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Effect of mechanical activation of red mud on the strength of geopolymer binder

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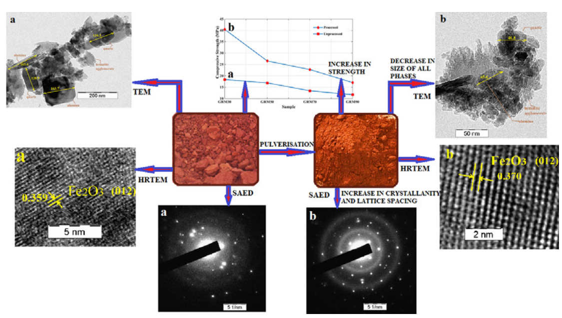
HIGHLIGHTS

- Utilized industrial waste like red mud, fly ash, slag and microsilica to produce alkali activated binders.
- Studied the effect of mechanical activation of red mud on strength of geopolymer paste.
- Ambient cured samples synthesized with pulverised red mud, fly ash and slag possessed higher strength.
- Heat cured samples exhibited lower strength with pulverised red mud in the binder.

GRAPHICAL ABSTRACT



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ABSTRACT

The growing interest in utilization of industrial waste and green construction has motivated the present work. Red mud is an industrial waste produced in the process of extraction of aluminum from bauxite by Bayer's process. The paper presents the studies conducted to assess the influence of mechanical activation of red mud and curing methods on the strength of red mud-fly ash geopolymer paste. Red mud was used in both unprocessed and pulverised form and the alkali activated paste samples were cured thermally as well as in ambient condition. The percentage of red mud varied from 0 to 90% and alkalinity from 6 M to 12 M NaOH solution. X-ray diffraction (XRD) was carried out to identify the mineral phases in pulverised and unprocessed red mud. SAED (selective area diffraction diagram) test was done on the red mud, along with SEM (scanning electron microscopy), TEM (transmission electron microscopy) and HRTEM analysis (high resolution transmission electron microscopy) to study the effect of mechanical activation and validate the experimental findings. Mechanical activation increased the reactivity of silica and the hematite phase of red mud as reflected in the silica reactivity and Fourier transform infrared spectroscopy (FTIR) test results. Use of pulverised red mud enhanced the mechanical properties of ambient cured paste and the specimens possessed maximum 7 day compressive strength of 40 MPa at 6 M alkalinity with 30% mechanically activated red mud content.

1. Introduction

Red mud (RM) is an inorganic waste generated during the process of extraction of alumina from bauxite. More than 120 million tons of red mud is generated each year which adds to the already existing inventory of 2.7 billion ton worldwide [1,2]. Its fineness and highly alkaline nature makes it a hazardous material and a threat to the environment [3,4].

Reusability of red mud is limited due to its alkaline nature. As the red mud contains silicon and aluminum containing minerals along with Na_2O, it could be used as a raw material for geopoly-

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merisation. The term geopolymerisation is a process comprising of dissolution of aluminosilicate solids in strongly alkaline medium followed by condensation of free alumina-silica oligomers to form a tetrahedral polymeric structure. The condensation occurs to the species in the liquid phase namely $[Al(OH)_4]^-$, $[SiO_2(OH)_2]^{2-}$, $[SiO(OH)_3]^-$. The bond formed between silicate species themselves (Si-O-Si) is stronger than that between the silicate and aluminate species (Si-O-Al) [5]. Hence, silica to alumina ratio which is the ratio of SiO_2/Al_2O_3, is a vital parameter influencing the strength of a geopolymer. Moreover, between the two silicate species, $[SiO_2(OH)_2]^{2-}$ and $[SiO(OH)_3]^-$, the latter forms larger aluminosilicate oligomers polymers and the concentration of $[SiO(OH)_3]^-$ is more as the alkalinity decreases [6]. This leads to further condensation between the aluminate and the silicate species, which gives larger oligomers that further results in a gradual build-up of aluminosilicate networks. When the alkalinity is too high, most of the silicate species may occur in the form of $[SiO_2(OH)_2]^{2-}$ which is unfavourable for the condensation reaction. Very low alkalinity may lead to the incomplete dissolution of the species. Hence, for every aluminosilicate feedstock source, there is an optimum SiO_2/Al_2O_3 ratio at a given range of alkalinity. P. Duxson et al., [7] reported the optimum value of SiO_2/Al_2O_3 ratio as 2.3 for metakaolin based geopolymer paste. Xu and Deventer [8] synthesised geopolymer binder from different combinations of fly ash, kaolinite and albite. They reported the optimum SiO_2/Al_2O_3 ratio for various blends of fly ash, kaolinite and albite geopolymer to be 4.2, whereas for geopolymer synthesised with only fly ash and kaolinite to be 4. For red mud and rice husk ash based geopolymer, the optimum SiO_2/Al_2O_3 ratio was reported to be 5.6, for 2–6 M alkaline solution.

Several investigations have been carried out in the past to explore the synergetic use of red mud with fly ash (FA) as a geopolymer binder. Zhang Guoping et al. [9] synthesised geopolymer paste using fly ash and red mud in the ratio of 80/20, 50/50, and 20/80. Mechanical properties of samples were determined after 28 days of curing. The strength obtained varied from 7 to 13 MPa. In another investigation using similar composition of red mud and fly ash, Jian He et al. obtained a strength of 10.5 MPa after 21 days [10]. Qingke Nie [11] studied the strength property of red mud – fly ash geopolymer added in 1:1 ratio. The 28 day strength achieved was 15.2 MPa at 2.5 molarity of NaOH that increased to 20.3 MPa at 3.5 molarity when red mud was used after desulfurization of flue gas from coal-burning power plant.

In most of the studies on red mud geopolymer, strength obtained was quite low and it took longer duration to set. Hence, the present investigation was undertaken as a feasibility study to enhance the strength of red mud based geopolymer by mechanical activation and in the process, to understand the effect of mechanical activation on the structure of red mud particles. The present study also aims at finding the optimum SiO_2/Al_2O_3 for the red mud – fly ash based geopolymer paste. Some of the prior investigations based on activation of raw material for geopolymer binder synthesis include the mechanical activation of fly ash [12] and alkali-thermal activation of phosphorous slag [13].

2. Materials and test methods

Red mud, fly ash, sodium silicate solution and NaOH flakes are the main constituents of the geopolymer paste. According to Rangan [14], the composition of aluminosilicate source material should be in a proportion to keep Si/Al ratio approximately as 2 ($SiO_2/Al_2O_3 = 4$) for cements and concretes. As red mud contains a low percentage of silica mostly being non-reactive (Tables 1 and 2) and the required SiO_2/Al_2O_3 ratio was not possible to obtain for most of the combinations of fly ash and red mud, there was a necessity to add a silica rich material, preferably an industrial waste. After some preliminary experiments, microsilica was added to geopolymer subjected to thermal curing and ground granulated blast furnace slag (GGBS) was adopted for ambient cured samples.

Table 1
Chemical composition of red mud, fly ash, GGBS and microsilica.

Oxide%	RM	FA	GGBS	MS
SiO_2	9.93	61.54	37.73	99.3
Al_2O_3	18.1	25.37	14.42	0.2
Fe_2O_3	42.9	6.73	1.11	0.09
CaO	2.3	3.1	37.34	0.1
K_2O	–	–	–	0.02
Na_2O	5.58	0.97	–	–
MgO	–	0.73	8.71	0.04
TiO_2	9.03	–	–	–
P_2O_5	0.35	–	–	–
V_2O_5	0.31	–	–	–
SO_3	–	0.62	0.39	–
L.O.I	10.5	0.39	1.41	0.01

Table 2
Properties of red mud and fly ash.

Material	Specific gravity	Surface area (m^2/kg)	Lime Reactivity (MPa)	pH	Reactive silica%
[a]URM	3.25	33,650	0.95	11.0	1.62
[b]PRM	3.2	39,400	3.61	10.8	5.12
FA	2.25	419	2.63	8.03	27.12

[a] Unprocessed red mud.
[b] Pulverised red mud.

Red mud was obtained from Ms. Hindalco, Belgaum and Class 'F' fly ash was procured from Raichur. Initially, it was in the form of boulders which was coarsely ground to breakdown the bigger lumps for carrying out the research. The ground red mud was passed through 300 μm sieve for ensuring uniformity in the test results. Further, for the tests on characterization, sampling was done by method of quartering for both unprocessed and pulverised red mud in order to ensure homogeneity. Commercially available sodium hydroxide flakes and sodium silicate solution (Na_2O = 16.64%, H_2O = 50.05%, SiO_2 = 33.31%) with 97% purity and 1.53 specific gravity were used in the study. Microsilica (MS), ground granulated blast furnace slag (GGBS) and river sand were provided by local suppliers.

The elemental composition of the dry binder materials was determined using XRF (X-ray Fluorescence) analysis. Table 1 lists the chemical composition of the constituents. Red mud mainly comprises of iron with substantial amount of alumina and silica whereas silica is the dominant constituent of fly ash. Apart from having silica and alumina, calcium is one of the main component of GGBS. Higher loss of ignition of red mud may not necessarily be due to incineration of organic carbon. Desorption of physically or chemically bound water and oxidation of iron based compounds may also be the reason for it [15]. Particle size analysis for red mud and fly ash was done with the help of laser particle size analyser, Mastersizer of Malvern Instruments having size range of 0.05 μm to 900 μm. Specific surface area of red mud was evaluated by BET (Brunauer, Emmett and Teller) test through physical adsorption of nitrogen vapors on the surface of red mud at 77 K temperature. X'Pert PRO, PANalytical X-ray Diffractometer was used for the mineralogical characterization of materials. Samples were exposed to Cu-K_α X-ray radiation and scanning was done with a speed of 1 deg/min over a range of 0 to 80° 2θ. The specimens were also subjected to microscopy analysis carried out using ESEM Quanta 200 Electron probe micro analyzer with a resolution of 3