Ash-Water Interaction and Its Effect on Ash Characteristics

Prabir K. Kolay* and D. N. Singh[†]

Introduction

Onventional applications of the ash viz. as a stabilizer of sub-grade or sub-base material in pavement construction, as a filler material for mines, as a constituent of cement and concrete, as a treatment medium for polluted water, and for treatment of soil for agriculture purposes (Joshi et al., 1975; Mehta, 1985; McLaren and DiGioia, 1987; Toth et al., 1987; Shi, 1996) do not take into account the quality of the ash and the subsequent changes it may undergo, before it can be used for these applications. In this context, some researchers have demonstrated and critically evaluated the influence of methods adopted for handling, collection, storage and disposal (viz. wet or dry disposal) of the ash (Theis and Gardner, 1990). It has also been demonstrated that the physical, chemical and mineralogical properties of the ash change to a great extent, when 'wetdisposal' or 'slurry disposal' method of the ash is adopted (Steenbruggen and Hollman, 1998; Grutzeck and Siemer, 1997; Henmi, 1987).

During wet disposal, the ash interacts with water and the alkalies present in it (mainly Na_2O and K_2O) react with major constituents of the ash (SiO₂ and Al₂O₃) leading to the formation of ash zeolites. This process is termed as 'zeolitization' of the ash, i.e. formation of zeolites, which alters the overall properties of the ash. Some efforts have been made in the recent past to synthesize zeolites from the fly ash (Singer and Berkgaut, 1995; Lin and Hsi, 1995; Xavier et al., 1997). These zeolites have been used for preventing degradation of the environment as well as for different industrial applications, such as removal of heavy metals from the industrial sludge and

Research Scholar, Department of Civil Engineering, Indian Institute of Technology, Bombay, Powai, Mumbai – 400 076, INDIA. E-mail: pkolay2001@yahoo.com

[†] Associate Professor, Department of Civil Engineering, Indian Institute of Technology, Bornbay, Powai, Mumbai – 400 076, INDIA. E-mail: dns@civil.iitb.ac.in

flue gas, ammonia removal, replacement of phosphate in detergent, removal of radioactive waste, etc.

However, studies related to the zeolitization of the ash and its effect on physical, chemical, mineralogical, thermal and geotechnical properties of the ash and their applications for various industrial uses are unexplored and needs a proper study. Efforts were made to characterize a typical Indian lagoon ash, based on its physical, chemical, mineralogical, thermal and geotechnical properties by Kolay (2000). However, how wet disposal of the ash influences its properties over a period of time, remains uninvestigated. Hence, an effort has been made in this paper to simulate ash-water interaction under controlled laboratory conditions (thermo-chemical activation), which replicates wet-disposal of the ash, and the changes undergone by it in the lagoons over a period of time. Studies are also conducted to establish the effect of zeolitization on physical, chemical, mineralogical, thermal and geotechnical properties of the ash. The paper also describes the application of the lagoon ash, and the zeolitized ash, for heavy metal removal, or retention, from the industrial sludge.

Experimental Investigation

Lagoon ash from Koradi Thermal Power Plant, Nagpur, Maharashtra, India, is chosen for the present study. Ash sampling is done randomly, in four batches during a span of seven days, so as to minimize the effect of heterogeneity. Later these batches of the samples were mixed together to prepare a representative sample of the ash. The oven-dried sample of this ash is designated as the original lagoon ash (OLA) sample. This sample has been characterized for its physical, chemical, mineralogical and thermal characteristics (Kolay, 2000).

To establish the compaction characteristics of the ash, a miniature compaction apparatus, capable of imparting compaction equivalent to the standard Proctor compaction, is fabricated (Kolay, 2000). The compaction mould is a cylindrical split mould of 38 mm internal diameter and 76 mm height. The consolidation characteristics of the ash, compacted at optimum moisture content (OMC) are determined by conducting one-dimensional consolidation tests. The variation of the permeability of the ash, compacted at different densities and water contents, is determined by conducting constant-head permeability tests. To establish shear strength characteristics of the ash, fast (undrained) and slow (drained) direct shear tests and the unconsolidated undrained (UU) and consolidated drained (CD) tests are conducted on the ash samples, compacted at their optimum moisture content (OMC). The fast and slow tests are conducted with rate of strain equal to 0.625 mm/min and 0.012 mm/min, respectively. For drained tests, the ash is consolidated prior to its shearing, for a period of 24 h (Kolay and Singh, 2001).

Alkali	Alkali Strength (M)	Time (h)					
		12	24	36	48		
NaOH	0.5	ALA1	ALA5	ALA9	ALA13		
	1.0	ALA2	ALA6	ALA10	ALA14		
	2.0	ALA3	ALA7	ALA11	ALA15		
	3.5	ALA4	ALA8	ALA12	ALA16		
КОН	0.5	ALA17	ALA21	ALA25	ALA29		
	1.0	ALA18	ALA22	ALA26	ALA30		
	2.0	ALA19	ALA23	ALA27	ALA31		
	3.5	ALA20	ALA24	ALA28	ALA32		

TABLE 1 : Designation of the Ash Sample Representing itsAlkali Activation

 TABLE 2 : X-Ray Crystalline Minerals Present in the OLA and ALA Samples (Treated with NaOH)

Sample	Mineral					
	Quartz	Mullite	NaP1 zeolite	Hydroxy-sodalite zeolite		
OLA	PD	Р	NP	NP		
ALA1	PD	Р	Р	NP		
ALA2	PD	Р	Р	NP		
ALA3	PD	Р	Р	NP		
ALA4	PD	Р	P	NP		
ALA5	PD	Р	Р	NP		
ALA6	PD	Р	Р	Р		
ALA7	PD	P	Р	NP		
ALA8	PD	Р	Р	NP		
ALA9	PD	Р	Р	NP		
ALA10	PD	Р	Р	NP		
ALA11	PD	Р	Р	NP		
ALA12	PD	Р	Р	NP		
ALA13	PD	Р	Р	NP		
ALA14	PD	Р	Р	NP		
ALA15	PD	Р	Р	NP		
ALA16	PD	Р	Р	NP		
ALA17	PD	Р	Р	NP		

PD = Predominant P = Present NP = Not Present

Simulation of Ash-Water Interaction

The ash sample (OLA) is activated with 160 ml alkali (NaOH and KOH) solution of 0.5, 1.0, 2.0 and 3.5 M, in an open system, maintaining a solid to liquid ratio of 0.125 g/l. The activation temperature of approximately 100 °C is maintained by using a water-bath and a reflux system. The process time is then varied from 12, 24, 36 and 48 h. At the end of these activation periods, the ash sample is filtered and repeatedly washed with distilled water. Table 1 presents details of the alkali activated ash samples (termed as ALA).

Results and Discussion

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X-ray diffraction analysis of the OLA sample indicates that Quartz and Mullite are the major crystalline phases present in it. To establish the influence of alkali activation on mineralogical characteristics of the ash,

Sample	Mineral						
	Quartz	Mullite	NaP1 zeolite	Hydroxy-sodalite zeolite			
OLA	PD	Р	Р	NP			
ALA1	PD	Р	Р	NP			
ALA2	PD .	Р	Р	NP			
ALA3	PD	Р	Р	NP			
ALA4	PD	P	Р	NP			
ALA5	PD	Р	Р	NP			
ALA6	PD	Р	Р	NP			
ALA7	PD	Р	Р	NP			
ALA8	PD	P	Р	NP			
ALA9	PD	P	Р	NP			
ALA10	PD	Р	Р	NP			
ALA11	PD	Р	Р	NP			
ALA12	PD	Р	Р	NP			
ALA13	PD	Р	Р	NP			
ALA14	PD	Р	Р	NP			
ALA15	PD	Р	Р	NP			
ALA16	PD	Р	Р	NP			
ALA17	PD	Р	Р	NP			

 TABLE 3 : X-Ray Crystalline Minerals Present in the

 OLA and ALA Samples (Treated with KOH)

PD = Predominant P = Present NP = Not Present



(a)



(b)

FIGURE 1 : SEM Micrographs of the (a) OLA (× 1600) and (b) ALA6 (× 200) Samples

X-ray studies are also conducted on ALA1 to ALA32 samples. This study reveals that only ALA1 to ALA16 samples exhibit formation of NaP1 zeolite. However, in addition to NaP1 zeolite, ALA6 sample exhibits formation of zeolite hydroxy-sodalite also, as shown in Table 2. However, KOH treatment of the OLA does not result in the formation of any zeolite, as shown in Table 3, and hence these samples (ALA17 to ALA32) are not characterized further. As ALA6 sample only exhibits the formation of two types of zeolites, detailed investigations are conducted to study its morphological, chemical and physical characteristics. Influence of these characteristics on thermal and geotechnical characteristics of the ash are also conducted in detail.

Figure 1 presents the SEM micrographs of the OLA and ALA6 samples. From the SEM studies on the OLA sample it can be observed that the OLA sample consists of different shapes of particles, viz. spherical, hollow (cenosphere), broken, plerospherical (i.e. a sphere within another sphere), and some other irregular shapes (Fig.1a). However, for ALA6 sample (Fig.1b), some overgrowth on the surface of the ash particles seems to have taken place. This may be attributed to the etching of silica present in the ash due to alkali activation.

The CEC of the OLA sample (100 meq/100g) is seen to increase as a result of alkali activation. However, ALA6 sample exhibits a very high CEC (= 244 meq/100g), which may be attributed to the presence of zeolites NaP1 and hydroxy-sodalite.

Table 4 presents the influence of alkali activation on the chemical composition (% by weight) of the OLA sample. The particle size distribution characteristics for the OLA and ALA6 samples are presented in Fig.2. From the figure, it can be seen that the OLA consists of 55% sand size fraction (< 4750 μ m), 41.5% silt size fraction (75 to 2 μ m) and about 3.5% clay size fraction (< 2 μ m). However, for the ALA6 sample the sand, silt, and clay

Oxides	OLA	ALA6	Oxides	OLA	ALA6
SiO ₂	59.89	54.01	Na ₂ O	0.06	0.063
Al ₂ O ₃	27.20	24.11	K ₂ O	0.93	0.698
Fe ₂ O ₃	4.33	6.391	MgO	0.03	0.380
CaO	1.01	0.948	TiO ₂	2.30	2.128
SO3	1.53	0.032	P ₂ O ₅	0.23	0.137

 TABLE 4 : Chemical Composition (% by Weight) of the OLA and ALA6 Samples



FIGURE 2 : Gradation Characteristics of the OLA and ALA6 Samples



FIGURE 3 : Grain-Size Distribution of the OLA and ALA6 Samples (Soft-Imaging Analysis)

size fractions are found to be 55, 45, and 0%, respectively. The study indicates that alkali activation of the OLA results in a decrease in its fines content. These observations are consistent with the results of the SEM studies also (Fig.1b). By conducting soft-imaging, these results are further substantiated. For this 206 particles were randomly selected for the analysis and the results obtained are presented in Fig.3. The minimum and maximum sizes of the particles are found to be 2.64 μ m and 45.77 μ m, respectively, for the OLA sample. However, for the ALA6 sample the range of particle size varies from 3.99 to 85.41 μ m. It can be further noted from the figure that the number of particles in the size ranges of 10 to 15 μ m, 20 to 30 μ m and 50 to 90 μ m are greater in the ALA6 sample than in the OLA sample. However, for the particle size range 30 to 45 μ m, the number of particles decreases in the ALA6 sample.

Table 5 presents the minimum and maximum void ratios and porosities of the OLA and the ALA6 samples. From the data presented in the table, it can be noticed that the minimum and maximum void ratios for the OLA sample increase by 47.37% and 23.61%, respectively, due to alkali activation. This indicates that on alkali activation, the ash alters to a more porous state and the porosity values increase by 23.25% and 8.47% for minimum and maximum void ratios, respectively. This observation is consistent with the fact that the ALA6 sample showed the presence of the zeolites NaP1 and hydroxy-sodalite, which are porous in nature.

Figure 4 presents the compaction characteristics for OLA and ALA6 samples. The ash samples starts bleeding beyond OMC. From the figure, it can be noticed that the maximum dry density and OMC of the OLA sample are 1.14 g/cm^3 and 30.05%, and the same for ALA6 are 1.05 g/cm^3 and 40%, respectively. This indicates a loss in the dry density of the alkaliactivated ash samples approximately by 8%. The increased optimum moisture content indicates the formation of a highly porous structure. The increased grain specific surface area also corroborates this observation (as shown in Fig.5). This shows that the controlled-condition-water-interaction is

TABLE	5	:	Void Rat	io (e)	and	Porosity	(1)	Values	of
			the OLA	and	ALA	5 Sample	S		

Properties	OLA	ALA6
Maximum void ratio	1.44	1.78
Minimum void ratio	0.76	1.12
Maximum porosity	0.59	0.64
Minimum porosity	0.43	0.53



FIGURE 4 : Compaction Characteristics of the OLA and ALA6 Samples



FIGURE 5 : Variation of Specific Surface Area of the OLA Sample with Alkali Activation

responsible for the formation of zeolites. These observations are consistent with the fact that alkali activation of the ash results in an increase in surface area and CEC value.

The consolidation characteristics of the ash samples, compacted at OMC, were determined. The compression index, C_c , for the OLA 'sample was found to be 0.038 and for the ALA6 sample it was 0.044. The increase in compression index value is approximately 16%. Studies have also been conducted on the collapse potential of these ash samples, corresponding to their loose and maximum dry density states. The study reveals that the collapse potential of ALA6 is less than the OLA sample.

The constant-head permeability tests were conducted on OLA and ALA6 samples, corresponding to their standard Proctor compaction states, as shown in Fig.6. For these samples, permeability decreases with increase in the moisture content up to about the OMC values (30.05% for OLA and 40% for ALA6). It is also evident from the figure that the permeability of ALA6 sample is greater than that for the OLA sample. This is consistent with the observation that alkali activation of the ash makes it more porous. The permeability values at OMC are found to be 6.26×10^{-5} and 8.45×10^{-5} cm/s for OLA and ALA6 sample is approximately 35% than the OLA sample at OMC.



FIGURE 6 : Variation of Permeability with Moisture Content for the OLA and ALA6 Samples (At Standard Proctor Densities)

Test Types		\$ (°)		
		OLA	ALA6	
Direct shear	Fast test	36	42	
	Slow test	30	36	
Triaxial shear	UU	35	40	
	CD	37	37	

TABLE 6 : Comparison of Shear Strength Parameters of the OLA and ALA6 Samples

The results of direct shear tests (fast and slow) and triaxial shear tests (UU and CD) of the OLA and ALA6 samples are presented in Table 6. From the table, it can be noticed that except for CD tests, the values of ϕ for alkali activated ash sample (ALA6) are higher. This may be attributed to the 'growth' of the particles due to alkali activation. This is in accordance with the results of SEM and gradation studies. However, for the consolidated drained (CD) tests, the ϕ values obtained for OLA and ALA6 samples are noticed to be same. This may be attributed to the



FIGURE 7 : Variation of Thermal Resistivity of the OLA and .' LA6 Samples with Moisture Content

high permeability of ALA6 sample. A high permeability for the ALA6 sample facilitates the expulsion of water from it during consolidation process. The loss of water from the ALA6 sample makes it similar to the OLA sample. This indicates that the basic difference between OLA and ALA6 samples is their water content/retention property, which is influenced by their porosity.

The thermal resistivity values of the OLA and ALA6 samples, corresponding to a dry density of 1.0 g/cm3, are estimated and their variation with moisture content of the ash is obtained, as shown in Fig.7. It can be seen from the figure that thermal resistivity values of the OLA and ALA6 samples (corresponding to their dry state) are 578 and 615 °Ccm/W, respectively. With the addition of 5% moisture to the dry samples the resistivity values drop to 459 and 513 °C-cm/W for OLA and ALA6 samples, respectively. The drop in resistivity values continues up to almost 20% and 30% moisture content for OLA and ALA6 samples, respectively. However, this drop is much less as compared to the drop in the resistivity values for moisture content less than 10% for both OLA as well as ALA6 samples. It can also be noticed that corresponding to 30% and 40% moisture contents, the OLA and ALA6 samples exhibit lowest resistivity values. These values remain practically same even with further addition of moisture. However, they could not be tested for moisture contents > 30% and > 40% due to the bleeding of these samples. Such a study is found to be useful in designing the fluidized thermal beds (FTBs).

Figure 8 presents the results of the TGA and DTA studies on OLA and ALA6 samples. The TGA studies on OLA and ALA6 samples, in dry air and inert atmosphere (Nitrogen), indicate loss of weight as the temperature increases. However, the weight loss is more for the ALA6 sample compared to the OLA sample which may be attributed to the release of moisture and oxidation of carbon and sulphur present in the ash samples, in the dry air combustion. However, when nitrogen (inert atmosphere) is used for combustion, the loss in weight may be attributed to the escape of volatile (as well as moisture) matter present in the ash samples. In the DTA studies, with similar atmospheric conditions, the OLA sample exhibits more exothermic reaction compared to the ALA6 sample. This indicates that OLA sample is a better conductor of heat, which may be attributed to the fact that ALA6 sample contains less carbon and sulphur (due to alkali interaction and subsequent washing with water).

Heavy Metal Retention Studies

To demonstrate application of ash zeolites for retention of heavy metals from the industrial sludge, studies are conducted on OLA and ALA6 samples. For this, 5 g of the ash sample is taken in a flask containing 30 ml of



FIGURE 8 : Comparison of TGA and DTA Results for the OLA and ALA6 Samples in (a) Dry Air, (b) Nitrogen



FIGURE 9 : Pb Retention Characteristics of the OLA and ALA6 Samples

 $0.05 \text{ M Pb}(\text{NO}_3)_2$ solution. The initial pH of the solution is adjusted to 2.0, 4.0, 6.0 and 8.0, respectively. These samples are stirred for 6, 12 and 24 h using an end-over-end shaker. This solution is transferred to a centrifuge tube to make a volume of 80 ml (i.e. initially lead added is 3885 μ g/ml) and is centrifuged at 6000 to 7000 rpm for 15 minutes. At the end of the centrifugation the solution is adjusted to the initially adjusted pH values. The supernatant solution is collected and analyzed to obtain the concentration of Pb present in the solution, with the help of an ICP unit. The difference between initial concentration of Pb and the concentration of Pb present in the solution indicates the concentration of Pb retained by the ash sample.

The results of Pb retention by the ash samples are presented in Fig.9. From the figure it can be noticed that the OLA sample retains 25 to 29% of the lead, for pH ranging from 2 to 4. However, at pH equal to 6, the precipitation of lead starts. This is responsible for 65 to 95% and 99% lead retention when the OLA and ALA6 samples are used, respectively. At pH equal to 8, the lead precipitates completely, indicating that all the lead loaded has been retained and hence the retention efficiency of the ash samples is 100%. It can also be noticed from the figure that as the period of equilibration increases from 6 to 24 h, the lead retention by the OLA increases, marginally (< 5%). The effect of alkali activation (i.e. zeolitization) of the OLA sample on its lead retention characteristics is also presented in



FIGURE 10 : Effect of Pb(NO₃)₂ Strength and pH on Pb Retention Characteristics of the ALA6 Sample (Equilibrium Time = 12 h)

Fig.9. It can be observed from the figure that the lead retention by ALA6 sample is 65 to 75%, when working at pH = 2, and 89 to 95%, for pH > 4 and a period of equilibrium ranging from 6 to 12 h is sufficient to achieve the desired retention. However, a rigorous experimentation is required for using these results for direct industrial applications.

Effect of different strength of $Pb(NO_3)_2$ solution on the retention capacity of the ALA6 sample, with different pH values and equilibrium time period of 12 h, is also studied and shown in Fig.10. It can be noticed from the figure that as the concentration of $Pb(NO_3)_2$ solution decreases, from 0.05 to 0.00005 M, a higher amount of Pb is retained by ALA6 sample, for a given pH value. However, it must be appreciated that 0.0005 M strength of Pb(NO_3)_2 solution is sufficient for almost 100% Pb retention and as such further dilution of the sludge is not recommended.

Conclusions

The ash-water interaction which occurs when the ash is disposed off using wet or slurry-disposal method, has been simulated under controlled laboratory conditions by imparting hydrothermal activation (alkali activation) to a Class 'F' lagoon ash. Based on various tests that were conducted on the ash samples, the following can be concluded:

- 1. Activation with NaOH leads to the formation of Zeolites. However, activation with KOH does not lead to zeolitization of the ash.
- 2. It has been noticed that the alkali activation is responsible for etching (and hence dissolution) of the silica present in the ash.
- 3. The alkali activation of the ash results in an increase in its specific gravity by 11.87 to 24.76% and its specific surface area by 0.72 to 142.51%, with different strength of NaOH and time periods.
- 4. The CEC of the ash increases by 5 to 157% as a result of alkali activation.
- 5. The alkali activation results in an increase in void ratio and porosity by 23.34 to 47.82% and 8.39 to 22.54%, respectively. As such, the maximum dry density of the ash decreases by 8.5%. However the water absorption capacity is noticed to increase by about 33%. This results in an increase of the hydraulic conductivity of the ash by approximately 35%, at the optimum moisture content.
- 6. The compression index of the ash is noticed to increase by about 16% due to its alkali activation.
- 7. The TGA and DTA studies confirm the formation of porous structure due to alkali activation of the ash.
 - 8. The thermal resistivity of ash increases due to alkali activation.
 - 9. Alkali activation leads to an increase in the shear strength of the ash.
 - 10. The amount of Pb retained by the ash increases as pH of the solution and contact time increases.
 - 11. It is observed that the alkali activated lagoon ash is much more efficient in retaining the heavy metals even at low pH value.

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