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Effect of Heavy metal and Magnesium Sulfate on Properties of Blended Cement Mortar

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Abstract

The effect of cadmium (Cd) present in mixing water on compressive strength, setting times, soundness and magnesium sulfate attack of high strength cement mortar was experimentally evaluated. Cement mortar specimens were cast using deionised water and cadmium (Cd) spiked deionized water for reference and test specimens as mixing waters respectively. On comparison with reference specimens, at higher concentrations of cadmium in mixing water, test samples had shown considerable loss of strength and also their setting times had significantly increased. However, at 2000 mg/L concentration of cadmium (Cd), the compressive strength marginally increased. Apart from that when reference specimens and test specimens were immersed in various concentrations of magnesium sulfate solution at different immersed ages, the loss in compressive strength was found to have been a slightly less in test specimens than that in reference specimens. XRD technique was employed to find out main compounds.

Key words: Cement mortar, cadmium (Cd), silica fume (SF), magnesium sulfate, superplasticiser (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[1]. 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[2]. 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[34]. Even though a huge volume of research 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 had worked on use of treated and partially treated wastewaters, but a particular constituent effect and its maximum permissible limit in mixing water was not reported[5]. 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 cadmium (Cd) present in mixing water for cement mortar and effect of magnesium sulfate in various concentrations on the same specimens. Pb, Zn, hg, Cu, Ni, Fe and Cr were friendly with cement mortar up to 600mg/L[6]. The tolerable limit of Cu, Pb, Zn, Mn was 500 mg/L[7]. The use of reclaimed wastewater for concrete mixing did not have any adverse effect on concrete[8]. Biologically contaminated water has given inexplicit results both positive and negative on cement mortar[9]. Biologically treated domestic wastewater was indistinguishable from distilled water when used as mixing water in concrete[10]. However, heavy metals such as Cu, Zn, Pb, caused a retardation of the early hydration and strength development of cement mortar[11]. These metals delayed setting and early strength development[12]. 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 and cement mortar made with metal spiked deionised water is exposed to sulfate environment. Hence, this investigation was carried out to understand the effect of cadmium (Cd) in mixing water on compressive strength, setting times, soundness of high strength cement mortar and to evaluate magnesium sulfate attack on the same cement mortar.

Material and Method

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

S. 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

S. 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

S. 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%

Superplasticiser: Commercial superplasticiser 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 cadmium 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

S. 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

Sulfate: Magnesium sulfate was used in different concentrations in order to study the magnesium sulfate attack on reference and test specimens.

Methods: Cadmium(Cd) was introduced into the deionised water in predetermined concentrations such as 10, 50, 100, 500, 1000, 2000, 3000, 4000, 5000mg/L. The concentrations were arrived based on the literature. After a 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

S. 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

Nine series of specimens were cast for test. The test specimens were cast with (cement + 9% SF + 0.8% SP + Cadmium). Cadmium concentrations of 10, 50, 100, 500, 1000, 2000, 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, 90, 180 and 365 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. In order to study magnesium sulfate attack, After 28 days curing, the reference mortar specimens were immersed in five plastic tanks. Magnesium sulfate concentrations maintained in the tanks were 1%, 1.5%, 2%, 2.5%, and 4% respectively. These concentrations represent very severe sulfate exposure conditions according to ACI 318-99, that are widely prevalent in many parts of the world[1314]. The exposure magnesium sulfate solutions were prepared by dissolving magnesium sulfate in deionised water. Fifteen specimens were immersed in each concentration for up to 12 months. The concentration of the solution was checked periodically and the solution was changed every 4 months. The above procedure was adopted for test specimens where a concentration of cadmium was 2000 mg/L. Three mortar specimens representing similar compositions were retrieved from the magnesium sulfate solutions after 1, 3, 6, 9, 12months of immersion. The effect of magnesium sulfate concentrations on the performance of reference and test specimens was evaluated by measuring the reduction in compressive strength. The reduction in compressive strength of reference and test specimens immersed in magnesium sulfate solutions were compared with that of reference specimens cured in deionised water.

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[15]. The reference sample (Cement + 9% SF + 0.8% SP + Deionised water) and test sample (Cement + 9% SF + 0.8% SP + Cadmium 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 copper Kα radiation.

Results and Discussions

Setting times: Figure 1 shows the effect of deioniesd water (Reference) and lead spiked deionised water (test) on initial and final setting times. The initial and final setting times increased as the concentration of cadmium increased. At a maximum concentration of 5000 mg/L, the test samples had 64 minutes increase in the initial setting time and 71 minutes increase in the final setting time, compared to the reference specimens. At the opted concentrations (10, 50, 100, 500, 1000, 2000, 3000, 4000, 5000mg/L), the increases in initial setting times observed were 0, 0, 0, 2, 12, 23, 38, 51 and 64 minutes respectively. The corresponding increases in the final setting times were 0, 0, 0, 6, 14, 26, 41, 56 and 71 minutes.

Compressive strength: figure 2 shows the change in compressive strength of test samples due to the use of cadmium spiked deionised water. The strength developments in reference and test specimens were the same for concentration of up to 100 mg/L. For the concentration of 500 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 concentration of 1000 mg/L the decrease in compressive strength at 3 days was 3.0%, but at 7, 28, 90, 180 and 365 days a slight increase in compressive strength was observed by 0, 0.60, 1.00, 0.41 and 0.4% respectively, compared with reference specimens. For the concentration of 2000 mg/L the decrease in compressive strength at an early age (3 and 7days) was by 8.12 and 3.28%, but from 28, 90, 180, 365 days a marginal increase in compressive strength was noticed of 1.95, 2.12, 1.45 and 1.52% respectively, compared with reference specimens. However, the rate of decrease in compressive strength increased from 3000 to 5000 mg/L. At 5000 mg/L, the decrease in compressive strength was by 32.25, 28.35, 21.10, 23.05, 25.42, 29.65% for 3, 7, 28, 90, 180, 365 days respectively. Eventually, compressive strength results reveal that at 2000 mg/L concentration, maximum increase in compressive strength is observed.

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 lead spiked deionised water (test) on soundness is shown in figure 3. The expansion measured were 0.7, 0.7, 0.7, 0.7, 0.88, 1.1, 1.4, 1.7, 2.0 and 2.4 mm for 0, 10, 50, 100, 500, 1000, 2000, 3000, 4000 and 5000mg/L concentrations respectively. Since all measured values were less than 10 mm, all the samples are considered sound.

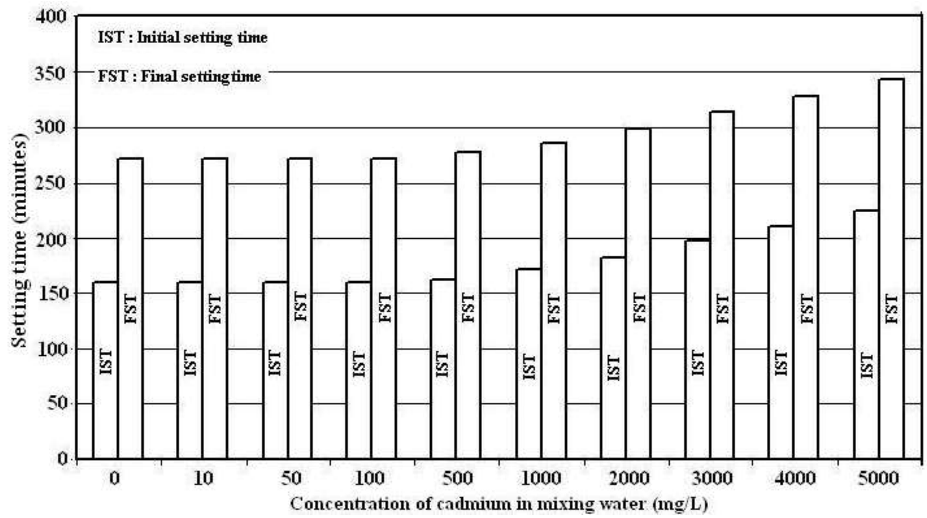

Figure-1
Effect of cadmium on setting time of blended cement

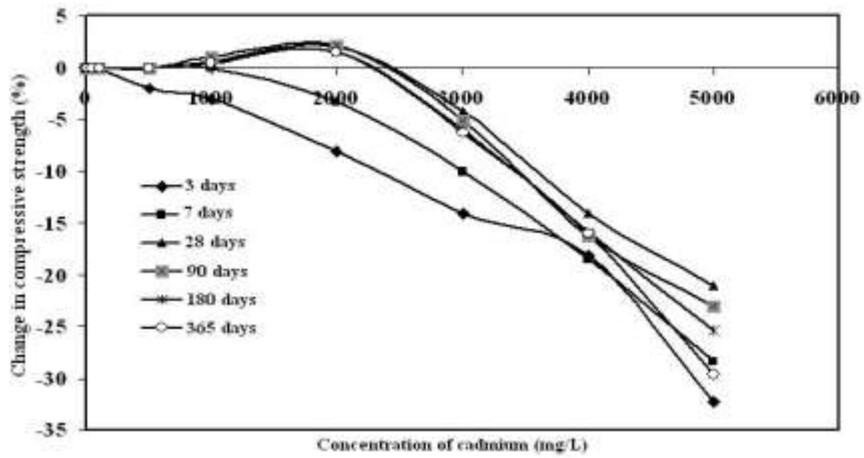

Figure-2
Change in compressive strength of mortar specimens made with various concentrations of cadmium at different age

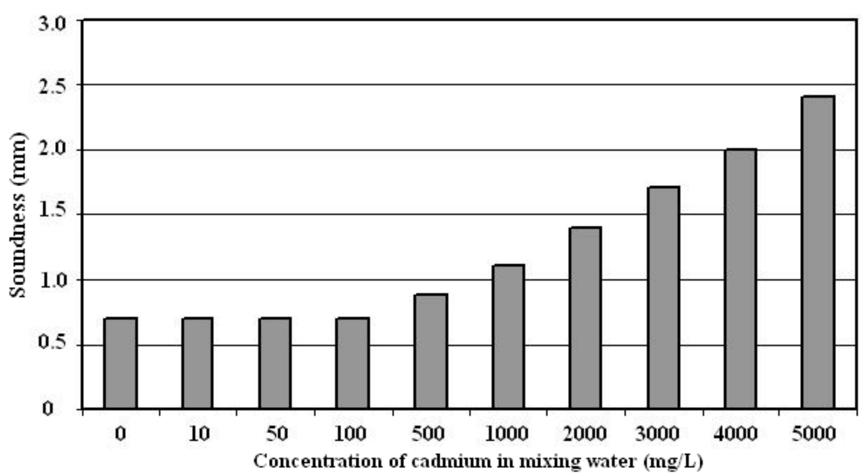

Figure-3
Effect of cadmium on soundness of blended cement

Sulfate attack: Figure 4-8 show reference and test specimens immersed in 1, 1.5, 2.0, 2.5 and 4% magnesium sulfate solutions for 12 months. The decrease in compressive strength, with increase in concentration and period of exposure, was noted in reference and test specimens, compared with reference specimens immersed in deionised water. The decrease in compressive strength was similar in reference and test specimens for any concentration of magnesium sulfate solution. The decrease in compressive strength was insignificantly less in test specimens, compared with reference specimens. However, at 12months, the decrease in compressive strength was by 2.4, 3.4, 4.7, 6.85, 10.5% in reference specimens and 2.3, 3.2, 4.5, 6.75, 10.1% in test specimens for 1, 1.5, 2.0, 2.5 and 4% concentration of magnesium sulfate solution respectively.

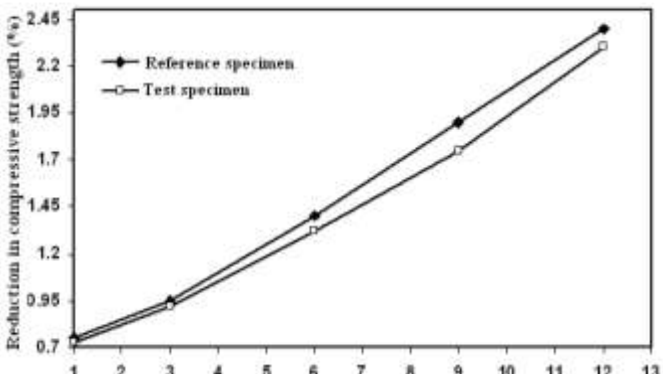

Figure-4
Reduction in compressive strength of mortar specimens immersed in 1% magnesium sulfate solution

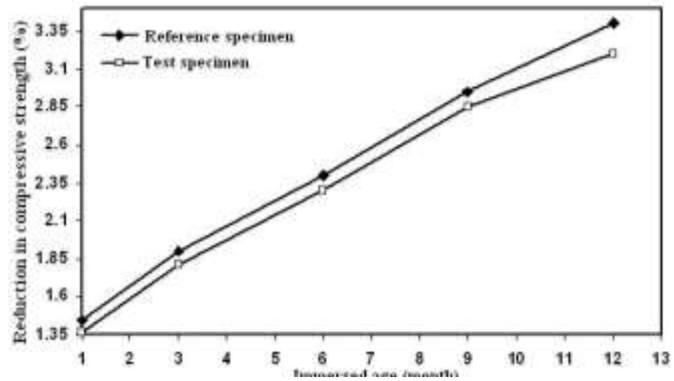

Figure-5
Reduction in compressive strength of mortar specimens immersed in 1.5% magnesium sulfate solution

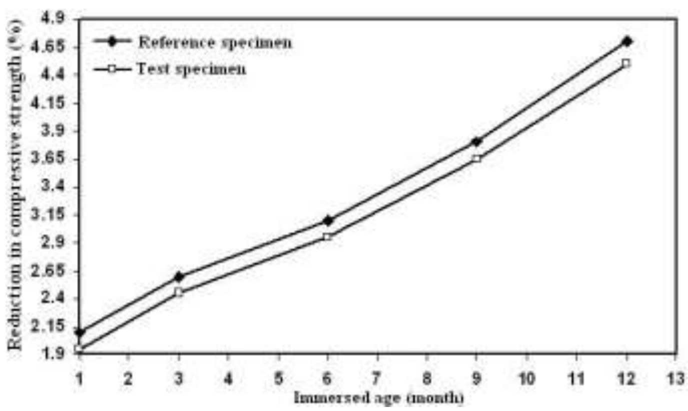

Figure-6
Reduction in compressive strength of mortar specimens immersed in 2% magnesium sulfate solution

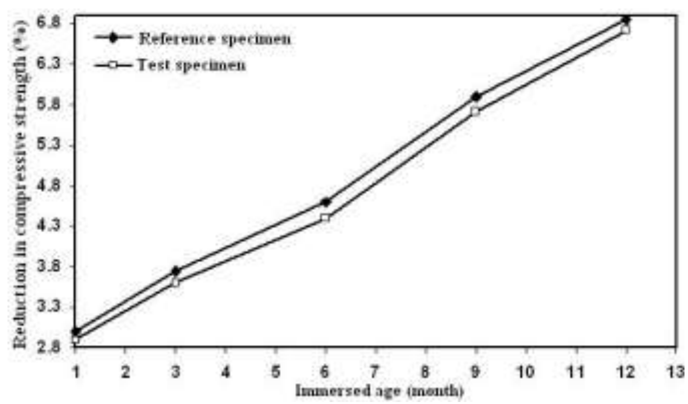

Figure-7
Reduction in compressive strength of mortar specimens immersed in 2.5% magnesium sulfate solution

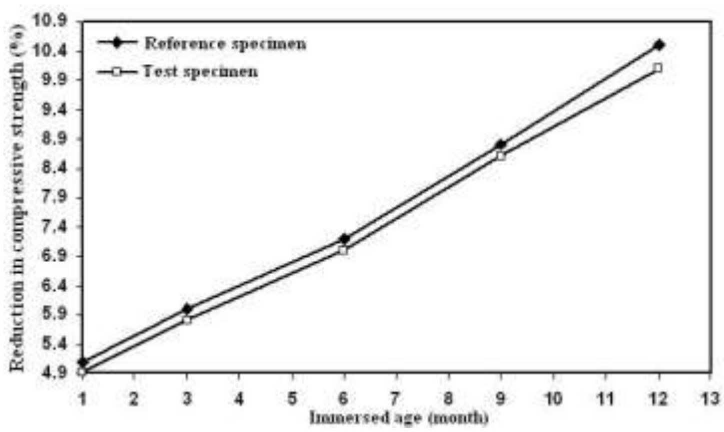

Figure-8
Reduction in compressive strength of mortar specimens immersed in 4% magnesium sulfate solution

XRD Analysis of blended cement paste made with deionised water and cadmium spiked deionised water: Figure 9 shows that powder X – ray diffraction patterns of reference and test samples. Both reference and test sample (2000 mg/L) were cured for 28 days before being subjected to XRD technique. After employing XRD for test sample, some new compounds were found along with hydrated compounds such as C_3S, C_2S, C-S-H, $Ca(OH)_2$, $Cd(OH)_2$, Cd-S-H, at 32.6^0, 32.6^0, 29^0, 20.6^0, 42.5^0, 31.5^0 respectively. Cadmium hydroxide precipitation is expected to form quickly in the high alkaline environment of a cement mix. The precipitated cadmium 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 cadmium above 2000 mg/L, delay in setting time was found to have increased. The compressive strengths of test specimens were considerably decreased compared with reference specimens as concentration of cadmium was increased. The possible reasons, as concentration of cadmium increases, cadmium hydroxide precipitation increases and may increase the replacement of Ca by Pb in hydrated compounds.

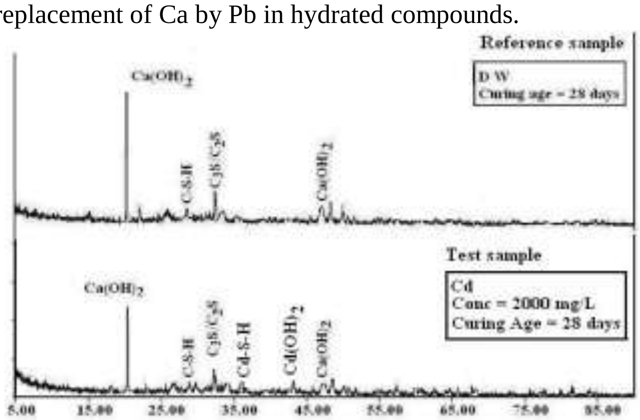

Figure-9
Comparison between XRD patterns of reference and test samples at age 28 days

Conclusions

Based on the results of this investigation, it was concluded that: Lead spiked deionised water affected setting times. For the concentration of 3000 mg/L and above, setting times were significantly increased. The presence of cadmium in high concentrations (≥ 3000 mg/L) in deionised water considerably decreased the compressive strengths. For a concentration of 2000 mg/L, at early ages of 3 and 7 days, compressive strength development was slow but for 28 days and onwards, compressive strength development was slightly higher than that of reference specimens. The presence of cadmium in cement matrix up to 2000 mg/L positively influences engineering properties of mortar. The compressive strength loss in reference and test specimens was almost the same when they were immersed in magnesium sulfate solutions. The strength loss exhibited was due to dissociation of calcium hydroxide and decalcification of C-S-H.

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