Session 1

Coal Combustion By-Products: The Basics

Session Chairperson:
Debra Pflughoeft-Hassett
Energy and Environmental Research Center
University of North Dakota
Grand Forks, North Dakota

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Debra Pflughoeft-Hassett, E.A. Sondreal, E.N. Steadman, K.E. Eylands, and B.A. Dockter, Energy and Environmental Research Center, University of North Dakota, Grand Forks, North Dakota

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PRODUCTION OF COAL COMBUSTION BY-PRODUCTS: PROCESSES, VOLUMES, AND VARIABILITY

D.F. Pflughoeft-Hassett[1], E.A. Sondreal,
E.N. Steadman, K.E. Eylands, and B.A. Dockter
Energy and Environmental Research Center
University of North Dakota
Grand Forks, North Dakota

Introduction

Coal is a vital part of energy production in the United States and both conventional and advanced coal conversion technologies result in the generation of solid by-products. The nearly 90 million tons of coal combustion/desulfurization by-products (CCBs) produced annually in the United States is a valuable national resource that is vastly underutilized. Current use of about 30% of the coal ash and only 2% of the flue gas desulfurization products represents a failed opportunity when compared to the nearly complete utilization already achieved in some western European countries. Future opportunities can be seized by concerted action to offer substantial benefits to the nation's electric generation, construction, and manufacturing industries; to agriculture; and to the environment; whereas failure to act will create, literally, mountains of solid waste that will be an unnecessary legacy of future energy production.

The value of CCBs is well established by research and commercial practice both in the United States and abroad. As engineering construction materials, these products can add value and enhance strength and durability while reducing cost. In agricultural applications, gypsum-rich products can provide plant nutrients and improve the tilth of depleted soils over large areas of the country. In waste stabilization, the cementitious and pozzolanic properties of these products can immobilize hazardous nuclear, organic, and toxic metal wastes for environmentally safe and effective disposal. Public benefits of CCB utilization are substantial, including conservation of land, energy, and natural resources; reduction in CO_2 emissions generated in the production of competing materials; improvements in the balance of trade (e.g., fewer cement imports); and prevention of solid waste pollution. Increasing cost and heightened regulation are making the disposal of CCBs an undesirable option.

U.S. Energy Production from Coal

U.S. coal production totaled a record high of 1,088.6 million short tons in 1997 according to preliminary data from the Energy Information Administration (EIA) (Hong, 1998). Utilities and industry continue to be the dominant coal consumers, using a record 922.0 million short tons in 1997 as a result of a substantial decline in nuclear-powered generation and moderate growth in electricity demand. U.S. coal consumption by all users in 1997 showed a 2.2% increase over 1996. Growth came entirely from the electric power industry, as coal consumption in the nonelectricity sectors decreased. Coal continued to be the principal energy source for electric power generation in the United States, accounting for 52% of total generation in 1996 (Hong, 1998). Coal consumption in the nonelectricity sectors (coke plants, other industrial plants, and residential/commercial users) totaled 105.8 million short tons in 1997, down by 2.6 % from the 1996 level of 108.7 million short tons.

It is forecast that the United States will continue to rely heavily on coal for energy production at least through 2020. It is further forecast that future coal consumption will be primarily in existing power generation facilities or in facilities that utilize clean coal technologies (CCTs) such as fluidized-bed combustion (FBC) and gasification. The CCT processes have been designed to meet ever-tightening emission control standards set by EPA and State agencies, but it is important to note that any use of coal in future energy production will continue to result in the generation of solid materials. These solids, referred to as wastes or by-products, vary with the type of coal used, the

conversion system, the emission controls applied to the system, the solid collection system, and the specific operating conditions.

Production of Coal Combustion By-Products

The type of coal or **coal rank** indicates the degree of coalification that has occurred for a particular coal. Coal is formed by the decomposition of plant matter without free access to air and under the influence of moisture, pressure, and temperature. Over the course of the geologic process that forms coal, coalification, the chemical composition of the coal gradually changes to compounds of lower hydrogen content and higher carbon content in aromatic ring structures. With an increase in degree of coalification, the percentage of volatile matter decreases and the calorific value increases. The common ranks of coal in the United States are anthracite, bituminous, subbituminous, and brown coal/lignite. Anthracite is the highest-ranked coal in the series, exhibiting the lowest volatile matter and higher calorific value, while lignite is the lowest-ranked coal in the series, with significantly greater volatile matter and lower calorific value. Figure 1 shows the geographic location of U.S. coal fields and the associated coal rank. It is generally true that the higher-ranked coals have a lower-percentage ash content and the lower-ranked coals have increasing percentages of ash, with the notable exception in certain Powder River Basin (Montana and Wyoming) subbituminous coals, which yield a very low ash percentage.

All coal contains minerals. These minerals are composed of inorganic constituents and can be present as included minerals, which are inherent in the coal particles, or as excluded minerals, which are separate from the coal substance. Excluded minerals may be dispersed in the coal or may be present simply because of the inadvertent mining of adjacent mineral strata by procedures used to extract the coal. This inorganic material becomes the ash or CCB following combustion or conversion.

Conventional Combustion Systems

The most common utility combustion systems in place in the United States today are pulverized coal (pc) combustion, cyclone firing, and stoker firing, with pc-fired units outnumbering the cyclone and stoker units. Figure 2 shows a simple schematic diagram for a typical pc combustion system. In this type of combustion system, the coal is prepared by grinding it to a very fine consistency for combustion. Typically, 70% of the coal is ground to pass through a 200-mesh per unit screen. There are several configurations for commonly used pc furnaces, which can impact ash formation, but the primary advantage of pc combustion is the very fine nature of the fly ash produced. In general, pc combustion results in approximately 65%–85% fly ash, and the remainder in coarser bottom ash (dry-bottom boiler) or boiler slag (wet-bottom boiler). Cyclone combustion uses coarsely pulverized coal (95% !¼ in.) and produces much higher percentages of bottom ash (up to 75%–90%, depending on coal type) and smaller amounts of fly ash. Stoker-fired units do not require the same level of coal grinding (e.g., !¾ in.) because the coal generally stays in the hot zone for an extended period of time, allowing complete combustion of larger coal particles.

Utilities use a variety of techniques for air pollution or emission control. Currently, emission control technologies are fairly broadly applied for control of particulates, SO_2, and NO_x. ESPs have been commonly installed on U.S. coal-fired steam–electric power plants to reduce particulate emissions. In recent years, baghouses have been specified for some new units as well as retrofits of existing units. At present, every operating U.S. utility-owned coal-fired unit is believed to have particulate control equipment in place.

U.S. utilities generally employ one of two strategies to control SO_2 in the flue gas stream: 1) use of compliance fuel or 2) use of flue gas desulfurization (FGD) units. Many western coals and some eastern coals are naturally of low sulfur content, and these can be used to meet SO_2 compliance requirements. Utilities may also physically clean or wash all or part of the fuel prior to combustion. Physical coal cleaning at the mine, transhipment point, or power plant is quite widespread in the United States not only because it results in reduced emissions, but also because some increase in steam generator efficiency is often possible if the fuel feedstock can be made more homogeneous. Utilities may also blend coals of different sulfur contents in order to obtain a mix allowing compliance with applicable regulations.

Control of NO_x emissions, which is relatively new for the utility industry, is complicated, since these emissions are related to both the nitrogen content of the fuel and the formation of various NO_x species during the combustion process. NO_x controls include combustion modifications such as use of overfire air or low-NO_x burners. Selective noncatalytic reduction and selective catalytic reduction are just beginning to be used as postcombustion NO_x control. Commercial installations have been made, but research and evaluation continue in the area of NO_x control.

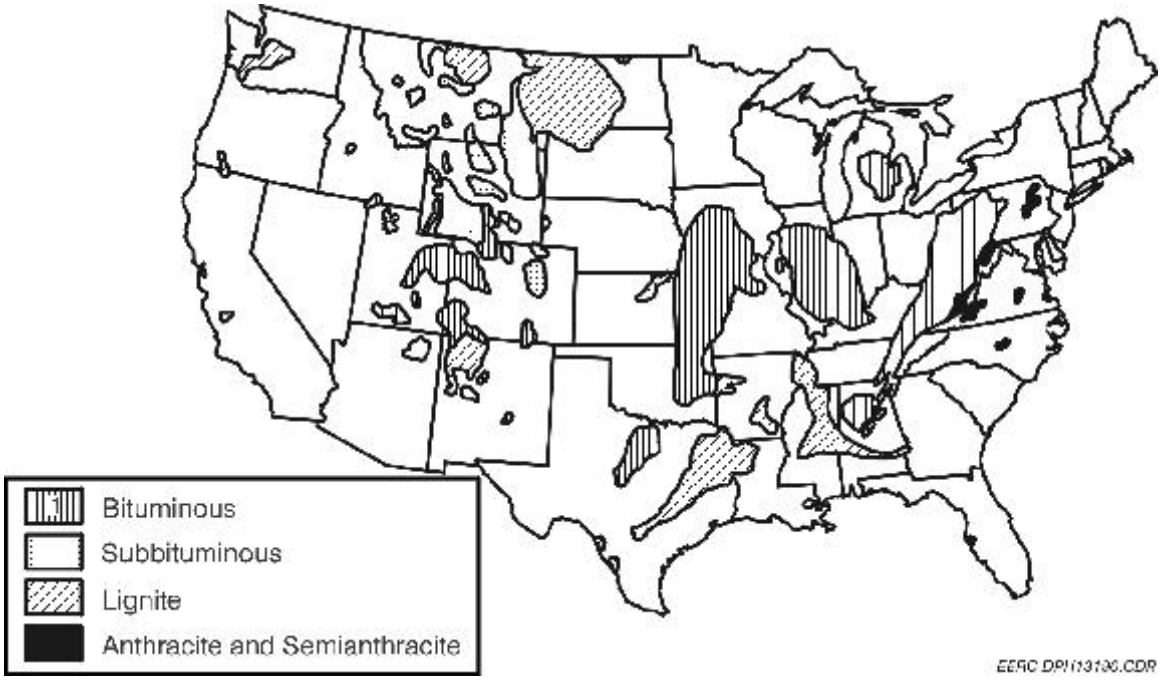

Figure 1. Geographic location of U.S. coal fields and the associated coal rank.

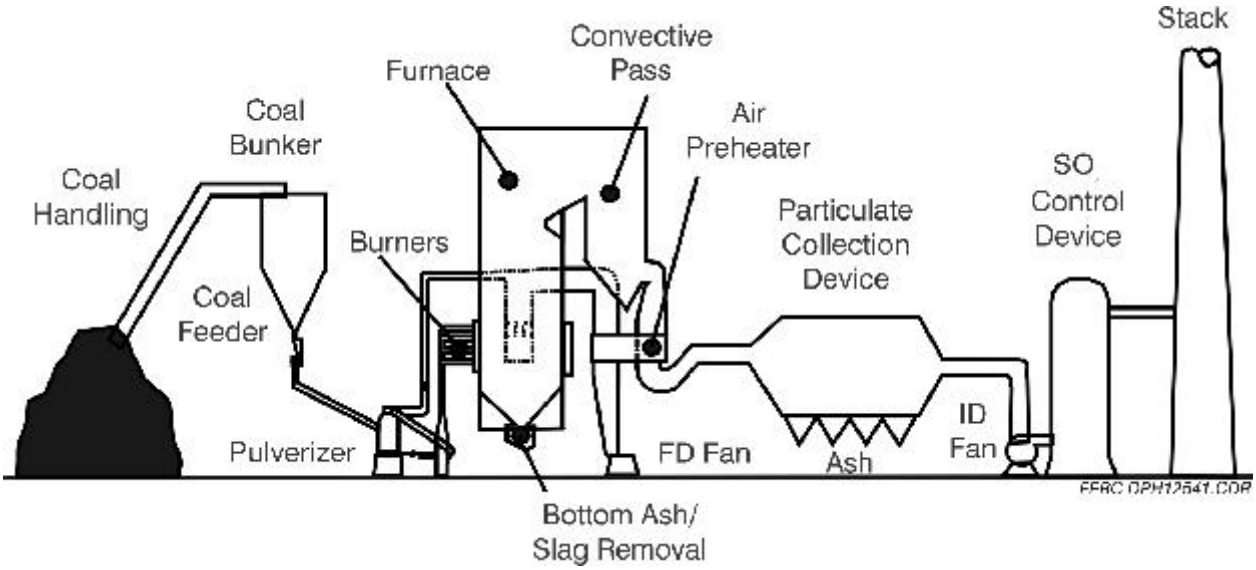

Figure 2. Schematic diagram for a typical pc combustion system.

Each of the emission control technologies that an individual coal-fired unit needs to use has the potential to impact the quantity and the character of the by-products generated. Current research on air toxic emissions (Benson and others, 1995; Miller and others, 1996; Pavlish and others, 1995) is evaluating the potential need for further emission controls for trace elements such as mercury and other hazardous air pollutants (HAPs). Technologies that may be required to control these emissions will also impact CCBs.

Fluidized-Bed Combustion

The FBC process consists of two subprocesses: 1) the fluidization of solids, by which solid particles/granules are suspended in an upward-flowing stream of gas, and 2) the combustion process, in which fuel particles are burned to sustain temperature. The solids in FBCs are typically fuel ash, bed material, sorbent used to control pollutants, and reaction products formed by sulfur capture and other sorbent–coal interactions. FBC systems operated at atmospheric pressure are classified as atmospheric fluidized-bed combustors (AFBCs), which usually also denotes low fluidization velocities resulting in a bubbling bed. Circulating fluidized-bed combustors (CFBCs) operate at fluidization velocities approximately 2 to 3 times higher. At these velocities, the rising gas entrains the bed materials; the resulting bed consists of a turbulent cloud of solids that fills the combustion chamber. A portion of the bed material is continuously carried out with the offgas and recirculated to the combustion chamber. Pressurized fluidized-bed combustor (PFBC) systems are similar to AFBCs, but operate under pressure. The compressed air used contains more oxygen per unit volume and, therefore, sustains a higher intensity of combustion, allowing for the design of smaller combustors. The other principal advantage of the PFBC is the increased conversion efficiency (coal-to-electricity) that can be achieved by passing the hot, pressurized combustion gases through both a gas turbine and a waste heat boiler serving a steam turbine to extract more useable energy in a combined cycle system.

The characteristics of the solid residues produced in FBCs depend on the bed material, fuel and ash compositions, unburnt carbon, desulfurization products, and unreacted sorbents. The residues can be collected from several locations in the system, including the bed offtake, primary cyclone, and final particulate control device. In most cases in the United States, these residues are combined.

Fluidized-bed combustion systems operate at low temperatures, typically less than 900EC, which prevents significant fusion and melting of the ash particles. The FBC fly ash particles are, therefore, angular and very different from the spherical fused ash particles produced in pc firing (Mann and others, 1985; Smith, 1990). Entrained bed material also influences the physical and chemical properties of the fly ash collected in the particulate control devices. The characteristics of the spent bed material depend on the properties of the coal ash, the bed material, and the sorbent and degree of sulfation due to sulfur capture. The solids recirculation of a CFBC and the higher pressure of a PFBC cause these systems to achieve higher sorbent utilization, resulting in a higher sulfation level in their residues. High-calcium materials used for sulfur capture (i.e., limestone or dolomite) produce residues containing high levels of calcium sulfate, free lime, and coal ash, which reflects the chemical characteristics of the sorbent and coal used. Selection of coal and sorbent combinations may provide an opportunity to adjust residue compositions to meet a particular utilization specification. The particle size of the fines collected from an FBC baghouse is similar to that of pulverized coal fly ash (mass mean diameter of 10 to 15 µm). The respective particle sizes of the bed offtake, cyclone, and baghouse residues were similar for eight test coals burned under similar conditions (Dearborn Environmental Consulting Services, 1988). Comparison of the AFBC and CFBC residues indicates finer particle-size distributions for the CFBC because of the high degree of solid recycle (Dearborn Environmental Consulting Services, 1986). Problems can arise in the disposal of FBC residues as a result of the high levels of CaO and $CaSO_4$, the alkalinity of leachate, and dust associated with residues that contain high levels of CaO. Rapid exothermic reactions and solidification occurring with the addition of water require that care be used in handling, utilizing, and disposing of the FBC residuals (Smith, 1990).

PFBC technology has been investigated under the DOE CCT program, including demonstration of commercial-scale systems. The current terminology applied to PFBC technologies is “first-generation PFBC” and “second-generation PFBC.” The first-generation PFBC technology was demonstrated at the Tidd Pressurized Fluidized-Bed Coal Technologies Project.

CCB Volumes

Annual summaries of CCB production and consumption have been prepared by the American Coal Ash Association (ACAA) since 1966. These surveys generally cover the highest-volume CCBs: fly ash, bottom ash, boiler slag, and FGD material. Production data from 1966, 1976, 1986, 1993, and 1998 (the most recent summary available from the ACAA) are presented in Table 1. A summary of CCB production and use for 1966 through 1993 that was published by ACAA (1996) indicates that CCB production increased from 1966 to about 1980. Since 1980, CCB production has remained relatively constant, with the exception of FGD materials. FGD material production began in 1987 and has remained relatively constant through 1996.

Table 1. Summary of CCB Production (ACAA, 1996).

	By-Product Production[1]				
	1966	1976	1986	1993	1998
Fly Ash	17.1	42.8	49.26	47.76	63.00
Bottom Ash	8.1	14.3	13.41	14.21	16.76
Boiler Slag	NA[2]	4.8	4.13	6.23	2.98
Combined Ash and Slag	25.2	61.9	66.80	68.20	82.74
FGD Material	NA	NA	NA	20.34	25.00

[1] All values shown in million short tons.
[2] No data available.

The quantity of CCBs produced is directly proportional to the amount of coal burned, the ash content of the coal, and the use of FGD. The average ash content of coal used by U.S. electric power utilities is approximately 10%; ash content has decreased significantly since 1975 (ICF Resources Inc., 1993). This reduction has resulted from a nominal increase in coal cleaning and a large increase in the use of low-sulfur, low-ash western coals to meet the sulfur dioxide emission requirements of the Clean Air Act. U.S. coal consumption for electric power generation has doubled since 1975 and is projected to increase an additional 25% by 2010 (EIA, 1993a). Approximately 22% of U.S. coal-fired generating capacity is currently equipped with FGD controls, and additional retrofit installations are projected to increase FGD coverage to about one-third of generating capacity by the year 2000, when the sulfur control provisions of the 1990 CAAA are fully implemented (EIA, 1993a, b).

CCB Variability

The characteristics of CCBs currently being produced vary widely. In the earlier discussion of processes from which CCBs are produced, the variability between different types of CCBs (fly ash, bottom ash, boiler slag, FGD material, and FBC by-products) was referred to as being related to the coal type, the combustion system, the emission control system, and collection method. There are physical and chemical differences in these by products. Fly ash is a finely powdered material comprised mainly of amorphous (glassy) spherical particles. Bottom ash is a coarse material with sintered and agglomerated amorphous particles. Boiler slag generally has the form of glassy pellets. FGD material is a generally crystalline fine powder, but may be a sludge (wet FGD) or a dry powder. FBC fly ash is a finely powdered mixture of coal ash and crystalline spent sorbent. FBC spent bed material is also a combination of coal ash and sorbent (both reacted and unreacted), primarily crystalline in nature. Table 2 summarizes the physical variability of these common CCBs.

CCBs also exhibit chemical variability. Fly ash and bottom ash from a single source have similar major chemical compositions; however, the trace element composition varies considerably, because many trace constituents of coal are volatile and tend to be associated with the fly ash. Some trace elements are also captured in FGD materials along with SO_2 gases. FGD material is generally high in calcium and sulfur-associated in crystalline phases. FBC by-products are also generally high in crystalline calcium–sulfur phases. The chemical variability of CCBs is also summarized in Table 2.

Table 2. Physical and Chemical Variability of CCBs.

CCB Type	Particle Size	Particle Morphology	Color	Major Composition	Trace Element Composition
Fly Ash	High % less than 325 sieve	Spherical	Tan to gray	Depends on coal source	Enriched in trace elements
Bottom Ash	Range from granular to ½ in.	Angular	Tan to black	Depends on coal source	Low concentrations
Boiler Slag	Granular	Approx. spherical	Black	Depends on coal source	Low concentrations of most traces
FGD	Fine powder	Angular (wet or dry)	White to off-white	Calcium and sulfur	May contain some trace elements

Variability within a single CCB type is generally understood as a range of characteristics exhibited by a particular CCB type. Ranges of performance are indicated by these characteristics and are important in considering CCBs for various management scenarios, including mine placement. Most of the variability is related to the source coal.

Variability in composition and physical properties can be an indicator of variability in performance, but performance testing is the most reliable means to determine the performance of a specific material.

Compositional Variability of Fly Ash

The bulk composition of fly ash is similar to that of many geologic materials. Fly ash is primarily composed of silicon, aluminum, iron, calcium, magnesium, sodium, potassium, and sulfur in association with oxygen as oxides, silicates, and aluminates. The combined silicon, aluminum, and iron content (reported as oxides) is frequently used to provide an indication of the pozzolanic or cementitious nature of fly ash (as in ASTM C 618). A combined value of 70% of these components is used to indicate a pozzolanic fly ash, and a value between 50% and 70% is used to indicate a cementitious fly ash. A pozzolan is a material that sets up when combined with water and a source of calcium. A cementitious material sets up when combined with water. Another indicator of pozzolanic/cementitious behavior is the calcium content of fly ash. Ranges of calcium content of fly ashes from different sources of U.S. coals are noted in Table 3.

Other major elements, most notably silicon and aluminum, vary inversely with the calcium content in the ash. Calcium content also provides an indication of the pH of the fly ash. Higher calcium content fly ashes tend to be more alkaline.

Table 3. Ranges of Calcium Content in Fly Ash Produced by Combustion of Coal from Various U.S. Sources (after Tishmack and Olek, 1999)

Source of Coal	Range of Calcium, as % CaO
Appalachian Region – Bituminous	1–6
Illinois Basin – Bituminous	1–6
Gulf Coast – Lignite	7–15
Fort Union – Lignite	18–25
Powders River Basin – Subbituminous	22–32

Total trace element concentrations and trace element leachate concentrations are frequently determined for fly ash. Leaching is the best available test to evaluate environmental performance of fly ash. Variability is noted in both total

and leachate trace element concentrations. The ranges of leachate concentrations for RCRA (Resource Conservation and Recovery Act) elements (arsenic, barium, cadmium, chromium, lead, mercury, selenium, and silver) fall below the RCRA limits for hazardous waste and usually below the Primary Drinking Water Standard limits.

Summary

CCBs will continue to be available throughout the United States for at least the next 20 years. Since only approximately one-third of these materials are used in construction, engineering, and manufacturing, large volumes are available for other applications, including mine reclamation. CCBs exhibit variability primarily related to the coal used and the production system. The range of characteristics exhibited by CCBs makes them useful in mine reclamation applications such as fills, treating acid mine drainage, and soil amendment for revegetation. As with any material, it is important to evaluate the properties and performance of CCBs in considering their use for any application.

References

American Coal Ash Association. *Coal Combustion Byproduct (CCB) Production & Use: 1966–1993;* American Coal Ash Association: Alexandria, VA, 1996.

Benson, S.A.; Pavlish, J.H.; Erickson, T.A.; Katrinak, K.A.; Miller, S.J.; Steadman, E.N.; Zygarlicke, C.J.; Dunham, G.E.; Pflughoeft-Hassett, D.F.; Galbreath, K.C. *Center for Air Toxic Metals Final Technical Report;* Energy & Environmental Research Center: Grand Forks ND, Dec 1995.

Dearborn Environmental Consulting Services. *Characterization of Circulating Bed AFBC Wastes;* DECS S10-512, CEA 432 G 494; Dearborn Chemical Company Ltd.: Ontario, Canada, Oct 1986; 119 p.

Dearborn Environmental Consulting Services. *Utilization Potential of CFBC Residue in Construction Applications: Final Report*; SSC 03SQ.23440-7-9216, DECG S10-608; Dearborn Chemical Company Ltd.: Ontario, Canada, Nov 1988; 51 p.

Energy Information Administration (EIA). *Electric Power Annual 1991*; DOE/EIA–0348(91);U.S. Department of Energy, Office of Coal, Nuclear, Electric, and Alternate Fuels: Washington, DC, Feb. 1993a, 162 p.

Energy Information Administration (EIA). *Annual Energy Outlook 1993—With Projections to 2010*; DOE/EIA–0383(93), Jan 1993b, 214 p.

Hong, B.D. U.S. Coal Supply and Demand: 1997 Review. U.S. Department of Energy, Energy Information Administration (http://www.eia.doe.gov//cneaf/coal/cia/summary/cia_sum.html). Published as Annual Review 1997: Coal. *Mining Engineering* **1998**, *50* (5).

ICF Resources Incorporated. *Coal Combustion Waste Management Study*; prepared for U.S. Department of Energy Contract DE-AC01-91FE62017; Washington, DC, Feb 1993.

Mann, M.D.; Willson, W.G.; Hendrikson, J.G. Gasifier Wastewater Treatment: Phase I—Cooling Tower Assessment. *Environ. Prog.* **1985**, *4* (1), 33–39.

Miller, S.J.; Ness, S.R.; Weber, G.F.; Erickson, T.A.; Hassett, D.J.; Hawthorne, S.B.; Katrinak, K.A.; Louie, P.K.K.A. *A Comprehensive Assessment of Toxic Emissions from Coal-Fired Power Plants: Phase I Results from the U.S. Department of Energy Study*; final report for U.S. Department of Energy Pittsburgh Energy Technology Center; Energy & Environmental Research Center: Grand Forks, ND, Sept 1996.

Pavlish, J.H.; Gerlach, T.R.; Zygarlicke, C.J.; Pflughoeft-Hassett, D.F. *Mitigation of Air Toxics from Lignite Generation Facilities*; final report; Energy & Environmental Research Center: Grand Forks, ND, Oct 1995.

Smith, I.E. *Management of AFBC Residues*; IEACR/21; IEA Coal Research, Feb 1990.

Tishmack, J.K.; Olek, J. Coal Consumption by U.S. Electric Utilities and Its Impact on Fly Ash Composition. In *13th International Symposium on the Management and Use of Coal Combustion Products*, Orlando, FL, Jan 11–15, 1999; Paper 81, 20 p.

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[1]Debra F. Pflughoeft-Hassett is a Research Manager in Residuals Research at the Energy and Environmental Research Center (EERC) of the University of North Dakota. She received her B.S. in Chemistry from the University of North Dakota in 1982. Pflughoeft-Hassett's principal areas of interest and expertise include utilization and characterization of coal by-products, waste management, and environmental impacts of coal by-product use and disposal. She has worked on the development of databases containing characterization information on coal by-products and on the development of chemical characterization protocols. Pflughoeft-Hassett also has expertise in analytical chemistry, primarily atomic spectroscopy, chromatography, classical analytical methods, molecular spectroscopy, and atomic absorption methods development, as well as environmental and geologic research. Pflughoeft-Hassett has participated extensively as an investigator on laboratory research investigations of groundwater contamination, sediment attenuation, coal conversion by-product characterization, leaching characterization, and chemical fixation of trace elements, and has developed and applied numerous analytical techniques for these tasks. She also participates as a principal researcher and project manager on several investigations of the utilization and disposal of coal combustion by-products and characterization of coal by-products and currently coordinates the research effort of the Coal Ash Resources Research Consortium (CARRC) and other coal by-product research at the EERC. In addition, she has coauthored over 50 publications.

THE COMPOSITION OF COAL COMBUSTION BY-PRODUCTS: EXAMPLES FROM A KENTUCKY POWER PLANT

Allan Kolker[1,3], Robert B. Finkelman[1], Ronald H. Affolter[2] and Michael E. Brownfield[2]
Energy Resources Program
U.S. Geological Survey
[1]Reston, Virginia and [2]Denver, Colorado

Abstract

A comprehensive study of feed coal, fly ash, bottom ash, feed limestone, and flue-gas desulfurization sludge was conducted at a Kentucky power plant over a 2-year period. Sampling was conducted monthly at two units, one burning high-sulfur coal (2.5 to 3.5 wt. % S), and another burning low sulfur coal (0.6 to 0.9 wt. % S). Determinations of mineralogy and elemental composition were integrated with directed studies of element modes of occurrence, magnetic properties, isotopic composition, organic chemistry, and leachability. Results show that the composition of the coal (element contents and modes of occurrence) is the primary determinant of the composition of the coal combustion products. Mass balance calculations show that with the exceptions of mercury and selenium, most elements are largely retained in the solid waste products. Ratios of element concentrations in fly ash versus bottom ash are very similar to the orders of element volatility reported in the literature. Nickel, chromium, and cobalt show substantial enrichment in the magnetic fly ash fraction from the low-sulfur plant, consistent with the occurrence of these elements in iron oxide minerals. Fission track studies show a uniform distribution of uranium in the larger glassy cenospheres, and possible enrichment of uranium in dark, iron rich glass versus clear glass. Electron microprobe results indicate a uniform distribution of arsenic at low levels throughout glassy fly ash particles, but possible trace element enrichments on particle surfaces were not detectable by this method. Environmental leaching studies show that leachate pH, and in the case of the low-sulfur fly ash, grain size, are important factors in determining element mobility. Our results help determine the suitability of these coal combustion products for recycling to beneficial uses and their potential environmental impact.

Introduction

The chemical composition of coal combustion by-products (CCBs) is a fundamental parameter in determining suitability for various applications. Element contents and their modes of occurrence in CCBs will determine the behavior of these materials upon disposal or use in the environment, and whether any metallic or chemical by-products can be economically extracted. The major purpose of this project is to provide a comprehensive chemical and physical characterization of these materials, including an assessment of their possible interaction with the environment, and to relate CCB properties to those of the feed coal precursor. In this paper, we summarize the mineralogy, chemistry, and other properties of CCBs and demonstrate the relation of these parameters to differences in the composition of feed coals. More detailed information is available primarily in recent proceedings papers and in USGS Open-File Report 98-342. This research was conducted jointly by the U.S. Geological Survey, the Kentucky Geological Survey, the University of Kentucky Center for Applied Energy Research, and the cooperating power plant.

Sampling Approach

Feed coal, fly ash, and bottom ash were collected monthly from July 1994 through June 1996 by the Kentucky Geological Survey. Feed coal and CCBs were taken from two units: Unit 1, a tangentially fired unit burning a blend of relatively high sulfur (~3 wt. %) Illinois Basin and Appalachian Basin coals; and Unit 3, a wall-fired unit burning a blend of low-sulfur (< 1 wt. %) Appalachian Basin coal. Grab samples of washed coal were collected at gravimetric feed units prior to pulverization and injection into the furnaces of each unit. For the low-sulfur unit, samples of fly ash were collected from two parallel banks of hoppers underneath the electrostatic precipitators, a coarse-side hopper closest to the flue gas entry point, and a fine-side hopper farther along the path through the precipitators (Eble, 1998). Fly ash from the high-sulfur unit, which has a different configuration, was collected from a single bank of hoppers. Samples of bottom ash were collected by suspending a hollow bucket covered with a nylon-mesh

screen into the water train carrying ash to the ash pond. This was the only available sampling point and possible modification of the bottom ash by interaction with water was unavoidable. A flue-gas desulfurization (FGD) system was installed on Unit 1 during the course of our study, and samples of feed limestone and FGD sludge were taken monthly following its installation. This report summarizes the results for fly ash and bottom ash, primarily representing the first year of the study.

Results

Mineralogy and Bulk Chemistry

Components of the CCBs and their mineralogy were determined using a combined approach that included reflected-light microscopy, X-ray diffraction, scanning electron microscopy (SEM), and electron microprobe analysis. Fly ash samples from both units consist predominantly of glassy, or partly devitrified spheres, cenospheres (hollow glassy spheres), or plerospheres (small spheres filling larger glass-rimmed spheres), and lesser amounts of crystalline mineral phases. Minerals present include mullite, quartz, and Fe- or Fe-Mg oxides derived primarily from oxidation of pyrite in the feed coal (Table 1; Pontolillo, 1998; Brownfield et al., 1999; Dulong, 1998). The most common oxide minerals are magnetite (Fe_3O_4), maghemite (?-Fe_2O_3), magnesioferrite ($MgFe_2O_4$), and hematite (a-Fe_2O_3) (Table 1). A host of other oxide trace-phases have been identified (Table 1). Oxide-mineral contents are greatest in fly ash from the high-sulfur unit, consistent with the higher pyrite content of its feed coal. Understanding the distribution of Fe-oxides and Fe-Mg oxides is especially important from the standpoint of disposal and use of fly ash because elements such as Ni, Cr, and Co are concentrated in these minerals, as shown by analysis of oxide-rich magnetic fractions (Cathcart et al., 1997), and by electron microprobe X-ray maps of individual Fe-oxide particles (Hower et al., 1999). SEM observation shows that many of the Fe-oxide-rich spheres consist of skeletal intergrowths of Fe-oxide in a glassy host (Figure 1; Brownfield et al., 1999; Hower et al., 1999). A small portion of the Fe-oxides in the CCBs is probably derived from residual magnetite contributed by the coal washing procedure (Brownfield et al., 1997).

Table 1. Mineralogy of CCBs from Unit 1 (high-sulfur) and Unit 3 (low-sulfur), after Brownfield et al. (1999).

Unit 1 Fly ash	Unit 1 Bottom Ash	Unit 3 Fly ash (combined)	Unit 3 bottom ash
	MAJOR PHASES		
Glass	Glass	Glass	Glass
Mullite	Mullite	Mullite	Mullite
Quartz	Quartz	Quartz	Quartz
	MINOR PHASES		
Illite/Muscovite	Illite/Muscovite	Illite/Muscovite	Illite/Muscovite
Hematite	Hematite	Anhydrite	Pyrite
Magnetite	Magnetite	Millosevichite	
Magnesioferrite	Magnesioferrite		
Maghemite	Maghemite		
	Pyrite		
	Anhydrite		
	Millosevichite		
	$(Al,Fe)_2(SO4)_3$		
	TRACE PHASES		
Franklinite ($ZnFe_2O_3$)	Franklinite	Hematite	Hematite
Trevorite ($NiFe_2O_4$)	Trevorite	Magnetite	Magnetite
Jacobsite ($MnFe_2O_4$)		Magnesioferrite	Magnesioferrite
Zincochromite ($ZnCr_2O_4$)		Maghemite	Maghemite
Corundum		Franklinite	Anhydrite
Sulfates		Trevorite	Millosevichite
		Nichromite ($NiCr_2O_4$)	Mn Oxide
		Magnesiochromite ($MgCr_2O_4$)	

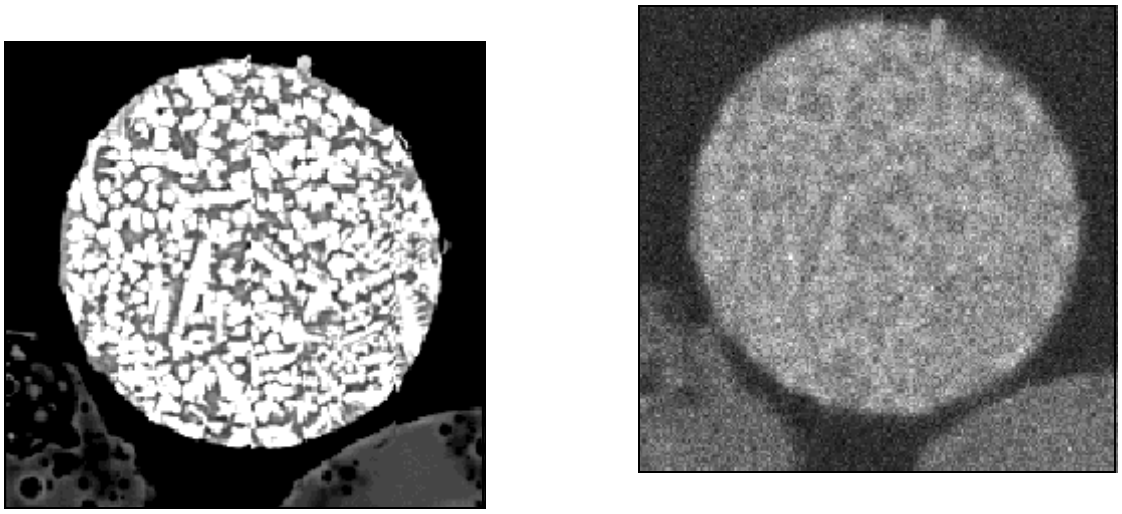

Figure 1. Backscattered electron image (left) and wavelength-dispersive elemental map for Ni (right) showing skeletal Fe-oxide in a glassy host, and correspondence of Ni distribution with Fe-oxide.

Fly ash from both units is classified as class F, having a minimum combined percentage of SiO_2 + Al_2O_3 + Fe_2O_3 of 70% (ASTM, 1988; Brownfield et al., 1999). In the present study, bulk concentrations were determined for most elements by inductively coupled plasma mass spectroscopy (ICP-MS) or by inductively coupled plasma atomic emission spectroscopy (ICP-AES). Selenium was determined by instrumental neutron activation analysis (INNA), whereas Hg contents were determined by cold vapor atomic absorption spectrophotometry (CVAA). Major and trace-element averages for feed coals and CCBs are given in Appendix 1. The averages show large standard deviations, especially for trace elements such as As, Cd, Ni, Pb, Sb, Se, and U, reflective of the variation in composition of the feed coals. In some cases, coals from more than 20 sources were utilized in a given month (Brownfield et al., 1999). Temporal (monthly) variations in the chemistry of CCBs and feed coal were investigated by Affolter et al. (1997) and Affolter (1998), as shown in Figure 2. For example, over a 12-month period, the arsenic content of feed coal in Unit 1 (high-sulfur) varied from 62 to 240 ppm (expressed on an ash basis, equivalent to 6.6 ppm to 26 ppm on a whole coal basis), resulting in a range of 100 to 330 ppm in fly ash, and <5 to 20 ppm in the bottom ash. On a month-to-month basis, the correlation between feed coal composition (expressed on an ash basis) and CCB chemistry is imperfect, due in part to differences in the ash contents of the coals used (Figure 2). Two of the bottom ash samples have high contents of Pb (>1000 ppm) and Mn (>1 wt. %), likely contributed by pulverizer discards such as pyrite and galena and boiler slag, as well as bolts, gears, etc. that are discarded in the bottom ash (Affolter et al., 1997).

Hower et al. (1999) investigated the partitioning of residual carbon and trace metals with particle size, comparing fly ash from the low-sulfur and high-sulfur units. Five size fractions, expressed by mesh size ranges +100, 100x200, 200x325, 325x500, and -500, were prepared from fly ash fractions collected from both units in November and December of 1994. The –500 (< 25 µm) fraction was the largest weight fraction (55.2 to 89.9 % of the sample) in all cases. Residual carbon, and carbon-bearing phases were determined by ultimate analysis, ash yield, and petrographic methods. The proportion of carbon is greatest in the +100 mesh (> 150 µm) fractions, comprising between 36.8 and 58.0 % of this fraction. However, the two sub 325-mesh (< 42 µm) fractions together constitute about 80 to 90% of each sample. This is potentially an important consideration in ash utilization , as carbon in this size fraction is more difficult to remove than that in the coarse fraction (Tondu et al., 1996; Hower et al., 1999). Trace-element data for the sized fractions show that arsenic, zinc, and lead are concentrated in the –500 fraction, consistent with enrichment of metals found in bulk samples of fine fly ash, relative to the coarse fly ash, in Unit 3 (Appendix 1). For Unit 1, there appears to be a correlation between carbon content and mercury concentration of the fly ash. Mercury contents in fly ash from Unit 3 were too low to establish any correlation with carbon content (Hower et al., 1999).

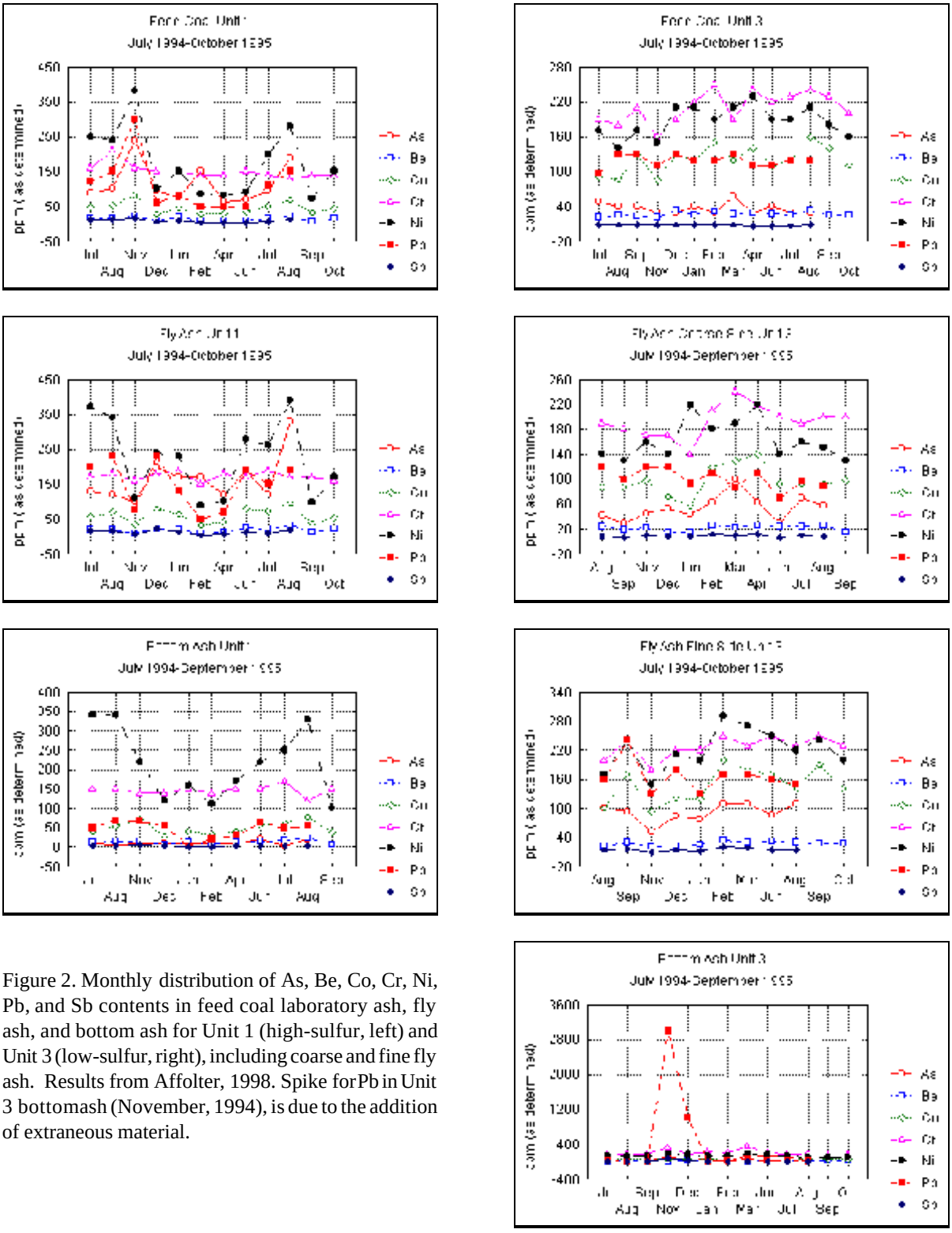

Figure 2. Monthly distribution of As, Be, Co, Cr, Ni, Pb, and Sb contents in feed coal laboratory ash, fly ash, and bottom ash for Unit 1 (high-sulfur, left) and Unit 3 (low-sulfur, right), including coarse and fine fly ash. Results from Affolter, 1998. Spike for Pb in Unit 3 bottomash (November, 1994), is due to the addition of extraneous material.

Element Modes of Occurrence and Mass Balance Calculations

Understanding the mode of occurrence of a given element in the CCBs is important from the standpoint of assessing its suitability for a given purpose, and evaluating the potential for groundwater contamination by leaching of arsenic, radionuclides, and other potentially harmful substances. Element associations in the Kentucky fly ash samples were investigated by Finkelman et al. (1997) and by Palmer et al. (1998a), who also investigated the bottom ash. These studies utilize a combination of approaches including sequential selective leaching, X-ray diffraction, SEM, and electron microprobe. In the selective leaching approach, CCB samples were leached with a 4-step sequence of reagents originally devised for determinations of element modes of occurrence in whole coals (Palmer et al. 1998b). Listed in order of application, the leaching sequence includes 1) 1N ammonium acetate ($NH_4C_2H_3O_2$); 2) 2N hydrochloric acid (HCl); 3) concentrated (48-51%) hydrofluoric acid (HF); and 4) 1.5N nitric acid (HNO_3). The mode of occurrence of an element is assessed by comparing the fraction removed by a given reagent to the concentration of that element in the bulk sample. As the bulk of the ash consists of silicate material, the largest fractions of material were leached by HF (Palmer et al., 1998a).

Leaching results were obtained for several elements of interest, including arsenic, nickel, cobalt, chromium, antimony, zinc, uranium and thorium (Palmer et al., 1998a). Fly ash samples from each unit show that a substantial portion (about 80%) of the arsenic is present as an HCl-soluble phase, possibly as $Ca_3(AsO_4)_2$ that has been identified as a condensate on fly ash particle surfaces (EPRI, 1998). Electron microprobe results for the Kentucky ash (McGee et al., 1995), and Canadian fly ash (Mukhopadhyay et al., 1996), show that arsenic is also present in solid solution in the glass phase in fly ash. Some of this Ca-silicate glass is leachable in HCl (C. A. Palmer, unpublished data). The electron microprobe studies show no enrichment in arsenic at the particle surfaces; however, the scale of this enrichment is likely to be too fine to resolve with the electron microprobe. Follow-up studies are underway to try to clarify the mode of occurrence of arsenic in fly ash. A much greater proportion (40-80%) of the arsenic in the bottom ash was found to be in silicates (HF soluble), compared to the fly ash.

Leaching results for iron, cobalt, nickel, and chromium in both fly ash and bottom ash show that these elements are primarily HF soluble, indicating they are present in silicates, and likely in Fe-oxides not exposed until their glassy matrix is dissolved by HF. Electron microprobe elemental maps confirm the presence of Ni and Cr in the Fe-oxides (Figure 1; Hower et al., 1999; Finkelman et al., 1997). Cobalt is likely to be present in pyrite, the precursor of Fe-oxides in the coal ash (Kolker et al., 1998). Analysis of magnetic separates, enriched in Fe-oxide phases, also shows enrichment in Ni, Co, and Cr, relative to bulk ash samples, especially in fly ash from the low-sulfur unit (Crowley et al., 1998; Cathcart et al., 1997). Leaching results for uranium and antimony in fly ash from the two units shows that significant (40-65%) portions of these elements are removed by HF. The presence of uranium in glassy portions of the fly ash is confirmed by fission track radiography (Zielinski and Budahn, 1998). Large (> 63 µm) cenospheres showed a uniform distribution of uranium with no apparent surface enrichment on the glassy rims. Opaque (oxide-rich) grains also contain moderate amounts of uranium that appear to be uniformly distributed, but the resolution of the radiography technique is not sufficient to distinguish skeletal magnetite from the host glass (Zielinski and Budahn, 1998).

Mass balance of elements between feed coal and solid CCBs was investigated by Crowley et al. (1998), who compared the concentration of selected elements in the feed coal ash to contents in the sum of the solid coal combustion products, calculated assuming the proportions of fly ash and bottom ash produced by the power plant are 75% and 25%, respectively. For most elements, including arsenic, beryllium, cadmium, cobalt, chromium, nickel, antimony, and uranium, the material balance equals or approaches 100%. A major exception is selenium. Only 10% (Unit 3) to 30% (Unit 1) of the selenium was retained in the solid CCBs, consistent with previous work indicating that selenium is a volatile element that can potentially escape in stack gasses. Similar, or even more highly volatile behavior is expected for mercury, but its mass balance was not determined. The mass fraction in the CCBs exceeds 100% for Pb in Unit 1 (140%) and for Mn in Unit 3 (130%). In the first case, the excess is controlled by the Pb content of the fly ash, which itself accounts for 125% of the Pb in the feed coal ash. In the second case, the bottom ash is enriched in Mn by a factor of 2, relative to the fly ash, possibly due to contamination.

Environmental Leaching Studies

In order to investigate the leachability of metals from the Kentucky CCBs, short-term deionized-water batch leaches were performed over periods ranging from a few minutes to 18 hours, with select samples placed into long-term (> 1 year) flow columns (Rice et al., 1999). Experimental conditions may provide an analogue to natural conditions in waste disposal sites exposed to infiltration of dilute meteoric water. The behavior of elements such as Cu, Ni, Cr, Zn, Mn, Mo, As, and U was investigated. Comparing averages for 12 monthly samples of high-S fly ash, low-S coarse fly ash, and low-S fine fly ash, all leached for 18 hours, significant differences were found in pH and average percentage of metals extracted. Average pH of the18-hour leachates ranged from 4.6 in the low-S fine ash to 11in the high-S ash. The low-pH leachates from the low-S fine ash had the highest percentages of metals that form cations in solution, and that are present as soluble oxides, extracted after 18 hours. Percentages extracted exceeded 2% of the amount present in the ash for Co (2.6%), Cr (4.4%), Mn (3.8%), Ni (3.8%), and Zn (4.3%). For Cu (28%) and Cd (21%), more than 20% of the total in the ash was extracted under these conditions.

Solution pH, and a series of reactions between the fly ashes and solutions, were found to be the most significant controlling factors determining the leachability and mobility of trace elements (Rice et al., 1999). In short-term (< 1 hour) experiments, leachates initially show a pH minumum, due to dissolution of aluminum sulfate surface coatings on fly ash particles. Within minutes, pH increases as a result of hydrolysis of metal oxides, and concentrations of metals in solution decrease, probably from co-precipitation and adsorption of metals onto secondary phases. In samples lacking sulfate grain coatings, such as the coarse low-S fly ash, initial pH of the leachates can be alkaline (Anderson and Leventhal, 1998). Concentrations of elements such as As, Mo, and U, that form oxy-anions in oxidizing solutions, are highest in the alkaline leachates. High pH-soluble elements like As and U continue to be leached over longer time periods, as seen in the column leaching experiments. The complexity of element speciation over varying pH and the influence of competing reactions between fly ash components and solutions make it difficult for standard short-term leaching tests to adequately predict the behavior of many metals of environmental concern (Rice et al., 1999).

Summary

The Kentucky power plant investigated provided a good opportunity to determine the composition ranges of fly ash and bottom ash produced by two units having differing firing geometries, and burning coals with differing sulfur contents. Monthly samples were investigated in detail using a combined analytical approach to assess mineralogy, bulk composition, element modes of occurrence, mass balance of environmentally sensitive elements, and the potential for mobility of these elements by infiltration of meteoric water into ash disposal sites. Significant chemical variations were found between monthly samples of a given CCB, between ash from the high- and low-S sources, and between coarse and fine fly ash fractions from the low-S boiler. These differences are primarily a consequence of differences and variation in the feedstock. Once in the environment, significant differences in leaching behavior are likely to result from these variations. Thorough characterization of coal ash composition is needed to predict its behavior during use and disposal.

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References

Affolter, R. H., 1998, The chemical composition of feed coal, fly ash , and bottom ash, section D., in Breit, G. N., and Finkelman, R. B., Characterization of coal and coal combustion products from a coal-burning power plant—Preliminary report and results of analyses: U. S. Geological Survey, Open-File Report 98-342, 101 p.

Affolter, R. H., Brownfield, M. E., and Breit, G. N., 1997, Temporal variations in the chemistry of feed coal fly ash, and bottom ash from a coal-fired power plant: Proceedings of the 1997 International Ash Utilization Symposium, Lexington, KY, p. 757-764.

American Society for Testing and Materials (ASTM), 1988, Annual Book of ASTM Standards, section 4: Construction Materials, vol. 04.01: Cement, Lime, Gypsum.

Anderson, T., and Leventhal, J. S., 1998, Coal ash environmental leaching: pH, section J., in Breit, G. N., and Finkelman, R. B., Characterization of coal and coal combustion products from a coal-burning power plant—Preliminary report and results of analyses: U. S. Geological Survey, Open-File Report 98-342, 101 p.

Brownfield, M. E., Cathcart, J. D., and Affolter, R. H., 1997, Characterization of feed coals and waste products from a coal-burning power plant in Kentucky: Proceedings of the 1997 International Ash Utilization Symposium, Lexington, KY, p. 780-784.

Brownfield, M. E., Affolter, R. H., Cathcart, J. D., O'Connor, J. T., and Brownfield, I. K., 1999, Characterization of feed coal and coal combustion products from power plants in Indiana and Kentucky: Proceedings of the 24th International Technical Conference on Coal Utilization and Fuel Systems, Clearwater, FL, p. 989-1000.

Cathcart, J, D., Reynolds, R. L., Brownfield, M. E., and Hower, J. C., 1997, Chemical, mineralogical, and, magnetic characterization of sized fly ash from a coal-fired power plant in Kentucky: Proceedings of the 1997 International Ash Utilization Symposium, Lexington, KY, p. 785-792.

Crowley, S. S., Finkelman, R. B., Palmer, C. A., and Eble, C. F., 1998, Characterization of hazardous trace elements in solid waste products from a coal-burning power plant in Kentucky, section E., in Breit, G. N., and Finkelman, R. B., Characterization of coal and coal combustion products from a coal-burning power plant—Preliminary report and results of analyses: U. S. Geological Survey, Open-File Report 98-342, 101 p.

Eble, Cortland F., 1998, Sample collection procedure, section B., in Breit, G. N., and Finkelman, R. B., Characterization of coal and coal combustion products from a coal-burning power plant—Preliminary report and results of analyses: U. S. Geological Survey, Open-File Report 98-342, 101 p.

EPRI (Electric Power Research Institute), 1998, Identification of arsenic species in coal ash particles, EPRI, Palo Alto, CA, TR-109002, 168 p.

Dulong, F., 1998, X-ray diffraction analysis, section R., in Breit, G. N., and Finkelman, R. B., Characterization of coal and coal combustion products from a coal-burning power plant—Preliminary report and results of analyses: U. S. Geological Survey, Open-File Report 98-342, 101 p.

Finkelman, R. B., Kolker, Allan, and Palmer, C. A., 1997, Modes of occurrence of arsenic and other trace elements in fly ash from a Kentucky power plant: Proceedings of the 1997 International Ash Utilization Symposium, Lexington, KY, p. 239-246.

Hower, J. C., Trimble, A. S., Eble, C. F., Palmer, C. A., and Kolker, Allan, 1999, Characterization of fly ash from low-sulfur and high-sulfur coal sources: Partitioning of carbon and trace elements with particle size: Energy Sources, v. 21, p. 511-525.

Kolker, Allan, and Finkelman, R. B., 1998, Potentially hazardous elements in coal: Modes of occurrence and summary of concentration data for coal components: Coal Preparation, v. 19, p. 133-157.

McGee, J. J., Finkelman, R. B., and Pontolillo, J., 1995, Microanalysis of hazardous air pollutants in fly ash and bottom ash from a coal-burning power plant: Geological Society of America, Abstracts with Programs, v. 27, no. 6, p. 139.

Mukhopadhyay, P. K., Lajeunesse, G., and Crandlemire, A. L., 1996, Mineralogical speciation of elements in feed coal and their combustion residues from an eastern Canadian coalfield and power plant: International Journal of Coal Geology, v. 32, p. 279-312.

Palmer, C. A., Finkelman, R. B., Krasnow, M. R., and Eble, C. F., 1998a, Laboratory leaching behavior of environmentally sensitive trace elements from fly ash and bottom ash samples, section F., in Breit, G. N.and Finkelman, R. B., Characterization of coal and coal combustion products from a coal-burning power plant—Preliminary report and results of analyses: U. S. Geological Survey, Open-File Report 98-342, 101 p.

Palmer, C. A., Crowley, S. S., Mroczkowski, S. J., Finkelman, R. B., and Bullock, J. H., Jr., 1998b, the use of sequential laboratory leaching to quantify the modes of occurrence of trace elements in coal: Proceedings of the 15th Pittsburgh Coal Conference, 28 p., CD-ROM.

Pontolillo, J., 1998, Fly ash petrography, section S., in Breit, G. N., and Finkelman, R. B., Characterization of coal and coal combustion products from a coal-burning power plant—Preliminary report and results of analyses: U. S. Geological Survey, Open-File Report 98-342, 101 p.

Rice, C. A., Breit, G. N., Fishman, N. S., and Bullock, J. H., Jr., 1999, Leachability of trace elements in coal and coal combustion wastes: Proceedings of the 24th International Technical Conference on Coal Utilization and Fuel Systems, Clearwater, FL, p. 355-366.

Tondu, E., Thompson, W. G., Whitlock, D. R., Bittner, J. D., and Vasiliauskas, A., 1996, Commercial separation of unburned carbon from fly ash: Mining Engineering, v. 48, p. 47-50.

Zielinski, R. A., and Budahn, J. R., 1998, Radionuclides in fly ash and bottom ash: Improved characterization based on radiography and low energy gamma-ray spectrometry: Fuel, v. 77, no. 4, p. 259-267.

Appendix 1. Averages of geochemical results for major elements and selected trace elements of interest.

1A: Results for high-sulfur unit (Unit 1). Modified from Affolter (1998) and Brownfield et al., 1999.

Oxide (wt. %) or Element (ppm)	Feed Coal Mean (whole coal basis) ± standard deviation[1]	Feed Coal Mean (ash basis) ± standard deviation[1]	Fly Ash Mean	Bottom Ash Mean
(ash %)	10		99	93
SiO_2		42 ± 4.1	47 ± 2.2	44 ± 2.7
TiO_2		0.98 ± 0.07	1.0 ± 0.07	0.85 ± 0.11
Al_2O_3		21 ± 1.2	22 ± 0.78	20 ± 1.7
Fe_2O_3		21 ± 3.7	19 ± 3.8	24 ± 5.1
MgO		0.76 ± 0.07	0.83 ± 0.06	0.71 ± 0.08
CaO		3.6 ± 0.72	3.6 ± 0.54	3.8 ± 0.63
Na_2O		0.61 ± 0.24	0.66 ± 0.21	0.58 ± 0.21
K_2O		1.8 ± 0.26	1.9 ± 0.27	1.5 ± 0.21
P_2O_5		0.26 ± 0.12	0.25 ± 0.09	0.16 ± 0.04
		Trace Elements (ppm)		
As	12 ± 6.1	120 ± 58	170 ± 67	11 ± 5
Be	1.5 ± 0.55	15 ± 5.4	19 ± 6.7	14 ± 5
Cd	0.36 ± 0.36	3.6 ± 3.6	5.5 ± 3.1	0.8 ± 0.25
Co	4.6 ± 1.8	45 ± 17	59 ± 20	49 ± 16
Cr	15 ± 2.6	150 ± 21	170 ± 12	150 ± 12
Hg[2]	0.07 ± 0.06	0.69 ± 0.6	0.39 ± 0.3	0.02 ± 0.01
Mn	25 ± 6.3	250 ± 57	270 ± 63	330 ± 63
Ni	18 ± 10	170 ± 97	220 ± 110	210 ± 92
Pb	11 ± 8.6	110 ± 77	150 ± 67	46 ± 21
Sb	0.87 ± 0.55	8.7 ± 5.2	13 ± 5.9	3.5 ± 1.6
Se[2]	2.5 ± 0.62	26 ± 6.2	8.9 ± 4.4	0.59 ± 0.76
Th	2 ± 0.24	20 ± 1.5	22 ± 3.1	21 ± 2.2
U	1.6 ± 1.3	16 ± 13	19 ± 8.1	14 ± 7.3

[1]Standard deviation based on a minimum of 10 determinations and a maximum of 12 determinations.
[2]Values for Hg and Se in coal ash computed from determinations on whole coal.

1B: Results for low-sulfur unit (Unit 3). Modified from Affolter (1998) and Brownfield et al., 1999.

Oxide (wt. %) or Element (ppm)	Feed Coal Mean (whole coal basis) ± standard deviation[1]	Feed Coal Mean (ash basis) ± standard dev.	Coarse Fly Ash Mean	Fine Fly Ash Mean	Bottom Ash Mean
(ash %)	9.1		98	98	97
SiO_2		53 ± 6.7	58 ± 3.3	55 ± 3.8	57 ± 5.2
TiO_2		1.6 ± 0.14	1.5 ± 0.15	1.6 ± 0.13	1.4 ± 0.22
Al_2O_3		30 ± 1.6	30 ± 1.4	30 ± 1.3	26 ± 2.9
Fe_2O_3		4.4 ± 1.0	4.2 ± 0.71	4.9 ± 0.4	8.2 ± 3.3
MgO		0.85 ± 0.16	0.97 ± 0.16	1.1 ± 0.11	0.81 ± 0.14
CaO		1.3 ± 0.3	1.2 ± 0.29	1.4 ± 0.16	1.1 ± 0.37
Na_2O		0.41 ± 0.09	0.37 ± 0.07	0.41 ± 0.06	0.32 ± 0.1
K_2O		2.1 ± 0.27	2.5 ± 0.46	2.6 ± 0.3	2.1 ± 0.37
P_2O_5		0.18 ± 0.07	0.18 ± 0.07	0.28 ± 0.06	0.11 ± 0.05
Trace Elements (ppm)					
As	3.3 ± 0.73	37 ± 8.8	54 ± 20	91 ± 19	54 ± 62
Be	2.4 ± 0.35	27 ± 3.7	22 ± 4.1	27 ± 4.3	16 ± 2.5
Cd	0.07 ± 0.03	0.8 ± 0.32	0.8 ± 0.22	1 ± 0.41	--
Co	11 ± 2.2	120 ± 23	97 ± 24	150 ± 37	61 ± 9.2
Cr	19 ± 3.1	210 ± 26	190 ± 26	230 ± 22	200 ± 64
Hg[2]	0.034 ± 0.04	0.31 ± 0.4	0.02 ± 0.005	0.02 ± 0.005	0.24 ± 0.3
Mn	14 ± 3.9	150 ± 45	210 ± 69	230 ± 36	480 ± 320
Ni	17 ± 2.5	190 ± 26	160 ± 32	220 ± 42	140 ± 25
Pb	11 ± 0.84	120 ± 11	100 ± 16	170 ± 33	380 ± 920
Sb	0.71 ± 0.07	7.9 ± 0.98	8.9 ± 1.7	15 ± 3.4	10 ± 23
Se[2]	5.6 ± 1.8	5.6 ± 1.8	0.82 ± 1.4	1.1 ± 1.7	1.7 ± 1.5
Th	2.9 ± 0.49	32 ± 5.6	30 ± 5.5	31 ± 2.9	29 ± 2.9
U	1.4 ± 0.32	16 ± 3.9	15 ± 3.4	21 ± 4.1	10 ± 2.7

[1]Standard deviations computed from a minimum of 9 determinations and a maximum of 14 determinations.
[2]Values for Hg and Se in coal ash computed from determinations on whole coal.
--Insufficient number of analyses with values above detection limit.

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[3]Allen Kolker has been a Geologist with the U.S. Geological Survey (USGS) Energy Resources Program in Reston, Virginia since 1996. He received his Ph.D. in Geochemistry from the State University of New York at Stony Brook in 1989, his M.S. in Geology from the University of Massachusetts in 1980, and his B.A. in Geology from Franklin and Marshall College, Lancaster, Pennsylvania, in 1977. Kolker's current research interests include coal geochemistry, trace elements, environmental geochemistry, microbeam analytical instruments (electron microprobe, ion probe, etc.), geochemistry and health issues, and trace elements in acid mind drainage and groundwater systems. He serves as Project Manager for a collaborative program on trace-element transformations during coal combustion.

PHYSICAL AND ENGINEERING PROPERTIES OF COAL COMBUSTION BY-PRODUCTS

Yoginder P. Chugh[1], Debasis Deb and C.B. Raju
Department of Mining and Mineral Resources Engineering
Southern Illinois University
Carbondale, Illinois

Coal Combustion By-Products Issue: An Overview

Over 80% of the 1.2 billion tons of coal annually produced in the USA are combusted for power generation. This results in generation of about 110 million tons of by-products known as "Coal Combustion By–products (CCBs)." These include fly ash, bottom ash, and boiler slag from conventional boilers, and Flue Gas Desulfurization (FGD) by-products from advanced clean coal technology combustors. Based on American Coal Ash Association collected statistics, the generation of CCBs has increased from about 78 metric tons in 1987 to about 110 metric tons in 1998; an increase of about 3% annually. Over 60% of the CCBs are generated as fly ash. An estimate of the average management cost for CCBs in the USA is about $15-20 per ton.

Cost-effective management of CCBs, in an environmentally friendly manner, has been, is, and will be an important problem impacting the economics of coal production and power generation. The U. S. Department of Energy, various States, Electric Power Research Institute, universities, private organizations, and entrepreneurs have provided leadership over the past 20 years to research, develop, demonstrate, and implement new technologies for CCBs management. With implementation of clean coal technologies and Clean Air Act Amendments of 1990, the generation volume of CCBs and FGD by-products will increase and their quality will decrease over the years requiring additional research and development for effective management. The development and recent funding of the Combustion By-Products Recycling Consortium (CBRC) by the National Energy Technology Laboratory is a very timely effort in this direction.

Coal Combustion By-Products Utilization: An Overview

CCBs beneficial use (excluding FGD by-products) has been steadily increasing over the past three decades from about 12% in 1967 to about 29% in 1994 and 34.7% in 1998. If FGD by-products are included, the usage has increased from about 23% in 1987 to about 29% in 1998. The remaining CCBs are disposed in on-site ponds, nearby abandoned or active mine sites, or landfills. Approximately 33-35% each of fly ash, bottom ash, and boiler slag was utilized in 1998.

Based on 1998 data, the major uses of fly ash include cement/concrete applications (16%), waste stabilization (5%), structural fills (4%), mining applications (3%), and road base/subbase (2%). Bottom ash is primarily used in road base/subbase (30%), structural fills (20%), snow and ice control (14%), and cement/concrete applications (12%). So boiler slag is mostly used for blasting grit/roofing shingles (75%). The FGD by-products are mostly consumed in wallboard industry (7%). These numbers may vary considerably from year to year; however, the overall use trend continues to be upward.

Coal Combustion By-Products as a Material: An Overview

CCBs represent incombustible materials left after combustion of coal in conventional and/or advanced clean coal technology combustors. Therefore, they represent inherent incombustible matter in coal, and sorbents for clean coal technologies and their chemical transformation during coal combustion and subsequent gas cleanup operations. Therefore, chemical composition of coal, inorganic matter associated with coal, and sorbents affect CCBs properties as a material.

Chemically, coal is an organic material and it primarily contains carbon, hydrogen, nitrogen, oxygen, and sulfur. The primary inorganic constituents associated with the coal include clay minerals, silica, carbonates, and sulfides. These constituents may decompose completely, partially or remain inert during the combustion process with temperatures ranging from 800-1500/C depending upon the technology used. Similarly, decomposed products may combine chemically to form new minerals based on reactivity, catalytic reactions, and temperature. The resulting CCBs are primarily made of silicon, aluminum, iron, calcium, magnesium, sulfur oxides, and several trace elements such as arsenic, selenium, lead, mercury, boron, etc. Most of these elements combine with oxygen to form corresponding oxides. Since combustion of coal is never complete, CCBs also contain varying amounts of unburned carbon and other matter (LOI). The chemical nature of CCBs may also vary based on clean coal and FGD technologies used such as fluidized bed combustion (FBC), wet scrubber, dry sorbent injection, etc. Tishmack (1997) and others have provided a good review of mineralogical composition of CCBs.

Typical Physical and Engineering Characteristics of Common CCBs

Fly Ash. A SEM micrograph of an F-ash from the Midwest and a C-ash is given in Figure 1. Table 1 shows a range of properties for F-fly ash and C-fly ash. It is a relatively dry (2-3% moisture content), cohesionless material with mean particle size of 20-30 μm (Figure 2). Particles range in size from 5 microns to about 7 mm. Specific area varies depending upon the mean particle size and the uniformity coefficient. The specific gravity of the ash varies from 1.9 to about 2.4. Most fly ash particles are hollow and spherical in shape. C-fly ash may also contain solid, irregular shaped particles. The size uniformity coefficient for both fly ashes is generally high. Since fly ash does not contain clays, it has no plastic limit. The fly ash may be classified as either F-ash or C-ash based on ASTM C-618 requirements shown in Table 2. The classification is primarily based on the sum of oxides of silicon, iron, and aluminum (50 to 70% for C-ash, 70% for F-ash). Bituminous coals invariably produce F-ash while lignite or subbituminous coal can produce either F-ash or C-ash based on calcium content in coal (Table 3). The free lime content indicated by calcium oxide must be less than 30% in F-ash and less than 40% in C-ash. Typical values of CaO in F-ash are less than 10% while for C-ash, they range from 15-20%.

Table 1. A Few Physical Properties of CCBs **.**

Properties	**C-Type Fly ash (Ref: McCarthy et al., 1987)**	**F-type Fly ash (Ref: Chugh et al., 1998)**
Mean particle size	45.0 μ	32.6 μ
As-received moisture	0.02 %	16.0%
CCE	44.46%	3.7%
Paste pH	NA	8.8

Table 2. Classification of Fly Ssh (ASTM C-618)**.**

Chemical:		**Class F**	**Class C**
$SiO_2 + Al_2O_3 + Fe_2O_3$	min	70	50
SO_3 , %	max	5	5
LOI, %	max	6	6
Alkalis, %	max	1.5	1.5
Physical:			
Fineness, %		34	34
Strength Activity 7 days (with PC), % of control		75	75
Strength Activity 28 day (with PC), % of control		75	75
Soundness, % (autoclave expansion)	max	0.8	0.8
Density, max variation from average (%)		5.0	5.0

Table 3. Calcium Content in Various Types.

Type of coal	CaO in ash
Bituminous	1- 8%
Subbituminous	6-12%
Lignite	10-32%

Typical oxide compositions for F-ash and C-ash are given in Table 4. ASTM C-311 dictates sampling and testing procedures for fly ash. Both types of fly ash demonstrate good compaction characteristics although C-ash demonstrates higher maximum density because of irregular particle shape. Figure 3 shows particle size distributions of different CCBs.

F-fly ash is a "pozzolonic" material only and requires addition of activators like cement or lime to initiate cementation reactions. C-fly ash on the other hand is both pozzolonic and self-cementing (because of available free lime) and does not require activation. Siliceous or alumino-silicate glass is the primary active component of F-fly ash, while for C-fly ash it is calcium alumino-silicate glass. Hydration of fly ash is not only governed by chemical composition but also by the crystallanity of ash.

Fluidized Bed Combustion By- Products. FBC is a well-established clean coal technology. An FBC combustor operates at a much lower temperature (about 800ºC) and reduces generation of nitrous oxides. However, the amount of LOI is increased in the ashes. Over the next decade, several new FBC units are being planned in the USA, particularly in the Midwest. Just as in a pulverized coal boiler, fly ash and bottom ash (or spent-bed ash) are produced in the ratio of about 60:40 in a FBC boiler. Typical SEM micrograph of FBC fly ash is shown in Figure 4. FBC fly ash mean particle size is similar to pulverized coal fly ash (about 20-30 μm) and most of the particles are of prismatic shape. The uniformity coefficient is also similar to F-fly ash and C-fly ash. The specific gravity varies from 1.9 to 2.4. The particle size of FBC is small and thus has the highest potential for fugitive dust generation (Figure 3).

Table 4. Chemical and Physical Characterization of Fly Ash.

Composition	SIPC	SIPC	SIUC	Cement
LOI	7.11	1.65	9.73	-
SiO_2	40.99	45.45	36.10	21.79
Al_2O_3	15.73	16.28	13.89	4.46
Fe_2O_3	22.15	23.72	11.08	2.96
CaO	4.31	7.38	18.00	62.20
NaO_2	0.7	0.29	0.55	0.09
MgO	0.57	0.55	0.43	4.06
SO_3	2.57	1.62	8.23	2.69
K_2O	3.43	1.92	1.44	0.48
Mn_2O_3	0.15	0.16	0.08	-
P_2O_5	1.21	0.16	0.40	-
TiO_2	1.08	0.81	0.40	-

Typical oxide composition for FBC fly ash and FBC spent bed ash is given in Table 5. The CaO content of FBC fly ash typically varies from 15 to 30%, while it is 30-45% for the spent-bed ash. Because of the high CaO content, the ash is highly self-cementing and produces very large amount of heat during the hydration process. The ash has much smaller amount of glassy material as compared to pulverized coal ash because of lower temperatures in the combustor. Since FBC technology is used for high sulfur coals, the ash contains more Fe as oxides.

The spent–bed ash is generally much coarser in size and resembles sand (70-80 μm) with lower uniformity coefficient than FBC fly ash. The LOI values in FBC fly ash and spent-bed material vary over a wide range depending upon the load on the boiler.

Table 5. Typical Oxide Composition of FBC Fly Ash and FBC Spent Bed Ash (Ref: Chugh, et al., 1998).

Chemical composition	FBC Fly Ash	FBC Spent Bed Ash	ASTM C 618 Fly ash Specifications
SiO_2	22.10	9.7	
Al_2O_3	6.80	3.69	
Fe_2O_3	6.67	2.16	
Total SiO_2+Al_2O_3+ Fe_2O_3	35.57	15.55	Class C: 50% Min Class F: 70% Min
SO_3	15.67	24.42	
CaO	38.70	53.10	
MgO	1.29	0.88	
LOI	5.46	0.80	6.0 Max
Free Moisture	0.11	0.00	
Water of Hydration	0.71	2.65	
Total Na_2O	0.50	0.16	
Total K_2O	1.12	0.39	
Others (TiO_2+P_2O_5+ SrO+BaO)	0.83	2.04	
Paste pH	12.2	12.00	

The use of FBC by-products in development of construction materials requires their prehydration to convert anhydrite to gypsum. This can be achieved through addition and thorough mixing of 10 to 25% water in two steps.

An additional area of concern in the use of FBC by-products is the higher amount of sulfates in ash. Limited available data indicates that sulfates in the range of 5 to 10% only delays the hydration reactions but have no effect on the ultimate strength. At higher sulfate contents, durability is significantly reduced. Formation of ettringite during initial hydration and its subsequent swelling can have a negative effect on the strength and performance of the structure. These issues can also be important for C-fly ash.

Flue Gas Desulfurization By-Products. Flue gas desulfurization is an established technology to remove SOx. The flue gases are forced to react with chemical sorbents in a wet slurry form or dry form in a scrubber. Over 90% of the existing FGD systems utilize limestone ($CaCO_3$), calcium hydroxide, Ca $(OH)_2$, or calcium oxide (CaO) as the sorbent. The resulting CCBs may be sulfite-rich or sulfate-rich depending upon whether the chemical reactions are oxygen inhibited or not.

Typical SEM microphotographs for sulfite-rich and sulfate rich FGD by-products are shown in Figures 5 and 6. Particle size and particle shape distributions vary significantly from plant to plant. Typical particle size ranges 0.88 mm to 1 mm. These variables have significant effect on compaction and strength development characteristics. FGD by-products contain some fly ash carried with flue gases. Because of the added sorbent, oxides of iron, silicon, and iron are smaller than for pulverized coal ash. Sulfite–rich by-products demonstrate thixotropic behavior and are extremely difficult to dewater. Sulfate-rich sludge has very similar characteristics to natural gypsum and is used primarily for wallboard applications. A common application for sulfite-rich wet scrubber sludge is to stabilize it with fly ash and 1-2% lime and use it as a structural fill.

Typical oxide compositions for wet scrubber sludge are given in Table 6. Free lime content is very low and therefore their reactivity is generally low.

Importance of Physical and Engineering Properties in CCBs Utilization

Based on an extensive literature review, the following physical properties have been identified as important.

- Particle Size Distribution (ASTM D 422)

- Minus 325 Sieve Fineness (ASTM C 311)
- Blaine Fineness (ASTM C 204)
- As received
- 325 Sieve Fraction
- Surface area
- Moisture Content (ASTM C 311)
- Specific Gravity (ASTM C311)

Table 6. Typical Oxide Composition of PCC Fly Ash and Scrubber Sludge (Ref: Chugh et al., 1998).

Chemical composition	PCC Fly Ash	Scrubber Sludge	ASTM C 618 Fly ash Specifications
SiO_2	55.90	0.45	
Al_2O_3	15.40	BDL	
Fe_2O_3	16.10	BDL	
Total SiO_2+Al_2O_3+ Fe_2O_3	87.40	0.45	Class C: 50% Min Class F: 70% Min
SO_3	1.15	58.73	
CaO	5.06	41.0	
MgO	0.78	BDL	
LOI	0.58	0.00	6.0 Max
Total Na_2O	1.48	BDL	
Total K_2O	1.93	0.02	
Free lime	0.10	0.23	
$CaSO_4$	--	99.87	
$CaSO_3$	--	BDL	
$CaCO_3$	--	BDL	
Paste pH	12.26	7.99	

Similarly, the following engineering properties have been identified as important.

- Loss on Ignition (ASTM C311)
- Compaction Properties (ASTM D-698, ASTM C-593)
- Pozzolonic Activity Index (ASTM C 618)
- Atterberg Limits (ASTM 4318)
- Swelling Properties
- Chugh's Engineering Test for air entrainment
- Calcium Carbonate Equivalent (CCE)
- Paste pH (ASTM D4972)
- Durability (ASTM 593)
- Flow properties (ASTM C 109)
- Sulfate resistance (ASTM C1012)

These properties will be discussed in relation to various applications for CCBs in later sections of this paper.

Classification of Beneficial Use Applications

Based on a literature review, which is rather extensive, an attempt is made here to classify beneficial use applications based on CCBs significant properties. These are:

- Large volume (structural fills, embankments, unstabilized road subbase)
- Cementitous/Pozzolonic (cement/concrete, flowable fills, structural materials, waste stabilization)

- Chemical/Neutralization properties (acid mine drainage, mine reclamation)
- Abrasive properties (blasting grit, roof shingles, snow and ice removal)
- Mineralogical properties (magnetite removal, aluminum alloys, silicon alloys, etc.)
- Soil enhancement properties (artificial soils, soil amendments)

Figure 7 shows utilization of CCBs for various applications in the United States for the year 1998. A discussion of desirable physical and engineering properties for each type of application follows.

Large Volume Applications

These applications generally represent low value, large volume applications such as structural fills, embankments, road subbase, etc. The important physical properties for CCBs will be particle shape and particle size distribution since both of these will impact their compaction characteristics, porosity, and permeability and strength and freeze–thaw durability. Particle size, particle shape, and moisture content will impact fugitive dust generation and control. FBC fly ash may not be well suited for this application unless it is modified by mixing with F-fly ash, and/or some amount of water. On the other hand, POZOTEC material (a combination of poor quality F-fly ash and wet scrubber sludge with 1-2% lime) may be best suited for this application, because of a combination of prismatic shape and spherical shape particles and appropriate water content to control dust and to achieve optimum moisture-density relationships. A ponded mixture of low quality F-fly ash and bottom ash also may be suitable for the above mentioned reasons. Such a mixture has found widespread use in housing construction around the Springfield, Illinois area. Such mixture materials are generally environmentally benign because most of the leaching has already occurred.

Cementitious/Pozzolanic Properties

This represents the largest use of CCBs and involves their most important property (pozzolonic and/or cementitous). ASTM C-618 test requirements for physical, chemical, and engineering properties adequately serve to determine if a CCB can be effectively used. The use of C-Fly ash is generally limited by the amount of LOI. Supplementary optional requirements for physical and chemical properties may be imposed depending upon the application. Flexible pavement design recommends similar requirements for CCBs except for LOI, which is 10% for F-fly ash and 6% for C-fly ash. The requirements for CCBs to be used in waste stabilization could be even less stringent. Pozzolonic activity index is a good measure of success in using the cementitious and pozzolonic properties. Sulfate resistance could be a very important variable for using FBC fly ash. Flow properties are important in using a fly ash for controlled low strength material (CLSM).

Hydration characteristics of a CCB are influenced by the form in which the calcium compounds exist. In soil/waste stabilization applications, where good cementation is essential, hydration chemistry could be very critical. Where fly ash is used as a drying agent or to reduce shrink–swell potential of clay soils, hydration characteristics may not be very important. Therefore, CCBs performance for each application should be studied.

In development of low and medium value and high fly ash volume lightweight structural materials, ability to foam CCBs is extremely critical. “Foam Index Test” has been used to some extent by the cement–concrete industries. Chugh (1998) developed and used a test similar to pozzolonic activity index test. In this test, 100 grams of CCBs–binder (Ordinary Portland Cement, Type I) mix is tested for increase in bulk density with increasing water content until an equilibrium value is achieved (Figure 8). Then, in a separate similar test, increasing amount of foam or foaming chemical may be added around point “A” in the figure to document decrease in bulk density and the lowest achievable density (Figure 9). Using this approach, the minimum amount of water/powder ratio, the point at which foam must be added, foamability, and minimum achievable density can be determined. This has helped tremendously to achieve maximum strength with least amount of foam in our research on development of lightweight materials for use in mines.

It is important to note that addition of CCBs will change compaction characteristics and, therefore, the moisture–density relationship. A delay in compaction may have a detrimental effect on the strength achievable with stabilized soil (Ferguson, 1993). This is clearly shown in Figure 10.

C-Fly ash and other self–cementing ashes may be used as a soil-drying agent to perform compaction. Moisture content can be easily reduced 10 to 20%. Similarly, fly ashes may also be used, instead of lime stabilization, to reduce swelling potential of clay soils. Fly ashes have also been successfully used for soil stabilization to increase shear strength.

Chemical and Neutralization Properties

Amendment of acidic soils and control of acid mine drainage from coarse coal refuse and fine coal refuse are examples of beneficial use applications using chemical and neutralization properties. Acid–base neutralization potential, paste pH, particle size distribution, and alkalinity rate release are some of the properties of interest. Some fly ashes demonstrate initially acidic pH which slowly changes to alkaline pH. FBC fly ash and FBC spent-bed material are good candidates for these applications because of high CaO content. Several mines in the Midwest are using poor quality C-fly ash to achieve the same goal.

Chugh (1998) demonstrated a novel application to effectively manage fine coal processing waste (FCPW) in conjunction with CCBs with financial support from the Office of Coal Development and Marketing of the State of Illinois, and National Energy Technology Laboratory of the U.S. Department of Energy. Currently, two of the paper authors (Chugh and Raju) are involved in extending the concept to develop direct vegetation concepts on FCPW as well as fly ash ponds. Paste pH, acid–base neutralization potential (CCE), CaO content, sulfate content, and particle size distribution properties have been used to achieve success.

Abrasive Applications

These represent low value applications. Particle size and shape and its strength and toughness are the primary physical properties of interest.

Mineralogical Properties

Recovery of magnetite from fly ash, use of fly ash in aluminum alloys, addition of fly ash as a raw material in cement manufacture, development of pozzolon and quick setting cements utilize mineralogical properties.

Soil Enhancement Applications

Addition of CCBs can benefit the soil as well as its vegetation characteristics by modifying its physical and chemical characteristics. Particle size and shape, alkalinity, and availability of several micronutrients in CCBs (except nitrogen and phosphorous) have been used to amend soil texture for increased water infiltration and acidity, and to supply some of the nutrient needs of the agricultural soil. FBC by-products, C-Fly ash, and FGD oxidized wet scrubber sludge are the primary CCBs used for this purpose. Most of the wet scrubber sludge around Springfield, Illinois is used in this manner. Korcak (1996) has identified Ca:Mg ratio, reduction in potassium (K) due to high calcium CCBs addition, reduction in availability of phosphorous (P) to plants, and high soluble salts as the major problems in using CCBs for soil enhancement and mine reclamation. Addition of organic matter to high calcium CCBs can help overcome some of the problems. For these applications, physical and engineering properties are not as critical as the chemical and micronutrient properties. The sulfite-rich scrubber sludge is generally much more difficult to manage than is sulfate-rich sludge. The use of CCBs can also increase infiltration rates, efficient use of water, and depth of roots. Korcak 1998), Dick et al (1999), and Dick et al (2000) have provided a more detailed discussion of beneficial uses of CCBs and FGD by-products/for agriculture.

Concluding Remarks

Coal combustion by-products (including flue gas desulfurization by-products) are complex, non-homogeneous materials with significant variability from plant to plant. The materials have potential for beneficial use in a variety of applications including construction materials, mine land reclamation, soil amendment, structural fills, and extraction of valuable trace elements. The use of physical and engineering properties must be evaluated for each project both because of high variability in properties, and because currently established tests may not be representative of the field performance. Tremendous opportunities exist to develop meaningful beneficial use applications for

CCBs—using their appropriate physical and engineering properties—with some applied research to make each project successful.

References

Chugh, Y.P, F. Brackebusch, and J. Carpenter, 1998, " Management of Dry Flue Gas Desulfurization By-Products in Underground Mines", US DoE Project Report Volume I, pp 176

Chugh, Y.P., and D. Dutta, 1998, "Development and Demonstration of a New Approach for Waste Slurry Management Using Natural Resources Utilization By-Products", Final Report, Illinois Clean Coal Institute

Dick W.A., J.M. Bigham, R. Forster, F. Hitzhausen, R. Lal, R. Stehouwer, S. Traina, W. Wolfe, R. Haefner, and G. Rowe, " land Application Uses for dry flue gas desulfurization by-products: phase 3. EPRI Report TR-112916, 1999, Electric Power Research Institute, Palo Alto, California.

Dick, W.A., R.C. Stehouwer, J.M. Bigham, W.E. Wolfe, Y.L. Hao, D.C. Adriano, J.H. Beeghley, and R.J. Haefner, " Beneficial uses of FGD By-Products: examples and case studies of land application, P.505-536. 2000, In J.F. Power and W.A. Dick (Eds.), Land Application of Agricultural, Industrial, and Municipal By-Products, Soil Science Society of America, Madison, WI

Ferguson, G., 1993, "Use of self-cementing fly ashes as a soil stabilization agent", textbook on Fly Ash for Soil Improvement, Ed. By Kevan D. Sharp, American Society of Civil Engineers, New York, NY, p115.

Gehler, J., 1991, "Recommended Practice: Coal Fly Ash in Pozzolanic Stabilization Mixtures for Flexible Pavement System", Flexible Pavement Manual, Published by ACAA, pp.40

Korcak, R.F, " Agricultural Uses of Coal Combustion By-Products, p.103-1019. In R.J. Wright, P.D. Millner, and R.F. Korcak (Eds.), Agricultural Uses of Municipal, Animal and Industrial By-Products. USDA Technical Information Center, Springfield, VA

McCarthy G.J, O.E. Manz, D.M. Johansen, S.J. Stainwand and R.J. Stevenson, 1987, "Correlations of Chemistry and Mineralogy of Western U.S. Fly Ash", Materials Research Society Symposium Proceedings, Vol. 86, pp. 109-112.

Saylak, D., G. Sorensen, and A. Gadalla, July 1994,"Use of FGD Gypsum and Bottom Ash in Roadway and Building Construction", EPRI Report, EPRI TR- 103856.

Stevenson R.J. and T.P. Huber, 1987, "SEM Study of Chemical Variation in Western U.S. Fly Ash", Materials Research Society Symposium Proceedings, Vol. 86, pp. 99-108.

Tishmack, Jody K.' Bulk Chemical and Mineral Characteristics of Coal Combustion By-Products (CCB)', Proceedings of the Coal Combustion By-Products Associated with Coal Mining–Interactive Forum, SIUC at Carbondale October 29-31, 1996, ed. by Yoginder P.Chugh, Brandi M. Sangunett and Kimery C. Vories.

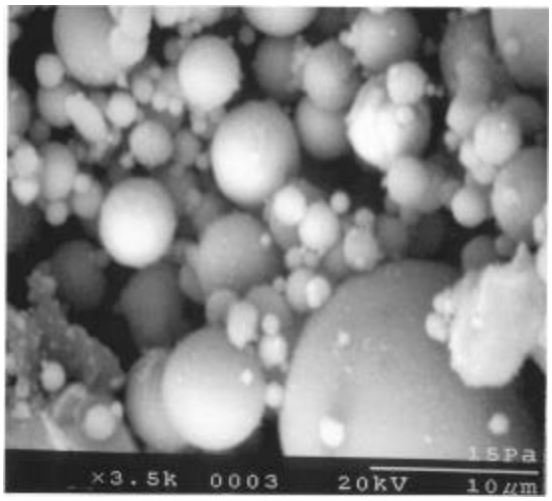

Figure 1: SEM microstructure of F Type -Fly Ash

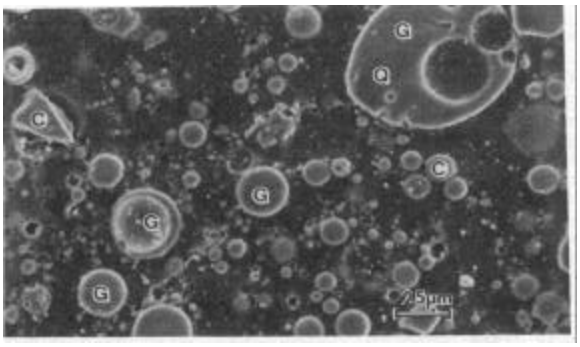

Figure 2. SEM microstructure of C-type fly ash (Ref: Stevenson et al., 1987)

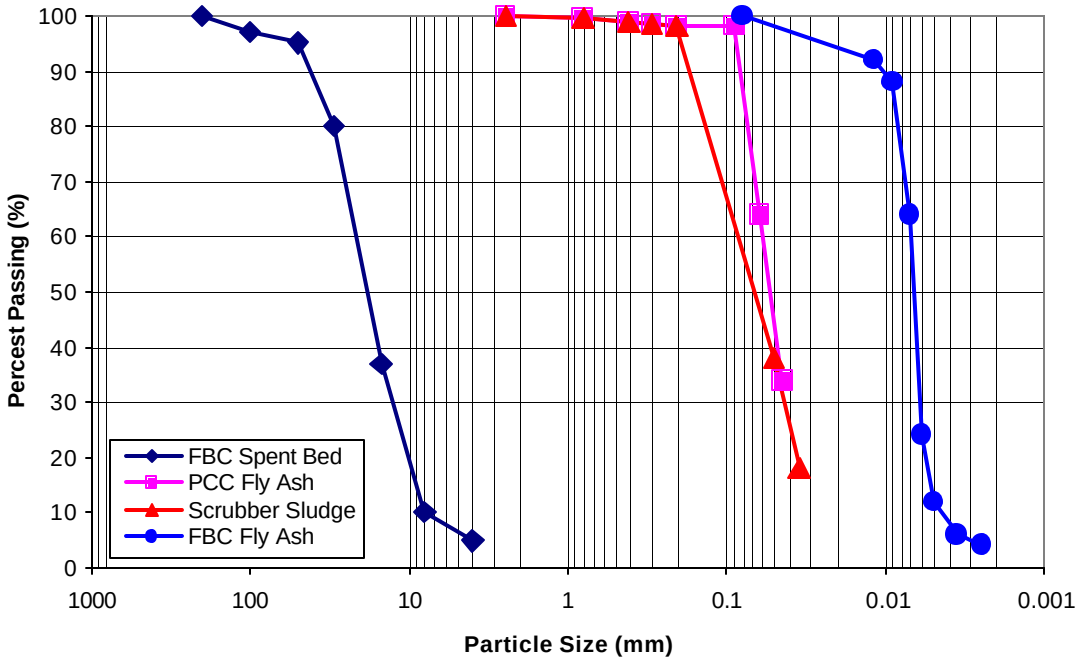

Figure 3. Particle size distribution of CCBs

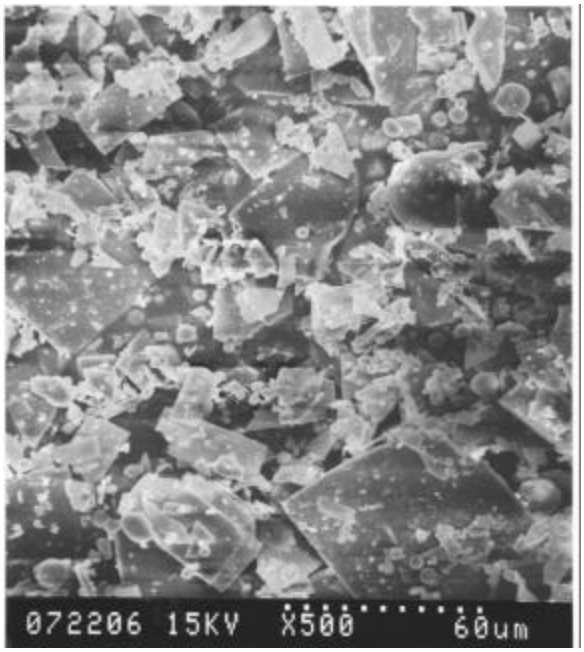

Figure 4: SEM micrograph showing irregular shape of particles in FBC fly ash

Figure 5. SEM of sulfite rich FGD by-products (Ref: Saylak et al., 1994)

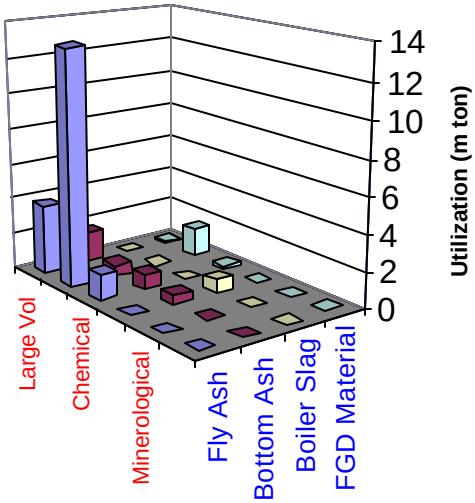

Figure 7. Usage of Dry and Moist CCBs based on Different Application

Figure 6. SEM of Sulfate rich FGD by-products (Ref: Saylak et al., 1994)

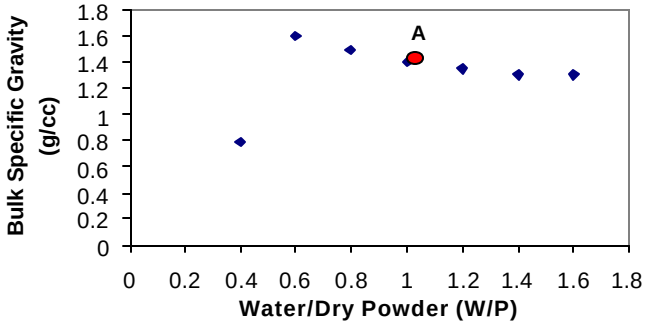

Figure 8. Variation in bulk specific gravity of mix with different W/P ratios (Ref: Chugh et al., 1998)

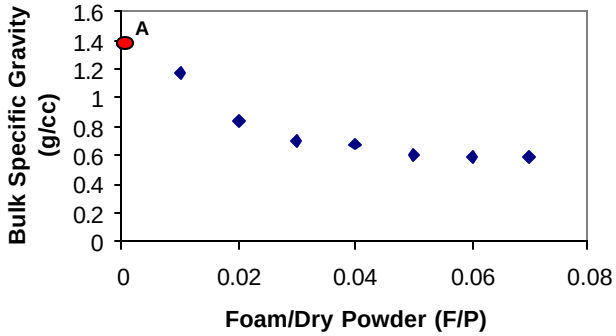

Figure 9. Variation in bulk specific gravity of mix with different F/P ratios (Ref: Chugh et al, 1998)

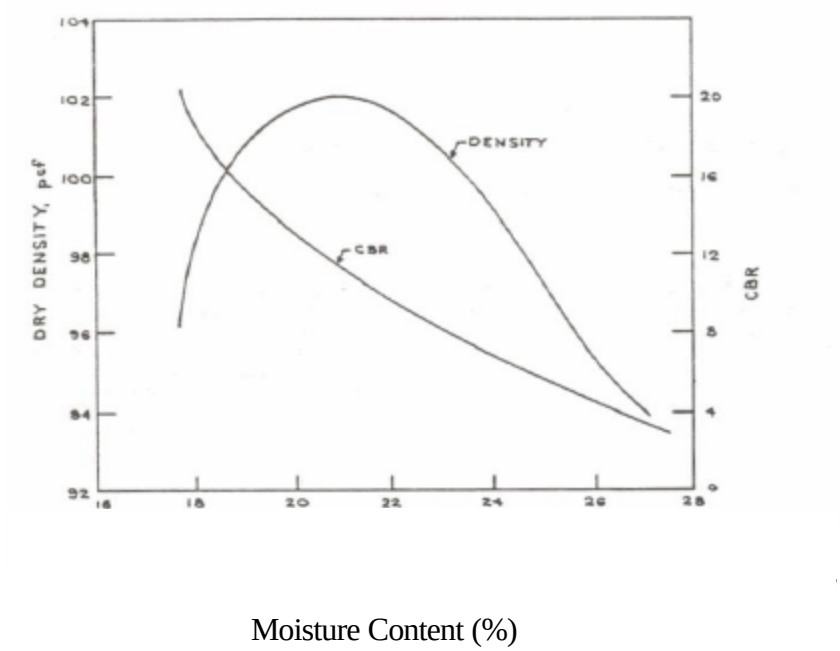

Figure 10. Density-moisture relation in the stabilization of soil using CCBs (Ref: Gehler et al, 1991)

[1]Paul Chugh has BS, MS, and Ph.D. degrees in Mining Engineering; the latter two are from The Pennsylvania State University. Chugh has been at Southern Illinois University for the past 23 years. For the past nine years, he has been actively engaged in research, development, and demonstration studies related to coal combustion by-products. He has commercialized three CCBs-based lightweight structural materials for use in mining industries. Currently, he is developing utility poles from CCBs and hopes to commercialize them in the near future. He is currently Director, Combustion By-Products Recycling Consortium-Midwestern Region.

ENVIRONMENTAL PERFORMANCE AND REGULATORY STATUS OF COAL COMBUSTION BY-PRODUCTS

D.J. Hassett[1] and D.F. Pflughoeft-Hassett
Energy and Environmental Research Center
University of North Dakota
Grand Forks, North Dakota

Introduction

The environmental performance of coal combustion by-products (CCBs) is, because of the nature of environmental science, both well documented and highly controversial. On the basis of scientific evidence, CCBs have been classified in a spectrum of potential for harm that ranges from "toxic-forming" to environmentally benign, and these two descriptions may be referring to a single material because of differences in interpretation of data. It is likely that CCBs can be found worldwide that fit well into either category, with the norm somewhere between the two extremes. It is the opinion of the authors that in truth, the potential for environmental impact for most CCBs is much closer to and often well within the environmentally benign classification. It would be expected that the polarization of positions regarding the environmental performance of CCBs has had an effect on the regulatory process. This appears to be the case.

Environmental Performance

There are two basic approaches to determining the environmental performance of disposed or utilized CCBs. One is to monitor an actual disposal site or utilization project; the other is to predict environmental performance through the use of laboratory studies, usually involving leaching tests. The best approach is field monitoring of actual sites; however, this is not always possible, especially in the case where environmental performance projections are to be determined in advance of actual disposal or use of CCBs. Volumes have been published regarding the use of laboratory leaching for the prediction of environmental impacts of CCBs. An excellent summary of leaching methods has been published that presents more than 50 different leaching tests (Sorini, 1997). As would be expected, some of the tests are suitable for use with CCBs, some are clearly not suitable, and many could be debated. The authors generally use a test developed at the University of North Dakota (UND) Energy & Environmental Research Center (EERC) called the synthetic groundwater leaching procedure (SGLP) (Hassett, 1987). This test was developed over a number of years prior to being published in order to facilitate ongoing ash research at the EERC.

The development of the SGLP was an evolutionary process that progressed as our ash research group gained a more fundamental understanding of the hydration of alkaline CCBs. We observed unusual leaching trends in alkaline CCBs that could lead to reductions in leachate concentrations of select trace elements. It became evident that many published leaching methods were unsuitable for use in the characterization of CCBs because they either utilized too short an equilibration time, thus not taking the effect of hydration reactions into account, or because they utilized leaching solutions that imposed artificial conditions on the ash–water system that would never be encountered under field conditions (Stevenson and others, 1988; Hassett and others, 1991; Hassett, 1994). The preferential use of SGLP by the ash research group at the UND EERC is not to be taken to suggest that there are not other suitable, published leaching methods for prediction of potential for environmental impact of CCBs. Many such tests exist. We simply continue to utilize and develop the SGLP as a part of our ongoing ash research program. There are, however, many leaching tests that are inappropriate for use with CCBs and many examples of the misuse or inappropriate use of leaching tests with CCBs for prediction of potential environmental impacts. It is beyond the scope of this manuscript to discuss the scientifically valid and invalid application of laboratory tests. It may be sufficient to say that in laboratory experiments to predict potential environmental impact, as in other disciplines, "garbage in, garbage out." The use of laboratory protocols to predict field phenomena must be carefully considered with a thorough understanding of the chemistry of the material being studied, field conditions at the site, and a realization of the limitations of laboratory studies to replicate field conditions.

Regulatory decisions have historically been made primarily by a regulatory body that performed research to support its own regulations, of which activity the objectivity has been sharply, and probably rightly, questioned. The primary objective of regulation is to protect the public interest, and many regulations have been developed to address, directly and indirectly, issues of safety and health. Regulatory objectives can usually be accomplished by several routes, but varying degrees of risk may be inherent within these options. The ideal regulation might be one that carries zero safety or health risk to the public; however, zero risk situations are not conducive to progress and are likely not even possible. It is the job of responsible scientists to provide unbiased information so risk can be reasonably assessed and, further, it is essential that scientists present their scientific results and evidence in a fashion understandable to regulators and the public sector. Both the regulators and scientists bear a heavy burden in the accomplishment of these objectives. The success of their interactions can only be measured by the reasonableness of the resulting regulations. Of course, the success rating will vary, depending on who is making the judgement.

CCBs can be held to numerous standards, especially in evaluating results of laboratory leaching. The expectation that leachate generated in a laboratory or collected at a field site meets primary drinking standards is, in the authors' opinion, rather extreme. Primary drinking water standards were developed to assist in evaluating if a water source is safe for human consumption. Leachate standards, however, have been developed with the expectation that leachate generated in disposed material with no interaction with the environment outside the disposal site will undergo changes through interactions with local sediments and through natural attenuation processes, including dilution, dispersion, and chemical attenuation. The argument is then often made, What if someone were to sink a well in an area of ash disposal? The obvious answer is simply that testing of the source water will tell if it is safe for consumption, irrigation, or other intended uses. It is important to realize that there are many natural sources of water as well as sources impacted by human activity that do not meet primary drinking water criteria, thus the need for water treatment plants in most cities. Most of the water on the earth (ocean water) is not potable. Additionally, trace element toxicity for most elements is a function of concentration, not identity; thus the simple presence of selenium or boron does not automatically indicate toxicity.

Public and private sector response to imposed regulations often leaves much to be desired and frequently adds another dimension to the interactions between regulators and scientists. The interpretation of regulations can lead to disagreements between regulators, scientists, and the public and private sectors. The difference between the spirit of the law and the letter is often the basis for the disagreements in interpretation, but it is important to note that development of regulation to cover all situations is not possible, because there are always exceptions. This of course adds to the burden of regulators and scientists. The existence of exceptions also makes it important that the public and private sectors maintain vigilance over regulations. The way to develop responsible and realistic regulations is for all concerned to become involved and begin working together. Working together successfully requires that a level of trust be developed that requires commitment and time as well as open and honest interaction.

Regulatory Status

The regulatory status of coal ash is well summarized in "Barriers to the Increased Utilization of Coal Combustion/Desulfurization By-Products by Government and Commercial Sectors" (Pflughoeft-Hassett, 1999).

The 1976 Resource Conservation and Recovery Act (RCRA) and the 1980 Solid Waste Disposal Act Amendments provide for comprehensive cradle-to-grave regulation of solid waste generation, collection, transportation, separation, recovery, and disposal (Jagiella, 1993; Findley and Farber, 1992; Butler & Binion, 1993). Subtitle C of RCRA and its implementing regulations impose specific federal requirements on materials deemed to be "hazardous," either because of being listed by the U.S. Environmental Protection Agency (EPA) as hazardous or by reason of having hazardous or toxic characteristics. Subtitle D of RCRA delegates regulation of nonhazardous solid wastes to the individual states. In its original form, RCRA did not specify whether coal ash fell under Subtitle C or D. The 1980 amendments temporarily excluded CCBs from Subtitle C regulation pending an EPA study report addressing appropriate classification. In the interim, CCBs were subject to regulation under state laws pertaining to solid wastes.

On August 2, 1993, EPA presented its final regulatory decision on fly ash, bottom ash, boiler slag, and flue gas emission control waste, stating that effective September 2, 1993, these materials are not regulated as hazardous wastes under Subtitle C and officially placing them under Subtitle D as solid wastes under the jurisdiction of

individual states (EPA, 1993). EPA will further evaluate the hazardous or toxic properties of industrial solid wastes, but at this time, CCBs are expected to remain under state regulation, where little positive change is expected regarding beneficial use.

Federal Action on CCB Utilization

In January 1983, EPA issued federal procurement guidelines on cement and concrete containing fly ash. In October of that year, Executive Order 12873 on Federal Acquisition, Recycling, and Waste Prevention required EPA to issue guidance for preference and purchase of environmentally preferable products. In July 1994, DOE submitted a report to Congress, "Barriers to the Increased Utilization of Coal Combustion/Desulfurization By-Products by the Government and Commercial Sector." In this document, DOE charged itself to:

- Consider CCBs under Executive Order 12873.
- Contribute data on RCRA performance of clean coal technology CCBs.
- Work with State and local governments to identify concerns regarding CCB use.
- Transfer technology targeting environmental/health-sensitive CCB markets.
- Cooperate with the States to review/revise/develop specifications and regulations relating to CCB use.
- Demonstrate high-volume CCB utilization.
- Explore ways to make CCBs easier to use or dispose of.

State Governments and CCBs

State departments of transportation (DOTs) are high-volume users of CCBs and have the potential to use more. DOTs rely on consensus standards for guidance and generally accept the use of fly ash in concrete. They can provide good opportunities for CCB demonstration projects.

State environmental health offices most frequently regulate CCB utilization on a case-by-case basis or under generic recycling laws. The State offices usually have limited resources and look to DOE or industry to provide data on new materials and projects. By 1996, 27 States had adopted laws, regulations, policies, and/or guidance authorizing at least limited CCB utilization in cement/concrete products. Notable efforts have been made in Illinois, Indiana, Iowa, North Carolina, Ohio, Pennsylvania, Texas, and West Virginia.

Regulatory approaches vary from State to State. Several States, such as Florida, Georgia, and Colorado, judge all proposed by-products and uses on a case-by-case basis, which may be costly and time-consuming. Other States, such as Pennsylvania, Tennessee, and Virginia, have several preapproved uses that require only notification to the regulatory agency. Iowa has generators register their by-products for use as a soil amendment, and reregistration is required only if there is a process change. West Virginia preapproves the use of CCBs as mine subsidence and mine fire control in a permitted coal mine. FBC by-products are regulated there the same as other CCBs and are preferred for mining applications.

An important barrier issue originating in RCRA legislation is the indiscriminate designation of CCBs as solid wastes whether they are recovered for use or disposed of in a landfill. In the absence of special State exemptions from solid waste regulations for beneficial use, which exist in only a few States, the "waste" designation can trigger case-by-case approval and permitting procedures that discourage CCB use because of unreasonable cost and delay. The remedies for this problem include both elimination of the "waste" designation *and* the creation of appropriate exemptions from regulation based on environmentally sound regulatory classifications for various classes of by-product use. While RCRA is the principal Federal law affecting the regulation of CCBs, a larger statutory framework of Federal law that is more or less integrated with State and local statutes may ultimately have to be considered. It is not within the scope of this study to unravel this potential regulatory maze. However, other Federal statutes that may apply to coal ash use or disposal in particular circumstances, as well as to virgin raw materials and derived products, include the Clean Water Act of 1972, the Safe Drinking Water Act of 1974, the Toxic Substances Control Act of 1976, and the Comprehensive Environmental Response, Compensation, and Liability Act of 1980 (CERCLA, the Superfund Act). All of these statutes deal with the control of toxic substances and ultimately rely on environmental testing and risk assessment to establish regulatory criteria. The final answer to regulatory questions constituting barriers to beneficial use, therefore, lies in obtaining adequate environmental data to demonstrate

environmental safety, a process that is well advanced for CCBs, but requires systematic compilation and refinement to provide the basis for regulatory classification.

Summary and Conclusions

The authors have had the opportunity to work with a number of citizen groups, regulatory agencies, industry groups, scientists, and engineers in a consulting or advisory capacity. Most of these experiences have been extremely positive and have pinpointed a single important requirement for scientists in working in the area of regulations: clear, factual information. In nearly all of the cases in which the authors have had a personal involvement, the presentation of factual information in a concise manner allowed the interested parties to make their own informed decisions, which has generally produced satisfactory results for all involved. There have been positive interactions with groups in North Dakota, South Dakota, Minnesota, Wyoming, and Indiana. In all of these locations, the application of reasonable science and discussions involving data that all parties found acceptable resulted in satisfactory resolutions to conflicts—resolutions that satisfied concerned citizens, local environmental groups, state regulatory agencies, coal ash producers, and coal ash users.

Coal ash is a material not likely to go away in the near future; thus proper handling, including engineering use options as well as disposal, must be properly conducted, even in light of the benign nature of most coal ash. With newer power-generating stations coming on-line or being converted for low-NO_x burners, it is likely that there will be some changes in the nature of the ash produced. This, of course, opens up an entirely new line of environmental and engineering performance issues.

It is hoped that this presentation and other issues, as they arise, will stimulate discussion conducive to a cooperative and trusting environment, thus allowing regulators, concerned citizens, power producers, ash marketers and users, and scientists to interact as colleagues with a common goal, that being the better interests of people and the environment. Since the decisions involving the potential for environmental harm are so important, it is imperative that objectivity be maintained, as well as a productive dialog among all concerned. Since that includes all of us, we had better keep talking and furthering our understanding of how things really work! Use rather than disposal is likely one of the best solutions to environmental problems concerning CCBs. Poor decisions where the environment is concerned are clearly unacceptable.

References

Butler & Binion. *Environmental Law Simplified: A Practical Guide for Oil and Gas Operations*; Robertson, G.L., Ed.; PennWell: Tulsa, OK, 1993; 132 p.

Findley, R.W.; Farber, D.A. *Environmental Law in a Nutshell*; West Publishing Co.: St. Paul, MN, 1992; 355 p.

Hassett, D.J. A Generic Test of Leachability: The Synthetic Groundwater Leaching Procedure. In *Proceedings of the Waste Management for the Energy Industries Conference*, University of North Dakota, April 29–May 1, 1987.

Hassett, D.J.; Pflughoeft-Hassett, D.F.; McCarthy G.J. Ettringite Formation in Coal Ash as a Mechanism for Stabilization of Hazardous Trace Elements. In *Proceedings of the 8th Annual International Pittsburgh Coal Conference*, Pittsburgh, PA, Oct. 14–18, 1991.

Hassett, D.J. Scientifically Valid Leaching of Coal Conversion Solid Residues to Predict Environmental Impact. In *Proceedings of the Trace Element Transformations in Coal-Fired systems Workshop*, Scottsdale, AZ, April 19–22, 1993; Special Issue of *Fuel Processing Technology* **1994**, *39* (1–3), 445–459.

Jagiella, D.M. Coal Combustion By-Products: A Survey of Use and Disposal Provisions. In *High-Volume Uses/Concrete Applications*, Proceedings of the 10th International Ash Use Symposium, Orlando, FL, Jan. 18–21, 1993; EPRI TR-101774, Project 3176, 1993; Vol. 1, pp 36-1 to 36–24.

Pflughoeft-Hassett, D.F.; Renninger, S. Review of Barriers t the Increased Utilization of CCBs by Government and

Commercial Sectors. Presented at the American Coal Ash Association 13th International Symposium on the Management and Use of Coal Combustion Products (CCPs), Orlando, FL, Jan 10–14, 1999.

Sorini, S.S. *A Summary of Leaching Methods*; prepared for the American Coal Ash Association, Inc.; Western Research Institute: Laramie, WY, April 1997.

Stevenson, R.J.; Hassett, D.J.; McCarthy, G.J.; et al. *Solid Waste Codisposal Study*; final report to Gas Research Institute for Contract No. 5083-253-1283; Energy & Environmental Research Center: Grand Forks, ND, Feb 1988.

U.S. Environmental Protection Agency. Final Regulatory Determination on Four Large-Volume Wastes from the Combustion of Coal by Electric Utility Power Plants. *Code of Federal Regulations;* Part 261, Title 40; *Federal Register* **1993**, 42466–42482 (Aug 9, 1993).

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[1] David J. Hassett is a Senior Research Advisor at the Energy and Environmental Research Center (EERC) of the University of North Dakota. He received his B.S. in Chemistry and Mathematics from Winona State University in Winona, Minnesota, in 1966 and continued with graduate studies in Chemistry from 1970 to 1975. He has authored or coauthored over 130 publications. Hassett's principal areas of interest and expertise include the application of analytical chemistry toward the solution of environmental problems associated with trace element occurrence, transport, and fate. The most recent research focus has been on trace element transformations during coal conversion processes and interaction between groundwater and coal conversion solids as related to the leachability of trace elements. Additional areas of expertise include hydration reactions of coal conversion solid residues as well as organic synthesis, radiochemistry, x-ray spectrometry, analytical chemistry, and vegetable oil diesel fuels.

ELECTRIC POWER UTILITY'S MATERIALS FLOW IN THE UNITED STATES

Samuel S. Tyson[1,3], Rustu S. Kalyoncu[2]
[1]American Coal Ash Association, Alexandria, VA;
[2]United States Geological Survey, Reston, VA

Abstract

Materials are essential in meeting our most fundamental needs – food and shelter—and to maintain and improve our standard of living. Materials processing requires significant amounts of energy. One of the most versatile and, therefore, desirable forms of energy is electricity. Electricity accounts for more than one third of the total energy consumption in the United States, and more than half of the nations' electricity is produced by burning coal. During 1998, approximately 1 billion tons of coal were burned by electric utilities. As a result, more than 100 million tons of coal combustion products (CCPs) were generated. As such, CCPs rank behind only sand and gravel and crushed stone as a produced 'mineral commodity,' and rank ahead of Portland cement and iron ore. Understanding the system of materials flow, from source to ultimate disposition, can help management and use of our natural resources and protect the environment. This study traces the flow of CCPs from the point of coal mining through their many applications as viable mineral commodities. The base year for this study was taken to be 1966, the first year for which statistical data for CCPs are available. Analysis tools such as life cycle assessment (LCA) are now used to provide quantitative scientific analysis of industrial systems. An LCA assessment that compared the use of coal fly ash in a highway embankment with using soil showed fly ash use is superior with respect to raw materials consumed and landfill space conserved. In addition, fly ash enables greater haul distances, and produces equal or lower air emissions, when compared to a soil embankment. The haulback of CCPs for use in mined land reclamation is particularly attractive from a "balance of materials" point of view. Scenarios for mine backhaul will be examined.

Introduction

ACAA's mission is to advance the management and use of coal combustion products (CCPs) in ways that are technically sound, commercially competitive, and environmentally safe. ACAA has a large volume and wide variety of information on all types of CCPs. This information is all available on its Website at www.acaa-usa.org or by contacting ACAA directly.

Some of the annual benefits of using CCPs are:

- by using 31 million tons of CCPs during 1998, 28 million cubic yards of landfill space were preserved for future use;
- assuming average landfill depths of 50 feet, the area preserved during 1998 would be about 350 acres;
- $620 million of disposal costs were avoided;
- revenues from the sales of CCPs are estimated to have been in excess of $150 million;
- the use of 1 ton of fly ash in concrete will avoid approximately 1 ton of carbon dioxide being emitted from cement production; and
- in 1998, 10.4 million tons of fly ash were used in cement and concrete products displacing 6.9 million tons of Portland cement, thereby avoiding 6.9 million tons of carbon dioxide emissions.

Reduction of Carbon Dioxide Emissions

Concerning the role of recycling power plant by-products into useful CCPs, the United States has developed a Climate Challenge Program to reduce the carbon dioxide emissions to below 1990 levels before 2010. The U.S. Department of Energy and the electric utilities have signed participation accords pledging to increase the use of CCPs, particularly fly ash that would displace Portland cement in concrete products. Increasing the fraction of mineral admixtures that utilize CCPs in all concrete products from the current level of 15 percent to 50 percent would eliminate up to 600 million metric tons of carbon dioxide. This would be the equivalent of removing twenty five percent of the carbon dioxide emissions from all of the cars in the world. This is the maximum level of replacement as

it would require the utilization of all of the fly ash now produced. Barriers that must be overcome in order to realize this type of utilization would include improving transportation of these materials to potential markets, beneficiation of materials so that they have a marketable quality, and improve the acceptance of these materials to the marketplace.

Production and Use of CCPs in the United States

Statistics on the production and use of CCPs for the last 30 years show that the use of fly ash and indeed all CCPs has been steadily increasing. This use, however, has not kept pace with the increase in the production of fly ash and other CCPs (See Figures on Fly Ash and Total CCP Production and Use). Concerning the rate of use for selected applications such as concrete, structural fill, road base, waste stabilization, snow and ice control, and flowable fill, the use of fly ash in concrete has been the application that has most dramatically increased over the last twenty years (See Figures on Fly Ash and Bottom Ash Use in Selected Applications). We do not show mining applications on these charts yet because they are still relatively small by comparison. Part of the reason they are not shown is that some mining applications are not yet classified as use but as disposal. Boiler slag has a very high rate of application being utilized almost completely for very high value applications such as blasting grit.

Potential for Use of CCPs as Flowable Fill

One of the areas that could be improved in terms of utilization of CCPs is as flowable fill. In support of this concept we have generated some statistics that show that based on the current U.S. population of 273,172,307, the entire 54 million tons of fly ash and bottom ash that would be available for use in flowable fill would amount to 390 pounds per person. A well developed flowable fill market in a major metropolitan area of one million persons may support about 65,000 cubic yards of flowable fill. Given a normal range of ash content in flowable fill mixtures from 400 to 2,000 pounds of ash per cubic yard of fill, that would represent about 26-130 pounds of ash per person per year in flowable fill usage. Since 80 percent of the U.S. population lives in metropolitan areas that results in a market of between 3.5 and 18 million tons of ash as flowable fill.

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[3]Samuel S. Tyson is the Executive Director of the American Coal Ash Association (ACAA) and President of the ACAA Educational Foundation with offices in Alexandria, Virginia. He earned both undergraduate and graduate degrees in Civil Engineering at the University of Virginia, and served for four years in the U.S. Army where he was a commissioned officer in the Corps of Engineers. He was a Research Engineer for nine years with the Virginia Transportation Research Council where he specialized in materials for construction and maintenance of concrete pavements and bridges. Sam is a registered professional engineer in the District of Columbia where he worked for five years as technical director for a ready mixed concrete company. He has both laboratory and field experience with fly ash concrete mixtures for construction of commercial and residential buildings, as well as for transportation and water treatment facilities. Sam joined ACAA in 1986 as its Director of Technical Services and was appointed as Executive Director in 1993.

Electric Power Utility's Material Flow in the United States

Sam Tyson, ACAA
Rustu Kalyoncu, USGS

Use of Fly Ash and Other CCPs at Coal Mines

Morgantown, WV - April 11, 2000

www.acaa-usa.org

ACAA INTERNATIONAL

Mission Statement

ACAA's mission is to advance the management and use of coal combustion products (CCPs) in ways that are technically sound, commercially competitive and environmentally safe

Annual Benefits of Using CCPs

- By using 31 million tons of CCPs (1998) 28 million cubic yards of landfill space were preserved for future use

Annual Benefits of Using CCPs

- Assuming average landfill depths of 50 feet; the area preserved would be about 350 acres (1998)

Annual Benefits of Using CCPs

- The productive use of 31 million tons of CCPs avoided $620 million in disposal costs (1998)

Annual Benefits of Using CCPs

- Revenues from the sales of CCPs are estimated to have been in excess of $150 million (1998)

Climate Challenge Program

- Reduction in CO_2 emissions to/below 1990 levels before 2010
- U.S. DOE and utilities have signed participation accords pledging increased use of CCPs, particularly fly ash to displace portland cement

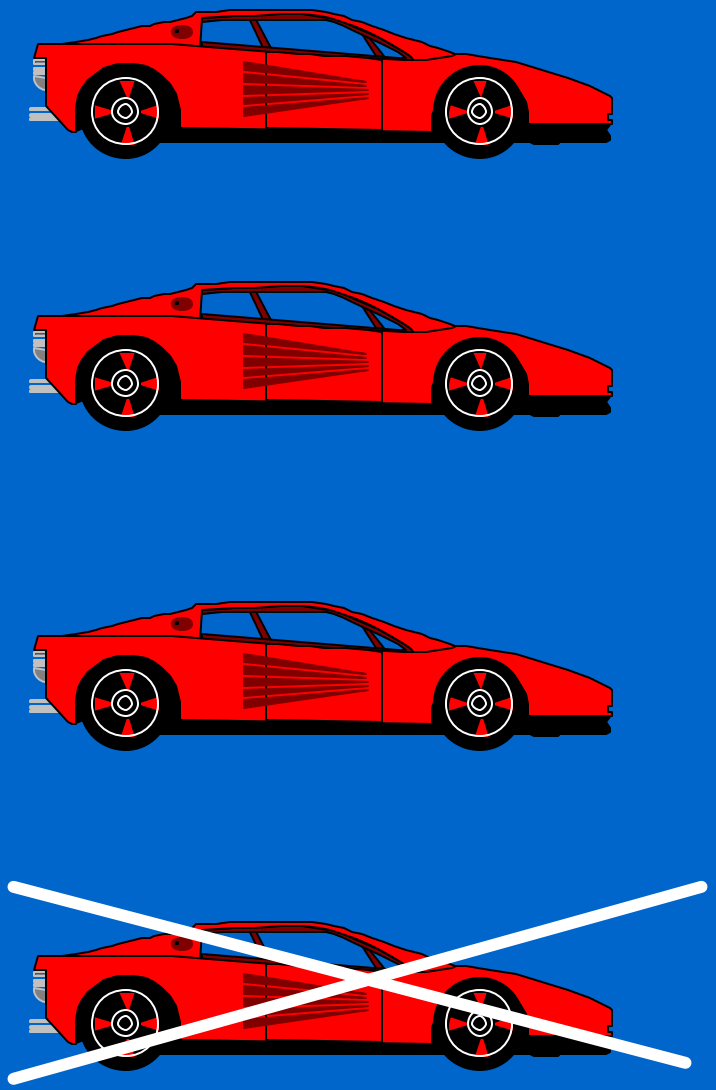
CO_2 Emission Avoidance

- Use of 1 ton of fly ash in concrete will avoid approximately 1 ton of CO_2 emitted from cement production

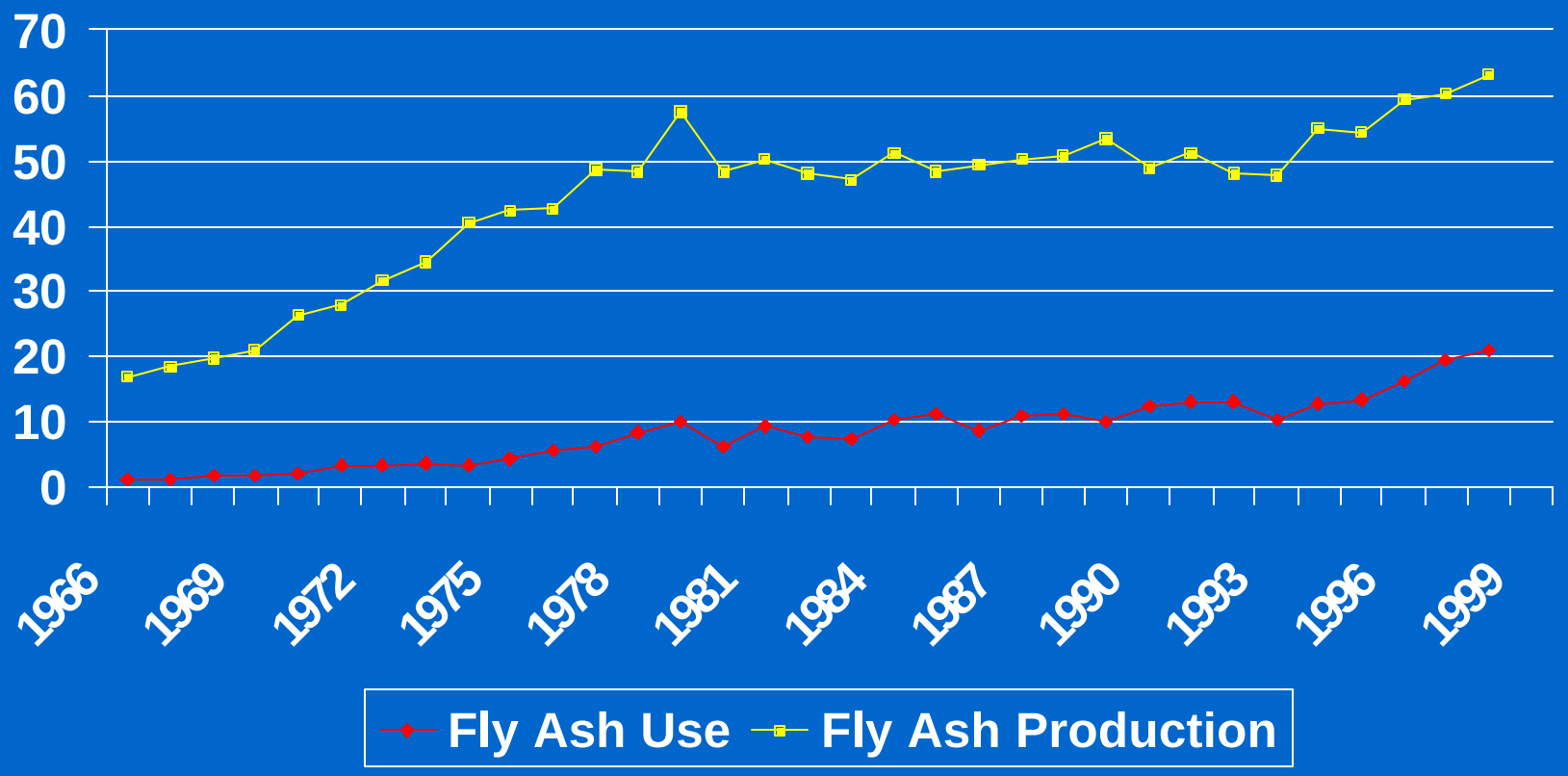
Annual Benefits of Using CCPs

- In 1998 10.4 million tons of fly ash were used in cement and concrete products displacing 6.9 million tons of portland cement; thereby avoiding 6.9 million tons of CO_2 emissions

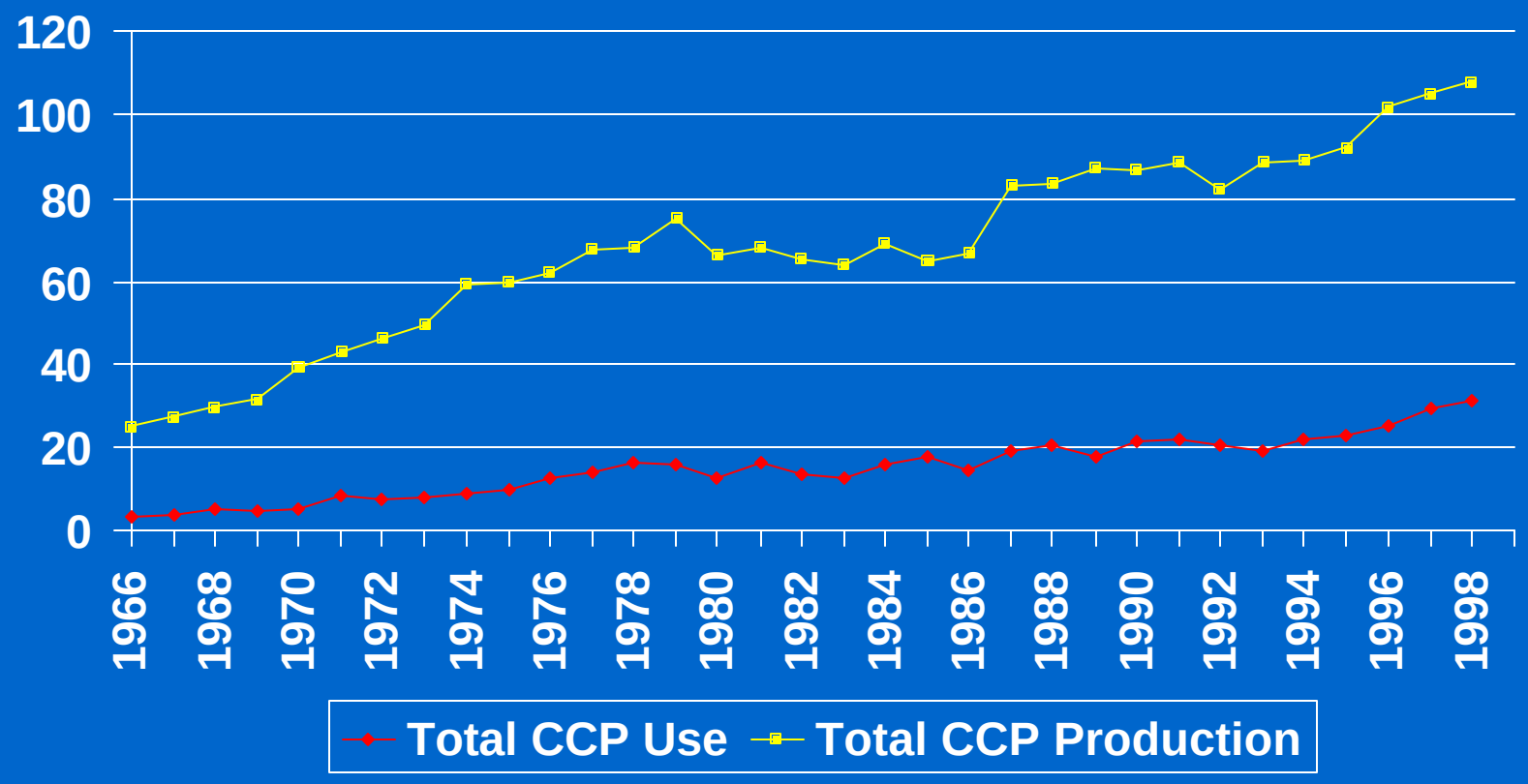
Increasing the fraction of mineral admixtures in all concrete from 15% of cementing materials to 50% would eliminate up to 600 million metric tons of CO_2 – equivalent to removing one quarter of all cars in the world. This level of replacement is the maximum possible, because it would require the utilization of all the fly ash produced. – Environmental building news-



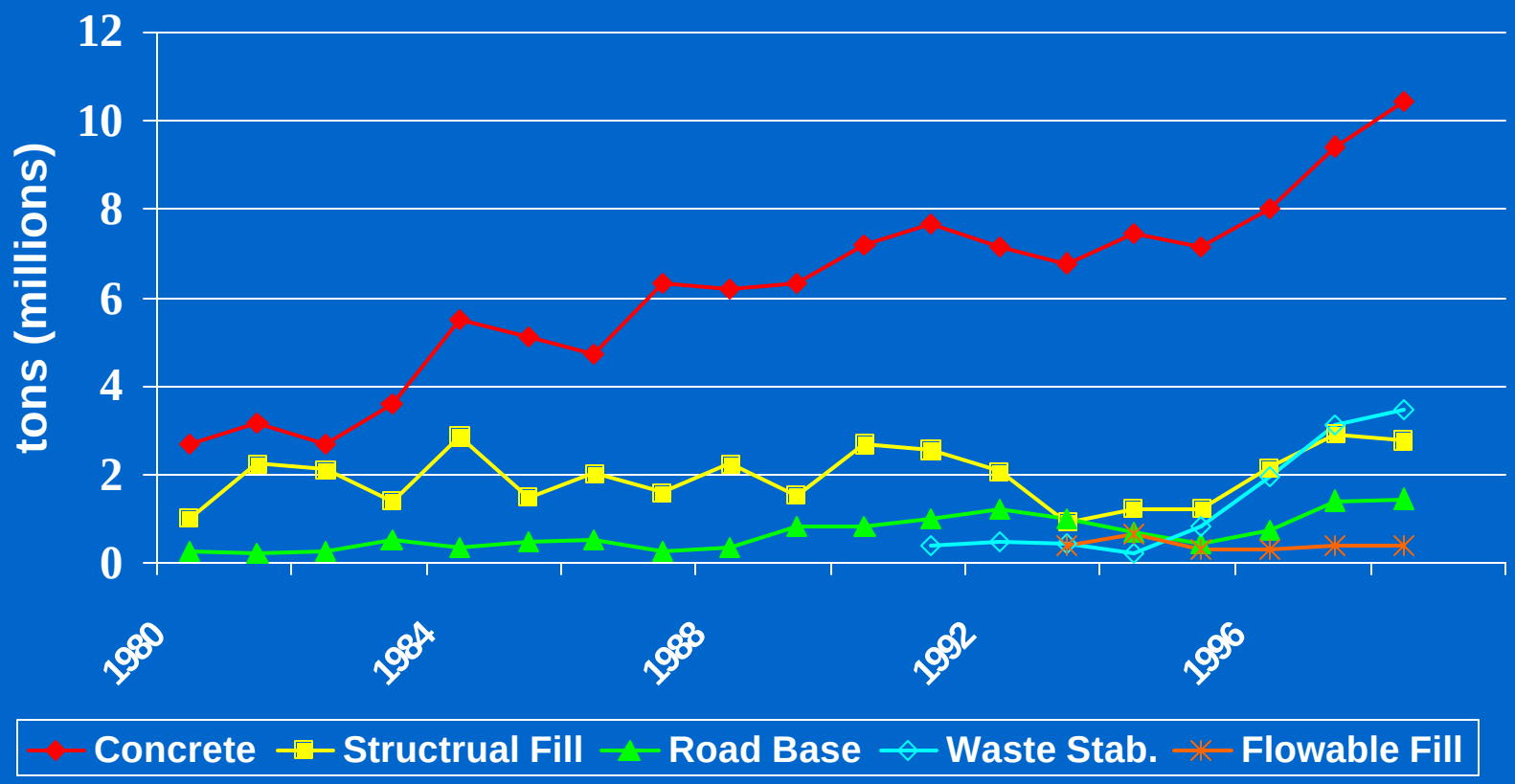
Fly Ash Production and Use



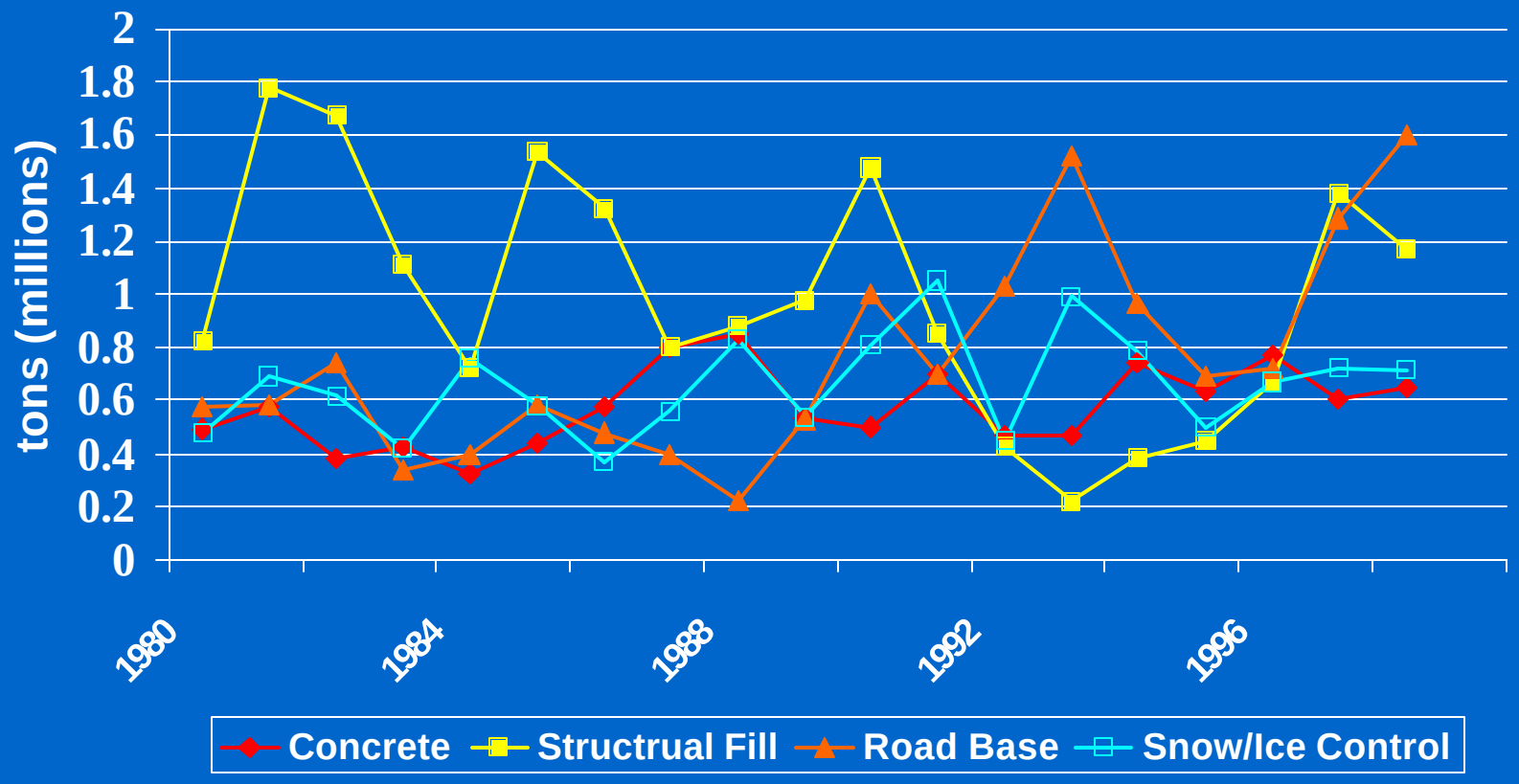
Total CCP Production and Use

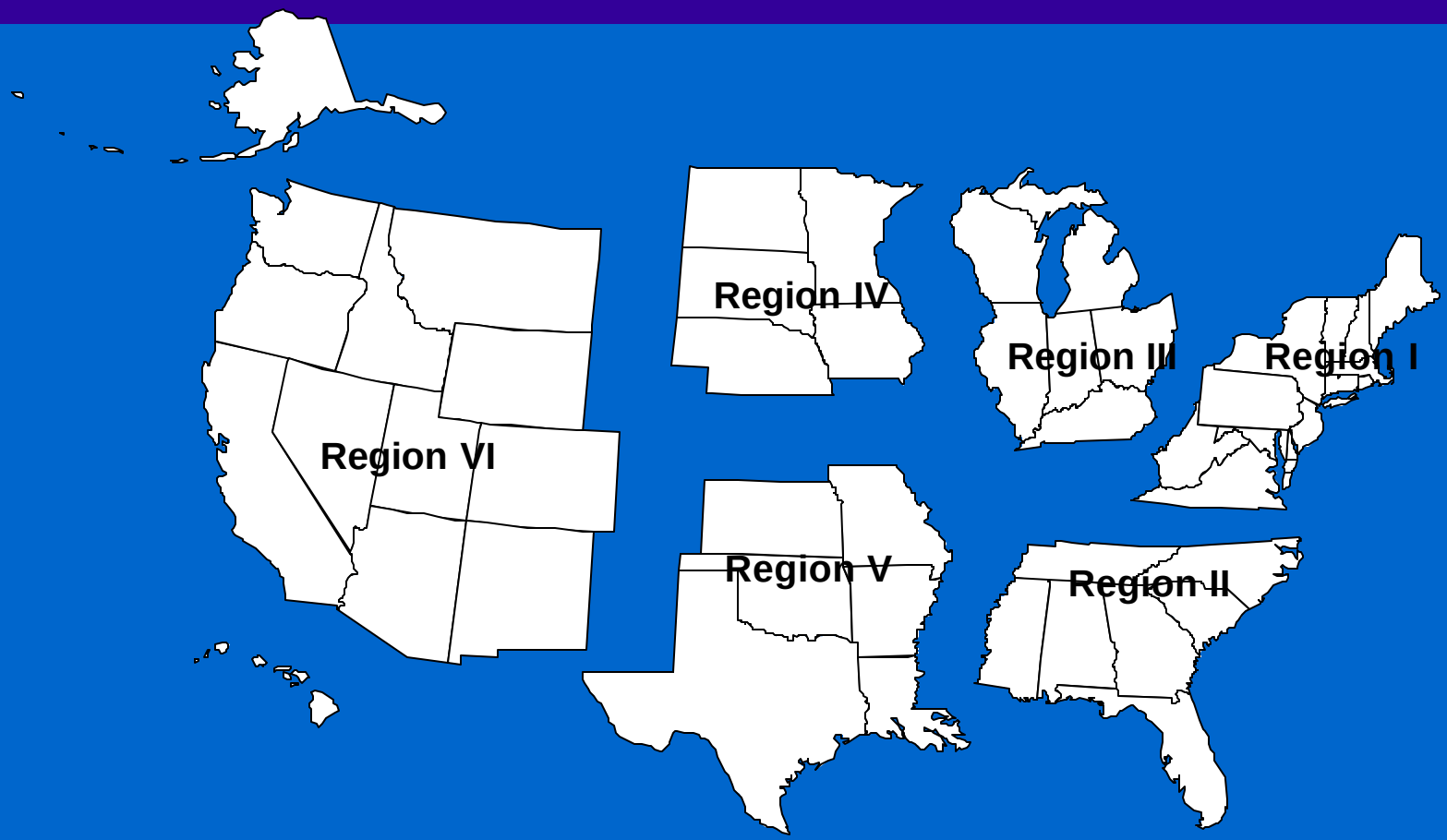


Fly Ash Use in Selected Applications



Bottom Ash Use in Selected Applications




Region IV
Region III
Region I
Region VI
Region V
Region II

Leading Mineral Resources in the USA

Mineral Resources	Annual Production (short tons, millions)
Crushed Stone	1,350
Sand & Gravel	980
CCPs	109
Portland Cement	90
Iron Ore	65

Flowable Fill Potential Materials

- Current U.S. Population is 273,172,307
- 54 million tons of fly ash & bottom ash are available for use in flowable fill
- That's 390 lbs per person

Flowable Fill Market Potential

- A well developed flowable fill market in a metropolitan area of one million people may support 65,000 yd^3 of flowable fill

- A high ash content mix may contain up to one ton of ash per yd^3, while a low ash mix might contain 400 lbs per yd^3

Flowable Fill Market Potential

- That come out to between 26 - 130 lbs of ash per person per year in flowable fill usage
- 80% of the U.S. population of 273,172,307 lives in metropolitan areas
- That gives a potential market of between 3.5 and 18 million tons of coal ash

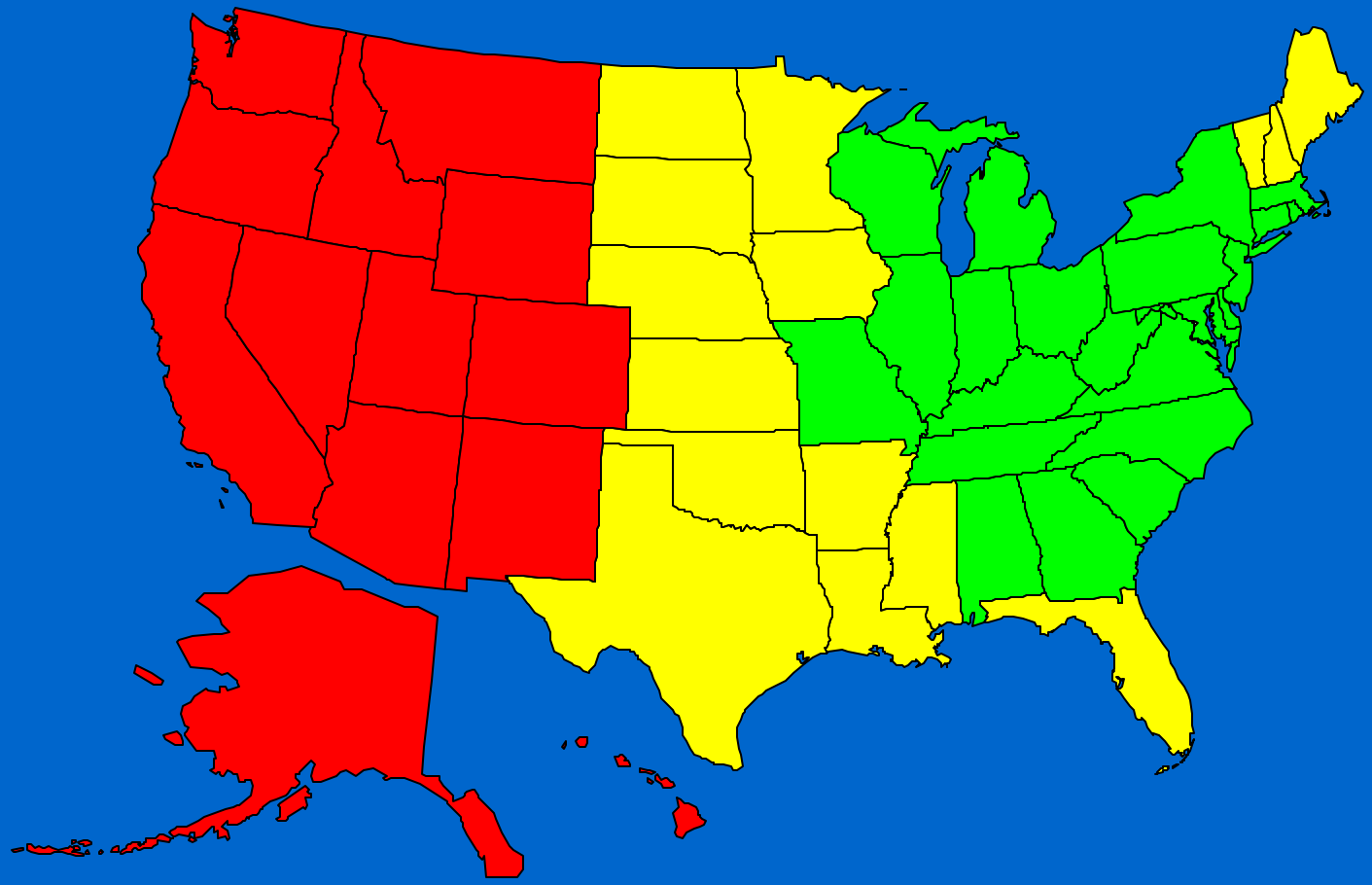
Future of Flowable Fill

- The number of future uses of flowable fill are limited only by the imagination of those using it

Future of Flowable Fill

- The use of coloring agents to code flowable fill may give it an advantage in utility cut work
- EPA Comprehensive Procurement Guideline (CPG) for flowable fill containing fly ash will lead to more fly ash being used

22 OTAG Affected States



The Cost of Compliance

- Compliance with all air regulations will cost coal fired electric utilities 22 BILLION dollars over the next 10 years

Source RDI, 1999

NOx Control Methods

• Low NOx Burners	33%
• SCR	45%
• SNCR	10%
• Natural Gas Re-burn	3%
• Fuel Switching	4.5%
• Other	4.5%

Source ACAA NOx survey 1998

1998 ACAA NOx Survey

- 60% of the units reporting will require additional NOx control*
- About half (52%) of these additional control measures will involve ammonia

*RDI estimates 207,000 MW of the 303,000 MW (68%) U.S. coal-fired generating capacity will be affected by this ruling

1998 ACAA NOx Survey

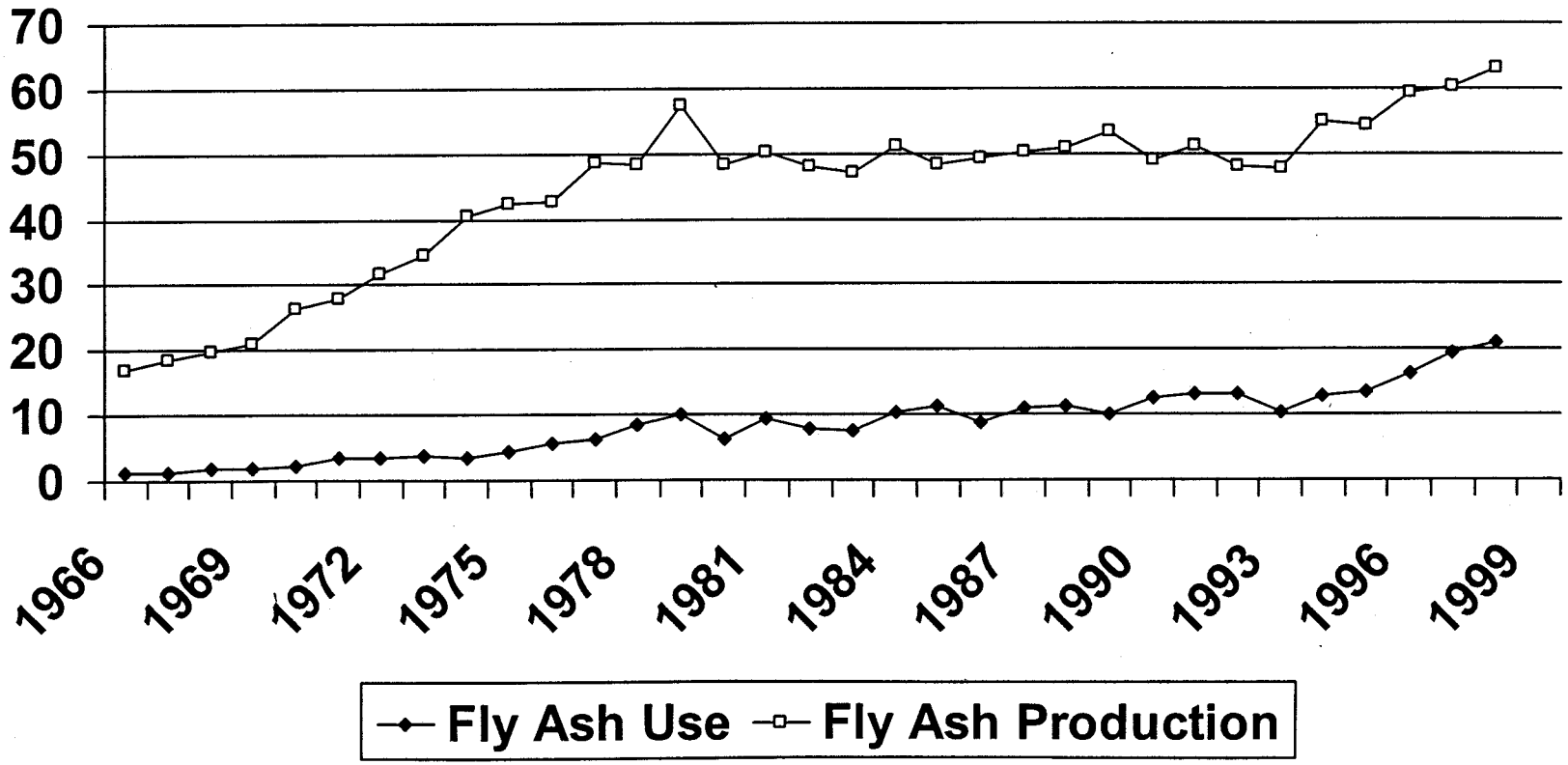
- The survey data indicates that 2.7 million tons of fly ash may be rendered unusable for pozzolan markets
- An additional 1.4 million tons will become unusable for their present uses
- In total, over 4 million tons of fly ash that is presently used will require disposal

Learn More

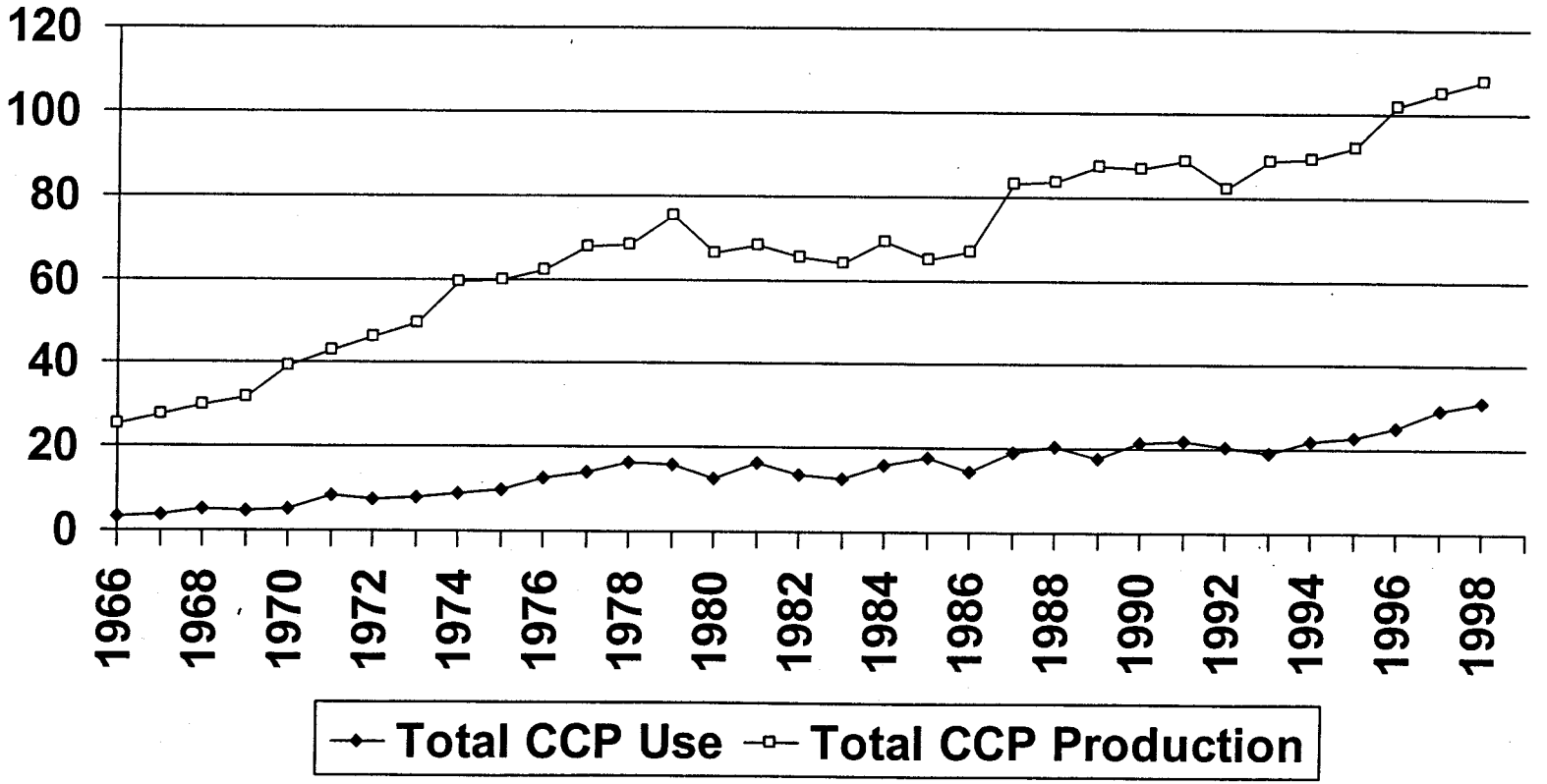
- ACAA Workshop: *Y2K Compliant Fly Ash at* ACAA's Annual Meeting, Workshop & Committee Meetings
  - Shelter Pointe Hotel & Marina - San Diego, CA
  - January 25, 2000
- Educational Program for the Managers of CCPs
  - NRCCE - WVU - Morgantown, West Virginia
  - June 5-9, 2000
- 14th International Symposium on the Management and Use of CCPs
  - Hilton Palacio del Rio - San Antonio, Texas
  - January 22 - 26, 2001

American Coal Ash Association
6940 South Kings Highway, Suite 207
Alexandria, Virginia 22310-3344
Internet: www.acaa-usa.org
E-mail: Styson@ACAA-USA.org
Phone: 703-317-2400
Fax: 703-317-2409

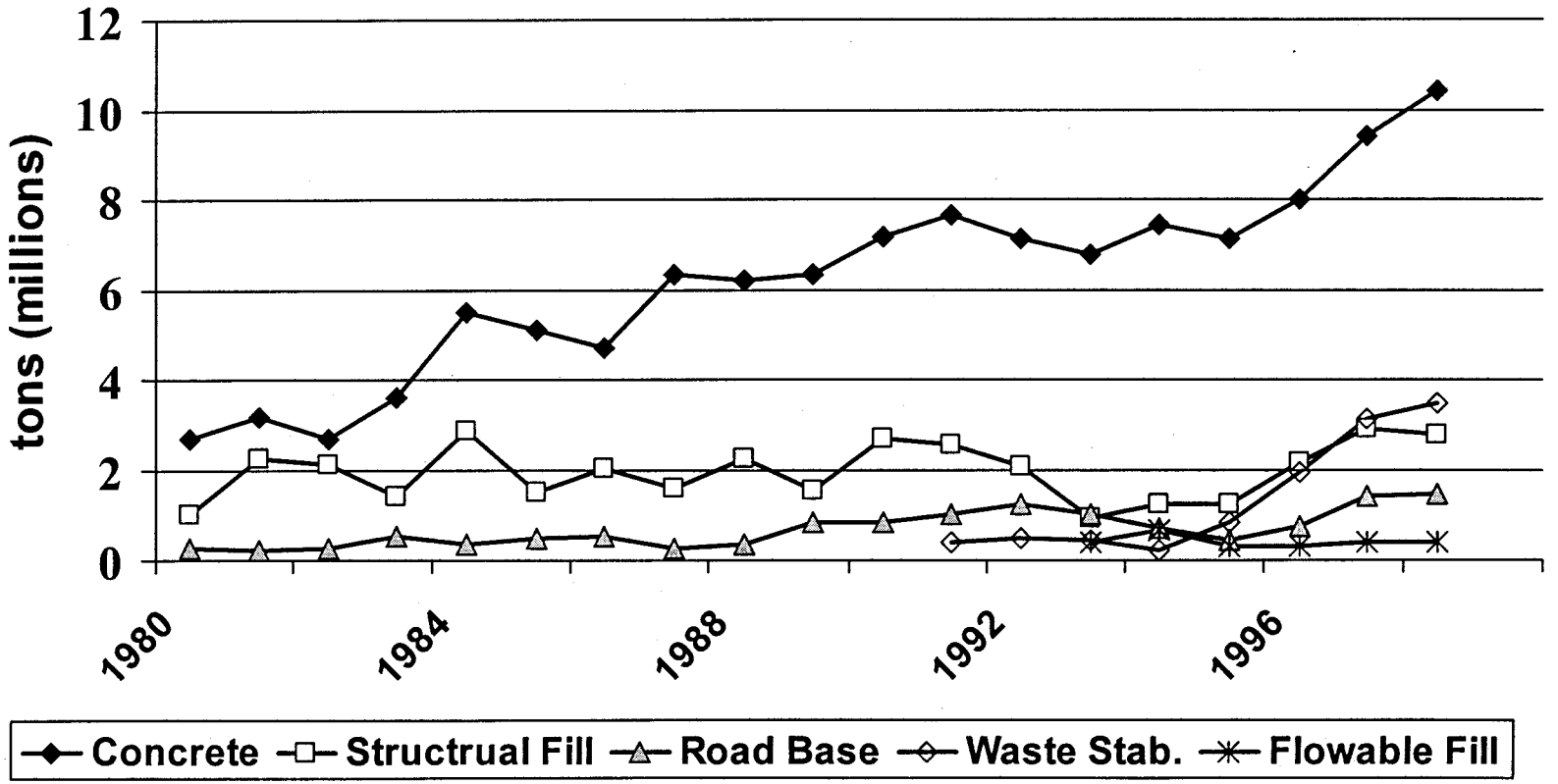
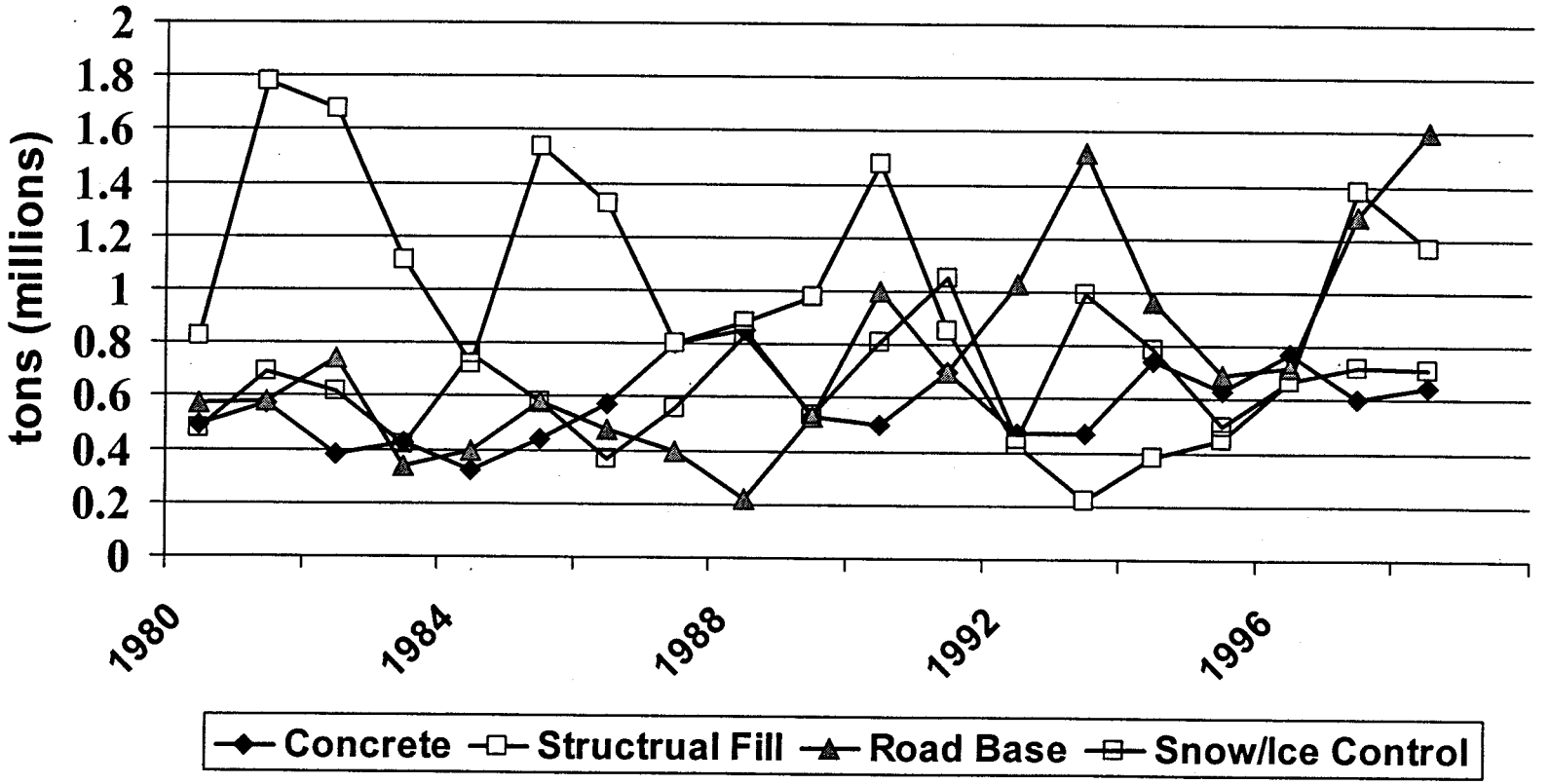
Fly Ash Production and Use



Total CCP Production and Use



Fly Ash Use in Selected Applications



Bottom Ash Use in Selected Applications