

Fly ash and its impacts

Fly ash is a particulate matter ranging in size from 0.01 to 100 μm released into the flue stream during combustion of coal in power generating stations. The mineralogical, physical and chemical properties of fly ash depend on the type of coal, combustion conditions, emission control devices and handling methods. Chemically it is a mixture of oxides, hydroxides, carbonates, silicates and sulphates of calcium, iron, aluminum and other metals in trace amount. It is grey to black in color, abrasive, alkaline and refractory in nature. Fly ash is regarded as a pollutant due to its negative impact on the ecosystem, although it has alternate, safe and viable utilities [1].

Formation of fly ash: Coal is a sedimentary rock formed millions of years ago from plant materials containing combustible organic matter in the form of dehydrogenated plant fragments as well as inorganic matter in the form of minerals like alumino-silicate clays, silica, carbonates of calcium, magnesium or iron and sulphides among other traces. On combustion at high temperatures, all elements in coal excluding carbon, hydrogen, nitrogen, oxygen and sulphur undergo physical and chemical transformation to form ash [2]. The mechanism of ash formation involves several particles that originate from a single coal particle through the initial process of fragmentation. As the combustible carbon matter surrounding the mineral components burnout, finely distributed ash components reach the particle surface. The molten ash components merge into larger particles and some part of the ash vapourise at high temperature, condense and coagulate. Vaporous pollutants and heavy metals accumulate over the ash particles. Coarse ash particles known as bottom ash (or slag), fall to the bottom of the combustion chamber, while the lighter fine ash particles called fly ash, remain suspended in the flue gas. In pulverized fuel firing systems, 70-90% is released as fly ash while 10-30% is removed as coarse-grained bottom ash [3]. Enrichment of components is found to be higher in fly ash when compared to bottom ash [4]

Constituents of fly ash: Apart from high percentage of silica (SiO_2), alumina (Al_2O_3) and magnetite (Fe_2O_3), listed in Table 1, fly ash also contains oxides, hydroxides, carbonates, silicates and sulphates of different elements like phosphorous, potassium, calcium, magnesium, iron, manganese etc. The chemical composition of fly ash enables its use for the synthesis of

zeolite, alum and precipitated silica [5]. Based on the nature of coal and combustion conditions, fly ash may contain various levels of heavy metals such as antimony, arsenic, barium, boron, cadmium, chromium, cobalt, copper, lead, mercury, molybdenum, nickel, selenium, silver, and zinc [6].

Table 1: Chemical composition for fly ash produced from different coal types [5].

Component (wt.%)	Bituminous	Sub-bituminous	Lignite
SiO ₂	20–60	40–60	15–45
Al ₂ O ₃	5–35	20–30	10–25
Fe ₂ O ₃	10–40	4–10	4–15
CaO	1–12	5–30	15–40
MgO	0–5	1–6	3–10
SO ₃	0–4	0–2	0–10
Na ₂ O	0–4	0–2	0–6
K ₂ O	0–3	0–4	0–4

Heavy metals in fly ash: Indian coal has very high ash content in the range of 35-40%. A study of 3 coal thermal plants based in and around Delhi reveals the amount of heavy metals in the fly ash generated (Table 2) [7]. According to an analysis on fly ash samples collected from 5 thermal plants (ranging from 90-3000 MW capacities) in India, concentrations of toxic heavy metals such as arsenic, mercury, lead and cadmium were in the range as given in Table 3 [4]. Analysis of heavy metals in groundwater near an ash disposal site in Orissa, India showed high concentrations of iron, barium, copper, manganese, sulphur, lead, vanadium and zinc. According to the study, the zone of attenuation for barium, iron, copper, manganese, sulphur and zinc in groundwater was about 600 – 900 m from the ash pond, while lead did not show any significant attenuation even at a distance of 1200 m [8].

Table 2: Heavy metals in fly ash samples of 3 coal thermal plants

Sample	Cr	Mn	Pb	Zn	Cu	Ni	Co
Fly ash (mg/kg)	87-103	47-139	20-56	60-124	56-83	28-63	8-18

Table 3: Heavy metals in fly ash samples of 5 coal thermal plants

Sample	As	Hg	Pb	Cd
Fly ash ($\mu\text{g/g}$)	0.19–0.35	0.51–2.13	7.6–35.3	0.6–0.93

Impact of heavy metals on natural ecosystem: Heavy metals like arsenic, lead, nickel, cobalt, chromium, boron and antimony found in fly ash are hazardous for living organisms. These elements can potentially be released to the soil, surface water, and groundwater by leaching processes also affecting the vegetation.

The leaching potential of ash ponds is higher due to diurnal and seasonal variations in temperature, moisture and other parameters [9]. Leaching of soluble ions from ash ponds into the ground water was observed in studies near Vijayawada Thermal Power Station [10]. Studies indicate that leachability of cationic metals such as cadmium, chromium, zinc, lead, mercury, and silver increases with decreasing pH or acidic conditions [11].

Bio-accumulation of heavy metals in plants lead to increased elemental composition eventually entering the food chain. An investigation of fly ash contaminated areas in Uttar Pradesh, India showed the bio-accumulation of heavy metals like Fe, Zn, Cu, Mo, B, Si, Al, Cr, Pb, Cd, Hg and As in native aquatic, terrestrial and algal species in the vicinity [12].

Leachate from fly ash dumpsites has genotoxic potential and may lead to adverse effects on vegetation and on the health of exposed human populations. A study on the mutagenicity and genotoxicity effects of fly ash leachate showed predominance of the metals like sodium, silicon, potassium, calcium, magnesium, iron, manganese, zinc, and sulphate. The Ames Salmonella mutagenicity assay conducted on two-tester strains and genotoxicity assay on fly ash leachate carried in vitro on human blood cells and in vivo on Nicotiana plants indicated that the leachate was directly mutagenic and resulted in DNA damage in whole blood cells, lymphocytes, and in Nicotiana plants [12].

Other pollutants in fly ash: Certain organic constituents contained in coal, during combustion results in formation of organic pollutants (mutagens and carcinogens) like Polycyclic Aromatic Hydrocarbons (PAH) and Polychlorinated biphenyls (PCB) which are adsorbed to the fly ash.

The impact of organic pollutants adsorbed to fly ash also reflects on water, soil and vegetation. Based on the fly ash generated from 5 thermal plants in India, the concentration of Benzo(a)Pyrene which is the most potent carcinogenic and mutagenic Polycyclic Aromatic Hydrocarbons (PAH) varied as 0.82- 18.14 ng/g. The total PAHs and PCBs in the fly ash samples were found to be in the range of 43.61-936.14 ng/g and 7.34-178.69 ng/g respectively [13]. Studies on fly ash also reveal the increased threat of radioactivity and its impact on the ecosystem including humans. According to a study based on 30 power plants in India, natural radionuclides like Ra-226, Th-228 and K-40 gets enriched by 2-5 times in the resulting fly ash compared to the parent coal.

Utilization of fly ash: Fly ash generated from coal based thermal power plants are usually stored in ash ponds which contaminate the top soil and water resources while also affecting the biodiversity. However, utilization of fly ash for alternative purposes has the following benefits [5]:

1. minimizing environmental impact of direct disposal,
2. minimizing disposal costs,
3. enabling other uses of the land since less area is reserved for fly ash disposal,
4. procuring financial returns from the sale of the by-product
5. replacing scarce or expensive natural resources.

In India, one of the major areas for fly ash utilization is in construction (cement production, brick manufacturing and road embankments) [1]. Typical highway engineering applications include fly ash for encapsulated purposes and unencapsulated purposes [4]:

Encapsulated purposes

- 1) Pozzolan in Portland Cement Concrete (PCC): Fly ash generated during pulverized coal combustion is categorized as pozzolan which are siliceous and/or aluminous materials that together with water and calcium hydroxide form cementitious products at ambient temperatures. The pozzolanic properties of the ash, including its lime binding capacity and

fineness makes it useful for the manufacture of cement, building materials concrete and concrete-admixed products.

- 2) Asphalt filler: The spherical shape and particle size distribution of fly ash makes it good mineral filler in Hot Mix Asphalt (HMA) applications which improves the fluidity of flowable fill and grout.

Unencapsulated purposes

- 3) Soil and road base stabilization: The geotechnical properties of fly ash like specific gravity, permeability, internal angular friction and consolidation characteristics make it suitable for use in construction of roads, embankments, structural fill etc. Fly ash also has important physicochemical characteristics such as bulk density, particle size, porosity, water holding capacity, and surface area. Roadways have high potential for large volume use of high carbon fly ash (HCFA) which can be activated with lime kiln dust (LKD) and used as a base layer for newly paved roads.
- 4) Flowable fills, grouts, structural fill/embankment: Flowable fill is a mixture of fly ash, water, and portland cement that flows like a liquid, sets up like a solid, is self-leveling, and requires no compaction to achieve maximum density.

Technical constraints: There are certain technical constraints to usage of fly ash for road construction. Loss on Ignition (LOI) is a measure of unburned carbon in the fly ash and is a critical parameter for concrete applications. Fly ash that contains significant amounts of unburned carbon due to the use of low nitrogen-oxide and sulphur-oxide burners cannot be reused in concrete production due to its reactivity with air entrainment admixtures. Fly ash which contains sulphur in excess of 5.0 percent as SO_3 or contain scrubber residue, should be carefully evaluated with specific project soils to evaluate the expansion potential of the materials combination [14].

Minimizing the environmental impact of fly ash usage in road construction [Water contamination] [4,5].

- While using fly ash for road construction, potential impacts to ground water and soil must be considered and studied.
- While determining the possible degree of leaching, it is necessary to have an understanding of the hydrological conditions and the permeability of materials and soil.
- The pavement structure and its designed thickness is an important parameter when evaluating harmful effects of fly ash on the environment.
- Take care when using or disposing off any construction material in a hydro-geologically vulnerable area.
- Follow proper engineering requirements when using unencapsulated fly ash.
- Dust control and erosion prevention measures are essential during construction phase.
- Scientific proportion of fly ash in the construction materials should be practiced.
- The amount of leachate produced should be controlled by assuring adequate compaction, grading to promote surface runoff, and daily proof-rolling of the finished subgrade to impede infiltration.
- When construction is finished, a properly seeded soil cover will reduce infiltration. For highway embankments, the pavement may be an effective barrier to infiltration
- Occupational issues include the handling of dry ash prior to or during its inclusion in a concrete mix or exposures during demolition of concrete structures. In such cases, work inhalation and skin contact precautions should be observed

Environmental impact of fly ash utilization in road construction: Fly ash is a waste material with variable chemical and mineralogical composition. Its unrestrained application could affect the environment adversely if proper and scientific methodologies are not adopted.

During road construction phase: When large quantities of fly ash are used, the quantities of toxic elements that can leach into the waters and soil become significant. Particularly, if the drainage from fly ash storage near the construction site is directly released into the watercourse, the aquatic living organisms in it are affected. These waters supplied to the people also threaten

their health [15]. Before embarking on construction activities involving fly ash, potential impact of water and soil must be studied.

- i. ***Encapsulated purposes:*** Fly ash used for encapsulated purposes like PCC, asphalt filler etc have shown minimal heavy metal leaching impact [16]. Since fly ash is bonded with asphalt or cement, significantly lower leaching abilities are observed for the following reasons: 1) ash particles are surrounded by asphalt or cement layer preventing water seepage, 2) bonded materials are mainly used for upper base courses that are thinner compared with the lower base courses. These materials when well compacted have a very low permeability and there is no significant influence of heavy metals on the surrounding waters and soil due to leaching [15].
- ii. ***Unencapsulated purposes:*** Studies on fly ash used for unencapsulated fly ash purposes like soil-road base stabilization, fill/embankments etc show leaching potential of heavy metals into the environment under certain conditions.
 - According to a case study on fly ash based fill in United States, the shallowness of the drinking water wells, **the porosity of the overlying sands, the location of the landfill, and the improper use of fly ash all contributed to the contamination of a town's drinking water with high levels of boron, manganese, and molybdenum [16].**
 - If the soil-road base stabilization layer is of average thickness and has reduced exposure to moist or damp conditions, leaching of heavy metals may be negligible [16]. Hence, it could be inferred that usage of fly ash in coastal regions with high moisture content might induce leaching of heavy metals.
 - It is not advisable to use flyash in high rainfall regions with laterite soil as the chances of contamination of groundwater sources and soil is higher due to leachate from fly ash, which gets transported faster in laterite media due to higher infiltration rate leading to contamination and hence affects the dependent population in the region.
 - The leaching potential of unpaved road materials (URM) mixed with lime activated high carbon fly ash and evaluation of groundwater (impacts of barium, boron, copper, and zinc leaching) indicate that an increase in fly ash and lime content has significant effects on

leaching behavior of heavy metals from URM–fly ash mixture. An increase in fly ash content and a decrease in lime content promoted leaching of Ba, B and Cu whereas Zn leaching was primarily affected by the fly ash content. The metal concentrations decreased with time and distance due to dispersion in soil vadose zone (top soil to water table section) [17]

- A study investigated the leaching potential of six metals, Al, Cr, Fe, Mn, Sb and V, from the fly ash-lime kiln dust (LKD) stabilized soils based on a series of batch water leach test and column leach test. The results indicated that an increase in LKD amount, pH, and fly ash content have significant effects on leaching behavior of heavy metals from soil–fly ash–LKD mixtures. The addition of fly ash caused an increase in pH values and in concentrations of Sb, V, Cr, Al and Mn [18]
- The potential for leaching of metals from fly ash stabilized subgrade soils used in highway construction was evaluated based on (1) water leach testing (WLT), (2) laboratory column testing, (3) field lysimeter testing, and (4) numerical modeling on soil-fly ash mixtures. The tests showed that 1) concentrations of metals in the leachate from soil-fly ash mixtures tend to be lower (1.5 to 2.5 times) than those from fly ash alone and the concentration increases non-linearly with increasing fly ash content, 2) the pH of the effluent and initial effluent concentration from soil-fly ash mixtures increases with increasing fly ash content, 3) the release pattern for metals from the soil-fly ash mixtures appears to be adsorption-controlled, 4) concentrations of most of the metals of concern are higher in leachate collected from the fly ash stabilized pavement section and decreased slightly over time, 5) the maximum concentration decreases by about 5 times within the first meter below a fly ash stabilized layer, and then decreases more gradually at deeper depths, 6) the maximum concentration at a given depth decreases with increasing dispersion coefficient and decreasing thickness of the stabilized layer, 7) the time to reach the maximum concentration at a particular depth is independent of the thickness of the stabilized layer, and increases as the dispersion coefficient decreases and the retardation factor increases [19]

References

1. Vimal Chandra Pandey, P.C. Abhilash, Nandita Singh, The Indian perspective of utilizing fly ash in phytoremediation, phytomanagement and biomass production, *Journal of Environmental Management* 90 (2009) 2943–2958
2. Robert A Meyers, Anthony D Walters, Janusz S Laskowski, *Encyclopedia of physical science and technology*, Third Edition Energy, AP publishers
3. H Spliethoff, *Power generation from solid fuels*, Springer
4. R.C. Bhangare, P.Y. Ajmal, S.K. Sahu, G.G. Pandit, V.D. Puranik, Distribution of trace elements in coal and combustion residues from five thermal power plants in India, *International Journal of Coal Geology* 86 (2011) 349–356
5. M. Ahmaruzzaman, A review on the utilization of fly ash, *Progress in Energy and Combustion Science* 36 (2010) 327–363
6. Rajarshi Chakraborty, Anita Mukherjee, Arsenic hazards in coal fly ash and its fate in Indian scenario, *Resources, Conservation and Recycling* 55 (2011) 819–835
7. Snigdha Sushil, Vidya S. Batra, Analysis of fly ash heavy metal content and disposal in three thermal power plants in India, *Fuel* 85 (2006) 2676–2679
8. T. Praharaaj, S.P. Swain, M.A. Powell, B.R. Hart, S. Tripathy, Delineation of groundwater contamination around an ash pond Geochemical and GIS approach, *Environment International* 27 (2002) 631–638
9. I.V. Suresh, C. Padmakar, Prabha Padmakaran, M.V.R.L. Murthy, C.B. Raju and R.N. Yadava, K. Venkata Rao, Effect of pond ash on ground water quality: a case study, *Environmental Management and Health* 9/5 [1998][ISSN 0956-6163]
10. Jianmin Wang, Heng Ban, Xinjun Teng, Hao Wang, Ken Ladwig, Impacts of pH and ammonia on the leaching of Cu(II) and Cd(II) from coal fly ash, *Chemosphere* 64 (2006) 1892–1898
11. S. Dwivedi, S. Srivastava, S. Mishra, B. Dixit, A. Kumar, R.D. Tripathi, Screening of native plants and algae growing on fly-ash affected near National Thermal Power Corporation, Tanda, Uttar Pradesh India for accumulation of toxic heavy metals areas, *Journal of Hazardous Materials* 158 (2008) 359–365
12. Rajarshi Chakraborty, Anita Mukherjee, Mutagenicity and genotoxicity of coal fly ash water leachate, *Ecotoxicology and Environmental Safety* 72 (2009) 838–842

13. S.K. Sahu, R.C. Bhangare, P.Y. Ajmal, S. Sharma, G.G. Pandit, V.D. Puranik, Characterization and quantification of persistent organic pollutants in fly ash from coal fueled thermal power stations in India, *Microchemical Journal* 92 (2009) 92–96
14. Fly ash facts for highway engineers, American coal ash association, <http://www.fhwa.dot.gov/pavement/recycling/fafacts.pdf>
15. Marija Šperac, Sanja Dimter, Water contamination by fly ash from road, construction, http://ksh.fgg.uni-lj.si/bled2008/cd_2008/03_Global%20climate%20change%20and%20hydrological%20processes/077_Sperac.pdf
16. Using coal ash in highway construction : A guide to Benefits and impacts, Federal Highway Administration
17. Bora Cetin, Ahmet H. Aydilek, Lin Li, Experimental and numerical analysis of metal leaching from fly ash-amended highway bases, *Waste Management* xxx (2012) xxx–xxx
18. Bora Cetina, Ahmet H. Aydileka,, Yucel Guneyb, Leaching of trace metals from high carbon fly ash stabilized highway base layers *Resources, Conservation and Recycling* 58 (2012) 8– 17
19. Md Sazzad Bin-Shafique, Craig H. Benson, and Tuncer B. Edil, Leaching of heavy metals from fly ash stabilized soils used in highway pavements, *Combustion Byproducts Recycling Consortium*, West Virginia University February 2003,

Coal Ash Is More Radioactive than Nuclear Waste

By burning away all the pesky carbon and other impurities, coal power plants produce heaps of radiation

By Mara Hvistendahl | December 13, 2007 |



CONCENTRATED RADIATION: By burning coal into ash, power plants concentrate the trace amounts of radioactive elements within the black rock. Image: ©ISTOCKPHOTO.COM

The popular conception of nuclear power is straight out of *The Simpsons*: Springfield abounds with signs of radioactivity, from the strange glow surrounding Mr. Burns' nuclear power plant workers to Homer's low sperm count. Then there's the local superhero, Radioactive Man, who fires beams of "nuclear heat" from his eyes. Nuclear power, many people think, is inseparable from a volatile, invariably lime-green, mutant-making radioactivity.

Coal, meanwhile, is believed responsible for a host of more quotidian problems, such as mining accidents, acid rain and greenhouse gas emissions. But it isn't supposed to spawn three-eyed fish like Blinky.

Over the past few decades, however, a series of studies has called these stereotypes into question. Among the surprising conclusions: the waste produced by coal plants is actually more radioactive than that generated by their nuclear counterparts. In fact, the fly ash emitted by a power plant—a by-product from burning coal for electricity—carries into the surrounding

environment 100 times more radiation than a nuclear power plant producing the same amount of energy. * [See Editor's Note at end of page 2]

At issue is coal's content of uranium and thorium, both radioactive elements. They occur in such trace amounts in natural, or "whole," coal that they aren't a problem. But when coal is burned into fly ash, uranium and thorium are concentrated at up to 10 times their original levels.

Fly ash uranium sometimes leaches into the soil and water surrounding a coal plant, affecting cropland and, in turn, food. People living within a "stack shadow"—the area within a half- to one-mile (0.8- to 1.6-kilometer) radius of a coal plant's smokestacks—might then ingest small amounts of radiation. Fly ash is also disposed of in landfills and abandoned mines and quarries, posing a potential risk to people living around those areas.

In a 1978 paper for *Science*, J. P. McBride at Oak Ridge National Laboratory (ORNL) and his colleagues looked at the uranium and thorium content of fly ash from coal-fired power plants in Tennessee and Alabama. To answer the question of just how harmful leaching could be, the scientists estimated radiation exposure around the coal plants and compared it with exposure levels around boiling-water reactor and pressurized-water nuclear power plants.

The result: estimated radiation doses ingested by people living near the coal plants were equal to or higher than doses for people living around the nuclear facilities. At one extreme, the scientists estimated fly ash radiation in individuals' bones at around 18 millirems (thousandths of a rem, a unit for measuring doses of ionizing radiation) a year. Doses for the two nuclear plants, by contrast, ranged from between three and six millirems for the same period. And when all food was grown in the area, radiation doses were 50 to 200 percent higher around the coal plants.

McBride and his co-authors estimated that individuals living near coal-fired installations are exposed to a maximum of 1.9 millirems of fly ash radiation yearly. To put these numbers in perspective, the average person encounters 360 millirems of annual "background radiation" from natural and man-made sources, including substances in Earth's crust, cosmic rays, residue from nuclear tests and smoke detectors.

Dana Christensen, associate lab director for energy and engineering at ORNL, says that health risks from radiation in coal by-products are low. "Other risks like being hit by lightning," he adds, "are three or four times greater than radiation-induced health effects from coal plants." And McBride and his co-authors emphasize that other products of coal power, like emissions of acid rain-producing sulphur dioxide and smog-forming nitrous oxide, pose greater health risks than radiation.

The U.S. Geological Survey (USGS) maintains an online database of fly ash-based uranium content for sites across the U.S. In most areas, the ash contains less uranium than some common rocks. In Tennessee's Chattanooga shale, for example, there is more uranium in phosphate rock.

Robert Finkelman, a former USGS coordinator of coal quality who oversaw research on uranium in fly ash in the 1990s, says that for the average person the by-product accounts for a miniscule amount of background radiation, probably less than 0.1 percent of total background radiation

exposure. According to USGS calculations, buying a house in a stack shadow—in this case within 0.6 mile [one kilometer] of a coal plant—increases the annual amount of radiation you're exposed to by a maximum of 5 percent. But that's still less than the radiation encountered in normal yearly exposure to X-rays.

So why does coal waste appear so radioactive? It's a matter of comparison: The chances of experiencing adverse health effects from radiation are slim for both nuclear and coal-fired power plants—they're just somewhat higher for the coal ones. "You're talking about one chance in a billion for nuclear power plants," Christensen says. "And it's one in 10 million to one in a hundred million for coal plants."

Radiation from uranium and other elements in coal might only form a genuine health risk to miners, Finkelman explains. "It's more of an occupational hazard than a general environmental hazard," he says. "The miners are surrounded by rocks and sloshing through ground water that is exuding radon."

Developing countries like India and China continue to unveil new coal-fired plants—at the rate of one every seven to 10 days in the latter nation. And the U.S. still draws around half of its electricity from coal. But coal plants have an additional strike against them: they emit harmful greenhouse gases.

With the world now focused on addressing climate change, nuclear power is gaining favor in some circles. China aims to quadruple nuclear capacity to 40,000 megawatts by 2020, and the U.S. may build as many as 30 new reactors in the next several decades. But, although the risk of a nuclear core meltdown is very low, the impact of such an event creates a stigma around the non carbon power source.

The question boils down to the accumulating impacts of daily incremental pollution from burning coal or the small risk but catastrophic consequences of even one nuclear meltdown. "I suspect we'll hear more about this rivalry," Finkelman says. "More coal will be mined in the future. And those ignorant of the issues, or those who have a vested interest in other forms of energy, may be tempted to raise these issues again."

**Editor's Note (posted 12/30/08): In response to some concerns raised by readers, a change has been made to this story. The sentence marked with an asterisk was changed from "In fact, fly ash—a by-product from burning coal for power—and other coal waste contains up to 100 times more radiation than nuclear waste" to "In fact, the fly ash emitted by a power plant—a by-product from burning coal for electricity—carries into the surrounding environment 100 times more radiation than a nuclear power plant producing the same amount of energy." Our source for this statistic is Dana Christensen, an associate lab director for energy and engineering at Oak Ridge National Laboratory as well as 1978 paper in Science authored by J.P. McBride and colleagues, also of ORNL.*

As a general clarification, ounce for ounce, coal ash released from a power plant delivers more radiation than nuclear waste shielded via water or dry cask storage.