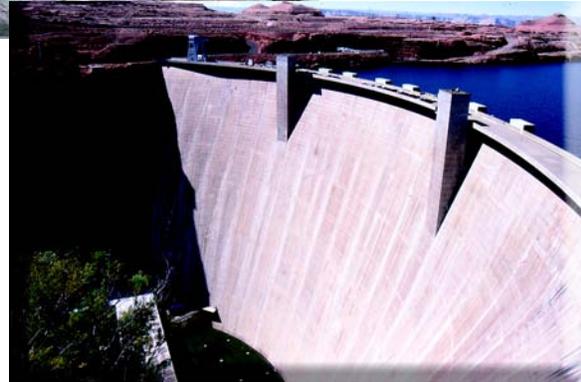
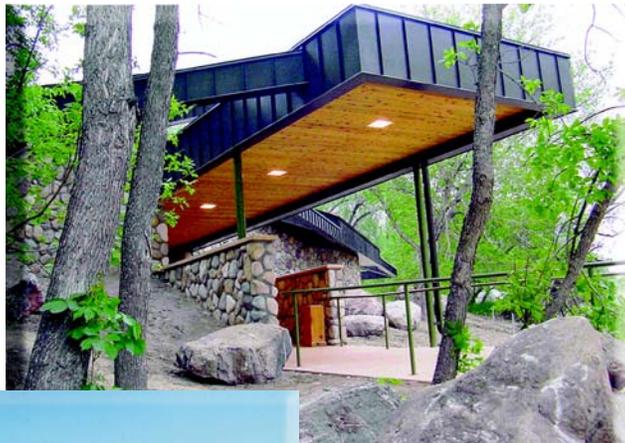




The logo for Clean Coal Technology features a thick blue horizontal bar at the top. Below it, the word "CLEAN" is written in a white, bold, sans-serif font with a black outline. The word "COAL" is written in a larger, blue, bold, sans-serif font with a black outline. Below "COAL", the word "TECHNOLOGY" is written in a smaller, blue, sans-serif font.



Coal Utilization By-Products



Acknowledgement:
DOE greatly appreciates the participation of the American Coal Ash Association in the preparation of this Topical Report.

Cover Photos:

Top: Building materials used in the Lewis & Clark Visitors Center in Fort Mandan, ND include fly ash-based mortar and stucco, wall board, and high-volume fly ash concrete.

Bottom left: The Ronald Reagan Building and International Trade Center in Washington, D.C. was built with concrete containing fly ash.

Bottom right: Fly ash is an important component in mass concrete projects, such as the Glen Canyon Dam near Page, AZ.



Coal Utilization By-Products

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Executive Summary

The Clean Coal Technology Demonstration Program (CCTDP) is a government and industry cofunded effort to demonstrate a new generation of innovative coal utilization processes in a series of facilities built across the country. These projects are carried out on a commercial scale to prove technical feasibility and provide information for future applications.

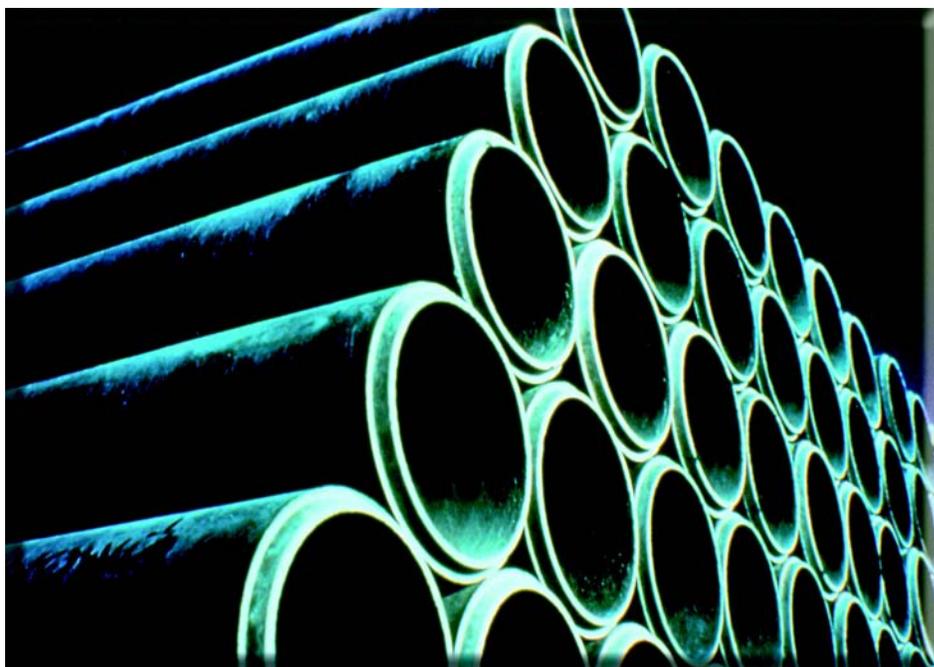
The goal of the CCTDP is to furnish the marketplace with advanced, more efficient coal-based technologies that meet strict environmental standards. Use of these technologies is intended to minimize the economic and environmental barriers that limit the full utilization of coal.

To achieve this goal, beginning in 1985, a multiphase effort consisting of five separate solicitations was administered by the U.S. Department of Energy (DOE) through its National Energy Technology Laboratory. Selected projects have demonstrated technology options with the potential to meet the needs of energy markets while satisfying relevant environmental requirements. Two follow-on programs have been developed that build on the successes of the CCTDP: the Power Plant Improvement Initiative (PPII) and the Clean Coal Power Initiative (CCPI).

Under the latter programs, three projects have been selected or are underway with the goal of increasing the use of coal utilization by-products (CUBs) in construction and other industries. One of these projects falls under PPII and is being conducted by Universal Aggregates, LLC. The others fall under CCPI and are being conducted by Western Greenbrier Co-Generation and the University of Kentucky.

CUBs are the solid materials formed during the combustion or gasification of coal during electric power generation. The primary large-volume CUBs are fly ash, bottom ash, slag, ash produced via fluidized bed combustion, and flue gas desulfurization by-products. Historically, CUBs have been disposed of in ashponds, landfills, and other sites. However, there are many incentives for developing more beneficial uses for these materials, including power generation economics, the conservation of natural resources and landfill space, and reductions in carbon dioxide emissions.

As time passes, more and more CUBs are being sold or reused—over 40 percent in 2004 compared to less than 25 percent in 1996 while at the same time production of CUBs has increased significantly. Government agencies and other stakeholders have established a goal of 50 percent utilization by 2010.



CUBs are used in the manufacture of pre-cast concrete pipe.

Coal Utilization By-Products

Topical Report Number 24

Introduction

Coal contains a substantial number of impurities, including mineral matter and sulfur. When coal is burned, the mineral matter is converted to ash and the sulfur is converted to sulfur oxides.

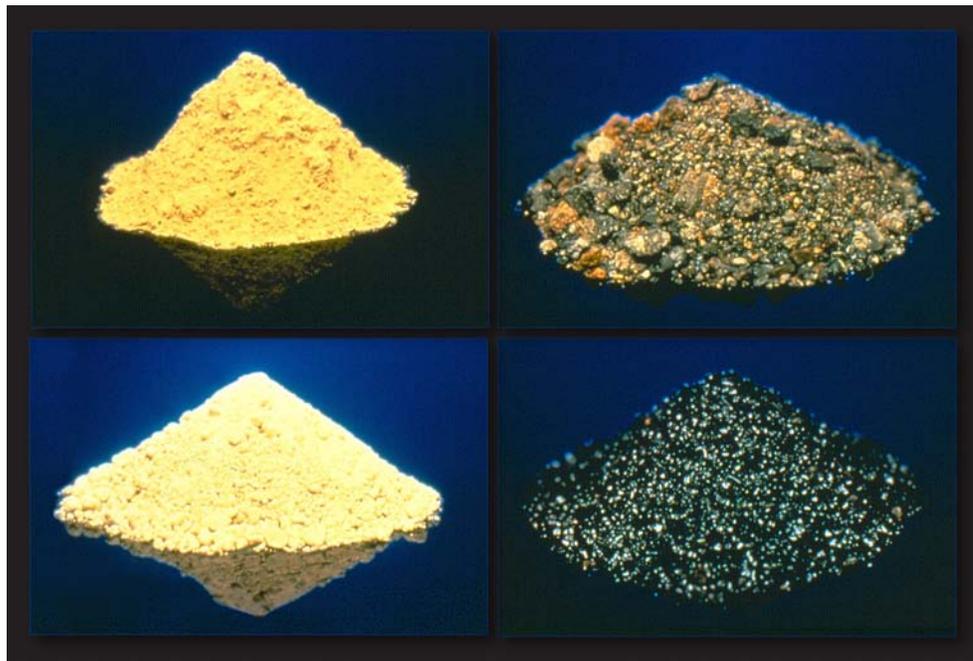
Coal-fired power plants have long been required to remove the bulk of the ash entrained in the flue gas. Now, environmental regulations are requiring more and more

sulfur oxides to be removed from power plant flue gas as well. Both actions result in increased generation of solid material referred to as coal utilization by-products (CUBs).

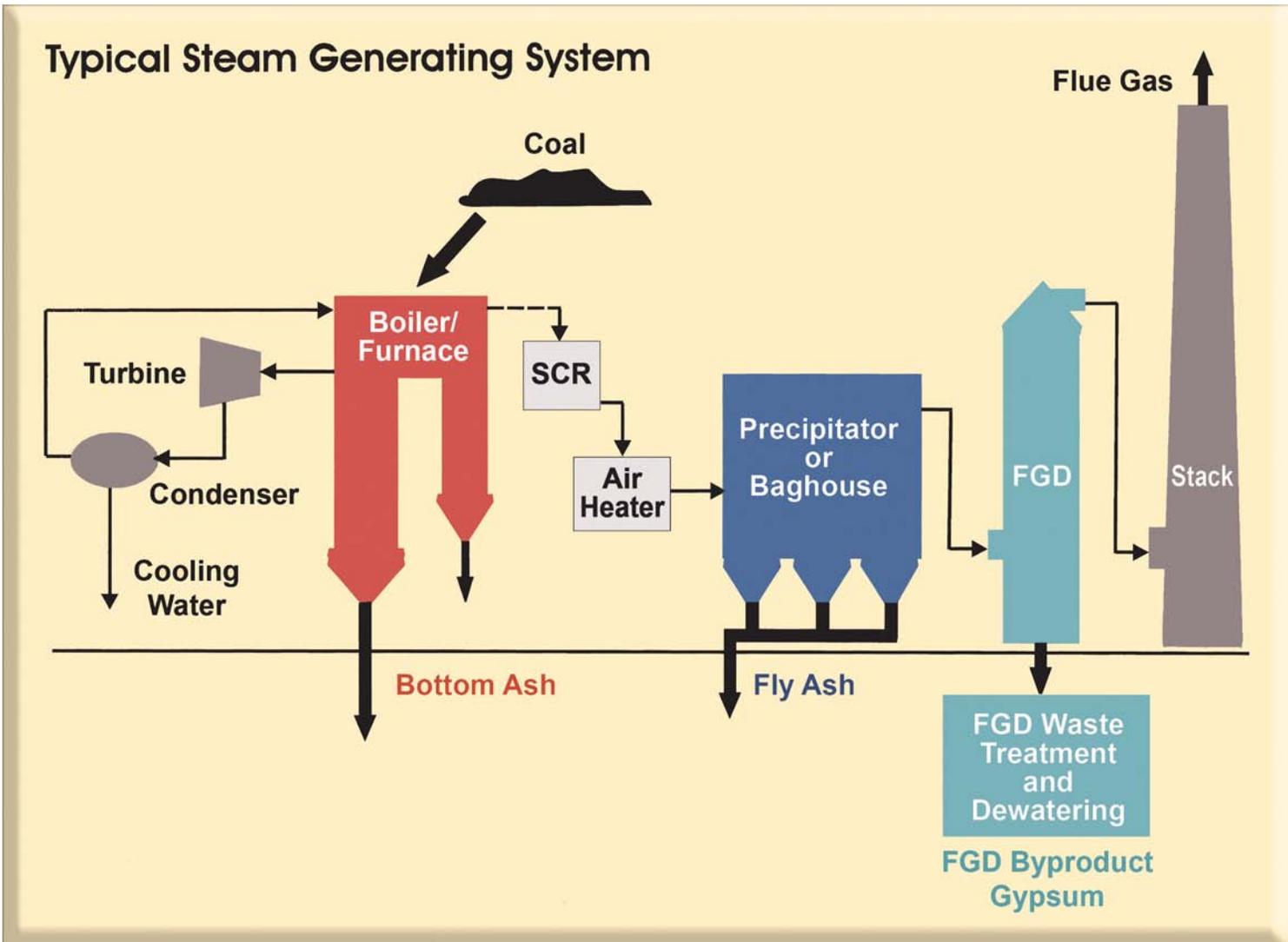
Although these materials have been referred to as coal combustion products (CCPs), residues, or wastes, the U.S. Department of Energy (DOE) prefers the term “utilization” over “combustion” because it accounts for coal gasification, which also produces solid by-products that must be managed. Similarly, DOE prefers the term “by-products” because it describes most accurately the nature of the materials at the moment they are generated. They become “products” when they are sold or beneficially utilized and “wastes” when they are sent to a permanent disposal site.

In 1980, CUBs were designated non-hazardous wastes by the Bevill Amendment to the Resource Conservation and Recovery Act. Further investigation has found that their properties often allow their beneficial use. In some cases, these properties make the CUB better suited for certain applications than the naturally occurring materials they replace.

CUB utilization improves the economics of power generation, conserves natural resources, avoids the consumption of increasingly scarce landfill space, and reduces emissions of carbon dioxide (CO₂) that would otherwise be required to produce



CUB samples, clockwise from upper left: fly ash, bottom ash, FGD material, and boiler slag.



the raw materials for which CUBs are substituted. CUBs are increasingly being sold or reused—more than 40 percent in 2004 compared to less than 25 percent in 1996. Government agencies and other stakeholders have established a goal of 50 percent utilization by 2010.

The principal organization promoting the beneficial use of CUBs is the American Coal Ash Association (ACAA). In addition, the U.S. Department of Energy’s Power Plant Improvement Initiative (PPII) and Clean Coal Power Initiative (CCPI) sponsor a number of projects that promote the utilization of diverse types of domestic CUBs. Several of these projects are noted throughout this report.



Magnified view of boiler slag

Where Do CUBs Come From?

The combustion of coal to generate electric power results in the formation of a variety of solid materials, collectively referred to as CUBs. The principal CUBs are fly ash, bottom ash, boiler slag, ash produced via fluidized bed combustion (FBC), and by-products of flue gas desulfurization (FGD).

Pulverized coal and cyclone boilers normally produce fly ash, bottom ash, and slag. A substantial quantity of fly ash is entrained in the boiler flue gas and collected

in electrostatic precipitators (ESPs) or baghouses. Bottom ash is formed when ash particles soften or melt and adhere to the furnace walls and boiler tubes, agglomerating and falling to hoppers located at the base of the furnace. Some bottom ash is transported to storage dry, but most is transported as a slurry to dewatering bins or ponds, where water is removed prior to the ash's transfer to utilization sites or storage stockpiles.

The yield ratio of fly ash to bottom ash depends on boiler type. In dry-bottom boilers, fly ash constitutes the major ash component at 80–90 percent, with bottom ash in the range of 10–20 percent.

Wet-bottom boilers yield molten ash, or slag, from the furnace bottom. Slag removed from the boiler in a molten state is dropped into a water-filled ash hopper. When it is quenched, it shatters and forms boiler slag particles.

In cyclone boilers, the slag yield is a greater percentage of total ash (70–85 percent). The ratio of slag to fly ash in other wet-bottom boilers is about the same as that of bottom ash to fly ash in dry-bottom units (10–20 percent slag and 80–90 percent fly ash).

Chemical Composition of Representative Fly Ashes, weight %

Compound	Class F Fly Ash		Class C Fly Ash		Portland Cement	
	Typical*	ASTM C-618	Typical*	ASTM C-618	Typical**	ASTM C-150
SiO ₂	53.6	---	40.9	---	20.3	---
Al ₂ O ₃	26.3	---	21.6	---	4.3	---
Fe ₂ O ₃	5.2	---	5.5	---	2.6	---
SiO ₂ +Al ₂ O ₃ +Fe ₂ O ₃	90.7	70.0 (min)	67.7	50.0 (min)	---	---
CaO (Lime)	4.1	---	19.1	---	63.6	---
MgO	1.5	---	3.9	---	2.2	6.0 (max)
Sulfate as SO ₃	0.9	5.0 (max)	1.4	5.0 (max)	---	3.0 (max)
Loss on Ignition	6.0	6.0	6.0	6.0	0.6	3.0 (max)
Moisture Content	0.2	3.0 (max)	0.0	3.0 (max)	---	---
Insoluble Residue	0.0	---	0.0	---	---	0.75 (max)
Available alkalis as Equivalent Na ₂ O	2.0	---	1.6	---	0.2	---

*Class F ash from We Energies Presque Isle Plant, Class C ash from We Energies Pleasant Prairie Plant – both normalized and adjusted to 6% LOI for ease of comparison with ASTM C-618

**Type 1 Portland cement – Lafarge Corporation

FGD material is produced when sulfur dioxide (SO_2) is removed from stack gases. This occurs in the flue gas scrubbers when slurried limestone or lime reacts with the gaseous SO_2 to produce calcium sulfite (CaSO_3).

In “wet” FGD systems, which are by far the most common in large, coal-fired utility boilers, SO_2 removal takes place downstream of the particulate removal device. In many installations, CaSO_3 is further oxidized to calcium sulfate (CaSO_4). Because the sulfate material is in an aqueous slurry, it forms the hydrate, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ (gypsum).

“Dry” FGD systems are installed upstream of the particulate removal device, which removes the sorbent reaction products (CaSO_3 or CaSO_4) along with the fly ash and the unreacted sorbent, lime.

When combustion takes place in an FBC, limestone is fed into the boiler with the coal for SO_2 removal. Bottom ash, fly ash, and sorbent (a small portion of which is unreacted) are removed. A dry FGD system may be added between the FBC and particulate removal device if greater SO_2 removal is required.



Flowable fill typically contains fly ash and water and may contain small amounts of Portland cement.

CUB Properties and Uses

Fly Ash

Fly ash is a fine, powdery material and by far the largest-volume CUB. Its particles are spherical in shape, glassy, with a size similar to that of silt. The chemical make-up of fly ash depends primarily on the chemical properties of the coal burned, but also on the grinding equipment, furnace, combustion process, and nitrogen oxide (NO_x)-control equipment used. The properties of a particular fly ash are the key factor in determining its potential use in manufacturing and construction applications.

ASTM International (formerly the American Society for Testing and Materials) classifies fly ash into two categories—Class F and Class C. Combustion of bituminous and anthracite coals (except in FBCs) usually produces Class F, a pozzolanic ash containing silicon, aluminum, and high levels of iron. Pozzolanic materials, a term originally applied to volcanic ash, form cement when mixed with water. The combustion of subbituminous and lignite coals usually produces Class C, a pozzolanic and cementitious ash high in calcium or lime.

The most common and economical use for Class C fly ash is as a partial replacement for Portland cement in concrete manufacturing (normally up to 30 percent, but can be as high as 50 percent in some applications). In 2004, approximately 14 million tons were used in this capacity, generating several hundred million dollars in revenue and demonstrating the wide acceptance fly ash enjoys in the concrete industry.

Two significant benefits are realized when fly ash is used to displace Portland cement. First, aluminosilicates in the ash react with calcium hydroxide, augmenting its cementitious properties and increasing the strength and durability of the final product. Second, Portland cement production releases high levels of CO₂. For every ton of fly ash used in replacement, one ton of CO₂ emission is avoided. This could prove to be a significant element of an overall U.S. greenhouse gas reduction strategy.

In addition to cement manufacture, fly ash is used to produce controlled low-strength material, also known as flowable fill, and as a filler in plastic compounds. Flowable fill pours freely, sets up quickly, and has the strength of compacted soil. In construction, it cuts man-hours and improves worker safety by allowing trenches to be backfilled remotely rather than manually. In mining, it is used as backfill and is especially useful in preventing underground mine subsidence. The finest-sized fly ash is used as filler in plastic compounds, increasing the stiffness of the plastic and reducing production cost by displacing plastic resin.

The applications noted above use fly ash with low carbon content, formally the predominant fly ash produced by U.S. coal-fired power plants. Due to changes in environmental controls, however, high-carbon fly ash is becoming more common. Efforts are underway to identify uses for such material, and two have been closely investigated.

The first is fuel. Carbon from the ash is high in surface area, which compensates for its low volatile matter content. Tests conducted by the University of Kentucky's Center for Applied Energy Research found a 99 percent burnout rate for the carbon when the fly ash is rebled with the coal feed. The second is as a sorbent material. The carbon's pore structure and high surface area help it adsorb odorous gases and organic pollutants. Applications could include removal of organic dyes and oils from waste streams.

In reconstructing and/or upgrading existing pavements, Class C fly ash is used during cold in-place recycling (also known as full-depth reclamation). The existing pavement is pulverized along with its base, and the mixture is stabilized by adding fly ash and water. A new asphaltic concrete surface is then installed above the stabilized section. The properties of the Class C ash enhance the recycled pavement's structural capacity to a much greater extent than either Class F ash or traditional crushed stone aggregate could do.

Class C fly ash is also widely used for soil stabilization. When properly proportioned, disked, and compacted, the ash increases the shear strength of soils in embankment sections. It can also serve as a drying agent. Soil with high moisture content can be difficult to compact during spring and fall. Adding fly ash to the soil quickly reduces the soil's moisture content to levels suitable for compaction. Finally, Class C ash is used to reduce the shrink-swell potential of clay soils. The cementitious products formed by hydrating the ash bond with the clay particles reduce the clay's swell potential to levels achievable with lime treatment.

Bottom Ash

Compared to fly ash, bottom ash is much coarser, often containing significant voids from gas bubbles. The chemical composition of bottom ash is somewhat similar to that of fly ash, but it typically contains more carbon and less volatile impurities (mercury, boron, etc.), which tend to report to the fly ash.

Bottom ash is also more inert. Because its particles have fused in the boiler, they show less pozzolanic activity and are unsuitable as an additive constituent in cement. Bottom ash can, however, be used as a coarse aggregate for cement blocks, with its porous nature often qualifying the product for lightweight classification. At one time this was a common use. However, quality and supply problems have reduced the amount of ash used in this type of product.

Today, bottom ash is most commonly used in structural fills, road base and sub-base pavement, and for snow and ice removal.

Boiler Slag

Boiler slags normally have a particle size in the range of 0.5–5.0 mm. Typically, its particles are smooth in texture, but if gases are trapped in the molten slag as it is tapped from the furnace, the slag can be somewhat porous. The maximum dry bulk density values of boiler slag are 10–25 percent lower than natural granular materials.

By far the most common use of boiler slag is for roofing granules and blasting grit. These applications account for over 88 percent of slag sold.

Boiler slag is also used in road construction. It enhances hot-mix asphalt because of its hard, durable particles and resistance to surface wear. It finds use in asphalt wearing surface mixtures because of its affinity for asphalt and its dust-free surface, which increases the asphalt's adhesion and anti-stripping characteristics. And, it has been used successfully as a seal-coat aggregate for bituminous surface treatments to enhance skid resistance. Because it has a uniform particle size, the slag is usually mixed with aggregates of other sizes to achieve target gradation.

FBC Ash

FBC ash is a relatively new CUB that already enjoys a utilization rate of over 50 percent. It is a mixture of unreacted lime, CaSO_3 , anhydrous CaSO_4 , and ash that is highly alkaline in nature. It is also self-cementing, although it has a tendency to swell.

FBC fly ash is used in structural fills where swelling is not an issue, soil modification, and mining applications. Efforts are also underway to find a use for this material in cement manufacturing.

Chemical Composition of Typical Bottom Ash, weight %

Compound	Bituminous Coal	Sub-bituminous Coal
SiO_2	61.0	46.8
Al_2O_3	25.4	18.8
Fe_2O_3	6.6	5.9
CaO	1.5	17.8
MgO	1.0	4.0
Na_2O	0.9	1.3
K_2O	0.2	0.3

FGD Material

Wet FGD scrubber material is initially formed and primarily generated as CaSO_3 . Calcium sulfite sludge can be fixated with lime, fly ash, or cement and used for road base. However, many wet scrubber systems include a forced oxidation step that converts CaSO_3 to CaSO_4 . Because this process is carried out in the aqueous phase, gypsum is produced.

The purity of synthetic gypsum ranges from 96 to 99 percent, depending on the sorbent used for desulfurization and the amount of fly ash collected in the scrubbers along with the gypsum. The quantity produced is directly proportional to the sulfur content of the fuel being burned and the system's SO_2 removal efficiency. Synthetic gypsum is widely used for wallboard—where its purity often makes it more desirable than natural rock gypsum—as a road base, and in cement manufacturing.

When used as a road base, the gypsum is stabilized with quicklime and pozzolanic fly ash. In cement manufacturing, it is mixed with the “clinker” product (calcium silicates) from the cement kiln. The gypsum acts to control the setting time of the resulting cement. When introduced in wet form, it also benefits the cement grinding process by introducing moisture into the ball mill, thus providing additional cooling.

Several uses for synthetic gypsum currently constitute small markets. These include agriculture and the manufacture of various products. However, gypsum production is expected to rise significantly over the next 10 years along with the increase in scrubber installations in response to environmental regulations. These small markets may prove increasingly important to synthetic gypsum utilization.



The purity of synthetic gypsum makes it more desirable than naturally occurring rock for the production of wallboard and other construction materials.

Chemical Composition of Typical Boiler Slag, weight %

Compound	Bituminous Coal	Sub-bituminous Coal
SiO_2	48.9	40.5
Al_2O_3	21.9	13.8
Fe_2O_3	14.3	14.2
CaO	1.4	22.4
MgO	5.2	5.6
Na_2O	0.7	1.7
K_2O	0.1	1.1

Agriculture

Gypsum has proven to be an effective soil amendment in many agricultural applications to improve drainage and provide sulfur and calcium nutrient. However, regulators are reluctant to allow the use of soil amendments that contain mercury, no matter how stable. In addition, the agriculture industry has yet to determine which crops would adequately benefit from gypsum application.

Ohio State University is a national leader in testing and research in FGD gypsum utilization in this area. The Electric Power Research Institute (EPRI) also is conducting data reviews and field tests of crop productivity to demonstrate the benefit and environmental acceptability of using gypsum in agriculture. Depending on the outcome of these efforts, EPRI is scheduled to conduct groundwater and subsurface migration tests for mercury. In addition, EPRI will conduct agronomic analyses to determine the economic value of FGD gypsum use with different crops, soils, and transportation scenarios (from power plant to farm). EPRI's work is being cofunded by DOE.

Typical Chemical Composition of Synthetic Gypsum

Constituent	Weight Fraction (%)
Ca	24.0
SO ₄	54.0
CO ₃	3.0
SiO ₂	2.7
Inert	1.3
H ₂ O	15.0
pH=7	

Other Applications

Gypsum can be heated to produce several hemihydrate and anhydrite forms of CaSO₄. The specific form of CaSO₄ produced is determined by the temperature to which it is heated, the length of time it remains at process temperature, and whether or not the material is agitated.

Higher-value uses for hemihydrates include plaster of Paris and a high-strength plaster sometimes referred to as gypsum cement. Gypsum cement can replace standard cement in some applications and has found broad application in self-leveling flooring, especially in Europe.

Anhydrites can be manufactured as either particulates or fibers. They are used in plastics and thermoplastics, paper, pharmaceuticals, food, adhesives, and paint. In plastics and thermoplastics, fibrous anhydrites add strength to the product.



CUBs improve the chemical and physical properties of soils, promoting plant growth and increasing productivity.

Market Analysis

In 2004, the United States produced over 122 million tons of CUBs, over 49 million tons of which were used constructively. This makes 2004 the first year in which over 40 percent of the CUBs from coal-fired power plants were effectively utilized.

The market value of various CUBs is determined by several factors. These include the uses for which the properties of the material make it suitable, distance to the user, and the state and local specifications that determine which purposes are allowed.

The ACAA estimates ranges of expected values for some of these products:

- Cement-quality fly ash—\$40–60/ton
- Self-cementing fly ash for soil stabilization—\$10–20/ton
- Bottom ash and fly ash for snow and ice control—\$3–6/ton
- Bottom ash and fly ash for road base—\$4–8/ton
- Self-cementing fly ash for oilfield grouting and waste stabilization—\$15–25/ton
- Fly ash for use in flowable fill—\$1/ton

Selling price is only one economic aspect of CUB utilization, however. If CUBs are not used beneficially, power plants incur costs associated with disposal, which can be as low as \$3/ton for onsite disposal but as high as \$50/ton for landfilling in areas where space is scarce or long hauls are required.

CUB Regulatory History

In the Solid Waste Disposal Act Amendments of 1980, which amended the 1976 Resource Conservation and Recovery Act (RCRA), Congress temporarily exempted from regulation as hazardous wastes a range of CUBs (fly ash, bottom ash, slag, and FGD wastes) under RCRA Subtitle C. Congress then directed EPA to study the adverse effects on human health and the environment caused by CUB disposal. The study was to be followed by a Report to Congress (RTC) and, six months later, a regulatory determination (RD) stating whether CUBs do or do not warrant permanent regulation.

In response, EPA took the following actions:

- 1988: Submitted the RTC, “Wastes from the Combustion of Coal by Electric Utility Power Plants,” in which it tentatively determined that CUBs do not warrant regulation under Subtitle C.
- 1992: In response to a suit filed by a citizens’ group because it did not publish its RD in the required timeframe, entered into a consent decree that divided CUBs into two categories: (1) those generated by electric utility and independent power production facilities and (2) all remaining wastes subject to RCRA Sections 3001(b) and 8002(n). The decree contained separate schedules for providing RDs for each category.
- 1993: Issued an RD determining that Category 1 materials do not warrant regulation when managed alone (i.e., not co-managed with low-volume wastes).
- 1999: Issued an RTC tentatively determining that Category 2 materials should also remain exempt from Subtitle C.
- 2000: Issued an RD determining that Category 2 materials do not warrant regulation. However, EPA also determined that “national regulations under subtitle D of RCRA are warranted for [CUBs] when they are disposed in landfills or surface impoundments, and that regulations under subtitle D of RCRA (and/or possibly modifications to existing regulations established under authority of the Surface Mining Control and Reclamation Act [SMCRA]) are warranted when these wastes are used to fill surface or underground mines.” The EPA also stated that it did not want to erect unnecessary barriers to the use of these materials because they conserve natural resources and landfill space.

To ensure the consistent regulation of CUBs across all waste management scenarios, EPA plans to develop national regulations for CUB disposal in surface impoundments, landfills, and as minefilling. EPA’s regulations will be applicable to CUBs that are generated at electric utility and independent power production facilities and not co-managed with low-volume wastes.

Fly Ash

Fly ash is the largest-volume CUB with respect to both production and utilization (70.8 and 28.1 million tons in 2004, respectively). It currently finds markets in concrete manufacturing and in road and other construction applications. However, with a 70 percent disposal rate, it is far from being fully utilized.

Of the 70.8 million tons of fly ash available annually, approximately 16.5 million tons are used as a replacement for Portland cement in concrete manufacturing and as a component of the kiln feed to produce clinker. In 2004, the United States used approximately 121 million tons of Portland cement, of which fly ash with acceptable properties could have replaced at least 30 percent (36.1 million tons). Therefore, substantial opportunity still exists for fly ash in this market—though not nearly enough to fully utilize annual production.

High-volume construction is another, potentially large market for fly ash and one favored by EPA. The ash can be used in road construction, as structural and mine fill, and for waste stabilization.

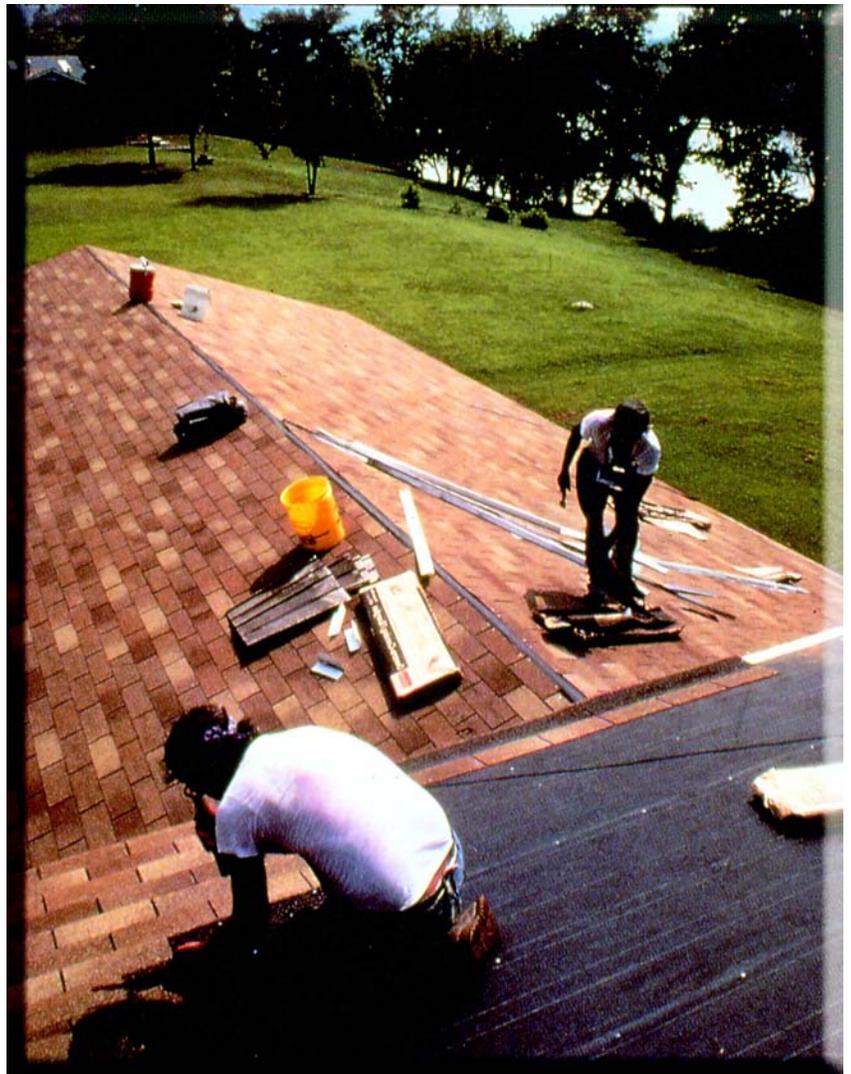
In a PPII demonstration project, Universal Aggregates is using spray dryer absorber ash, a mixture of fly ash and spent sorbent, to manufacture aggregate. According to the United States Geological Survey (USGS), the United States uses more than 1.2 billion tons/year of crushed stone, sand, and gravel as aggregate. Barriers to tapping this market with fly ash include non-acceptance in some states of fly ash as a base material, widely varying specifications for use where it is accepted, and potential cost. USGS reports that sand and gravel sold for an average price of \$5.28/ton in 2004 (f.o.b. quarry) while crushed stone sold for \$6.08/ton. The cost of manufactured aggregate must be competitive and it must continue to gain acceptance as a safe, reliable material. If these conditions are met, the potential market for manufactured aggregate is expected to be quite large.

Bottom Ash

Just under 50 percent of annual bottom ash production currently finds a market as structural fill, road base material, and a snow and ice control product. As acceptance for these applications increases, these large markets have the potential to absorb all of the bottom ash produced annually.

Boiler Slag

Nearly 90 percent of the boiler slag currently generated each year is sold on the market, primarily as blasting grit and roofing granules. However, much of the slag is produced in cyclone boilers, which have fallen out of favor due to their high NO_x emissions.



The most common uses of boiler slag are roofing granules and blasting grit. However, quantities available are decreasing as cyclone boilers are being retired.

As the older cyclone boilers are retired, the quantities of boiler slag available will decrease. According to ACAA data, 2.57 million tons were produced in 1996 compared to 1.97 million in 2004. The boiler slag that is produced will certainly find a ready market.

FBC Ash

The quantities of available FBC ash are currently small compared to other forms of ash. However, it already enjoys a utilization rate of over 50 percent. Its highly alkaline nature makes FBC ash especially useful in soil modification and to mitigate acid mine drainage. Work is also underway to find a use for this material in cement manufacturing.

While FBC technology has been available for some time, recent trends indicate that installations will increase dramatically in the coming decade. Therefore, the use of FBC ash also needs to grow. If utilization rates are to be maintained or increased, continuing work is needed to expand the use of this CUB in its current applications and to develop new ways to utilize this important product.

FGD Material

In 2004, just under 12 million tons of synthetic gypsum were produced in U.S. FGD systems, and over 9 million tons were sold. Of product sold, over 8 million tons went into wallboard.

Because of its purity, which ranges from 96 to 99 percent, the $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ produced in FGD systems competes effectively with natural gypsum. Some wallboard producers have built manufacturing plants near power plants. When the gypsum is to be used in a remote wallboard plant, transportation costs are critical.

Conversely, approximately 17.5 million tons of CaSO_3 FGD material were produced in 2004, but less than 7 percent found a market, primarily in structural fills and mining applications. It would be relatively easy to convert this material to gypsum if the market would support it. Conversion of all CaSO_3 FGD material would nearly triple current gypsum production to almost 30 million tons/year. An almost certain rise in gypsum production will result from industry compliance with SO_2 emission restrictions embodied in EPA's Clean Air Interstate Rule (CAIR). CAIR is expected to greatly increase the number of plants equipped with wet FGD systems, which in turn will substantially increase the amount of available FGD gypsum.

Because the United States uses a total of only 39 million tons of gypsum/year, and given the constraint of transportation costs, it is unlikely that current uses can effectively absorb all FGD material in the future. To fully utilize future production, development of other potential markets must continue, including agriculture, gypsum cement, paper, plastics, pharmaceuticals, food, adhesives, and paint.



Fly ash and FGD material can be used as filler in paints.

DOE-Sponsored CUB Demonstrations

As mentioned earlier, DOE has selected projects under the PPII and CCPI programs that will demonstrate effective use of CUBs. These projects are currently in various stages of development.

Western Greenbrier

One of the DOE-sponsored projects intended to increase the use of CUBs is the CCPI project being conducted by Western Greenbrier Co-Generation, LLC. This project will co-generate electric power and steam for export to nearby users, as well as produce cement from a portion of the ash from the combustion system.

The Western Greenbrier project, to be located in Rainelle, WV, will produce 75 megawatts (MW) of electric power while burning beneficiated waste coal. The waste coal will be obtained from the 4-million ton Anjean waste coal pile. The combustion system will be a circulating fluidized bed (CFB). Limestone will be injected into the bed to control SO₂. The limestone will be converted to lime in the CFB. SO₂ removal will be enhanced with a spray dryer absorber (SDA). Particulate matter will be controlled in a pulse jet baghouse located downstream of the SDA. A portion of the fly ash/lime mixture removed by the baghouse will be hydrated and recycled. The balance will be used for remediation of the acid runoff from the Anjean waste coal pile.

Spent bed material (lime and ash) will be processed in a horizontal kiln to produce clinker, which will then be crushed to produce a fast-setting, high-strength cement.

University of Kentucky

Another CCPI project that will demonstrate ash processing is being sponsored by the University of Kentucky. Collaborators in this project are CEMEX USA and LG&E Corporation, the parent of Kentucky Utilities (KU). The demonstration will be carried out at KU's Ghent Power Station. The technology being demonstrated will process the ash from a boiler and convert it all into saleable products. The demonstration will also use the plant's ash pond as a feed source during boiler outages or when demand for the ash product is high.

The process moves the ash through a series of separation equipment that includes screens, crushers, hydraulic classifiers, concentrating spirals, sieve bends, flotation cells, and dryers. The end result is a series of products that completely utilize the boiler ash. These products are pozzolan, lightweight aggregate, fill-sand, unburned carbon, and cenospheres.



Light-weight concrete block made with CUBs.
(Photo courtesy of FlexCrete Building Systems, LC.)

Universal Aggregates

This PPII project is being conducted by Universal Aggregates, LLC, at the Birchwood Power Facility in King George County, VA. This demonstration will transform 115,000 tons/year of spray dryer solids into 167,000 tons/year of lightweight aggregates that can be used to manufacture light- and medium-weight masonry blocks.

In this process, spray dryer ash is mixed with water and other recycled products and fed to a mixer that produces a moist, granular material. The product from the mixer is fed directly to an extruder that produces short, soft, wet extrusions (green pellets). These are sent to a slow-turning tumbler where the green pellets are mixed with a dry embedding material. The embedding material coats the green pellets to keep them from agglomerating and to fill voids between the pellets to cushion them during subsequent processing. The green pellets are then fed to a curing vessel where they are allowed to cure via cementitious/pozzolanic reactions. The hardened pellets are screened to remove fines and embedding material and sent to storage or to a final crushing and screening process to generate the final product.

Other Projects

In addition to these PPII and CCPI projects, DOE is sponsoring 10 additional projects under the Combustion Byproducts Recycling Consortium, which is managed by the National Energy Technology Laboratory and the West Virginia University Water Research Institute. These projects have a total value of over \$1.8 million.

Examples of Best-Practice Utilization of CUB Materials

We Energies

We Energies (Wisconsin Electric Power and Wisconsin Gas LLC) is a leader in CUB utilization, with more than 98 percent of its total CUB production (645,000 tons/year) going to reuse applications. The utility developed a patented process designed to remove coal ash from company landfills and restore the land in accordance with all applicable regulations. The process includes identifying a disposal site that has the appropriate CUBs and excavating cover materials to access the deposited ash. A portion of the ash is recovered to determine loss-on-ignition (LOI) value. If it is cost effective to do so, the ash material is removed to a pulverized coal furnace for reburning, utilizing one of two coal ash beneficiation processes developed by We Energies. These processes convert a high-carbon ash into a more useable and marketable product while extracting its residual fuel heating value.

The utility also patented a process to remove ammonia (NH₃) compounds from fly ash. This process is applicable to ash generated from units equipped with selective catalytic reduction (SCR) or selective non-catalytic reduction (SNCR) technologies, which use NH₃ to control NO_x. The process involves the application of heat to the ash using a high-temperature air slide. We Energies patented two processes related to the use of fly ash in producing metal matrix composites (e.g., aluminum casings). Prototype automotive parts, such as manifolds and brake drums, have been produced for testing. In these types of products, fly ash is used in the composite to alter the density, hardness, crack propensity, and mechanical properties of the metal matrix. These composite materials hold promise for producing lower cost alloys and providing a higher value use for fly ash.

We Energies also has a patent (and one pending) for producing controlled low-strength material and concrete material that is less electrically resistant. These materials have potential applications in the utility and construction industry for electrical grounding, lightning protection, transportation system sensors, and ice prevention on bridges, sidewalks, and airport runways.

The utility has also produced a structural lightweight aggregate that blends a mixture of fly ash, paper mill sludge, and municipal wastewater sludge. The process pelletizes and dries the mixture, then fires the pellets in a co-current flow rotary kiln to produce a low-density, ceramic aggregate. From 1994 to 2000, We Energies owned and operated a commercial-scale pilot plant for the production of this product.

Great River Energy

Great River Energy markets fly ash from the Coal Creek Power Station, a 1,100-MW plant, located in Underwood, ND, and the Stanton Station, a 180-MW plant located near Stanton, ND. Sales of fly ash in 2004 from the Coal Creek Power Station are projected to have been about 390,000 tons out of the 440,000 tons produced. A significant portion of the fly ash marketed from both plants is mixed with cement to make concrete that is stronger and more durable than concrete made with cement alone. In addition, the fly ash from these plants is being used by the Amerada Hess Corporation to restore oil production sites in North Dakota after oil rigs are removed. It is also used in manufacturing FlexCrete (an aerated concrete) that will be used to help construct the National Energy Technology Training and Education Center at Bismarck State College. The fly ash is also being tested in new product development for ceramic tiles and a spray product to protect and extend the life of wooden power transmission poles.

Charah Inc.

Charah has explored new ways to bag concrete mix to address issues of cleanliness and container damage loss to appeal to big-box retailers, who are the largest sellers of these products. Working with Automatic Packaging Machinery of Atlanta, GA, and Concetti of Rome, Italy, Charah developed a method to successfully place its CUB-based concrete mix into totally sealed plastic bags fitted with two handles. In addition, the plastic bags are more durable than paper bags. These innovations will eliminate leakage problems experienced by retailers and make the product more appealing to consumers.

Charah built a manufacturing plant in Virginia that started production in January of 2005. This plant includes automated, state-of-the-art equipment and will have the capacity to annually produce six million bags of the CUB-based concrete mix. Over the next three years, Charah plans to build seven additional manufacturing plants to utilize ash resources throughout the United States.

EERC

The University of North Dakota Energy and Environmental Research Center (EERC) has the country's most extensive research program focused on the release of mercury via leachates and vapor from CUBs impacted by mercury emission controls. EERC has developed the following technologies:

- Methods for determining the direct leachability of mercury from CUBs
- Methods for evaluating vapor-phase transport of mercury
- A method to evaluate the release of mercury from CUBs at elevated temperatures (up to 750 °C) in real time
- Experimental protocols to evaluate the effect of microbiological activity on CUB leachate.

The DOE Clean Coal Technology Programs

The DOE commitment to clean coal development has progressed through three phases. First was the Clean Coal Technology Demonstration Program (CCTDP), a model of government and industry cooperation that advanced DOE's mission to foster secure and reliable energy systems.

With 33 of its 34 active projects completed, the CCTDP has yielded technologies that provide a foundation for meeting future energy demands and utilizing the vast U.S. reserves of coal in an environmentally sound manner. Begun in 1985, the CCTDP represents a total investment value of nearly \$3.3 billion. DOE's share of the total cost is about \$1.3 billion, or approximately 40 percent. The projects' industrial participants (i.e., non-DOE) have provided the remainder, about \$2.0 billion.

Two follow-on programs have been developed that build on the successes of the CCTDP and are patterned after it. The Power Plant Improvement Initiative (PPII) is a cost-shared program directed toward improved reliability and environmental performance of the nation's coal-burning power plants. Authorized by the U.S. Congress in 2001, PPII involves six projects that focus on technologies enabling coal-fired power plants to meet increasingly stringent environmental regulations at the lowest possible cost.

The Clean Coal Power Initiative (CCPI), authorized in 2002, is aimed at accelerating commercial deployment of advanced technologies to ensure the nation will continue to have clean, reliable, and affordable electricity. Total Federal funding will equal up to \$2 billion over 10 years, with a matching cost share by industrial participants of at least 50 percent. To date, nine CCPI projects are either active or in negotiation.



In ancient times the Romans added volcanic ash to concrete to strengthen structures and roads.



CUBs are used to enhance modern road construction.

LCRA

In 2004, the Lower Colorado River Authority (LCRA) achieved a utilization rate of nearly 150 percent of current production of FGD CUBs by using material that was deposited in landfills years ago. LCRA plans to install scrubbers on Units 1 and 2 at the Fayette Power Project by 2012 and projects that its market will accommodate the additional volume of FGD by-products that it anticipates generating in the near future.

LCRA's bottom ash uses include production of road-base materials (bottom ash mixed with fly ash) and brick manufacturing. Until 2002, LCRA's utilization rates of bottom ash averaged nearly 50 percent. By 2004, LCRA pushed its utilization rate to over 100 percent, again using stored material produced in earlier years to make up the difference. The increased use is primarily due to a higher local demand in surrounding counties for road-base material. In addition, the demand for bottom ash as an ingredient in brick increased when a new brick plant opened in the area. LCRA's fly ash use, primarily in ready-mix concrete, road stabilization, and road-base mixtures, has also seen an increase beyond 100 percent.

Kansas City Power and Light; Lafarge North America; and the University of Missouri, Kansas City

The partners are testing the "*Full Depth Cold In-Place Recycling of Asphalt Pavement.*" This process is used to rehabilitate low-volume rural roads by recycling existing asphalt pavement and base materials in place, instead of hauling them away and bringing virgin materials to the site. The old road is ground up and left in place. Self-cementing (Class C) fly ash and water are then mixed in, and the blend is compacted into a new road base.

PMET

Pittsburgh Mineral and Environmental Technology (PMET) developed and patented the innovative Brixx Technology to produce building products. The process produces stand-alone building products from CUBs, including both fly ash and bottom ash. Unlike many concrete applications, the Brixx process can utilize fly ash with LOI exceeding 3 percent. The process consists of mixing the raw materials, pressing the mixture into desired shapes, and curing the resulting product. The process produces tobermorite (a calcium silicate hydrate) crystals in the Brixx product that result in a strong, weather-resistant material. PMET has taken this technology from a laboratory-scale process to the pilot scale. Currently, PMET is producing paving brick as a demonstration project for a Pennsylvania Department of Environmental Protection-sponsored Energy Harvest grant.

The fly ash used in this project has an LOI of 6.3 percent, which is too high to use as an additive in concrete. The Brixx paving bricks have a compressive strength that exceeds ASTM standards. For a full-scale plant, energy consumption is expected to be 430,000 Btu/ton of product, which is 67 percent less energy than a modern clay brick high-efficiency kiln. Production costs are expected to be approximately \$0.11/piece, compared to an estimated selling price of \$0.20. PMET estimates that a plant producing 13.6 million paving bricks/year would have a payback time of two years.

Xcel Energy and Lafarge North America

During the spring of 2002, Xcel Energy and Lafarge North America demonstrated use of fly ash alongside other materials (including lime and oil emulsions) on a trial highway project in Randall County, TX. The paving contractor used approximately 200 tons of CUB material to stabilize the road base. The fly ash performance on this project was strong compared to the alternative materials, and Lafarge has seen geotechnical applications grow from 20 percent of the stabilization work in the Amarillo market in 2002 to 90 percent of the market today.

The success of Xcel Energy and Lafarge's success in the traditional and nontraditional CUB markets in Texas has resulted in the beneficial use of all of the 500,000 tons of CUBs produced annually at Xcel's Harrington and Tolk power stations. Xcel Energy estimates that in 2003, 15,865 tons of these CUBs were used in Texas stabilization projects. Assuming that 75 percent of fly ash used for soil stabilization replaces the use of lime, the corresponding ratio of CUB to lime use is about 2:1. With an emission factor for lime manufacture of 0.17 metric tonnes of carbon equivalent (MTCE)/ton, then greenhouse gas emissions reduction attributable to this CUB use in stabilization projects is 1,350 MTCE/year.



CUBs are used in a range of construction materials, including masonry products.

Factors Limiting the Use of CUBs

Unburned Carbon on Fly Ash

Increasingly strict limits on U.S. NO_x emissions have led to the widespread use of low-NO_x burners, reburning, and overfire air. Often these strategies impair complete coal combustion and produce high-carbon fly ash, which is unsuitable for use in cement manufacturing. The excessive carbon adsorbs concrete's air-entraining agent, which impacts the setting process, causes air entrainment problems, and reduces the material's strength and durability, especially during freeze-thaw conditions.

In some cases, careful design and operation of low-NO_x combustion systems can mitigate the problem of excessive carbon. Several organizations have also developed processes to separate the unburned carbon from the fly ash or developed cement additives to block adsorption of the air-entraining chemicals by the carbon. The University of Kentucky Center for Applied Energy Research is currently demonstrating a DOE-sponsored CCPI project that addresses the former application.

Ammonia Deposition on Fly Ash

Two other NO_x-reduction technologies—SCR and SNCR—introduce NH₃ into the flue gas. Unreacted NH₃, referred to as ammonia slip, contaminates the system's fly ash via adsorption or other mechanisms. This effect can be detrimental to both utilization and disposal of the ash.

In the manufacture of building materials, fly ash must meet permissible limits of ammonia content based on exposure limits for employees and product performance. Even if exposure limits are not exceeded, ammonia can present problems for sensitive individuals.

If the ash is placed in a landfill, odor becomes a factor. Further, in landfills, rainwater can leach ammonia along with other components of ash, resulting in violation of groundwater pollution regulations.

These effects must be taken into account in establishing SCR/SNCR operations, and several thermal and chemical techniques have been developed to counteract the effects

of ammonia slip. One process subjects the fly ash to an additional FBC step to remove both the unburned carbon and the residual ammonia. Another process treats the fly ash with an alkali, such as lime, to release and recover the ammonia. In addition, several methods have been developed to remove ammonia and other pollutants from the wastewater that results from exposure of fly ash in landfills to rainwater.

Increasing CUB Utilization

In 2003, the ash industry, in partnership with EPA, DOE, and the Federal Highway Administration, established the Coal Combustion Products Partnership (C²P²). This effort has been successful in making end-users, specifiers, regulators, and others aware of how CUBs can enhance highway and construction activities.

C²P² has also recognized a number of organizations for their initiatives to increase the use of CUBs. Awardees exemplify best practices for promoting the commercial utilization of CUBs and demonstrating the environmental benefits that can result.

In mid-2005, a number of C²P²'s founders began working on a new program, the Green Highways Partnership. The partnership combines public and private efforts to integrate transportation planning with environmental protection. This includes addressing such factors as watershed protection, ecosystem management, and the use and reuse of recycled industrial materials.

By looking at the design, planning, construction, operation, and maintenance of transportation systems in the broadest environmental context, there will be less impact on the environment and many opportunities for collaborative partnerships. Coal ash and other industrial by-products can contribute to the greening of America's highways by conserving natural materials, reducing greenhouse gas emissions, and lowering overall costs.

ACAA Coal Utilization By-Product Data for 2004—All quantities are 1000s of tons.

CUBs used for:	Fly Ash	Bottom Ash	Boiler Slag	FGD Gypsum	Wet FGD Product	Dry FGD Product	FGD Other	FBC Ash
Concrete/concrete products/grout	14,122	789	0	291	0	37	0	0
Structure/fills embankments	4,685	3,065	7	0	267	0	0	62
Cement/raw feed for cement clinker	2,345	615	34	449	39	0	0	0
Road base/subbase/pavement	488	1,092	7	0	0	0	0	0
Snow & ice control	6	830	88	0	0	0	0	0
Agriculture	52	19	0	131	11	3	0	0
Aggregate	8	409	38	0	0	3	0	0
Flowable fill	180	0	0	0	0	11	0	0
Mineral filler in asphalt	90	0	40	0	0	0	0	0
Wallboard	0	0	0	8,148	0	0	0	0
Waste stabilization/solidification	2442	257	5	0	0	0	0	71
Mining applications	1,113	40	0	0	282	123	0	135
Blasting grit/roof granules	0	70	1,747	0	0	0	0	0
Soil modification/stabilization	501	21	0	0	0	0	0	190
Miscellaneous	2,037	944	8	25	597	0	3	16
Total used	28,069	8,152	1,973	9,045	1,196	177	3	473
Total produced	70,800	17,200	2,202	11,950	17,500	1,829	115	867
Percent used	39.7	47.4	89.6	75.7	6.8	9.7	2.9	54.6

To Receive Additional Information

To be placed on the Department of Energy's distribution list for future information on the Clean Coal Demonstration Programs, the projects they are financing, or other Fossil Energy Programs, please contact:

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Mercury

Recent regulations to control mercury emissions in stack gases could also have a deleterious effect on the utilization of CUBs.

One method likely to be widely used for mercury control is the injection of powdered, activated carbon into the flue gas. Currently, the carbon is removed along with the fly ash using standard fly ash removal equipment. This results in ash contaminated with high carbon levels.

We Energies Inc. is conducting a CCPI project at its Presque Isle Power Plant to demonstrate EPRI's TOXECON™ mercury-control process. Using this process, the bulk of the fly ash is removed by existing ESPs before carbon is injected into the system. The carbon is later removed, along with any residual ash, via a baghouse installed downstream of the ESP.

Wet FGD processes can also be effective for mercury removal, especially if the mercury in the flue gas is in the oxidized state when it enters the FGD system. There is currently some interest in enhancing these processes to achieve higher levels of mercury removal. One concern is the possibility of FGD by-products containing elevated levels of mercury. However, tests to date indicate that mercury contamination will not be a problem for either the disposal or constructive use of these CUBs.

A second concern is the re-release of gaseous mercury during the manufacture of wallboard, cement, and other products that contain FGD CUBs. The Innovations for Existing Plants program of DOE's National Energy Technology Laboratory is currently investigating the extent to which such re-releases of mercury may occur.



Agriculture is a potentially significant market for gypsum and other CUBs.

Conclusions

CUB reuse carries with it many economic and environmental advantages, including cost savings to the power industry, conservation of natural resources and landfill disposal space, and reduced CO₂ emissions. The challenges are to ensure that CUBs produced are available and salable and continue to find profitable market outlets.

Through research and increased public awareness, these challenges are being addressed by government and private stakeholders. The quantities of CUBs generated are increasing, but the utilization of CUBs is increasing faster.

We have nearly reached the goal of 50 percent utilization to be achieved by 2010. With continued product and market development, this goal will be met and exceeded, and our nation will have come a long way in the responsible stewardship of its CUBs.

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List of Acronyms and Abbreviations

ACAA	American Coal Ash Association
ASTM	American Society for Testing and Materials
CaSO ₃	calcium sulfite
CaSO ₄	calcium sulfate
CaSO ₄ •2H ₂ O	gypsum
CCPs	coal combustion products
CCPI	Clean Coal Power Initiative
CCWs.....	coal combustion wastes
CFB	circulating fluid bed
CO ₂	carbon dioxide
CCTDP	Clean Coal Technology Demonstration Program
CUBs	Coal Utilization By-Products
DOE	U.S. Department of Energy
EERC	University of North Dakota Energy and Environmental Research Center
EPA	U.S. Environmental Protection Agency
EPRI	Electric Power Research Institute
ESP	electrostatic precipitator
FBC	fluidized bed combustion
FGD	flue gas desulfurization
KU	Kentucky Utilities
LCRA	Lower Colorado River Authority
LOI	loss on ignition
MTCE	metric tonnes of carbon equivalent
MW	megawatts of electric power
NH ₃	ammonia
NO _x	nitrogen oxides
PMET	Pittsburgh Mineral and Environmental Technology, Inc.
PPII	Power Plant Improvement Initiative
RCRA	Resource Conservation and Recovery Act
RD.....	regulatory determination
RTC	Report to Congress
SCR.....	selective catalytic reduction
SDA	spray dryer absorber
SNCR.....	selective non-catalytic reduction
SO ₂	sulfur dioxide
USGS	United States Geological Survey

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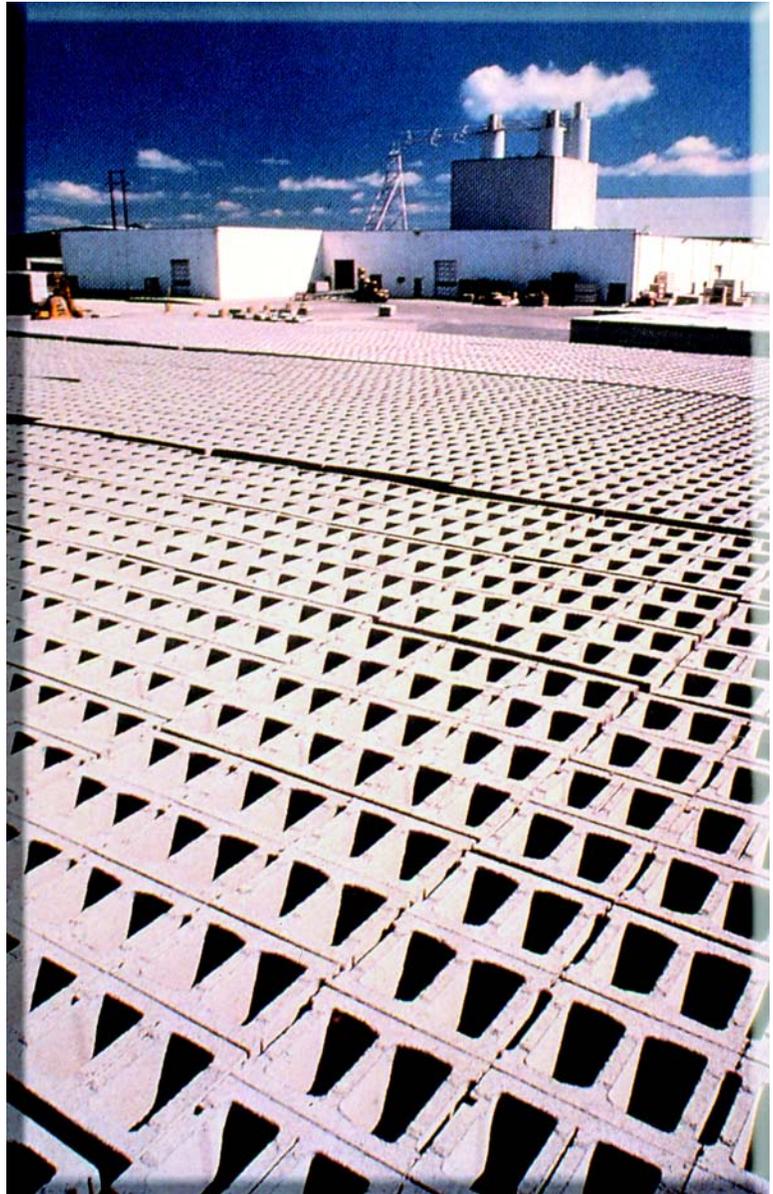
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The most common and economical use for fly ash is in the manufacture of concrete and concrete products.



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