was 0.5 wt% or perhaps even greater. Therefore, the calcite content was calculated from the chemically determined CaO content of coal. This approach was judged to be reasonable because no other Ca minerals were detected in the samples by the XRD, and the amount of Ca associated with clay minerals and plagioclase was insignificant relative to that associated with calcite. The steps for calculating the mineralogical composition of the coal samples from the XRD spectra and chemical analyses were as follows:

1. Deconvolute XRD patterns and transfer data electronically to a computer spreadsheet.
2. From the percent of insoluble LTA and chemically determined pyritic-S (S_{py}) content of coal, %(pyrite + marcasite) in LTA = %S_{py} in LTA × 1.871.
3. From bulk pack XRD peak areas, calculate the percentages of quartz, K-feldspar, plagioclase, calcite, pyrite, and marcasite on a 100% basis.
4. Decimal non-clay minerals (DNC) in the LTA = (%[pyrite + marcasite] from step 2) ÷ (%[pyrite + marcasite] from step 3).
5. Percentage of each non-clay mineral in the LTA = (its percentage in the non-clay fraction) × (DNC).
6. From smear slide XRD peak areas, calculate the percentages of mixed-layered illite/smectite, illite, kaolinite, and chlorite on a 100% clay basis.
7. Percentage of each clay mineral in the LTA = (percentage in the clay fraction) × (1–DNC).
8. Recalculate the percentage of calcite in LTA using the %LTA and chemically determined CaO contents of coal, replace this chemical calcite content for the XRD calcite content from step 5, and adjust the percentages of other minerals from steps 5 and 7 accordingly.
9. Percentage of each mineral in whole coal = (%LTA ÷ 100) × (percentage in the LTA).

Mineralogical Analysis of CCRs and Limestone

The CCRs from the power plants contained large amounts of amorphous (glass) material and variable amounts of lime and anhydrite, which react with water. Therefore, a somewhat different procedure of mineralogical analysis was followed for the fly and bottom ashes as well as for the limestone sample: the water extraction step was omitted, 8 wt% dolomite was added to the sample as the internal standard, and the samples were micronized in propanol. Among a small number of available standards, the dolomite was the best because its peaks did not overlap with other mineral peaks, and 8 wt% dolomite produced enough XRD counts to ensure accuracy without diluting the other peaks too much.

RESULTS AND DISCUSSION

Mineralogical Composition of Marketed Coals

On average, the most abundant minerals in the 35 marketed Illinois coals were kaolinite ($\bar{x} = 2.07\%$) and quartz ($\bar{x} = 2.06\%$)(table 2, fig. 3). K-feldspar was the least abundant mineral; its average concentration was 0.01%. The clay mineral fraction generally was more abundant than the non-clay fraction in the 35 samples (fig. 4), and the clay mineral composition was slightly skewed towards kaolinite (fig. 5). The average clay content was 5.11% on whole coal basis or 52% on an LTA basis. This proportion of the clay fraction in the LTAs of the marketed Illinois coals is only slightly less than the 56% value for channel samples of Illinois coals reported in Harvey and Ruch (1986), which suggests that conventional cleaning does not significantly alter the ratio of clay to non-clay minerals compared with that of standard channel samples.

Table 2 Mineralogical composition of marketed Illinois coals and CCRs. All values are in weight percent on a dry weight basis.[1]

Sample no.	Region	I/S	I	Kaol	Chl	Qtz	Pyr	Marc	Calc	K-f	Plag
C32773	1	1.67	0.79	1.50	0.07	2.24	1.42	0.24	0.71	0.05	0.07
C32774	1	0.43	0.53	0.93	0.05	1.26	2.35	0.26	0.27	<0.01	0.04
C32777	1	1.12	1.20	1.78	0.16	2.66	1.47	0.03	4.46	<0.01	0.08
C32778	1	1.79	1.23	2.31	0.23	1.82	0.91	<0.01	0.87	<0.01	0.06
C32782	1	0.61	1.10	1.69	0.06	3.62	2.00	0.06	1.27	<0.01	0.11
C32783	1	1.94	1.18	2.02	0.12	1.37	2.00	0.37	0.52	<0.01	0.10
C32785	1	1.83	1.21	1.77	0.09	2.16	1.54	0.29	0.64	0.03	0.05
C32797	1	1.87	1.06	1.89	0.13	1.87	1.64	0.06	0.77	<0.01	0.06
C32814	1	0.69	0.47	0.66	0.02	1.19	1.71	0.01	0.87	<0.01	0.07
C32779	2	1.87	0.77	1.34	0.21	2.25	1.68	0.09	0.77	<0.01	<0.01
C32794	2	1.09	1.20	2.34	0.17	2.36	2.02	0.12	0.79	<0.01	0.04
C32798	2	2.30	1.17	2.00	0.10	2.70	1.78	0.16	1.62	<0.01	0.06
C32800	2	2.70	1.17	2.23	0.20	2.17	1.41	0.18	0.82	<0.01	0.05
C32813	2	3.11	2.50	2.19	0.32	3.07	2.42	0.12	0.96	<0.01	0.05
C32815	2	1.65	1.03	1.88	0.13	2.95	2.17	0.11	1.52	<0.01	<0.01
C32784	3	1.81	1.00	2.34	0.18	1.41	1.26	0.09	0.20	<0.01	0.05
C32795	3	0.59	1.29	1.81	0.15	1.20	0.31	<0.01	0.18	<0.01	0.03
C32796	3	2.95	1.42	3.22	0.44	4.06	0.73	0.02	0.61	<0.01	0.11
C32799	3	1.06	2.65	3.21	0.44	1.42	0.34	0.01	1.89	<0.01	0.18
C32801	3	1.08	1.44	2.44	0.28	1.26	1.17	0.07	0.41	<0.01	0.07
C32802	3	1.39	1.73	2.09	0.60	1.32	1.42	0.10	0.71	<0.01	0.05
C32803	3	1.69	1.34	2.45	0.07	1.53	1.31	0.09	0.50	<0.01	0.05
C32661	4H	1.41	1.22	1.84	0.11	1.80	1.78	<0.01	0.34	<0.01	<0.01
C32664	4H	2.04	1.55	2.86	0.12	1.84	2.05	0.09	0.36	<0.01	0.06
C32665	4H	1.33	1.41	1.83	0.12	2.29	1.83	0.05	0.36	<0.01	0.03
C32771	4H	2.94	1.63	2.15	0.10	2.33	2.11	0.03	0.79	<0.01	0.05
C32776	4H	1.44	0.88	1.57	0.12	1.87	1.71	0.20	0.86	0.05	0.08
C32662	4S	1.48	1.20	1.64	0.19	1.15	1.01	0.06	0.23	<0.01	0.09
C32663	4S	1.31	1.18	2.80	0.19	1.77	1.30	0.53	0.29	<0.01	0.05
C32772	4S	1.10	1.19	2.19	0.18	2.24	1.50	0.19	0.80	0.02	0.09
C32775	4S	1.09	0.84	1.83	0.03	1.51	1.97	0.13	0.25	<0.01	0.14
C32780	4S	0.53	2.05	2.42	0.27	1.47	1.59	0.21	0.82	<0.01	0.06
C32781	4S	0.93	1.01	1.71	0.05	2.86	1.63	0.32	0.48	<0.01	0.07
C32793	4S	2.13	1.90	2.18	0.37	3.85	1.43	0.20	0.68	0.07	0.29
C35564	5	2.05	1.09	2.92	0.28	1.57	1.39	0.23	1.70	<0.01	0.06
Mean[2]	all	1.57	1.29	2.07	0.18	2.06	1.56	0.13	0.84	0.01	0.07
SD[2]	all	0.70	0.46	0.56	0.13	0.78	0.50	0.12	0.78	0.01	0.05

Power plant coals

Sample no.	Sample type	I/S	I	Kaol	Chl	Qtz	Pyr	Marc	Calc	K-f	Plag
C35300	FBC feed	1.78	2.07	2.70	0.16	1.70	0.89	0.30	0.86	<0.01	0.00
C35301	CYC1 feed	0.46	1.47	2.14	0.04	3.03	1.12	<0.01	1.00	<0.01	0.13
C35302	CYC2 feed	0.60	1.54	2.13	0.30	2.79	1.06	0.05	1.05	<0.01	0.03
C35303	PC feed	0.35	2.32	3.47	0.19	1.61	1.27	0.07	1.00	<0.01	0.02

Power plant ashes

Sample no.	Sample type	Mul	Qtz	Calc	Hemat	Magn	Anhyd	Gyps	Lime	Portl	Glass
C35304	FBC-fly ash	ND	8.44	ND	3.03	0.69	17	ND	2.30	11	57
C35308	FBC-bottom ash	ND	8.18	1.95	ND	ND	16	2.03	40	13	19
C35305	CYC1-fly ash	1.87	7.57	0.75	2.96	4.03	ND	5.02	ND	ND	78
C35309	CYC1-bottom ash	ND	1.29	ND	ND	0.44	ND	0.50	ND	ND	98
C35306	CYC2-fly ash	2.29	6.83	1.11	2.16	3.79	0.60	ND	ND	ND	83
C35310	CYC2-bottom ash	ND	1.27	ND	ND	0.48	ND	0.29	ND	ND	98
C35307	PC-fly ash	5.09	0.008	ND	2.07	4.74	0.71	ND	ND	ND	87
C35311	PC-bottom ash	ND	0.97	0.37	1.97	4.95	ND	ND	ND	ND	92
C35312	FBC - limestone3.4% illite, 1.5% kaolinite, 1.5% chlorite, 5% quartz, 86% calcite, and 4.0% dolomite										

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[1] I/S, mixed layered illite/smectite; I, illite; Kaol, kaolinite; Chl, chlorite; Qtz, quartz; Pyr, pyrite; Marc, marcasite; Calc, calcite; K-f, K-feldspar; Plag, plagioclase; Mul, mullite; Hemat, hematite; Magn, magnetite; Anhyd, anhydrite, Gyps, gypsum; Portl, portlandite; Glass, amorphous material (calculated by difference); SD, standard deviation; H, Herrin Coal; S, Springfield Coal; ND, not detected

[2] For values below detection limits, one-half of the detection limits were used in statistical calculations of means and standard deviations.

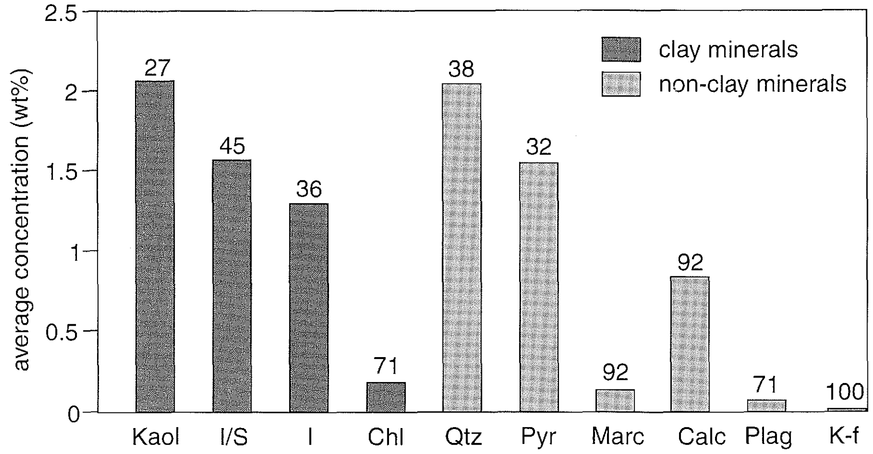


Figure 3 Average mineral content of 35 marketed coals. Numbers above bars are relative standard deviations ((standard deviation/mean) × 100). Keys: Kaol, kaolinite; I/S, illite/smectite; I, illite; Chl, chlorite; Qtz, quartz; Pyr, pyrite; Marc, marcasite; Calc, calcite; Plag, plagioclase; K-f, K-feldspar.

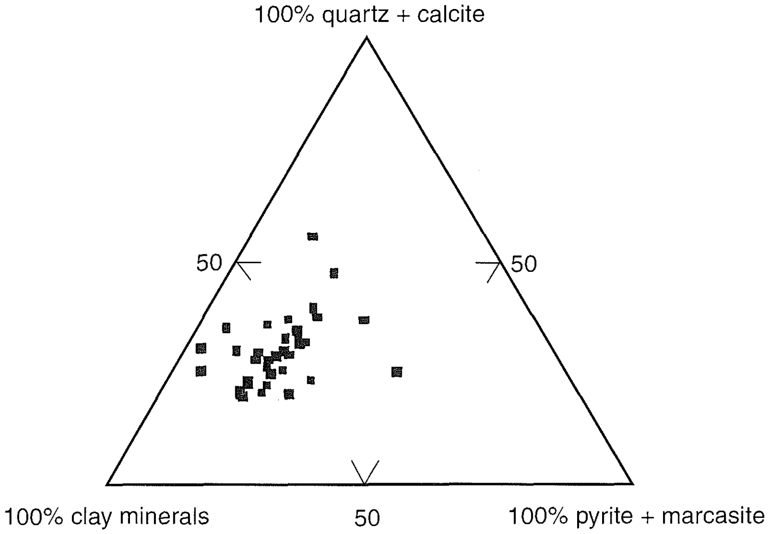


Figure 4 Major mineral composition of mineral matter from 35 marketed Illinois coals.

Relationships between Minerals and Minor and Trace Elements

By using the mineralogical and chemical data (tables 2 and 3), statistical correlations were sought among the minerals and minor and trace elements in the marketed Illinois coals. The statistical analysis yielded many significant correlations (table 4). The square of the correlation coefficient (r^2) for some of the correlations was greater than 0.5 (figs. 6–10). Statistical correlations may or may not indicate that an element is located in the mineral with which it is positively correlated. For example, the correlation between quartz and Mg indicates that most of the quartz and the Mg-bearing mineral (illite/smectite) was incorporated into the coal by the same geological and geochemical conditions. The same interpretation can be made for the correlation between calcite and Zn. Calcite and the main Zn-bearing mineral (sphalerite) were incorporated into the coal by the

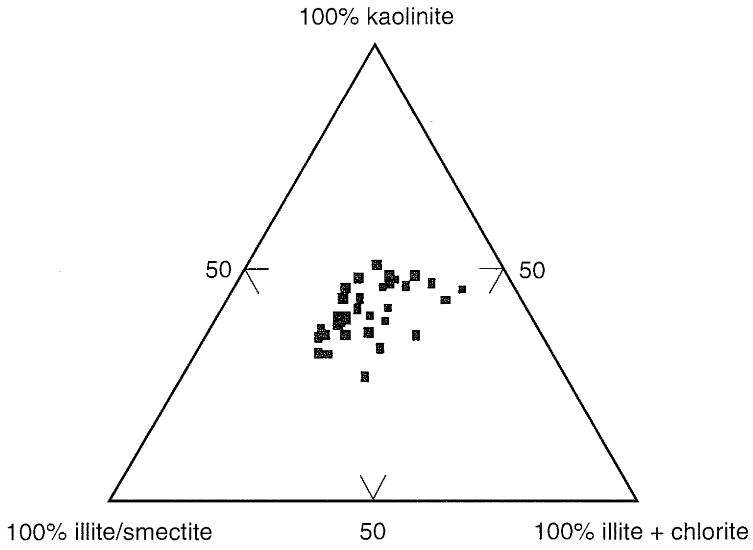


Figure 5 Clay mineral composition of the mineral matter from 35 marketed Illinois coals.

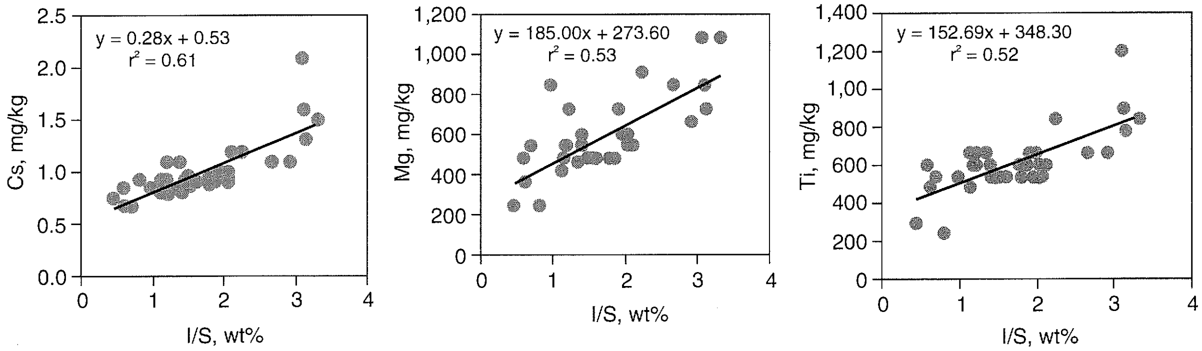


Figure 6 Relationships of $r^2 > 0.5$ between elements and mixed-layered illite/smectite in marketed Illinois coals.

same geochemical conditions, namely epigenetic precipitation; sphalerite was apparently present in the samples, but its concentration was too small to be detected by the XRD method. There is some evidence that F may be part of the illite and mixed-layered illite/smectite structure (Thomas et al. 1977). Manganese is known to replace Ca in the calcite structure, and, therefore, the Mn/calcite correlation was not surprising. Although the overall Hg-pyrite correlation is weak (fig. 11), there appear to be two populations, one above and one below the regression line, each with a different slope. This evidence suggests that Hg may be partitioned distinctly between pyrites of different origins (syngenetic vs. epigenetic). The modes of occurrence of most trace elements in coal are subject to multiple interpretations unless constricted by separating and directly analyzing individual minerals in coal.

Combustion Behavior of Minerals in Coal

Upon combustion, coal minerals (fig. 3) were converted to other minerals and amorphous phases that made up the CCRs (fig. 12). Among the minerals present in coal, only some of the quartz survived the combustion process; the rest of the quartz that was present in the coal was converted to silica glass. The clay minerals and feldspar were converted largely to aluminosilicate glass and;

Table 3 Chemical composition of 35 marketed Illinois coals from preparation plants and of feed coals and combustion residues from four selected power plants. The values are in milligrams per kilogram (unless indicated otherwise) on a moisture-free basis.

Lab no.	Region[1]	%Moisture	%Ash	Btu/lb	%Volatile	%Fixed C	%C	%H	%N	%O	%Total S	%Organic S	%Pyritic S	%Sulfate S	Ag	Al	As	B	Ba	Be
C32773	1	14.02	8.72	12,810	41.22	50.06	71.47	5.04	1.21	9.41	4.14	3.03	0.97	0.14	<1	8,997	1.3	135	41	1.0
C32774	1	13.45	7.07	13,270	40.87	52.06	74.58	5.38	1.31	8.09	3.58	1.56	1.46	0.56	<1	5,345	20	116	17	4.0
C32777	1	14.94	14.52	12,450	38.60	46.88	69.44	5.04	1.22	6.63	3.14	2.05	1.01	0.08	<1	8,574	5.1	119	66	1.2
C32778	1	17.36	9.80	12,710	36.68	53.53	71.95	5.16	1.42	10.08	1.60	0.98	0.54	0.07	<1	10,955	10	202	50	2.2
C32782	1	14.99	11.62	12,500	38.98	49.40	69.45	5.17	1.25	8.61	3.90	2.45	1.25	0.20	<1	8,574	2.4	106	38	<1.0
C32783	1	15.59	9.74	12,690	40.50	49.76	70.02	5.36	1.26	9.21	4.42	2.96	1.34	0.12	<1	9,421	2.2	155	33	1.4
C32785	1	13.98	9.75	12,740	41.43	48.81	70.22	5.34	1.30	9.22	4.17	3.00	1.05	0.12	<1	9,738	2.3	178	43	1.5
C32797	1	15.73	10.29	12,730	40.27	49.45	71.11	5.06	1.23	8.68	3.62	2.45	0.99	0.18	<1	10,215	4	147	44	1.2
C32814	1	11.39	6.00	13,840	45.68	48.31	76.20	5.49	1.28	7.35	3.68	2.41	1.09	0.18	<1	3,811	6.4	83	33	2.0
C32779	2	12.73	9.63	12,750	39.39	50.98	71.19	5.13	1.24	8.62	4.20	3.07	1.04	0.09	<1	9,685	1.7	114	40	<1.0
C32794	2	11.13	10.52	12,690	38.49	51.00	71.22	4.92	1.31	8.37	3.67	2.29	1.24	0.14	<1	10,585	2.3	128	36	1.1
C32798	2	12.38	13.16	12,290	38.31	48.53	68.84	4.97	1.27	8.28	3.48	2.13	0.20	0.15	<1	12,543	2.2	128	82	<1.0
C32800	2	11.93	11.39	12,600	38.42	50.19	70.45	4.94	1.20	8.39	3.63	2.49	0.92	0.22	<1	11,696	2	137	49	<1.0
C32813	2	10.80	14.70	12,090	36.49	48.80	67.69	4.72	1.26	8.16	3.47	1.97	1.45	0.05	<1	15,507	2.4	127	69	1.4
C32815	2	12.65	12.03	12,420	37.16	50.82	69.42	4.93	1.41	8.48	3.73	2.19	1.41	0.12	<1	11,855	3	126	44	<1.0
C32784	3	10.00	8.13	13,330	35.62	56.24	74.81	5.22	1.57	8.48	1.79	0.77	0.74	0.13	<1	10,056	18	74	32	1.8
C32795	3	10.06	5.76	13,780	35.25	58.99	78.02	5.11	1.63	8.75	0.73	0.55	0.17	0.02	<1	7,992	3.6	57	26	1.0
C32796	3	9.81	16.10	12,120	32.00	51.90	69.01	4.64	1.49	7.71	1.05	0.53	0.42	0.10	<1	21,541	9.8	49	81	1.0
C32799	3	9.67	11.42	12,730	34.40	54.18	72.42	4.82	1.94	8.62	0.76	0.52	0.21	0.03	<1	15,983	17	58	91	1.0
C32801	3	10.38	8.36	13,280	35.93	55.71	75.08	5.19	1.56	7.82	1.98	1.11	0.70	0.17	<1	10,479	10	64	38	1.0
C32802	3	8.56	9.36	13,090	38.34	52.30	73.74	5.11	1.41	7.25	3.12	2.01	0.88	0.23	<1	10,056	3.1	78	36	<1.0
C32803	3	10.08	9.19	13,150	36.62	54.19	74.10	5.11	1.46	7.59	2.54	1.56	0.79	0.19	<1	10,638	4.1	78	45	1.2
C32661	4H	7.60	8.17	13,240	36.60	55.23	74.99	5.11	1.48	7.36	2.89	1.76	0.99	0.14	<1	9,262	3.4	47	33	1.6
C32664	4H	5.80	9.87	13,150	36.67	53.45	73.80	0.00	1.41	7.06	2.87	1.64	1.18	0.05	<1	12,490	5.4	41	36	1.4
C32665	4H	6.80	9.39	13,150	36.31	54.30	74.17	5.05	1.44	7.23	2.73	1.61	1.05	0.07	<1	11,114	4.4	60	39	1.2
C32771	4H	6.50	12.57	12,620	35.06	52.37	71.65	4.75	1.34	6.75	2.93	1.59	1.22	0.12	<1	13,972	3.7	58	51	1.1
C32776	4H	10.15	9.27	13,180	37.92	52.81	72.98	5.14	1.44	8.05	3.13	1.90	1.13	0.10	<1	9,579	2.7	76	33	1.5
C32662	4S	8.20	7.00	13,530	34.88	58.12	77.02	5.12	1.59	7.75	1.51	0.85	0.59	0.08	<1	9,209	14	40	51	1.4
C32663	4S	6.70	8.96	13,100	35.39	55.65	75.05	5.07	1.59	7.15	2.18	1.02	1.01	0.15	<1	10,109	34	45	40	1.1
C32772	4S	6.62	9.33	13,270	35.44	55.23	75.10	5.08	1.58	6.53	2.38	1.29	0.99	0.10	<1	9,844	8	40	33	1.0
C32775	4S	2.76	7.67	13,780	35.88	56.45	77.09	5.11	1.40	5.76	2.98	1.78	1.16	0.04	<1	8,362	4.9	38	29	1.8
C32780	4S	6.82	9.57	13,120	37.75	52.68	73.46	5.03	1.44	7.17	3.32	2.07	1.05	0.21	<1	9,632	3.1	64	37	<1.0
C32781	4S	4.96	9.71	13,770	34.44	55.84	75.69	5.30	1.60	4.68	3.02	1.80	1.10	0.12	<1	8,997	4.3	24	32	<1.0
C32793	4S	11.19	14.14	12,400	33.52	52.35	70.37	4.86	1.49	7.50	1.64	0.69	0.92	0.04	<1	15,189	33	82	70	1.2
C35564	5	8.99	14.90		43.75	56.25	-	-	-	-	2.39	0.94	1.32	0.13	<1	16,407	6.4	146	154	2.5
Mean[2]	all	10.40	10.20	12,952	37.60	52.70	72.70	4.90	1.40	7.80	2.90	1.70	1.00	0.10	0.5	10,812	7.4	92	48	1.3
SD[2]	all	3.40	2.50	476	2.90	3.00	2.70	0.90	0.20	1.10	1.00	0.80	0.30	0.10		3,240	8.1	45	25	0.7

Power plant samples

Lab no.	Sample type	%Moisture	%Ash	Btu/lb	%Volatile	%Fixed C	%C	%H	%N	%O	%Total S	%Organic S	%Pyritic S	%Sulfate S	Ag	Al	As	B	Ba	Be
C35300	FBC-coal	12.45	10.96		40.81	48.24	-	-	-	-	4.21	2.94	0.69	0.57	<0.2	9,897	1.8	195	39	1.7
C35301	CYC1-coal	12.86	10.63		39.05	50.31	-	-	-	-	3.95	2.48	0.67	0.80	<0.2	8,045	2.6	190	35	4
C35302	CYC2-coal	13.72	10.70	39.11	50.19	-	-	-	-	-	4.02	2.49	0.67	0.85	<0.2	8,203	2.4	198	38	1.9
C35303	PC-coal	12.94	10.64	-	38.77	50.60	-	-	-	-	4.00	2.52	0.79	0.69	<0.2	8,150	2.2	181	37	1
C35304	FBC-fly ash														<0.3	33,925	6.1	429	158	6
C35305	CYC1-fly ash														1.1	70,179	51	1,450	320	14
C35306	CYC2-fly ash														<1	72,296	145	1,870	368	15
C35307	PC-fly ash														<0.5	84,733	34	1,100	387	9
C35308	FBC-bottom ash														<0.2	10,903	4	27	506	<1
C35309	CYC1-bottom ash														<0.3	80,076	1.2	289	357	5.5
C35310	CYC2-bottom ash														<0.3	79,758	<1	359	334	10
C35311	PC-bottom ash														<0.3	69,067	3	385	352	9
C35312	FBC-limestone														<0.1	6,298	3.3	<10	20	1.2

Lab no.	Br	Ca	Cd	Ce	Cl	Co	Cr	Cs	Cu	Dy	Eu	F	Fe	Ga	Ge	Hf	Hg	K	La	Li	Lu	Mg	Mn	Mo
C32773	6.5	2,859	<0.3	6.3	100	2.3	12	0.88	7.4	0.64	0.16	90	11,890	3.2	<5	0.36	0.13	1,577	3.5	3.9	0.1	482	39	<6
C32774	3.9	1,072	<0.3	4.1	30	3.1	5.8	0.75	13.6	1.5	0.32	68	21,123	4.0	27	0.32	0.22	913	2.2	5.8	0.11	241	18	<5
C32777	3.6	17,867	5.1	5.0	120	1.5	11	0.8	8.0	0.44	0.10	78	11,890	2.3	11	0.39	0.05	1,909	3.0	2.3	0.08	603	205	<6
C32778	7.7	3,502	0.6	11	70	4.6	12	0.98	15.4	0.86	0.21	70	7,834	3.7	7	0.49	0.04	1,826	6.6	9.6	0.1	603	38	<5.7
C32782	10	5,074	0.4	5.1	150	1.6	14	0.68	6.2	0.45	0.10	78	15,038	2.1	6	0.4	0.07	1,577	3.1	2.8	0.07	543	55	11.0
C32783	9.4	2,073	<0.3	6.9	160	2.7	11	0.96	7.7	0.76	0.17	81	15,457	3.1	5	0.4	0.07	1,743	3.5	3.4	0.09	543	37	9.7
C32785	7.2	2,573	0.4	7.2	120	2.6	17	1.0	8.8	0.68	0.16	115	12,310	2.9	5	0.41	0.07	1,909	4.0	3.8	0.08	603	39	10.3
C32797	5.9	3,073	1.3	8.0	90	3.0	13	1.0	10.0	0.74	0.18	116	11,960	3.2	<5	0.44	0.04	1,826	4.4	4.7	0.1	603	32	12.0
C32814	2.0	3,502	1	5.0	10	2.5	5.7	0.92	8.8	1.9	0.30	63	12,590	2.2	16	0.17	0.07	747	1.7	0.9	0.12	241	30	15.0
C32779	5.8	3,073	0.4	7.9	80	2.0	17	0.9	10.3	0.8	0.19	91	11,820	2.7	<5	0.38	0.05	1,660	4.3	4.7	0.09	543	29	19.0
C32794	2.5	3,145	<0.1	7.6	40	2.8	12	0.93	7.2	0.82	0.18	95	15,318	3.0	<5	0.4	0.08	1,660	4.1	7.5	0.08	543	40	11.7
C32798	5.4	6,504	0.4	9.1	80	3.3	23	1.1	10.6	0.94	0.21	134	13,779	3.5	<5	0.5	0.05	2,158	4.9	6.0	0.08	844	54	10.3
C32800	6.0	3,288	<0.2	8.6	80	2.8	23	1.1	9.6	0.89	0.20	89	12,870	3.3	<5	0.47	0.06	1,992	4.6	6.7	0.08	663	30	9.0
C32813	4.0	3,859	1.1	13	50	3.5	42	1.5	14.0	1.2	0.28	263	15,597	4.2	<5	0.6	0.06	3,072	6.8	10.1	0.10	1,085	40	14.3
C32815	2.2	6,075	<0.2	9.0	20	2.7	14	1.0	8.5	1.0	0.21	88	15,178	3.3	<5	0.46	0.06	1,743	4.7	8.4	0.08	724	61	9.0
C32784	16	786	<0.3	13	390	4.2	11	0.9	7.7	0.87	0.24	67	10,002	3.2	7	0.52	0.11	1,577	7.6	15.6	0.08	482	17	<5
C32795	21	715	<0.1	9.2	450	4.8	8.6	0.68	7.1	0.66	0.16	53	2,798	2.5	<5	0.37	0.03	1,162	5.4	8.6	0.06	362	11	<5
C32796	17	2,430	0.85	21	380	8.5	19	2.1	15.6	1.3	0.35	123	7,204	4.4	<5	0.9	0.06	3,487	12	41.6	0.12	1,085	41	<6
C32799	7.1	7,576	<0.2	13	10	4.4	12	1.1	10.4	1.1	0.29	127	3,567	4.2	<6	0.5	0.02	2,573	7.2	13.2	0.09	724	64	<5
C32801	16	1,644	<0.1	11	350	4.4	12	0.8	7.8	0.79	0.20	76	10,701	2.9	<5	0.5	0.04	1,660	6.0	12.3	0.08	482	21	<5
C32802	14	2,859	<0.1	8.3	290	2.5	12	0.97	6.5	0.68	0.17	88	11,890	2.9	<5	0.42	0.04	1,743	4.8	8.6	0.07	482	23	<5
C32803	14	2,001	<0.1	9.0	320	2.7	12	0.94	11.0	0.98	0.21	94	10,771	3.6	<5	0.45	0.04	1,826	5.2	13.6	0.08	482	28	5.5
C32661	20	1,358	<0.3	10	260	3.9	16	0.92	9.2	0.86	0.19	81	11,471	3.0	<5	0.44	0.07	1,660	5.3	7.6	0.1	482	18	<8.3
C32665	12	1,429	<0.3	12	130	3.6	13	1.1	8.2	0.95	0.21	84	12,100	3.1	<5	0.48	0.16	1,992	6.0	13.7	0.11	543	25	15.3
C32771	8.0	3,145	<0.5	13	90	4.1	14	1.3	9.3	1.2	0.26	131	14,548	3.8	<5	0.57	0.15	2,656	7.8	12.5	0.12	724	36	12.3
C32776	9.5	3,431	<0.3	8.1	150	3.6	15	0.9	8.3	0.79	0.18	74	12,520	3.3	<5	0.44	0.07	1,660	4.4	5.3	0.10	482	38	14.7
C32662	27	929	<0.3	16	350	4.4	10	0.87	11.5	1.4	0.37	83	7,484	2.8	<5	0.39	0.08	1,743	8.5	10.3	0.11	482	15	<7.3
C32663	18	1,286	<0.3	11	210	4.1	11	0.84	8.6	0.8	0.19	78	12,240	3.1	<5.5	0.59	0.25	1,577	6.7	12.6	0.09	464	18	<7.5
C32772	21	3,216	<0.2	11	240	3.9	9.2	0.78	5.2	0.79	0.19	62	12,170	2.6	<5	0.47	0.19	1,743	6.6	10.7	0.09	543	39	<5
C32775	26	1,001	1.05	10	170	4.7	14	0.93	8.8	0.79	0.19	87	13,219	3.4	5	0.41	0.21	1,494	4.9	7.9	0.09	422	16	19.7
C32780	15	3,288	<0.55	7.9	210	1.9	12	0.85	6.1	0.55	0.14	75	13,009	2.4	5	0.42	0.07	1,992	4.4	6.3	0.08	482	24	11.3
C32781	29	1,930	0.5	8.9	190	2.7	12	0.84	6.3	0.62	0.15	61	12,590	2.4	6	0.45	0.11	1,743	5.2	8.1	0.07	844	37	12.0
C32793	11	2,716	<0.2	14	200	5.5	13	1.2	10.1	1.1	0.27	124	11,261	4.2	<5.5	0.79	0.13	3,155	7.8	11.5	0.09	905	39	<5.5
C35564	6.4	6,790	0.71	15.3		7.2	17.2	1.6	11.0		0.31	90	15,248	4.6	11	0.9	0.1	2,407	7.1	30.0	0.15	844	80	5.0
Mean	11.4	3,353	0.5	10.0	167	3.6	14.0	1.0	9.2	0.9	0.2	93	12,058	3.2	4.8	0.5	0.1	1,890	5.5	10.0	0.1	592	39	8.3
SD	7.4	3,060	0.9	3.5	121	1.5	6.1	0.3	2.5	0.3	0.1	36	3,378	0.6	4.9	0.1	0.1	562	2.0	7.8	0.0	196	33	5.8
C35300	8.6	3,431	1	8.4	-	4.6	25	1.5	9.0	ND	0.20	137	12,660	3.7	4	0.6	0.1	1,909	4.6	3.8	0.2	724	80	13.0
C35301	12.9	4,002	0.20	5.0	-	4.0	17	1.0	5.8	ND	0.10	63	15,178	2.6	7	0.5	0.08	1,411	2.7	3.0	0.2	482	80	<10
C35302	12.9	4,217	0.2	6.7	-	3.5	18	0.9	5.5	ND	0.10	61	15,457	2.8	7	0.3	0.08	1,494	3.2	3.1	0.1	543	80	<10
C35303	13.2	4,002	0.42	7.1	-	3.5	17	1.0	5.0	ND	0.10	63	15,457	2.4	7	0.6	0.08	1,494	2.9	3.3	0.1	543	80	8.0
C35304	22.6	230,988	2.48	34	-	12.3	75	4.3	35.8	ND	0.80	53	44,764	10.8	13	2.4	0.25	7,720	18.3	7.0	0.4	59,459	620	16.0
C35305	18.7	24,657	11.5	60	-	24.2	227	11.5	110.0	ND	1.00	230	111,420	56.3	200	5.2	0.73	18,180	25	37.0	0.8	4,945	310	89.0
C35306	14.3	29,302	16.2	81.8	-	46.5	220	14.65	159.0	ND	1.64	200	94,633	65.9	220	5.05	0.41	20,837	35.9	56.0	0.95	4,945	310	90.0
C35307	<1	36,449	4.89	63	-	20.2	175	8.4	66.8	ND	1.20	67	118,904	36.7	114	5.1	0.1	15,441	29.4	37.0	0.8	5,126	460	67.0
C35308	0.5	446,753	0.63	15	-	4.3	35	1.0	16.9	ND	0.40	48	10,561	3.3	4	1	0.01	1,992	7.5	<6	0.2	9,468	310	11.0
C35309	<1	63,179	0.48	63.1	-	20.2	112	4.2	34.3	ND	1.10	15	137,299	11.7	9	4.6	0.02	11,124	31.3	28.0	0.7	5,246	540	<10
C35310	<1	49,528	0.49	61	-	17.2	125	4.3	28.8	ND	1.00	<10	147,930	8.6	8	4.8	<.01	11,290	29	23.0	0.7	4,885	540	30.0
C35311	<1	39,237	0.47	55	-	22.5	136	5.0	39.1	ND	1.00	<10	214,236	10.5	20	4.4	<.01	11,041	24.4	18.0	0.7	4,583	460	<16
C35312	0.6	356,988	0.55	9.4	-	3.5	11	0.7	15.0	ND	0.20	5	7,100	1.5	8	0.4	<0.01	1,743	5.0	<5.0	0.1	7,297	1,394	<4

Continued

Table 3. *Continued* Chemical composition of 35 marketed Illinois coals from preparation plants and of feed coals and combustion residues from four selected power plants. The values are in milligrams per kilogram (unless indicated otherwise) on a moisture-free basis.

Lab no.	Na	Ni	P	Pb	Rb	Sb	Sc	Se	Si	Sm	Sn	Sr	Ta	Tb	Th	Ti	Tl	U	V	W	Yb	Zn	Zr
C32773	1,039	11	44	<6	11	0.2	1.9	1.9	20,988	0.65	<5	28	0.1	0.12	1.2	539	<1	1.7	16	0.35	0.29	32.9	20
C32774	148	15	87	124	5	1.2	1.9	1.2	11,312	1.2	<5	17	0.07	0.25	0.84	300	<1	<0.8	11	0.2	0.61	70.8	19
C32777	445	7	44	36.0	10	1.1	1.6	1.6	27,298	0.45	<5	26	0.11	0.1	1.1	539	<1	1.1	18	<0.2	0.29	447	22
C32778	1,187	31	87	13.5	12	2.2	2.6	1.5	23,886	0.97	<5	50	0.12	0.15	1.5	659	<1	0.9	25	0.35	0.43	105	26
C32782	1,113	7	87	<6	8.2	0.5	1.6	1.9	27,438	0.49	<5.5	25	0.1	0.07	1.1	539	1	1.3	23	0.35	0.26	42.2	23
C32783	1,484	8	44	<5.5	12	0.1	2.0	1.3	20,520	0.75	<5	28	0.11	0.13	1.3	539	<1	1.1	17	0.3	0.44	54.1	22
C32785	1,261	17.5	131	<5.3	11	0.4	2.0	3.9	23,091	0.73	<5	30	0.12	0.13	1.3	539	<1	1.8	29	0.4	0.37	59.9	22
C32797	1,113	16	87	8.5	11	0.6	2.2	1.4	23,232	0.72	<5	44	0.11	0.13	1.5	599	<1	1.9	27	0.45	0.39	105	25
C32814	74	12	<44	23.0	5.1	1.9	1.1	1.3	9,956	1	<5	17	0.05	0.29	0.61	240	<1	8.0	16	0.25	0.76	67.9	11
C32779	1,039	11	44	7.0	10	0.4	2.0	2.3	22,203	0.8	<5	27	0.1	0.13	1.3	539	<1	3.1	41	0.55	0.41	77.9	22
C32794	371	14	44	14.5	10	0.3	2.1	1.9	23,559	0.8	<5	20	0.1	0.14	1.4	599	<1	2.0	23	0.3	0.43	120	24
C32798	1,039	18	87	12.0	13	0.3	2.5	3.2	28,701	0.93	<5	24	0.12	0.16	1.7	659	<1	2.7	46	0.45	0.47	78	28
C32800	964	15.5	87	8.0	14	0.4	2.4	2.8	26,457	0.89	<5	22	0.12	0.13	1.6	659	<1	2.9	30	0.4	0.42	68.5	26
C32813	890	24	305	12.5	19	0.7	3.1	5.4	35,572	1.2	<5	27	0.14	0.2	2.1	839	<1	3.7	65	0.5	0.65	141	34
C32815	371	10	44	12.3	11	0.6	2.4	2.1	25,849	0.91	<5	20	0.13	0.13	1.7	659	<1	1.9	27	0.25	0.45	101	24
C32784	890	15	44	39.5	13	1.1	2.6	1.4	18,510	1.2	<5	30	0.1	0.16	1.4	599	<1	1.0	18	0.4	0.47	28.8	31
C32795	1,039	18	44	16.0	8.8	1.1	1.9	1.1	15,005	0.82	<5	27	0.1	0.09	1.2	480	<1	0.6	15	0.25	0.33	39.9	20
C32796	1,261	23.5	87	31.3	24	1.0	3.8	2.0	44,079	1.8	<5	30	0.21	0.23	3	1,199	<1	1.0	39	0.3	0.74	318	51
C32799	519	14.5	436	63.7	15	3.6	2.8	1.3	26,363	1.4	<5	156	0.12	0.19	1.6	659	<1	0.7	28	0.75	0.47	121	28
C32801	816	14	44	22.0	11	0.6	2.4	1.5	20,146	0.97	<5	22	0.11	0.14	1.5	659	<1	1.0	21	0.75	0.42	34.5	27
C32802	593	7	44	7.0	11	0.3	2.2	1.5	20,801	0.78	<5	29	0.11	0.13	1.4	539	<1	1.2	32	0.35	0.38	32.1	24
C32803	816	13	44	12.5	11	0.4	2.6	1.5	20,661	0.93	<5	27	0.1	0.15	1.6	599	<1	1.1	34	0.4	0.43	25.4	25
C32661	519	13.5	44	19.0	10	0.5	2.4	2.0	18,791	0.85	<6.5	22	0.1	0.13	1.5	539	1	7.5	33	0.4	0.47	68.2	27
C32664	245	11	31	32.5	14	0.5	3.1	1.6	23,746	1.1	<5.5	21	0.1	0.18	1.7	599	<1	2.2	22	0.4	0.53	38.7	29
C32665	297	11	44	18.5	13	0.4	2.5	1.7	22,764	0.98	<7.5	22	0.1	0.14	1.6	599	<1	5.7	35	0.5	0.45	23.5	26
C32771	445	10	44	21.5	18	0.3	2.8	1.4	30,570	1.3	<5	23	0.14	0.16	1.8	779	<1	2.2	26	0.5	0.55	104	35
C32776	668	12	44	10.0	11	0.6	2.6	1.7	20,053	0.79	<5	14	0.11	0.16	1.4	539	<1	1.8	45	0.45	0.44	32	25
C32662	593	17	175	22.5	11	1.0	2.5	1.3	16,173	1.7	<5	62	0.1	0.24	1.9	539	<1	1.9	27	0.4	0.61	28.4	22
C32663	252	13	144	96.0	9.7	1.4	2.4	1.5	21,549	0.88	<10	46	0.1	0.13	1.4	659	1	0.9	23	0.45	0.44	61.8	39
C32772	371	13	87	27.0	10	0.7	2.4	1.3	22,343	0.95	<5	43	0.13	0.14	1.3	599	<1	<1	19	0.45	0.39	39.8	32
C32775	148	17.5	44	51.5	11	1.2	2.3	3.6	16,360	0.9	<5	44	0.1	0.14	1.3	480	<1	6.8	29	0.35	0.43	109	24
C32780	445	7.5	44	11.7	10	1.4	2.0	2.3	20,941	0.7	<5	19	0.11	0.1	1.2	599	<1	2.0	64	0.5	0.33	35.7	27
C32781	223	11	44	46.0	11	1.4	1.7	2.5	22,343	0.74	<5	28	0.1	0.1	1.2	539	<1	2.0	91	0.35	0.34	62.4	27
C32793	1,039	22	175	35.5	18	1.2	2.9	1.1	33,655	1.3	<5	40	0.16	0.17	1.8	839	<1	0.8	32	0.5	0.56	91.3	49
C35564	1,335	25	87	35.4	17.6	2.1	3.7	2.2	31,084	1.3	<5	35	0.2	0.17	2.4	899	<1	0.9	26	0.1	0.62	252	12
Mean	716	14.4	87	25.8	12.0	0.9	2.4	1.9	23,314	1.0	2.6	33	0.1	0.2	1.5	611	0.5	2.2	31	0.4	0.5	89	27
SD	397	5.5	83	25.9	3.7	0.7	0.6	0.9	6,605	0.3	0.5	24	0.0	0.0	0.4	163	-	1.9	16	0.1	0.1	87	8
C35300	1,113	18	131	4.3	19	0.4	2.5	5.5	26,597	1.0	<5	34	0.1	0.2	1.8	539	<1	1.9	41	0.3	0.5	77	10
C35301	1,039	8	44	3.3	14	0.7	1.8	2.7	24,961	0.7	<5	25	0.1	0.1	1.2	480	<1	2.0	34	<0.3	0.5	34	9
C35302	964	17	44	3.2	13	0.8	1.9	2.0	25,475	0.6	<5	25	0.1	0.1	1.3	539	<1	1.8	37	<0.5	0.3	39	9
C35303	1,039	11	44	3.2	12	0.6	1.9	2.9	25,475	0.7	<5	26	0.1	0.1	1.4	480	<1	2.3	41	0.4	0.5	34	9
C35304	3,858	66	567	14.1	54	1.3	7.8	14.4	96,572	3.8	<5	300	0.4	0.5	5.6	1,978	2	7.1	69	3.8	1.7	193	10
C35305	14,615	173	742	89.7	132	13.6	19.4	43.3	217,404	6.3	11	264	1.3	1.0	14.6	6,114	10	21.7	420	4.0	3.9	962	111
C35306	16,247	308	873	170	178	49.9	23.1	24.3	189 451	8.5	10	371	1.5	1.12	15.8	6,114	4	18.1	560	5.55	4.35	1,286	131
C35307	11,425	77	524	48.9	104	7.9	18.0	7.4	243,347	6.7	5	264	1.1	0.8	12.6	5,455	4	16.8	428	3.4	3.8	306	105
C35308	1,113	14	480	4.8	15	0.8	2.4	<1	61,327	1.7	6	506	0.2	0.2	1.9	659	<1	4.0	18	0.9	0.7	73	ND
C35309	6,380	70	524	<5.3	90	1.1	16.3	2.1	244,235	6.7	18	255	0.9	0.8	11.3	4,016	2	11.1	197	<.6	3.1	97	74
C35310	6,751	62	349	<4.8	70	1.0	16.1	1.8	246,852	5.5	14	231	1.0	0.7	11.1	4,136	2	13.2	244	1.0	3.2	93	73
C35311	5,935	85	349	10.2	88	2.2	14.4	2.2	217,638	4.8	26	194	0.8	0.6	10.4	3,896	3	12.5	231	<1.5	2.7	133	56
C35312	816	9.4	262	5.03	11	0.2	1.5	<0.5	21,409	1.1	<5	526	<0.1	0.2	1.0	360	<1	2.8	14	<1.7	0.5	39	ND

[1] Regions: H, Herrin Coal; S, Springfield Coal.

[2] For those values indicated with "<" sign, one-half of the values were used in the statistical computations to determine the mean and standard deviation values.

Table 4 Mineral-element correlations in marketed Illinois coals at $\alpha = 0.001$ levels of significance, which correspond to $r^2 > 0.30$ for the number of samples used.

Mineral-element pair		r^2	Mineral-element pair		r^2
Illite/smectite	Cs	0.62	Illite + Illite/smectite	Mg	0.66
	Mg	0.53		F	0.63
	Ti	0.52		Ti	0.63
	Ta	0.49		Cs	0.60
	Sc	0.48		Rb	0.59
	Cr	0.47		Sc	0.56
	Rb	0.46		Th	0.56
	Hf	0.42		Ta	0.55
	Ga	0.41		Hf	0.49
	Ba	0.36		Ba	0.47
				Ga	0.45
				Ce	0.37
				La	0.34
Kaolinite	Hf	0.58	Chlorite	Ta	0.34
	Sc	0.55		Ti	0.33
	Ba	0.53		Hf	0.31
	Ti	0.53			
	Li	0.51	Quartz	Mg	0.53
	Ta	0.51		Ti	0.32
	Th	0.46		Ta	0.31
	Ce	0.38			
	La	0.36	Calcite	Mn	0.94
	Cs	0.32		Zn	0.54
Marcasite	B	0.48			
	Br	0.37			

to a lesser extent, to mullite. Pyrite and marcasite were converted to hematite, magnetite, and amorphous Fe oxides. Some of the calcite reacted with sulfur released from pyrite, marcasite, and organic matter and formed anhydrite, which later reacted with moisture and partially hydrated to gypsum. The rest of the calcite was converted to CaO (lime) and $Ca(OH)_2$ (portlandite); some of these minerals subsequently changed back to calcite through reaction with atmospheric CO_2. At the FBC plant, large amounts of lime and portlandite were generated (mostly in the bottom ash) because of the limestone addition; subsequent reaction with atmospheric CO_2 most likely took place only on the exterior surfaces of these relatively coarse Ca minerals from the FBC ashes. The mineral conversion reactions apparently varied from one type of combustion unit to another, which resulted in distinct differences in the mineralogical as well as chemical compositions of the CCRs from the four coal-fired power plants. These differences have important implications for the effect of plant type on the HAPs emissions and on the suitability of the CCRs for use in cement, ceramic, and other commercial applications.

Emission of HAPs from Power Plants

If a HAP element is entirely retained in CCR, its emission into the atmosphere at coal-fired power plants is prevented. However, a portion of each HAP generally is mobilized and becomes airborne. The mobilized portions of the HAPs may be partially adsorbed on surfaces of hardware on the cool side (between the boiler and the stack) of a power plant and partially emitted into the atmosphere. Thus, the mobility values of HAPs would overestimate their atmospheric emissions, except in the case of highly volatile HAPs (F, Hg, Se). Therefore, it is difficult to obtain mass balance for trace elements from power plant samples, and the mobility values reported here should be used cautiously.

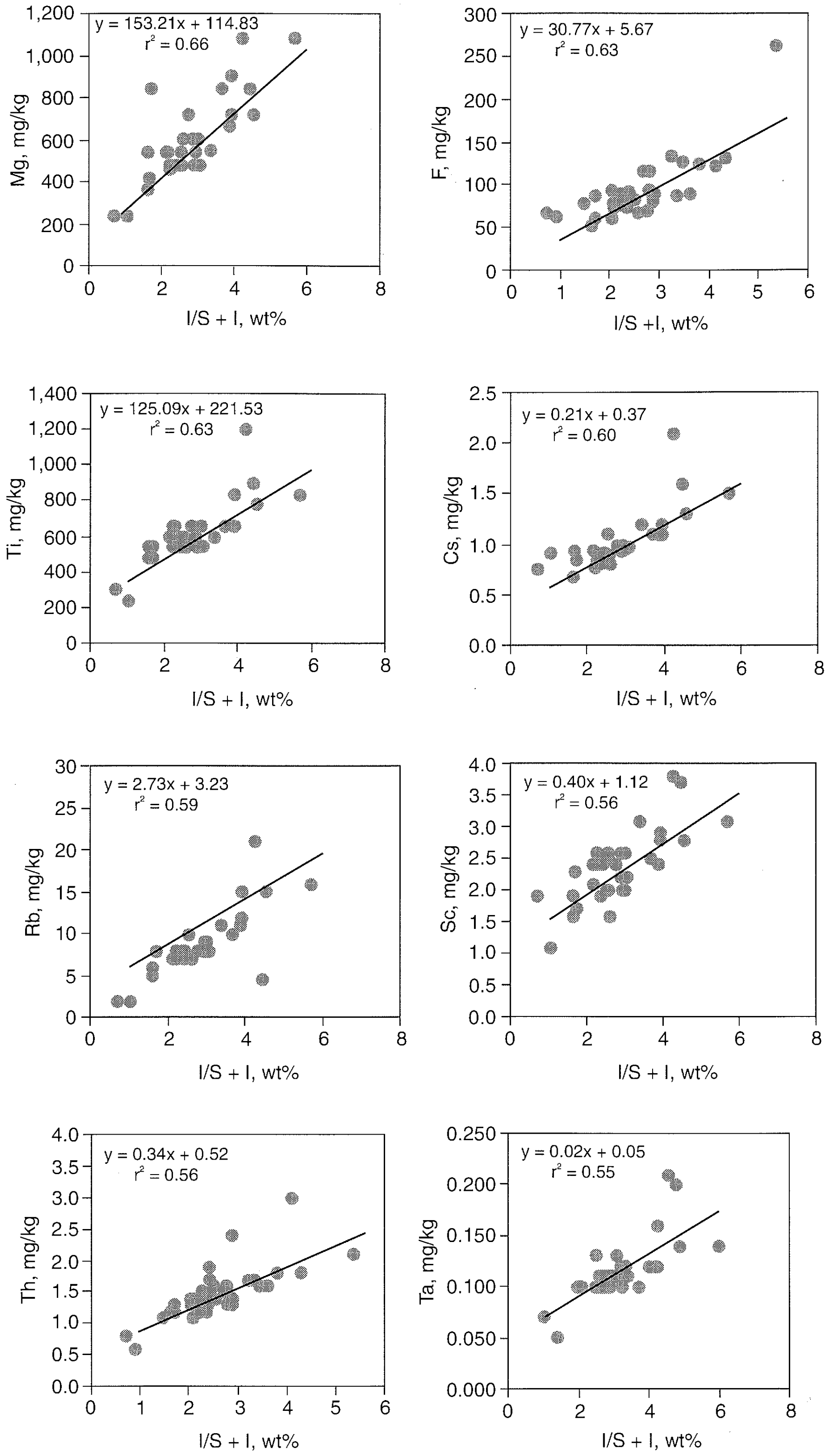


Figure 7 Relationships of $r^2 > 0.5$ between elements and mixed-layered illite/smectite plus illite in marketed Illinois coals.

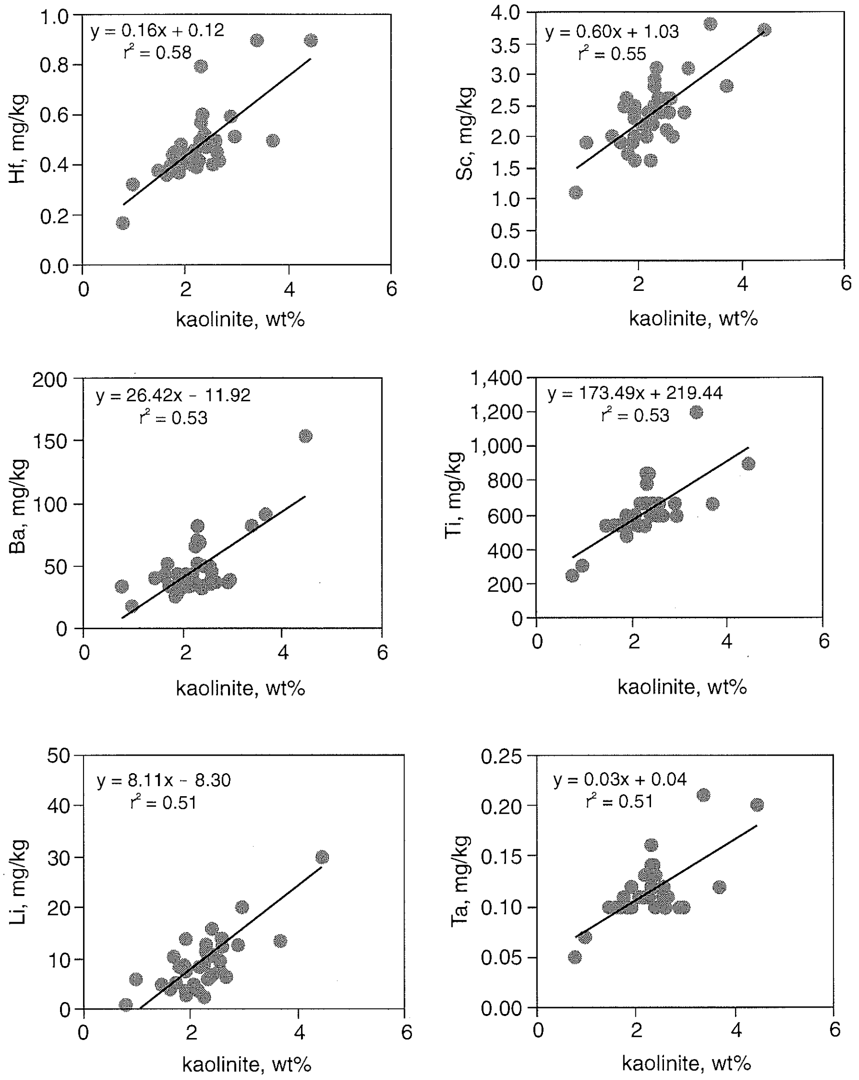
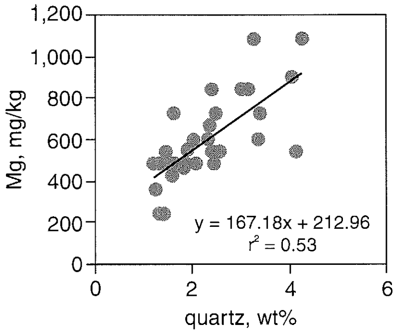


Figure 8 Relationships of $r^2 > 0.5$ between elements and kaolinite in marketed Illinois coals.

Figure 9 Relationship between quartz and Mg in marketed Illinois coals.



The mobilities of 15 HAP elements from the four power plants were determined by using mass balance calculations (table 5). The mass balance of an element was calculated by comparing its mass in the feed (w_F) and in the CCRs (w_{CCRs}):

$$\text{Mass balance (\%)} = (w_{CCRs} / w_F) \times 100.$$

The calculations of w_{CCRs} and w_F took into consideration the mass ratios of fly ash to bottom ash as well as the measured concentrations of elements and high-temperature ash in the samples. The fly ash to bottom ash ratios were 80/20 for the FBC plant, 25/75 for the CYC plants, and 75/25 for the PC plant. The feed for the FBC plant included not only coal but also the limestone added to the bed at a ratio of 75% coal to 25% limestone.

The mass balances of the 15 elements were normalized to that of Al (by dividing them by Al mass balance and multiplying the result by 100) to minimize the effect of sampling and analytical errors on the mass balance computations. Aluminum was used for normalization because it is a refractory element with a relatively large concentration in coal and is expected to be retained almost completely in the combustion ashes; no more than 5% (most of the time <1%) of Al was expected to escape the particulate collection systems with ultra-fine, airborne fly ash particles. Aluminum mass balances of approximately 100% for the CYC and PC units (Table 5) indicated that the mass balance calculations performed for these two types of plants were highly accurate. The Al mass balance for the FBC plant (76%) was somewhat small but still reasonable. The Al mass balance deficiency for the FBC plant could have resulted from variations in the composition of the feeds that would make it difficult to obtain a truly representative sample during a few hours of operation. The limestone and the coal used in the FBC furnace were blends of products from many different quarries and mines in Illinois. Therefore, future studies should consider collecting at least several

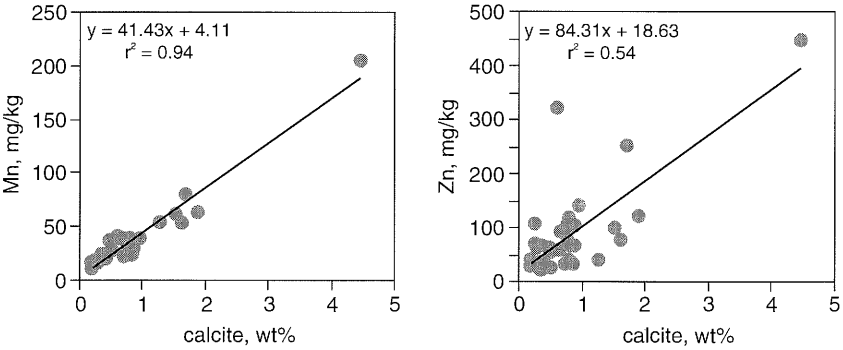


Figure 10 Calcite-Mn and calcite-Zn relationships in marketed Illinois coals.

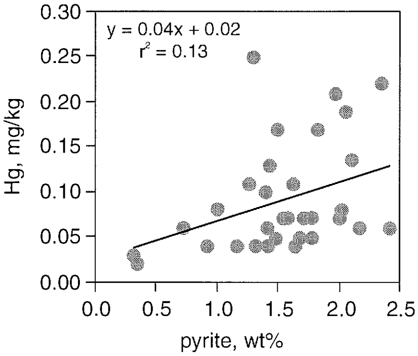


Figure 11 Relationship between pyrite and Hg in marketed Illinois coals.

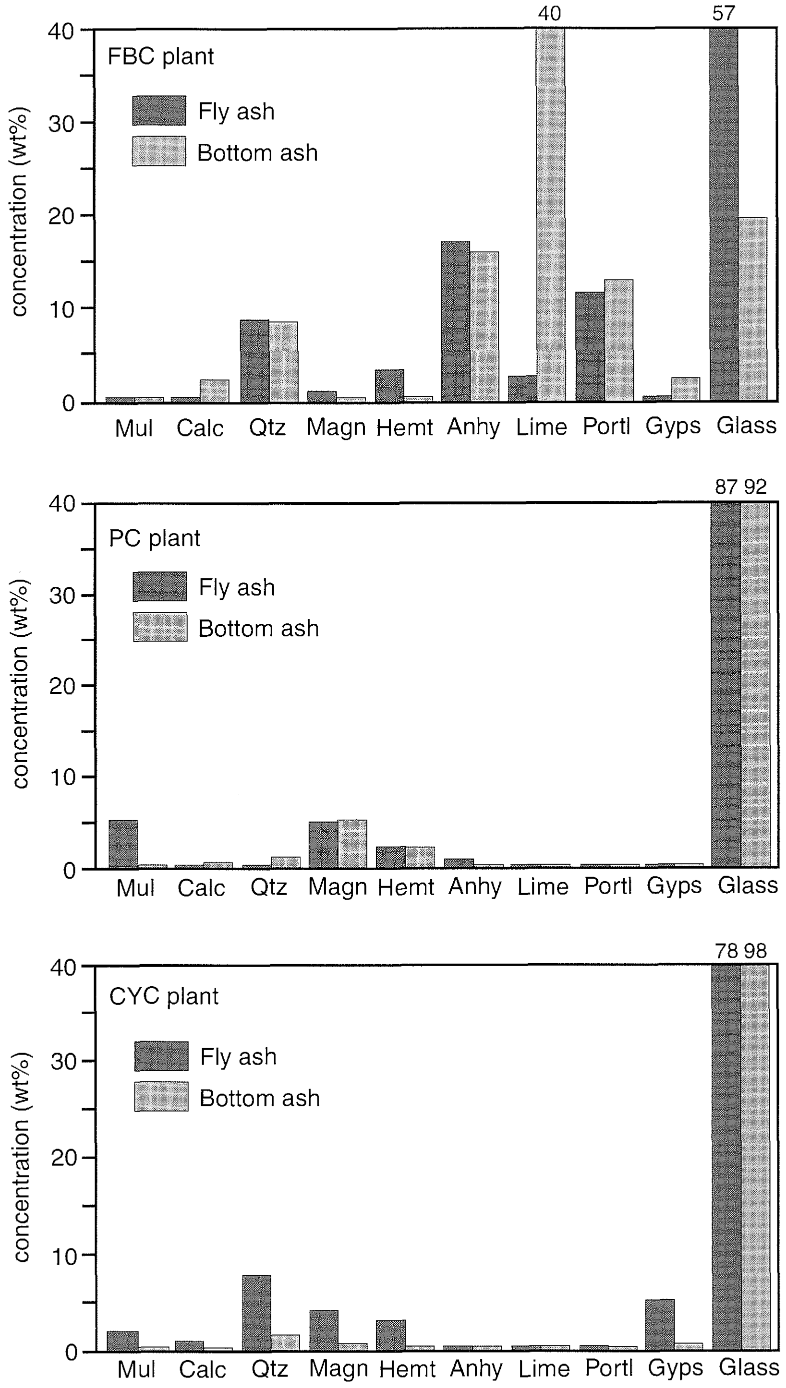


Figure 12 Mineralogical composition (from table 2) of CCRs from three types of plants (FBC, PC, CYC) in Illinois. The cyclone plant values were the averages of two plants. Key: Mul, mullite; Calc, calcite; Qtz, quartz; Magn, magnetite; Hemt, hematite; Anhyd, anhydrite; Portl, portlandite; Gyps, gypsum; Glass, amorphous phase.

Table 5 Concentrations of Al and 15 elements of environmental concern in coal, CCRs, and limestone samples from the four power plants and related combustion mobility and relative enrichment (RE) values. The concentration values are in milligrams per kilogram unless indicated otherwise. All values are on a dry weight basis.

Item	Plant and sample type	Al (%)	As	Be	Cd	Co	Cr	F	Hg	Mn	Ni	P	Pb	Sb	Se	Th	U
C35300[1]	FBC-coal	1.00	1.8	1.7	1.00	4.6	25	137	0.10	77	18	131	4.34	0.4	5.5	1.8	1.9
C35304	FBC-fly ash	3.39	6.1	6.0	2.48	12.3	75	53	0.25	620	66	567	14.1	1.3	14.4	5.6	7.1
C35308	FBC-bottom ash	1.09	4.0	0.5	0.63	4.3	35	48	0.01	310	14	480	4.8	0.8	<1	1.9	4.0
C35312	FBC-limestone	0.63	3.3	1.2	0.55	3.5	11	5	<0.01	1,394	9.4	262	5.03	0.2	<0.5	1.0	2.8
Mass balance (%)		76	81	96	73	76	96	15	82	42	108	104	84	106	87	94	94
Mobility (%)		24	19	4	27	24	4	85	18	58	0	0	16	0	13	4	6
RE for fly ash		0.9	0.6	0.9	0.6	0.6	0.8	0.1	0.7	0.3	1.0	0.8	0.7	0.8	0.8	0.8	0.8
RE for bottom ash		0.3	0.4	0.1	0.2	0.2	0.4	0.1	0.0	0.2	0.2	0.7	0.2	1.5	0.0	0.3	0.4
C35301	CYC1-coal	0.80	2.6	4.0	0.19	4.0	17	63	0.08	77	8	44	3.34	0.7	2.7	1.2	2.0
C35305	CYC1-fly ash	7.02	50.6	14.0	11.5	24.2	227	230	0.73	310	173	742	89.7	13.6	43.3	14.6	21.7
C35309	CYC1-bottom ash	8.01	1.2	5.5	0.48	20.2	112	15	0.02	542	70	524	2.65	1.1	2.1	11.3	11.1
Mass balance (%)		102	54	20	170	54	85	11	25	65	123	135	75	62	47	104	71
Mobility (%)		0	46	80	0	46	15	89	75	35	0	0	25	38	53	0	29
RE for fly ash		0.9	2.0	0.4	6.2	0.6	1.4	0.4	1.0	0.4	2.3	1.8	2.8	2.0	1.7	1.3	1.1
RE for bottom ash		1.0	0.0	0.1	0.3	0.5	0.7	0.0	0.0	0.7	0.9	1.2	0.1	0.2	0.1	1.0	0.6
C35302	CYC2-coal	0.82	2.4	1.9	0.20	3.5	18	61	0.08	77	17	44	3.22	0.8	2.0	1.3	1.08
C35306	CYC2-fly ash	7.23	146	15.0	16.2	45.8	208	200	0.41	310	262	873	170	48	22.2	15.6	19.2
C35310	CYC2-bottom ash	7.97	0.05	10.0	0.49	17.2	125	5	0.005	542	62	349	2.4	1.0	1.8	11.1	13.2
Mass balance (%)		107	160	62	232	73	85	9	14	66	69	115	144	167	36	99	86
Mobility (%)		0	0	38	0	27	15	91	76	34	31	0	0	0	64	1	14
RE for fly ash		0.9	6.5	0.8	8.7	1.4	1.2	0.4	0.5	0.4	1.7	2.1	5.7	6.4	1.2	1.3	1.1
RE for bottom ash		1.0	0.0	0.6	2.6	0.5	0.7	0.0	0.0	0.8	0.4	0.8	0.1	0.1	0.1	0.9	0.8
C35303	PC-coal	0.82	2.2	1.0	0.42	3.5	17	63	0.08	77	11	44	3.2	0.6	2.9	1.4	2.3
C353307	PC-fly ash	8.47	34.0	9.0	4.89	20.2	175	67	0.10	468	77	524	48.9	7.9	7.4	12.6	16.8
C35311	PC-bottom ash	6.91	3.0	9.0	0.47	22.2	136	5	>.01	468	85	262	10.2	2.2	2.2	10.4	12.5
Mass balance (%)		105	121	91	92	60	99	8	10	62	73	106	124	110	21	87	69
Mobility (%)		0	0	9	8	40	1	92	90	38	27	0	0	0	79	13	31
RE for fly ash		1.1	1.6	1.0	1.2	0.6	1.1	0.1	0.1	0.6	0.7	1.3	1.6	1.4	0.3	1.0	0.8
RE for bottom ash		0.9	0.1	1.0	0.1	0.7	0.9	0.0	0.0	0.6	0.8	0.6	0.3	0.4	0.1	0.8	0.6

[1] Lab number.

Table 6 Mobilities of HAPs during combustion.

	Mobility (%)		
Plant type	Low (<25%)	Moderate (25–50%)	High (>50%)
FBC	As, Be, Co, Cr, Hg, Ni, P, Pb, Sb, Se, Th, U	Cd	F, Mn
CYC[1]	As, Cd[2], Cr, Ni, P[2], Pb, Sb[2], Th, U	Be, Co, Mn	F, Hg, Se
PC	As[2], Be, Cd, Cr, P, Pb, Sb[2], Th	Co, Mn, Ni, U	F, Hg, Se

[1] Average of two CYC plants. The two plants varied significantly with respect to the mobilities of some elements (see table 5).

[2] Negative mobilities resulting from excess mass balance suggest the possibility of contamination of combustion ashes by erosion or corrosion of hardware (see text for more on the definition of mobility).

sets of samples over a period of several months of operation from the FBC plant, and the average mass balance data on these samples should be used to smooth out the variance.

The mobility of HAP elements from the four plants was calculated as follows:

$$\text{Mobility (\%)} = 100 - \text{mass balance}.$$

According to this mobility relationship, if the amount of an element recovered from the CCRs accounted for 100% of the amount in the feed, then the element was assumed to be immobile. If the mass balance of an element was less than 100%, then the difference was considered to indicate the percentage of the element that entered and remained in the gas phase or condensed on the ultra-fine, airborne fly ash particles or on the power plant hardware.

For convenience, the mobility values were divided into low, moderate, and high categories (table 6). Negative mobility values caused by the excess mass balance (101–167%) in some cases (table 5) probably resulted mainly from contamination of the CCRs by the erosion or corrosion of hardware in the combustion process. In particular, the excess mass balances observed for Cd for the CYC1 unit and for As, Cd, Pb, and Sb for the CYC2 unit (table 5) were too large to explain as sample variability or analytical error. Analysis of the CYC2 fly ash was repeated three times, and no significant variation was found between the three analyses. Although the negative mobility values were arbitrarily assumed to be in the low-mobility category, we recommend that periodic sampling of the CYC2 plant and analysis of the samples be carried out in the future to better understand the combustion behavior of As, Cd, Pb, and Sb at this unit.

For the FBC plant, only the mobilities of F (85%) and Mn (58%) were large (table 6). The mobilities at the FBC plant were surprisingly low for the normally volatile elements Hg (18%) and Se (13%). Overall, the HAPs mobilities were lower at the FBC plant than at the other plants (table 5). Apparently, a relatively low combustion temperature (~900°C) or the chemical environment created by the addition of limestone resulted in generally lower HAPs mobilities. The FBC fly and bottom ashes naturally contained large amounts of anhydrite and lime-portlandite (table 3). Several investigators (Clarke and Sloss 1992; Meij 1993, 1994a; Gullet and Ragnunathan 1994; Bool and Helble 1995; Querol et al. 1995; DeVito and Bhagwat 1997) reported that Ca-rich materials such as lime and limestone can capture substantial amounts of As, Hg, Sb, and Se during combustion. Suarez-Fernandez et al. (1996), however, did not find any major differences between the combustion behavior of trace elements in a laboratory-scale FBC unit with or without the addition of limestone. This result suggests that low temperatures may influence the mobility of certain elements more than does limestone addition.

For the CYC and PC plants, mobilities of the volatile elements F (89–92%), Hg (75–90%), and Se (53–79%) were high (table 6), as expected. The mobility values of some elements for the CYC and PC plants were inconsistent with the volatility data summarized in figure 7 of Clarke and Sloss (1992). According to Clarke and Sloss (1992), As, Cd, Pb, and Sb are moderately volatile. However, our data indicated that all four elements had low mobilities at the PC plant, and Cd and Pb had low mobilities at the two CYC plants. Also, the Mn mobility was supposed to be low, which is inconsistent with the moderate Mn mobility calculated for the CYC and PC plants.

Although Mn is not a volatile element at normal coal combustion temperatures, its mobility from the FBC plant was surprisingly large. Querol et al. (1995) reported that Mn has an affinity for Fe oxide in the CCRs. The Mn content of the feed coal from the CYC and PC plants was less than the Mn content of the feed (a blend of coal and limestone) from the FBC plant (table 5). Furthermore, CCRs from the CYC and PC plants contained more Fe oxide minerals (magnetite + hematite) than did the CCR from the FBC plant (table 3). These differences could be the reason Mn mobility was considerably greater at the FBC plant than at the CYC and PC plants.

Studies reviewed by Clarke and Sloss (1992) and Davidson and Clarke (1996) indicated that among the 15 HAPs investigated, substantial portions of only F, Hg, and Se were mobilized in the gas phase and emitted into the atmosphere during coal combustion. The emission of other elements generally resulted from their enrichment in the submicron-size, fly ash particles that passed through the particulate control systems.

Partitioning of HAPs between Fly Ash and Bottom Ash

The atmospheric emission of elements from coal-fired power plants is directly related to the partitioning of elements among CCRs. For example, the enrichment of an element in the bottom ash would reduce its atmospheric emission. However, if an element is preferentially enriched in submicron-size, airborne, fly ash particles, its emission would be enhanced. The partitioning of elements in CCRs affects not only their atmospheric emissions but also the commercial value of the CCRs. To compare the distribution of HAP elements in fly and bottom ashes relative to their concentrations in coal, a relative enrichment factor (RE) was calculated for each HAP using the formula of Meij (1992):

$$RE = (C_{CCR}/C_F) \times (\%ash_F/100).$$

where C_{CCR} and C_F are the concentrations of an element in the CCR (fly ash or bottom ash) and feed, respectively, and $\%ash_F$ is the percentage of ash in the feed. The feed refers to coal or, in the case of the FBC unit, a mixture of coal and limestone. Elements that are neither enriched nor depleted in the CCR should ideally have relative enrichment values of 1. Elements with relative enrichment values of significantly greater or less than 1 are enriched or depleted, respectively, in the CCR. Based on the literature (Meij 1992) and for convenience, the relative enrichment values in this study were divided into "normal," "enriched," and "depleted" categories (table 7).

In most cases, the relative enrichment factor of the HAPs was greater for the fly ash than for the bottom ash samples from the four plants (table 5). The only reverse cases were Sb at the FBC plant, Mn at the CYC plants, and Co and Ni at the PC plant. The greater relative enrichment values for fly ash than for bottom ash probably resulted from the combination of two factors: (1) large portions of most HAP elements were volatilized during combustion and then, upon cooling, condensed on the fly ash particles, and (2) some elements were enriched in finely disseminated coal minerals that ended up in the fly ash in greater proportions than they did in the coarse coal minerals.

Some elements with large relative enrichment values could be recovered from the respective CCR and sold. For example, Se was highly enriched in the CYC1 fly ash (RE = 1.7). The average concentrations of Se in the earth's crust, shale, and soils are 0.05, 0.5, and 0.4 mg/kg, respectively (Clarke and Sloss 1992). As a result, the Se concentration in the CYC1 fly ash was 866, 87, and 108 times greater than the earth's crust, shale, and soil averages, respectively. Therefore, the

Table 7 Relative distribution of HAPs among combustion ashes.

Plant and ash type	Distribution Normal (RE = 0.7–1.3)	Depleted (RE < 0.7)	Enriched (RE > 1.3)
FBC-fly	Be, Cr, Hg, Ni, P, Pb, Sb, Se, Th, U	As, Cd, Co, F, Mn	none
FBC-bottom	P	As, Be, Cd, Co, Cr, F, Hg, Mn, Ni, Pb, Se, Th, U	Sb
CYC[1]-fly	Be, Co, Hg, U	F, Mn	As, Cr, Cd, Ni, P, Pb, Sb, Se, Th
CYC-bottom	Cr, Mn, Ni, P, Th, U	As, Be, Co, F, Hg, Pb, Sb, Se	Cd
PC-fly	Be, Cd, Cr, Ni, P, Th, U	Co, F, Hg, Mn, Se	As, Pb, Sb
PC-bottom	Be, Co, Cr, Ni, Th	As, Cd, F, Hg, Mn, P, Pb, Sb, Se, U	none

[1] Average of two CYC plants.

CYC1 fly ash can be considered to be a potential source for commercial Se production. Rose et al. (1979) reported that Se is produced industrially as a by-product of Cu refining; for an Arizona Cu ore deposit, for example, Se concentration was ~8 mg/kg. This value is much greater than the crustal average of 0.05 mg/kg Se, but similar in magnitude to the range of 7.4 to 43.3 mg/kg for Se found in the fly ashes from the three Illinois plants (table 3).

In the past, relative enrichment values in the combustion products were used to assign the inorganic elements in coal to differing volatility classes (Clarke and Sloss 1992, Meij 1992, Davidson and Clarke 1996). However, such a task is often complicated by substantial variations in the combustion behavior of elements depending on the characteristics of coal, the type and operating conditions of power plants, and sampling and analytical errors. For example, some elements were enriched in the fly ashes from CYC or PC plants but not in the fly ash from the FBC plant (table 7). The only obvious trend common to all four power plants was that most HAPs were depleted or normally distributed in the bottom ashes (table 7). Although depletion of Al, a non-HAP conservative element, is not expected in the CCRs, its depletion in the FBC bottom ash (RE = 0.3; table 5) is not surprising. The likely reason for the observed Al depletion is that the abundant and Al-rich clay minerals from the FBC feed coal ended up in the fly ash in greater proportions than the Al-deficient calcite that was the principal component of the limestone. This study did not examine the enrichment of the trace elements in particle-size fractions of the fly ash samples. Previous studies (Tumati and DeVito 1991, 1993; Dale et al. 1992; DeVito and Jackson 1994; Helble 1994; Meij 1994b; Querol et al. 1995; Cereda et al. 1995; Suarez-Fernandez et al. 1996) indicate that there is generally a negative correlation between ash particle size and the concentrations of As, Co, Cr, Hg, Mn, Ni, Sb, and Se.

Temporal Variations in the Characteristics of Marketed Coals

Marketed coals from four of the Illinois preparation plants were sampled twice with a 4-year interval between the two sampling times. The mineralogical and chemical characteristics of these as-shipped coals changed somewhat over the 4 years (table 8); some of these changes could partly be the result of the simple sample variation that can occur any time. There was no apparent systematic change that was common to all four coals. For example, the ash content increased for two of the coals and decreased for the other two. The temporal change in coal quality for some individual mines is not surprising because over time the production in a mine moves to different reserve blocks, commonly with somewhat differing coal qualities. And, in some cases, coal cleaning efficiency is altered over time to meet the specifications of coal buyers. For example, if the customer of a mine changes from a PC boiler without a scrubber to a PC boiler with a scrubber, a FBC unit, or gasification plant, the run-of-mine coal does not have to be cleaned as much for sulfur (pyrite) removal. The average coal quality for the entire basin, however, would not change significantly over a 4-year period. The coal C35300 from the FBC unit (Tables 3 and 5) was a blend of production from 17 different and mostly high-sulfur coal mines; thus, this sample probably represented a typical marketed coal from high-sulfur Illinois coal mines.

Table 8 Temporal variations in the mineralogical and chemical composition of marketed coals from four selected Illinois preparation plants. Sample 1 from each plant was collected in 1992 (Demir et al. 1994), and sample 2 from each plant was collected in 1996. All values are on a dry weight basis, except equilibrium moisture.

	Plant A		Plant B		Plant C		Plant D	
Composition	Sample 1 (C32773)	Sample 2 (C35559)	Sample 1 (C32774)	Sample 2 (C35562)	Sample 1 (C32782)	Sample 2 (C35303)[1]	Sample 1 (C32814)	Sample 2 (C35561)
Mineralogical (wt%)								
Illite/smectite	1.67	1.94	0.43	3.21	0.61	0.35	0.69	0.63
Illite	0.79	1.72	0.53	1.96	1.10	2.32	0.47	0.87
Kaolinite	1.50	2.85	0.93	1.60	1.69	3.47	0.66	1.33
Chlorite	0.07	0.14	0.05	0.20	0.06	0.19	0.02	0.05
Quartz	2.24	2.04	1.26	0.79	3.62	1.61	1.19	0.35
Pyrite	1.42	1.52	2.35	2.87	2.00	1.27	1.71	1.31
Marcasite	0.24	0.55	0.26	0.56	0.06	0.07	0.01	0.60
Calcite	0.71	0.91	0.27	0.21	1.27	1.00	0.87	0.45
K-feldspar	0.05	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Plagioclase	0.07	<0.01	0.04	0.11	0.11	0.02	0.07	<0.01
Ash	8.7	11.2	7.1	10.7	11.6	10.6	6.0	4.9
Volatile M	41.2	40.9	40.9	41.1	40.0	38.8	45.7	42.6
Fixed C	50.1	48.0	52.1	48.2	49.4	50.6	48.3	52.6
Pyritic S	0.97	1.20	1.46	1.87	1.25	0.79	1.09	1.11
Organic S	3.03	3.27	1.56	1.89	2.45	2.52	2.41	1.43
Sulfate S	0.14	0.19	0.56	0.19	0.20	0.69	0.18	0.51
Eq. moisture	13.9	12.1	13.4	12.2	14.3	14.7	11.3	13.9
Al	0.90	1.02	0.53	1.21	0.86	0.82	0.38	0.34
Si	2.10	2.53	1.13	1.94	2.74	2.55	1.00	0.67
Fe	1.19	1.41	2.11	2.25	1.50	1.55	1.26	1.67
Ca	0.29	0.36	0.11	0.09	0.51	0.40	0.35	0.18
K	0.16	0.20	0.091	0.27	0.16	0.15	0.075	0.06
Na	0.10	0.10	0.015	0.022	0.11	0.10	0.007	0.007
Chemical (mg/kg)								
As	1.3	1.6	20	26	2.4	2.2	6.4	46
B	135	163	116	98	106	181	83	161
Br	6.5	8.3	3.9	5	10	13.2	2	3.6
Ba	41	44	17	61	38	37	33	11
Be	1.0	<1	4.0	6.5	<1	1.0	2.0	3.0
Cd	<0.3	1.0	<0.3	0.7	0.4	0.4	1.0	0.7
Ce	6.3	8.0	4.1	13.6	5.1	7.1	5.0	2.7
Co	2.3	3.4	3.1	7.5	1.6	3.5	2.5	11
Cr	12	3.4	5.8	14	14	17	5.7	5.7
Cs	0.88	1.1	0.75	1.8	0.68	1.0	0.92	0.80
Cu	7.4	8.2	13.6	18.2	6.2	5.0	8.8	20.5
Eu	0.16	0.21	0.32	0.52	0.1	0.10	0.3	0.35
F	90	141	68	133	78	63	63	50
Ga	3.2	2.9	4.0	5.3	2.1	2.4	2.2	2.7
Ge	<5	<5	27	61	6	7	16	125
Hf	0.36	0.5	0.32	0.6	0.4	0.6	0.17	0.2
Hg	0.13	0.07	0.22	0.15	0.07	0.08	0.07	0.13
La	3.5	4.3	2.2	7.1	3.1	2.9	1.7	1.2
Li	3.9	4.3	5.8	14.1	2.8	3.3	0.9	1.2
Lu	0.1	0.09	0.11	0.17	0.07	0.10	0.12	0.14
Mg	482	603	241	663	543	543	241	121
Mn	39	42	18	24	55	43	30	20
Mo	<6	6.5	<5	<5	11	8.0	15	<3
Ni	11	11	15	22	7	11	12	20
P	44	87	87	87	87	44	30	87
Rb	11	14	5	19	8.2	12	5.1	4.3
Pb	<6	5.4	102	169	<6	3.2	23	184
Sb	0.2	0.3	1.2	2.3	0.5	0.6	1.9	5.1
Sc	1.9	2.0	1.9	3.4	1.6	1.9	1.1	1.5
Se	1.9	2.7	1.2	1.6	1.9	2.9	1.3	1.9
Sm	0.65	1.0	1.2	2.4	0.49	0.70	1.0	1.3
Sn	<5	<5	<5	<5	<5.5	<5	<5	<5
Sr	28	33	17	33	25	26	17	10
Ta	0.1	0.1	0.07	0.1	0.1	0.1	0.05	<0.1
Tb	0.12	0.11	0.25	0.44	0.07	0.10	0.29	0.29
Th	1.2	1.4	0.8	2.1	1.1	1.4	0.6	0.6
Tl	<1	<1	<1	<1	1	<1	<1	<1
Ti	539	599	300	599	539	480	240	240
U	1.7	1.3	<0.8	1.0	1.3	2.3	8.0	0.8
V	16	36	11	26	23	41	16	16
W	0.35	0.50	0.2	0.3	0.35	0.4	0.25	0.10
Yb	0.29	0.40	0.61	1.1	0.26	0.5	0.76	0.73
Zn	33	99	71	287	42	34	68	179
Zr	20	11	19	21	23	9	11	9

[1] Two other newly collected coals (tables 3 and 5, CYC 1 and CYC 2 feed coals) came from the same mine as the sample C35303.

SUMMARY AND CONCLUSIONS

The mineralogical and chemical composition of (1) marketed Illinois coals from 35 mines and (2) feed coal, fly ash, and bottom ash from three different types of power generating units (PC, CYC, and FBC) burning Illinois coals were investigated. This investigation was the first time the nature and combustion behavior of mineral matter in marketed Illinois coals were determined in such a systematic and detailed manner. The general findings were as follows:

- The mean clay mineral content of the marketed Illinois coals was about 52% of the total mineral matter present in these coals. The mean values for abundances of the individual minerals in the coals (with standard deviations shown as ± values) were kaolinite, 2.07 ± 0.56%; quartz, 2.06 ± 0.78%; mixed-layered illite/smectite, 1.57 ± 0.70%; pyrite, 1.56 ± 0.50%; illite, 1.29 ± 0.46%; calcite, 0.84 ± 78%; chlorite, 0.18 ± 0.13%; marcasite, 0.13 ± 0.12%; plagioclase, 0.07 ± 0.05%; and K-feldspar, 0.01 ± 0.01%. Quartz partially survived the combustion process and was partially converted to silica glass at the power plants. The clay minerals and feldspars were converted to aluminosilicate glass and to mullite. Pyrite and marcasite were converted to hematite, magnetite, and amorphous Fe oxides. Calcite was converted to lime, portlandite, anhydrite, and gypsum.
- Concentrations of some minor and trace elements increased with increased concentrations of certain minerals in the 35 coals. Among the 15 HAP elements (As, Be, Cd, Co, Cr, F, Hg, Mn, Ni, P, Pb, Sb, Se, Th, U) in the coals, the concentrations of Cr, F, and Th were strongly and positively correlated with the content of mixed-layered illite/smectite or the combination of mixed-layered illite/smectite and illite. Strong positive correlations existed also between Th and kaolinite contents and between Mn and calcite contents. There were weak positive correlations between Co and chlorite, Hg and marcasite, and Hg and pyrite. These relationships between minerals and elements are important considerations for designing methods for pre- and post-combustion control of HAP emissions from coal-fired power plants.
- Upon combustion, a portion of each HAP element is mobilized and becomes airborne. The mobilized portions of an element could partially be adsorbed on surfaces of hardware on the cool side of a power plant instead of being emitted into the atmosphere. In that case, the atmospheric emission of HAPs, except highly volatile ones (F, Hg, Se), could be less than the emission values reported here. Therefore, in this study, the term "mobility" instead of "emission" was used to express the portion of an element that was not retained in CCRs. The mobilities of 15 HAPs from the FBC plant were generally less than the mobilities from the other plants. Relatively large mobilities (more than 50% of the original amount in coal) were observed for F and Mn at the FBC plant and for F, Hg, and Se at the CYC and PC plants.
- Combustion mobilities of trace elements are controlled by their volatility and affinity for various coal combustion phases. The elements investigated in this study occurred in greater concentrations in the fly ash than in the bottom ash in most cases, which is generally consistent with the literature data. The relative enrichment of the elements in the fly ash most likely resulted from the combination of (1) the partial volatilization of the elements from the bottom ash and their subsequent condensation on the fly ash particles upon cooling and (2) preferential enrichment of some elements in finely disseminated coal minerals that ended up largely in the fly ash. Some CCRs contained high concentrations of certain elements that could be recovered and sold.
- There were differences in the mineralogical and chemical compositions of two sets of marketed coal samples taken from four Illinois preparation plants at a 4-year interval. Some of the differences could result from expected sample variations independent of when the samples were collected. However, it is likely that the observed differences largely resulted from changes in characteristics of in-place coal as mining moved to different reserve blocks over time and from changes in coal cleaning in response to market demands. Therefore, historical coal quality data on clean coal products from a given mine cannot be used to accurately determine the quality of the current production from the same mine.

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