Some Studies on Sustainable Utilization of Iron Ore Tailings (IOT) as Fine Aggregates in Fly Ash Based Geopolymer Mortar

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Abstract. This study presents the sustainable utilization potential of Iron Ore Tailings (IOT) as a replacement material against natural fine aggregates in the preparation of fly ash based geopolymer mortar. Low calcium fly ash is used as the source material and a mixture of sodium hydroxide and sodium silicate is used as the alkaline activator in the mix. Systematic studies such as setting times and compressive strength of the various mixes with different alkali binder ratio’s were investigated in detail. It is to be noted that setting times of the mixes were found to be increasing with the increase in alkali binder ratio (0.4 to 0.8). Alkali binder ratio of 0.6 is found to be the optimum with respect to the compressive strength, irrespective of the type of fine aggregate. Scanning electron microscopy also reveals that microstructure of the fly ash based geopolymer mortar produced had a dense matrix with utilization of the Iron ore tailing. It can be concluded from the study that IOT is found to be a best alternative against the natural sand as a fine aggregate.

1. Introduction
Concrete is the second most consumed substance on earth after water. Estimated yearly consumption of concrete is approaching 30 billion tonnes, worldwide demand of the concrete is out passing the demand of all other materials. Due to the calcination of the raw materials and fuel combustion, the manufacture of one tonne of cement releases approximately one tonne of CO₂. Studies predicted that a 50% of increase in annual production of cement can be expected by 2050 [1]. In connection with this fly ash, which is a by-product of burning coal is available in abundance worldwide creates an opportunity to utilize this as complete replacement for OPC can be an alternative material, which lead towards the reduction of carbon emission and sustainable utilization of the resources.

On the other hand, minerals like Iron and Steel, the vital components of any national economy, with the rapid industrialisation has brought about a great deterioration in the quality of our environment. India, alone with iron ore reserves of about 19.3 billion tonnes produces a waste material referred as iron ore tailings, whose generation is estimated to be 10-25% by mass of the total iron ore mined, thus amounting to around 18 million tonnes per year [2]. Therefore, utilization of this material for making valuable products will also be a great step towards the protection of the environment.
In 1978, Davidovits succeeded in producing amorphous to semi-crystalline polymeric three-dimensional silico-aluminate material from metakaolin and sodium hydroxide at 100 - 150 °C, which he named as Geopolymers, stated that these binders can be produced by a polymeric synthesis of the alkali activated material from geological origin or from the by-product materials.

Many researchers made their effort in the production of geopolymers with materials such as metakaolin, fly ash, and ground granulated blast furnace slag or combination of any of the materials were investigated in the past as source materials for geopolymerisation [3] and the most common alkaline activator used in geopolymerisation is a combination of sodium hydroxide (NaOH) or potassium hydroxide (KOH) and sodium silicate (Na₂SiO₃) or potassium silicate (K₂SiO₃) [4-10]. The rheological properties of the fresh geopolymer mixtures are workability, setting time and engineering properties are highly influenced by a number of factors such as type of alkali activator, alkali binder ratio, curing regime and types of source material [4-9].

Hardjito et al. (2008) [8], studied on strength and setting times of low calcium fly ash based geopolymer mortar. Curing was done at 65°C, 70°C, and 80°C for 24 hours and specimens were tested for 7, 14, and 28 days compressive strength. The change in setting time of Geopolymer mortar due to different curing temperature has been determined. The higher the curing temperature, less setting time is required. Higher concentration of sodium hydroxide solution results in a higher compressive strength of geopolymer mortar. The activator to fly ash ratio, by mass of 0.40 produced the highest compressive strength. Curing temperature plays an important role in the geopolymerisation process. As the ratio of alkali to binder by mass increases, the compressive strength of geopolymer mortar decreases. Hardjito et al. (2009) [9], studied the effect of concentration of sodium hydroxide solution, alkali to binder ratio and curing temperature on the compressive strength of geopolymer mortar with natural sand as the fine aggregate. It was observed that alkaline concentration was proportionate to the compressive strength of Geopolymer mortar. The compressive strength was found to be increasing with the increase of the concentration of the sodium hydroxide. As the amount of activator content increases, and consequently increasing the activator to fly ash ratio up to 0.40; the compressive strength of geopolymer mortar increased. However, when additional activator content is added, increasing the activator to fly ash ratio to 0.45, the compressive strength decreased. Optimum dosage of the alkali binder ratio was found as the 0.4 by mass. Li et al. (2013) [10], studied the workability, compressive strength and microstructure for geopolymer pastes and mortars made of class C fly ash at mass ratios of alkali to fly ash ranging from 0.30 to 0.35. A solution of sodium hydroxide and the sodium silicate was used as the alkaline activator. Microstructural characteristics of the samples were analysed using scanning electron microscope (SEM) and it indicated that the dense structure of the geopolymer contribute to the high compressive strength.

The present study concentrates on the investigation of the influence of varying alkali to binder ratio on the setting time and strength properties of fly ash based geopolymer mortar with natural sand and the iron ore tailings as the fine aggregates under ambient curing condition and to have a detailed assessment of the ongoing geopolymerisation process, scanning electron microscopy (SEM) analysis was also carried out.

2. Materials and Methodology

The materials used in the making of concrete have equally diverse properties and behaviour. The properties of these materials were determined in the laboratory as per standard specifications, the following materials are used in our present study are Fly-Ash, Natural River Sand and the Iron Ore Tailings and a mixture of sodium hydroxide and sodium silicate is used as the alkaline activator.

2.1. Materials

2.1.1. Fly ash

The fly ash used for the present study was procured from Udupi Power plant, Karnataka. The fly ash was of Class F type as per IS 3812 (part 1)-2013, classification [11]. The fineness of fly ash was assessed using Blaine’s air permeability as per the guidelines described in IS 1727:1967 [12]. The physical properties of Fly-Ash are shown in Table 1.
Table 1. Physical Properties of Fly-Ash.

| Sl No. | Properties       | Values Obtained |
|--------|------------------|-----------------|
| 1      | Specific Gravity | 2.12            |
| 2      | Fineness         | 2161.86 cm²/g   |

2.1.2. Fine Aggregates
Iron ore tailings used for this study was provided by KIOCL Ltd, Mangalore, Karnataka, India, shown in Figure 1. Locally available natural river sand and the iron ore tailings were used as the fine aggregates for the present study. Particle size distribution of fine aggregates are presented in the Figure 2. The physical properties of fine aggregates were determined as per IS 2386-1963 (Part I) [13] are presented in Table 2.

![Figure 1. Iron Ore Tailings Sample.](image)

Table 2. Physical properties of fine aggregates.

| Sl. No | Properties       | Sand            | IOT            |
|--------|------------------|-----------------|----------------|
| 1      | Specific gravity | 2.56            | 2.83           |
| 2      | Bulk density     | Loose 1520 kg/m³| 1580 kg/m³    |
|        |                  | Compacted 1760 kg/m³| 1830 kg/m³ | |
| 3      | Moisture Content | NIL             | NIL            |
| 4      | Water Absorption | 1%              | 4%             |
| 5      | Zone             | Zone 1          | Zone III      |

![Figure 2. Particle Size Distribution of Fine Aggregates.](image)
2.1.3. Alkaline Activator
Laboratory grade sodium hydroxide (NaOH) pellets of purity 97% and sodium silicate solution (Na₂SiO₃) with SiO₂/Na₂O = 3.3 (8.0% Na₂O, 26.5% SiO₂, 65.5% H₂O by mass) were used to prepare the alkaline solution.

2.2. Mix Proportions
Fly ash and fine aggregates were mixed at a ratio of 1:3. Alkaline activators were made by using ten moles per liter (10M) solution of sodium hydroxide and sodium silicate solution at a ratio of 1:2.5. Alkali to fly ash ratio of 0.4, 0.6 and 0.8 were used respectively in three mixes. Mix designations used for this study is tabulated in Table 3.

| Table 3. Mix designation of the mortar mixes. |
|---------------------------------------------|
| Alkali Fly ash ratio | Natural River Sand | Iron ore Tailings |
| 0.4               | RS1               | IOT1           |
| 0.6               | RS2               | IOT2           |
| 0.8               | RS3               | IOT3           |

Note: Mixes with alkali to fly ash ratios varying in an order of 0.4, 0.6 and 0.8 were represented 1, 2, and 3 respectively. Based on fine aggregates used, mixes with natural river sand is represented as ‘RS’ and mixes with iron ore tailings is represented as ‘IOT’.

2.3. Preparation of solution and mortar specimens
The alkali solution is prepared with NaOH, Na₂SiO₃ and water in required mix proportions. The weighted NaOH pellets are dissolved in weighed amount of water to form a NaOH solution followed by thorough mixing of weighed Na₂SiO₃ solution into it. The entire solution is finally transferred into a closed container and allowed to cool for 24 hours before using the solution in the mix. All the ingredients are weighed and then batched according to their respective proportions. The fine aggregates used for this study are dried in an oven for at least 24 hours and it was made sure that there is no moisture content present. Hand mixing is adopted for the production of the mortar. The mixing is done over a non-absorbent mixing plate. Initially, fine aggregates and fly ash is mixed according to the proportion for about two minutes followed by gradual addition of alkaline solution to it. Once the mortar is ready, it is filled into the respective moulds in three layers by carefully compacting each layer using a tamping rod in order to achieve full compaction. All the ready specimens are kept under the ambient conditions. Demoulding of all the specimens were done after final setting of the mortar and they are kept for curing under ambient condition until it is tested for the compressive strength.

2.4. Tests on Mortar
In the present study, to evaluate the fresh and hardened properties of the mortar, the setting times and compressive test were carried out and details of the tests are described in the following section.

2.4.1. Setting Times
Finding out of the setting times of the geopolymer will help to get an idea about in-situ usability of the geopolymer materials. The test is performed in accordance to the IS 8142:1976 [14]. In this test both initial and final setting time of geopolymer mortar is found out.

2.4.2. Compressive Strength
The compressive strength test was carried out in accordance to IS 4031:1988-Part 6 [15]. The cubes were tested at different ages such as 7-days, 14-days and 28-days.

2.4.3. Scanning Electron Microscopy (SEM)
Samples for the scanning electron microscopy were collected from the core portion of the specimen during compressive strength. The samples are analysed for the degree of geopolymerization.

3. Results and Discussions

3.1. Setting Time Test
The Initial and Final Setting time test are conducted as described in the section 2.4 and test results are presented in Figure 3. From the Figure, it can observed that the both initial and final setting time largely depends on the alkali fly ash ratio. Initial setting time is found to be ranging from 18 hours to 53.45 hours for natural sand samples and 20.52 to 40.12 hours for IOT samples. Final setting time is found to be ranging from 33.30 hours to 78.02 hours for natural sand samples and 49.70 to 64.15 hours for IOT samples. General trend in setting time shows that in lower alkali fly ash ratios 0.4, geopolymer mortar with natural sand as the fine aggregate have lower setting time. As the alkali fly ash ratio increases (0.6 and 0.8) the geopolymer mortar with IOT set faster comparing to that of natural river sand.

![Figure 3. Comparison of Initial and Final Setting Time.](image)

3.2. Compressive Strength
The compressive strength of geopolymer mortar with river sand and iron ore tailings as fine aggregate is presented in Figure 4. It is observed from the test results that, 7th and 14th day strength attained for the natural river sand samples were 1.45 MPa and 3.5 MPa respectively for an alkali binder ratio of 0.4 and maximum 28th day was 5.87 MPa for an alkali binder ratio of 0.6. Similarly, maximum 7th, 14th and 28th day strength attained for iron ore tailings samples were 1.80, 4.55 and 8.27 MPa respectively for an alkali binder ratio of 0.6.
The test results indicated that variation of the alkali binder ratio has greater influence on the compressive strength of both natural sand and the iron ore tailing geopolymer mortar mixes. From the above graph, it is evident that all the mixes provided their highest compressive strength at alkali binder ratio of 0.6 irrespective of the fine aggregates. All the mixes provided their lowest compressive strength at the alkali binder ratio of 0.8.

4. Scanning Electron Microscopy Study
Scanning Electron Microscopy (SEM) is done for all the 28\textsuperscript{th} day samples for the three different alkali binder ratios. Samples were dried and vacuumed prior to the test. SEM images were taken for all samples with uniform magnification are presented Figure 5 and Figure 6.

![Figure 4. Compressive strength of geopolymer mortar with varying alkali binder ratio.](image)

![Figure 5. SEM images of (A) RS1 (B) RS2 (C) RS3.](image)
Figure 6. SEM images of (A) IOT1 (B) IOT2 (C) IOT3.

Scanning electron microscopy helped to identify the microstructure of the geopolymer mortar. From figure, it can be observed that, the unreacted and partially reacted fly ash can be observed in the form of micro spheres and found to be less dense. Samples with higher alkali binder ratio have denser matrix comparing to that of lower alkali binder ratio. The samples which has denser matrix can be recognized as the sample with higher extend of the geopolymerisation.

5. Conclusions

Based upon on the results obtained and the observations during the experimental investigations, the following conclusions can be drawn:

- The use of iron ore tailings in the production of geopolymer mortar the setting time has reduced.
- Compressive strength of the Geopolymer mortar with natural sand and iron ore tailings is ranges from 2.9 to 4.9 MPa and 3.47 to 8.27 MPa respectively.
- Irrespective of the aggregates in geopolymer mortar mix with alkali fly ash ratio of 0.6 is found to be optimum alkali binder ratio based on the compressive strength.
- SEM results showed that use iron ore tailings increase the density of the matrix, along with compressive strength increment as compared to mix with natural river sand.

From the present study, it can be understood that utilization of iron tailings in the production of geopolymer mortar significantly improves the setting times and the compressive strength.

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