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Effect of Chromium on High Performance Cement Mortar

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ABSTRACT

The effect of chromium (Cr) present in mixing water for high performance cement mortar was experimentally evaluated. The properties investigated are setting times, soundness, compressive strength, durability aspects like acid attack, alkaline attack, sulphate attack and chloride ion penetration. High performance cement mortar specimens were cast using Chromium (Cr) spiked de-ionized water and de-ionized water for test specimens and reference as mixing waters respectively. It is observed that, the initial and final setting times of cement paste with test specimens got retarded with increase of Chromium concentration in de-ionized water. The change in expansion of cement mortar is insignificant at all concentrations of the Chromium. Very slight decrease in compressive strength was observed at low concentrations of Chromium than that of controlled cement mortar and gradually increases for remaining concentrations of chromium. The compressive strength and weight of the specimen mortar cubes immersed in acid, alkaline and sulphate solutions decreases with age. The chloride ion permeability is observed low.

Key words— Chromium (Cr), Compressive Strength, De-ionized Water, High Performance Cement Mortar (HPCM), Micro Silica, Setting Times, Soundness, Super Plasticizer (SP).

1. INTRODUCTION

Mechanization, increases in population and human activities are continuously generating lot of liquid and solid waste causing many environmental problems in the world. Waste water generated from industrial sector is being diverted directly into rivers and streams without proper treatment in most of the cases. Construction industry is one of the largest consumers of water. Generally, potable water is suitable as mixing water for cement concrete. Due to pollution of water bodies, availability of potable water is becoming scarce for the construction industry there by forcing it to use alternate sources of water. In this regard, industrial waste water plays an important role. Reuse and recycling of industrial waste water may be practiced to attain sustainable development of construction industry.

Heavy metals like Hg, Zn, Pb, Cu, Ni, Fe and Cr showed good results with cement mortar up to concentration of 600mg/L [1]. Non-potable water, such as treated industrial waste water, which contains heavy metals like Ni, Zn, Hg, Cu, Cr, Pb, Cd, and Fe was used in making cement mortar and got satisfactorily results [2]. Concrete cast with reclaimed wastewater as mixing water did not have any adverse effect. Concrete with improved initial compressive strength could be made with reclaimed wastewater used partially or totally for the mixing water [3]. Cadmium spiked de-ionized water for the concentration of 3000 mg/L and above, setting times were significantly increased, for the concentration of 3000 mg/L and above, the compressive strength were considerably decreased, For a concentration of 2000 mg/L, at early ages of 3 and 7 days, the compressive strength development was slow but for 28 days and onwards, Compressive strength development was slightly higher than that of reference specimens. The compressive strength loss in reference and test specimens was almost the same when they were immersed in magnesium sulfate solutions [4]. Retardation of the early hydration process and strength development of cement mortar is caused by presence of Heavy metals such as Zn, Pb, Cu [5].Amount and quality of mixing water in concrete and cement mortar mix are important in determining properties of concrete and cement mortar [6].Supplementary materials like GGBS and silica fume play main role in cement replacing at different percentages [7]. It was found that the strengths of both cement mortar and cement paste increases when 15% of the cement is replaced by silica fume [8]. It was suggested the term HPC for concrete mixtures that possess the following three properties: high strength, high workability, and high durability [9]. Equivocal results that are both positive and negative results are observed in cement mortar mixed with biologically contaminated water [10]. Silica Fume added to concrete increases water demands, often requiring one additional pound of water for every pound of added Silica Fume. This is due to high surface area of silica fume. This problem can be easily overcome by using super plasticizer or HRWR [11]. In case of low concentrations, hydrochloric acid and nitric acid caused higher deterioration compared to sulfuric acid during the testing period. Sulfuric acid that produced the least soluble calcium salt had caused the least damage on test specimens especially in terms of both strength and weight loss [12]. It was investigated the effect of acid attack on concrete with fly ash and micro silica. 150 mm size concrete cubes which were cured for 28 days and immersed in water with 1 % of sulfuric acid for 45 day were tested and it was reported that the loss in weight of control concrete was 2.5% where as the concrete with 15% fly ash and 7.5% micro silica showed only 1.09% loss in weight [13]. Though reclaimed industrial wastewater are reported to be used in cement mortar for mixing, there is very tiny information is available on the permissible limit of heavy metals in mixing water and cement mortar made with heavy metal spiked de-ionized water exposed to acid attack, alkaline attack and sulphate attack. Hence, this exploration was carried out to understand the consequence of Chromium (Cr) in mixing water on soundness, setting times, compressive strength, acid attack, alkaline attack, sulphate attack and chloride ion penetration on high performance cement mortar.

2. MATERIALS AND METHODS

The materials used in this investigation include:

1. 53 – Grade OPC
2. Fine aggregate (Ennore sand – grade I, grade II and grade III)
3. Micro Silica
4. Water (De-ionized)
5. Super plasticizer
6. Heavy Metal (Chromium)
7. Chemicals

2.1 Cement

Ordinary Portland cement (53 Grade) was used for this study. Initial experiments like initial setting time, final setting, soundness and compressive strength test on mortar cubes were conducted. The physical and chemical properties of cement are within the permissible limits as per IS 12269:1987 and are given in Table 1 and Table 2 respectively.

Table 1: Physical Properties of Cement

S. No.	Property	Result
1	Specific gravity	3.20
2	Fineness	325 m^2/kg
3	Initial setting time	150 minutes
4	Final setting time	260 minutes
5	Compressive strength	MPa
	a) 3 days	29
	b) 7 days	38
	c) 28 days	54
6	Soundness	0.5 mm

Table 2: Chemical Composition of OPC

S.No.	Oxide Composition	Percent
1	CaO	64.58
2	SiO_2	21.83
3	Al_2O_3	5.48
4	Fe_2O_3	4.46
5	MgO	1.10
6	Alkalies(Na_2O,K_2O)	0.002
7	SO_3	1.5

2.2 Fine Aggregate

The fine aggregate used throughout this investigation was obtained from Ennore, Tamil Nadu minerals limited, Chennai. It is approved by Bureau of Indian Standards (BIS) to manufacture and supply of Indian Standard sand conforming to IS 650:1991. The physical and chemical properties of the sand are presented in Table 3 & Table 4:

Table 3: Physical properties of Ennore Sand

Physical property	Results
Specific gravity	2.64
Bulk density(kg/m3)	15.54
Fineness modulus	2.72
Particle size variation(mm)	0.09 to 2
Color	Grayish white
Water absorption in 24 hours	0.8%
Shape of grains	Sub angular

Table 4: Chemical properties of Ennore Sand

Chemical Property	Results
SiO2	99.30%
Fe2O3	0.10%
Loss on ignition	0.11%

2.3 Micro Silica

Micro silica used throughout this investigation was obtained from Mumbai, India. The physical and chemical properties of the Micro silica are presented in the Table 5 and Table 6.

Table 5: Physical Properties of Silica Fume

Physical Properties	Specific gravity	2.22
	Average particle size	0.1 microns
	Bulk density	223 kg/m^3

Table 6: Chemical Properties of Silica Fume

Chemical Compound	Percent of Total Weight
SiO_2	95.65
Al_2O_3	0.37
Fe_2O_3	0.21
CaO	0.16
MgO	0.09
SO_3	0.42
Na_2O	0.51
Loss on ignition	1.43

2.4 Water

For reference specimens, De-ionized water was used and Chromium spiked de-ionized water was used for test specimens in different concentrations.

2.5 Super Plasticizer

Commercially available 'conplast SP-430' water reducing agent was used. The properties are given in the Table 7.

Table 7: Properties of conplast SP-430

Property	Value
Specific gravity	1.20 – 1.22 at 30°c
Chloride content	Nil as per IS: 9103-1999 and BS : 5075
Air entrainment	Approx. 1% additional air over control

2.6 Heavy Metal

Chromium (Cr) is a heavy metal with atomic number 24. It is slightly soluble in water. Chromium heavy metal introduced into the de-ionized water in predetermined concentrations such as 10, 50, 100, 500, 1000, 2000, 3000, 4000 and 5000mg/L. The physical properties of Chromium are presented in the Table 8.

Table 8: Physical properties of Chromium (Cr)

Physical Properties	Density	2.87 gm/cc
	Melting point	1152 °C
	Boiling point	1300 °C

2.7 Chemicals

2.7.1 Acids -Sulfuric acid of 2.5 % concentration mixed in de-ionized water and Hydrochloric acid of 2.5 % concentration mixed in de-ionized water.

2.7.2 Alkalies -Sodium hydroxide of 2.5 % concentration mixed in de-ionized water.

2.7.3 Sulphates -Magnesium sulphate of 2.5% concentration mixed in de-ionized water.

2.7.4 Sodium Chloride – 3 % by mass (reagent grade) mixed in de-ionized water.

2.7.5 Sodium Hydroxide – 0.3 N (reagent grade) mixed in de-ionized water.

2.8 Methods

The experimental methods adopted were in accordance with the standard procedures laid down in Bureau of Indian standards. Chromium was added into the de-ionized water in different concentrations such as 10 mg/l, 50 mg/l, 100 mg/l, 500 mg/l, 1000 mg/l, 2000 mg/l, 3000 mg/l, 4000 mg/l, and 5000mg/l. As per standard specification, Cement is replaced with silica fume [14]. As per literature, the concentrations of admixtures used are arrived at 9% Micro Silica replacement in cement and addition of Super Plaster of 0.8% was fixed for reference high performance cement mortar specimens.

Seventeen reference mixes were cast for test and finally the test specimens were cast with (cement + 9% SF + 0.8% SP) based on maximum compressive strength. Chromium concentrations such as 10, 50, 100, 500, 1000, 2000, 3000, 4000, and 5000mg/L were introduced in de-ionized water as mixing water for test specimens. The physical properties obtained for reference specimens are given in Table 9.

Table 9: Physical properties of High performance Cement mortar

S. No	Property	Result
1	Initial setting time	72 minutes
2	Final setting time	135 minutes
3	Compressive strength	MPa
	a) 3 days	48
	b) 7 days	62
	c) 28 days	67
4	soundness	1mm

The amount of cement, fine aggregate and mixing waters for preparing each specimen were 200gms, 600gms and "(P/4) + 3" where 'P' denotes the percentage of mixing water required on combined weight of cement and fine aggregate to make a paste of standard consistency. Vicat's apparatus was used to find the Initial and final setting times[15]. As per IS 456-2000, to test the quality of water under question for its suitability to use for construction purpose, the compressive strength of the specimens made with water in question should not differ by 10 percent with that of the cubes made from de-ionized water. Also, if the difference in initial setting time of the sample under question is more than 30 minutes it is significant otherwise it is in significant. Le-Chatelier equipment was used to find the soundness of reference and test specimens. If the expansion of the sample is more than 10mm, it is significant otherwise it is insignificant.

The specimens were cast using standard metallic cube mould of size 70.6 mm X 70.6 mm X 70.6 mm for compressive strength of cement mortar. The mix proportion of cement mortar that is cement to sand ratio is 1: 3 by weight throughout [16]. The compressive strength of specimens was studied at different ages, i.e., 3 days, 7 days, 28 days, 90 days and 180 days[17]. The specimens in mould were maintained at a controlled temperature of 27^0 c ± 2^0 c and at 90 % relative humidity for 24 hours by covering the moulds with gunny bags wetted by the de-ionized water. After 24 hours specimens were de-molded and cured in de-ionized water for further 27 days. Three test specimens were tested for each mix and average of three values are taken to compare with reference specimens. The maximum Compressive strength was obtained at Chromium concentration of 5000 mg/l. Hence the resistance to aggressive chemical nature was found at Chromium concentration of 5000 mg/l.

In order to study the durability aspect, effects of acidic alkaline and sulfate were investigated. Solutions of Sulfuric acid, Hydrochloric acid, Sodium hydroxide and Magnesium sulphate were prepared with de-ionized water at 2.5% concentration in four non absorbent plastic tanks. Mortar cubes of 500 mm^2 cross sectional area were cast and cured in the prepared solutions and tested for compressive strength and weight loss at 30 days, 60 days, 90 days and 180 days and it was compared with reference specimens cured in de-ionized water for the same period. The Chloride Ion Permeability was determined by using Rapid Chloride Permeability Test. Cylinders of dimensions 100mm diameter and 200mm height were cast and cured in water for 28 days.

By using the diamond saw, cut a 50 mm slice from the top of the cylinder so that cylinder specimen of size 100 mm in diameter and 50mm in thickness was prepared and this specimen was used for Rapid Chloride Permeability test to determine the Chloride Ion Permeability. The diffusion cell consists of two chambers. NaCl solution concentration 2.4M was filled in one chamber and in another chamber 0.3M NaOH solution was taken. This two component cell assembly checked for air and water tightness. Turn DC power supply on, set to 60 V, and record initial current reading. During the test, the air temperature around the specimens shall be maintained in the range of 20 to 25 °C. Read and record current values at an interval of 30 minutes and monitored up to 6 hours. From the observed current values, the chloride ion permeability is calculated in terms of coulombs at the end of 6 hours by using the formula as given in ASTM C1202.

$$Q=900(I_o+2I_{30}+2I_{60}+2I_{90}+\ldots+2I_{300}+2I_{330}+I_{360})$$

Where

Q = Charge passed (Coulombs)

I_0 = Current immediately after voltage is applied in Amperes,

I_t = Current at't' minutes after voltage is applied in Amperes,

3. RESULTS AND DISCUSSIONS

Effect of chromium metal present in mixing water on the properties of high performance cement mortar are analyzed by laboratory testing for respective parameters .They include setting times, soundness, compressive strength, acidic & alkaline environment tests and rapid chloride permeability test.

3.1 Effect on Setting Times

The effect of Chromium present in different concentrations in the mixing water on setting times is represented graphically in Fig.1. It is observed that the initial and final setting process of cement got retarded with increase of Chromium concentration in de-ionized water.

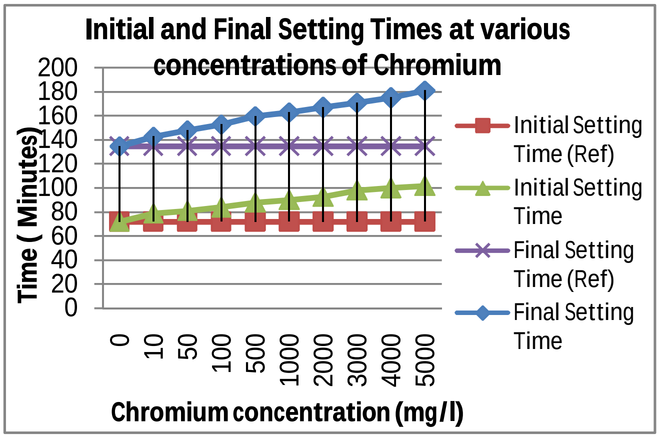

Figure 1: Variation of initial and final setting times of cement of various concentrations of Chromium

The increase in the initial setting time is insignificant at all concentrations of chromium (i.e. up to 5000 mg/l), but the increase in the final setting times are insignificant up to 1000 mg/l concentration and are significant at 2000mg/l, 3000 mg/l, 4000 mg/l and 5000mg/l concentrations of Chromium. The increase in the initial setting time is less than 30 minutes for all concentrations of chromium when compared with that of the test blocks made with de-ionized water.

The increase in the final setting time is 32 minutes at 2000 mg/L,36 minutes at 3000mg/l,40 minutes at 4000 mg/L and 46 minutes at 5000mg/l concentration of chromium when compared with that of the test blocks made with de-ionized water, for all other concentrations it is less than 30 minutes. Hence, the effect of Chromium on an average over setting times is insignificant for all the specimens tested.

3.2 Effect on Soundness

The effect of Chromium on soundness of blended cement mortar is represented graphically in Figure2. The effect of Chromium at all concentrations on soundness of the cement was studied. The expansion after soundness test obtained with de-ionized water is 1mm.

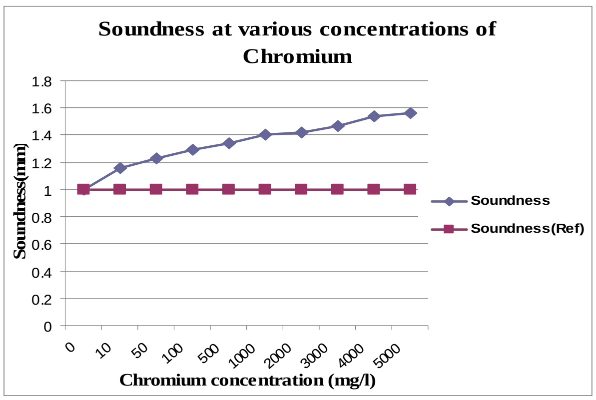

Figure 2: Soundness of specimens at various concentrations of Chromium

The same was obtained as 1.16mm for 10mg/L Chromium concentrated mixing water and 1.56 mm at 5000 mg/L Chromium concentrated mixing water. Expansion of cement mortar with all concentrations of Chromium is well within the prescribed limits. Therefore, the effect of Chromium metal present in mixing water for High performance cement mortar is insignificant.

3.3 Effect on Compressive Strength

The effect of Chromium present in mixing water at different concentrations on compressive strength of high performance cement mortar is graphically represented in Fig 3. Cement mortar cubes cast with chromium spiked de-ionized water for 7 Days, 28 Days and 180 Days of curing showed very slight decrease in compressive strength than that of controlled blended cement mortar cubes up to 50 mg/l. Beyond 50 mg/l concentration of chromium, the compressive strength gradually increases and reaches maximum at 5000 mg/l concentration of Chromium. But for 3Days and 90 Days of curing showed gradual increase in compressive strength than that of controlled blended cement mortar cubes for all concentrations of Chromium.

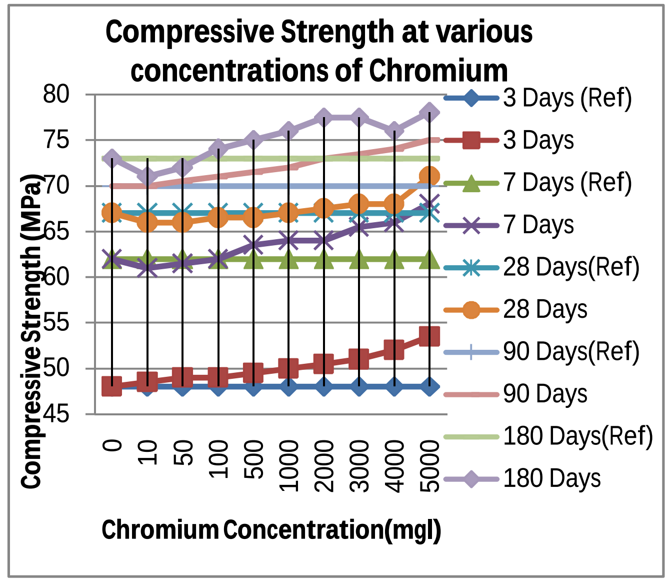

Figure 3: Compressive strengths of mortar cubes at various concentrations of Chromium at different ages

The percent change in compressive strength of blended cement mortar cubes cast with different concentrations of Chromium in de-ionized water was graphically represented in Fig 4. The percent change in compressive strength at all concentrations of Chromium is below 10 percent except at 5000 mg/L at 3 days when compared with that of the compressive strength of blended cement mortar cubes cast with de-ionized water. Hence, the effect of Chromium heavy metal on compressive strength up to 5000mg/L is insignificant.

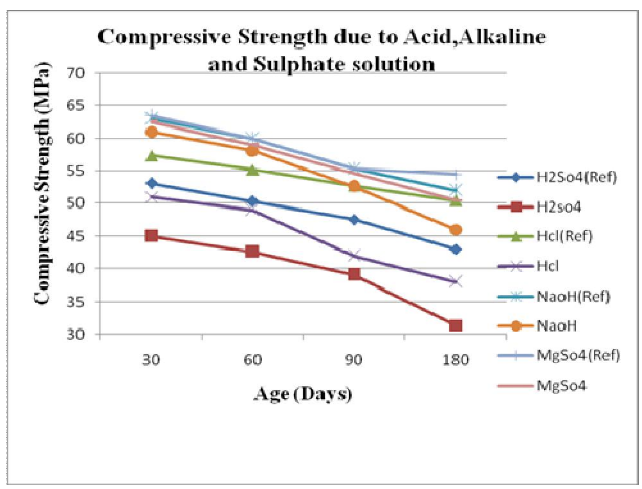

Figure 4: Percent change in compressive strengths at various concentrations of Chromium at different Ages

3.4 Effect on Durability

For conducting durability tests among the reference mix cubes made with de-ionized water, cement mortar cubes made with 5000mg/l Chromium concentrated mixing water were taken for testing, at which the maximum compressive strength was attained.

3.4.1 Resistance against Acid Attack

The compressive strength results and the loss in weight of the acid attacked blended cement mortar cubes cast with different mixing compounds in de-ionized water are graphically represented in Figure 5 and Figure 6.

3.4.2 Resistance against Alkaline Attack

The compressive strength results and the loss in weight of the alkaline attacked blended cement mortar cubes cast with different mixing compounds in de-ionized water and Chromium spiked de-ionized water are graphically represented in Figure 5 and Figure 6.

3.4.3 Resistance against Sulphate Attack

The compressive strength results and the loss in weight of the sulphate attacked blended cement mortar cubes cast with different mixing compounds in de-ionized water and Chromium spiked de-ionized water are graphically represented in Figure 5 and Figure 6.

The strength of the mortar cubes decreases with age. And also the strength changes with the change in curing solution. The lowest strength is observed for acid attack and less reduction in strength is observed for sulphate attack. The lowest strength is observed for the Sulfuric acid and then for hydrochloric acid and less reduction in strength is observed for Magnesium sulphate. Next to Magnesium sulphate, slight increase in strength is observed for alkaline solution

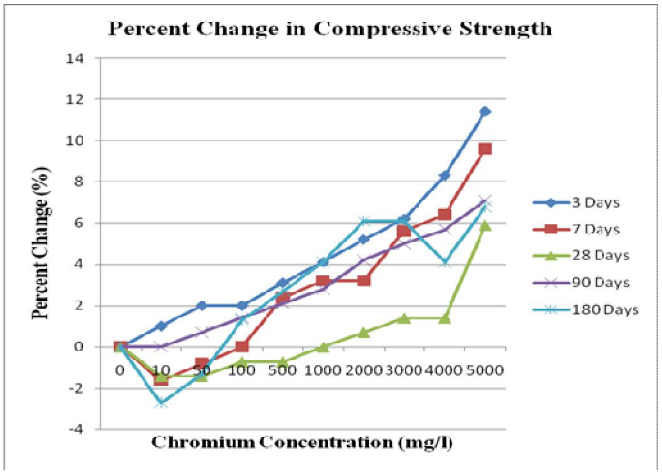

Figure 5: Compressive strength of control cement mortar cubes and that of cubes cast with Chromium containing water immersed in different solutions.

The change in the strength of the mortar cubes cast with Chromium when compared with control mortar increases as the age increases. And as the age increases, the change in the compressive strength decreases, it can be seen in Figure 5. The main reason is the surface of the cube erodes initially at higher rates and as the age increases the rate of erosion decreases slowly.

The percentage change in the compressive strength ranges from 36.6 % at 30 days exposure to 55.7 % at 180 days when exposure to Sulphuric acid. The percentage change in the compressive strength ranges from 28.1 % at 30 days exposure to 46.4 % at 180 days when exposure to Hydrochloric acid. The percentage change in the compressive strength ranges from 14 % at 30 days exposure to 35.2 % at 180 days when exposure to Alkaline media. The percentage change in the compressive strength ranges from 11.9 % at 30 days exposure to 28.8 % at 180 days when exposure to Sulphate media.

The weight loss of the blended Cement Mortar cubes cast with de-ionized water when immersed in acidic media is more and considerable and the same is negligible when exposed to Alkaline and Sulphate solutions. The maximum loss in weight was found to be at 180 days in acidic media.

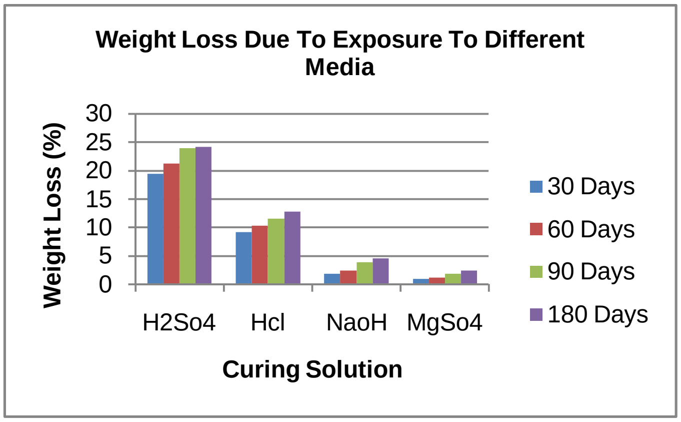

Figure 6: The graph showing the loss in weight of blended cement mortar cubes cast with water containing Chromium immersed in different solutions

The minimum loss in weight was found to be at 30 days in sulphate solution. This is due to the variation in P^H values. The Figure 6 shows the loss of weight of blended cement mortar when immersed in different media.

3.5 Rapid Chloride Permeability Test

The values of ion penetration of the cylinder specimens cast with de-ionized water and Chromium spiked de-ionized water are graphically represented in Figure 7. The charge passing is less for the cylinder specimen cast without metal. The charge passing through the cylinders cast with Chromium is high when compare with that of the control mortar, as shown in Figure 7 . As per ASTM C1202 penetrating rate for both cylinder specimens cast with de-ionized water and Chromium spiked de-ionized water is categorized as low.

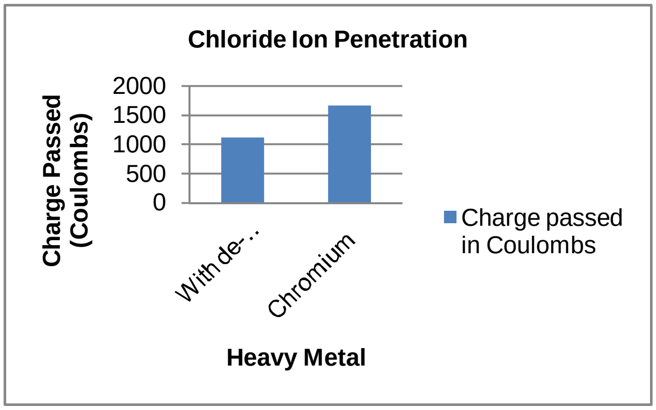

Figure 7: The graph showing the charge passed through the cement mortar specimens cast with De-ionized water and Chromium spiked De-ionized water

4. CONCLUSIONS

Based on the results and analysis of this investigation**,** The following conclusions may be drawn on the properties of High Performance Cement Mortar

1. As the chromium concentration in spiked water increased, the initial setting time of cement paste were retarded and is insignificant at all concentrations, the final setting time of cement paste were retarded and are insignificant up to 1000 mg/l and is significant beyond 1000 mg/l.

2. Expansion of blended cement spiked with Chromium de-ionized water is well within limits at all concentrations.

3. As the chromium concentration in spiked water increased, gradual increase in Compressive strength was observed except at some concentrations of Chromium at 7 days, 28 days and 180 days of curing.

4. The blended cement mortar cubes cast with Chromium de-ionized water immersed in H_2So_4, HCl solutions showed more reduction in compressive strength than that of the controlled blended cement mortar and showed very less reduction in compressive strength than that of the controlled blended cement mortar cubes exposed to NaOH solution, $MgSo_4$ solution. The reduction in compressive strength of the controlled blended cement mortar is significant at 30 days exposure to H_2So_4, HCl solutions and is insignificant for exposure to NaOH, $MgSo_4$ solutions.

5. Weight loss of the specimens is significant for the blended cement mortar cubes cast with Chromium spiked de-ionized water immersed in H_2So_4 solution and it is insignificant for the blended cement mortar cubes cast with Chromium de-ionized water immersed in HCl solution up to 60 days beyond that it is significant. Weight loss is insignificant when the specimens were exposed to NaOH and $MgSo_4$ solutions.

6. Permeability of blended cement mortar specimens cast with Chromium spiked de-ionized water is low.

7. The results obtained from this study indicates that industrial waste water containing Chromium up to concentration of 5000 mg/l has positive effect on engineering properties of High Performance Cement mortar and can be used as mixing water in High Performance Cement Mortar and the present investigation can be extended for concentrations of chromium above 5000 mg/l.

8. High Performance cement mortar cast with Chromium spiked de-ionized water up to concentration of 5000 mg/l showed retarding nature and is suitable for hot weather condition to counter the rapid hardening due to high temperature.

9. In the present study, the effect of individual metals present in the waste water from electroplating industry is studied to find the properties of the High performance Cement Mortar . In the same way, the effect of other metals present in the waste water emerging from the other industries like steel, bewerages, textiles etc. can be used to find the properties of the High performance Cement Mortar. Not only the single metal but also the combination of the metals in the industrial waste water can be used to study further the properties of the High performance Cement Mortar.

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