

Fly ash

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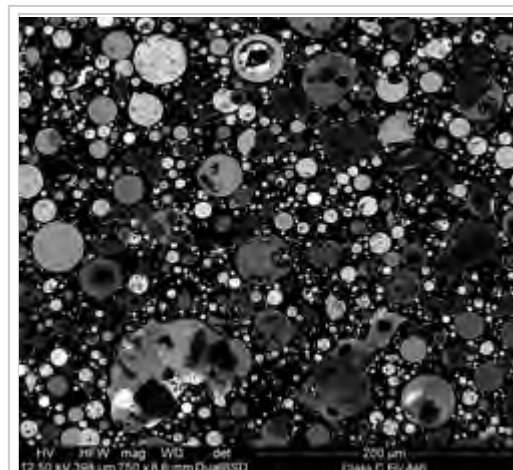
Fly ash, also known as "pulverised fuel ash" in the United Kingdom, is one of the coal combustion products, composed of the fine particles that are driven out of the boiler with the flue gases. Ash that falls in the bottom of the boiler is called bottom ash. In modern coal-fired power plants, fly ash is generally captured by electrostatic precipitators or other particle filtration equipment before the flue gases reach the chimneys. Together with bottom ash removed from the bottom of the boiler, it is known as **coal ash**. Depending upon the source and makeup of the coal being burned, the components of fly ash vary considerably, but all fly ash includes substantial amounts of silicon dioxide (SiO_2) (both amorphous and crystalline), aluminium oxide (Al_2O_3) and calcium oxide (CaO), the main mineral compounds in coal-bearing rock strata.

Constituents depend upon the specific coal bed makeup but may include one or more of the following elements or substances found in trace concentrations (up to hundreds ppm): arsenic, beryllium, boron, cadmium, chromium, hexavalent chromium, cobalt, lead, manganese, mercury, molybdenum, selenium, strontium, thallium, and vanadium, along with very small concentrations of dioxins and PAH compounds.^{[1][2]}

In the past, fly ash was generally released into the atmosphere, but air pollution control standards now require that it be captured prior to release by fitting pollution control equipment. In the US, fly ash is generally stored at coal power plants or placed in landfills. About 43% is recycled,^[3] often used as a pozzolan to produce hydraulic cement or hydraulic plaster and a replacement or partial replacement for Portland cement in concrete production. Pozzolans ensure the setting of concrete and plaster and provide concrete with more protection from wet conditions and chemical attack.

After a long regulatory process, the EPA published a final ruling in December 2014, which establishes that coal fly ash is regulated on the federal level as "non-hazardous" waste according to the Resource Conservation and Recovery Act (RCRA). Coal Combustion Residuals (CCR's) are listed in the subtitle D (rather than under subtitle C dealing for hazardous waste, which was also considered).^[4]

In the case that fly or bottom ash is not produced from coal, for example when solid waste is used to produce electricity in an incinerator (see waste-to-energy facilities), this kind of ash may contain higher levels of contaminants than coal ash. In that case the ash produced is often classified as hazardous waste.



Photomicrograph made with a scanning electron microscope (SEM) and back-scatter detector: cross section of fly ash particles at 750x magnification

Contents

- 1 Chemical composition and classification

- 1.1 Class F fly ash
 - 1.2 Class C fly ash
- 2 Disposal and market sources
- 3 Fly ash reuse
 - 3.1 Portland cement
 - 3.2 Embankment
 - 3.3 Soil stabilization
 - 3.4 Flowable fill
 - 3.5 Asphalt concrete
 - 3.6 Geopolymers
 - 3.7 Roller compacted concrete
 - 3.8 Bricks
 - 3.9 Metal matrix composites
 - 3.10 Waste treatment and stabilization
 - 3.11 As a catalyst
- 4 Environmental problems
 - 4.1 Present production rate of fly ash
 - 4.2 Groundwater contamination
 - 4.3 Spills of bulk storage
 - 4.4 Contaminants
- 5 Exposure concerns
- 6 See also
- 7 References
- 8 External links

Chemical composition and classification

Fly ash material solidifies while suspended in the exhaust gases and is collected by electrostatic precipitators or filter bags. Since the particles solidify rapidly while suspended in the exhaust gases, fly ash particles are generally spherical in shape and range in size from 0.5 μm to 300 μm . The major consequence of the rapid cooling is that few minerals have time to crystallize, and that mainly amorphous, quenched glass remains. Nevertheless, some refractory phases in the pulverized coal do not melt (entirely), and remain crystalline. In consequence, fly ash is a heterogeneous material. SiO_2 , Al_2O_3 , Fe_2O_3 and occasionally CaO are the main chemical components present in fly ashes. The mineralogy of fly ashes is very diverse. The main phases encountered are a glass phase, together with quartz, mullite and the iron oxides hematite, magnetite and/or maghemite. Other phases often identified are cristobalite, anhydrite, free lime, periclase, calcite, sylvite, halite, portlandite, rutile and anatase. The Ca-bearing minerals anorthite, gehlenite, akermanite and various calcium silicates and calcium aluminates identical to those found in Portland cement can be identified in Ca-rich fly ashes.^[5] The mercury content can reach 1 ppm,^[6] but is

Component	Bituminous	Subbituminous	Lignite
SiO₂ (%)	20-60	40-60	15-45
Al₂O₃ (%)	5-35	20-30	20-25
Fe₂O₃ (%)	10-40	4-10	4-15
CaO (%)	1-12	5-30	15-40
LOI (%)	0-15	0-3	0-5

generally included in the range 0.01 - 1 ppm for bituminous coal. The concentrations of other trace elements vary as well according to the kind of coal combusted to form it. In fact, in the case of bituminous coal, with the notable exception of boron, trace element concentrations are generally similar to trace element concentrations in unpolluted soils.^[7]

Two classes of fly ash are defined by ASTM C618: Class F fly ash and Class C fly ash. The chief difference between these classes is the amount of calcium, silica, alumina, and iron content in the ash. The chemical properties of the fly ash are largely influenced by the chemical content of the coal burned (i.e., anthracite, bituminous, and lignite).^[8]

Not all fly ashes meet ASTM C618 requirements, although depending on the application, this may not be necessary. Ash used as a cement replacement must meet strict construction standards, but no standard environmental regulations have been established in the United States. 75% of the ash must have a fineness of 45 μm or less, and have a carbon content, measured by the loss on ignition (LOI), of less than 4%. In the U.S., LOI must be under 6%. The particle size distribution of raw fly ash tends to fluctuate constantly, due to changing performance of the coal mills and the boiler performance. This makes it necessary that, if fly ash is used in an optimal way to replace cement in concrete production, it must be processed using beneficiation methods like mechanical air classification. But if fly ash is used also as a filler to replace sand in concrete production, unbeneficiated fly ash with higher LOI can be also used. Especially important is the ongoing quality verification. This is mainly expressed by quality control seals like the Bureau of Indian Standards mark or the DCL mark of the Dubai Municipality.

Class F fly ash

The burning of harder, older anthracite and bituminous coal typically produces Class F fly ash. This fly ash is pozzolanic in nature, and contains less than 7% lime (CaO). Possessing pozzolanic properties, the glassy silica and alumina of Class F fly ash requires a cementing agent, such as Portland cement, quicklime, or hydrated lime—mixed with water to react and produce cementitious compounds. Alternatively, adding a chemical activator such as sodium silicate (water glass) to a Class F ash can form a geopolymer.

Class C fly ash

Fly ash produced from the burning of younger lignite or sub-bituminous coal, in addition to having pozzolanic properties, also has some self-cementing properties. In the presence of water, Class C fly ash hardens and gets stronger over time. Class C fly ash generally contains more than 20% lime (CaO). Unlike Class F, self-cementing Class C fly ash does not require an activator. Alkali and sulfate (SO₄) contents are generally higher in Class C fly ashes.

At least one US manufacturer has announced a fly ash brick containing up to 50% Class C fly ash. Testing shows the bricks meet or exceed the performance standards listed in ASTM C 216 for conventional clay brick. It is also within the allowable shrinkage limits for concrete brick in ASTM C 55, Standard Specification for Concrete Building Brick. It is estimated that the production method used in fly ash bricks will reduce the embodied energy of masonry construction by up to 90%.^[9] Bricks and pavers were expected to be available in commercial quantities before the end of 2009.^[10]

Disposal and market sources

In the past, fly ash produced from coal combustion was simply entrained in flue gases and dispersed into the atmosphere. This created environmental and health concerns that prompted laws that have reduced fly ash emissions to less than 1% of ash produced. Worldwide, more than 65% of fly ash produced from coal power stations is disposed of in landfills and ash ponds, although companies such as Duke Energy are starting initiatives to excavate coal ash basins due to the negative environmental impact involved.

The recycling of fly ash has become an increasing concern in recent years due to increasing landfill costs and current interest in sustainable development. As of 2005, U.S. coal-fired power plants reported producing 71.1 million tons of fly ash, of which 29.1 million tons were reused in various applications.^[11] If the nearly 42 million tons of unused fly ash had been recycled, it would have reduced the need for approximately 27,500 acre·ft (33,900,000 m³) of landfill space.^{[11][12]} Other environmental benefits to recycling fly ash includes reducing the demand for virgin materials that would need quarrying and cheap substitution for materials such as Portland cement.

As of 2006, about 125 million tons of coal-combustion byproducts, including fly ash, were produced in the U.S. each year, with about 43% of that amount used in commercial applications, according to the American Coal Ash Association Web site. As of early 2008, the United States Environmental Protection Agency hoped that figure would increase to 50% as of 2011.^[13]

Fly ash reuse

There is no U.S. governmental registration or labelling of fly ash utilization in the different sectors of the economy - industry, infrastructures and agriculture. Fly ash utilization survey data, acknowledged as incomplete, are published annually by the American Coal Ash Association.^[14]

Many of the following uses are discussed further below. Coal ash uses include (approximately in order of decreasing importance):

- Concrete production, as a substitute material for Portland cement and sand
- Embankments and other structural fills (usually for road construction)
- Grout and Flowable fill production
- Waste stabilization and solidification
- Cement clinkers production - (as a substitute material for clay)
- Mine reclamation
- Stabilization of soft soils
- Road subbase construction
- As Aggregate substitute material (e.g. for brick production)
- Mineral filler in asphaltic concrete
- Agricultural uses: soil amendment, fertilizer, cattle feeders, soil stabilization in stock feed yards, and agricultural stakes
- Loose application on rivers to melt ice^[15]
- Loose application on roads and parking lots for ice control^[16]

- Other applications include cosmetics, toothpaste, kitchen counter tops,^[17] floor and ceiling tiles, bowling balls, flotation devices, stucco, utensils, tool handles, picture frames, auto bodies and boat hulls, cellular concrete, geopolymers, roofing tiles, roofing granules, decking, fireplace mantles, cinder block, PVC pipe, Structural Insulated Panels, house siding and trim, running tracks, blasting grit, recycled plastic lumber, utility poles and crossarms, railway sleepers, highway sound barriers, marine pilings, doors, window frames, scaffolding, sign posts, crypts, columns, railroad ties, vinyl flooring, paving stones, shower stalls, garage doors, park benches, landscape timbers, planters, pallet blocks, molding, mail boxes, artificial reef, binding agent, paints and undercoatings, metal castings, and filler in wood and plastic products.^{[12][18][19]}

Portland cement

Owing to its pozzolanic properties, fly ash is used as a replacement for Portland cement in concrete.^[20] The use of fly ash as a pozzolanic ingredient was recognized as early as 1914, although the earliest noteworthy study of its use was in 1937.^[21] Roman structures such as aqueducts or the Pantheon in Rome used volcanic ash or pozzolana (which possesses similar properties to fly ash) as pozzolan in their concrete.^[22] As pozzolan greatly improves the strength and durability of concrete, the use of ash is a key factor in their preservation.

Use of fly ash as a partial replacement for Portland cement is particularly suitable but not limited to Class C fly ashes. Class "F" fly ashes can have volatile effects on the entrained air content of concrete, causing reduced resistance to freeze/thaw damage. Fly ash often replaces up to 30% by mass of Portland cement, but can be used in higher dosages in certain applications. In some cases, fly ash can add to the concrete's final strength and increase its chemical resistance and durability.

Fly ash can significantly improve the workability of concrete. Recently, techniques have been developed to replace partial cement with high-volume fly ash (50% cement replacement). For roller-compacted concrete (RCC)[used in dam construction], replacement values of 70% have been achieved with processed fly ash at the Ghatghar dam project in Maharashtra, India. Due to the spherical shape of fly ash particles, it can increase workability of cement while reducing water demand.^[23] Proponents of fly ash claim that replacing Portland cement with fly ash reduces the greenhouse gas "footprint" of concrete, as the production of one ton of Portland cement generates approximately one ton of CO₂, compared to no CO₂ generated with fly ash. New fly ash production, i.e., the burning of coal, produces approximately 20 to 30 tons of CO₂ per ton of fly ash. Since the worldwide production of Portland cement is expected to reach nearly 2 billion tons by 2010, replacement of any large portion of this cement by fly ash could significantly reduce carbon emissions associated with construction, as long as the comparison takes the production of fly ash as a given.

Embankment

Fly ash properties are unusual among engineering materials. Unlike soils typically used for embankment construction, fly ash has a large uniformity coefficient and it consists of clay-sized particles. Engineering properties that affect the use of fly ash in embankments include grain size distribution, compaction characteristics, shear strength, compressibility, permeability, and frost susceptibility.^[23] Nearly all the types of fly ash used in embankments are Class F.

Soil stabilization

Soil stabilization is the permanent physical and chemical alteration of soils to enhance their physical properties. Stabilization can increase the shear strength of a soil and/or control the shrink-swell properties of a soil, thus improving the load-bearing capacity of a sub-grade to support pavements and foundations. Stabilization can be used to treat a wide range of sub-grade materials from expansive clays to granular materials. Stabilization can be achieved with a variety of chemical additives including lime, fly ash, and Portland cement. Proper design and testing is an important component of any stabilization project. This allows for the establishment of design criteria, and determination of the proper chemical additive and admixture rate that achieves the desired engineering properties. Stabilization process benefits can include: Higher resistance (R) values, Reduction in plasticity, Lower permeability, Reduction of pavement thickness, Elimination of excavation - material hauling/handling - and base importation, Aids compaction, Provides “all-weather” access onto and within projects sites. Another form of soil treatment closely related to soil stabilization is soil modification, sometimes referred to as “mud drying” or soil conditioning. Although some stabilization inherently occurs in soil modification, the distinction is that soil modification is merely a means to reduce the moisture content of a soil to expedite construction, whereas stabilization can substantially increase the shear strength of a material such that it can be incorporated into the project’s structural design. The determining factors associated with soil modification vs soil stabilization may be the existing moisture content, the end use of the soil structure and ultimately the cost benefit provided. Equipment for the stabilization and modification processes include: chemical additive spreaders, soil mixers (reclaimers), portable pneumatic storage containers, water trucks, deep lift compactors, motor graders.

Flowable fill

Fly ash is also used as a component in the production of flowable fill (also called controlled low strength material, or CLSM), which is used as self-leveling, self-compact backfill material in lieu of compacted earth or granular fill. The strength of flowable fill mixes can range from 50 to 1,200 lbf/in² (0.3 to 8.3 MPa), depending on the design requirements of the project in question. Flowable fill includes mixtures of Portland cement and filler material, and can contain mineral admixtures. Fly ash can replace either the Portland cement or fine aggregate (in most cases, river sand) as a filler material. High fly ash content mixes contain nearly all fly ash, with a small percentage of Portland cement and enough water to make the mix flowable. Low fly ash content mixes contain a high percentage of filler material, and a low percentage of fly ash, Portland cement, and water. Class F fly ash is best suited for high fly ash content mixes, whereas Class C fly ash is almost always used in low fly ash content mixes.^{[23][24]}

Asphalt concrete

Asphalt concrete is a composite material consisting of an asphalt binder and mineral aggregate. Both Class F and Class C fly ash can typically be used as a mineral filler to fill the voids and provide contact points between larger aggregate particles in asphalt concrete mixes. This application is used in conjunction, or as a replacement for, other binders (such as Portland cement or hydrated lime). For use in asphalt pavement, the fly ash must meet mineral filler specifications outlined in ASTM D242 (http://www.astm.org/cgi-bin/SoftCart.exe/DATABASE.CART/REDLINE_PAGES/D242.htm?

L+mystore+ndfm2845). The hydrophobic nature of fly ash gives pavements better resistance to stripping. Fly ash has also been shown to increase the stiffness of the asphalt matrix, improving rutting resistance and increasing mix durability.^{[23][25]}

Geopolymers

More recently, fly ash has been used as a component in geopolymers, where the reactivity of the fly ash glasses can be used to create a binder similar to a hydrated Portland cement in appearance, but with potentially superior properties, including reduced CO₂ emissions, depending on the formulation.^[26]

Roller compacted concrete

Another application of using fly ash is in roller compacted concrete dams. Many dams in the US have been constructed with high fly ash contents. Fly ash lowers the heat of hydration allowing thicker placements to occur. Data for these can be found at the US Bureau of Reclamation. This has also been demonstrated in the Ghatghar Dam Project in India.

Bricks

There are several techniques for manufacturing construction bricks from fly ash, producing a wide variety of products. One type of fly ash brick is manufactured by mixing fly ash with an equal amount of clay, then firing in a kiln at about 1000 °C. This approach has the principal benefit of reducing the amount of clay required. Another type of fly ash brick is made by mixing soil, plaster of paris, fly ash and water, and allowing the mixture to dry. Because no heat is required, this technique reduces air pollution. More modern manufacturing processes use a greater proportion of fly ash, and a high pressure manufacturing technique, which produces high strength bricks with environmental benefits.

In the United Kingdom, fly ash has been used for over fifty years to make concrete building blocks. They are widely used for the inner skin of cavity walls. They are naturally more thermally insulating than blocks made with other aggregates.

Ash bricks have been used in house construction in Windhoek, Namibia since the 1970s. There is, however, a problem with the bricks in that they tend to fail or produce unsightly pop-outs. This happens when the bricks come into contact with moisture and a chemical reaction occurs causing the bricks to expand.

In India, fly ash bricks are used for construction. Leading manufacturers use an industrial standard known as "Pulverized fuel ash for lime-Pozzolana mixture" using over 75% post-industrial recycled waste, and a compression process. This produces a strong product with good insulation properties and environmental benefits.^{[28][29]}



The upper reservoir of Ameren's Taum Sauk hydroelectric plant was constructed of roller-compacted concrete that included fly ash from one of Ameren's coal plants.^[27]

Metal matrix composites

Hollow fly ash can be infiltrated by molten metal to form solid, alumina encased spheres. Fly ash can also be mixed with molten metal and cast to reduce overall weight and density, due to the low density of fly ash. Research is underway to incorporate fly ash into lead acid batteries in a lead calcium tin fly ash composite in an effort to reduce weight of the battery.

Waste treatment and stabilization

Fly ash, in view of its alkalinity and water absorption capacity, may be used in combination with other alkaline materials to transform sewage sludge into organic fertilizer or biofuel.^{[30][31]}

As a catalyst

Fly ash, when treated with sodium hydroxide, appears to function well as a catalyst for converting polyethylene into substance similar to crude oil in a high-temperature process called pyrolysis.^[32]

In addition, fly ash, mainly class C, may be used in the stabilization/solidification process of hazardous wastes and contaminated soils.^[33] For example, the Rhenipal process uses fly ash as an admixture to stabilize sewage sludge and other toxic sludges. This process has been used since 1996 to stabilize large amounts of chromium(VI) contaminated leather sludges in Alcanena, Portugal.^{[34][35]}

Environmental problems

Present production rate of fly ash

In the United States about 131 million tons of fly ash are produced annually by 460 coal-fired power plants. A 2008 industry survey estimated that 43% of this ash is re-used.^[36]

Groundwater contamination

Since coal contains trace levels of trace elements (like e.g. arsenic, barium, beryllium, boron, cadmium, chromium, thallium, selenium, molybdenum and mercury), fly ash obtained after combustion of this coal contains enhanced concentrations of these elements, and therefore the potential of the ash to cause groundwater pollution needs to be evaluated. In the USA there are documented cases of groundwater pollution which followed ash disposal or utilization without the necessary protection means.^[37]

In 2014, residents living near the Buck Steam Station in Dukeville, North Carolina, were told that "coal ash pits near their homes could be leaching dangerous materials into groundwater."^{[38][39]}

Spills of bulk storage

Where fly ash is stored in bulk, it is usually stored wet rather than dry to minimize fugitive dust. The resulting impoundments (ponds) are typically large and stable for long periods, but any breach of their dams or bunding is rapid and on a massive scale.

In December 2008, the collapse of an embankment at an impoundment for wet storage of fly ash at the Tennessee Valley Authority's Kingston Fossil Plant caused a major release of 5.4 million cubic yards of coal fly ash, damaging 3 homes and flowing into the Emory River. Cleanup costs may exceed \$1.2 billion. This spill was followed a few weeks later by a smaller TVA-plant spill in Alabama, which contaminated Widows Creek and the Tennessee River.

In 2014, tens of thousands of tons of ash and 27 million gallons (100,000 cubic meters) of contaminated water spilled into the Dan River near Eden, NC from a closed North Carolina coal-fired power plant that is owned by Duke Energy. It is currently the third worst coal ash spill ever to happen in the United States.^{[40][41]} A 48-inch (120 cm) pipe spilled arsenic and other heavy metals into the river for a week, but was successfully plugged by Duke Energy. The U.S. federal government plans to investigate, and people along the river have been warned to stay away from the water. Fish have yet to be tested, but health officials say not to eat them.^[42]

New regulations published in the Federal Register on December 19, 2015, stipulate a comprehensive set of rules and guidelines for safe disposal and storage.^[43] Designed to prevent pond failures and protect groundwater, enhanced inspection, record keeping and monitoring is specified. Procedures for closure are also included and include capping, liners, and dewatering.^[44]

Contaminants

Fly ash contains trace concentrations of heavy metals and other substances that are known to be detrimental to health in sufficient quantities. Potentially toxic trace elements in coal include arsenic, beryllium, cadmium, barium, chromium, copper, lead, mercury, molybdenum, nickel, radium, selenium, thorium, uranium, vanadium, and zinc.^{[45][46]} Approximately 10% of the mass of coals burned in the United States consists of unburnable mineral material that becomes ash, so the concentration of most trace elements in coal ash is approximately 10 times the concentration in the original coal.^[47] A 1997 analysis by the U.S. Geological Survey (USGS) found that fly ash typically contained 10 to 30 ppm of uranium, comparable to the levels found in some granitic rocks, phosphate rock, and black shale.^[47]



In 2000, the United States Environmental Protection Agency (EPA) said that coal fly ash did not need to be regulated as a hazardous waste.^[48] Studies by the U.S. Geological Survey and others of radioactive elements in coal ash have concluded that fly ash compares with common soils or rocks and should not be the source of alarm.^[47] However, community and environmental organizations have documented numerous environmental contamination and damage concerns.^{[49][50][51]}

A revised risk assessment approach may change the way coal combustion wastes (CCW) are regulated, according to an August 2007 EPA notice in the Federal Register.^[52] In June 2008, the U.S. House of Representatives held an oversight hearing on the Federal government's role in addressing health and environmental risks of fly ash.^[53]

Exposure concerns

Crystalline silica and lime along with toxic chemicals represent exposure risks to human health and the environment. Although industry has claimed that fly ash is "neither toxic nor poisonous," this is disputed. Exposure to fly ash through skin contact, inhalation of fine particulate dust and ingestion through drinking water may well present health risks. Fly ash contains crystalline silica which is known to cause lung disease, in particular silicosis. Crystalline silica is listed by the IARC and US National Toxicology Program as a known human carcinogen.^[54]

Lime (CaO) reacts with water (H₂O) to form calcium hydroxide [Ca(OH)₂], giving fly ash a pH somewhere between 10 and 12, a medium to strong base. This can also cause lung damage if present in sufficient quantities.

Material Safety Data Sheets recommend a number of safety precautions be taken when handling or working with fly ash.^[55] These include wearing protective goggles, respirators and disposable clothing and avoiding agitating the fly ash in order to minimise the amount which becomes airborne.

The National Academy of Sciences noted in 2007 that "the presence of high contaminant levels in many CCR (coal combustion residue) leachates may create human health and ecological concerns".^[1]

See also

- Alkali–silica reaction (ASR)
- Alkali–aggregate reaction
- Cement
- Energetically modified cement (EMC)
- Health effects of coal ash
- Pozzolanic reaction
- Silica fume

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External links

- Evaluation of Dust Exposures at Lehigh Portland Cement Company, Union Bridge, MD, a NIOSH Report, HETA 2000-0309-2857 (<http://www.cdc.gov/niosh/hhe/reports/pdfs/2000-0309-2857.pdf>)



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- Determination of Airborne Crystalline Silica Treatise by NIOSH (<http://www.cdc.gov/niosh/docs/2003-154/pdfs/chapter-r.pdf>)
- "Coal Ash: 130 Million Tons of Waste" (<http://www.cbsnews.com/stories/2009/10/01/60minutes/main5356202.shtml>) *60 Minutes* (Oct. 4, 2009)
- American Coal Ash Association (<http://www.aaa-usa.org>)
- Fly Ash Information Center (<http://www.fly-ash-information-center.org.in>) : Site explaining the history and uses of fly ash.
- United States Geological Survey - Radioactive Elements in Coal and Fly Ash (<http://greenwood.cr.usgs.gov/energy/factshts/163-97/FS-163-97.html>) (document)
- Public Employees for Environmental Responsibility: Coal Combustion Waste (<http://www.peer.org/campaigns/publichealth/coalash/index.php>)
- UK Quality Ash Association (<http://www.ukqaa.org.uk>) : A site promoting the many uses of fly ash in the UK
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