Abstract: Concrete being the most widely and extensively used material in the construction industry, has application in wide- range of structures. Structures such as chimneys, reactors and furnaces are subjected to high temperatures. However, most of the structures need to withstand high temperatures under circumstances of fire breakouts and accidents. The present study is focused on the study of Alkali Activated Slag Concrete (AASC) mixes incorporating Copper Slag (CS) as fine aggregate replacement (0%, 25%, 50%, 75% and 100%) subjected to elevated temperature. AASC specimens with/without CS are prepared and exposed to elevated temperatures at 200, 400, 600 and 800°C in an electric furnace. The specimens are exposed for duration of 4 hours after the oven reached the required peak temperature and then immediately were allowed to cool to room temperature in ambient condition. Concrete specimens were tested for ultrasonic pulse velocity (UPV), residual compressive and split tensile strength. The results indicated that relative compressive strengths of AASCs with sand/CS were higher than that of OPC based control concrete up to 600°C. The strength loss at 800°C for AASCs with/without CS was found to be severe. The splitting tensile strength of both OPC and AASCs with sand/CS was found to be more sensitive to high temperatures as compared to the compressive strength. It may be concluded that the AASC mixes with sand/CS significantly promotes the residual mechanical properties up to a temperature of 600°C. However after 600°C, the replacement of sand with CS reduces the resistance of AASC mixes to elevated temperature.

Keywords: Alkali Activated Slag Concrete, Copper Slag, Elevated Temperature, Residual Strength, UPV

1. Introduction

From a decade, awareness on the utilization of industrial byproducts and wastes for concrete production is increasing. Amongst all alkali activated slag or fly ash has been the subject of great interest due to their outstanding properties [1–5]. Ground Granulated Blast furnace slag (GGBFS) activated by means of alkalis like carbonate, hydroxide, and silicates of sodium or potassium. Since alkali activated materials do not have Portland cement, they display dissimilar properties compared to Ordinary Portland Cement Concrete (OPCC), such as greater resistance to acid and sulphate attack [6, 7], and high temperatures [8].

Copper slag (CS) is a derivative obtained in the course of the manufacturing and decontaminating of copper. The manufacture of one ton of copper nearly generates 2.2–3 tons of CS as a by-product [9]. Even in India, about 2.5 million tons of copper slag is generated annually, which is conventionally disposed of as an industrial waste. However, it can be gainfully utilized in concrete mixes as a partial replacement to sand [10].

Studies have indicated that High Performance Concrete (HPC) mixes made with CS, as a replacement to river sand, exhibit improved workability; their 28-day compressive strengths increased up to 50% replacement (by weight) of sand with CS beyond which the strengths tended to decline [10]; At constant workability, the compressive strengths of the mixes were amplified [11]. The high density and glassy surface with shape ‘rough’ of CS may often lead to undesirable effects, like excessive bleeding leading to weaker top surface layers and the formation of water pockets below particles of coarse aggregate. Such effects are also observed to increase with increased content of CS as a fine aggregate. However, the amount of bleeding can be regulated by limiting the copper slag content to 40%, or by adding fines [12-14]. Increased presence of particles finer than 0.15mm in copper slag is shown to cause delays in the setting time of concrete mixes, without affecting their durability properties [9]. The shrinkage characteristics of concrete mixes containing copper slag fine aggregate are found to be similar to, or quite often better than those of corresponding control concrete mixes without copper slag [14-16].

In contrast to OPCC, alkali-activated materials after exposure to elevated temperatures showed better performance [17–21]. Several studies have reported the properties AASC mixes with dissimilar kinds of aggregates [22–24]; however, the use of Copper Slag...
(CS) as fine aggregate in alkali activated slag concrete (AASC) mixes have not yet been studied.

Rashad et al. [18] compared the residual strengths of AAS pastes using sodium sulphate as activator subjected elevated temperatures on with those of OPC. According to them the relative strengths of AAS pastes, up to 600 °C, were higher than those of OPC paste. Guerrieri et. al. [24] activated AASC mixes with powdered sodium metasilicate and hydrated lime and compared the results with OPC and blended GGBFS/cement (50/50) concrete after exposure to elevated temperature upto 1200 °C. They observed that between 400 °C and 1200°C, the residual strengths of AASCs were comparable to 50/50 blended GGBFS/cement concrete mixes while higher than OPCCs. The study on the behavior of AAS subjected to elevated temperatures was carried out few more researchers [26, 27].

Guerrieri and Sanjayan [27] studied the behavior of alkali-activated GGBS/fly ash pastes exposed to elevated temperature up to 800 °C, for 1 h. It was observed that the samples having lower initial strengths (7.6 MPa) exhibited an increase in residual strength up to 90% gain. Concrete mixes with initial strengths around 28 MPa reported decrease in the residual strength by around 70%, while samples with initial strengths around 83 MPa displayed residual strength loss by 90% after exposure to 800 °C.

Indeed, there is no available research on the performance of AASC mixes subjected to elevated temperature with CS as fine aggregate. Hence the resent study is focused to study to the behavior of AASC mixes with CS after exposure to elevated temperatures. This present study presents the residual strength properties of AASC mixes with CS as fine aggregate at replacement levels of 0% to 100% (at an increment level of 25%) by volume, after exposure to elevated temperatures ranging from 200 °C to 800 °C at an increment of 200 °C.

2. Experimental Program

2.1. Materials

2.1.1. Cement

OPC conforming to IS 8112 – 2013, was used for preparing reference concrete mix. The cement was having a fineness of about 340 m²/kg (Blaine) and specific gravity of 3.14. Compressive strengths of cement at 7 and 28 days were 40.5 and 54.0 MPa, respectively.

2.1.2. GGBFS

In the present investigation, Ground Granulated Blast Furnace Slag (GGBFS) conforming to IS: 12089 – 1987 was used as the starting material to produce alkali-activated slag concrete mixes. The same was obtained from M/S Jindal Steel Works, Bellary, India. The slag has a fineness of about 370 m²/kg (Blaine) and specific gravity of 2.9. The chemical composition of GGBFS used is shown in Table 1. With a computed basicity coefficient $K_b = (CaO+MgO)/(SiO_2+Al_2O_3)$ of 0.88, it can be classified as an ‘acidic slag’.

2.1.3. Alkali solution

Commercial grade Sodium Hydroxide (NaOH) flakes (97% purity) and Liquid Sodium Silicate (LSS) (14.7% Na₂O + 32.8% SiO₂ + 52.5% H₂O by mass, and density = 1570 kg/m³), were used in the preparation of alkali activator solution. The alkali activator solution used herein is a combination of LSS and sodium hydroxide flakes, formulated to provide a SiO$_2$/Na$_2$O ratio (module, Ms) of 1.25 and Na₂O concentration of 4%. The desired Ms was obtained by adding NaOH to appropriate amount of LSS. Tap water available in the institute laboratory was then added to bring the total water to binder ratio to 0.4, for all AASC mixes, taking into account the amount of water readily present in the LSS. Alkali solution was immediately transferred to a container with air tight cap, left for at least 24 hours to cool, before using in a concrete mix.

2.1.4. Aggregates

Crushed granite chips of maximum aggregate size (MAS) of 20 mm were used as coarse aggregate. The specific gravity and water absorption of the coarse aggregate were 2.69 and 0.4%, respectively. The specific gravity, water absorption and fineness modulus (FM) of river sand used were 2.64, 1.50% and 2.58, respectively. The chemical composition of CS used in this study is shown in Table 1. It was observed that the CS, as-received from the industry consisted of 3.3% friable particles when tested as per ASTM C 142.

The specific gravity, water absorption and fineness modulus (FM) of resulting CS used were 3.6, 0.50% and 2.61, respectively. Indian Standard IS: 383–1970 classifies, the fine aggregate into four different zones on the basis of grading. The fine aggregate grading can vary between a ‘coarse’ for zone I to ‘fine’ for zone IV. The results of sieve-analysis of both sand and CS used as fine aggregates here in this study are compared with the four suggested standard grading zones shown in Table 2. The results show that both sand and CS conform to Zone II, as per IS: 383 – 1970.

**Table 1 Chemical composition of GGBS and Copper Slag (wt% by weight)**

<table>
<thead>
<tr>
<th>Constituent</th>
<th>GGBS</th>
<th>Copper Slag</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaO</td>
<td>33.77</td>
<td>0.84</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>16.7</td>
<td>6.06</td>
</tr>
</tbody>
</table>
The total volumes of aggregates were appropriately varied in these mixes. The alkaline activator was incorporated in the mixes, at a constant dosage of activation of 4% Na₂O with modulus Ms=1.25. With the known properties of all ingredients, AASC mixtures containing 25%, 50%, 75%, and 100% of CS as replacement for river sand as fine aggregate were prepared. The total volume of fine aggregate comprising of sand/CS was kept constant in all the AASC mixtures. The mass fraction CS used were more than that of sand of equal volume at each replacement level due to much higher density of the CS. Details of mix proportions of all the trial mixes tested herein are presented in Table 3. AASC mixes prepared with sand/CS showed no indications of segregation or bleeding.

2.2.2. Sample Preparation, Curing and Testing

Concrete cube samples of 100x100x100 mm size were prepared with each of the above mixes, to determine their compressive and split tensile strength. Concrete specimens were demoulded after 24 hours; OPC concrete cubes were cured in water, while alkali-activated slag concretes were kept at ambient laboratory condition having 85±10% relative humidity at 27±3°C until testing in order to prevent leaching. For each mix, six specimens were tested using calibrated testing machines. Cube compressive tests, were conducted as per the guidelines in IS 516:1959, while split tensile strength tests on cube specimens were performed as per provisions of IS 5816:1999. The Ultrasonic Pulse Velocity (UPV) test was performed on cubes of 100 mm size before and after exposure to high temperature according to ASTM C 597-09.

The cube samples from every mix were kept in temperature controlled furnace and were subjected to heating from room temperature (27 °C) to higher elevated temperatures of 200, 400, 600 and 800 °C at a rate of 7°C/min. The specimens are exposed for duration of 4 hours after the oven reached the required peak temperature, allowed to cool to room temperature gradually inside the furnace, then specimens were tested for ultrasonic pulse velocity (UPV), residual compressive and split tensile strength.

### Table 3 Details of mix design (all ingredients are in kg/m³)

<table>
<thead>
<tr>
<th>Mix ID</th>
<th>OPC</th>
<th>GGBFS</th>
<th>Fine Aggregates</th>
<th>Coarse Aggregate</th>
<th>LSS</th>
<th>NaOH</th>
<th>Added water</th>
<th>Total water</th>
<th>SP</th>
<th>Total quantity</th>
</tr>
</thead>
<tbody>
<tr>
<td>OPCC</td>
<td>440</td>
<td>-</td>
<td>650</td>
<td>-</td>
<td>178</td>
<td>-</td>
<td>140.8</td>
<td>176</td>
<td>2.64</td>
<td>2445</td>
</tr>
<tr>
<td>ACS-0</td>
<td>-</td>
<td>440</td>
<td>630</td>
<td>-</td>
<td>1141</td>
<td>10</td>
<td>140.8</td>
<td>176</td>
<td>-</td>
<td>2429</td>
</tr>
<tr>
<td>ACS-25</td>
<td>-</td>
<td>440</td>
<td>473</td>
<td>216</td>
<td>1141</td>
<td>10</td>
<td>140.8</td>
<td>176</td>
<td>-</td>
<td>2488</td>
</tr>
<tr>
<td>ACS-50</td>
<td>-</td>
<td>440</td>
<td>315</td>
<td>432</td>
<td>1141</td>
<td>10</td>
<td>140.8</td>
<td>176</td>
<td>-</td>
<td>2547</td>
</tr>
<tr>
<td>ACS-75</td>
<td>-</td>
<td>440</td>
<td>156</td>
<td>648</td>
<td>1141</td>
<td>10</td>
<td>140.8</td>
<td>176</td>
<td>-</td>
<td>2606</td>
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<tr>
<td>ACS-100</td>
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<td>440</td>
<td>864</td>
<td>-</td>
<td>1141</td>
<td>10</td>
<td>140.8</td>
<td>176</td>
<td>-</td>
<td>2665</td>
</tr>
</tbody>
</table>

2.5. Super Plasticizers

A commercially available, chloride-free Naphthalene sulfonate-based admixture (Conplast SP 430) with 40% solids in solution was used to enhance the workability of the OPC-based control concrete mix.
3. Results and Discussions

A slump of around 50-75mm had been aimed at, for the various concrete mixes during the mix design stage. At a moderately lower w/c ratio of 0.40, this was achieved with a small 0.8% dosage (% by weight of cement) of super-plasticizer content for OPC-based concrete mix.

However the various AASC mixes achieved desired levels of workability with no requirement of a super-plasticizer and also it is observed that, increase in replacement of sand by CS showed more or less same workability.

Compared to those of CS admixed concrete mixes reported to increase in workability by earlier researchers [10, 11, 30]. This may be possibly due to similar FM of river sand and CS used herein, and also changes in the mix proportions, binder (AAS).

3.1. Compressive strength of AASC mixes

The compressive strength at various ages of OPC-based mix and AASC mixes, are presented in Figure 1. It is observed that the compressive strength of both OPCC and AASC mixes gradually increased as curing period progressed up to 90-days.

All the AASC mixes showed development of higher early-strengths as compared to the control OPCC mix; such initial strength development can prove very advantageous in the construction industry, from the viewpoint of cost-effectiveness in terms of early formwork removal and faster advancement of work.

It was observed that the compressive strengths with CS are more or less similar to those with sand-based AASC mix.

The variations in the physical and structural characteristics of the binders in AASC mixes are responsible for the high early strength of AASC mixes. The hydration reactions occurring in AAS type binders are quite faster as compared to that occurring in OPC type binders, mainly due to faster dissolution and precipitations of GGBFS at highly alkaline environment [29, 30].

The formation of calcium silicate hydrate (C–S–H) due to the use of sodium based activators is mainly responsible for the development of strength [30, 31].

Also, the AASC mixes are believed to have a very uniform and dense interfacial transition zone having minimal differences in these regions [26].

3.2. Split Tensile Strength of AASC Mixes

Figure 2 depicts the results for split tensile strengths of different AASC mixes with sand/CS. All AASC mixes have gained higher split tensile strengths than that of the control OPC mix; tensile strengths of AASCs seem to be not sensitive to the level of replacement of sand with CS.

3.3. Residual Compressive Strength

Figure 3 presents profile of the residual compressive strength of OPCC and AASC mixes with sand/CS after being subjected to elevated temperatures of 200, 400, 600 and 800 °C. It can be noted that the compressive strength of OPCC slightly increased for about 2% and AASC mixes with sand/CS showed higher increment in the range of 5.3%-7.7% after exposed to 200 °C for 4 h. The strength increase upto 200°C may be due to the evaporation of the water, which lead to the increased
friction between the failures planes [34]. The strength gain may be also attributed to phenomenon called “dry hardening” in which there is an increase in the strength of the concrete after being exposed to temperatures between 150 to 350 °C. The evaporation of the free water leads to strengthening of the hydrated cement paste, resulting in stronger Van der Waal’s forces due to cement gel layers getting closer to each other [35-37]. Under the action of heat, secondary hydration of unhydrated cementitious components occur, which fill the unoccupied pores thus forming a dense and closed structure with increase in chemical bonding within the paste [38, 39]. However, with further increase in the temperature from 200 °C to 400 °C, the compressive strength of OPCC reduced by 12.8% , which is mainly due to the dehydration of portlandite to calcium oxide at approximately 400 °C causing reduction of the volume and strength of the mixes [40]. AASCs with sand/CS showed 8.9-12.1% strength increment compared to original 28-day compressive strength. The increase in the strength in AASC mixes may be on account of the absence of portlandite, which is formed in OPCC [2, 8, 25, 26, 42]. With the increase in the temperature from 400°C to 600 °C, strength of OPCC further reduced to 56.3%. This decrease in OPCC may be attributed to the coarsening of the pore-structure of the hardened cement paste [42-45] along with the reduction and disintegration of the C-S-H [40, 46] accompanied by decompositions of calcium hydroxide. A sharp reduction in relative strength of AASC mixes occurred beyond 600 °C, due to the loss of crystal water and increased replacement of CS in AASCs further decreased strength as probably due to difference in the rates of expansion of aggregates and binder [38, 47, 48]. Once again at 800°C, as the replacement of CS increased, strength reduction is also increased, loss in strength for ACS-0 is as high as 75.7% and for ACS-100 a higher 83.3%. However OPC based concrete retained upto 37% of its strength.

3.4. Residual Splitting Tensile Strength

Residual splitting tensile strength test results at various temperatures are presented graphically in Figure 4. A comparison of relative splitting tensile strength of the various concretes is shown in Figure 5. sharp drop in the splitting tensile strength was noticed in OPCC mixes exposed to 400 °C around 57% while for AASC mixes with sand/CS the reduction is in in the range of 31% to 40%. After exposure at 600 °C, the concrete cubes exhibited considerable loss in the splitting tensile strength. The decomposition of the products of hydration along with the incompatibility between the paste and the aggregates may have resulted in this severe loss of strength. The crack coalescence effect is usually higher in splitting tensile strength compared to that in compressive strength. This can be related to the quicker rate of strength loss in splitting tensile strength as compared to compressive strength loss at higher temperatures. The development and growth of new cracks lead to the reduction in the area available for load-carrying, thus increasing the stresses at the critical crack tips [49]. Moreover, under compressive loads have a tendency to close up, while under tensile loads the cracks tend to open up. Under the influence of high vapor pressure along with thermal incompatibility between aggregates and the paste and decomposition of products of hydration at high temperatures, the crack propagation is significantly affect and leads to localization of micro cracks into macro cracks. Hence, The Loss in splitting tensile tensile strength is more sensitive to cracks, formed as a result of elevated temperature exposure, either on macro or on micro scale [50].

3.5. UPV values of concrete mixes tested at elevated temperature exposed to elevated temperature

Relative performances of OPCC and AASCs with sand/CS with reference to UPV recordings for various
temperatures are given in Figure 5. It is evident that, pulse velocity characteristics deteriorate in OPCC more than that of AASC mixes with sand/CS upto 600°C. Transmission of ultrasonic pulse waves through the concrete mass is highly influenced by micro cracking. The presence of micro cracks highly influences the transmission the pulse waves passing through concrete specimens. Above 600°C, the amount of air voids increase on account of disintegration of C-S-H gel and thermal incompatibility between aggregate and paste, thus decreasing the UPV values [51], which is also reflected in higher strength reduction of AASC mixes than OPCC at 800°C.

4. Conclusions
The key conclusions drawn from the present study are summarized as follows:

![Figure 5 UPV values for concrete tested at elevated temperatures](image)

Figure 5 UPV values for concrete tested at elevated temperatures

1. Increase in replacement of sand by CS in AASC show no significant change in workability.
2. AASCs with sand/CS show higher early compressive strength and higher split tensile strength properties than those of OPCC mix of similar compressive strength.
3. At all levels of replacement, AASCs containing CS exhibited satisfactory performance at high temperature.
4. The overall residual compressive strength of AASCs with sand/CS was not much affected particularly at initial rise of temperature. The reduction in residual compressive strengths was, however, more prominent in concrete exposed to temperature 600°C or higher and also as the replacement of CS increases, reduction of strength increases from 600°C compared to ACS-0, but still residual strength off 100% CS replaced mix showed better strength retention than OPCC mix at 600°C.
5. At 800°C, OPCC mixes showed better residual strength characteristics than AASC mixes with sand/CS, which is also reflected in decreased UPV values of the corresponding mixes.
6. Elevated temperatures have more detrimental effect on splitting tensile strength than on compressive strengths.

References


exposed to temperatures up to 700 °C”, *ACI Material Journal*, 87 (2), 160–166, 1990.


