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Research Article

Groundwater contamination due to fly ash disposal: A Review

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Abstract

Increased use of coal for electrical power generation results in large quantity of fly ash and other residues, which require proper handling and disposal. In India, about 75% of the electricity is generated by coal based thermal power plants which produces nearly 65 million tons/year of fly ash as by product. Disposal of fly ash has adverse impacts on terrestrial and aquatic ecosystems due to leaching of toxic substances from the ash into soil and groundwater as well as plant establishment and growth. The ash is generally being disposed of by hydraulically slurry with water into artificial lagoons called ash ponds. If the ash pond are not properly designed, the contamination of surface and groundwater may take place due to leaching of metals leaching in the disposal environment is one of the major problems associated with the holding of coal combustion residues in the ash ponds. Thus, the proper utilization of fly ash is required and should be approach towards minimum disposal. Therefore the proper disposal of fly ash is required and should be minimized.

Keywords: Ash pond, Fly ash, Heavy metals, Leachate.

Introduction

The global energy needs has enormously been increased and to a large extent this is met from fossil fuels. Coal is the only natural resource and fossil fuel available in abundance in India. Consequently, it is used widely as a thermal energy source and also as fuel for thermal power plants producing electricity (Mishra, 2004). Power generation in India has increased manifold in recent decades to meet the demand of increasing population (Jamil et al., 2009). India is heavily dependent on coal for meeting its energy requirement which is nearly 60% of commercial energy demand. Thus coal is at the centre stage of India's energy scene (Mishra and Mahakur, 2006). Coal is derived from peat and as geological processes apply pressure to peat over time, it is transformed into the following types based on their organic maturity (WCI, 2009):

Lignite (brown coal) is the lowest rank of coal and used solely as fuel for steam electricity power generation.

Sub bituminous coal properties lies in between lignite and bituminous coal and are used primarily as fuel for steam electricity power generation.

Bituminous Coal is a dense coal usually black, sometimes dark brown, used primarily as fuel in steam electric power generation with substantial quantities also used for heat and power application in manufacturing and to make coke.

Anthracite is the highest rank of coal and a harder glossy and black coal used primarily for residential and commercial space heating.

Indian coal is generally of low quality with 40-45% ash content. The power plants in India presently consume about 250 MT of coal generating about 100MT ashes (Fly and bottom ash) annually, the disposal of such a huge quantity of fly ash is herculean task. A single

thermal power plant uses around 1,000 tons of coal and churns out 13.34 tones of fly ash. Fly ash contains a variety of toxic elements that damage the living and non living constituents of the environment. With 100 tons of coal burnt produces about 100 kg Pb, 40 kg Zn, 15 kg Cu, 8 kg Cd, 40 kg Cr, 3 kg As which ultimately find their way in surrounding environment (Sahu, 1990). Different environmental issues of concern due to disposal of such huge quantity of ash on land are the effects on air, soil, vegetation, ground and surface water. The major constraint in block disposal of fly ash is the land requirement as for every 20-25 years (Mishra, 2011).

The usual methods of ash disposal are (a) dumping in disposal area (b) placement and compaction in controlled fill (c) slurring with water followed pumping into a lagoon or impoundment (Eisenberg et al., 1986).

Wet disposal system is the most common practice taken in thermal power plants for the fly ash disposal. In wet disposal system, the fly ash is mixed with water and transported as slurry through pipe and disposed of in ash ponds or dumping areas near the plants (Nawaz, 2013). Terrestrial disposal of fly ash has been considered as potential source of contamination (Figure 1), due to enrichment and surface association of trace elements in the ash particles. There are two impacts associated with the ash pond decant. The first point is that this water slowly seeps into the ground while carrying with it the ash leachates. The water may contain harmful heavy metals like lead which has a tendency to leach out over a period of time. Due to this groundwater gets polluted and may become unsuitable for domestic use.

The second factor affecting the water environment is the release of ash pond decant into the local water bodies. Such a release of ash pond decant tends to deposit ash along its path thereby causing fugitive dust nuisance when it dries up. Also when such water mixes with a water body, it increases the turbidity by decreasing the primary productivity. This is harmful to the fisheries and other aquatic biota in water (Patra, 2010).

Chemical composition of fly ash

Fly ash varies in its physical, chemical and mineralogical composition depending on the parent coal, the operating conditions of the furnace, efficiency of emission control devices, storage and handling of by products and climate (Adriano et al., 1980). Fly ash occurs as spherical particle of alumino-silicate glass usually ranging in diameter of 0.5-100 μm . Particle

diameter between 0.5-75 μm has surface area ranging from 1.27-0.45 m^2/g where as ash fractions with particle diameter greater than 75 μm have unusually high surface area because of the presence of large porous and carbonaceous particles (Schure et al., 1985). Chemically fly ash consist of more than 90% oxides of silicon, aluminium, titanium, iron, sodium, calcium, magnesium, potassium and trace amounts of toxic elements are also present, such as mercury, arsenic and chromium (Prasad et al., 1996). On the basis of chemical analysis and x-ray diffraction measurements, it was found that in fly ash, soluble fractions consist of mostly of anhydrous CaSO_4 , 3MgSO_4 , CaSO_4 , $\text{Na}_2\text{Ca}(\text{SO}_4)$ and other double sulphates (David et al., 1993). Investigators have defined some less abundant, yet significant mineral forms of gypsum, calcite, ferrous, carbonates and manganese oxide in the fly ash (Bauer and Natusch, 1981; Henry et al., 1980). Fly ash can be separated into three major matrices: glass, mullite-quartz and magnetic spinal. The ratio of crystalline material to glassy amorphous material increases with particle size (Hulett et al., 1981; Hensen et al., 1984). The quartz content varies in the range of 15-17% depending on the type of coal and mullite content varies from 0-22%. The fractioned surface indicated that about 90% by wt of the fly ash was composed of 50 μm particles (David et al., 1993).

Based on the chemical composition, fly ash is grouped into two classes-F and C (ASTM, 1994). They primarily differ in the amount of calcium and the silica, alumina and iron content in the ash, which also vary among the types of coal used (Table 1). Class F fly ash is highly pozzolanic and has total calcium content typically ranging from 1 to 12% mostly in the form of calcium hydroxide and calcium sulphate. In contrast, class C fly ash contains calcium content as high as 30 to 40%. Another difference between class F and Class C is that the amount of alkalies (combined sodium and potassium) and sulphates (SO_4) are generally higher in the class C fly ashes than in the class F fly ash (Seshadri et al., 2010).

It is known that fly ash particles emitted from coal fired power plants show an enrichment of several toxic trace elements (Burcu et al., 1997; Campbell et al., 1978). Baba (2001) used atomic absorption spectrophotometric techniques for the geochemical analysis of the coal, fly ash and bottom ash obtained from the aforementioned power plant. The major components determined were SiO_2 , Al_2O_3 , Fe_2O_3 , MgO , CaO , Na_2O , K_2O , TiO_2 , MnO and trace elements were Ba, Cd, Cu, Cr, Co, Ni, Pb, Sb and Zn. The concentrations of nine major and minor elements for the collected samples are listed in Table 2

and Table 3 in order to provide a general idea of the relative metal concentration of each sample type.

An analytical study being carried out by Prasad and Mondal (2008) to determine the chemical composition of fly ash and to determine the minor metals in the fly ash of Chandrapura Thermal Power Plant, Jharkhand and Ramagundam Super Thermal Power Plant, Andhra Pradesh. Visually, the colour of fly ash was blackish grey in Chandrapura thermal power plant and ash was light grey in Ramagundam super thermal power plant. The most abundant component in both the ashes found was SiO_2 followed by Al_2O_3 , Fe_2O_3 and CaO . The least abundant major components in both the ashes found were TiO_2 , Na_2O , K_2O and SO_3 . The minor metals present in both the fly ashes indicate that Mn has been the most abundant trace elements, whereas Cd has been least abundant (Prasad and Mondal, 2008). The results of analysis are listed in Table 4 and 5 respectively.

Choi et al. (2002) studied the composition of coal and fly ash samples collected from five different power plants in Korea; Boryona (BR), Samcheonpo (SCP), Seocheon (SC), Yongwol (YW) and Yongdong (YD). Chemical compositions of the fly ashes were determined using ICP-AES. It has been observed that smaller the particle, higher the specific surface area and therefore the size distribution of fly ash is an important in controlling elemental retention and release to the environment. The major solid phases in five fly ashes are mullite, quartz and iron oxides including hematite and magnetite. Clay minerals were not detected in the sample.

Contrary to the coal chemistry, the fly ash from bituminous coals was higher in SiO_2 , Fe_2O_3 , CaO and MgO concentrations. However, K_2O concentration was still higher in the anthracite fly ash and the fly ash chemistry seems to higher mineral matter contents in the feed coal. The higher concentrations of Si, Al, Fe, Ca and Mg in the bituminous coal fly ash appear to be due to lower content of mineral matter. The higher K contents in the anthracite coal fly ash however could be attributable to the illite in anthracite coal. In the size fractioned anthracite coal fly ash samples, the under 45 μm fractions generally show higher concentrations for Si, Al, Na and K than the over 90 μm size. Fractioned samples indicating surface association of the major elements. On the contrary, the Si, Al, Na and K in the sub bituminous coal fly ash show little difference between the two different size fractions. As for trace element concentrations, the two different types of ashes do not show any significant differences, although Cu, Pb

and Zn concentrations were slightly higher in SC (Seocheon thermal power plant) and Yd (Yongdong thermal power plant) anthracite fly ashes. Cr shows extremely high concentrations for YD anthracite coal fly ash recording up to 498 ppm. Nearly all the trace elements except for the Cr in the YD samples showed size dependence. Such size dependence also implies surface enrichments for the trace elements. Chemical composition of fly ash is given in Table 6.

Marnkovic et al. (2010) analyzed the chemical composition of fly ash and bottom ash from the Serbian Nikola Tesla power plant by using classic chemical analysis. The "Nikola Tesla" power plant is the biggest power plant in Serbia. It is producing about 5-6 million tones of coal ashes (fly ash and bottom ash) per annum. On the basis of chemical analysis, the fly ash from the Nicola Tesla power plant is classified as a low calcium fly ash. This fly ash satisfies the chemical requirements for use as a pozzolan, because the content of pozzolanic oxides ($\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3$) in it (80-66%) is greater than the minimum content for these oxides required by ASTM 618(70%). Also, the contents of SO_3 (2.74%) and Na_2O (0.14%) as well as the loss of ignition (1.85 %) are lower than allowed maximum values proposed by ASTM 618 (5%, 1.5%, and 6% respectively). The content of oxides: SiO_2 , Al_2O_3 and Fe_2O_3 were lower (49.39%, 19.70% and 5.83%) but loss on ignition higher (8.91%) in the bottom ash from the Nicola Tesla Power Plant than in the fly ash. On the basis of X-ray diffraction study, it can be stated that major crystalline phase in the fly ash is quartz- SiO_2 . The other crystalline phase in fly ash, present in small amounts were mullite $\text{Al}_6\text{Si}_2\text{O}_{13}$, anhydrite CaSO_4 , Feldspar $\text{NaAlSi}_3\text{O}_8$, diopside $\text{CaMgSi}_2\text{O}_6$, hematite Fe_2O_3 and gehlenite $\text{Ca}_2\text{Si}_2\text{O}_7$.

In the bottom ash, the major crystalline phase was quartz then calcite CaCO_3 and small amounts of anhydrite, feldspar, diopside and hematite. Besides the mentioned crystalline phases, a significant amount of amorphous aluminosilicate (glass) was also found in the XRD pattern of fly ash and bottom ash. The SiO_2 present as quartz or in the crystalline aluminosilicate phase is inert. Similarly, the part of the alumina in the crystalline phase is inactive. Both the silica and alumina in the amorphous aluminosilicate (glass) are reactive.

Coal is also radioactive due to primordial ^{238}U , ^{232}Th and ^{40}K . Earlier work on coal ash has shown that Indian coals contained 1.8-6.0 ppm ^{238}U and 6.0-15.0 ppm of ^{232}Th (Mishra and Ramachandran, 1991). But recent studies have shown that pond ash generated from coal

contains as high as 50 ppm ^{232}Th and 10 ppm of ^{238}U . Mandal and Sengupta (2005) analyzed the coal samples in terms of trace elements and radionuclide listed in Table 8 and Table 9. Ash samples were taken from ash ponds of Kolaghat Thermal Power Station, West Bengal. Laboratory measurement ^{238}U , ^{232}Th and ^{40}K in coal and ash samples were under taken using a low level gamma-ray spectrometric set up. The detector was a 5 ×6 inch NaI (Tl) crystal coupled to a 5 inch diameter photomultiplier tube. In closed, systems the activity concentrations of all nuclei in the decay chain reach secular equilibrium (Evans, 1969), meaning that the activity concentration of all nucleids were the same. As a result, measuring the activity concentration of one member in a closed system provides information on the presence of all the members (Macdonalds, 1997). Results of chemical analysis showed that the feed coal is dominated by SiO_2 , Al_2O_3 , followed by Fe_2O_3 , K_2O , TiO_2 , CaO , MgO and Na_2O (Table 8). Coal from KTPS is thus aluminosilicious in nature. Chemical analysis of the ash samples Kolaghat shows that the ash is dominant by iron with minor amounts of TiO_2 , K_2O , CaO , MgO , MnO and Na_2O . Trace element concentration of the ash shows that the ashes of Kolaghat contain sufficient amounts of As, Cu, Pb, Ni, Zn, Co, V, Sc, Be, Cs and Zr decomposition of organic and inorganic matter. Trace elements associated with the organic material get released and accumulate in the refractory phases e.g. mullite and other aluminous phases as clays are the highest repositories of trace elements.

Leaching Behavior of Fly Ash

Trace elements present on the surface of ash particles are most immediately available for release into aqueous environment. Release of metals from ash surface depends on the pH of aqueous media. Maximum metals release at low pH of 2 from the surface of ash into leachate. As the pH increases the dissolution of metal from ash surface decreases (Prasad and Mondal, 2008). When the water flows through the porous media it follows diversified set of paths. However, certain set of path may occur more frequently to yield an uniformly declined concentration profile in the continuously leaching water, which are known as the most probable set of paths. Figure 2 shows the diversified and most probable set of paths followed by water during its flow through the porous media. These sets of flow paths do not only vary with respect to the variation in the flow rate but the continuous deformation phenomenon occurring in the particulate matter may also cause diversified paths. For example, the water initially flows through the path P_1 , may be leached out through two

paths; P_{11} and P_{12} , which later leached out through either P_{11} or P_{12} or even entirely a new path P_{13} . If it is assumed that $(P_{11}, P_{12}, P_{13}, \dots, P_{1n})$. where $n =$ any natural number is the set of diversified paths of P_1 at any time, then path of flow of leaching metals can be expressed by equation- $P_1 = P_{11} + P_{12} + P_{13} + \dots + P_{1n} = \sum_{i=1}^n P_{1i}$. As the set of paths vary with respect to time, the concentration profile of the leachates also varies (Singh et al., 2007). Figure 3 shows the concentration profile of sodium (Na) when water flows through the set of most probable paths and randomly diversified paths. From figure it is evident that though the variation in the concentration is non uniform. However, it essentially decreases with increase in time. Thus the rate of change in the dissolved contaminants can be reasonably assumed to be inversely proportional to the time (t) when the water flows through the most probable set of paths.

Further, if the initial time be zero and the time taken to pass through the porous media is (t) then it can be assumed that the concentration profile declined at the end of the successive time series i.e. $t=h, t+h, t+2h, t+3h, t+4h, \dots$ etc. where $h > 0$ and as much as small (Sunderrajan et al., 1994).

Based on the above facts concentrations of trace metal in the water successively passing through the porous media can be theoretically drawn and is shown in figure 4.

Singh et al. (2007) have used open percolation column used for studying behavior and characteristics of leachates generated. The set up consist of PVC columns of 10 cm diameter and 75 m height, open at the top and fitted with an outlet at the bottom to collect the leachates (Fig. 5). The columns are filled up into layers with the fly ash collected from ash ponds of thermal power plants. Sufficient ramming and scratching was done during the addition of each new layer to ensure proper interlocking and packing of fly ash into the column. All the columns were packed up to 60 cm height with fly ash collected from the ash ponds. Leaving a 15 cm space at the top as per standard guidelines and procedure adopted for design in the open percolation column experiments. The guidelines were followed in order to maintain a constant head of 15 cm water and to stimulate the solid liquid ratio of ash ponds in the real field conditions (Singh and Kumar, 2004). Leachates were collected in polypropylene beakers placed below the outlet of the column.

Groundwater contamination due to ash leaching effects

Groundwater is vulnerable to metal contamination due to waste disposal and leachate percolation (Theis et al., 1978; Theis et al., 1990; Carlson et al., 1993). However, it has been stated in a study conducted by Mondal and Sengupta (2005) that when large quantities of ash accumulate for long periods of time in the disposal site, hazardous substances are likely to be released by leaching, percolate through the soil layers and eventually reach the groundwater.

Terrestrial disposal of fly ash has been regarded as potential source of contamination due to enrichment and surface association of trace elements in the ash particles. Much concern has been paid to the leaching behavior and possible contamination, especially for the aquatic environment; when ash is in contact with water. The groundwater environment is more vulnerable than surface water due to lower velocity under low permeability and the possible accumulation of leached elements in the groundwater. In this case, not only more soluble sublimes on the surface of the fly ash particles but also the longer term dissolution of the glassy particles which are unstable under natural conditions, is expressed to influence the groundwater (Choi et al., 2002).

The slurry and the ash pond water is found to be strongly alkaline and saline, with an average pH of 9.7 and TDS of 7,290 mg/l. The ash water is sodium- sulphate-chloride type water, with minor amounts calcium, carbonate, potassium and magnesium. The molar ratio of sodium to sulphate is about 2. With sodium and sulphate comprising 80% of the molar mass and chloride 11%. Ionic strength is moderate at about 0.16. The major ion chemistry and pH are considered to be controlled by impurities such as Al and Ca in the coal. The ash leachate seeping from the base of the pond is expected to have similar chemistry but the exact concentration depends on a number of factors, including the long term leaching behavior of the ash and height and consolidation of final ash deposited (Mudd et al., 1998). Spencer and Drake (1987) investigated chemical quality of the shallow groundwater regime at a coal fly ash land fill near Montpelier Iowa. The fly ash land fill was operated between 1964-1973 and was subsequently capped with a thin loess layer and seeded to pasture. The ash is underlain by loess, over clay rich till, over sand stone. Groundwater now saturates the lower one half of the ash. Calcium, sulphates and alkalinity were the dominant components in groundwater at the site. The

local native groundwater was a calcium bicarbonates type whose pH ranges from 6.7 to 8.2 with an average value of 7.2. Ca^{2+} , Mg^{2+} and HCO_3^- ions were derived from the dissolution of carbonates in loess and till. Sulfate ions may have been generated either from native gypsum dissolution or from oxidation of sulfide to sulfate in the unsaturated zone. The groundwater that entered the landfill exhibited a significant increase in total dissolved solids mainly due to increase in Ca^{2+} and SO_4^{2-} concentrations. The pH of landfill groundwater samples was consistently higher than that of native groundwater ranging from 7.7 to 9.2 and averaging 8.5. Corresponding landfill bicarbonate concentrations were consistently lower than those in the native groundwater. Oxides on ash surface may supply hydroxyl ions responsible for the elevated pH. The background water was under saturated with respect with respect to CaSO_4 , and nearly saturated with respect to CaCO_3 . Landfill groundwater contained calcium concentrations in considerable excess of those predicted to be in equilibrium with CaCO_3 as calcite, but was only slightly over saturated with respect to gypsum due to common ion effect. Detectable traces of As were found in one third of total samples, and the rest were at or below the analytical detection limit of 0.01 mg/l. At one landfill well location, selenium was recorded to be in excess of the 0.01 mg/l EPA drinking water standard. Samples from the downward gradient well had slightly elevated selenium, which suggested some mobility of selenium through the saturated loess.

Monica and Violeta (2008) conducted a study to assess the groundwater contamination around ash pond of Arad Thermal Power Plant which is extended over 65 ha. Fourteen interceptions and nine control drillings (PC1–PC9) were put into execution around the ash storage pit with depths varying with 16.50-18.00 m. The interception drillings were situated to the west of the storage pit and were made in order to certify the phreatic water quality. In case of pollution the purpose of these drilling is to capture the water and introduce it into the technological circuit. The control drillings were situated to the north, east and south of the storage pit and were put into execution in order to verify if there were possible polluted water leakages towards east where tapping of groundwater for Arad city drinking water is performed. The results obtained from the analysis of water samples (sampled from PC1 and PC4-PC9) shows low level of pH at PC4, PC5 and PC7, higher concentration of chloride at PC4-PC8 and sulphate at PC4 and PC7 given in Table 10.

The thermal power plant uses the wet disposal scheme. The ash is transported as slurry through pipes and

Table 1 Normal range of chemical composition for fly ash produced from different coal types (expressed as percentage by weight) ASTM (1994).

Chemical Composition (%)	Coal Types		
	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

Table 2 Major elemental concentrations of the collected solid waste sample from Yenikoy Thermal Power Plant (Baba 2001).

Chemical Composition (%)	Coal	Bottom Ash	Fly Ash
SiO ₂	5.39-9.41	10.80-38.50	14.80-38.50
Al ₂ O ₃	1.36-4.36	2.51-14.71	3.43-17.32
Fe ₂ O ₃	0.08-2.2	0.5-8.09	0.86-11.75
MgO	0.05-3.5	1.15-4.61	0.53-9.13
CaO	21.38-30.45	23.31-45.13	22.31-54.13
Na ₂ O	0.01-0.18	0.15-0.62	0.25-1.23
K ₂ O	0.37-0.77	0.10-3.60	0.41-4.89
TiO ₂	0.03-0.43	0.18-1.32	0.23-1.68
MnO	0.06-0.94	0.14-0.18	0.15-0.21

Table 3 Metal concentration of the collected solids waste sample from Yenikoy Thermal Power Plant (Baba 2001).

Metal (mg/kg)	Coal	Bottom Ash	Fly Ash
Ba	53-98	62-109	67-109
Cd	<5	<5	<5
Cu	9-49	18-121	58-141
Cr	4-44	47-194	174-252
Co	3-5	3-7	8-12
Ni	18-58	30-293	69-306
Pb	0.8-25	5-33.4	20.3-82
Sb	<5	<5	<5
Zn	30-70	33-226	49-270

Table 4 Chemical composition of fly ash (Prasad & Mondal 2008).

Chemical Composition	Percentage	
	Ramagundam	Chandrapura
Silica as SiO ₂	60.11	56.70
Alumina as Al ₂ O ₃	26.53	23.80
Iron as Fe ₂ O ₃	4.25	4.70
Sulphur as SO ₃	0.35	0.30
Calcium as CaO	4.00	2.10
Magnesium as MgO	1.25	1.40
Sodium as Na ₂ O	0.22	0.25
Potassium as K ₂ O	0.75	0.50
Loss of ignition	0.88	10.35

Table 5 Total minor metal concentration in fly ash (Prasad & Mondal 2008).

Chemical composition	Concentration (mg/kg)	
	Ramagundam	Chandrapura
Cu	27.2	74.7
Mn	127.0	1124.0
Pb	65.3	27.7
Ni	7.6	21.4
Zn	46.5	53.3
Cd	1.0	1.7
Cr	43.5	16.2

Table 6 Chemical composition of the coal and fly ash from five different coal fired power station in Korea (Choi et al. 2002).

Chemical Composition (wt %)	Fly Ash				
	Sub bituminous		Anthracite		
	SCP	BR	SC	YW	YD
SiO ₂	55.2	55.2	43.5	44.6	47.3
Al ₂ O ₃	23.1	19.9	27.5	25.1	29.2
Fe ₂ O ₃	6.1	9.7	4.7	3.8	4.4
MgO	1.0	1.2	0.9	0.8	0.7
CaO	3.7	3.7	0.9	0.5	0.5
Na ₂ O	0.3	0.3	0.3	0.2	0.2
K ₂ O	1.0	1.0	3.8	3.3	3.9
TiO ₂	1.1	1.2	1.5	1.5	1.6
P ₂ O ₅	0.5	0.3	0.2	0.2	0.2
MnO	0.1	0.1	0.1	0.0	0.0
S	0.1	0.1	0.1	0.1	0.1
Co	18	53	12	8	8
Cr	69	95	86	80	498
Cu	63	66	109	77	109
Ni	74	174	66	41	72
V	210	147	175	130	157
Pb	32	29	103	36	68
Zn	93	93	167	43	97

Table 7 The concentrations of trace elements in the fly ash and bottom ash, mg/kg (Marinkovic et al. 2010).

Elements (mg/kg)	Fly Ash	Bottom Ash
Cu	263	200
Zn	190	124
Cd	0.52	0.25
Pb	102	72
Ni	175	155
Mn	317	222
Cr	275	205
Sb	3.3	4.1
Fe	90.9	99

Table 8 Bulk chemical composition of feed coal and pond ash from KTPS (Mandal & Sengupta 2005).

Chemical composition	Unit	Average (Coal)	Average (Ash Pond)
Na ₂ O	wt%	0.05	0.10
MgO	wt%	0.24	0.56
Al ₂ O ₃	wt%	9.52	26.00
SiO ₂	wt%	23.14	57.81
P ₂ O ₅	wt%	0.22	0.48
K ₂ O	wt%	0.48	1.19
CaO	wt%	0.39	0.83
TiO ₂	wt%	0.69	1.82
MnO	wt%	0.02	0.04
Fe ₂ O ₃	wt%	2.49	4.95
C	wt%	48.10	3.48
S	wt%	0.39	0.03
Be	ppm	2.27	5.70
Sc	ppm	10.70	28.68
V	ppm	61.20	238.18
Co	ppm	7.78	24.16
Ni	ppm	22.50	80.70
Cu	ppm	32.00	63.3
Zn	ppm	46.10	100.48
As	ppm	5.41	18.63
Rb	ppm	28.97	75.89
Sr	ppm	84.28	204.60
Zr	ppm	157.80	444.58
Ba	ppm	252.00	708.62
Pb	ppm	18.5	66.70

Table 9 Radioactivity in pond ash and coal samples from KTPS (Mandal & Sengupta 2005).

S. No.	Location	²³⁸ U (Bq/Kg)	²³² Th (Bq/Kg)	⁴⁰ K (Bq/Kg)
IIT-KAP1	Ash Pond	117.42	145.84	403.00
IIT-KAP2	Ash Pond	119.82	146.65	279.00
IIT-KAP3	Ash Pond	114.95	144.23	282.10
IIT-KAP4	Ash Pond	117.42	143.02	266.60
IIT-KAP5	Ash Pond	98.88	141.80	372.00
IIT-KAP6	Ash Pond	110.0	146.65	272.80
IIT-KAP7	Ash Pond	117.53	136.15	372.00
IIT-KAP8	Ash Pond	108.03	136.35	372.00
IIT-KAP9	Ash Pond	113.71	126.05	359.60
IIT-KAP10	Ash Pond	108.40	138.70	384.40
IIT-KAP11	Ash Pond	107.20	139.70	368.90
IIT-KAP12	Ash Pond	107.53	146.25	415.40
IIT-KAP13	Ash Pond	113.95	141.44	403.00
IIT-KAP14	Ash Pond	105.18	129.72	359.60

Table 10 Groundwater quality around ash storage pit of Arad Thermal Power Plant (Monica & Violeta 2008).

Parameter	Unit	Sample						
		PC1	PC4	PC5	PC6	PC7	PC8	PC9
pH	pH unit	7.33	6.26	5.85	7.67	6.31	6.97	8.2
Chlorides	mg/l	53.25	340.8	468.6	268.02	404.7	276.9	243.17
Sulphates	mg/l	2.4	620	12.5	115	890	250	230
Calcium	mg/l	10	232	112	36	624	136	28
Magnesium	mg/l	2.4	76.8	24	26.4	33.6	9.2	14.4
Total Hardness	^o d	1.96	50.4	21.3	11.2	95.2	21.3	7.28
Copper	mg/l	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
Cadmium	mg/l	<0.0005	<0.0005	<0.0005	<0.0005	0.015	<0.0005	<0.0005
Total Chrome	mg/l	<0.005	<0.005	<0.005	<0.005	0.074	<0.005	<0.005
Nickel	mg/l	<0.001	0.027	0.011	0.012	0.036	0.012	<0.001
Zinc	mg/l	<0.0005	0.032	<0.0005	<0.0005	<0.0005	0.0025	<0.0005
Lead	mg/l	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005

Table 11 Characteristics of hydraulic transport water Arad Thermal Power Plant (Monica & Violeta 2008).

Indicator	Unit	Value
pH	pH Unit	9.18
Chloride	mg/l	447
Calcium	mg/l	416
Magnesium	mg/l	38.4
Sulphates	mg/l	203
Total Hardness	^o d	67.2
Copper	mg/l	<0.001
Cadmium	mg/l	<0.0005
Total Chrome	mg/l	0.062
Nickel	mg/l	0.023
Zinc	mg/l	<0.0005
Lead	mg/l	<0.005

Table 12 Enrichments of elements in tube well waters around ash pond of Kolaghat Thermal Power Plant (Mandal & Sengupta 2005).

S.No.	Al	Cr	Mn	Fe	Ni	As	Ba	Pb
4B	1.6	0.2	4.5	1.1	0.5	0.3	-	29.9
4A1	1.1	0.2	1.2	0.9	1.1	9.5	0.7	13.1
4A2	2.1	0.2	1.2	1.2	1.2	16.4	0.8	4.2
1A1	0.8	0.2	2.7	0.8	0.9	0.4	-	27.4
1A2	0.9	0.2	1.2	0.9	1.1	14.5	0.7	4.0
1B	0.9	0.2	2.8	1.1	1.3	0.5	0.4	12.9
B1	0.8	0.2	4.6	1.0	0.9	0.3	0.3	15.2
B2	0.8	0.2	1.6	1.1	1.3	1.1	0.1	10.6
R1	0.7	0.2	3.4	1.0	0.8	0.2	0.2	3.3
R2	0.7	0.2	2.1	1.1	0.7	0.4	0.3	12.3
R3	0.8	0.2	1.2	1.1	0.5	0.7	-	1.6
R4	0.9	0.2	1.2	1.1	0.6	0.6	-	4.7
M1	1.4	0.7	1.4	0.8	1.6	0.5	0.6	18.7
M2	0.7	0.2	2.1	0.9	0.9	0.5	0.3	4.1
M3	0.8	0.2	5.3	1.1	1.2	0.8	0.1	3.5

Figure1. Schematic representation of air water and soil pollution due to ash disposal (Monica and Violeta, 2008).

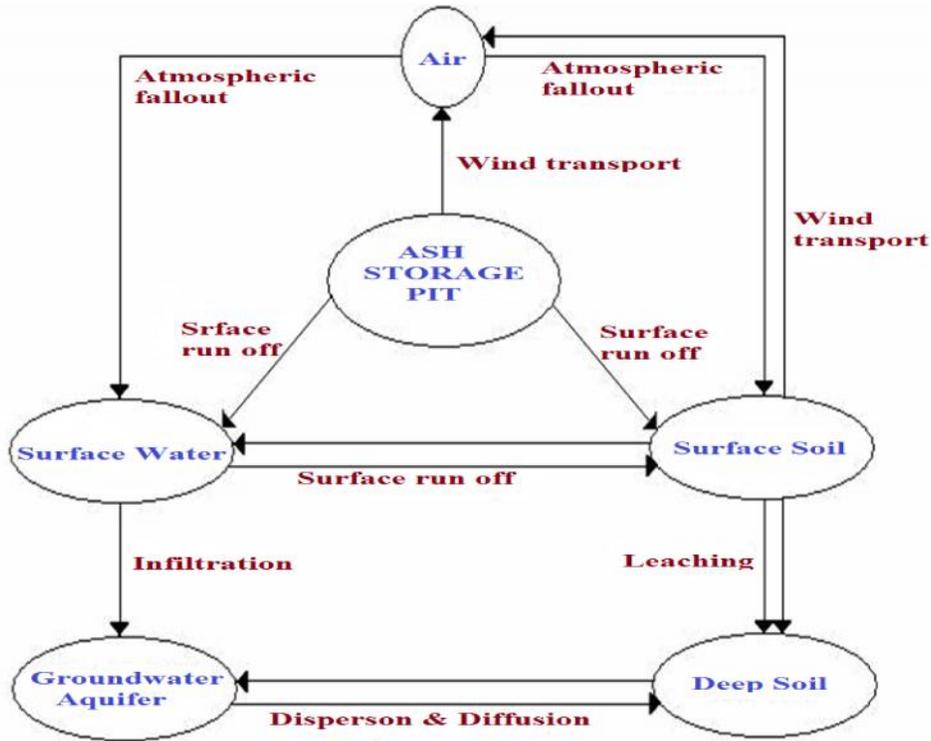


Figure 2. Pictorial view of water flow through the most portable paths (Singh et al., 2007).

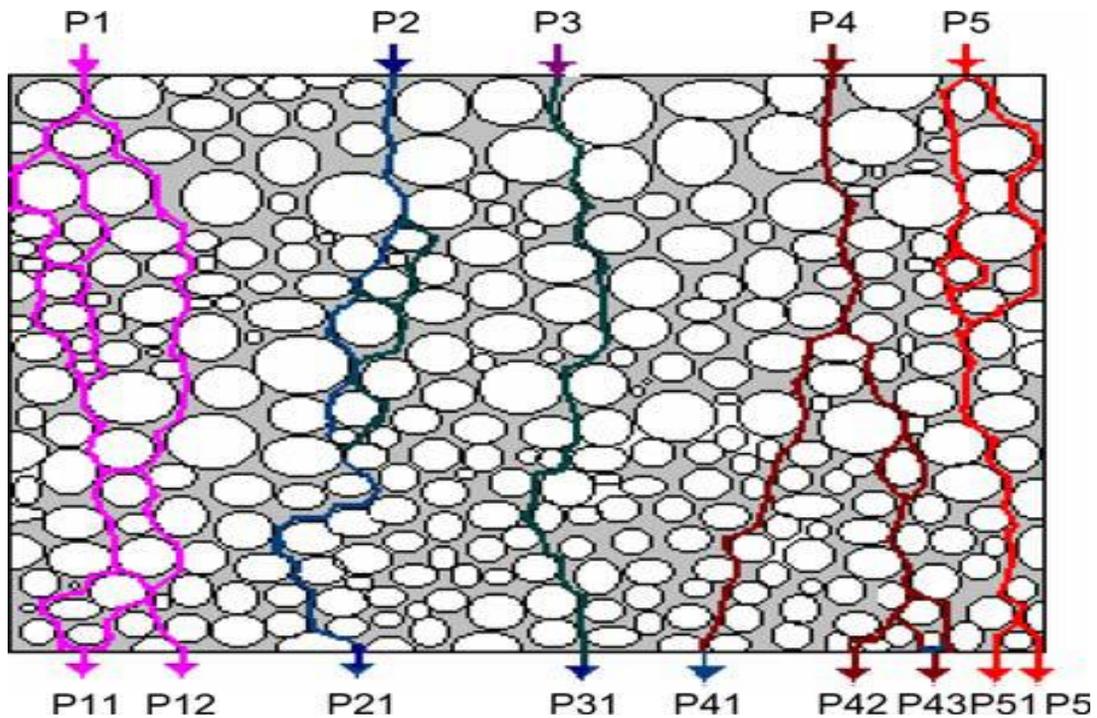


Figure 3. Concentration profile of sodium when water flows through the set of most probable paths and randomly diversified paths (Singh et al., 2007).

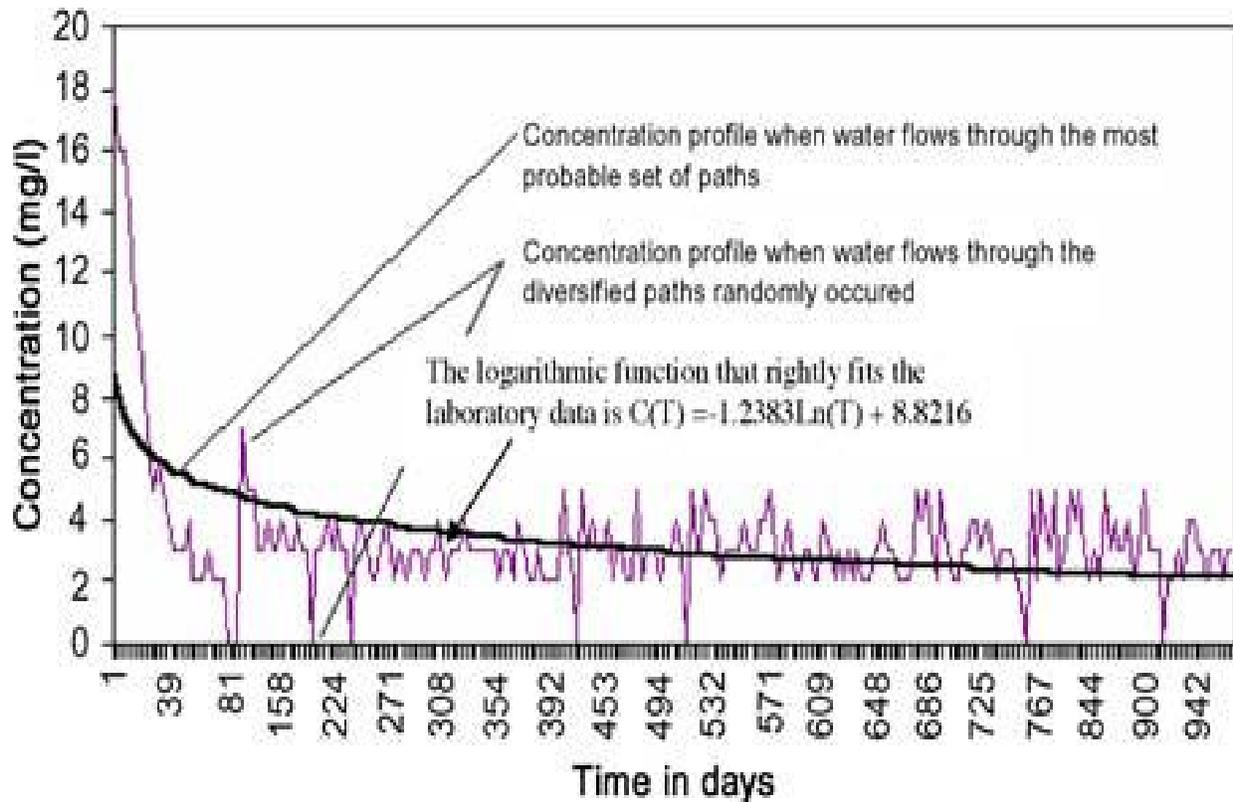


Figure 4. Hypothetical concentration profile of trace metals at successive series of time when the water flow passes through the ash sample (Singh et al., 2007).

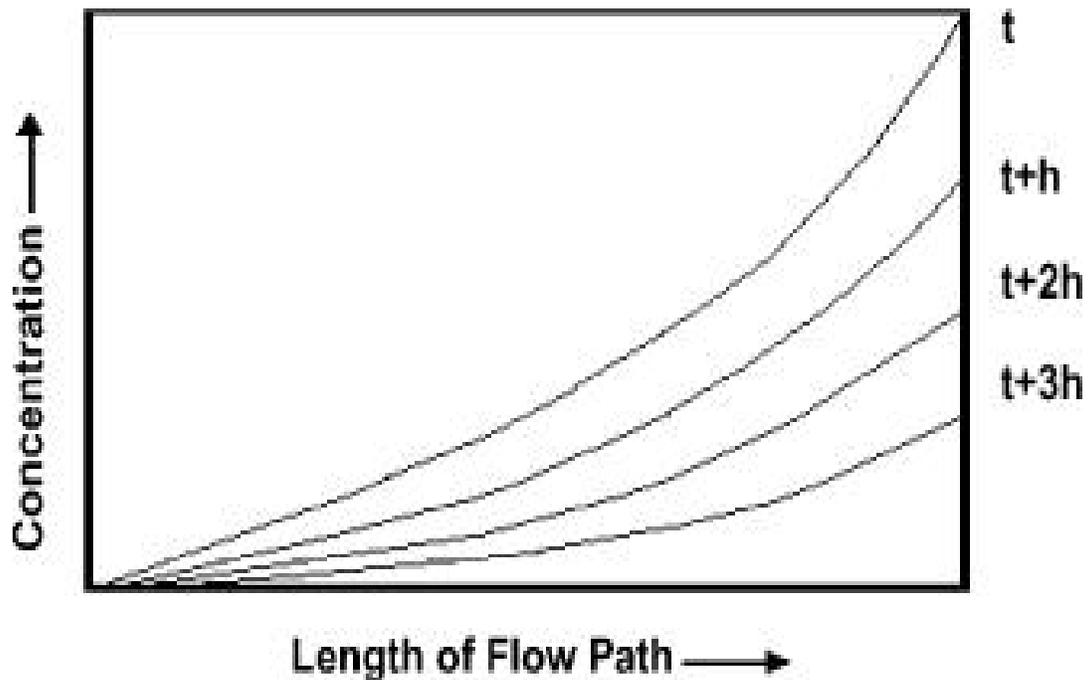


Figure 5. Open column experimental set up for leaching study (Singh et al., 2007).

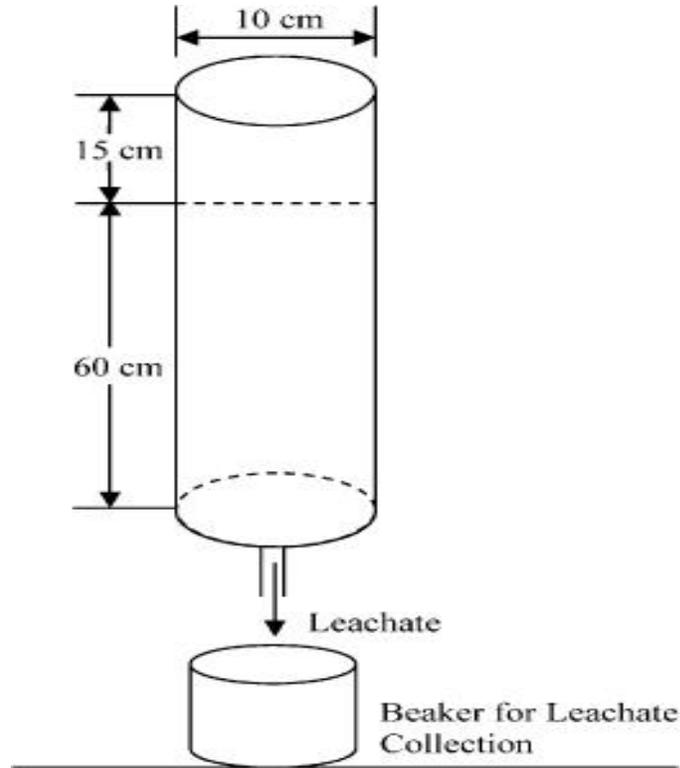
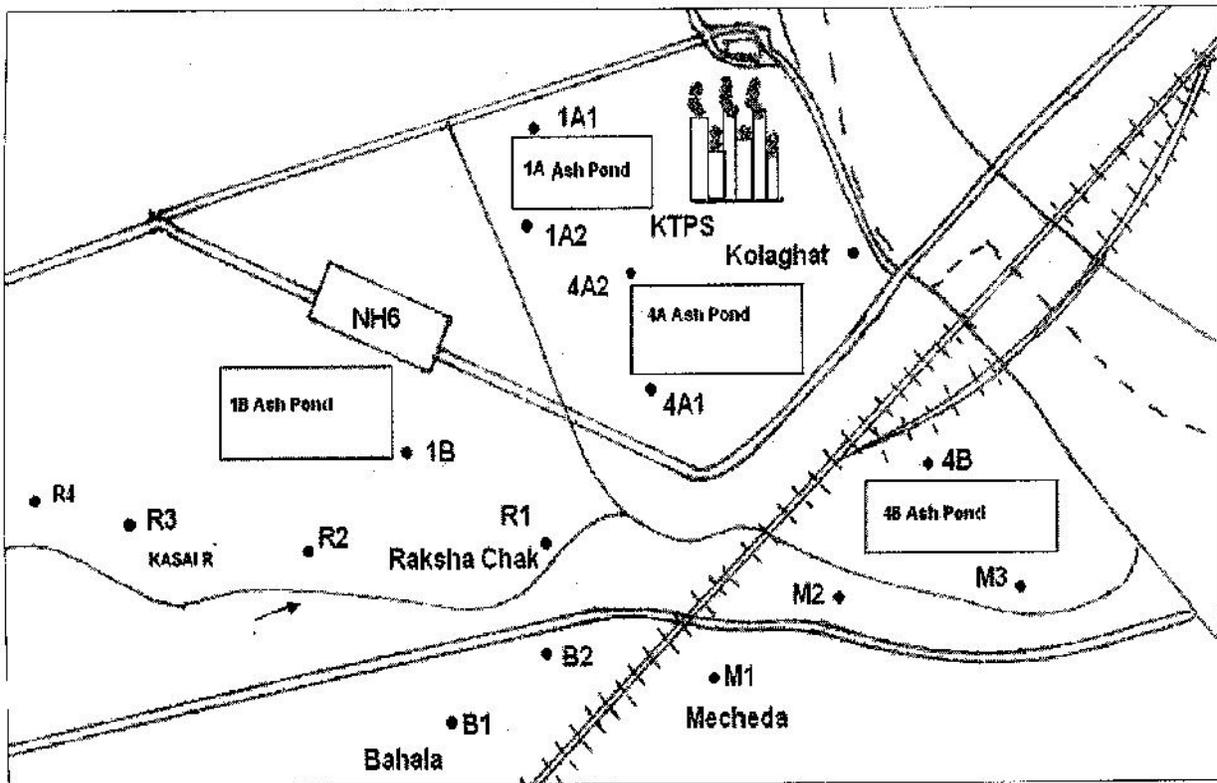


Figure 6. Location map of study area around ash pond of Kolaghat Thermal Power Plant (Mandal and Sengupta, 2005).



disposed off in the storage pit. The transport water and phreatic water both show high values of for chloride, sulphate and hardness (Table 11). Because of this similitude in indicator values between transport water and phreatic water sampled from the drillings the high impact of the ash storage pit over environment was confirmed.

Mandal and Sengupta (2005) analyzed the groundwater quality around the ash ponds of Kolaghat Thermal Power Plant, West Bengal. Water samples were collected from tube wells located near the ash ponds 1A, 1B, 4A, 4B (Figure 6) and from the surrounding villages Bahala (B1, B2) Raksha (R1, R2, R3, R4) and Mecheda (M1, M2 and M3). pH of the water samples ranged from 7.02 to 8.70, indicating alkaline nature of the water. Elements found in the tube well waters were Ca followed by Na, Mg and K. Na and K were present in higher amount in the tube well waters in the villages than those near the ash pond. Ca, on the other hand, is enriched in the tube well waters of the ash pond, implying a significant input from the ash pile. According to the enrichment factor given in Table 12, the tube well water near the ash ponds show maximum enrichment in the elements compared to other places. This is especially true for Al, Mn, Pb and As implying significant input from the ash pile. The high concentration of trace elements in waters of tube wells, possibly, can be attributed to the leaching of the elements from the ash pile and subsequent mixing of ash pond leachate with groundwater.

Conclusion

The ash residue after coal burning may contain significant level of heavy metals, ions of calcium, magnesium, chloride and bicarbonates may cause serious surface and groundwater pollution when disposed off through ash pond effluent into river water. The ash storage pit of Thermal Power Plants impact heavily over the environment. Underground water monitoring in the area around ash pond is of much environmental significance and needs a lots of attention. The data obtained by monitoring and analysis of groundwater proves to be helpful in assessing the possible contamination from fly ash around the thermal power plant area. Underground water aquifers can be protected through the regulation and standardization of toxic substances and establishing standards.

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