

SYNTHESIS OF ALKALI-ACTIVATED MATERIAL USING COPPER SLAG AS SOURCE OF ALUMINOSILICATE

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ABSTRACT. Alkali-activated materials (AAM) have gain most attention recently as energy incentive materials and have a successful future as alternative binder in construction industry due to its comparable mechanical and durability properties to Portland cement. The present study was conducted to synthesis AAM using Copper Slag (CS) as source of aluminosilicate. The effect of different alkali contents (4%, 6%, 8% and 10%) and silicate modulus (1.0, 1.25 and 1.5) on the compressive strength of the Alkali-activated Copper Slag (AACS) was determined. Test results reflected that compressive of AACS mixes was increased with increase in alkali content and silicate modulus. These results demonstrate that CS can be used as source of aluminosilicate for the development the AAM. Based on the compressive strength test results, the optimum alkali content and silicate modulus for the synthesis of AACS was 8% and 1.5 respectively.

Keywords: Alkali-activated materials, Compressive Strength, Copper Slag, Alkali Content, Silicate Modulus

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INTRODUCTION

Alkali-activated materials (AAM) are induced by a chemical reaction of aluminosilicate materials (termed the ‘precursor’) under an alkaline environment [1]. Due to low carbon footprints and equivalent performance to Portland cement, AAM have been widely accepted as alternative binders [2]. Alkali-activated materials have been synthesized using a large variety of precursors and activators or combination of activators [3]. However, to develop the low-cost AAM in any specific region, locally available sources of aluminosilicate have to be identified and also specified the correct activator for the activation of these aluminosilicate [4].

Copper slag (CS) is a metallurgical waste generated during primary and secondary refining process of copper. In India during the year 2017, the production of 8.4 million tonnes of copper produced approximately 17 million tonnes of CS [5]. Environmental issues have arisen with the dumping of CS and these problems can be minimized with the utilization of CS in the construction industry, which consumes a large amount of materials such as cement and aggregates. Intense research has been carried out on the utilization of CS as replacement of fine aggregates and Portland cement in concrete [6]. However, very little or no information is available on the use of CS for the development of AAM.

The present study was carried out to synthesis AAM using copper slag as source of aluminosilicate. The influence of alkali content and silicate modulus on the compressive strength of Alkali-activated Copper Slag (AACS) was determined.

MATERIALS AND METHODS

Materials Used

In this investigation, CS obtained from Rajasthan (India) was used as source of aluminosilicate. Copper Slag was first ground in Laboratory Ball Mill using 20mm and 25 mm stainless steel balls for 2 hours. Subsequently, CS was sieved through 45-micron sieve to attain the required fineness. The specific gravity and specific surface area of CS was 3.21 and 405 m²/g. The chemical composition of CS determined using X-ray fluorescence is given in Table 1. X-Ray Diffraction (XRD) pattern of CS is shown in Figure 1, which reflects that CS is a fully amorphous material with minor peaks of crystalline mineral such as Fayalite (F) and Clinoferrosilite (C). Slags which are highly amorphous in nature reflect higher reactivity towards alkali-activation.

Table 1 Chemical composition of CS

Compound (%)	Si ₂ O	Al ₂ O ₃	Fe ₂ O ₃	CaO	Na ₂ O	K ₂ O	TiO ₂	SO ₃	Loss on ignition (%)
Composition	37.6	11.5	42.4	3.80	0.74	0.76	0.37	0.01	1.50

Stranded sand conforming to IS 650 was used to prepare alkali-activated cement mortar. Locally supplied 12M sodium hydroxide solution (NaOH= 35%, H₂O= 65%) and sodium silicate solution (Si₂O= 29.4%, Na₂O= 14.7%, H₂O= 55.9% by weight) were used to prepared alkali-activator solution.

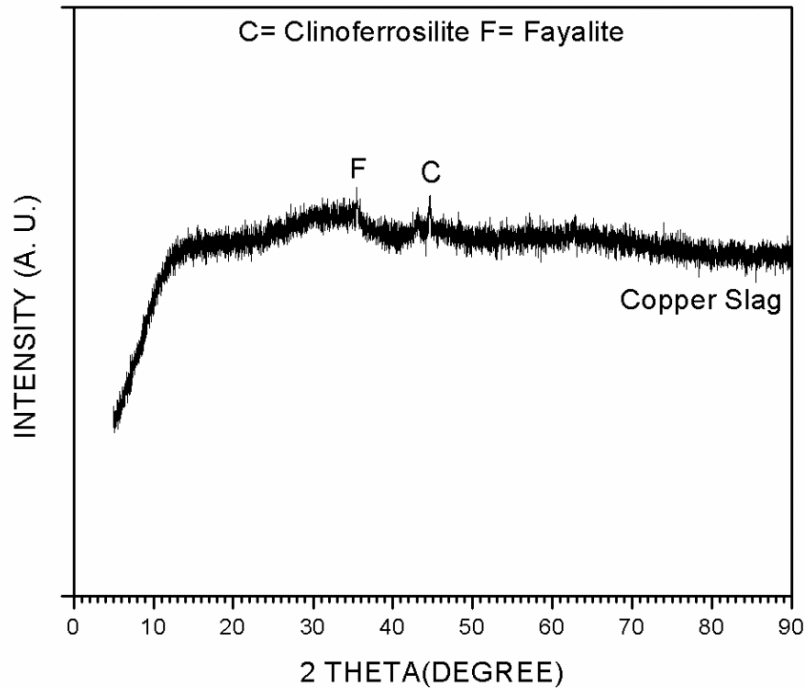


Figure 1 XRD Pattern of CS

Mix Proportions of Alkali-Activated CS Mortar Mixes

Alkali-activated Copper Slag (AACS) mortar mixes were prepared using three different silicate modulus ($\text{Si}_2\text{O}/\text{Na}_2\text{O} = 1.0, 1.25$ and 1.5) and four different alkali contents ($\text{Na}_2\text{O} = 4\%, 6\%, 8\%$ and 10%). Mixes were identified using notation AXMY, where A= alkali content, M= silicate modulus and X, Y are variables. Mix proportions of different mixes for 1000g of CS are given in Table 2. To prepare AACS mortars, standard sand to binder ratio of 3 and water to binder ratio of 0.3 was used.

Preparation of AACS Mortar and Testing

Alkali-activation solution for each mix was prepared by mixing of sodium hydroxide, sodium silicate and water in required amount as presented in Table 2. Alkali-activation solution was kept for 24 hours to cool down the temperature. Standard sand and CS was mixed in mortar mixer for 5 minutes. Subsequently, alkali activator solution was added in the mixer and mixed for another 2 minutes. After the mixing, the mortar was poured into cube specimens of size $50 \times 50 \times 50 \text{mm}$ and sealed to prevent any moisture loss. Two types of curing regimes were selected; ambient curing and heat curing. In ambient curing, specimens were de-moulded after 24 to 48 hours of casting and placed in laboratory conditions ($T = 25 \pm 3^\circ\text{C}$ and $\text{RH} = 50 \pm 5\%$) until testing. In heat curing, specimens were put into oven along with moulds for 24 hours at 80°C . Then, specimens were de-moulded and placed in laboratory conditions ($T = 25 \pm 3^\circ\text{C}$ and $\text{RH} = 50 \pm 5\%$) until testing. The compressive strength test on AACS mixes was conducted as per IS 516 at the curing age of 3, 7 and 28 day.

Table 2 Mix proportions for 1000g of CS (By weight)

Mix	CS (g)	Sand (g)	SH (g)	SS (g)	Water (g)	Alkali Content (Na ₂ O %)	Silicate Modulus (Si ₂ O/ Na ₂ O)	W/S ratio
A4M1.0	1000	3000	74	136	202	4	1.0	0.3
A6M1.0	1000	3000	111	204	153	6	1.0	0.3
A8M1.0	1000	3000	148	272	104	8	1.0	0.3
A10M1.0	1000	3000	185	340	55	10	1.0	0.3
A4M1.25	1000	3000	55	170	197	4	1.25	0.3
A6M1.25	1000	3000	83	255	146	6	1.25	0.3
A8M1.25	1000	3000	111	340	95	8	1.25	0.3
A10M1.25	1000	3000	139	425	44	10	1.25	0.3
A4M1.5	1000	3000	37	204	193	4	1.5	0.3
A6M1.5	1000	3000	55	306	139	6	1.5	0.3
A8M1.5	1000	3000	73	408	85	8	1.5	0.3
A10M1.5	1000	3000	91	510	31	10	1.5	0.3

SH= Sodium Hydroxide, SS= Sodium Silicate, W/S ratio= Water/Solid ratio, where water is water in activators and extra water; Solid is solid part of activators and CS.

RESULTS AND DISCUSSION

Compressive Strength

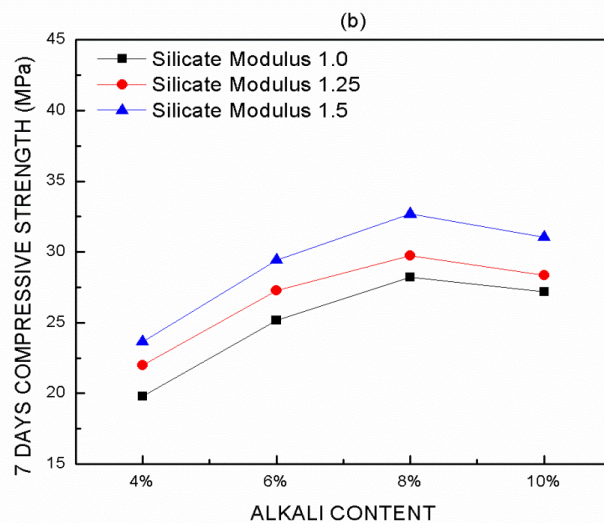
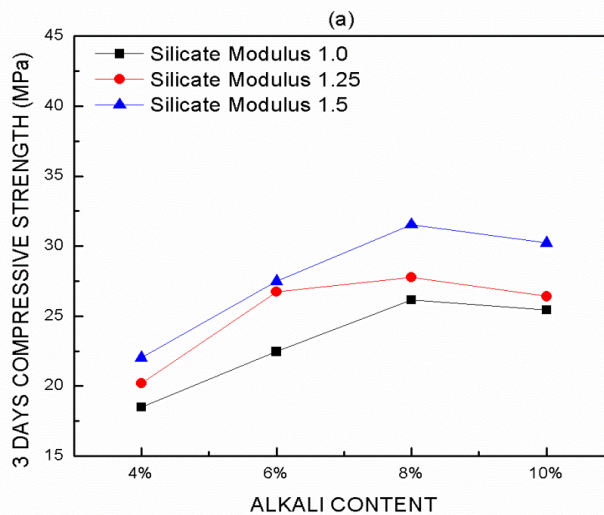
Effect of alkali content (Na₂O content)

The effect of alkali content on compressive strength of different AACS mixes is shown in Figure2. It was found that compressive strength of AACS was increased with increase in alkali content in all curing ages. In Figure2 (c) for silicate modulus of 1.0, 28 days compressive strength of AACS with 4%, 6%, 8% and 10% alkali content was 21.86MPa, 26.64MPa, 28.36MPa and 27.45MPa respectively. For silicate modulus of 1.25, the 28 days compressive strength of AACS with 8% alkali content was 33.47MPa as compare to 24.08MPa for 4% alkali content as shown in Figure2 (c). The 28 days compressive strength of AACS for silicate modulus of 1.5 was increased from 25.92MPa to 38.75MPa, when alkali content was increased from 4% to 8%. Similar behavior was also observed for 3 days and 7 days compressive strength of AACS in Figure2 (a) and Figure2 (b) respectively. In general, compressive strength of AACS was improved with addition of alkali content, but most significant improvement in compressive strength was observed for 8% alkali content in all curing ages and silicate modulus.

The increase in alkali content raised the pH of the alkali-activator solution, which increase the leaching of Si and Al from CS [7-8]. These aluminosilicate reacts with sodium cations to develop the aluminosilicate gel, which improves the compressive strength [9]. However, the increment in compressive strength was significant up to 8% of alkali content and beyond this compressive strength was decrease due to the saturation of alkalis [10]. The alkalis require aluminosilicate for the formation of gel, but the limited availability of aluminosilicate in CS does not contribute in further formation of gel. Thus saturation of alkalis in alkaline solution takes place, which decreases the compressive strength of AACs mortar.

Effect of silicate modulus ($\text{Si}_2\text{O}/\text{Na}_2\text{O}$)

The effect of silicate modulus on the compressive strength of AACs mixes can also observed from the Figure 2. It was found that compressive strength of AACs mixes was increased with increase in silicate modulus for all alkali contents and curing ages. In Figure 2(a) for 8% alkali content, 3 days compressive strength of AACs for silicate modulus of 1.0, 1.25 and 1.5 was 26.15MPa, 27.78MPa and 31.55MPa respectively.



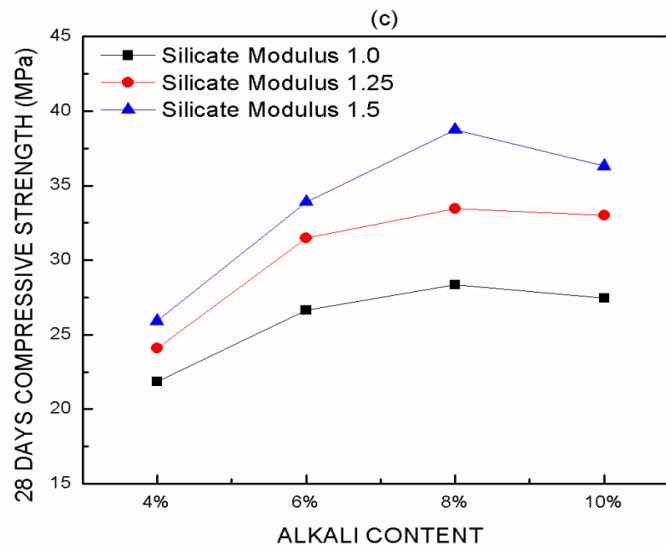


Figure 2 Effect of alkali content and silicate modulus on compressive strength of AACCS mortar mixes (a) 3 days compressive strength (b) 7 days compressive strength (c) 28 days compressive strength

In Figure 2(b) for 8% alkali content, 7 days compressive strength of AACCS for silicate modulus of 1.0, 1.25 and 1.5 was 28.20MPa, 29.72MPa and 32.68MPa respectively. In Figure 2(c) for 8% alkali content, 28 days compressive strength of AACCS for silicate modulus of 1.0, 1.25 and 1.5 was 28.36MPa, 33.47MPa and 38.75MPa respectively. Same trend was also observed for 4%, 6% and 10% alkali contents in all curing ages and it reflects that increase in silicate modulus increases the compressive strength. The AACCS mixes with silicate modulus of 1.5 demonstrates the maximum compressive strength.

As silicate modulus increases, the amount of soluble silicates in the mixes increased without altering the alkali content. The compressive strength of AACCS is directly affected by the degree of polymerization which is depends upon amount of soluble silicate [11]. With the addition of soluble silicate in the alkali activator solution the degree of polymerization increases, which enhanced the compressive strength of AACCS mortar mixes [12-13].

Except the alkali content and silicate modulus, curing regime also effect on the compressive strength of AACCS mortar mixes which is shown in Figure3. It was observed that the compressive strength of heat cured specimens was more than the ambient cured specimens. This behavior was similar in 3 days, 7 days and 28 days compressive strength of AACCS as shown in Figure3(a), Figure3(b) and Figure-3 (c) respectively. In ambient cured specimens, the gain in compressive strength was linear with curing age and the maximum compressive strength was observed at the curing age of 28 days. However in heat cured specimens maximum gain in the compressive strength was observed within 3 days of curing. In AACCS, heat curing accelerates the polymerization and compressive strength development take place in shorter curing periods as compare to ambient curing [14]. Similar behavior was also observed in the literature during the alkali-activation of CS, where heat cured specimens shows better results in terms of compressive strength than ambient cured specimens [15-16].

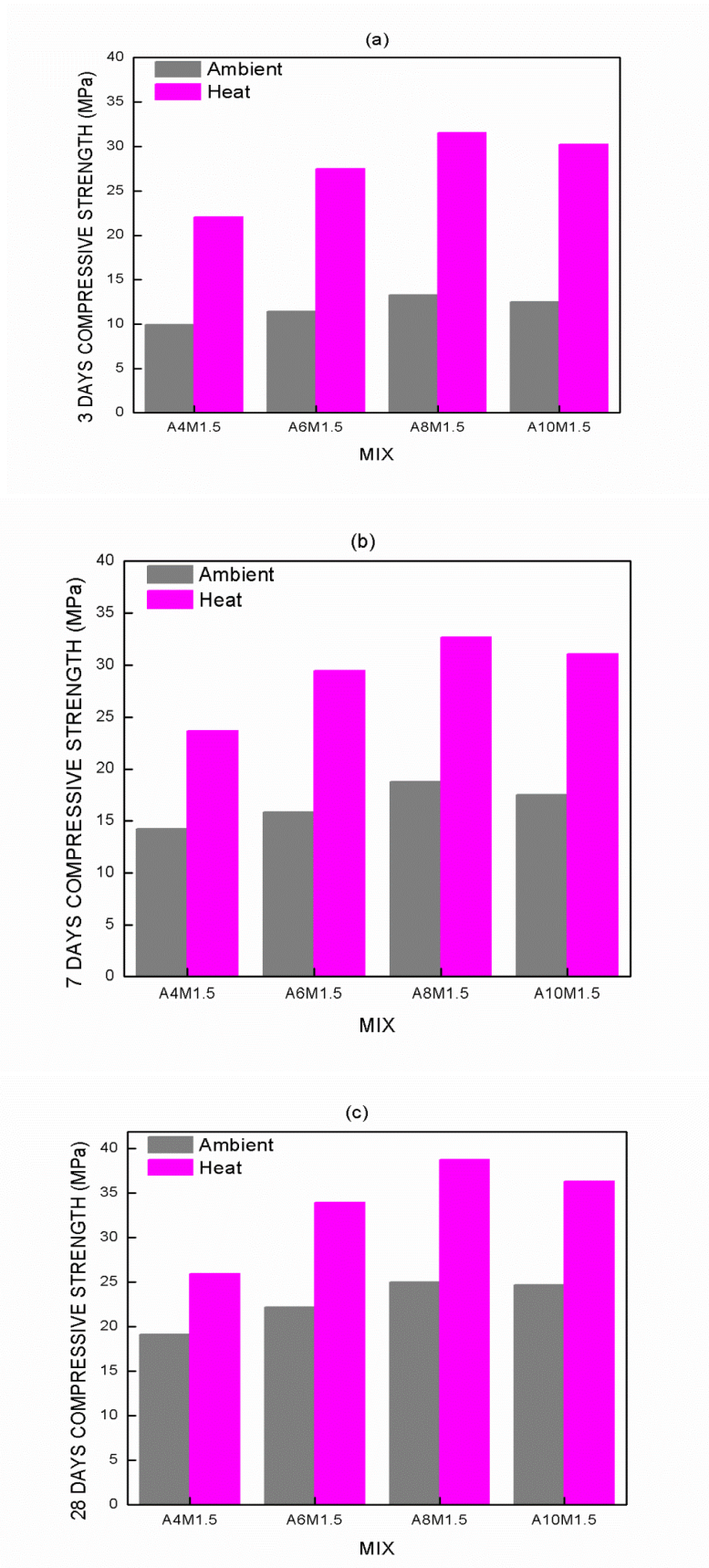


Figure 3 Effect of curing regime on compressive strength of AACs mortar mixes
 (a) 3 days compressive strength (b) 7 days compressive strength
 (c) 28 days compressive strength

CONCLUSIONS

The main conclusions are as follow:

1. The compressive strength of AACs mortar mixes was increased with increase in alkali content up to 8%, beyond this compressive strength was decreased.
2. As silicate modulus increases the compressive strength of AACs mortar mixes was increased. The mixes with silicate modulus of 1.5 exhibited the maximum compressive strength.
3. The AAM can develop using CS as a source of aluminosilicate with optimum alkali content and silicate modulus of 8% and 1.5 respectively.

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