Technical Update - Coal Combustion Products - Environmental Issues

Coal Ash: Characteristics, Management and Environmental Issues

Table of Contents

Coal-fired power plants in the United States produce more than 92 million tons of coal ash per year. About 40% is beneficially used in a variety of applications, and about 60% is managed in storage and disposal sites. This technical update summarizes information and data on the physical and chemical characteristics of coal ash, beneficial use applications, disposal practices, and management practices to mitigate environmental concerns.

Introduction

The U.S. electric utility industry burns more than 1 billion tons of coal annually, with coal-fired generation supplying about 50% of the electricity used in the United States. The solids collected from the furnace and removed from the flue gas after the coal is combusted are collectively referred to as coal combustion products (CCPs), and can be broadly categorized as coal ash and flue gas desulfurization (FGD) solids. Information on FGD gypsum, the solid product from wet FGD systems with forced oxidation, is presented in a companion technical update document.

Coal is composed primarily of carbon and hydrogen, but all coal also contains some mineral matter (for example, clays, shales, quartz, and calcite); the percentage varies by coal type and source. Coal ash is the mineral matter that is collected after the coal is combusted, along with some unburned carbon. The amount of coal ash produced at a power plant depends on the volume of coal burned, the amount of mineral matter in the coal, and the combustion conditions. In 2007, U.S. coal-fired power plants produced about 92 million tons of coal ash, including 72 million tons of fly ash, 18 million tons of bottom ash, and 2 million tons of boiler slag.[1]

Formation and Physical Characteristics

The physical and chemical properties of coal ash are determined by reactions that occur during the high-temperature combustion of the coal and subsequent cooling of the flue gas. A considerable amount of research has gone into understanding how coal ash forms, its characteristics, and how it weathers in the environment.

Fly Ash

Fly ash refers to the lightweight particles that travel with the flue gas as it exits the furnace and moves away from the high-temperature combustion zone. Power plants are equipped with particulate collection devices, either electrostatic precipitators (ESPs) or baghouses, designed to remove nearly all of the fly ash from the flue gas prior to the stack to prevent it from being emitted to the atmosphere (Figure 1). An ESP uses electrically charged wires and plates to capture the fly ash; baghouses use fabric filters, similar to vacuum cleaner bags. Dry fly ash collected in the ESP or baghouse is then either pneumatically conveyed to a hopper or storage silo (dry management), or mixed with water and sluiced through a series of pipes to an on-site impoundment (wet management).

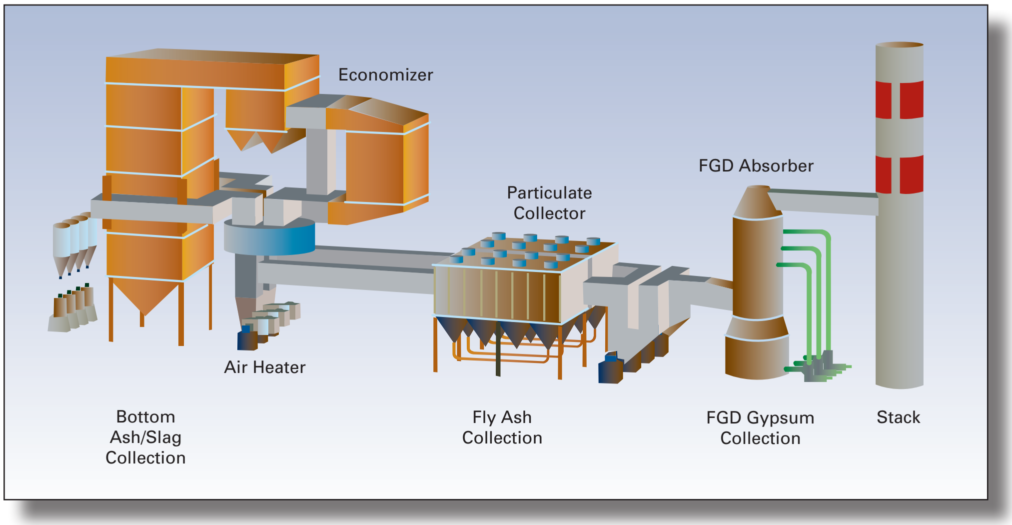

Figure 1. Typical power plant layout showing location of fly ash and bottom ash collection.

Fly ash is composed mainly of amorphous or glassy aluminosilicates. Fly ash particles are typically silt-sized spheres, ranging from 1 to 100 microns in diameter.

Fly ash particles are composed mainly of amorphous or glassy aluminosilicates. However, the particles also contain some crystalline compounds that either pass through the combustion zone unchanged or are formed at high temperatures. Elements such as arsenic and selenium that become volatile at high temperatures, preferentially condense on the surface of the ash particles as the flue gas cools.

Fly ash particles are typically spherical in shape, either solid or with vesicles (Figure 2). A small percentage are thin-walled hollow particles called cenospheres. The particles are fine-grained, typically silt-sized, ranging from 1 to 100 microns in diameter, with median particle diameter of 20 to 25 microns.[2] Fly ash is usually tan to dark gray in color.

Bottom Ash/Boiler Slag

Bottom ash consists of heavier particles that fall to the bottom of the furnace (see Figure 1). Bottom ash is also composed primarily of amorphous or glassy aluminosilicate materials derived from the melted mineral phases. Most bottom ash is produced in dry-bottom boilers, where the ash cools in a dry state. Boiler slag is a type of bottom ash collected in wet-bottom boilers (slag-tap or cyclone furnaces, which operate at very high temperatures), where the molten particles are cooled in a water quench.

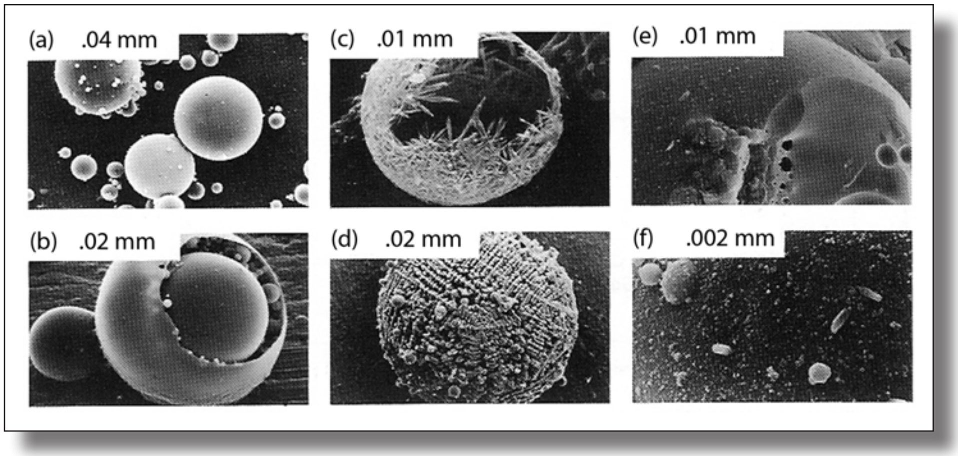

Figure 2. Scanning electron micrographs of fly ash. (a) Typical spherical morphology of glassy particles. (b) A large hollow sphere formed when entrapped gas expanded during thermal decomposition of calcium carbonate ($CaCO_3$). (c) A particle etched with hydrofluoric acid to remove surface glass and reveal a shell of interlocking mullite crystals. (d) A typical magnetic spinel mineral (magnetite) separated from ash after removal of encapsulating glass. (e) A fractured ash particle containing numerous vesicles. (f) The accumulation of tiny granules of inorganic oxides, crystals, and coalesced ash on the surface of a larger particle.

Whether collected from dry-bottom or wet-bottom boilers, bottom ash is usually mixed with water and conveyed away from the furnace in a sluice pipe. It is transported either to a dewatering bin or to an on-site impoundment.

Bottom ash is coarser than fly ash, with a sandy texture and particles ranging from about 0.1 mm to 50 mm in diameter.

Bottom ash is coarser than fly ash, with a sandy texture and particles ranging from about 0.1 mm to 50 mm in diameter. Bottom ash from dry-bottom boilers is generally dull black and porous in appearance. It typically has the consistency of coarse sand to gravel and higher carbon content than fly ash. Boiler slag is black and angular, and has a smooth, glassy appearance.

The properties of fly ash and bottom ash make them useful for a variety of construction applications. Table 1 lists ranges for some of the important geotechnical properties of fly ash and bottom ash.

The properties of fly ash and bottom ash make them useful for a variety of construction applications.

Table 1. Typical ranges for geotechnical properties of fly ash and bottom ash.[3]

Property	Fly Ash	Bottom Ash
Specific Gravity	2.1 – 2.9	2.3 – 3.0
Bulk Density (compacted), lbs/ft^3	65 – 110	65 – 110
Optimum Moisture Content, %	10 – 35	12 – 26
Hydraulic Conductivity, cm/s	10^{-4} – 10^{-6}	10^{-1} – 10^{-3}
Porosity	0.40 – 0.50	0.25 – 0.40
Angle of Internal Friction, degrees	25 – 40	35 – 45

Chemical Composition

The chemical composition of coal ash is determined primarily by the chemistry of the source coal and the combustion process. Because ash is derived from the inorganic minerals in the coal, such as quartz, feldspars, clays, and metal oxides, the major elemental composition of coal ash is similar to the composition of a wide variety of rocks in the Earth's crust (Figure 3). Oxides of silicon, aluminum, iron, and calcium comprise more than 90% of the mineral component of typical fly ash (Figure 3). Minor constituents such as magnesium, potassium, sodium, titanium, and sulfur account for about 8% of the mineral component, while trace constituents such as arsenic, cadmium, lead, mercury, and selenium, together make up less than 1% of the total composition. Table 2 provides the typical range of major and trace constituents concentrations in fly ash and bottom ash, along with the range for rock and soil for comparison.

Because ash is derived from the inorganic minerals in the coal, the major elemental composition of coal ash is similar to a wide variety of rocks. Oxides of silicon, aluminum, iron, and calcium make up more than 90% of the mineral component of fly ash; trace constituents collectively make up less than 1 percent.

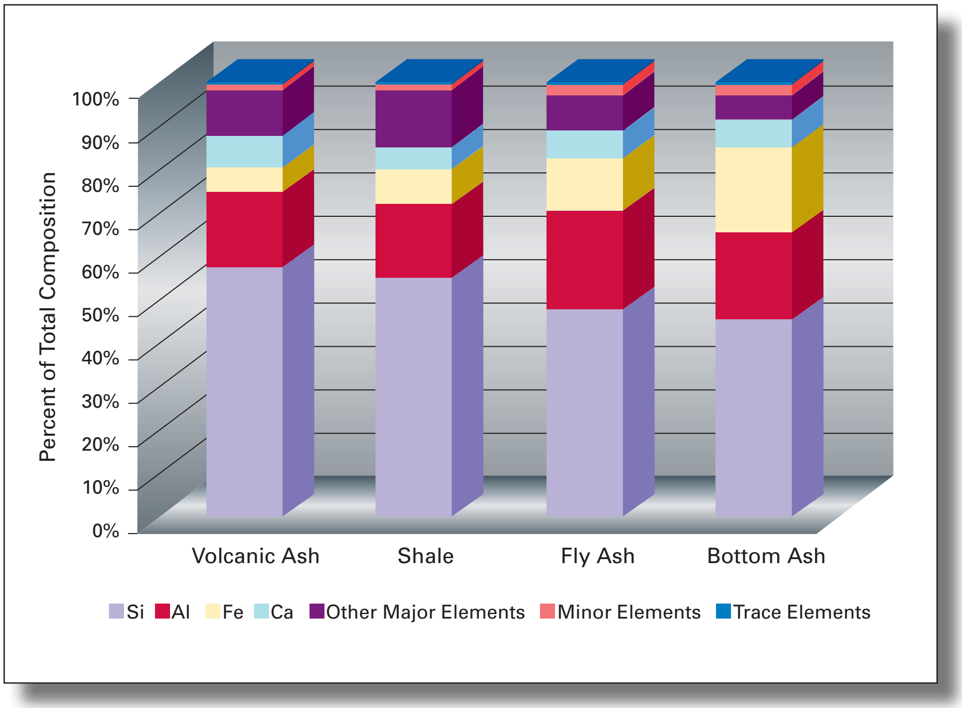

Figure 3. Elemental composition for bottom ash, fly ash, shale, and volcanic ash. Median values for ash are from EPRI database[3], and for rock are from Taylor and Litche (1980)[4] and Hem (1992).[5]

Fly ash also contains a variable amount of unburned carbon, depending on the combustion conditions. Unburned carbon is often measured by a laboratory test called loss-on-ignition (LOI). LOI values can range from less than 1% to more than 20%.

The relative calcium, iron, and sulfur contents of fly ash influence its fundamental chemical properties and reactivity. Subbituminous and lignite coal ashes typically contain relatively high concentrations of calcium, with concentrations exceeding 15% (expressed as CaO), and produce alkaline solutions (pH 11 – 12) on contact with water. Bituminous coal ashes generally contain much less calcium, and yield slightly acidic to slightly alkaline solutions (pH 5 – 10) on contact with water.

The chemical composition of coal ash can change as power plants change fuels or add new air emissions controls to prevent releases to the atmosphere.[10] Examples of air emissions controls that can impact fly ash composition include the use of ammonia-based systems to control NO_X, powdered activated carbon injection to control mercury, and sodium-based sorbents to control SO_3. Examples of fuel changes include blending of different coal types, and co-firing of biomass with coal. EPRI maintains active research programs to evaluate the impacts of changes in emissions controls on the environmental and engineering characteristics of the ash.[11-13]

Table 2. Range (10th percentile – 90th percentile) in bulk composition of fly ash, bottom ash, rock, and soil.

	Fly Ash*	Bottom Ash*	Rock**	Soil***
Aluminum, mg/kg	70,000 – 140,000	59,000 – 130,000	9,800 – 96,000	15,000 – 100,000
Calcium, mg/kg	7,400 – 150,000	5,700 – 150,000	6,000 – 83,000	1,500 – 62,000
Iron, mg/kg	34,000 – 130,000	40,000 – 160,000	8,800 – 95,000	7,000 – 50,000
Silicon, mg/kg	160,000 – 270,000	160,000 – 280,000	57,000 – 380,000	230,000 – 390,000
Magnesium, mg/kg	3,900 – 23,000	3,400 – 17,000	700 – 56,000	1,000 – 15,000
Potassium, mg/kg	6,200 – 21,000	4,600 – 18,000	4,000 – 45,000	4,500 – 25,000
Sodium, mg/kg	1,700 – 17,000	1,600 – 11,000	900 – 34,000	1,000 – 20,000
Sulfur, mg/kg	1,900 – 34,000	BDL – 15,000	200 – 42,000	840 – 1,500
Titanium, mg/kg	4,300 – 9,000	4,100 – 7,200	200 – 5,400	1,000 – 5,000
Antimony, mg/kg	BDL – 16	All BDL	0.08 – 1.8	BDL – 1.3
Arsenic, mg/kg	22 – 260	2.6 – 21	0.50 – 14	2.0 – 12
Barium, mg/kg	380 – 5100	380 – 3600	67 – 1,400	200 – 1,000
Beryllium, mg/kg	2.2 - 26	0.21 – 14	0.10 – 4.4	BDL – 2.0
Boron, mg/kg	120 – 1000	BDL – 335	0.2 – 220	BDL – 70
Cadmium, mg/kg	BDL – 3.7	All BDL	0.5 – 3.6	BDL – 0.5
Chromium, mg/kg	27 – 300	51 – 1100	1.9 – 310	15 – 100
Copper, mg/kg	62 – 220	39 – 120	10 – 120	5.0 – 50
Lead, mg/kg	21 – 230	8.1 – 53	3.8 – 44	BDL – 30
Manganese, mg/kg	91 – 700	85 – 890	175 – 1400	100 – 1,000
Mercury, mg/kg	0.01 – 0.51	BDL – 0.07	0.1 – 2.0	0.02 – 0.19
Molybdenum, mg/kg	9.0 – 60	3.8 – 27	1.0 – 16	All BDL
Nickel, mg/kg	47 – 230	39 – 440	2.0 – 220	5 – 30
Selenium, mg/kg	1.8 – 18	BDL – 4.2	0.60 – 4.9	BDL – 0.75
Strontium, mg/kg	270 – 3100	270 – 2000	61 – 890	20 – 500
Thallium, mg/kg	BDL – 45	All BDL	0.1 – 1.8	0.20 – 0.70
Uranium, mg/kg	BDL – 19	BDL – 16	0.84 – 43	1.2 – 3.9
Vanadium, mg/kg	BDL – 360	BDL – 250	19 – 330	20 – 150
Zinc, mg/kg	63 – 680	16 – 370	25 – 140	22 – 99

BDL – Below Detection Limit

* Source for most fly ash and bottom ash data is EPRI CP-INFO Database[3]. Beryllium, thallium, mercury (bottom ash only) and boron (bottom ash only) are from the EPRI PISCES Database[6]

** Source for rock data is US Geological Survey National Geochemical database.[7]

*** Source for most soils data is Shacklette and Boerngen (1984)[8]; cadmium and thallium data are from Smith et al (2005).[9]

In 2007, 32 million tons of fly ash and 9.0 million tons of bottom ash and boiler slag were beneficially used. The primary use for fly ash was as a replacement for portland cement in making concrete.

Beneficial Use

The physical and chemical properties of coal ash make it suitable for many construction and geotechnical uses. In 2007, 32 million tons of fly ash were beneficially used, representing 44% of the total fly ash produced.[1] Similarly, 7.3 million tons of bottom ash (40%) and 1.7 million short tons of boiler slag (80%) were used. Figure 4 shows the amounts of fly ash used in various applications.

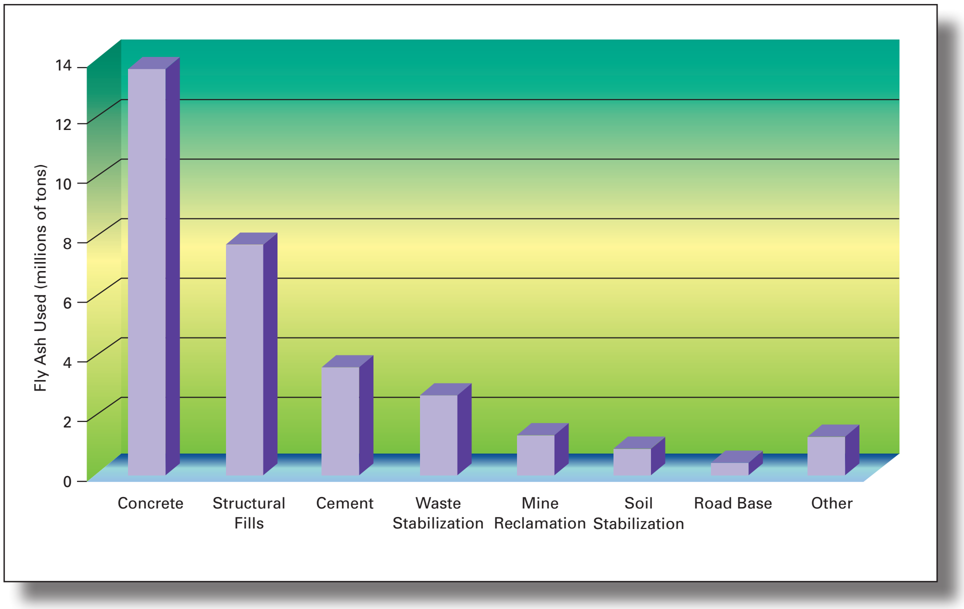

Figure 4. Beneficial uses of coal fly ash. Data are from the 2007 ACAA survey.[1]

In 2007, the use of fly ash to replace cement in concrete yielded energy savings equivalent to the annual energy use by over a half million households, and reduced CO_2 emissions equivalent to removing over 1.5 million cars from the road.

The primary use for fly ash is as an ingredient in concrete. Fly ash act as a pozzolan, a siliceous/aluminous material that develops cementitious properties when combined with calcium hydroxide and water. Fly ash can be used as a direct replacement for portland cement in concrete, and has been used in a wide variety of concrete applications in the United States for more than 60 years. The use of fly ash can significantly improve many concrete qualities, for example, strength, permeability, and resistance to alkali silicate reactivity. Standard specification ASTM C618 establishes the physical and chemical requirements of fly ash for use in concrete.[14]

In addition to improving the quality of concrete, the use of fly ash greatly reduces the energy use and CO_2 emissions associated with the production of concrete. In 2007, use of fly ash in concrete resulted in an estimated 55 trillion Btu in energy savings, and 10 million tons in avoided CO_2 emissions.[15] These numbers are equivalent to the annual energy use for over 600,000 households and removal of 1.7 million cars from the road, respectively. Other benefits of using ash include conservation of virgin materials such as limestone used in cement production, and reduced need for disposal sites.

In addition to concrete, applications that use more than 1 million tons per year of fly ash are structural fills, cement production, waste stabilization, and mine reclamation. The primary uses for the coarser bottom ash and boiler slag are for structural fills and road base materials, as blasting grit/roofing granules, and for snow and ice traction control.

US EPA actively promotes coal ash use under the Coal Combustion Partnership Program (C^2P^2), and has set a goal of 50% utilization by 2011.[16] The Federal Highway Administration provides technical guidance on the use and benefits of fly ash for highway construction projects.[17]

Disposal

Coal ash that is not beneficially used is placed in landfills and impoundments. About 60% of disposed fly ash is managed dry in landfills, and 40% is managed wet in impoundments. There is a long-term trend toward increased use of dry management practices.[18,19]

Dry fly ash is typically loaded on trucks, wetted to prevent dusting, and then transported to a dedicated landfill facility. The landfill may be located on or off the power plant property. Wet-managed fly ash is typically sluiced to an on-site impoundment or series of impoundments, where the fly ash settles to the bottom of the ponds. In some cases, treatment chemicals may be added to the ash pond to improve settling, remove dissolved constituents, or control pH. The settled ash solids may either be dredged for beneficial use or for disposal, or may be left in place.

Ash management sites vary in age, size, and design. In most cases, the sites are operated under state-issued permits that specify applicable requirements for siting criteria, engineering controls (for example, liners, leachate collection, caps, slopes, and runoff control), groundwater monitoring, site closure, corrective action, and financial assurance. A study by US EPA and US Department of Energy (DOE) published in 2006 found that regulatory and engineering controls for new or expanded units permitted between 1994 and 2004 had tightened considerably, establishing engineering controls and groundwater monitoring as standard practice.[18] For example, 55 of 56 units assessed in that study employed engineered liners, with the only exception being one landfill that managed only bottom ash.

A study performed by US DOE and US EPA found that nearly all new CCP disposal units (55 of 56 units) studied between 1994 and 2004 employed liners to control leachate release.

In 1993 and again in 2000, following several years of study, the US EPA published regulatory determinations that coal ash and other combustion products did not warrant regulation as a hazardous waste.[20,21] Disposal is currently regulated under non-hazardous provisions by individual states. In 2009, US EPA is again evaluating the appropriate federal role in regulating disposal of coal combustion products.

Environmental Issues

Leaching

One of the primary environmental concerns at large storage and disposal sites is leaching and release of trace constituents to groundwater and surface water. Extensive testing has shown that coal ash rarely, if ever, exceeds hazardous waste criteria contained in the the Toxicity Characteristic Leaching Procedure (TCLP) promulgated under the Resource Conservation and Recovery Act.

Laboratory studies have demonstrated that the leaching process is complex and depends on a number of factors, primarily chemical speciation of the constituent, solution pH, and availability of the constituent for leaching. Availability for leaching depends on whether the element resides on the surface of the ash particle, in the outer glass hull, or within the interior glass matrix (see Figure 2).

In addition, subsequent chemical interactions and secondary mineral formation can further modify leaching characteristics of the ash. For example, because arsenic typically condenses on the surface of the fly ash particle, it may initially be available for leaching. However, the presence of calcium in the ash can limit the release of dissolved arsenic by formation of calcium-arsenic precipitates.[22] Weathering and formation of iron hydroxide compounds can also serve to sequester arsenic. Detailed leaching studies under controlled conditions are used to elucidate the mechanisms controlling constituent release and provide the best indication of the long-term potential for release and environmental risk.

While laboratory studies are used to define long-term leaching mechanisms, field studies provide

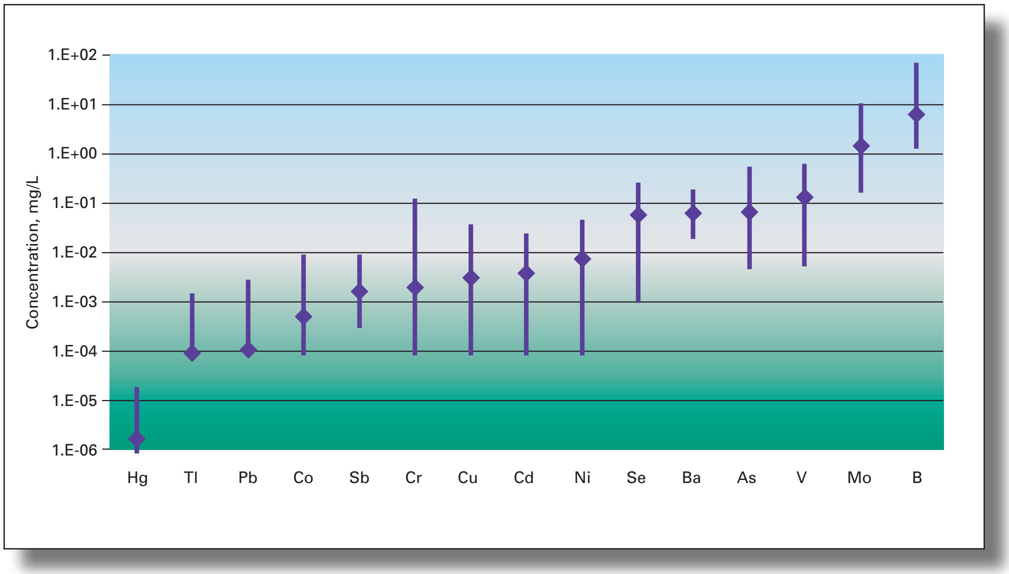

Figure 5. Field leachate concentrations for coal ash disposal sites. Bars show 10th percentile to 90th percentile, and diamond shows median. Source: EPRI CP-INFO Database.[3]

Coal ash rarely, if ever, exceeds hazardous waste criteria contained in the the Toxicity Characteristic Leaching Procedure (TCLP). While laboratory studies are used to understand leaching mechanisms, field studies provide the best information on leachate quality under actual environmental conditions.

the best information on leachate quality under actual environmental conditions. In 2006, EPRI, with support from the US DOE, completed an extensive characterization of field leachates at over 30 coal combustion product disposal facilities (Figure 5).[23] This study provides the most comprehensive database available for ash leachate characteristics representative of typical environmental conditions at disposal sites. The data in Figure 5 represent initial concentrations in the management facility, not the concentration that the public is exposed to; these data can be used as input to infiltration and groundwater transport models to assess the risk of contamination to a receptor, either a drinking water well or surface water body, and to develop the best management methods to prevent or mitigate those risks.

Leachate runoff and infiltration to groundwater can be controlled by a variety of standard engineering practices employed at disposal facilities. Depending on site-specific conditions, these practices may include use of liners, leachate collection systems, diversion ditches, caps, and vegetation. Monitoring networks are used to ensure the performance of the engineering controls in protecting groundwater and surface water resources.

Windblown Ash

Because of its fine-grained texture, dry fly ash is susceptible to blowing under windy conditions. Studies of the potential health effects associated with ash dust have largely focused on power plant workers, for whom exposure to dusty conditions is much more common than for the general public. While direct inhalation of fly ash or any respirable dust should be avoided, research has shown that worker exposure to ash dust during normal power plant operation does not result in exposures above health criteria.[24,25] Standard precautions such as dust masks are recommended when working in high-dust environments at power plants. At disposal sites, windblown ash is generally controlled by periodic wetting of open ash areas, and by covering inactive areas with bottom ash, soil, or vegetation.

Research by US EPA, EPRI, and others has all shown that mercury is stable on fly ash at ambient temperatures, with very little potential for leaching or volatilization.

Mercury

Mercury is an element of significant environmental interest because of its toxicity and occurrence in lakes and rivers. The median mercury concentration in coal is 0.11 mg/kg, and 80% of coal samples contain less than 0.25 mg/kg.[26] Information collected by the US EPA in the late 1990s indicated that in the United States about 40% of the mercury in coal was captured by the fly ash and/or the then existing SO_2 control, and 60% was released to the atmosphere.[27] The amount of mercury captured at any particular plant was found to depend on a number of factors, including coal type, coal chlorine content, particulate collection device, NO_x control, and flue gas desulfurization systems.

Mercury in fly ash generally ranges from about 0.05 mg/kg up to about 2 mg/kg, with typical concentrations between 0.1 mg/kg and 0.5 mg/kg. One of the leading approaches to further reduce mercury emissions from power plants is injection of activated carbon into the flue gas. The mercury sorbs onto the carbon, which is then captured with the fly ash in the ESP or baghouse. Although the mercury and carbon content in the fly ash are increased by this process, research by US EPA, EPRI, and others, has consistently shown that the carbon-bound mercury is very stable on the fly ash at ambient temperatures, with very low potential for leaching or volatilization.[13,28,29] Similarly, concrete containing fly ash exhibits very little mercury release and does not present a significant risk to the public.[30,31] High-temperature fly ash uses, such as use in cement kilns and hot-mix asphalt, may release mercury from fly ash to the air due to volatilization.

"Radioactive elements in coal and fly ash should not be sources of alarm. The vast majority of coal and the majority of fly ash are not significantly enriched in radioactive elements, or in associated radioactivity, compared to soil or rocks."—US Geological Survey

Radioactivity

Coal contains naturally occurring radioactive constituents, such as uranium and thorium and their decay products. Uranium and thorium are each typically present in coal at concentrations of 1 to 4 mg/kg.[32] These constituents are captured by the fly ash following combustion of the coal. Any radon gas present in the coal is lost to stack emissions.

Although the radionuclides are enriched in the fly ash in comparison to the coal itself, the US Geological Survey determined that the average radionuclide concentrations in ash are within

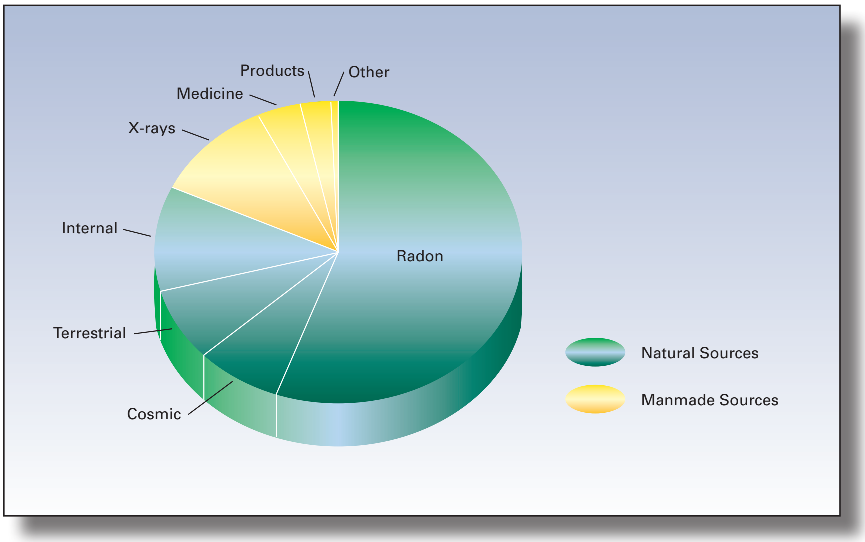

Figure 6. Distribution of background radiation sources comprising the total annual average radiation dose in the United States.[32,33]

the range of concentrations found in other geologic materials, such as granite and shale.[32] Background radiation exposure to the U.S. population is about 360 mrems/yr, with natural sources, primarily geologic materials and cosmic rays, accounting for about 82% of that total (Figure 6).[32,33] Man-made sources account for the remaining 18% of total exposure, with X-rays being the largest single source.

In a worst case evaluation, exposure to an outdoor worker at an ash storage facility (8 hrs/day for 225 days/yr) was estimated as 8 mrems/yr, or only about 2.3% of background exposure.[33] Similar results have been found in examining potential for radioactivity exposure to concrete made with a high proportion of fly ash.[32] Research by US EPA, US Geological Survey, EPRI, and others has shown that exposure to radiation from coal ash or concrete products made with fly ash does not represent a significant health risk.

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