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Research Paper

Leaching behaviour and compressive strength of cement solidified fly ash used for adsorption of metal ions from aqueous solutions

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ABSTRACT

It is very important to ensure that the fly ash produced, after adsorbing metal ions from aqueous solution, is disposed of in a manner that it does not adversely affect the environment. In this study, the used fly ash loaded with heavy metal ions is solidified with cement and sand mixture in a certain ratio. The studies reveal that cement solidified fly ash does not reduce the compressive strength of this mortar cube and also does not leach out the adsorbed metal ions in presence of water over a period of time. It makes cement solidified fly ash safe for use in various Civil Engineering purposes without adversely affecting the environment. The results of this study also suggest that fly ash may be a promising adsorbent for environmental technologies in the future.

1 Introduction

With the rapid development of industrial growth across the world, a lot of pollutants are generated to satisfy the need of human beings. This industrial growth results in more and more discharge of wastewater containing heavy metal ions, directly or indirectly into the water bodies especially in developing countries. These heavy metal ions are essential for human health if they are present in very small quantity. In fact, it is very important for the proper functioning of living tissue and other human organs. However, too much dose of heavy metal ions may cause eminent health problems [1].

Nowadays various technologies are available for removing heavy metal ions from wastewater. Most of these technologies are not cost-effective [2]. However, adsorption is an efficient and easily available technique for the removal of metal ions present in wastewater [3-5]. There are some adsorbents which are very efficient but are very expensive and difficult to separate after use [6, 7]. Hence fly ash, a low-cost adsorbent has been universally accepted as a cost-effective and efficient

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adsorbent for removing heavy metals from wastewater [8-10]. The chemical and mineral compositions of fly ash vary widely, depending upon the minerals associated with the coal and the burning condition [11]. It is very important to ensure that the fly ash produced, after adsorbing the metal ions, is disposed of in such a manner that it does not adversely affect the environment.

The objective of this study is to evaluate the effectiveness of a technique used for the safe disposal of used fly ash which consists of cementitious properties in presence of Portland cement. In the present investigations, the fly ash loaded with metal ions is solidified with cement and sand. The cube compressive strength of cement solidified fly ash is determined to ensure its suitability for use in various civil engineering applications [12, 13]. The semi-dynamic leaching test is carried out to study any release of metal ions from the fly ash in presence of water over a period of time, if it is solidified [14, 15] with the cement and used for various civil/mining engineering purpose.

2 Material and Methods

2.1 Fly ash

The fly ash used in the investigations was collected from a coal-fired thermal power plant, situated at Koradi, Nagpur, India. The properties of fly ash such as the particle size distribution, chemical composition, morphology and surface characteristics of fly ash play a significant role when it is used as an adsorbent. Therefore, the fly used in the study was characterized before using it as an adsorbent, by using chemical methods and instrumentation techniques such as particle size distribution, X-ray diffraction (XRD), scanning electronic microscopy (SEM), surface charge (Zeta potential) and surface area etc.

2.1.1 Particle Size Distribution

Physically, fly ash is a heterogeneous mixture containing particles with a wide size distribution between few millimeters to sub-micron sizes. The fly ash collected was sieved, to study the particle size distribution as per Indian Standard [16] and is as given below in Table 1.

Table 1- Particle Size distribution of fly ash

Particle size (µm)	> 1000	1000 - 600	600 - 425	425 - 300	300 - 212	212 - 150	150 - 75	< 75
% by weight	0.028	0.048	0.052	0.084	0.176	1.124	7.364	91.124

Table 1 shows that approximately 91.12 % of the fly ash particles have size less than 75 µm.

2.1.2 Chemical Composition of Fly Ash

The chemical analysis of the fly ash used is presented in Table 2.

Table 2- Chemical constituents of the fly ash sample

Constituent	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	CaO	MgO	Na_2O	K_2O	SO_3	P_2O_5	Mn	LOI
% by weight	65.01	24.41	4.04	0.69	0.35	0.55	0.22	0.21	0.15	0.037	0.28	2.04

It is depicted in Table 2 that major constituents of the fly ash are SiO_2 and Al_2O_3 contributing about 89.4%. The other important constituent is Fe_2O_3 and other constituents present in the fly ash are in traces. The sum of SiO_2, Al_2O_3 and Fe_2O_3 is usually used to assess the pozzolanicity of supplementary cements. The pH of fly ash collected was in the range of 6.9 to 7.9 and it was classified as 'class F' fly ash as per ASTM C-618 classification [17].

2.2 Preparation of fly ash sample loaded with metal ions

The fly ash was used without any pre-treatment for the adsorption of three metal ions i.e. Ni^{+2}, Zn^{+2}, and Pb^{+2} from an aqueous solution in which the concentration of each metal ion was 100 mg/l. Five liters of aqueous solution, containing these three metal ions (initial pH = 5.85), was taken in a container and 500 gm fly ash was added to it. The mixture was stirred manually every hour for twenty-four hours. After twenty-four hours the fly ash and solution were separated and this solution was used to determine the amount of each metal ions adsorbed by fly ash. From the results generated by Atomic Adsorption Spectrophotometer (AAS), it was depicted that fly ash produced after adsorption was loaded with Zn^{+2}=0.416 mg/gm, Ni^{+2}=0.2005 mg/gm, and Pb^{+2}=1.0 mg/gm. After adsorption of three metal ions, this fly ash was available for its safe disposal.

2.3 Compressive strength test

The compressive strength of mortar cubes containing fly ash in different proportion was measured as per code of Indian standards. For this purpose, test samples were prepared by mixing of cement, sand and fly ash in the ratio of 1:3:0 (sample 1), 1:3:0.25 (sample 2) and 1:3:0.5 (sample 3). In each sample cement and water ratio was maintained as 1: 0.4 to maintain the consistency of the mix. The cement, sand, fly ash and water mixture was mixed properly and standard size cubes (7.06 cm × 7.06 cm × 7.06 cm) were prepared [18]. Ordinary Portland Cement 43 grade conforming to the code of Indian standards [19] were used for sample preparation. These mortar cubes i. e. sample 1, 2 and 3 were tested on uniaxial compression testing machine as per code of Indian Standards [20] for their cube compressive strength.

2.4 Semi-dynamic leaching tests

Semi-dynamic leaching test was performed to study the leaching behavior of three metal ions (Ni^{+2}, Zn^{+2}, and Pb^{+2}) from the hardened mortar cubes as per the guidelines given by Ameriacan Nuclear Society (ANS 16.1) [21]. As per these guidelines, a cylindrical test specimen with a length to diameter ratio of 4 was prepared using a mix which is prepared for compressive strength test. The length of the test specimen was found to be equal to 4.786 cm and its average diameter was calculated as 1.192 cm. Thus, length to diameter ratio was maintained as 4.015 i.e. approximately 4. The specimen mass was found to be 35.002 gm. The leaching agent used to conduct the test was freshly prepared double distilled water.

2.5 Equipments

The mineralogical components of fly ash were determined using the X-ray diffraction spectra (XRD) by X-Pert-ProXRD diffractometer. A scanning electron microscope (SEM) (Model Philips SEM 515) between 25kV to 30kV was used to analyze the surface characteristics of fly ash. Atomic absorption spectrophotometer (Model – GBC 932 AA) was used to determine the metal ion content in the aqueous solution. Micromeritics ASAP 2020 was used to determine the surface area of fly ash, using liquid nitrogen gas.

3 Results and discussion

3.1 X-ray Powder Diffraction (XRD) Analysis

The adsorption characteristics of the fly ash can be understood using X-ray study. XRD-analysis was conducted to study the change in the mineralogical composition of fly ash before and after adsorption of heavy metals. Fig. 1 shows the X-ray diffraction pattern for the fly ash sample collected before adsorption of metal ions.

The various peaks of the minerals are indicated: A as Quartz , Silicon dioxide (SiO_2), B as Mulite, Aluminum silicon oxide ($3Al_2O_3.SiO_2$), C as Magnetite (Fe_3O_4), D as Hematite (Fe_2O_3), E as Leucite, Potassium aluminumsilicate $K(AlSi_2O_6)$, F as Magnesium silicate (Mg_2SiO_4), G as Silicon oxide (SiO_4), H as Rutile (TiO_2) and I as Calcium aluminum sulphite Hydrate ($Ca_6Al_2O_6(SO_3).32H_2O$).

It can be seen from the figure 1 that crystalline minerals compounds are mainly in oxide form. The oxides are basically the insulating materials and posses the dielectric property. The dielectrics are the materials which have an electric dipole and dipole moment. The electric dipole, when oriented in particular direction, gives rise to polarization in the sample. This polarization has the property to attract the charged particles and makes the fly ash as a good adsorbent to adsorb the metal ions.

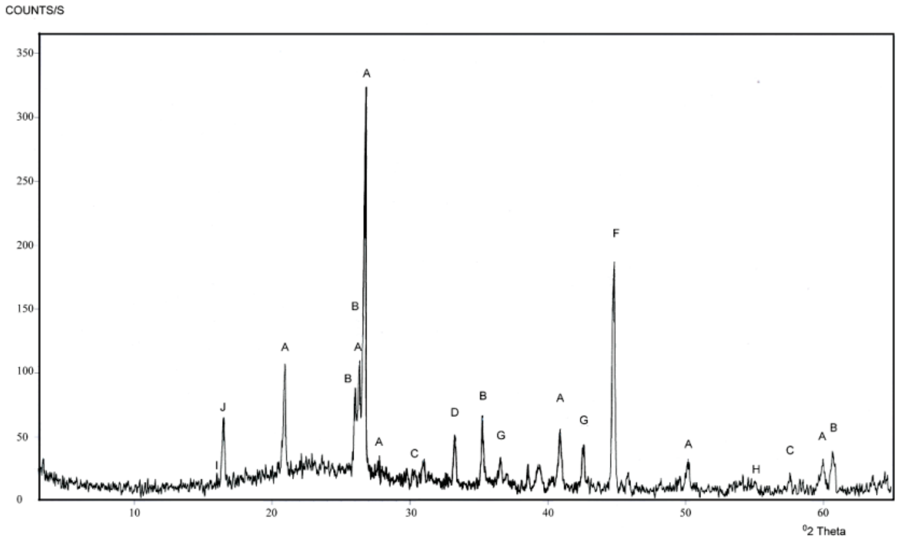

Fig. 1- XRD spectra of fly ash sample

The XRD graph for the fly ash sample after the adsorption of the three metal ions namely Ni^{+2}, Zn^{+2}, and Pb^{+2} have been shown in Fig. 2. It shows a variation in the peaks which were obtained for unused fly ash.

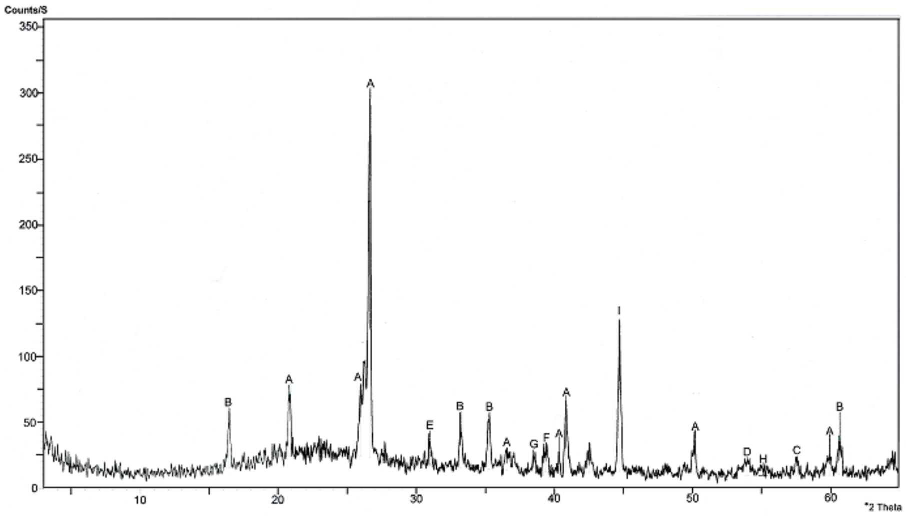

Fig. 2- XRD spectra of fly ash after adsorption of metal ions

The various peaks of the minerals are indicated :A as Quartz, Silicon dioxide (SiO_2), B as Mulite, Aluminum silicon oxide ($3Al_2O_3.SiO_2$), C as Magnetite, (Fe_3O_4), D as Hematite, (Fe_2O_3), E as Dolomite, $CaMg(CO_3)_2$, F as Katoite, Calcium aluminum Hydrogen Oxide ($Ca_3Al_2(O_4H_4)_3$), G as Diaspore, Aluminum oxide Hydrate ($Al_2O_3.H_2O$), H as Rutile, (TiO_2), I as Akermanite, Calcium Magnesium silicate ($Ca_2MgSi_2O_7$) etc. However, during the adsorption process, some other peaks for some other minerals are also surfaced such as - Dolomite $CaMg(CO_3)_2$, Katoite ($Ca_3Al_2(O_4H_4)_3$), Diaspore ($Al_2O_3.H_2O$) and Akermanite ($Ca_2MgSi_2O_7$).

3.2 Scanning Electron Microscope (SEM) Analysis

This analysis is required to analyze the distribution of shape and size of fly ash particles. Fig. 3 shows a magnified image of fly ash sample. It clearly depicts that the fly ash particles are generally spherical in shape. However, there are some irregularly-shaped particles are also present such as angular particles of quartz. It also indicated that a large number of particles are present in the size range below 10 μm.

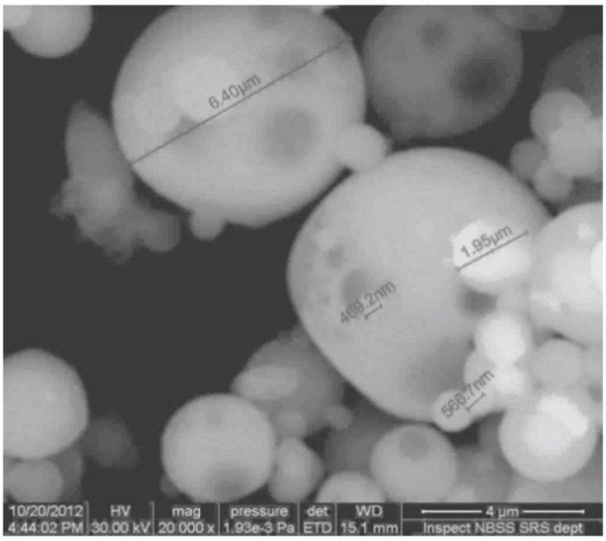

Fig. 3- Magnified image of fly ash sample (magnification: 20000x)

3.3 Surface Area Analysis

Information about the characteristics of the adsorbent used is an important requirement for modeling and simulation studies for any adsorption separation process. Value of surface area is one of the factors that govern the intensity of physical forces acting between adsorbate and the adsorbent molecules. The intensity of these forces, in turn, affects the amount of adsorbate to be adsorbed on the adsorption site. Obviously, the adsorbent having larger surface area are preferred in purification and bulk separation process. In the present study, the surface area of the fly ash was determined by BET method using liquid nitrogen gas [4] and was found to be 10.5777 ± 0.1429 m^2/gm, This surface area is comparable with the surface area of rice husk ash and peat coal [22]. Activated charcoal, activated carbon and zeolite have a very large surface area as compared with the fly ash sample. Adsorbent having high surface area is highly desirable for the adsorption process, but these adsorbents posses very high cost.

3.4 Disposal of fly ash

For the safe disposal of fly ash two tests namely: Compressive strength test and semi-dynamic leaching tests were carried out.

3.4.1 Compressive Strength Test

The mortar cubes i.e. sample 1, 2 and 3 were tested on uniaxial compression testing machine as per code of Indian Standards [20] for their cube compressive strength after 28 days of curing are shown in Table 3.

Table 3- Compressive strength of Cement, Sand, and Fly ash mortar

Sr. No.	Ratio of Cement: Sand: Fly ash	Av. Cubical Compressive Strength (N/mm^2)	Decrease in strength with respect to no fly ash sample
1	1:3:0	12.65	-
2	1:3:0.25	12.52	1%
3	1:3:0.5	12.15	4%

It can be seen from the Fig. 4 that the cube compressive strength which was 12.65 N/mm^2 without any fly ash, has been decreased by 4% to 12.15 N/mm^2 when the cement: sand: flyash ratio was 1:3:0.5. This decrease in strength is very low therefore, it can be concluded that the used fly ash can be solidified by mixing with cement and sand in the proper ratio and this mortar can be used for various civil engineering purposes.

3.4.2 Semi-Dynamic Leaching Test

To conduct the semi-dynamic leaching test, the specimen prepared (Length to diameter ratio =4) was immersed in 350 ml of distilled water to attain liquid-to-solid ratio equal to 10 as per the ANS 16.1 test [21]. The test water was renewed every twenty-four hours. These water samples were collected and concentrations of different metal ions were recorded by using AAS technique for 90 days. The results are plotted in Fig. 4. During the leaching test, it was observed, that no traces of Zn^{+2} and Pb^{+2} ions were detected in the water samples from the first day to end of the test. Therefore, it was concluded that leaching of Zn^{+2} and Pb^{+2} could not take place due to the presence of strong binding force between positively charged Zn^{+2} and Pb^{+2} ions and negatively charged fly ash particles.

Thus, for these two metals, the cumulative fraction released up to 90 days was zero. However, Ni^{+2} ions were leached up to 63 days and after that, no traces of Ni^{+2} were detected in solution.

To study the leaching behavior of Ni^{+2}, graphs were plotted between the number of days versus concentration of Ni^{+2} ions leached as shown in Fig. 4. It is depicted from the Fig. 4 that the maximum leaching of the Ni^{+2} was reported after day one (0.098 mg/l) but this concentration was also very less as compared to the maximum safe limit (3 mg/l) as given by The Environment (Protection) Rules of India, 1986 [23].

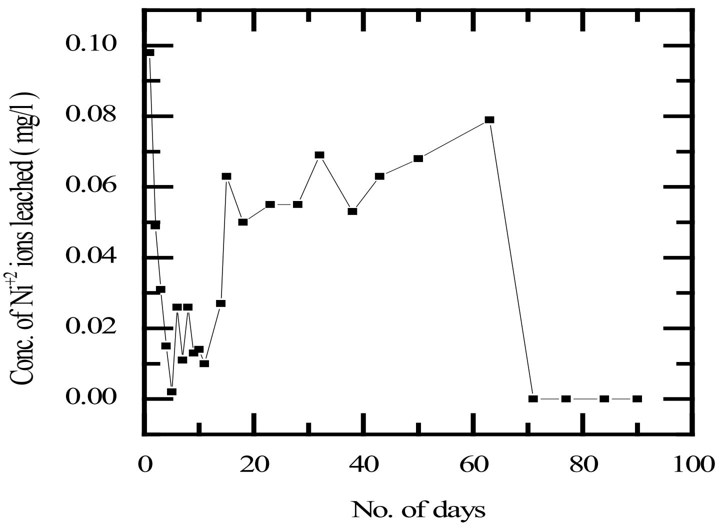

Fig. 4- Variation in concentration of Ni^{+2} ions in the leachate against number of days

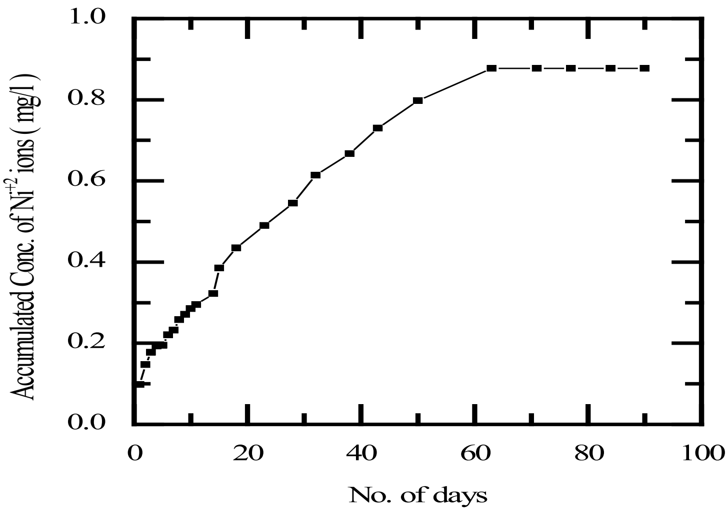

Fig. 5- Variation of accumulated leached material (Ni^{+2}) in cement solidified fly ash waste

It was also observed that the amount of Ni^{+2} ions leached out in the water samples varies with respect to time and such behavior was observed up to 63 days but later on, no traces of Ni^{+2} ions were detected in our study till the end of semi-dynamic leaching study. The cumulative amount of Ni^{+2} released during 63 days was obtained by adding the traces of Ni^{+2} ions released in semi-dynamic leaching test. Fig. 5 indicates that the variation of the cumulative released fraction of Ni^{+2} ions leach out with respect to the number of days.

It can be seen from the Fig. 5 that even during the complete course of the study, the cumulative released fraction in terms of the amount was found to be 0.877 mg/l which is well below the safe disposal limit.

4 Conclusion

It can be concluded that fly ash which is a waste material and readily available in thermal power plants, can be used as an adsorbent for the removal of metal ions present in aqueous solution. Cement solidified fly ash does not reduce the compressive strength of this mortar cube and also does not leach out the adsorbed metal ions in presence of water over a period of time and make it safe for use in various Civil Engineering purposes without adversely affecting the environment. The results of this study suggest that fly ash may be a promising adsorbent for environmental technologies in the future.

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