

# Performance of Fly Ash and Copper Slag based Geopolymer Concrete

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## Abstract

**Background/Objectives:** Recycling and utilization of industrial by-products in the construction industry significantly complements the sustainable technology and development. Geopolymer is a new generation binder material which forms an eco-friendly alternative for the conventional Portland cement binders. **Methods/Statistical analysis:** This paper aims to analyse the performance of copper slag as an alternative for fine aggregate in geopolymer concrete. The combination of sodium hydroxide solution of 14 moles concentration and sodium silicate are used as an alkaline activator. The ratio between alkaline liquid and fly ash ratio is 0.4 for all the mixtures. The oven temperature at 60°C for a period of 24 hours and ambient curing conditions are considered. Each specimen tested on the compressive strength, water absorption and density of the concrete. **Findings:** The test results show that the compressive strength increases with the increase of the copper slag content and a marginal change is observed with the decrease in strength gain as there is increase in the copper slag content. **Application/Improvements:** These results, thereby substantiates the fact that the copper slag is an alternative material for sand.

**Keywords:** Compressive Strength, Copper Slag, Fly Ash, Geopolymer, Sodium Hydroxide, Sodium Silicate

## 1. Introduction

The production of cement consumes natural resources and huge amount of energy is spent on the manufacturing process, and it also releases a large quantity of greenhouse gases into the atmosphere<sup>1</sup>. Quarrying of coarse aggregates and mining of sand causes environmental impact. In addition to this, industrial by-products like fly ash, ground granulated blast furnace slag, steel slag, copper slag generated from various industries are disposed as landfills and into marine that causes environmental degradation<sup>2</sup>. The above facts motivates the researchers to develop of a new alternative binding materials for construction, which is eco-friendly and that leads to the new cement less binder called geopolymers, an alternative cementitious material prepared from the combination of silica-alumina rich source material with alkali solution. Geopolymers, developed by Joseph Davidovits are amorphous aluminosilicate materials,

synthesized at slightly elevated temperature or ambient condition<sup>3</sup>.

Geopolymer concrete has many advantages over the normal concrete as it is stronger and durable than Ordinary Portland Cement (OPC) concrete. It has a better spalling resistance to rapidly rising temperature exposure as compared to the OPC concrete<sup>4</sup>. It has the capability of utilizing industrial by-products for its manufacturing process. The silica and alumina components of the source material which are dissolved by the alkaline solution, helps in hardening of the geopolymer concrete. During the geopolymerization, water is gradually split out and tetrahedral units are alternatively linked to polymeric precursors by sharing oxygen atoms between two tetrahedral units and hence forming amorphous geopolymers<sup>5</sup>.

Curing temperature and durations are the most important factors which influence the strength of the geopolymer concrete. As the presence of sodium silicate in gel form delays the setting time of the concrete at

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ambient temperature, to overcome this problem, concrete is cured at 60°C for about 24 hours to 48 hours<sup>6</sup>. The effect of curing time on the compressive strength of the geopolymer concrete cannot be generalized within 5 to 6 hours. However, 21 hours of curing is observed to be very effective for the development of the compressive strength beyond which there is no considerable increase in the strength of concrete<sup>7</sup>. The ratio between alkaline liquid to ash influences the compressive strength and workability of the geopolymer concrete<sup>8</sup>.

The present study investigates the possibilities of using copper slag as a fine aggregate in geopolymer concrete in ambient curing and hot air oven curing condition has been examined. The strength development in the concrete is studied, with different percentage of copper slag added as a partial replacement of the fine aggregate in the mix.

## 2. Materials and Methods

### 2.1 Fly Ash

Fly ash is the most commonly used industrial by-product in which it has a high amount of silica and alumina. The same were collected from Tuticorin thermal power station, Tamil Nadu, India. The collected fly ash confirms the low calcium fly ash category and specific gravity of the fly ash is tested as per IS 1727-1697. The elemental composition by EDAX analysis is shown in the Table 1 and Scanning Electron Microscope (SEM) analysis showed that the fly ash consists of glassy, spherical sphere of smooth surface<sup>9</sup>.

### 2.2 Coarse and Fine Aggregates

The hard broken granite stone of 12 mm size having a specific gravity of 2.76 is used as a coarse aggregate. The

**Table 1.** Elemental composition of fly ash

El	AN	Series	Unn. (wt %)	C norm. (wt %)	C Atom (at %)	Sigma (wt%)
O	8	K-series	61.06	56.40	69.70	7.80
Si	14	K-series	26.16	24.17	17.01	1.20
Al	13	K-series	17.86	16.50	12.09	0.93
Fe	26	K-series	1.61	1.48	0.53	0.08
K	19	K-series	0.71	0.66	0.33	0.06
Ti	22	K-series	0.57	0.52	0.22	0.05
Ca	20	K-series	0.29	0.27	0.13	0.04

locally available river sand and copper slag are used as fine. The specific gravity, water absorption test for copper slag and sand are determined and tabulated in Table 2.

The sieve analysis is done for sand and copper slag and results show that both conforming to zone – II, as per IS: 383 – 1970 and the gradation is presented in the Table 3.

The copper slag is procured from Sterlite Industries Ltd, Tuticorin, Tamil Nadu, India for the replacement of sand in geopolymer concrete. The slag appears as black glassy particle and granular. The particle sizes are similar to the sand. The elemental composition of the copper slag and sand from EDAX analysis is presented in Table 4 and Table 5 and the microstructure of the, sand and copper slag is presented in the Figure 1.

### 2.3 Alkaline Activator

The alkaline activator used in this study is the combination of sodium hydroxide and sodium silicate in the ratio

**Table 2.** Physical properties of copper slag and sand

Physical properties	Copper Slag	Sand
Particle Shape	Irregular	Irregular
Specific Gravity	3.90	2.52
Water Absorption	0.23%	0.94%
Fineness Modulus	2.83	2.57

**Table 3.** Grading of fine aggregates

IS Sieve Size (mm)	Sand (% passing)	Copper Slag (% passing)
4.75	100	99.9
2.36	99	98.5
1.18	95.3	70.2
0.6	76.1	42.5
0.3	52.5	5.3
0.15	16.7	0.2

**Table 4.** Elemental composition of copper slag

El	AN	Series	Unn. (wt %)	C norm. (wt %)	C Atom (at %)	Sigma (wt%)
Si	14	K-series	30.88	57.43	61.92	1.41
Al	13	K-series	12.17	22.64	25.41	0.64
Fe	26	K-series	6.33	11.77	6.38	0.20
K	19	K-series	3.36	6.25	4.84	0.14
Ca	20	K-series	1.03	1.91	1.44	0.06

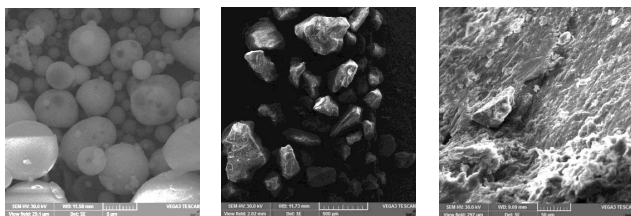
1:2.5<sup>10</sup>. Sodium hydroxide solution of 14M is prepared by dissolving the sodium hydroxide flakes in distilled water one day prior to use<sup>11</sup>. The sodium silicate is supplied by the local manufacturer having Na<sub>2</sub> to SiO<sub>2</sub> ratio of 2:1 is used in this work.

## 2.4 Mix Proportion

The mix proportion for the study is carried out by keeping the quantity of fly ash and coarse aggregate as constant. The ratio between sodium hydroxide to sodium silicate is taken as 1:2.5 and the ratio between alkaline liquid to fly ash is kept as 0.4. A dosage 4% of the super plasticiser Conplast SP430 (Sulphonated naphthalene formaldehyde condensate) conforming to IS: 9103-1999 and ASTM C-494 is added to the mix, to improve the workability of the concrete. The sand is replaced with copper slag by its weight with an increment of 10% in each mix and the mix proportion is presented in Table 6.

**Table 5.** Elemental composition of sand

El	AN	Series	Unn. (wt %)	C norm. (wt %)	C Atom (at %)	Sigma (wt%)
O	8	K-series	24.42	60.71	64.85	7.80
Si	14	K-series	7.83	19.46	11.84	0.38
Al	13	K-series	0.62	1.53	0.97	0.06
Fe	26	K-series	0.89	2.22	0.68	0.05
Mg	12	K-series	0.17	0.42	0.29	0.04
K	19	K-series	0.23	0.58	0.25	0.04
Ca	20	K-series	0.14	0.36	0.15	0.03



**Figure 1.** Microstructure of fly ash, sand and copper slag.

**Table 6.** Mix proportion

Mix ID	M1	M2	M3	M4	M5	M6	M7	M8	M9	M10	M11
Materials	0 % Kg/m <sup>3</sup>	10% Kg/m <sup>3</sup>	20% Kg/m <sup>3</sup>	30% Kg/m <sup>3</sup>	40% Kg/m <sup>3</sup>	50% Kg/m <sup>3</sup>	60% Kg/m <sup>3</sup>	70% Kg/m <sup>3</sup>	80% Kg/m <sup>3</sup>	90% Kg/m <sup>3</sup>	100% Kg/m <sup>3</sup>
Copper Slag	0	61.3	112.6	183.9	245.2	306.5	367.8	429.1	490.4	551.7	613
Fine Aggregate	613	551.7	490.4	429.1	367.8	306.5	245.2	183.9	122.6	61.3	0
NaOH	53					Fly ash – 460 Kg/m <sup>3</sup>					
Na <sub>2</sub> SiO <sub>3</sub>	132.5					Coarse Aggregate – 1139 Kg/m <sup>3</sup>					

## 2.5 Specimen Preparation

The prepared sodium hydroxide and the sodium silicate are premixed. The fly ash and dry aggregates are mixed in a pan mixture for about three minutes. The premixed alkaline activator along with super plasticizer is added to the dry mixed materials and then mixed for about five minutes and then transferred to the mould in three layers, each layer is compacted by table vibrator for 10 seconds to eliminate air voids and the surface is levelled. Then the specimens are sealed off with poly vinyl sheet, to prevent the loss of water due to evaporation<sup>12</sup>.

The specimens are left in the room temperature for a day as a rest period<sup>13</sup>. After completion of rest period the specimens are demoulded and cured at 60 °C for 24 hours and also remaining cube specimens are left to cure at ambient condition.

## 3. Results and Discussion

The appearance of the copper slag looks black and glassy with a specific gravity of 3.90 which is higher than that of the sand 2.52 (Figure 2). The measured water absorption of the copper slag is 0.23% as it is lesser compared the sand of 0.94%. Figure 2 shows the sieve analysis report of sand and copper slag and it show that they both conforming to zone – II, as per IS: 383 – 1970 and the gradation is presented in the Table 3.

An elemental analysis performed for the copper slag, sand and fly ash are present in the above table shows that, the presence of Si in copper slag is higher as compared to sand. Also it is noted that the presence of Al in copper slag is higher as compared to both fly ash and sand. The presence of these Si and Al in copper slag may leads to the improvement of the strength in the concrete as the percentage replacement of copper slag increases.

The average slump value for all the mixes is in the range of 225 – 270 mm and it shows a high workability due to addition of the super plasticizer. Without super

plasticizer the mixes are stiff and cohesive due to lack of water content in the concrete.

The compressive strength of the oven cured and ambient cured specimens at 3rd, 7th and 28th days of testing are presented in Figure 3 and Figure 4. It is observed that, as the percentage of copper slag increases the compressive strength also increases. The maximum compressive strength of 58.95Mpa is obtained for the specimen cured

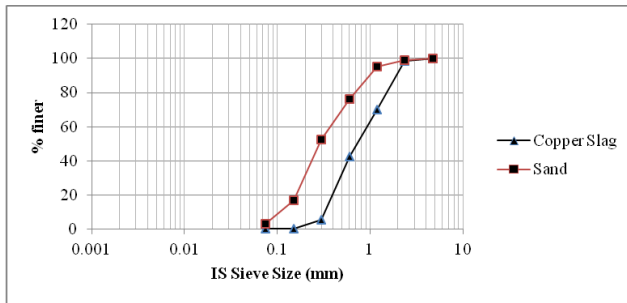


Figure 2. Sieve analysis of sand copper slag

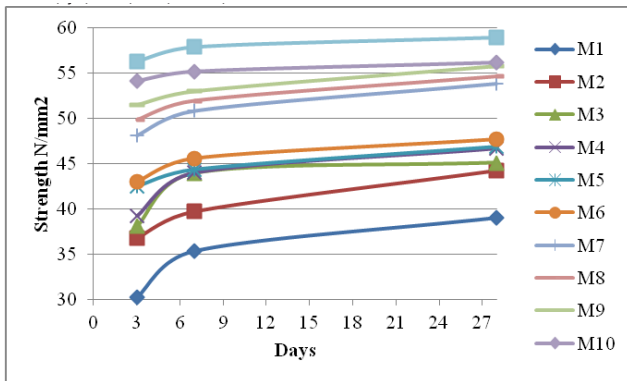


Figure 3. Compressive strength of hot air cured geopolymer concrete.

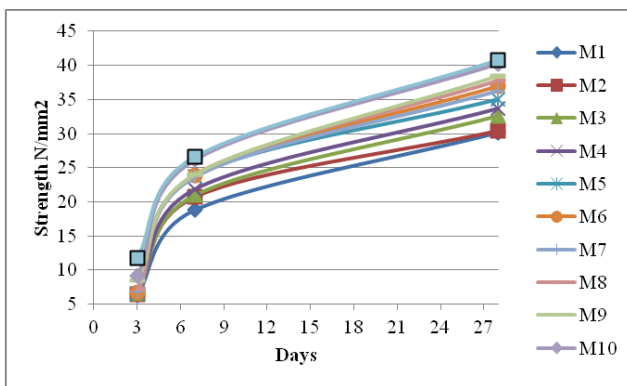


Figure 4. Compressive strength of ambient cured geopolymer concrete.

at 60 °C for 24 hours heating whereas in ambient curing condition 40.78Mpa for the mix M11 having 100% replacement of copper slag, while control mix M1 with sand as fine aggregate achieved a compressive strength of 39.08Mpa and 30.08Mpa. The strength of geopolymer concrete having replacement of sand with copper slag shows the similar strength behavior<sup>14</sup>. When GGBS used as a binder in the replacement of copper slag in place of sand shows that marginal change in the compressive strength<sup>15</sup>. The geopolymer activated by the sodium hydroxide and sodium silicate in the concrete developed a higher compressive strength<sup>16</sup>. It is found that the amount of soluble silica in the activator solution influences the development of the compressive strength<sup>17</sup>. The maximum compressive strength in geopolymer concrete is due to the oven curing resulting with low porosity and makes the specimen denser material<sup>18</sup>.

It is observed by comparing the mixes with one another for the strength gain from third day to twenty eight day, shows the mix M1 has higher strength gain of 1.29 times in oven curing condition, while for ambient cured condition M6 mix has 5.50 times strength gain. It is observed that an average 95% of strength is achieved in 7 days if concrete is cured in oven and 55% in ambient curing as compared with 28th day results. As comparing the 28th day results with M1 and M11 mix, it is noted that the M11 mix of oven cured concrete has 1.5 times and ambient cured concrete has 1.35 times higher than the M1 mix. The reaction kinetics is higher in the oven cured concrete resulting in maximum strength at early ages, while it is lower in ambient cured concrete resulting in lower compressive strength at the initial stages. The mix M11 has lower strength gain in both ambient and hot air cured condition, even though it exhibits lower strength gain the compressive strength reaches the maximum compared to the other mixes both oven and ambient curing condition. It is observed as the percentage of replacement of copper slag increases the strength gain decreases in oven cured concrete specimens, while ambient cured specimens the strength gain is increasing upto M6 mix after that it starts to reduce. The Fe<sub>2</sub>O<sub>3</sub> in the copper slag may retard the gain in strength of geopolymer concrete<sup>19</sup>.

The density of geopolymer concrete of the mixes at 28 days ranges from 2398 kg/m<sup>3</sup> to 2431 kg/m<sup>3</sup> for hot air cured and 2361 kg/m<sup>3</sup> to 2387 kg/m<sup>3</sup> for ambient cured concrete is presented in the Figure 5. It is noted that the copper slag replacement increases, the density of the concrete also increases, due to high specific gravity of copper



slag<sup>20</sup>. The density of geopolymer concrete is close to a density of ordinary Portland concrete in practice, which varies in the range 2200kg/m<sup>3</sup>–2600 kg/m<sup>3</sup>. The density of the hot air cured concrete is slightly higher than the ambient cured concrete, this may due to better geopolymerization process resulting in lower porosity<sup>18</sup>.

Figure 6 shows the 28-days water absorption of geopolymer concrete, it is observed that the percentage of water absorption are reduced as the copper slag content in concrete increased in both ambient and hot air cured concrete. It is also noted that water absorption percentage is much higher in ambient cured condition compared to hot air cured concrete this is because of lower adsorption of sodium silicate on the surface of the source material and it creates macro-cavities which increase the porosity of the ambient cured concrete resulting in higher water absorption<sup>18</sup>.

The SEM images presented in the Figure 7 determines the microstructures of the geopolymer concrete specimen which has homogenous matrix, also unreacted fly ash and partially reacted fly ash in the specimen surface. The micro cracks and pores are also seen on the surface of the concrete might be due to the thermal movement, and a dissolution of fly ash by alkalis observed over the partially reacted fly ash covered with the reaction products<sup>21,22</sup>.

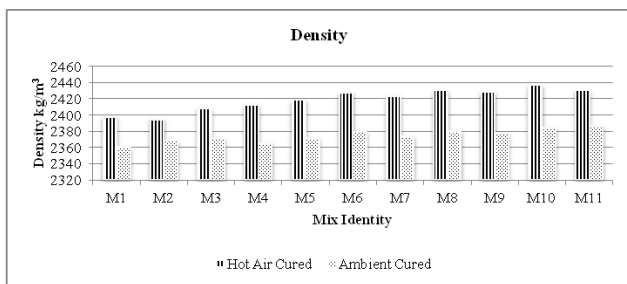


Figure 5. Density of Geopolymer concrete..

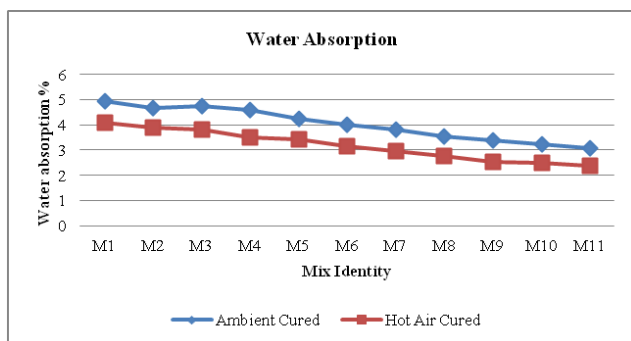


Figure 6. Water absorption.

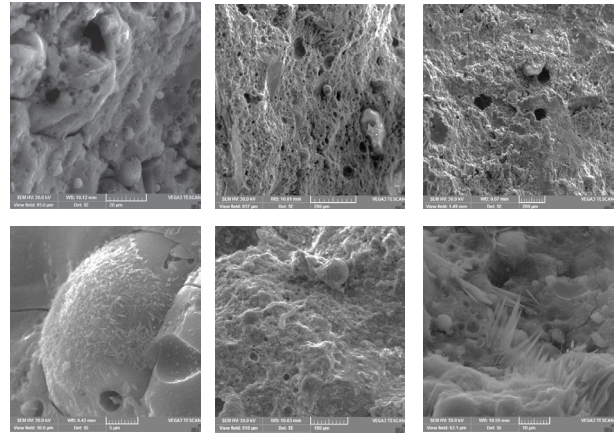


Figure 7. Microstructure of geopolymer concrete.

## 4. Conclusion

The copper slag percentages greatly influences the strength of the geopolymer concrete. The strength of the geopolymer concrete having copper slag as a fine aggregate is compared with control concrete found to be 1.35 and 1.51 times increase in strength, when cured it in ambient and oven curing. The maximum compressive strength of oven cured geopolymer concrete is found to be 58.95 Mpa whereas in ambient cured the compressive strength is reduced to 40.78 Mpa. It is observed that the percentage of the copper slag has been increased in the geopolymer concrete and the compressive strength also be increased. There is a marginal variation found in the density of the concrete when cured in oven and ambient condition. The water absorption of the oven cured geopolymer concrete is found to be minimum when compared with the ambient curing condition. The microstructure of geopolymer concrete shows the homogeneity of the geopolymer concrete and dissolution of fly ash is also found on the specimen surfaces.

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