



Influence of Copper Slag on Early Age Properties of Cement

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Abstract

The influence of Copper slag on early-age properties of ordinary Portland cement (OPC) has been investigated using various experimental methods. Several properties were tested by preliminary tests such as Normal consistency, Setting Time, Fineness, Specific Gravity, Chemical Composition, and Compression Strength. Energy Dispersive X-ray Analysis (EDAX), X-ray diffraction (XRD), Scanning Electron Microscopy (SEM) tests are conducted to know material composition and bonding. All the Tests are carried for OPC, Copper Slag and OPC Mixed with Various Percentages of Copper Slag (CS) Viz. 5%, 10%, 20%, 25%, 30%, 35% & 40% by weight of cement. Experimental Results showed that Compression Strength Increased to Maximum extent of 5.37% at 25% replacement level copper slag. Preliminary test results shows decrease in consistency, setting time and increase in fineness, specific gravity but all the results were found to be in permissible limits at 25% replacement level of copper slag. From Chemical Composition and XRD Results it is observed that the Major compound Present in OPC is Calcium Oxide, in Copper Slag is Silicon Dioxide and for composite material (i.e. at 25% replacement level of Copper Slag) Calcium Oxide and Silicon Dioxide are responsible for Compression strength increase. The SEM image at 25% replacement level of Copper Slag with OPC shows thicker fibers which is responsible for increase in Compression strength.

Keywords: Copper Slag, Cement, Strength.

1. Introduction

In India due to quick economic development the natural resources are exhausting rapidly. Hence it is very important to preserve the natural resources by finding alternate materials to natural resources thereby preserving the integral part of our environment. Number of research studies has completely shown the use of micro silica, fly ash, Metakolin, Ground Granulated Blast Furnace Slag (GGBS) etc., which are the products left out in their respective industries. as aggregates and cement replaced materials in the preparation of concrete without losing its basic properties also sometimes the composites perform better than the normal concrete which gifts important financial and environmental benefits such as, the use of zero-cost raw material, disposal problems and fresh environment. Copper is also one such metal with wide applications in several industries. The discarded material in the production of copper during smelting and refining of copper from copper ore is called copper slag. It is produced during mate smelting and converting steps. From previous investigation it is observed that copper slag can replace either cement or aggregates partially or fully therefore it has a favorable future in construction industry. It is estimated that in India around 600000 to 6500000 tons of copper slag was produced from copper producers Sterlite, Birla Copper and Hindustan Copper at different sites. Copper slag exhibits good strength property that helps designate in concrete as a partial or fully replacement to OPC or aggregates.

Present study is focused on evaluating the impact of copper slag on properties of cement by replacing cement by copper slag by different percentages Viz. 5%, 10%, 20%, 25%, 30%, 35% & 40% by weight of OPC.

The present study is focused on the following.

1. Examine the significance of CS addition as a secondary cementitious material on Normal Consistency, Setting Time, Specific Gravity, Fineness and Soundness of Cement.
2. Measure the reactivity of Copper Slag with OPC at different replacement levels.
3. Evaluate the Compression Strength of Cement by replacing OPC with copper slag at various percentages.

2. Previous Works

Romy S. Edwin et al. [1] presented the experimental results on mortar compression strength with altered proportions of copper slag and concluded that mortar compression strength with copper slag is equivalent to compression strength of control mix in some cases even better. From Isothermal calorimetry test it is found that increase in the replacement of copper slag reduces hydration. Dale P. Bentz et al. [2] conducted a research on influence of fineness of cement on early age properties of cement and concluded that high early age properties results in early age cracking. Dale P. Bentz et al. [3] considered the effect of water cement ratio (ranging from 0.325 to 0.425) on early age properties of cement. The results shows that decrease in water cement ratio increases strength, semi adiabatic temperature rise and autogenous shrinkage, which results in increase of tendency for early age cracking. Zhenjun Wang et al. [4] considered the effect of compression strength value and microwave absorption performance of mortars containing various proportions of copper slag up to 70% and stated that 50% replacement level of copper slag is possible in the cement mortars with the better compression strength values. Seyed Reza Mirhosseini et al. [5] in their examination on mechanical properties of concrete with copper slag stated that copper slag can be replaced

up to 30% without effecting engineering properties of concrete and replacement of copper slag above 30% results in the decrease of strength by more than 25%. Al-Jabri et al.[6] in their test take a shot at the impact of copper slag as a fine aggregate on the properties of mortar and cement announced that the compression strength quality was enhanced by 70% for the mortar at half substitution level of copper slag and for concrete density was slightly increased at 5% replacement level of copper slag, while increase in the addition of copper slag causes increase in workability. they inferred that copper slag can be replaced up to 50% by fine totals with great quality and toughness prerequisites. Amin Nazer et al. [7] directed research on antiquated copper slag in Portland concrete and concluded that the copper slag has intense binding properties. Caijun Shi et al. [8] in their survey on usage of copper slag in cement and concrete reasoned that use of copper slag gives both specialized and natural advantages. J Vijayaraghavan et al. [9] contemplated the impact of copper slag on mechanical properties of concrete and concluded that 40% copper slag replacement with cement possesses more strength than control mix. Mobasher et al. [10] in their experimental work about examined about the hydration of cement blends with the substitution of copper slag.

3. Materials

Cement

The cement utilized in this examination is Ordinary Portland Cement 43 grade which fulfills the necessities IS 8112-1989 specification.

Fine Aggregate

Characteristic waterway sand which is locally accessible has been utilized as fine total. The sand utilized was having fineness modulus 4.11 and affirmed to reviewing zone-II according to IS: 383-1970.

Copper slag

The copper slag utilized in the test program was obtained from Ingaldal Copper Mines, a unit of Hutti Gold Mines Company Limited, Chitradurga (Tq. and D).

Water

Customary convenient water free from natural substance, turbidity and salts was utilized for blending and for relieving all through the test work.

4. Results and Discussion

4.1 Chemical Analysis

The chemical analysis test results on cement, copper slag and the cement replaced with 25% copper slag by weight of cement were classified in table 4.1. From the chemical analysis data it is observed that the copper slag displays pozzolonic properties since it contains low Calcium Oxide (CaO) content and different oxides, for example, Silicon Dioxide (SiO₂), Ferric Oxide (Fe₂O₃), Ferric Oxide (Fe₂O₃), Alumina (Al₂O₃) and Magnesium oxide (MgO). Variation of these chemical compounds along with their mass percentage of chemical composition is shown in the Fig 4.1

Table 4.1: Chemical compounds and their percentages

Chemical Compound	% of Chemical Composition		
	OPC	Copper Slag	Cement replaced with 25% of copper slag
Silicon Dioxide (SiO ₂)	22.22	53.46	29.9
Ferric Oxide (Fe ₂ O ₃)	4.47	16.53	7.40
Alumina (Al ₂ O ₃)	5.51	11.47	8.27
Calcium Oxide (CaO)	59.72	3.82	45.74
Magnesium oxide (MgO)	2.02	6.91	2.83

Tri Calcium Silicate (C3S)	7.05	-	-
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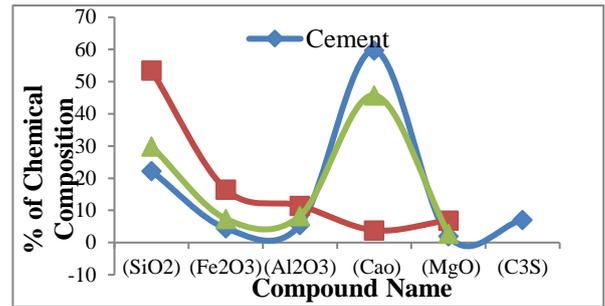


Fig 4.1: Chemical compounds and their mass percentage

4.2 Preliminary test results

Fineness test results at various replacement levels of copper slag are revealed in Table 4.2. As replaced levels of copper slag rises the Fineness test values increases because high particle size of Copper slag in contrast with cement. Variation of same is shown in Fig 4.2

Table 4.2: Fineness test results

Copper Slag replaced in %	0	5	10	15	20
Fineness Value in %	2.5	2.6	7.5	12	12.5
Copper Slag replaced in %	25	30	35	40	
Fineness Value in %	14.3	18.6	20.2	21.7	

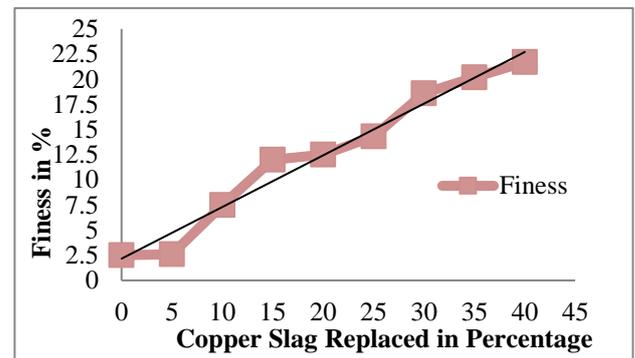


Fig 4.2: Fineness v/s CS Replacement Level

Initial and Final Setting time results at various replacement levels of Copper Slag by weight of cement is shown in Table 4.3. As the replaced levels of CS increases the Initial and Final Setting time values decreases in comparison with mortar without copper slag due to increase of Silicon Dioxide content which is predominant in copper slag but are in permissible limits i.e. greater than 30 minutes and less than 600 minutes respectively. The variation of initial and final time with respect to Copper Slag replaced in percentage by weight of cement is shown in Fig 4.3

Table 4.3: Initial and Final Setting time test results

Copper Slag replaced in %	0	5	10	15	20
Initial setting Time in minutes	45	43	42	40	38
Final setting Time in minutes	480	468	443	413	389
Copper Slag replaced in %	25	30	35	40	
Initial setting Time in minutes	37	36	35	33	
Final setting Time in minutes	365	324	301	289	

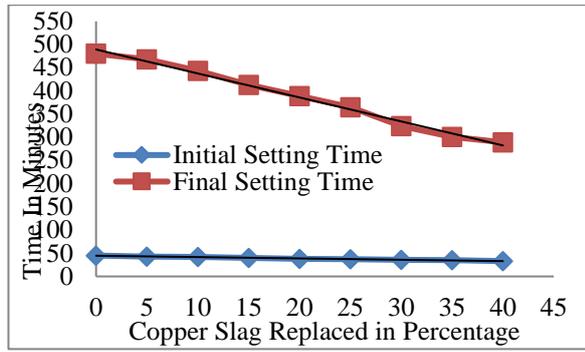


Fig 4.3: Initial and Final setting v/s CS Replacement level

The Specific Gravity of cement at various replacement levels of copper slag are tabulated in table 4.4 and the variation of the same is shown in Fig 4.4. The value of Specific gravity increases gradually with the replacement of copper slag in to cement due to the high density of copper slag.

Table 4.4: Specific gravity test results

Copper Slag re- placed in %	0	5	10	15	20
Specific gravity	3.06	3.086	3.113	3.14	3.167
Copper Slag re- placed in %	25	30	35	40	
Specific gravity	3.194	3.221	3.248	3.275	

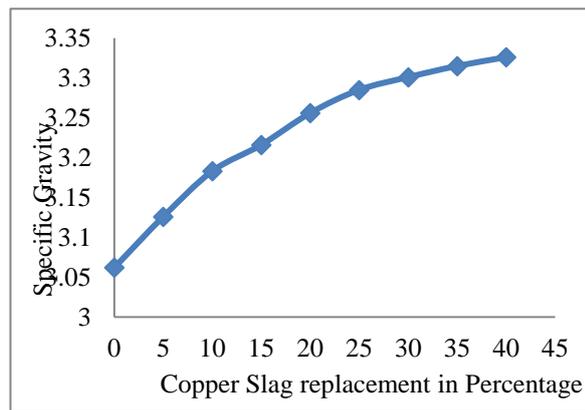


Fig 4.4: Specific gravity v/s CS Replacement level

The Normal consistency of cement at various replaced levels of copper slag is tabulated in table 4.5 and the variation of the same is shown in Fig 4.5. The value of Normal consistency decreases gradually with the replacement of copper slag in to cement due do the reduction in availability of lime for the hydration because of increase in silicon dioxide and reduction in calcium oxide content with the replacement of copper slag.

Table 4.5: Normal consistency test results

Copper Slag re- placed in %	0	5	10	15	20
Normal Consisten- cy in %	28	28	26	26	26
Copper Slag re- placed in %	25	30	35	40	
Normal Consisten- cy in %	26	25	25	24.5	

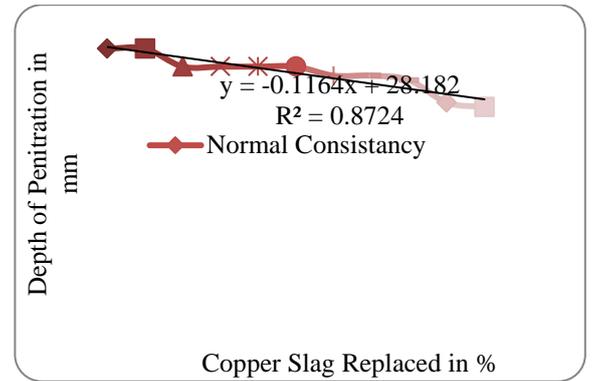


Fig 4.5: Normal Consistency v/s CS replacement level

4.3 Microscopic analysis and Mechanical property

The SEM picture of cement example as appeared in Fig 4.6 and its substance creations evaluated are appeared in Fig 4.7 and table 4.6. Using Energy Dispersive X-Ray Spectroscopy. It was observed from Fig 4.6, the cement sample has irregular appearance and the formation of large amount of platelets and Needles. The Fig 4.7 and Table 4.6 demonstrates the aggregate mass division of Carbon , Aluminum, Silica, Calcium, Iron and Oxide components in the concrete example is 99.78% and alternate components are 0.22 %. Furthermore the XRD example of the Cement test appeared in Fig 4.8 reveals the presence of Haturite and low Quartz.

Table 4.6: Element Percentage in Cement Sample

Element	C	O	Al	Si	Ca	Fe	Cu
Weight %	06.80	49.82	1.29	18.96	21.71	1.20	0.22
Atomic %	11.38	62.67	0.96	13.59	10.90	0.43	0.07

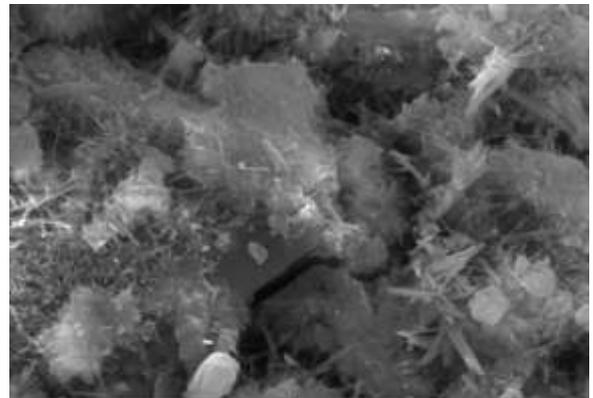


Fig 4.6: SEM Image of Cement Sample

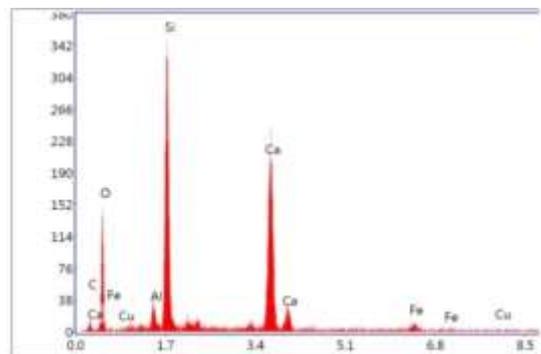


Fig 4.7: EDS Spectrum of Cement Sample

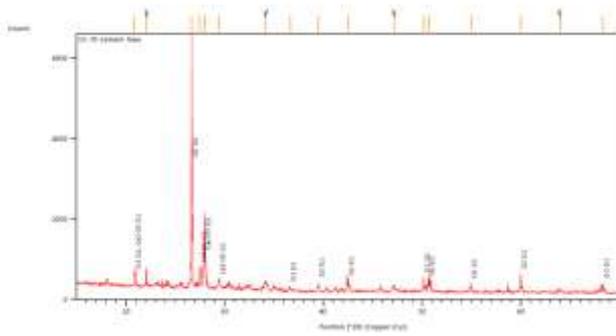


Fig 4.8: XRD Spectrum of Cement Sample

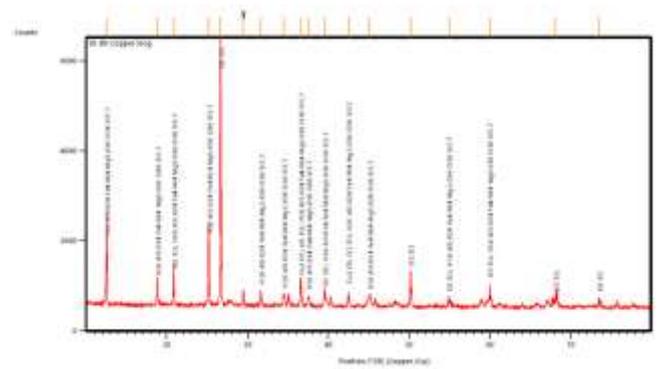


Fig 4.11: XRD Spectrum of Copper Slag

The SEM picture of copper slag shown in Fig. 4.9 along with its quantified chemical compositions are shown in Fig 4.10 and table 4.7 using Energy Dispersive X-Ray Spectroscopy. As can be seen in Fig 4.9 the copper slag has ir-regular appearance and the formation of large amount of platelets. The total mass fraction of carbon , Aluminum, Silica, Calcium, Iron and Oxide components in the copper slag is 98.8% and alternate components is 1.2 % as shown in Fig 4.10 and table 4.7. Moreover the XRD example of the copper slag appeared in Fig 4.11 uncovers the nearness of Cuprite, Quartz low and Chamosite among them Quartz has been given careful consideration because of its strength property.

Table 4.8: Element Percentage in 25% Copper Slag replacement with Cement

Element	O	Al	Si	Fe	Ca	Cu
Weight %	32.84	45.10	2.19	16.42	0.03	2.35
Atomic %	43.36	44.70	1.29	9.27	0.01	0.67

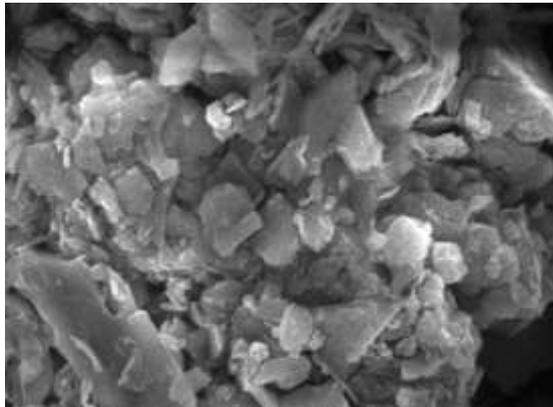


Fig 4.9: SEM Image of Copper Slag

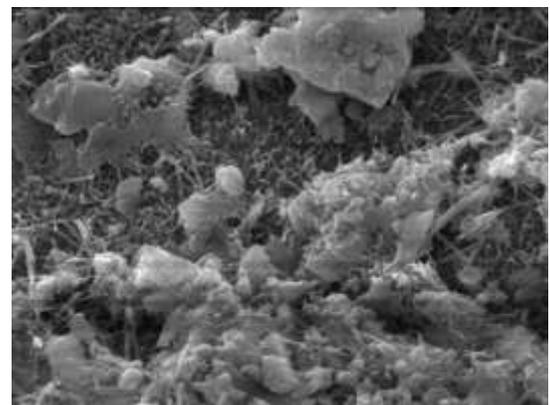


Fig 4.12: SEM Image of 25% CS with Cement

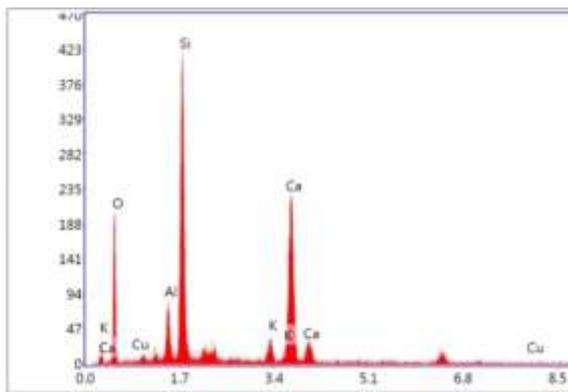


Fig 4.10: EDS Spectrum of Copper Slag

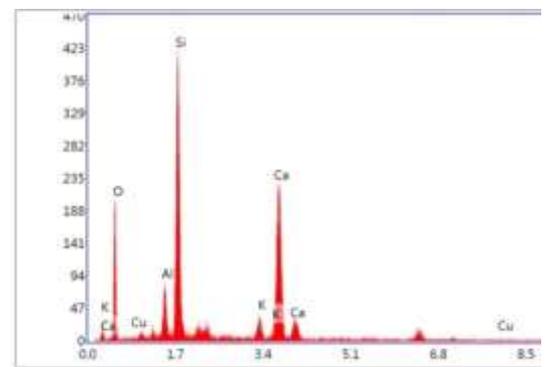


Fig 4.13: EDS Spectrum of 25% CS with Cement

Table 4.7: Element Percentage in Copper Slag

Element	C	O	Al	Si	Ca	Fe	Mg
Weight %	32.84	45.10	2.19	16.42	0.03	2.35	1.07
Atomic %	43.36	44.70	1.29	9.27	0.01	0.67	0.70

The SEM picture of the mortar consolidated 25% copper slag is appeared in Fig 4.12 and its chemical compositions quantified are shown in Fig 4.13 and table 4.8 using Energy Dispersive X-Ray Spectroscopy.

From Fig 4.12 it is observed that that the formation of few irregular needles and platelets which helps in the in-crease of strength. The aggregate mass portion of Aluminum, Silica, Calcium, Iron and Oxide components in the copper slag is 98.9% while the substance of alternate components is 1.1 % appeared in Fig 4.13 and table 4.8. In substitution the XRD example of the mortar fused with 25% copper slag appeared in Fig 4.14 uncovers the nearness of Quartz and Sinnerite among them Quartz has been given careful consideration because of its strength property.

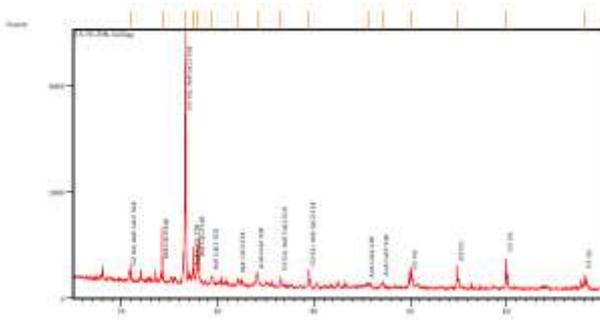


Fig 4.14: XRD Spectrum cement replaced with 25% CS

Compression strength results at various replaced levels of copper slag for different ages of 3, 7 and 28 days are shown in Table 4.9 and Fig 4.15. The Compression strength varies linearly and gives maximum strength at 25% replacement of cement by copper slag. It was observed that the compression strength increases gradually and gives maximum strength at 25% their after the strength values decreases rapidly mainly because of increased silica content in the copper slag after reaching its optimum value tends to reduce bonding by increasing brittleness hence the strength of mortar reduces rapidly.

To assess pressure quality of six 3D shape specimens of 50 cm² surface region are utilized. Mortar with 0% replacement of cement

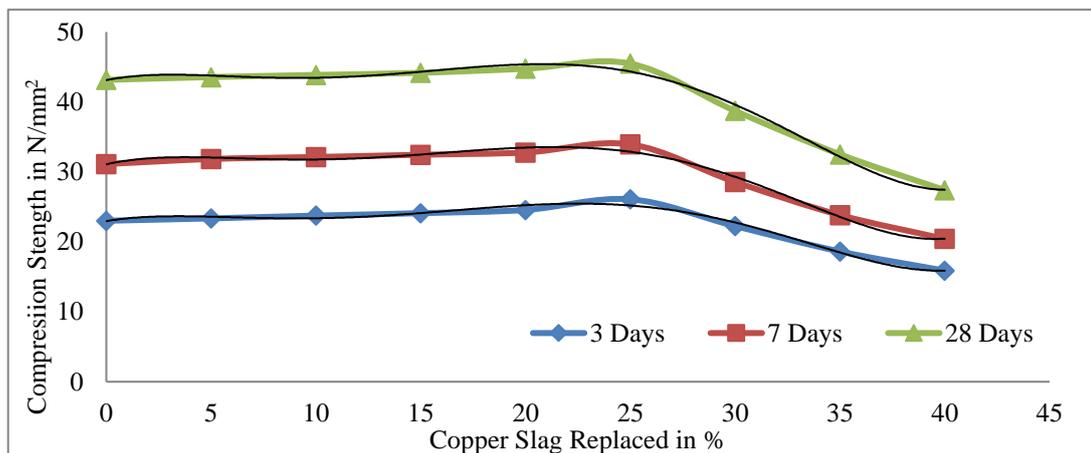


Fig 4.15: Compression Strength Results

5. Conclusions

In this examination, the accompanying decisions about the impact of copper slag on the early age properties of the cement are arrived:

1. The copper slag shows pozzolonic properties due to the presence of Calcium Oxide (CaO), Silicon Dioxide (SiO₂), Ferric Oxide (Fe₂O₃), Ferric Oxide (Fe₂O₃), Alumina (Al₂O₃) and Magnesium oxide (MgO) hence it can be used as secondary cementitious material. Presence of Silicon dioxide by an amount 53.46 % by mass in the copper slag is found responsible for strength increase.
2. The SEM image of the mortar containing 25% copper slag shows formation of few thick needles which accounts for increased strength and XRD pattern reveals the presence of Sinnerite and free Quartz which are responsible for increase in compression strength.
3. By replacing cement by the copper slag up to 25 % by weight of the cement Maximum compression strength of 45.47 N/mm² is achieved, which is 5.37 % more in comparison with control mix.
4. The copper slag exhibits good performance with the OPC up to 25 % replacement level which shows nearly linear improvement in compression strength from 43.15 N/mm² to 45.47 N/mm².

by copper slag is shown with the mark M, Mortar with 5% replacement of cement by copper slag is shown with the mark M+05CS, Mortar with 10% replacement of cement by copper slag is shown with the mark M+10CS, Mortar with 15% replacement of cement by copper slag is shown with the mark M+15CS, Mortar with 20% replacement of cement by copper slag is shown with the mark M+20CS, Mortar with 25% replacement of cement by copper slag is shown with the mark M+25CS, Mortar with 30% replacement of cement by copper slag is shown with the mark M+30CS, Mortar with 35% replacement of cement by copper slag is shown with the mark M+35CS, Mortar with 40% replacement of cement by copper slag is shown with the mark M+40CS.

Table 4.9: Compression strength test results at different replaced levels

Mortar Mix	Average compression strength (N/mm ²)		
	3 Days	7 Days	28 Days
M	23.01	31.12	43.15
M+05CS	23.35	31.84	43.55
M+10CS	23.75	33.13	43.86
M+15CS	24.10	32.45	44.16
M+20CS	24.56	32.77	44.74
M+25CS	26.08	33.93	45.47
M+30CS	22.25	28.56	38.72
M+35CS	18.62	23.83	32.50
M+40CS	15.88	20.43	27.39

5. The Substitution of copper slag more than 25% leaves free silica which results in greater reduction of strength. There is 11% reduction in strength at 30% replacement level in comparison with control mix.
6. Environmental issues can be reduced by using copper slag in construction industry. Also the production of cement is reduced to some extent this reduces the carbon dioxide emission to environment.

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