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Research Article

INFLUENCE OF COPPER ON PROPERTIES OF BLENDED CEMENT MORTAR

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ABSTRACT
The effect of copper (Cu) present in mixing water on compressive strength, setting times, soundness on blended cement mortar was experimentally evaluated. Cement mortar specimens were cast using deionised water and copper (Cu) spiked deionized water for reference and test specimens as mixing waters respectively. On comparison with reference specimens, at higher concentrations of copper in mixing water, test samples had shown considerable loss of strength, and also their setting times had significantly increased. However, at 2500 mg/L concentration of copper (Cu), the compressive strength marginally increased. XRD technique was used to find out main compounds.

Key Words: *Cement mortar, Copper (Cu), Silica fume (SF), Superplasticizer (SP)*

INTRODUCTION
It is a well known fact that quality and quantity of mixing water in fresh cement mortar and concrete are important in determining properties of cement mortar and concrete. Water has both beneficial and detrimental effect on concrete (Neville, 2000). Generally, if water is potable, it is also suitable as mixing water for concrete. However, non-potable water, such as treated industrial wastewater, which contains heavy metals (Hg, Cu, Ni, Zn, Cr, Pb, Cd, and Fe), was satisfactorily used in making cement mortar (Reddy Babu, *et al.*, 2009). The water quality with respective to impurities could be made less stringent for curing if no chemicals that harm concrete remain on the surface after evaporation. Even greater amounts of impurities could be permitted in water if it was used for washing concrete equipment (Hooton, 1993; Steinour, 1990). Even though considerable volume of work was carried out to understand the interaction of different ingredients of concrete such as cement, aggregate, chemical and mineral admixtures, considerable research work was not carried out in the role of mixing water on concrete. However, few researchers (Reddy Babu, 2009) had worked on use of treated and partially treated waste waters, but a particular constituent effect and its maximum permissible limit in mixing water was not reported. For this reason, a guideline based on careful scrutiny on tolerable limit of a specific constituent in mixing water is highly needed.

Research Significance
This paper examines the maximum permissible limit of copper (Cu) in mixing water of cement mortar. Madhusudana Reddy et al 2013 had studied influence of Pb in mixing water in blended cement mortar. Reddy Babu et al 2007, reported Pb, Zn, hg, Cu, Ni, Fe and Cr were friendly with cement mortar up to 600mg/L. (Mindess and Young, 1981) reported the tolerable limit of Cu, Pb, Zn, Mn was 500 mg/L. (Tay and Yip, 1987) showed that the use of reclaimed wastewater for concrete mixing did not have any adverse effect on concrete. (Ramana Reddy et al., 2006) reported inexplicit results both positive and negative with biologically contaminated water. (Cebeci and Saatci, 1989) found that biologically treated domestic wastewater was indistinguishable from distilled water when used as mixing water in concrete. However, heavy metals such as Cu, Zn, Pb, caused a retardation of the early hydration and strength development of cement mortar (Tashiro, 1980). These metals delayed setting and early strength development (Barth, 1990). Even though biologically treated sewage and reclaimed wastewater are reported to be usable in

concrete for mixing, there is very little information on the maximum permissible limit of heavy metals in mixing water. Hence, this investigation was carried out to understand the effect of copper (Cu) in mixing water on compressive strength, setting times, soundness of blended cement mortar.

MATERIALS AND METHODS

Cement 53-grade ordinary Portland cement conforming to IS: 12269-1987 was used. The physical properties and chemical composition of major compounds of cement are given in Table .1 and 2 respectively.

Table 1: Physical properties of cement

Sl. No	Property	Result
1	Specific gravity	3.17
2	Fineness	225 m^2/kg
3	Initial setting time	114 minutes
4	Final setting time	224 minutes
5	Compressive strength	MPa
a)	3 days	33
b)	7days	43
c)	28 days	54
6	soundness	0.5 mm

Table 2: Chemical composition of cement

Sl. No	Oxide composition	percent
1	CaO	64.59
2	SiO_2	23.95.
3	Al_2O_3	6.89
4	Fe_2O_3	3.85
5	MgO	0.78
6	SO_3	1.06
7	K_2O	0.46
8	N_2O	0.12
9	Loss on ignition	1.2
10	Insoluble residue	0.35

Sand Ennore sand conforming to IS: 650-1966 was used. Physical properties are given in Table.3. The cement to fine aggregate ratio was maintained at 1:3(by weight) in the mortar mixes.

Table 3: Physical properties of sand

Sl. No	Property	Result
1	Specific gravity	2.65
2	Bulk density	15.84 kN/m^3
3	Grading	percent
4	Passing 2mm sieve	100%
5	Passing 90µ sieve	100%
6	Particle passing 2mm and retained 1mm	33.33%
7	Particle passing 1mm and retained 500µ	33.33%
8	Particle passing 500µ and retained 90µ	33.33%

Superplasticizer: Commercial superplasticizer was used. Based on a number of trials, 0.8% (by weight of cement) was arrived.

Water Deionised water was used in reference specimens and copper spiked deionised water in different concentrations was used in test specimens.

Silica Fume: Silica fume was used in the present investigation. 9% of the cement was replaced by silica fume, where maximum compressive strength was achieved. The chemical composition is given in Table. 4

Table 4: Chemical composition of silica fume

Sl. No	Oxide composition	Percent
1	CaO	0.5
2	SiO_2	92.3
3	Al_2O_3	2.7
4	Fe_2O_3	1.4
5	MgO	0.3
6	SO_3	0.1
7	K_2O	0.1
8	N_2O	0.1
9	Loss on ignition	1.8

Copper(Cd) was introduced into the deionised water in predetermined concentrations such as 500, 1000, 1500, 2000, 2500, 3000, 4000, 5000mg/L. The concentrations were arrived based on the literature. After number of combinations tried, a combination (cement + 9% SF + 0.8% SP) was fixed for reference specimens where maximum compressive strength was attained. The physical properties of reference specimens are given in Table. 5.

Table 5: Physical properties of reference cement mortar

SL No	Property	Result
1	Initial setting time	160 minutes
2	Final setting time	272 minutes
3	Compressive strength	MPa
a)	3 days	49
b)	7 days	59
c)	28 days	75
d)	90 days	77
e)	180 days	81
f)	365 days	82
4	Soundness	0.7 mm

Eight series of specimens were cast for test. The test specimens were cast with (cement + 9% SF + 0.8% SP + Copper). Copper concentrations of 500, 1000, 1500, 2000, 2500, 3000, 4000, and 5000mg/L were introduced into the deionised water used as mixing water for test specimens. The quantities of cement, Ennore sand and mixing waters for each specimen were 200g, 600g and (P/4) + 3 where P denotes the percentage of mixing water required to produce a paste of standard consistence. Initial and final setting times were found out by Vicat's apparatus. Le-Chatelier equipment was used to find soundness of reference and test specimens. The reference and test specimens were prepared using standard metallic cube mould of size 7.06 X 7.06 X 7.06cm for compressive strength of mortar. The blended cement to sand ratio was 1: 3 by weight throughout the tests. The compressive strength of reference and test specimens was studied at different ages, i.e., 3, 7, 28, and 90 days. The compacted specimens in mould were maintained at a controlled temperature of 27 ± 2^0 and 90 percent relative humidity for 24 hours by keeping the moulds under gunny bags wetted by the deioned water and then demolded. After demolding, the specimens were cured in deionised water for 27 days. From the experiments of setting and soundness tests, an average of three values was used to compare the results of the reference specimens. In the case of compressive strength tests, three test specimens were compared with three reference specimens.

Powdered X – Ray Diffraction Studies

Powder X – ray diffraction (XRD) is one of the commonly used techniques for investigation of crystalline compounds in hydrated cement paste (Knudsen, 1976). The reference sample (Cement + 9% SF + 0.8% SP + Deionised water) and test sample (Cement + 9% SF + 0.8% SP + Copper spiked (2000 mg/L) deionised water) for XRD were ground to a fine powder and a flat specimen was prepared on a glass surface using an adhesive. The diffracted intensities were recorded with powdered diffractometer using monochromatic Kα radiation.

RESULTS AND DISCUSSION

Soundness The Le-Chatelier's test result for expansion measurement in cement should not be more than 10 mm. The effect of deionised water (Reference) and Copper spiked deionised water (Test) on soundness is shown in Fig.1. The expansion measured was 0.7, 0.7, 0.72, 0.75, 0.79, 0.81, 0.86, 0.92, and 0.98 mm for 0, 500, 1000, 1500, 2000, 2500, 3000, 4000 and 5000mg/L concentrations respectively. Since all measured values were less than 10 mm, all the samples are considered sound.

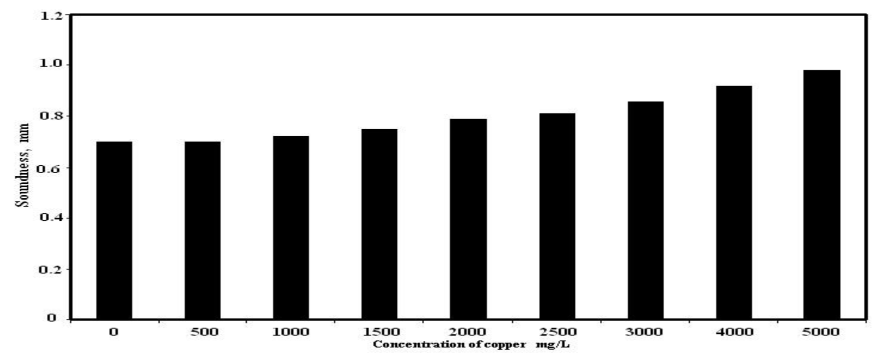

Figure 1: Effect of copper on soundness of blended cement

Setting times Figure 2 shows the effect of deioniesd water (Reference) and Copper spiked deionised water (Test) on initial and final setting times. The initial and final setting times increased as the concentration of copper increased. At a maximum concentration of 5000 mg/L, the test samples had 63 minutes increase in the initial setting time and 57 minutes increase in the final setting time, compared to the reference specimens. At the opted concentrations (500, 1000, 1500, 2000, 2500, 3000, 4000, 5000mg/L), the increases in initial setting times observed were 4, 10, 17, 21, 28, 35, 51 and 63 minutes respectively. The corresponding increases in the final setting times were 6, 10, 17, 23, 30, 36, 46 and 57 minutes.

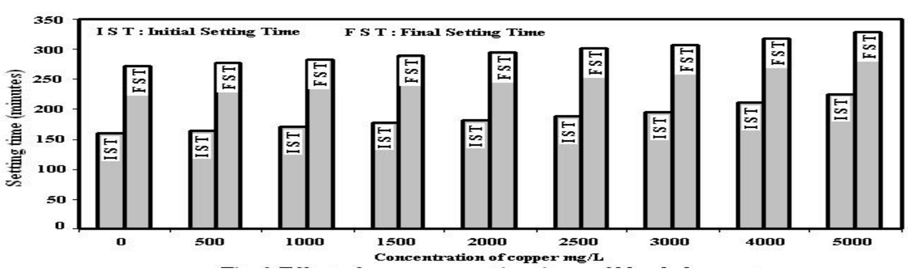

Figure 2: Effect of copper on setting times of blended cement

Compressive strength Figure 3 shows the change in compressive strength of test samples due to the use of copper spiked deionised water. The strength developments in reference and test specimens were the same for concentration of 500 mg/L. For the concentration of 1000 mg/L, the observed decrease in compressive strength at 3 days was 2.01%, compared to reference specimens. After 3 days, compressive strength developments in reference and test samples were the same. For the concentrations of 1500 mg/L and 2000mg/L the decrease in compressive strengths at 3 days were 2.9% and 3.5%, after 7 days, in either concentrations , compressive strength of reference and test was same. For the concentration of 2500 mg/L the decrease in compressive strength at an early age (3 days) was by 4.6%, at 7, 28 and 90 days a marginal increase in compressive strength was noticed of 0.5, 1.2 and 1.% respectively, compared with reference specimens. However, increase in concentrations 3000 to 5000 mg/L and age, decrease in compressive strength was observed. Decrease in compressive strength at 5000 mg/L was 18.5, 18.0, 17.6 and 17.1%% for 3, 7, 28, and 90 days respectively. Eventually, compressive strength results reveal that at 2500 mg/L concentration, a little increase in compressive strength is observed.

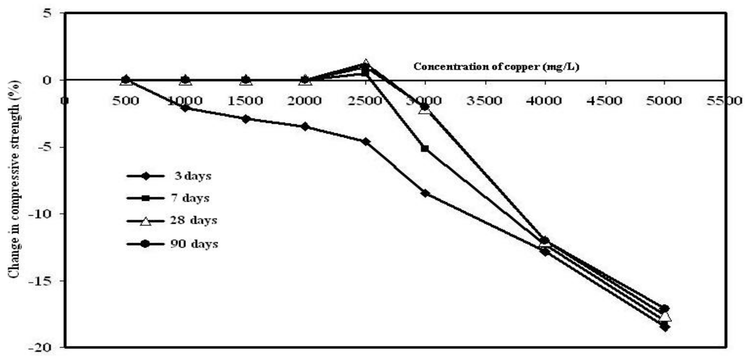

Figure 3: Effect of copper on percentage change in compresive strength

XRD Analysis of blended cement paste made with deionised water and copper spiked deionised water: Figure 9 shows that powder X – ray diffraction patterns of reference and test samples. Both reference and test sample (2500 mg/L) were cured for 28 days before being subjected to XRD technique. After employing XRD for test sample, new compound was found along with hydrated compounds such as C_3S, C_2S, C-S-H, $Ca(OH)_2$, $Cu(OH)_2$, at 32.6^0, 32.6^0, 29^0, 20.6^0, 28.2^0 respectively. Copper hydroxide precipitation is expected to form quickly in the high alkaline environment of a cement mix. The precipitated copper hydroxide might be coated on hydrated and anhydrate cement compounds, there by delaying the setting process and slowing early strength development. However, for concentrations of copper above 2500 mg/L, setting times were significantly increased and compressive strengths of test specimens were considerably decreased compared with reference specimens. The possible reasons, at higher concentrations, copper hydroxide precipitation increases and may increase the replacement of Ca by Cu in hydrated C-S-H.

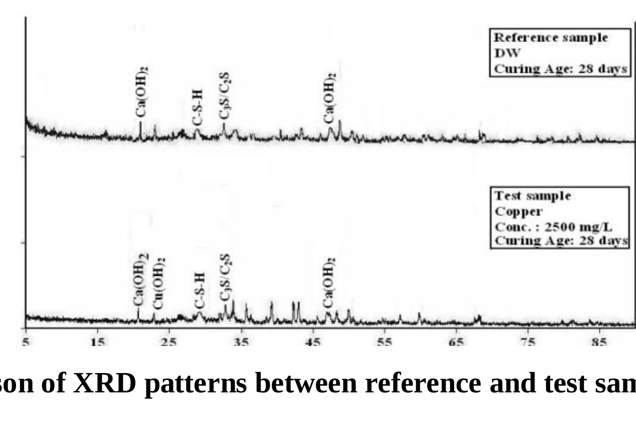

Figure 4: Compartson of XRD patterns between reference and test sample at age of 28 days

Conclusion

Lead spiked deionised water affected setting times. For the concentration of 3000 mg/L and above, setting times were significantly increased. The presence of copper in high concentrations (≥ 3000 mg/L) in deionised water considerably decreased the compressive strengths. For a concentration of 2500 mg/L, at early ages of 3, compressive strength development was slow but from 7 days and above, compressive strength development was a little higher than that of reference specimens. The presence of copper in cement matrix up to 2500 mg/L positively influences engineering properties of mortar. The strength loss exhibited was due to dissociation of calcium hydroxide and decalcification of C-S-H.

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