Materials Characterization Paper
In Support of the
Advanced Notice of Proposed Rulemaking –
Identification of Nonhazardous Materials That Are Solid Waste

Coal Combustion Products - Coal Fly Ash, Bottom Ash, and Boiler Slag

December 17, 2008

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1. Definition of CCPs

Coal combustion products (CCPs) are formed during coal-burning processes in power plants and industrial boilers. Coal combustion produces various forms of CCPs that are categorized by the process in which they are generated. The CCPs that can be used as ingredients in the manufacture of portland cement include:[1]

- Fly ash: Exhaust gases leaving the combustion chamber of a power plant entrain particles during the coal combustion process. To prevent fly ash from entering the atmosphere, power plants use various collection devices to remove it from the gases that are leaving the stack. Fly ash is the finest of coal ash particles.
- Bottom ash: With grain sizes ranging from fine sand to fine gravel, bottom ash is coarser than fly ash. Utilities collect bottom ash from the floor of coal burning furnaces used in the generation of steam, the production of electric power, or both. The physical characteristics of the products generated depend on the characteristics of the furnace.
- Boiler Slag: Boiler slag consists of molten ash collected at the base of cyclone and pulverized coal boilers. Facilities cool boiler slag with water, which then shatters into black, angular pieces that range in size from course sand to fine gravel and have a smooth appearance.

2. Annual Quantities of CCPs Generated and Used

(1) **Sectors that generate CCPs:**

- The coal-fired power industry, represented by NAICS sector 221112 – Fossil Fuel Electric Power Generation, is the largest generator of CCPs. Other industries, such as commercial boilers and mineral and grain processors that use coal as a fuel source, also produce small quantities of CCPs.

(2) **Quantities and prices of CCPs generated:**

- In 2007, the coal-fueled electric power industry generated approximately 71.7 million tons of fly ash, 18.1 million tons of bottom ash, and 2.1 million tons of boiler slag.
- In 2003, the price per ton of concrete-quality fly ash, freight on board (FOB) (i.e., costs net of shipping or transport costs), ranged from $0-$45 (ACAAa).

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[1] This paper focuses on CCPs used primarily as an ingredient in cement manufacture; see the Materials Characterization Paper for Coal Refuse for further information on mining rejects and combustion applications.

- In 2003, the price per ton of bottom ash ranged from $3-$8 FOB (ACAAa).
- The price of boiler slag could not be determined at this time; as with many small markets, it may be that most transactions involving boiler slag are private.

(3) **Trends in generation of CCPs:**

- The coal-fired power industry is the largest generator of CCPs in the United States. Coal-generated electricity supplies approximately 50 percent of the electricity consumed in the United States (American Coal Foundation). Since electricity demand is projected to increase in coming years, and coal will continue to be an important fuel source, the quantity of CCPs produced and available for beneficial reuse may also increase (USDOE 2008, p.10). While other industries that use coal as a fuel source in commercial or industrial boilers (e.g., mineral and grain processors) also produce CCPs, these quantities tend to be small, and increases or decreases in their production will not have a significant impact on the overall trend in CCP production.

3. Uses of CCPs

(1) **Ingredient and combustion uses of CCPs:**

- Fly ash, bottom ash, and boiler slag can be added to the raw material feed in clinker manufacturing to contribute specific required constituents, such as silica, alumina, and calcium, in the final cement composition.
- Fly ash with high unburned carbon content can also be reburned in cement kilns for energy recovery at the same time as it provides ingredient value.

(2) **Non-combustion uses of CCPs:**

- Fly ash can be used in a number of non-combustion applications. It’s most common, and most high-value, use is as a supplementary cementitious material in concrete (i.e., a substitute for, or amendment to, portland cement in concrete mixes). In this application, fly ash can provide certain material advantages such as greater workability, higher strength, and increased longevity in the finished concrete product. Fly ash is also used as a partial substitute for virgin dirt, sand, or gravel in structural fill, or as a substitute for portland cement in waste stabilization (ACAA 2006).
- Bottom ash can be used to offset virgin sand and gravel in applications such as structural fill, road base, and concrete (ACAA 2006).
- Boiler slag can be used to offset virgin sand and gravel in applications such as structural fill and blasting grit (ACAA 2006).

(3) **Quantities of CCPs landfilled:**

- In 2007, 40 million tons fly ash, 9.2 million tons bottom ash, and 0.41 million tons boiler slag were landfilled, representing roughly 56 percent, 60 percent, and 20 percent of production, respectively.

(4) **Quantities of CCPs stockpiled/stored:**

- The American Coal Ash Association (ACAA) estimates that between 100 million and 500 million tons of fly ash have accumulated in U.S. landfills since the 1920s, when the disposal of fly ash in landfills began. It is unclear, however, how much of this fly ash is available for beneficial use.
- The recoverability of fly ash depends significantly on the manner in which it is disposed. Fly ash disposed of in a monofill or holding pond likely would be suitable for beneficial use because it has generally not been commingled with other materials. Unfortunately, the ACAA is unaware of data indicating how much of the 100-500 million tons of stockpiled fly ash is deposited in monofills or holding ponds
- The recovery of landfilled ash for beneficial reuse does not appear to be widely practiced. Although a portion of the fly ash located in stockpiles across the U.S. may be available for beneficial use, a recent analysis of the market for fly ash found that approximately 49 percent of the 72.4 million tons of fly ash generated in 2006 was beneficially used (ACAA). Therefore, even if large quantities from stockpiles were made available, it is unlikely that the quantity re-used would increase significantly. In other words, the demand for fly ash appears to be met by existing production.
- Certain electric utilities, however, have pursued programs to recover ash for use of its residual unburned carbon in power plants. Examples include:
  - Wisconsin Energy Corporation began reburning ash at its Pleasant Prairie Power Plant in 2000 and expanded reburning to include ash recovered from landfills in 2001 after receiving approval under Wisconsin's first Environmental Cooperative Agreement. The patented process can use either dry high-carbon fly ash directly from the company's older power plants, or use moist high-carbon ash from WEC's power plants, stockpiles, existing landfills, and remediation projects. According to its 2006 Performance Report, WEC reburned approximately 11,023 short tons of recovered landfill ash in 2002 (WEC 2006a, p.69).[2]
  - In 2001, Western Kentucky Energy's Coleman station in Hawesville, Kentucky, inaugurated an ash-recovery program developed by staff at the University of Kentucky Center for Applied Energy Research (CAER). The CAER researchers developed a system to remove fly ash from holding ponds and extract carbon to create a reburning fuel or several other products (BNET 2002, pp. 1-2).
- Wisconsin Energy Corporation also recovers landfilled ash for sale as a construction material. Under the Environmental Cooperative Agreement and Wisconsin regulations for beneficial industrial byproduct use, the company recovered 31,967 short tons (706.293 cubic feet) of coal ash from its P4 landfill and sold it as a base material to replace stone or gravel under roads, parking lots,

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[2] The report indicates that between 2003 and 2006, the facility did not reburn any recovered coal ash from its landfill. During these years, however, the facility continued to reburn coal ash generated by power plants.

and buildings. Since 2002, more than 93,696 short tons have been recovered (WEC 2006a, p.70).

Exhibit 1: Overview of Generation and Use of CCPs in 2007

Commodity	**Annual Quantity Generated**	**Annual Quantity Used as Ingredient**		**Annual Quantity Landfilled**	**Annual Quantity in Other Uses**	**Total Quantity Stockpiled as of 2006**
		Fuel	**Cement Ingredient in Kilns**			
	----------------------------*Short Tons* -------------------------					
Coal fly ash	71.7 million	Undetermined	3.6 million	40.07 million	28.03 million	100 – 500 million[a]
Bottom ash	18.1 million	0	0.61 million	10.80 million	6.69 million	Undetermined
Boiler slag	2.1 million	0	0.007 million	0.41 million	1.65 million	Undetermined

Sources:
Unless otherwise noted, data is from American Coal Ash Association. (ACAA), 2006, *Coal Combustion Product (CCP) Production and Use Survey,* accessed at: http://www.acaa-usa.org/associations/8003/files/2007_ACAA_CCP_Survey_Report_Form%2809-15-08%29.pdf.

Notes:
a. Personal communication with Dave Goss, ACAA, November 27, 2006.

4. Management and Combustion processes for CCPs

(1) **Types of units using CCPs:**
- When used in clinker manufacture, fly ash, boiler slag, and bottom ash are fed into cement kilns with other raw material feed.

(2) **Sourcing of CCPs:**
- Although electric utility companies produce ash at their coal-fired power plants, most utilities do not handle, dispose of, and/or sell the ash that they produce. There are approximately 40 to 50 commercial ash marketing firms operating throughout the United States, in all states except Hawaii. In addition to commercial ash marketing organizations, certain coal-burning electric utility companies have formal ash marketing programs of their own. Most coal-burning electric utility companies currently employ an ash marketing specialist whose responsibility it is to monitor ash generation, quality, use or disposal, and to interface with the ash marketers or brokers who are under contract to the utility companies (Turner Fairbank Highway Research Center).

(3) **Processing of CCPs:**
- Use of CCPs as a raw feed in cement kilns does not require processing. However, kilns do require feed of consistent quality, quantity, and composition in order to ensure that the feed mix in the kiln is appropriate. In particular, levels of key metals (e.g., iron and alumina) in CCPs are carefully calibrated with other

ingredients to ensure that the final cement product has the correct mineral and metal content.

- Due to its pozzolanic properties, stockpiled class C fly ash may harden over time if exposed to moisture. (Class F fly ash does not exhibit this characteristic). Hardened class C fly ash must be crushed prior to beneficial use but is typically limited to use as an aggregate in concrete. Class F fly ash does not loose reactivity over time and can be recovered from stockpiles for use in concrete, but it is unclear to what extent stockpiled Class F fly ash can be used in cement kilns, or whether it requires processing prior to use.
- Bottom ash may require stockpiling for a short period of time (at least 1 or 2 days) to allow excess water to drain prior to beneficial use. Ponded bottom ash reclaimed from a lagoon should be stockpiled and allowed to drain for a somewhat longer time period, perhaps up to 1 or 2 weeks, depending on the amount of rainfall. After size reduction, bottom ash can be screened to produce different size ranges, if desired. (Turner Fairbank Highway Research Center).
- An example of the recovery process used by Wisconsin Energy Corp. includes:
  - Identifying a disposal site that contains the byproducts (typically fly ash and bottom ash) and removing a portion of the byproduct;
  - The removed materials are crushed, screened, and periodically sampled in accordance with ASTM D2234;[3]
  - Analyzing a sample of the portion of the byproducts to determine the loss on ignition of the portion of the byproducts;
  - Either fly ash or bottom ash or a mixture of both is added in a fine particle condition to the furnace of a pulverized coal boiler in a small proportion to the pulverized coal fed to the furnace. The ash is burned with the pulverized coal. The proportion of coal ash is preferably in the range of 1 percent to 3.5 percent, by weight, of the pulverized coal.
  - Introducing the portion of the byproducts along with pulverized coal into a pulverized coal furnace if the portion of byproducts has a loss on ignition greater than or equal to a predetermined loss on ignition value (typically greater than or equal to 1 to 5 percent); and
  - Burning the portion of the byproducts in the furnace with the pulverized coal to render the byproducts into a commercially valuable fly ash and bottom ash having very low loss on ignition, typically lower than 3 percent (WEC 2003, p.7; WEC, p.1).[4]

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[3] During a pilot project to reprocess landfilled combustion products that was conducted by Wisconsin Energy Corporation in July and October 1998, samples were collected every 30 minutes from the transfer point where the ash fell onto the stacker conveyor during the entire operation per the ASTM standard, and a composite sample was prepared for every 5,000 tons processed and tested.

[4] Landfill ash recovery operations at the Western Kentucky Energy (Coleman Station) involves the following activities. Ash first must be recovered from the pond or landfill and then separated into its fundamental components: carbon, silicates, and high-density, iron-rich materials. A coarse carbon-fuel product is recovered by density separation using concentrating spirals. A fine carbon-fuel product is recovered with flotation cells.

(4) **State status of CCPs use as ingredient:**

- In the state of Wisconsin, Wisconsin Energy Corporation has an agreement with the state to burn recovered landfill ash at their power plants.
- At this stage, we have not identified any other states that have specifically given beneficial use designation to the use of CCPs in clinker manufacture, or that prohibit fly ash use in clinker, but we have not performed an exhaustive investigation of state activities and regulations.

5. CCP Composition and Impacts

(1) **Composition of CCPs:**

- The chemical properties of fly ash are influenced to a great extent by those of the coal burned. There are basically four types, or ranks, of coal, each of which varies in terms of its heating value, its chemical composition, ash content, and geological origin: anthracite, bituminous, subbituminous, and lignite. The principal components of bituminous coal fly ash are silica, alumina, iron oxide, and calcium pxide, with varying amounts of residual, unburned carbon, as measured by the loss on ignition. Silica, alumina, and calcium are also the primary ingredients in portland cement, along with iron oxide. Lignite and subbituminous coal fly ashes are characterized by higher concentrations of calcium and magnesium oxide and reduced percentages of silica and iron oxide, as well as a lower residual carbon content, compared with bituminous coal fly ash. Very little anthracite coal is burned in utility boilers, so there are only small amounts of anthracite coal fly ash. Fly ash contains trace metals, such as vanadium, zinc, copper, chromium, nickel, lead, arsenic, and mercury.[5]
- Bottom ash and boiler slag are composed principally of silica, alumina, and iron oxide, with smaller percentages of calcium and magnesium oxides, sulfates, and other compounds. The composition of the bottom ash or boiler slag particles is controlled primarily by the source of the coal and not by the type of furnace. Bottom ash or boiler slag derived from lignite or sub-bituminous coals has a higher percentage of calcium oxide than the bottom ash or boiler slag from anthracite or bituminous coals. (Turner-Fairbank Highway Research Center).
- All of these materials provide effective substitutes for most or all of the raw materials in cement, but the relative levels of different oxides must be carefully managed to ensure that the kiln product meets industry specifications.

(2) **Impacts of CCPs use:**

- In clinker manufacture, CCPs partially offset the need for virgin silica, iron, and alumina sources. Using CCPs in the cement kiln can reduce the unit consumption of virgin feed stock materials, which may reduce the overall emissions associated with materials extraction and processing, since CCPs generally require less pre-processing than the virgin materials they replace.
- With respect to emissions from the cement kiln itself, to the extent CCPs have a lower emission profile than the virgin materials they replace, overall emissions

[5] Listed by relative frequency. See USEPA, March 15, 1999.

will be reduced. However, CCPs may have higher emissions of pollutants such as mercury than virgin silica, iron and alumina sources when burned in the kiln.

- The specific lifecycle impacts of CCP use as a raw material in clinker production are not evaluated here because of uncertainties in lifecycle scenario development. For example, it is difficult to determine the replacement ratio between CCPs and other raw feed materials in clinker production. Thus, the correct quantity of material to be modeled is unclear. In addition, CCPs may substitute for a combination of virgin raw materials and other secondary materials (e.g., blast furnace slag, foundry sand, cement kiln dust, etc.); the choice of material often depends on location-specific factors such as the proximity of material sources to the cement kiln and relative availability of different materials. Avoided upstream impacts depend heavily on the specific material being displaced in the lifecycle scenario.
- When fly ash with a high unburned carbon content is introduced to the cement kiln during clinker manufacture, fuel supply may be reduced to accommodate the additional energy provided by the carbon in the fly ash (Bhatty, Javed et al. 2001).
- One health risk issue is currently gaining attention in the use of fly ash in high-heat applications such as cement manufacture. When exposed to elevated temperatures (approximately 2,750 degrees Farenheit) in a cement kiln, laboratory experiments have found that mercury is readily released from fly ash (Pflughoeft-Hasset et al. 2007). At this time, the level of mercury in fly ash has not been considered significant enough to create a health risk. However, as coal utilities increasingly employ mercury capture technologies, some facilities may implement technologies that result in fly ash with much higher mercury content that is not suitable for use in cement manufacture. Other, more expensive technologies would ensure that most or all fly ash is separate from mercury capture; at this point it is not clear how much, if any, fly ash would be affected by mercury capture technology.
- Combustion of stockpiled CCPs to produce a low loss on ignition (LOI) coal ash has several potential advantages:
    - Removal, recovery, and characterization of landfilled CCPs so that recovered CCPs may be put to beneficial use. Characterization includes energy content, sulphur content, moisture, and trace metals content for energy and air emissions analyses.
    - Preservation of licensed landfill space.
    - Preservation of coal reserves by recovering heat from reclaimed CCPs.
    - Production of low LOI coal ash that may be substituted for portland cement thereby reducing the need for portland cement and reducing air emissions from its production process.
    - Reduced need for limestone quarries (due to the use of ash as a substitute for portland cement) and landfill sites (WEC, p.2).[6]

[6] Recovery of landfilled ash may require extra screening. For example, during the removal of ash from a landfill in Wisconsin in 2000, the removed materials were crushed, screened and periodically sampled in accordance with ASTM D2234. It was found that over 99 percent of the material removed consisted of coal combustion products, with foreign materials consisting of lost items from landfill operators (e.g., soda cans, safety ribbon, gloves, etc.) (WEC, 2006, p3).

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