



ISSN: 0976-3031

Available Online at <http://www.recentscientific.com>

International Journal of Recent Scientific Research
Vol. 7, Issue, 7, pp. 12502-12505, July, 2016

**International Journal of
Recent Scientific
Research**

Research Article

CHEMICAL CHANGES OF FLY ASH IN CONTACT WITH SEAWATER AND THEIR IMPACT ON MARINE ENVIRONMENT

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ARTICLE INFO

Article History:

Received 20th April, 2016

Received in revised form 29th May, 2016

Accepted 30th June, 2016

Published online 28th July, 2016

Key Words:

Chemical changes, thermal power plant, fly ash, trace elements, seawater.

ABSTRACT

In this present study the chemical changes of fly ash exposed to prolonged, large scale contact with sea water in the earlier ash dumpsite of Tuticorin thermal power plant in Tuticorin Bay was determined. The chemical characteristics of pH, organic carbon, calcium were studied by taking different ash samples at one time during May, 2015. Chemical changes of dumpsite ash was studied by comparing with fresh fly ash taken from electrostatic precipitator of thermal power plant. Two stations were fixed in and around the earlier ash dumpsite. Four trace elements (Fe, Cu, Pb & Cd) were studied for 3 ash types: ash from electrostatic precipitator, dumpsite ash (S1) and ash from station 2 sediment. The pH in dumpsite ash was decreased due to high temperature of dumpsite area, all the trace elements were high in fresh fly ash except iron. Chemical changes occurred in ash contact with sea water and altered the quality of seawater. The organic matter present in water may bring some of the trace element in water by means of chelation and complexation reactions. The present study revealed that the mobilizations of fly ash constituents were influenced by various environmental factors and further need to be studied in details.

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INTRODUCTION

Fly ash is generally captured from the chimneys of coal-fired power plants, whereas bottom ash is removed from the bottom of the furnace. In the past, fly ash was generally released into the atmosphere, but pollution control equipment mandated in recent decades now requires that it be captured prior to release. Depending upon the source and makeup of the coal being burned, the components of the fly ash produced vary considerably, but all fly ash includes substantial amounts of silicon dioxide (SiO₂) (both amorphous and crystalline) and calcium oxide (CaO). The disposal of the fly ash is a serious hazard to the environment that consumes millions of rupees towards the cost of its disposal. The mineralogical, physical and chemical properties of fly ash [1, 2] depend on the parent coal, conditions of combustion, type of emission control devices and storage and handling methods. Therefore, ash produced by burning of anthracite, bituminous and lignite coal has different compositions. Chemical changes occur in coal ash exposed to prolonged (300 days), large scale, Contact with running seawater. Four major components (Al, Ca, Mg, Fe) and seven minor and trace elements (Cd, Cr, Cu, Mn, Zn, Pb, Hg) were measured in four coal ash types: fly and bottom ash freshly obtained from coal-fired power plant, and old ash (crushed and blocks) recovered from the sea after 3–5 years

contact with seawater. Changes occurred in the chemical composition of the coal ash along the experiment: Fe increased in fresh ash, Al increased in old ash and Ca increased in all ash types except old ash blocks. Cu and Hg decreased in fresh fly ash while Cr increased, Cd decreased in all ash types except bottom ash, and Mn decreased in bottom ash. Most of the changes occurred in the fresh fly ash, and not in the old ash, indicating equilibrium after prior exposure to seawater. In addition, more changes occurred in fresh fly ash than in bottom ash, emphasizing the differences between the two ash types [3]. In this present study the tentative physical and chemical changes of prolonged contact of ash (earlier it was dump in deep sea) in marine environment was determined by studying chemical characteristics, trace elements. In the marine environment some element may leach from ash, some may get adsorbed and there may increase the element quantity in ash.

Study area

Tuticorin Bay is situated in the South east coast of India in the Gulf of Mannar along the Tamil Nadu coast. Tuticorin Thermal Power Station (TTPS) is located about 2 km to the east of Tuticorin Port and the northern boundary of the complex is on the brim of the intertidal area of the Tuticorin Bay (Lat.08° 46' 20" N; Long. 78° 10' 46" E). TTPS is a coal – fired thermal power station and hence large amount of fly ash (6,000 Metric

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Tonnes per day) is generated during the process. Tuticorin Thermal Power Station functioning since 1976 and is generating 1050 MW of electricity. About 17,000 metric tons of coals are used as fuel for the power generation per day. Presently the hot water effluent generated by cooling the condenser has pumped directly into the Bay.

In this present investigation the study area is located near the earlier fly ash dumpsite in Tuticorin coastal water and this also contains the water outfall from the coolant. So this area received high temperature of water. Two stations (station 1 and 2) were fixed at distance of 500 meter and 2 km from the outfall of TTPS and shown in Figure 1

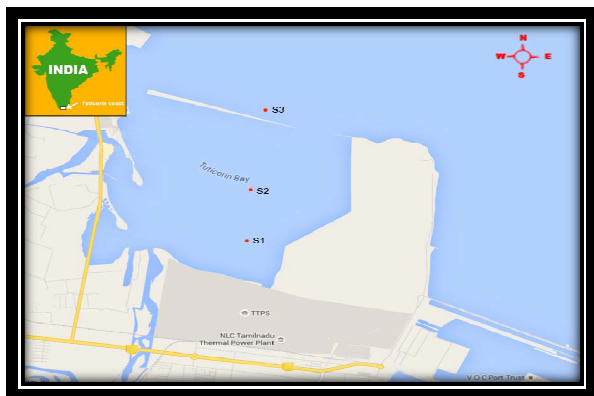


Figure 1 Map showing the study area (Tuticorin Bay) with 3 stations

Station 1: 500 meters away from water outfall of power plant (earlier ash dumpsite) (N 08° 46' 48.3" & E 078° 10' 76.3"). This area do not containing any biological system due to the water with high temperature from outfall of thermal power plant and the presence of fly ash.

Station 2: 2 km away from the water outfall of power plant. (N 08° 47' 32.0" & E 078° 10' 80.3"). This area also do not containing any biological system. The impact of outfall water from power plant and fly ash extents over in this area too.

Sample collection

For the determination of chemical changes of fly ash in marine environment, ash sample was collected one time during May, 2015 from thermal power plant. Three types of fly ashes were used for the analysis. Fresh fly ash from electrostatic precipitator was collected. Second sample from earlier ash dumpsite of Tuticorin coast and third sediment sample from station 2 were also collected by deep grab sampling during May 2015. The inner part of the grab sample was taken for the analysis to avoid contamination and collected in polythene bags. The collected fly ash was air dried under the shade.

MATERIALS AND METHODS

Chemical characteristics

To study the chemical characteristics of ash samples pH was determined in 'Elico' pH meter, calcium was estimated by extraction with ammonium acetate and titrated with EDTA [4]. Organic carbon content was determined by wet oxidation method [5].

Analysis of trace elements by Atomic Absorption Spectrometry

Fly ash samples were collected and rinsed with deionized distilled water and dried, crushed, homogenized and kept in closed plastic containers until the chemical analysis. Then transferred to prewashed glass wares, kept in an oven at $80^{\circ}\text{C} \pm 1^{\circ}\text{C}$ till complete dryness. Dried samples were then ground with mortar and pestle into fine powder. Then sieved through a $102\ \mu$ mesh size sieve, weighed out 1 g and sieved samples in triplicate [6] put into 100 ml digestion flask. Samples were digested with 9 mL concentrated HNO_3 acid and 1 mL of perchloric acid over a hot plate, heated the samples until the solution become clear. Then it was cooled, filtered through Whatmann No.1 filter paper and made up to 25 ml in a volumetric flask. The made up samples were stored in prewashed polythene bottles and analyzed for various metals on an Atomic absorption Spectrometry (AAS; Elico-SD 164 India). Blank also prepared by the addition of same quantity of reagents without sample.

RESULTS AND DISCUSSION

Chemical characteristics of fly ash

pH of fly ash samples

Fly ashes were collected from ESP (Electrostatic precipitator), from dumpsite of thermal power plant into coastal water and sediment from station 2. The pH of fresh fly ash was 9.4, ash from dump site showed 8.36 and station 2 sediment showed pH of 8.5 (Figure 2). pH of all the fly ash showed alkaline nature. In the present study all the fly ash samples showed high value of pH due to alkaline in nature (Table 1). Sample taken from dumpsite and station 2 showed low pH than fresh fly ash. Station 1 dumpsite sample showed low pH than station 2 sample. This is because the high temperature of water outfall from power plant.

Organic carbon in fly ash samples

Organic carbon of fresh fly ash from ESP (Electrostatic precipitator) was 2.77 %, fly ash from dump site showed the maximum value of 4.894 % and sediment from station 2 showed 3.253 % (Figure 3). During our study period, the ash from dumpsite showed the maximum value of organic carbon (Table 1). The distribution of organic carbon closely followed the distribution of sediment type (i.e.) sediment low in clay content was low in total organic carbon and as the clay content increased the organic carbon content also increased which as reported by [7]. It is also evident from result of that low organic carbon may be due to coarse sandy nature of the sediments, as the organic carbon variation has largely controlled by the fine fraction of the sediment. In this present study fly ash from ash dumpsite showed maximum value (4.894%) due to low sandy nature and high fine nature which also confirmed by sediment texture study, station 2 sample showed low organic carbon than station 1. So the impact of ash decreased with increase of distance has proven by above observations.

Calcium in fly ash samples

Fresh fly ash showed the amount of calcium was 184 mg/g, ash from dumpsite showed maximum of 464 mg/g and sediment

from station 2 showed 302.4 mg/g (Table 1). In the present study, ash from dumpsite showed the higher value of calcium (Figure 4). Calcium is present in fly ash in multiple modes of occurrence, primarily lime, anhydrite, calcite and within the glassy matrix. It is the most largely released cation regardless of the extractant used [8]. The leachable concentrations range over several orders of magnitude as a function of the mode of Ca occurrence and concentration in the fly ash, the proportion of each phase and the leaching test performed. With only water, the amounts of Ca leached could easily fall in the 100-15,000 mg/kg range [9, 10, 11, 12]. Increase element concentration may be due to chemical exchange or to adsorption. The increase of calcium found in this research. In the present study calcium level in fly ash and in sediment, also recorded very low amount compared to other studies.

Table 1 Chemical characteristics of ash

Ash samples	pH	Organic carbon %	Calcium mg/g
Fresh fly ash	9.4	2.77	184
Ash from dump site (Station 1)	8.36	4.894	464
Sediment from station 2	8.5	3.253	302.4

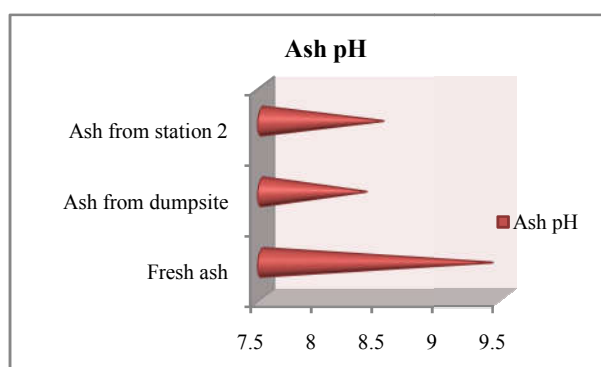


Figure 2 pH of ash samples

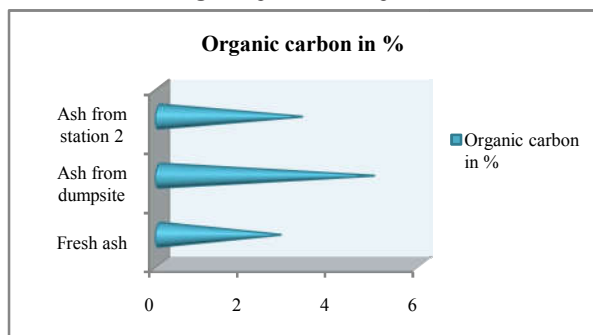


Figure 3 Organic carbon of ash samples

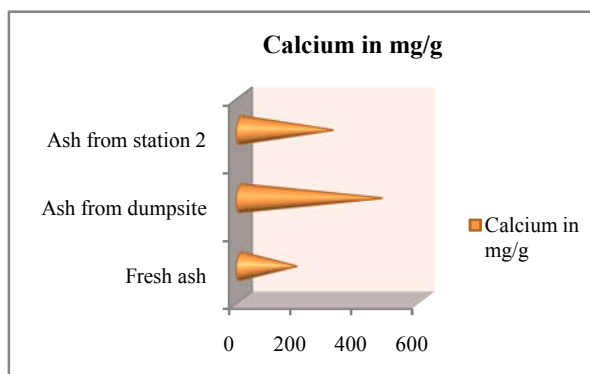


Figure 4 Calcium of ash samples

Heavy metals in ash samples

Heavy metals of ash samples were analyzed by atomic absorption spectrometry and the results are shown in Table 2. Iron, copper, lead and cadmium were analyzed and showed all the metals were high in fresh fly ash except iron (Figure 5-8). The mineral fraction in coal undergoes different transformations during and after combustion, namely decomposition, volatilization, fusion, agglomeration or condensation [13]. As the flue gas cools down after combustion, volatile elements such as As, B, Hg, Cl, Cr, Se and most prominently S, condense on the surface of the fly ash particles, forming compounds with a variable solubility (commonly on the high side) and essentially combined with Ca. These result not only in a strong gradient of element concentrations within fly ash particles [14], but also in a gradient of leachability. Iron content increased in ash dumpsite which confirmed the observation of [15]. All other elements were showed high value in fresh fly ash that confirmed the impact of ash decrease with increase of distance from station 1 and metals are leached from dumpsite ash.

Table 2 Heavy metals in ash samples

Elements mg/kg	Fresh fly ash	Ash from dumpsite	Ash sample from station 2
Fe	5565	6573	3244.5
Cu	65	35.2	27.5
Pb	45.3	43	38.2
Cd	2.5	0.320	0.245

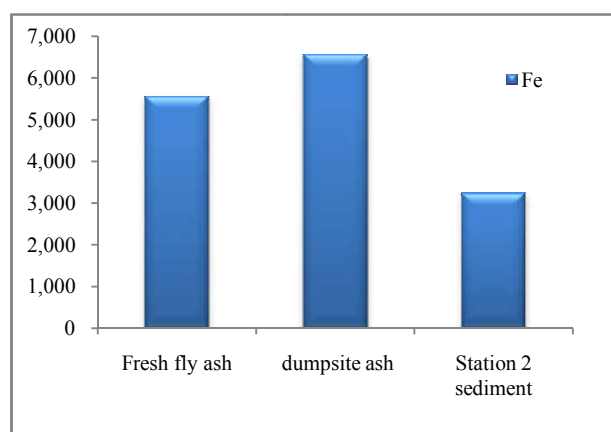


Figure 5 Iron in ash samples (mg/kg)

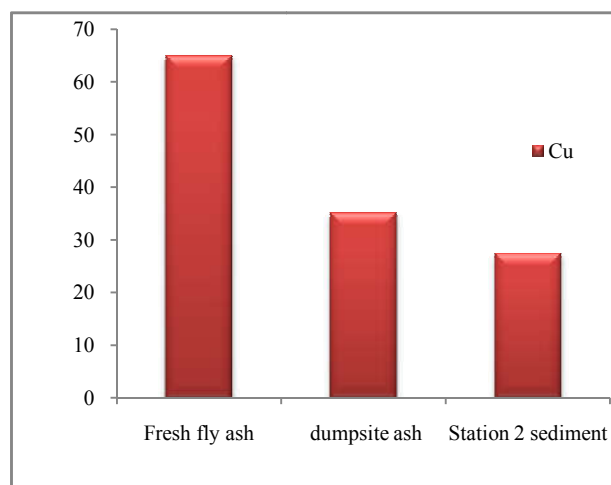


Figure 6 Copper in ash samples (mg/kg)

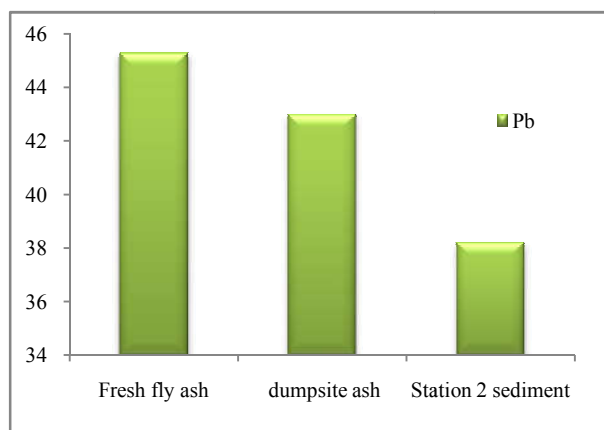


Figure 7 Lead in ash samples (mg/kg)

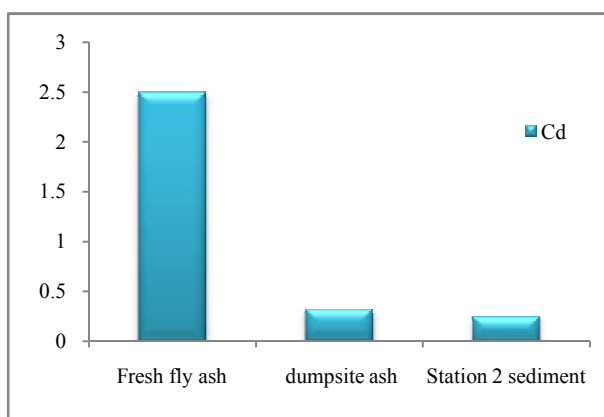


Figure 8 Cadmium in ash samples (mg/kg)

CONCLUSION

The chemical changes of fly ash in marine environment was studied by pH of fresh fly ash compared with ash sample taken from dumpsite that showed 11.06% of pH value decreased in dumpsite ash. But in the case of organic carbon the values have increased with 76.6% in dumpsite ash. The heavy metal content in ash samples were determined and the results of ash from dumpsite area compared with fresh fly ash which showed iron content in dumpsite 18 % gets increased. The percentage of other metals like copper, lead and cadmium decreased in dumpsite ash like 45%, 5%, and 87% respectively. The impact of ash in marine environment was decreased as the distance increase from the dumpsite. The disposal, management and proper utilization of waste products has become a concern for the scientists and environmentalists. Proper management of solid-waste of fly ash from thermal power plants is necessary to safeguard our environment.

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