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KENTUCKY GEOLOGICAL SURVEY
UNIVERSITY OF KENTUCKY, LEXINGTON
Donald C. Haney, State Geologist and Director

IMPACT OF HAZARDOUS AIR POLLUTANTS ON MINERAL PRODUCERS AND COAL-BURNING PLANTS IN THE OHIO VALLEY

(Title III, Clean Air Act Amendments of 1990)

ABSTRACTS

March 19-21,1995
Hyatt Regency Lexington
Lexington, Kentucky

SPECIAL PUBLICATION 21 Series XI, 1995

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INTRODUCTION

This conference, "Impact of Hazardous Air Pollutants on Mineral Producers and Coal-Burning Plants in the Ohio Valley," focuses on Title III of the Clean Air Act Amendments of 1990. Title III established an initial list of hazardous air pollutants, or air toxics, that are subject to regulation by the U.S. Environmental Protection Agency. The list includes elements commonly found in trace amounts in coal and carbonate rocks.

Regulation of hazardous-air-pollutant elements would affect the coal industry of the Ohio Valley, an important part of the region's economy. Ohio Valley states are major coal producers, and coal-fired power plants burning large quantities of locally produced coal are the region's principal source of electricity.

Technical sessions of the conference address the potential impact of Title III, trace elements in coal, air-toxics control technology, and ash disposal and by-product recovery. Detailed information on trace-element concentrations in Ohio Valley coals and carbonate rocks, available in data bases at state geological surveys and the U.S. Geological Survey, is exhibited in posters prepared by the geological surveys.

Principal sponsors of this Title III conference are the Ohio Valley Mineral Consortium (OVMC) and the coal associations of the region. The OVMC consists of the state geological surveys of Illinois, Indiana, Kentucky, Ohio, Pennsylvania, and West Virginia.

This is the second OVMC-sponsored conference. In 1992, a conference on Title IV of the Clean Air Act Amendments of 1990, which deals with acid deposition control, was sponsored by the OVMC, aggregate and crushed stone associations of the Ohio Valley, and the National Stone Association. The availability of limestone and lime in the region for SO_2 emission control was addressed at that meeting.

OVMC conferences promote increased interaction between state geological surveys and industry. They provide an opportunity for an exchange of information by the stone and coal industries, operators of coal-fired boilers (utility- and industrial-scale), research institutions, government agencies, and state geological surveys.

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MARKET IMPACTS OF THE CLEAN AIR ACT AMENDMENTS OF 1990

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The Clean Air Act Amendments of 1990 will have impacts on the markets for coal, products produced from coal, and employment in those industries. The impacts will involve a change in the distribution of coal demand and production, and will directly affect employment in producing areas. Indirect impacts on employment and income are likely to be small relative to the direct impacts.

THE EFFECTS ON AND THE ROLE OF THE INDUSTRY IN IMPLEMENTING THE AIR TOXIC PROVISION OF THE CLEAN AIR ACT

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Implementation of Title III of the 1990 Clean Air Act Amendments is progressing rapidly. The sheer workload and pace of this legislation is requiring new and innovative approaches to regulation development as well as an overhaul to the historical concept of program implementation. The Maximum Achievable Control Technology (MACT) standards for over 40 source categories will be in place by the end of 1995. Air toxic rules issued under Title III to date will achieve more emission reductions than all combined air-toxic rules issued under previous versions of the Clean Air Act. And the work has only begun. The MACT standards to be issued by 1997 will cover another 42 source categories and the 10-year standard (to be promulgated by the year 2000) will cover still another 87 source categories.

Numerous programmatic rules have also been issued, including the so-called hammer provisions under section 112 (j) and the provisions for approving State programs under section 112 (l). Numerous studies have also been completed. In 1995, the final rules for modifications under section 112 (g) are to be issued. Thus, by mid-1995 the full force of Title III will begin to be felt, and many industries will be actively involved in air-toxic programs.

This presentation outlines the activities that will take place over the next few years. The discussions focus on both the regulatory activity and implementation aspects. On the regulatory front, new concepts for developing regulations will be outlined, and experiences gained with these concepts will be shared. On the implementation front, the massive efforts that Title III places on the permit program will be discussed, along with potential mechanisms for reducing these impacts. Finally, a challenge to industry and public-interest groups will be issued for participation in the regulatory development process.

PANEL: TITLE III OF CLEAN AIR ACT AMENDMENTS—IMPACT ON STATE UTILITY REGULATORY PROCESS

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The primary focus of state utility commissions is the economic regulation of utilities. These commissions are specifically interested how reasonable the rates being charged are and how reliabile the utility service is. Relative to Title III of the Clean Air Act Amendments of 1990, these commissions are concerned about the cost of control of hazardous air pollutants (HAPS). A report published by the Electric Power Research Institute indicates that the cost of controlling HAPS will be significant. Public utility commissions are concerned about the interrelationship of Title III and Title IV of the Clean Air Act Amendments; the interrelationship with carbon dioxide reductions, whether they be voluntary or mandatory; and the overlapping and possibly additive costs caused by these interrelationships.

State commissions are mostly familiar with Title IV of the Clean Air Act Amendments and the impact of sulfur dioxide and nitrogen oxide reductions on electric utilities. Ninety-eight percent of the electricity generated in Indiana and 87 percent in Ohio is produced by coal, mostly locally mined. Indiana law provides for the prior approval by the Indiana Utility Regulatory Commission of the "environmental compliance plans" of electric utilities. Such prior approval guarantees recovery of the costs associated with development and implementation of the plan. The law requires that the environmental compliance plan must be "least cost," while preserving the use of Indiana coal. In considering such plans, if the use of Indiana coal is to be diminished, the Commission must take into consideration the economic and employment effects of the reduced coal use on the coal-mining region and the service territory of the utility.

The Indiana Commission has authorized four scrubbers for compliance with Title IV requirements on three different utility systems, and there are several existing scrubbers that predate the 1990 Clean Air Act Amendments. The Ohio Commission has authorized one scrubber for Title IV, and there are several existing scrubbers. However, scrubbers do not provide sufficient removal of hazardous air pollutants to meet potential proposed standards. We are, therefore, concerned about the interrelationship between control technologies for Title III and Title IV and the possibility of additive costs.

TRACE ELEMENTS IN COAL: THEIR LIFE AND TIMES

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Geologic processes control the concentration, modes of occurrence, and textural relations of the inorganic constituents (minerals and trace elements) in coal. These processes thereby influence the environmental impact, technological behavior, and by-product potential of the inorganic constituents. Trace elements can be incorporated into coal as components of plants or they may be added during peat formation and the coalification process, and after the formation of the coal. Some coal minerals and amorphous solids that contain trace elements may undergo transformations, such as dissolution, that mobilize the elements. These mobilized elements may be removed or may be precipitated as new minerals (such as PbSe and $CuFeS_2$) that fill voids in the organic matter. The resulting trace-element modes of occurrence and associations can have profound effects on the behavior of the elements during coal cleaning and combustion. Trace elements that occur in organic matter and in fine-grained minerals will be difficult to remove by conventional coal-cleaning processes, whereas trace elements that occur with late-stage cleat and fracture-filling minerals commonly can be separated from the organic matter. The associations of trace elements may also affect their behavior during coal combustion. Elements intimately associated with organic matter, sulfide minerals, or carbonate minerals are likely to end up in the fly ash or to escape with the flue gas. If the same elements are associated with silicate or oxide minerals, they then are more likely to end up in bottom ash or slag. These elements pose concerns for the safe disposal of coal-combustion waste products.

PANEL: COAL-QUALITY DATA BASES IN THE PUBLIC DOMAIN

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Linda J. Bragg, *U.S. Geological Survey*
Heinz H. Damberger, *Illinois State Geological Survey*
David C. Glick, *Pennsylvania State University*
William C. Grady, *West Virginia Geological and Economic Survey*

Title IV of the Clean Air Act Amendments of 1990 placed tight restrictions on the amount of SO_2 that could be emitted per million Btu generated. This legislation forced many electric utilities, which are the primary consumers of coal, to install costly sulfur-reduction devices on one or more of their coal-fired boilers or switch to lower sulfur coal. This effectively places limitations on the coal that can be mined, especially in terms of total sulfur content and calorific value.

Title III of the Clean Air Act Amendments, which addresses the subject of air toxics, may place similar restrictions on the use of coal. Title III covers 190 substances, including 13 elements that naturally occur in coal. If any of these elements are to be regulated, more knowledge of their spatial distribution in coal, both within and between coal basins, will be required.

Several coal-quality data bases containing a wide variety of information on United States resources, including trace-element concentrations, are presently available to the public. Information in these data bases covers every major coal basin in the Nation, and can be obtained in several different electronic formats for a minimal cost.

DETERMINING THE ABUNDANCE AND ASSOCIATION OF TRACE ELEMENTS IN COAL

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The Clean Air Act Amendments of 1990 have spurred the development of analytical methods for trace metals, historically some of the most difficult substances to measure accurately in coal. Wet chemical methods involving atomic absorption or atomic emission spectrophotometry are widely used to obtain bulk trace-metal measurements for coal. Lower limits of quantification (LLQ) of 0.5 ppm for arsenic, 0.01 ppm for mercury, and 0.2 ppm for selenium have been obtained. One disadvantage is that sample digestion is required, significantly affecting the precision of the results.

X-ray analytical methods present an alternative approach for some trace metals. Wavelength-dispersive X-ray fluorescence spectrometry has proven useful for measuring chromium, nickel, and lead in bulk coal samples, generally providing better analytical precision than wet chemical methods. Energy-dispersive X-ray fluorescence spectrometry yields better LLQ values, although precision is compromised.

X-ray methods can also be employed to obtain information on trace-metal content of individual mineral grains in coal using scanning electron microscopy with wavelength-dispersive spectrometry (SEM–WDS). Measurements of trace metals in mineral grains as small as a few microns can be made. SEM–WDS has shown that mercury and other trace metals occur in levels as high as hundreds of parts per million in individual mineral grains, considerably higher than their abundance in the overall samples. Trace metals are associated with pyrite and other dense minerals in coal. These results support density-based coal-cleaning methods as a possible means to control trace-metal emissions.

Several other speciation methods are being considered. These include selective extraction and X-ray absorption fine structure analysis.

A STUDY OF AIR-TOXIC EMISSIONS FROM COAL-FIRED UTILITY BOILERS

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The U.S. Department of Energy has developed a program to assess the toxics emissions from fossil-fuel–fired power plants. The program involved field testing eight coal-fired utility boilers for the hazardous air pollutants listed in Title III of the Clean Air Act Amendments of 1990. The objects of the program were to: (1) determine the concentrations of toxics emissions emanating from coal-fired electric utilities, (2) determine the ability of conventional pollution control equipment to remove selected species from flue gas, (3) determine the concentration of toxic substances associated with particulate matter, (4) quantify toxic materials on the surfaces of particulate matter, and (5) calculate material balances for selected trace elements in all major input and output streams of a utility boiler.

Data will be presented on the concentrations of specific trace and minor species in all the major input and output streams of the power plants. The removal efficiencies of trace metals across air-pollution–control equipment will also be discussed. Data will be presented on the partitioning of trace metals in various process streams. The emission factors for selected toxics will also be discussed.

CHARACTERIZATION OF AIR-TOXICS EMISSIONS FROM CLEAN-COAL TECHNOLOGY PROCESS CONFIGURATIONS

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The U.S. Department of Energy's Clean Coal Technology Program is demonstrating a variety of new, advanced coal-utilization technologies. To better assess the commercial readiness and environmental performance of these technologies, the Department's Pittsburgh Energy Technology Center is coordinating air-toxics studies at several Clean Coal Technology project sites. The demonstration technologies involved include advanced wet scrubbers and low-NO_x combustion systems for power-plant applications. Air-toxics measurements span a wide variety of trace-metal, inorganic, semi-volatile and volatile-organic, and radionuclide substances. Sampling episodes and laboratory analyses have already been completed for some facilities. This survey paper summarizes the results to date, and describes the potential ramifications of these data under Title III of the Clean Air Act Amendments of 1990.

AIR-TOXICS REMOVAL BY WET-LIMESTONE SCRUBBERS

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Over the past 2 years the Tennessee Valley Authority (TVA) has partnered with the U.S. Department of Energy (DOE) Pittsburgh Energy Technology Center (PETC) and the Electric Power Research Institute. Extensive field investigations of the toxic inventories at a wet-limestone–scrubbed coal-fired power plant in Kentucky were made. The results of the first study are being finalized, while preliminary analytical results of the second test program are now being obtained.

TVA and DOE/PETC have teamed up to conduct one of the most extensive air-toxics inventories ever conducted at a coal-fired utility boiler. TVA staff from Technology Advancements and the Environmental Research Center in Muscle Shoals, Alabama, teamed with technologists from the Southern Research Institute in Birmingham, Alabama, and Brooks Rand in Seattle, Washington. The test plan included the coal-wash plant, boiler, electrostatic precipitator, wet-limestone scrubber under varied operating conditions, stack, and plume. Residence times in the scrubber modules have been calculated, and mercury speciation throughout this system was investigated. A complete understanding of the mercury chemistry and speciation is essential for successful emissions control. This million-dollar toxics inventory was conducted in late October 1994.

CONTROLLING TRACE ELEMENTS IN COAL BY COLUMN FLOTATION

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This paper describes selected findings from an ongoing research project supported by the Pittsburgh Energy Technology Center of the U.S. Department of Energy. The project involves the evaluation of an advanced fine-coal cleaning method, column flotation, for the selective removal of trace elements from the Pittsburgh coal seam. Scanning-electron-microscopy–automated image analysis and advanced washability analyses are applied with state-of-the-art analytical procedures to compare the predicted and actual removal of antimony, arsenic, barium, beryllium, cadmium, chromium, cobalt, manganese, mercury, nickel, lead, selenium, and zinc from coal cleaned in our pilot-scale 20-foot flotation column.

Early results indicate that nearly all elements of concern show some affinity with mineral constituents. Barium, arsenic, cadmium, manganese, lead, and zinc show a strong affinity for the mineral constituents and can thus be greatly reduced through coal preparation. The other elements show some affinity for the organic components and so cannot be reduced as effectively; nevertheless, some reduction as a result of cleaning has been observed.

FURTHER REDUCTION OF TRACE ELEMENTS IN PRODUCT COALS FROM ILLINOIS MINES THROUGH FLOTATION-BASED PROCESSES

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Thirty-four samples of washed coals from Illinois mines were tested at –100, –200, and –400 mesh sizes for the cleanability of ash and of trace and minor elements using a froth flotation/release analysis (FF/RA) procedure. Composite samples of 80 percent of the total combustibles of the feed were prepared for each run by proportionately combining individual FF/RA concentrates. These composite samples, as well as individual concentrate and tailing fractions, were analyzed for ash and trace and minor elements. Mass balances, calculated from the chemical analysis data on the concentrates and tailings, were within experimental errors, indicating a high degree of reliability for the data obtained. The data were used to evaluate further potential beneficiation of washed Illinois coals from conventional preparation plants through the use of standard froth-flotation or column-flotation techniques. At 80 percent combustibles recovery, up to 69, 76, and 83 percent reductions in ash content were achieved beyond conventional coal cleaning for the –100, –200, and –400 mesh sizes, respectively. Average percentage reductions for those elements that are classified as Hazardous Air Pollutants (HAPS) by the Clean Air Act Amendments of 1990 are generally less than those for ash. However, reductions for some elements in individual samples approach or exceed reductions for ash. For example, reductions for manganese and phosphorus are similar to or higher than those for ash for the majority of the samples. For many samples, reductions for arsenic and mercury also approach or exceed that for ash. On average, additional beneficiation achieved by grinding the coal finer than –200 mesh is relatively small for most HAPS elements.

BY-PRODUCT RECOVERY OF COAL-WASTE PRODUCTS—CAN IT WORK IN THE UNITED STATES?

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The U.S. Environmental Protection Agency estimates that by the year 2000 the annual amount of coal-waste products will increase from approximately 100 million to 170 million tons. Only about 30 percent of the waste presently generated at coal-fired electric utility power plants is reused; the remainder is disposed of, primarily in surface impoundments and landfills. Because landfill sites are becoming increasingly scarce and because migration of soluble, potentially hazardous elements from waste sites can occur, the costs of disposing of the wastes are expected to increase substantially. One way to decrease disposal costs may be to extract hazardous and useful elements from coal waste. Potentially hazardous elements such as arsenic, lead, mercury, selenium, and antimony are often incorporated into pyrite and other sulfide minerals. For example, chemical analyses of samples from several mined Appalachian coal beds show arsenic concentrations as high as 4,000 ppm (ash basis). Electron microscopy of the samples shows that the arsenic is incorporated in large pyrite grains (larger than 100 µm) that can readily be separated from the coal during physical coal cleaning. In waste piles, these grains may be susceptible to oxidation and leaching. Leaching may be enhanced because the observed grains have a high surface area and the presence of extraneous elements in the lattice tends to destabilize the mineral structure. If leaching occurs, arsenic can migrate into surface and ground water. We have also observed similar occurrences of lead, mercury, and selenium in pyrite grains from other coals. Extraction and processing of the sulfide fraction of these coals could significantly decrease the likelihood of pollution.

Most of the world's largest coal-producing nations have investigated the possibility of using by-product recovery procedures to extract potentially economic elements from coal and coal-waste products. The greatest success has been reported by coal scientists from the former Soviet Union and Central European countries, who have extracted gallium, germanium, uranium, molybdenum, vanadium, zinc, cadmium, and, in one case, platinum, gold, and silver, by a variety of physical and chemical processes. The apparent success of these operations may be dependent on government subsidies to the coal industry and the use of very high-ash (up to 40 percent) and high-sulfur (up to 6 percent) coals.

Efforts to extract elements from United States coal waste are probably not economic at this time. Because the coal that is mined is relatively low in ash and sulfur, the resulting coal waste probably does not contain sufficient concentrations of economic elements to justify the expense of by-product recovery procedures. However, if toxic elements are concentrated in the wastes in unstable minerals that can be leached, then extraction and processing may be less costly than mitigating the effects of those elements.

TRACE-ELEMENT MOBILITY/STABILITY IN ASH-DISPOSAL SITES IN KENTUCKY

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The effects of coal-ash disposal on ground water were evaluated at three Kentucky sites having different geologic settings and disposal methods. Two sites, one in an alluvial setting and one in a karst setting, utilize pond disposal, and one site, in an upland setting, utilizes dry-ash disposal.

At the alluvial site, geochemical processes along flow paths affect leachate concentration and movement. Leachate generated in the reducing environment of a closed-out pond (shallow flow zone) migrates into the underlying oxidized alluvium (intermediate flow zone). Wells constructed in the ash have arsenic values that exceed the maximum contaminant level (MCL); however, arsenic concentration is attenuated by adsorption onto iron oxides in the intermediate flow zone. A reducing zone adjacent to the river attenuates sulfate, although sulfate still exceeds the secondary contaminant level (SMCL) in down-gradient alluvial wells.

An upland site, located in interbedded limestones and shales, contains a dry-ash valley fill. Ground-water seepage into the sides and base of the fill has caused highly leachable constituents in the ash to migrate into the shallow, fractured bedrock underlying the fill. MCL's and SMCL's are exceeded for arsenic and sulfate within the ash. Sulfate, however, is the only leachate-generated constituent that exceeds the SMCL in the shallow bedrock.

A karst site containing active and closed-out ponds was evaluated using dye-tracing techniques and spring monitoring. Separate conduit flow systems were identified for each disposal pond. The active pond is contributing to down-gradient spring flow via sinkholes. Down-gradient springs meet all MCL's and SMCL's. Wells installed in the closed-pond indicate that arsenic, boron, and manganese exceed MCL's and SMCL's; however, water quality in down-gradient springs does not exceed these standards.

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EFFECT OF CLEAN AIR ACT AMENDMENTS ON COAL-COMBUSTION BY-PRODUCT UTILIZATION

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Over the past several years, requirements for compliance with ever-stricter air-regulatory programs have placed increasing challenges on utilities in the realm of coal-combustion by-product (CCBP) management. Fly ash, bottom ash, boiler slag, and flue-gas desulfurization sludges constitute the majority of coal-combustion by-products. Clean-coal technologies such as coal washing and fluidized-bed combustion also generate significant quantities of by-products requiring management at some utility sites. Utilities save money on disposal costs, generate revenue, and conserve landfill space and other natural resources by marketing and utilizing these by-products.

However, in addition to increasing the sheer volume of these materials that require management, air-regulatory programs affect CCBP quality. The most notable impact on quality has been the effect of low NO_x burners on unburned carbon (measured as loss on ignition—LOI) in fly ash. Fly ash is marketed extensively as a low-cost replacement for cement in concrete products. However, fly ash must meet strict quality standards, especially for LOI, if it is to be utilized in this way. Many utilities are seeing markets for fly ash evaporate as LOI increases.

Other air regulations or air-compliance strategies that affect CCBP utilization or have the potential to affect utilization in the future include the use of ammonia injection for SO_x, reduction of air toxics, and fuel switching. Balancing compliance strategies with CCBP marketing and utilization considerations will be discussed.

GYPSUM DILEMMA: AN UPDATE

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Of the approximately 18 million metric tons of flue-gas desulfurization (FGD) material generated in 1993 in the United States, it is estimated that less than 5 percent was marketed as a substitute for natural gypsum, specifically in agriculture and wallboard manufacturing. Synthetic gypsum represented less than 4 percent of the total gypsum consumed and approximately 5 percent of the crude gypsum produced from 112 mines in the United States. As provisions of the 1990 Clean Air Act Amendments move toward the second phase, the quantities of FGD material generated are likely to increase significantly. Several mineral industries, not the least of which is the coal industry, will continue to have a major interest in the increased number and types of scrubbers being installed. Other interested industries include the limestone, lime, soda ash, and gypsum industries. For the sorbent and higher sulfur coal industries, increased commercial use of FGD by-product, such as synthetic gypsum, would be economically beneficial. For other mineral industries, the implications of such an outcome are mixed.

THE EFFECT OF THE CLEAN AIR ACT ON THE UTILIZATION OF COAL-COMBUSTION BY-PRODUCTS: LOW NO_X BURNER CONVERSION

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The Clean Air Act will have a substantial impact on altering the amounts and types of coal-combustion by-products. The production of conventional wet-scrubber sludge will substantially increase, as will the amount of dry flue-gas desulfurization material produced from fluidized-bed combustion and SO_2 spray dryers. We estimate that the amount of these materials produced in Kentucky will essentially double by the end of the millennium. In addition, the conversion of conventional burners to low NO_x configurations is having a significant impact on the nature and utilization potential of conventional fly ash.

To assess the impact of the low NO_x conversion, the fly ash from a power plant in Kentucky was studied before and after conversion. Samples of coal were taken before and after the pulverizers, and fly ash was sampled from all major collection equipment, including the air-cyclones, electrostatic precipitators, and economizer bins. These materials were analyzed for carbon as well as major and trace elements.

It was found that the amount of carbon in all of the ash collection devices increased by a factor of two or more. The average particle size of the ash increased, primarily as a function of the higher and coarser carbon load. Within the limits of variability induced by the coal feedstock, no observable impact on the distribution of major or trace elements was found for the fly ash. The effect of conversion on the utilization potential of the ash will be discussed.

B&W'S ADVANCED EMISSIONS CONTROL DEVELOPMENT PROGRAM

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Babcock & Wilcox (B&W) is conducting a 5-year project aimed at the development of practical, cost-effective strategies for reducing the emissions of hazardous air pollutants (common called "air toxics") from coal-fired electric utility plants. Project participants include the Ohio Coal Development Office within the Ohio Department of Development and the U.S. Department of Energy's Pittsburgh Energy Technology Center. The need for air-toxics–emissions controls will likely rise as the U.S. Environmental Protection Agency proceeds with implementation of Title III of the Clean Air Act Amendments of 1990. Data generated during the program will provide utilities with the technical and economic information necessary to reliably evaluate various air-toxics–emissions compliance options, such as fuel switching, coal cleaning, and flue-gas treatment.

The development work is made possible by B&W's new Clean Environment Development Facility (CEDF), wherein air-toxics–emissions control strategies can be developed under controlled conditions, and with proven predictability to commercial systems. The CEDF will provide high-quality, repeatable, comparable data over a wide range of coal properties, operating conditions, and emissions-control systems. As part of the Advanced Emissions Control Development Program (AECDP), back-end flue-gas cleanup equipment, including an electrostatic precipitator (ESP), a fabric filter, and a wet scrubber, has been incorporated into the CEDF facility.

The specific objectives of the AECDP project are to: (1) measure and understand the production and partitioning of air-toxics species for a variety of steam coals, (2) optimize the air-toxics removal performance of conventional flue-gas cleanup systems (ESP's, bag houses, scrubbers), (3) develop advanced air-toxics–emissions control concepts, (4) develop and validate air-toxics–emissions measurement and monitoring techniques, and (5) establish a comprehensive, self-consistent air-toxics data library. Development work is currently concentrated on the capture of mercury, fine particulate, and a variety of inorganic species, such as the acid gases (hydrogen chloride, hydrogen fluoride, etc.). The capture of fine particulate is of importance because many of the trace elements initially volatilized in the furnace tend to preferentially recondense on the small fly-ash particles, due to their high surface area per unit weight.

TRACE-ELEMENT DISTRIBUTION IN WEST VIRGINIA COALS

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The modes of occurrence and stratigraphic distribution of 15 trace elements were examined to assess the impact of the 1990 amendments to the Clean Air Act on mining and utilization of West Virginia coal resources. The Title III hazardous air pollutants studied were antimony, arsenic, beryllium, cadmium, cobalt, chromium, lead, manganese, mercury, nickel, selenium, chlorine, fluorine, and the radionuclides uranium and thorium. Data from the U.S. Geological Survey USCHEM data base were integrated with stratigraphic, petrographic, X-ray–diffraction–mineralogic, and scanning-electron-microscope investigations performed at the West Virginia Geological and Economic Survey.

Five of the elements (beryllium, chromium, lead, selenium, and thorium) displayed stratigraphic abundance trends. These elements were most abundant in the Middle Pennsylvanian coals and low in abundance in Upper Pennsylvanian coals. Most of the elements (antimony, arsenic, cadmium, cobalt, mercury, manganese, nickel, uranium, and fluorine) showed no apparent stratigraphic trends. Statistical analyses indicate poor but tentative negative correlations between vitrinite and chromium, lead, and selenium, and positive correlations between exinite and selenium, and between petrographic mineral matter and chromium, lead, and selenium. Chromium also positively correlated with illite, kaolinite, and quartz in the coals. Micron-size crystals of lead selenide (clausthalite) were the most common mode of occurrence of lead and selenium in West Virginia coals.

COAL IN PENNSYLVANIA

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Pennsylvania has important bituminous coal resources, as well as approximately 95 percent of the anthracite resources of the United States. Bituminous coal is found in the western third of the Commonwealth and in isolated basins in north-central and south-central Pennsylvania. Anthracite is found in five basins in east-central and northeastern Pennsylvania.

The rank of coal in Pennsylvania increases from west to east, ranging from high-volatile bituminous in the west to anthracite in the east. The fixed-carbon content on a dry, ash-free basis varies from 55 to 98 percent. The heat value on a dry, ash-free basis ranges from a low of 14,700 Btu/lb. in Beaver County on the west to a maximum of 15,800 Btu/lb. in northern Somerset and southern Cambria Counties. From this high, the heat value declines to the east to a low of about 14,400 Btu/lb. in Carbon County. The inherent moisture content generally varies from 2 to 7 percent, and the ash content ranges from 4 to 20 percent for most coals. The sulfur content, as received, is generally from 1.5 to 3 percent for bituminous coal, and less than 1 percent for anthracite coal.

The Pennsylvania Geological Survey has been providing coal samples to the U.S. Geological Survey for trace-element analysis since 1975. To date, we have obtained more than 800 bench or whole-seam analyses of trace elements in Pennsylvania coal.

The first record of mining of bituminous coal in Pennsylvania was at Fort Pitt (downtown Pittsburgh) in 1761. Eight years later, anthracite was reportedly used by a blacksmith in Wilkes-Barre. Production records for anthracite date from 1870, and 6.1 billion tons have been produced since that time. Production records for bituminous coal date from 1877, and 10.5 billion tons have been produced. Total production, therefore, has been nearly 17 billion tons.

Pennsylvania currently ranks fourth in the United States in annual coal production with 58 million tons of bituminous coal and 5 million tons of anthracite in 1993. This is approximately one-quarter of the annual maximum of 272 million tons produced in 1917.

No detailed study has been done on the remaining coal resources in Pennsylvania. Estimates range up to 16 billion tons of anthracite and 62 billion tons of bituminous coal.

TRACE ELEMENTS OF OHIO COALS

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The Ohio Division of Geological Survey (OGS), in cooperation with the U.S. Geological Survey, has collected coal samples for trace-element analysis since 1975. Analytical results have been published in four OGS Information Circulars (47, 50, 52, and 55). Trace-element analyses of 660 whole-bed samples from 29 Ohio coal seams have been included in the U.S. Geological Survey coal-quality data base (COALQUAL, version 1.3). Ohio coal-bed samples analyzed include 151 from the Middle Kittanning, 103 from the Lower Kittanning, 66 from the Pittsburgh, 57 from the Upper Freeport, 42 from the Lower Freeport, 40 from the Clarion, 30 from the Brookville, 27 from the Meigs Creek, 24 from the Waynesburg, 17 from the Pomeroy/Redstone, 11 from the Anderson, 11 from the Mahoning, and 10 from the Strasburg coals.

Title III of the Clean Air Act Amendments of 1990 identified 189 hazardous air pollutants, including chlorine, phosphorus, and compounds of antimony, arsenic, beryllium, cadmium, chromium, cobalt, lead, manganese, mercury, nickel, selenium, thorium, and uranium. Trace-element content of the analyzed Ohio coal samples averaged, in ppm, 738.163 chlorine, 129.782 phosphorus, 0.888 antimony, 24.832 arsenic, 2.566 beryllium, 0.131 cadmium, 6.149 cobalt, 16.209 chromium, 8.525 lead, 30.905 manganese, 0.204 mercury, 17.118 nickel, 4.008 selenium, 2.267 thorium, and 1.870 uranium. Of these elements listed in COALQUAL, 1 antimony, 1 arsenic, 15 phosphorus, 16 thorium, and 96 chlorine values are qualified (zero values) and were not used in this examination. The maximum trace-element values analyzed, in ppm, include 3,300 chlorine (unnamed coal), 980 phosphorus (Lower Kittanning coal), 19 antimony (Upper Freeport coal), 390 arsenic (Anderson coal), 16 beryllium (unnamed coal), 1.5 cadmium (Lower Kittanning coal), 77 cobalt (unnamed coal), 88 chromium (unnamed coal), 73 lead (unnamed coal), 690 manganese (Lower Freeport coal), 1.1 mercury (Upper Freeport coal), 73 nickel (Lawrence coal), 150 selenium (Lower Freeport coal), 12 thorium (Bear Run coal), and 35 uranium (Brookville coal).

Ohio coals are lower in cadmium, manganese, thorium, and uranium in comparison to Wyoming coals. All Ohio coal samples and nearly all the coal samples, including Western coals, listed in COALQUAL are excluded by Title III.

TRACE ELEMENTS IN KENTUCKY COAL

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Title III of the Clean Air Act Amendments of 1990, entitled "Hazardous Air Pollutants," cites 190 chemical substances that may require monitoring with the implementation of Phase I in 1995. The list includes 13 elements that naturally occur in Kentucky coal: antimony (Sb), arsenic (As), beryllium (Be), cadmium (Cd), cobalt (Co), chlorine (Cl), chromium (Cr), lead (Pb), manganese (Mn), mercury (Hg), nickel (Ni), phosphorus (P), and selenium (Se). Two other elements, thorium (Th) and uranium (U), may also be considered, as they fall under the category of radionuclides. Figure 1 shows the distribution of the average concentrations of the 13 elements in coal beds from the Eastern Kentucky Coal Field. Figure 2 shows the distribution of the same elements in coal beds from the Western Kentucky Coal Field. In the eastern field, arsenic, chlorine, chromium, manganese, and nickel have the highest values, whereas beryllium, cadmium, mercury, antimony, and selenium are all present in relatively low concentrations. In the western field, coals have higher manganese, nickel, and lead concentrations than coals from the eastern field. In addition, the average chlorine concentration for coals in the western field is about half that for coals in the

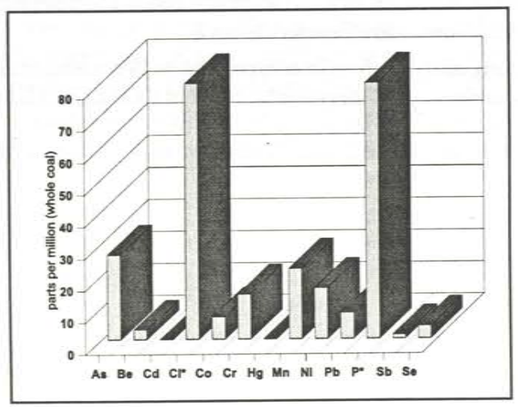

Figure 1. Distribution of average concentrations for 13 elements in eastern Kentucky coal beds with ash yields less than or equal to 25 percent. These elements are cited in Title III of the Clean Air Act Amendments of 1990, and may require monitoring. Chlorine (Cl*, actual value, 1,196 ppm) and phosphorus (P*, actual value, 128 ppm) are scaled to fit the diagram.

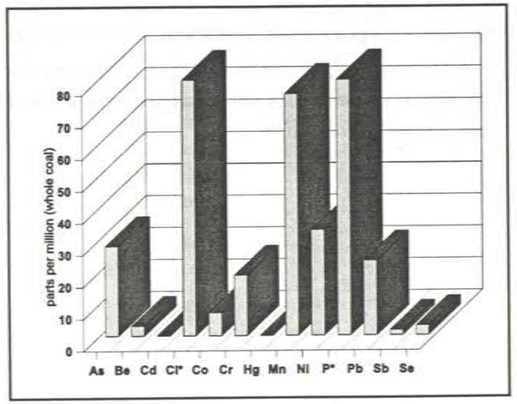

Figure 2. Distribution of 13 elements in western Kentucky coals with ash yields less than or equal to 25 percent. Chlorine (Cl*, actual concentration, 585 ppm) and phosphorus (P*, actual concentration, 118 ppm) are scaled to fit the diagram.

eastern field. Stratigraphically, the distribution of arsenic and lead roughly parallels the distribution of sulfur, suggesting that these elements are, at least in part, associated with disulfide minerals.

Trace-element investigations have been performed on a small scale in the Pond Creek and Fire Clay coal beds, both of which are major mineable coal beds in the Eastern Kentucky Coal Field. Results indicate a wide range of variability for many elements, even over a distance of only a few thousand feet (Fig. 3). Caution should be exercised, therefore, when applying regional data to smaller areas (e.g., quadrangle, individual coal mine). Analyses of beneficiated Fire Clay and Pond Creek coal indicate that many element concentrations are reduced during coal preparation. This reduction is significant since a majority of eastern and western Kentucky coals undergo beneficiation prior to use.

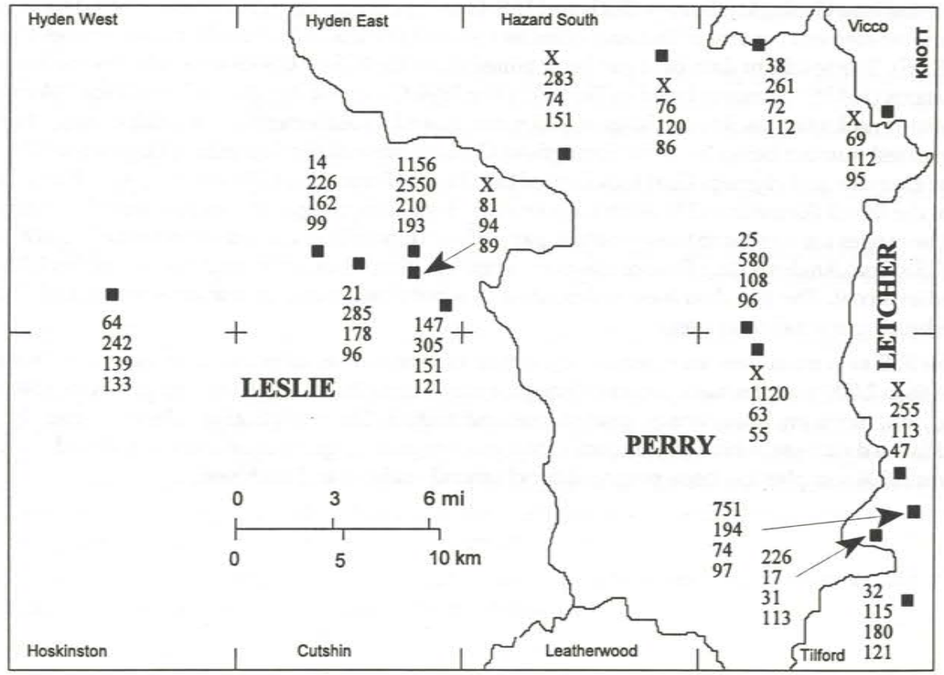

Figure 3. Concentration (parts per million, ash basis) of, in descending order, arsenic, manganese, nickel, and lead in the Fire Clay coal bed in an area of eight 7.5-minute quadrangles in the Eastern Kentucky Coal Field. X indicates that the element concentration was below analytical detection limits.

MAJOR, MINOR, AND TRACE-ELEMENT CONTENT OF INDIANA COALS AND LIMESTONES

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The Indiana Geological Survey (IGS) and U.S. Geological Survey (USGS) developed data on the trace- and minor-element content of Indiana's coal as a part of the USGS National Coal Resources Data System (NCRDS). The resultant data base can be obtained from the IGS or USGS and includes the hazardous air pollutants (HAPS) elements listed in Title III of the 1990 Clean Air Act Amendments for 244 coal and 144 associated rock samples. The analyses of major, minor, and trace elements are available from 14 coal seams, the greatest number being from the Springfield Coal Member of the Petersburg Formation (61), followed by the Danville and Hymera Coal Members of the Dugger Formation (27) and the Upper Block Coal Member of the Brazil Formation (23). All trace elements show wide ranges of concentration for every coal bed, and the ranges are similar to those in other parts of the Illinois Basin. In addition to the NCRDS data base, the IGS's Coal Analysis Data Base contains proximate, ultimate, calorific, and fusion data on 1,416 samples of Indiana coal. The IGS data base is described in a publication and is available on a set of diskettes for DOS-based personal computers.

The IGS also maintains an extensive collection of crushed samples of carbonate rocks from Indiana. More than 2,000 samples have been analyzed for major constituents (calcium, magnesium, silicon, aluminum, iron, titanium, phosphorus, manganese, and sulfur). The analytical results are currently being entered into a data base, which also includes stratigraphic and geographic information. An additional group of over 8,000 samples has been prepared for chemical analysis and archived.

TRACE ELEMENTS IN ILLINOIS COALS AND LIMESTONES

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Abundances and distribution of trace elements in Illinois coals have been studied at the Illinois State Geological Survey (ISGS) since the early 1970's. This research effort helps answer several important questions about the potential impact of coal utilization on the environment. The main areas of the research are described below:

- Abundances of up to 60 elements in about 220 channel and 150 bench samples of Illinois coals were determined using several instrumental methods to provide information on the trace-element content of coal seams prior to mining. Lateral variation of trace-element abundances in individual seams across the basin was studied, particularly in relation to geological factors that control their distribution.
- The washability characteristics of trace elements were studied by float-sink techniques to determine their removability from coal and association with inorganic and organic portions of coal.
- Shipped coals from currently active mines were analyzed for trace-element hazardous air pollutants (HAPS) to determine the effect of conventional coal-preparation and advanced coal-cleaning techniques on removability of HAPS.
- Hand-picked coal lithotypes from a vertical column were analyzed to determine the lithologic control on trace-element distribution.

Trace-element studies of agricultural limestone products in the 1950's at the ISGS mainly concerned the abundance and variability of certain elements, including manganese, iron, zinc, strontium, and barium, that may benefit crop production. Currently, a larger number of trace elements, including mercury, chlorine, fluorine, and other HAPS, are being determined in 10 samples of limestone and dolomite aggregate products. Sulfur dioxide sorption tests indicate that high calcium content and high porosity (low density) are the most predictive properties for an effective sorbent.

Future research will focus on the occurrence and nature of HAPS in coals and limestones and on their behavior during utilization of various coals and limestones.

TRACE ELEMENTS IN OHIO VALLEY CARBONATE ROCKS

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Title III of the Clean Air Act Amendments of 1990 established an initial list of 190 hazardous air pollutants (HAPS), including compounds of 11 elements commonly found in trace amounts in coal and carbonate rocks. Trace elements from coal are the main source of HAPS from coal-burning power plants, but limestone used in controlling SO_2 emissions may also contribute to the trace-element load.

In the Ohio Valley, a number of coal-burning power plants employ limestone- and lime-based emission-control systems. Trace-element data for limestones are limited relative to data for coal, but the U.S. Geological Survey's National Geochemical Data Base (NGDB) includes analyses for Ohio Valley carbonate rocks. Chemical analyses of 749 samples in the NGDB show the following range of concentrations (in parts per million) for the 11 elements listed under Title III (antimony, cadmium, and selenium showed no value exceeding the lower analytical threshold):

Antimony	< 68
Arsenic	0.41–250
Beryllium	< 1–10
Cadmium	< 2
Chromium	< 1–300
Cobalt	0.84–30
Lead	< 1–200
Manganese	10–7,000
Mercury	0.01–0.1
Nickel	< 1.5–100
Selenium	< 200

The sample population from the Ohio Valley is relatively small, but the data give an indication of elemental concentrations. The range of values can serve as a guide for evaluating carbonate rocks of the region for industrial uses, in which the trace-element concentrations of the rocks may affect air and water quality.