SYNERGISING RED (MUD) AND GREY (ASH) FOR GREENER GEOPOLYMERS

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Abstract

The paper covers the synergistic use of two major industrial waste namely red mud and fly ash for developing building materials through geopolymerisation. Geopolymerisation behaviour of red mud fly ash mixture has been studied using Isothermal conduction calorimeter. Evaluation of the geopolymers synthesised from red mud fly ash mixture showed that upto 20 % red mud can be used to develop products. Paving blocks have been produced at pilot scale which meets IS 15658 specification and exhibited good mechanical properties and durability.

Introduction

Red mud and fly ash are integral to the primary aluminium production. Large quantities of red mud are generated during Bayer process for alumina from bauxite. Fly ash is a byproduct in captive coal based power plants supplying electrical energy, notably Hall Heroult cell to convert alumina into aluminium. Use of fly ash in place of natural alumino-silicate raw materials (e.g. clays) results in green geopolymer, due primarily to benefits accrued from resource conservation. The term geopolymer is used for alumino-silicate polymers formed in alkaline environment.[1] During the process of geopolymerisation, alumino-silicates are dissolved into alkali solution to form free SiO_4 and AlO_4 tetrahedral units. Further these SiO_4 and AlO_4 tetrahedrons linked alternatively where charge-balancing cations are provided by alkali metal cations and yield polymeric precursors ($–SiO_4–AlO_4–$, or $–SiO_4–AlO_4–SiO_4–$, or $–SiO_4–AlO_4–SiO_4–SiO_4–$) by sharing oxygen atoms between two tetrahedra and forming geopolymer products[1,2].

Fly ash based geopolymers are now a commercial reality. Synergistic use of red mud and fly ash offers the possibility for greener geopolymers. The rationale for the synergistic use of red mud in geopolymer lies in the presence of: (a) caustic in red mud which can complement as a cheaper source for alkali; (b) alumino-silicate phases, including those which belong to zeolite/ geopolymer family; and (c) oxide and hydroxide of iron which can provide framework for ferro-sialate formation. Figure 1 shows the ternary map with location of fly ash and red mud based on SiO_2, Al_2O_3 and Fe_2O_3 content. The geopolymer form will either be dominant in poly-sialate or ferro-sialate depending on the proximity with fly ash or red mud. Ferro-sialate is an iron rich molecular structure consisting of Fe atoms as tetrahedral Fe [IV] in structural position within the ferro-sialate geopolymeric sequence [-Fe-O-Si-O-Al-O-].[3] The formation of ferro-sialate forms the scientific basis of using red mud in geopolymer.

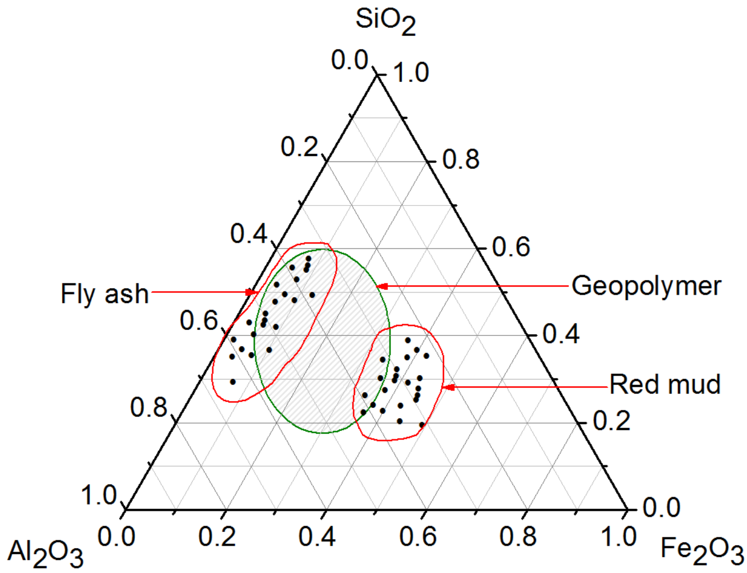

Figure 1: Ternary diagram showing geopolymer formation zone

Many researchers have studied the role of red mud in geopolymer system. It was reported that in the geopolymerisation of red mud and pressurised fluidised bed boiler ash (PFBC ash), red mud behaves as inactive filler which can be solidified with the help of active PFBC ash.[4]Use of red mud and metakaolin mixture was tried by many researchers.[5, 6] They have obtained the compressive strength in the range of 2-13 MPa with red mud addition upto 40 %. Almost similar results were obtained with red mud and fly ash mixture where with class C fly ash, an unconfined compressive strength in the range of 7-13MPa.[7]

The focus of this presentation is on greener geopolymers using fly ash and red mud. The effect of red mud addition on geopolymerisation kinetics has been investigated using isothermal conduction calorimeter. The paper touches upon the up-scaling and production at pilot scale to produce red paving blocks which meets IS 15658 specification.

Materials and Methods

A high silica red mud (Source: ALCOA, Australia) and class F fly ash (Source: Tata Power) was used for the studies. The chemical analysis of red mud and fly ash was carried out using XRF analysis and is given in Table 1.

Table 1: Chemical composition and physical properties of fly ash and red mud

Constituents	SiO_2	Fe_2O_3	Al_2O_3	CaO	MgO	Na_2O	K_2O	LOI
Fly ash	60.48	4.52	28.15	1.71	0.47	0.14	1.41	1.59
Red mud	29.2	31.5	15.2	4.5	0.2	3.1	--	10.2

Mixtures of red mud and fly ash in different proportions were used for geopolymerisation. The amount of red mud was varied between 0-40 %. The reference batch was only fly ash and labelled as FARM0. Different batches were prepared by replacing fly ash by 10, 20, 30 and 40 % red mud and labelled as FARM1, FARM2, FARM3 and FARM4 respectively.

Isothermal conduction calorimetry was used to measure the rate of heat evolution during the reaction ($d\propto/dt$) using an eight channel isothermal conduction calorimeter (TAM AIR, Thermometric AB, Jarafalla, Sweden). The sample was prepared by mixing 3.5 ml alkaline activator (6M NaOH solution + Na2SiO3 into 1:1 ratio) with the 7 gm powder sample. Calorimetric studies were carried out at 27 and 60 °C. The reaction products were characterised by powder X-ray diffraction (XRD) technique. Pilot scale studies were carried out using fully automatic pilot plant with vibro-casting facility.

Results and Discussion

In the calorimetric study, the heat flow at ambient temperature was very minor and the curve appeared as straight horizontal line, but at 60 °C, prominent calorimetric curve has been obtained. Figure 2 shows the heat evolution curve obtained by isothermal conduction calorimetry of the samples at 60 °C for 24 hours. The peak intensity was maximum in FARM0, which decreased with the addition of red mud. The time of occurring peak maxima also increased with red mud addition. This clearly indicates the change in reactivity of geopolymer with red mud addition. Interestingly, this peak behaviour is opposite to the peak behaviour of similar samples subjected to calorimetry at ambient temperature in our previous study.[8] Thus it can be concluded that the red mud plays a dominant role at ambient temperature geopolymerisation whereas fly ash plays dominant role at elevated temperature geopolymerisation.

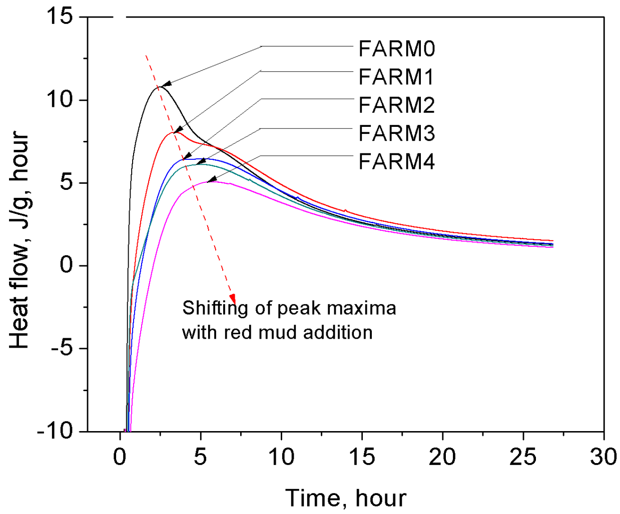

Figure 2: Calorimetric curve of the samples at 60 °C

Figure 3 shows the XRD of finally reacted geopolymer. Two types of peak were observed, peak corresponding to mineral phases derived from parent raw materials fly ash and red mud, and peaks corresponding to reaction product. In the first category, quartz, mullite, hematite and cancrinite were the major phases whereas in the second category sodalite was the main crystalline peak. Hump formation between 15-30° was due to the formation of amorphous gel corresponding to N-A-S-H (N = NaO, A = Al_2O_3, S = SiO_2, H = H_2O).

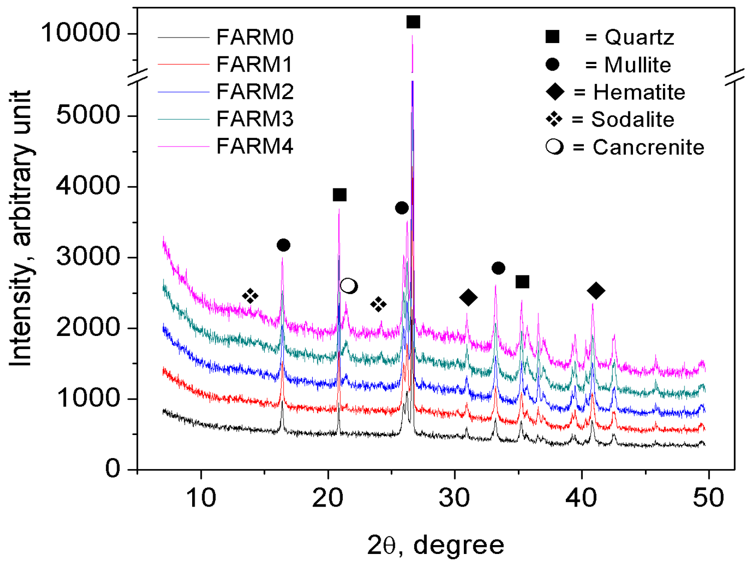

Figure 3: XRD of finally reacted geopolymer

Pilot scale production of building blocks

To explore the possibility of producing building material for commercial application, paving blocks have been produced on 1 tonne scale. The process flow sheet used is given in Figure 4.

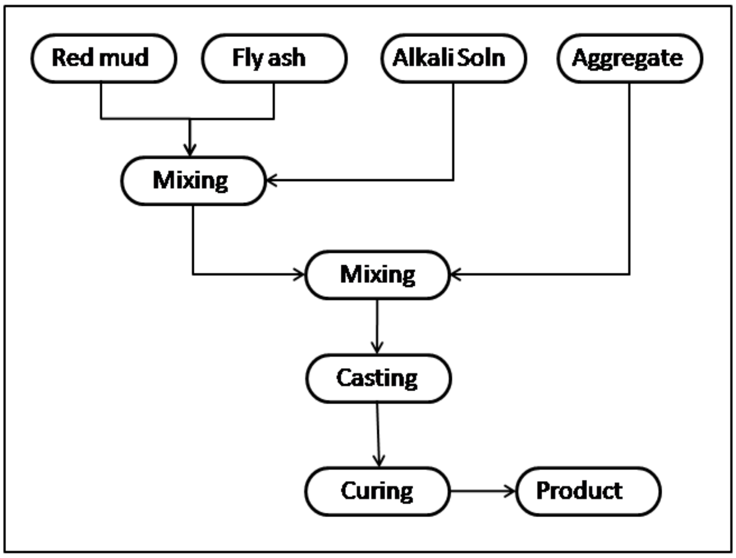

Figure 4: Process flow sheet adopted for pilot scale production

First red mud and fly ash were dry mixed in a mechanical mixer for 3 minutes followed by mixing with alkali solution for another three minutes. The alkali solution used was 1:1 mix of NaOH (6M) solution and $Na_2SiO_3.9H_2O$ solution. Aggregates were added into the prepare dough and then vibro-casted in polyvinyl chloride mould for 1 minute on a vibration table. The mould was then covered with plastic lid to reduce the moisture loss and cured under suitable conditions. Table 2 shows the properties of paving blocks produced at pilot scale. It is obvious from table that only FARM0, FARM1 and FARM2 confirm the IS 15658 specification.

Table 2: Properties of paving block & its compliance with IS specification

Sl. No	Property	IS 15658: 2006	FARM 0	FARM 1	FARM 2	FARM 3	FARM 4
1	Visual Inspection	95% free of defect	Meets spec	Meets spec	Meets spec	Meets spec	Blister s
2	Size tolerance, mm (L+W)	± 2	± 1	± 1	± 1	± 1	± 1
3	Water absorption, %	7	6	6	7	9	12

4	Compressive strength, N/mm^2	30	32	36	32	26	21
5	Tensile split strength, MPa	No Spec	> 2.5	> 2.5	>2.1	> 2.0	> 1.5
6	Flexural strength, MPa	3	4	4.5	3.2	2.8	2.5
7	Abrasion resistance, mm	2	0.68	0.62	0.78	0.9	1.2
8.	Electrical conductivity,Ϭ(s/cm)	No Spec	132	177	212	250	277

Conclusions

It is possible to use red mud and fly ash synergistically for developing geopolymer products. Calorimetry and XRD results indicate the formation of reaction product as a result of geopolymerisation. Pilot scale studies showed that paving blocks meeting IS 15658 specification can be produced using 10-20 % red mud.

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