Durability of Bricks Coated with Red mud Based Geopolymer Paste

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Abstract. The present study is undertaken to assess the durability of concrete blocks coated with red mud – fly ash based geopolymer paste. Concrete blocks of size 200 x 200 x 100mm were coated with geopolymer paste synthesized by varying the percentages of red mud and fly ash. Uncoated concrete blocks were also tested for the durability for comparison. In thermal resistance test, the blocks were subjected to 600°C for an hour whereas in acid resistance test, they were kept in 5% sulphuric acid solution for 4 weeks. The specimens were thereafter studied for surface degradation, strength loss and weight loss. Pastes with red mud percentage greater than 50% developed lot of shrinkage cracks. The blocks coated with 30% and 50% red mud paste showed better durability than the other blocks. The use of blocks coated with red mud - fly ash geopolymer paste improves the aesthetics, eliminates the use of plaster and improves the durability of the structure.

Keywords
red mud, fly ash, silica fume, alkaline liquids, acid resistance, thermal analysis, XRD

1. Introduction
Replacing natural raw materials with wastes may offer a much sought after opportunity to mitigate today’s waste management problems. Red mud is an industrial waste produced during the extraction of Alumina from Bauxite by Bayer’s process. Approximately 70 million tons of red mud is produced annually across the world [1]. In India alone around 4 million tons of red mud is generated every year [2]. It is a hazardous material due to its high alkalinity. Mostly the disposal of red mud is done by stockpiling; hence it is harmful to the people residing nearby, surrounding atmosphere, flora and fauna and water bodies [3].

Red mud is being utilized in the construction industry but not extensively. Some of its applications as enumerated by the researchers are in the field of ceramics, additive to cement, production of bricks, blocks and tiles, road and airfields bases [4-6]. Red mud can also be used in geopolymerisation technology as it contains a good amount of silica and alumina. Geopolymer binders are sustainable,
environment friendly alternative to OPC. It has been established in previous works that it is also possible to obtain a comparable strength with ambient curing [7, 8]. One of the possible applications of red mud geopolymer paste is as a coating material. In India, concrete blocks are widely used as masonry units. As it is highly porous, it allows the ingress of water laden with chemicals, thus affecting the durability of the structure. Moreover, it does not offer a pleasant aesthetics. This initiated the need to investigate the use of red mud based geopolymer paste as a coating to the concrete blocks.

2. Experimental Program

Material characterization of red mud and fly ash were carried out by conducting physical, chemical, mineralogical and morphological test. As red mud consists of very fine particles, the particle size distribution was done by wet sieve analysis. Hydrometer analysis was done for the particles passing through 75 micron sieve. Next, the compressive strength test of the paste with varying red mud percentage and varying molarity was carried out in accordance with the test procedure as specified in the IS : 1727-1967. A particular molarity was selected for the coating of blocks based on the compressive strength test results. The coated blocks were tested for acid resistance and fire resistance.

2.1. Materials

Materials utilized in the research are red mud, fly ash, microsilica, sodium hydroxide and sodium silicate solution and sulphuric acid. Ms. Hindalco, Belgaum readily extended their support and supplied red mud for the present research. Fly ash was obtained from Cashutec, an agency which promotes green building construction in Raichur, Karnataka. Alkalies and sulphuric acid were procured from Amar chemicals, Bangalore.

2.2. Material Properties

Red mud comprises of extremely fine particles which are cohesive in nature. It is finer than the fly ash particles as seen from the grading curve fig 1. The percentage of particles passing through 75 micron was 86% for red mud and 83% for fly ash. Table 1 lists the physical properties and pH of red mud and fly ash. Fineness of red mud as per Blaine’s permeability test is 766 m$^2$/kg. Its specific gravity is 3.14 and is highly alkaline with pH of 13. Red mud contains about 10% silica most of it being crystalline and non-reactive as evident from the lime reactivity test in table 1. Chemical compositions of red mud and fly ash are tabulated in table 2. Around 40% is iron, which imparts the characteristic red colour to it. XRD pattern as obtained from the mineralogical test performed on red mud shows the presence of silica, hematite, alumina, calcite and quartz, fig 2. SEM micrograph from morphological test shows red mud to be comprised of irregularly shaped fine particles forming a cluster, whereas fly ash particles are spherical in shape, fig 3.

Fly ash particles are slightly coarser than red mud and consist of around 60% silica and 25% alumina. Microsilica was added to make silica/alumina ratio for any variation greater than 1.6. Ratio of silica to alumina should fall between 1.65 and 2.8 for higher concentration of Si-O-Si bond in the geopolymer [9].

2.3. Casting and testing procedure

2.3.1. Compressive strength of paste: The paste cubes of size 50 x50 x50 mm were casted by varying different percentages of red mud (RM) along with fly ash (FA) and silica fume (SF) of different molarities starting from 6M to 12M with an increment of 2M by keeping sodium hydroxide to sodium
silicate solution ratio as 2.5. To keep the silica to alumina ratio within permissible limits, 10% microsilica was added to all the variations except RM100. The different variations of the binding materials are 100%RM + 0%FA + 0%SF: (RM100), 90%RM + 0%FA + 10%SF: (RM90), 70%RM + 20%FA + 10%SF: (RM70), 50%RM + 40%FA + 10%SF: (RM50), 30% RM + 60%FA + 10%SF: (RM30), 10%RM + 80%FA + 10%SF: (RM10), 0% RM + 90%FA + 10%SF: (RM0). Each of above combination was mixed with different molarities of NaOH solution and tested for compressive strength according to the test procedure specified in the IS: 1727-1967. A uniformly increasing loading rate of 3.5 N/mm²/min was applied using a Universal Testing Machine and a load range of 0 – 100 kN was selected.

Table 1 Physical Properties and pH of red mud and fly ash

| Sample | Fineness (m²/kg) | Specific gravity | Lime reactivity (MPa) | pH |
|--------|-----------------|------------------|----------------------|----|
| RM     | 766             | 3.14             | 0.58                 | 13 |
| FA     | 342             | 2.15             | 6.42                 | 8.24 |
Table 2 Chemical composition of red mud, fly ash and microsilica

| Sample | SiO₂ | Al₂O₃ | Fe₂O₃ | CaO | K₂O | Na₂O | MgO | TiO₂ | P₂O₅ | V₂O₅ | S | L.O.I |
|--------|------|-------|-------|-----|-----|------|-----|------|------|------|---|------|
| RM     | 9.93 | 18.1  | 42.9  | 2.3 | -   | 5.58 | -   | 9.03 | 0.35 | 0.31 | - | 10.5 |
| FA     | 61.54| 25.37 | 6.73  | 3.1 | -   | 0.97 | 0.73| -    | -    | -    | - | 0.62 |
| MS     | 99.32| 0.2   | 0.09  | 0.1 | 0.02| -    | 0.04| -    | -    | -    | - | 0.01 |

2.3.2. Preparation of geopolymer coated Concrete blocks: Based on the compression test results carried out on the red mud – fly ash based paste cubes; the molarity which gave the maximum compressive strength was selected. For the selected molarity, geopolymer paste was prepared for all variations of red mud and applied on the concrete blocks of size 200 x 200 x 100 mm of 3 mm thickness. Coating was done manually with the help of a wooden float and trowel. The coated blocks were placed inside a hot air curing chamber (HACC) cured at 60°C for 24 hours. HACC was a box of size 1.5x1.5x0.75m made up of 12 mm thick plywood. Inside face of chamber was flushed with GI sheet supported over wooden reapers of size 25mm x 50mm. The space between plywood and GI sheet was filled with a low thermal conductivity material i.e. thermocol sheets, to minimize temperature losses. Two electrically operated coiled room heaters 2000 watts each, was used as the heating source. The chamber was designed to maintain the temperature in the range of 30°C to 100°C. Tests were performed on the blocks only after seven days of applying the paste.
2.3.3. Test for Elevated Temperature: Resistance heating electric industrial furnace, designed for a maximum temperature of 1200°C was used, fig 4. Thermostats were used for the control of temperature and thermocouples were used to observe and monitor the temperature. Kanthal alloy formed of iron, chromium and aluminum was used as heating element. The concrete blocks coated with paste were kept in the furnace at temperature of 600°C at an incremental rate of 4.4°C per minute. The temperature of 600°C was sustained for 1 hour. The specimens were allowed to cool inside the furnace for two hours and were later kept at an ambient temperature to cool down further till constant temperature was reached [10]. The blocks were then observed visually and tested for loss of weight and compressive strength.

2.3.4. Acid resistance test: In acid resistance test, the paste coated blocks were immersed in a tank containing sulphuric acid of 5% concentration for a period of 4 weeks, fig 5. The blocks were then taken out from the tank and allowed to become dry at room temperatures for two days. They were brushed lightly with nylon brush to remove any loosely sticking debris. Finally the acid treated geopolymer coated blocks were inspected visually and tested for loss of weight and compressive strength. The compressive strength of bricks were tested according to the procedure laid down in IS 3495 (Part I):1992. The test results were compared with that of strength of control bricks that were initially cured in the same way as the test specimens and later kept at an ambient temperature.
3. Results and discussion

Fig. 6 and 7 show the compressive strength and weight of all the variations of geopolymer paste before the durability test. The compressive strength of the paste increases with increase in molarity of the alkaline solution from 6M to 12M. As the molarity increases, the leaching of silica and alumina accelerates, resulting in increased polymerization. The variation of strength with red mud content is observed. Initially, there is an increase in strength as the red mud percentage increases up to the addition of 30% of red mud. Thereafter, a steep fall in the strength is observed as the red mud percent exceeds 50%. The strength of the geopolymer reaches its peak when the red mud percentage is 30%. Red mud itself contributes little to amorphous silica as evident from fig 2, but the addition of red mud increases the alkalinity of the geopolymer mix. This results in faster rate of dissolution of silica and hence increased polymerisation rate. Alkalinity is one of the significant factors affecting the geopolymerisation process [11]. Shrinkage cracks occur when the percentage of red mud is more in the geopolymer mix, fig 8. The cracks increase in number and become wider when the red mud is greater than 50%. This can be one of the explanations for low strength of the geopolymer when the red mud is more than 50%. Also, the amount of inert material which does not participate in the polymerization increases as the red mud percent increases. They hinder the polymerization process resulting in a weaker matrix.

A molarity of 12M was selected for preparing the coating for the blocks. At this molarity the strength of RM0 was 31.7 Mpa and the strength of RM30 was 38 Mpa which is greater than RM0 by 6.3%.

3.1. Paste

Fig. 8 Blocks coated with a) RM0, b) RM10, c) RM30, d) RM50, e) RM70, f) RM90, g) RM100 and h) uncoated block after fire resistance test.
3.2. Thermal resistance

The coated bricks were examined visually after being subjected to 600°C for 1 hour. Minor cracks were observed for bricks coated with RM0, RM10, RM30 and RM50. The number of cracks and the crack width increased when the percentage of red mud was more than 50%. Disintegration of the coating at some places was also observed. There was bulging of the uncoated concrete block and the presence of very wide cracks was observed. Strength loss and weight loss of the coated blocks were recorded after the thermal treatment. Fig 9 and Fig 10 show the percentage strength and weight loss after fire resistivity test. Strength loss was least for blocks coated with RM30 and RM50 composition. The strength loss of 30.9% was observed for bricks coated with RM30 composition and 37.37% for RM50 coated blocks. The uncoated block showed 51.8% strength loss. Weight loss too followed more or less similar pattern. Thermal stability of the red mud and fly ash was tested. Fig. 11 and fig 12 show the thermogravimetric (TG) and differential thermal analysis (DTA) curve of red mud and fly ash respectively. Total loss of weight of red mud up to a temperature of 600°C is found to be 5.48% and 7.38% up to a temperature of 900°C. Up to 150°C, the rate of weight loss is more, which would be due to the loss of physical water. Endothermic peaks are observed up to 550°C due to the release of physical water and bound water. After that reactions are mostly exothermic and the loss in weight is predominantly due to decomposition of calcite (CaCO₃) into CaO.
3.3. Acid resistance

Visual inspection was made for the coated bricks immersed in 5% sulphuric acid solution for 30 days. There was slight disintegration of the concrete blocks without any coating. In the uncoated concrete blocks, ettringite and gypsum are formed when C₃A reacts with the sulphate ions in the presence of Ca(OH)₂ [13].

There was no sign of any surface deterioration in bricks coated with RM0, RM10, RM30 and RM50. Strength loss for RM30 was 24.53% which was the least followed by RM50 with a strength reduction of 32.33%, fig 13. Weight loss for 50% red mud was 4.38% which was least of all the variations, fig 14. Red mud has lesser calcium content than the fly ash; hence the geopolymer paste with red mud incorporated has a better resistance to sulphuric acid than RM0, the paste without any red mud. Also the alkalinity of red mud adds to its resistance against acid attack. For the paste with red mud greater than 50%, porosity increased due to the presence of shrinkage cracks and thereby exposing the concrete block for corrosion.

4. Conclusions

From the present study, following conclusions are drawn.

i. Strength of red mud paste increases with molarity from 6M to 12M.

ii. There is an increase in the strength of the geopolymer due to the addition of red mud in the geopolymer matrix up to 30%. The strength reduces significantly when the red mud percentage is more than 50%.

iii. Formation of numerous cracks occurs in the geopolymer paste upon hardening when the percentage of red mud is greater than 50% and hence cannot be used for structural applications.

iv. Thermal analysis shows that Red mud is more stable than fly ash at higher temperatures. RM30 and RM50 showed better thermal stability than other variations. Increase in red mud percentage beyond 50% causes lot of shrinkage cracks and hence show poor thermal stability.

v. Addition of red mud in the geopolymer paste increases its resistance to sulphuric acid because of lesser calcium content and greater alkalinity than fly ash. Strength loss of the block coated with fly ash geopolymer paste, RM0, was more than those of blocks coated with all the variations of red mud geopolymer paste.

vi. The coating of the concrete blocks increases its durability. Increase in red mud percentage up to 50% improved the resistance of the block to high temperature and sulphuric acid. The addition of red mud also enhances the aesthetics of the concrete block.
5. References

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