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RESEARCH ARTICLE OPEN ACCESS

Behaviour of Heavy Metals on the Properties of "High Performance Cement Mortar"

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ABSTRACT
Cement is one of the most widely used material in the construction field.. Due to growing population and rapid industrialization, as a result, there is a concomitant increase in waste water volume contaminated with various constituents i.e., organic, inorganic and biological substances. Because of over population and rapid growth of industries, fresh water resources have been drastically diminishing. Metals used for plating are heavy metals having superior qualities like Nickel, Copper, Lead, Cadmium, Platinum, Mercury, Silver, Chromium etc. It has been noted that out of the total amount of these metals used in electroplating, 4% goes as waste in sludge spent wash, electroplating solutions etc. If these waters are used for farming, drinking etc, it may give detrimental effect. Hence, use of these waters has to be thoroughly examined for the purpose for which they have meant. Cement concrete industry is one such which requires lot of water. Concrete is one of the highly consumable product in now a days. Experimental studies are carried out in the present investigation to check the suitablity of industrial waste water containing heavy metals such as Mercury, Lead and Copper on compressive strength development, setting times, soundness and durability against acidic, alkaline and sulphate attack is studied. The goal was to search for the optimal specifications to maximise the replacements of fresh water with an alternative source. Results obtained in these studies indicate that the use of industrial waste water yields compressive strength, setting times, soundness and durability which is insignificant in comparison to the concrete made with de-ionized water. Detailed description about the results was presented with help of graphs, and future scope was discussed.

Keywords: Mercury, lead, copper, alkaline and sulphate attack is studied.

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I. INTRODUCTION

For obtaining high performance cement mortar, the optimum dosage of silica fume and Superplasticizer was fixed on the basis of compressive strength. The compressive strength of cement mortar cubes was found which were casted by varying the percentages of silica fume and Superplasticizer. The percentage of silica fume used was 7% to 10% as replacement of cement by weight. The percentages of Superplasticizer used were 0.6%, 0.8%, 1.0%, and 1.2%, by weight of cement. The mortar cubes were casted by various combinations of percentages of silica fume and Superplasticizer. The maximum compressive strength was obtained at 9% of silica fume and 0.8% of Superplasticizer.

The pollutants from the electroplating industries are invariably hazardous, as the effluents contaminate air, water and soil. The common metals they contain in the water disposed from the electroplating industry even after treating them to limited standards are Mercury, Lead, and Copper etc. Some of the polluting agents have deleterious effect on human health also. The environmental load in electroplating industry mainly consists of process waste water, hydroxide sludge and Sulphuric acid. In the present investigation an attempt is made to find the suitability of water emits from the electroplating industry in making high performance cement mortar

High strength phenomenon allows applying the high performance cement for production of the wide range of mortars with 28th day compressive strength in the range of 40 to 145 MPa. To obtain high performance cement mortar we have taken silica fume as an admixture in association with Conplast SP-430 Superplasticizer. We have replaced cement by 9% silica fume and with 0.8% of Superplasticizer by weight of cement. We obtained high performance cement mortar whose characteristic compressive strength is about **72 N/mm²**.

The parameters considered for the hardening of cement are initial and final setting times. Setting times of cement was found out by a standard Vicat's apparatus. Setting times, both initial and final indicate the hardening of cement. The compression test is the most common test conducted on hardened concrete because most of the desirable characteristic properties of concrete are qualitatively related to its compressive strength. The compressive strength of cement mortar cubes was determined at different ages (3 days, 7 days, 28 days). These mortar cubes casted with water containing different metals (i.e., Mercury, Copper, and Lead) with different concentrations of 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 5000 mg/l are used.

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In the present study, the effect of these heavy metals on high performance cement mortar is compared with the normal high performance cement mortar. High strength and durability of high performance cement are provided by the application of silica fume based complex admixture. High performance cement mortars possess low permeability, high resistance to chemical attack and thermal resistance.

II. Silica Ratio: Silica ratio is the ratio of percentage by weight of silica to that of the sum of the alumina and ferric oxide.
Mathematically it is expressed as

Silica ratio = $$\frac{SiO_2}{\left(Al_2O_3 + Fe_2O_3\right)}$$

The significance of this ratio is that it shows whether the cement is rich or poor in silica in Portland cement. An average value of this ratio should be from 1.7 to 3.5. High silica ratio means a value from 2.5 to 3.5 and a low silica ratio ranges from 1.7 to 2.0 approximately.

Alumina Ratio: Alumina ratio is the ratio of alumina to ferric oxide.

Alumina ratio = $$\frac{Al_2O_3}{Fe_2O_3}$$

With a high value of this ratio we have an alumina rich and ferric oxide free Portland cement. On the other hand for iron ore, which contains no alumina, this ratio is practically zero.

Lime Saturation Factor (L.S.F): L.S.F. has very high significance in the technology of Portland cement. It is the ratio of the quantity of lime present by weight to that required by the acidic oxides (SiO_2, Al_2O_3, Fe_2O_3) to form the main mineralogical clinker compounds.

L.S.F. = $$\frac{CaO - 0.7(SO_3)}{2.8SiO_2 + 1.2Al_2O_3 + 0.65\,Fe_2O_3}$$

The cause for the deduction of SO_3 from the total lime percentage is due to the addition of gypsum during grinding of clinker, which is added to regulate the setting process of cement. The CaO derived from this addition of gypsum enters into the total lime percentage when determined analytically during chemical analysis of cement. The extra CaO induced into cement by addition of gypsum must therefore be subtracted from the total lime content. The actual extra CaO content is obtained by multiplying the quantity of SO_3 obtained by the chemical analysis of cement by a factor 0.70.
BS 12-1978 specifies that the Portland cement shall have the L.S.F. corresponding to a high proportion of dicalcium silicate and also a value corresponding to a high proportion of tricalcium silicate.
Tricalcium aluminate content C_3A is calculated by the formula

$$C_3A = 2.65\ Al_2O_3 - 1.69\ Fe_2O_3$$

Where each symbol refers to the percent by mass of total oxide present in cement, excluding any contained in insoluble residue.

ADMIXTURES:

Admixtures are those ingredients in concrete other than Portland cement, water and aggregates that are added to the mixture immediately before or during mixing. Admixtures can be classified by function as Air-entraining admixtures, water reducing admixtures, plasticizers, accelerating admixtures, hydration-control admixtures, corrosion admixtures, shrinkage admixtures, alkali-silica reactivity inhibitors, coloring admixtures and miscellaneous admixtures such as workability, bonding, damp-proofing, permeability reducing, grouting, gas forming, antiwashout, foaming and pumping admixtures. The major reasons for using admixtures are:

1. To reduce the cost of concrete construction.
2. To achieve certain properties in concrete more effectively than by other means.
3. To maintain the quality of concrete during the stages of mixing, transporting, placing and curing in adverse weather conditions.
4. To overcome certain emergencies during concreting operations.

MATERIALS:

The materials which were used in the present investigation include:

1) 53 grade Ordinary Portland Cement
2) Fine aggregate (Ennore sand)
3) Admixtures
(i) Silica fume – 9% by replacement of cement
(ii) Superplasticizer (Conplast SP - 430) - 0.8% by weight of cement
4) De-ionized water
5) Heavy metals like Lead, Mercury, and Copper are used with different concentrations in (mg/L).
6) Chemicals like Sulphuric acid, Hydrochloric acid, Sodium Hydroxide and Magnesium Sulphate of solutions at 2.5%.
7) 3% of Sodium Chloride and 0.3N of Sodium Hydroxide solutions are prepared with distilled water separately for testing of Rapid Chloride Permeability Test.

ADMIXTURES:

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- To reduce the cost of concrete construction.
- To achieve certain properties in concrete more effectively than by other means.
- To maintain the quality of concrete during the stages of mixing, transporting, placing and curing in adverse weather conditions.
- To overcome certain emergencies during concreting operations.

Despite these considerations, it should be borne in mind that no admixture of any type or amount can be considered a substitute for good concreting practice. The effectiveness of an admixture depends upon factors such as type, brand and amount of cementing materials, water content, aggregate shape, gradation and proportions, mixing time, slump and temperature of the concrete. Trail mixtures should be made with the admixture and the job materials at temperatures and humilities anticipated on the job. In this way the compatibility of the admixture with other admixtures and job materials, as well as the effects of the admixture on the properties of the fresh and hardened concrete, can be observed. The amount of admixture recommended by the manufacturer or the optimum amount determined by laboratory tests should be used.

SILICA FUME:

Microsilica (also known as condensed silica fume or silica fume) was first tested in 1947, and related tests revealed a variety of potential application benefits. The development of large scale production equipment of micro silica in 1970's allowed the increased use of it in concrete. This led to the introduction of national and international standards for the use of the material as an additive to improve the quality of concrete.

Microsilica is produced due to reduction of quartz at high temperature to give silicon or ferro-silicon metal. At 2000^0 C when electric arc is fired through the furnace, quartz releases silicon monoxide gas besides forming the metal. The gas rises and reacts with oxygen in the upper parts of the furnace and condenses as it cools and terms into the pure spherical particles called micro silica. The physical and chemical properties of the silica fume are mentioned in the table 4.7.

The primary chemical properties of silica fume are shown in the table.

Silicon dioxide (SiO_2) content:

The minimum requirement of silicon dioxide is 85%. Because SiO_2 is the reactive ingredients of silica fume, a limit on the content is deemed appropriate.

2.6 **Moisture content:**

The maximum limit of moisture content is 3%. The intent here is to minimize the amount of moisture that is brought along with the silica fume

2.7 Loss on ignition:

The maximum limit of loss on ignition is 6%. Fly ashes have had this requirement for many years because of the potential for partially combusted coal particles being included in fly ash.

This coal can be of a form with a very high surface area, which significantly increases the demand for air entraining admixture in air-entrained concrete. It is not clear whether any coal of this same nature is present in silica fume, do the loss on ignition requirement is more of a control on any unburned coal or other material from the electric arc furnace.

Over size material:

This requirement limits the amount of oversize material retained on a 45 µm (No.235) sieve to a maximum of 10%. There is a further requirement that the maximum variation from average be no more than 5%. As silica fume is an extremely fine material and a sieve analysis will not provide any significant information on particle size or surface area. This requirement is aimed at minimizing the amount of foreign material in the silica fume. Such material could include uncombusted materials from the furnace or rust particles from the silica fume collection system.

Accelerated pozzolanic activity:

The accelerated pozzolanic activity of a silica fume must be at least 105% of the control made without silica fume. The silica-fume mixtures use a dry super plasticizer to achieve a flow value equal to the cement only mixtures.

Specific surface:

Specific surface for silica fume is determined by using a technique known as nitrogen adsorption technique. The minimum specific surface should be $15m^2/kg$. Specific surface is an important parameter for silica fume because the higher the surface, the smaller the particles.

SUPERPLASTICIZER:

The use of superplasticizers (high range water reducer) has become a quite common practice. This class of water reducers was originally developed in Japan and Germany in the early 1960s, they were introduced in the United States in the mid-1970s. Superplasticizers are linear polymers containing sulfonic acid groups attached to the polymer backbone at regular intervals (Verbace 1968).

Most of the commercial formulations belong to one of the four families:

1. Sulfonated Melamine – Formaldehyde Condensates (SMF)
2. Sulfonated Napthalene – Formaldehyde Condensates (SNF)
3. Modified Lignosulfonates (MLS)
4. Polycarboxylate ether Superplasticizers (PCE)

Conplast SP-430 is based on Sulphonated Napthalene Polymers and supplied as a brown liquid instantly dispersible in water. Conplast SP-430 has been specially formulated to give high water reductions upto 25% without loss of workability or to produce high quality concrete of reduced permeability.

The sulfonic acid groups are responsible for neutralizing the surface charges on the cement particles and causing dispersion, thus releasing the water tied up in the cement particle agglomerations and thereafter reducing the viscosity of the paste and concrete (Mindess and Young 1981). The properties of the Superplasticizer are mentioned in the table .

TEST PROCEDURE:

The details of the spiked de-ionized water used in the experimental work are presented in table. A total of 255 reference mortar cubes of 50 cm^2 cross-sectional area were casted and cured in de-ionized water and tested for compressive strength at different ages (3 days, 7 days, 28 days). These mortar cubes were casted with different proportions of Ordinary Portland cement, silica fume and super plasticizer. The details of the proportion of cement and admixtures are presented in table 4.12.

A total of 28 samples of standard mould used in Vicat's apparatus were casted and tested for initial and final setting time experiments. The same numbers of samples of standard mould were used in Le-Chatelier's equipment to test for soundness. A total of 405 mortar cubes of 50 cm^2 cross-sectional area were casted and cured in de-ionized water and tested for compressive strength at different ages (3 days, 7 days, 28 days). The details of the second phase test programme are shown in table 4.13.

A total of 192 mortar cubes of 50 cm^2 cross-sectional area were casted and cured in solution of sulphuric acid, Hydrochloric acid, Sodium Hydroxide and Magnesium Sulphate, and tested for compressive strength and weight loss at different ages (30 days). The details of the durability test programme are shown in table.

A total of 4 samples of cylinders of dimension 100 mm diameter and 200 mm height were casted and cylindrical discs of size 100 mm diameter and 50 mm thickness were prepared and tested for Ion Permeability. The details of the Rapid Chloride Permeability Test programme are shown in table

EXPERIMENTAL PROCEDURE:

Normal consistency, initial and final setting times are determined by the Vicat's apparatus, which measures the resistance of cement paste of standard consistency to the penetration of a needle under a total load of 300 g. The standard consistency of a cement paste is defined as that consistency which will permit the Vicat's plunger to penetrate to a point 5 to 7 mm from the bottom of the Vicat's mould when the cement paste is tested.

Vicat's apparatus conforming to IS 5513-1976 consists of a frame to which a movable rod having an indicator is attached which give the penetration. The rod weights 300 g and has diameter and length of 10 mm and 50 mm respectively. Vicat's mould is in the form of cylinder and it can be split into two halves. Vicat's apparatus includes three arrangements – plunger for determining consistency, square needle for initial setting time and needle with annular collar for final setting time.

The initial set is an arbitrary time in the setting process, which is reached when the needle is no longer able to pierce the 40 mm deep pat of cement paste to within about 5 to 7 mm from the bottom. The final set is reached, when the needle makes an impression on the surface of the paste but does not penetrate.

III.FIGURES AND TABLES

Characteristics of De-ionized Water

S.NO.	Parameter	Deionized water
1.	pH	6.5
2.	TDS(mg/L)	8
3.	Alkalinity(mg/L)	10
4.	Acidity(mg/L)	2
5.	Hardness(mg/L)	1
6.	Sulphates(mg/L)	0.2
7.	Chlorides(mg/L)	8

Permissible limits for solids in water

Sl.No.	Material	Tested as per	Permissible limit (max)
1.	Organic	IS 3025 (part-18)	200 mg/L
2.	Inorganic	IS 3025 (part-18)	3000 mg/L
3.	Sulphates	IS 3025 (part-24)	400 mg/L
4.	Chlorides	IS 3025 (part-32)	2000 mg/L for P.C.C and 500 mg/L for R.C.C
5.	Suspended Matter	IS 3025 (part-17)	2000 mg/L

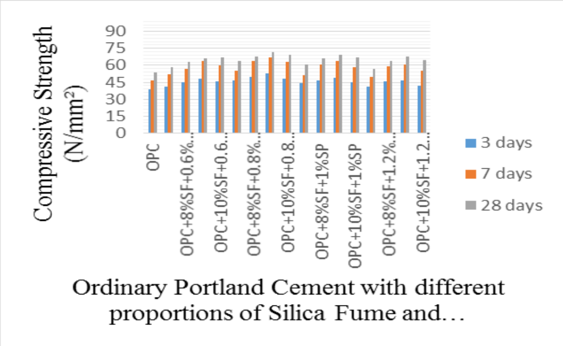
Effluents of Electro Plating Industry

S.NO.	Parameter	Maximum value (mg/L)
1.	pH	7-10
2.	Total Suspended Solids	25
3.	Oil and Grease	10.0
4.	Arsenic	0.10
5.	Cadmium	0.10
6.	Chromium (hexavalent)	0.10
7.	Chromium (total)	0.50
8.	Copper	0.50
9.	Lead	0.20
10.	Mercury	0.01
11.	Nickel	0.50
12.	Silver	0.50
13.	Zinc	2.00
14.	Total Metals	10.0
15.	Cyanides (free)	0.20
16.	Fluorides	20.0
17.	Trichloroethane	0.05
18.	trichloroethylene	0.05
19.	Phosphorous	5.00

To ensure a high-quality product, diagrams and lettering MUST be either computer-drafted or drawn using India ink.

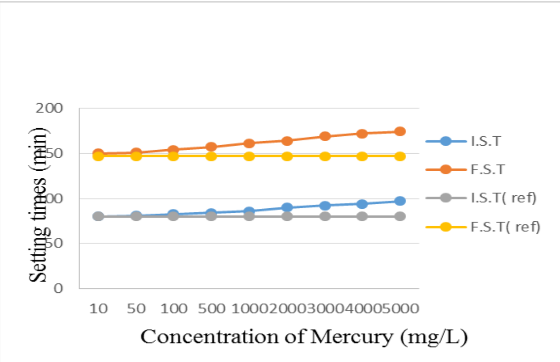
Figure captions appear below the figure, are flush left, and are in lower case letters. When referring to a figure in the body of the text, the abbreviation "Fig." is used. Figures should be numbered in the order they appear in the text.

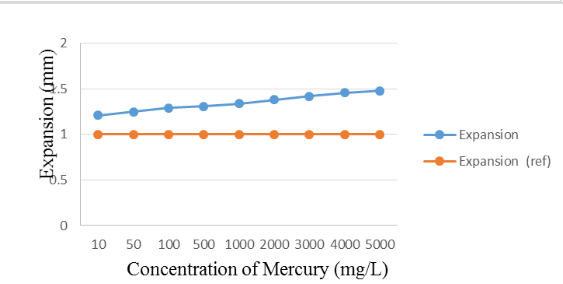
Table captions appear centered above the table in upper and lower case letters. When referring to a table in the text, no abbreviation is used and "Table" is capitalized.



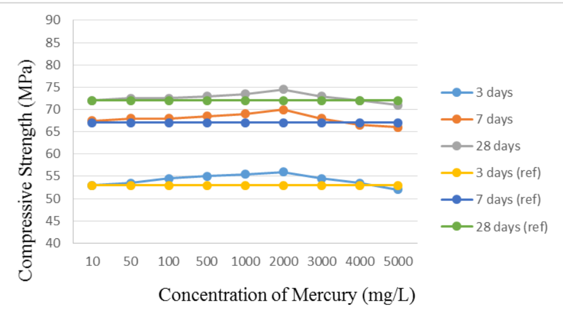
Compressive strengths of OPC with different proportions of Silica fume and Conplast SP-430

INFLUENCE ON INITIAL AND FINAL SETTING TIME

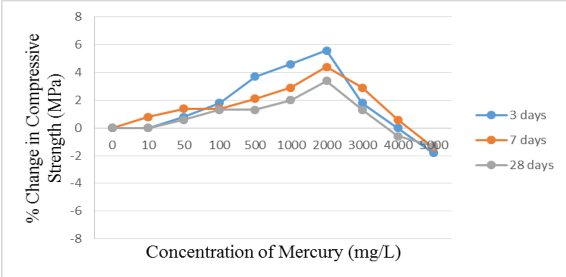




INFLUENCE ON COMPRESSIVE STRENGTH



Compressive strength of high strength cement mortar cubes at various concentrations of Mercury at different ages

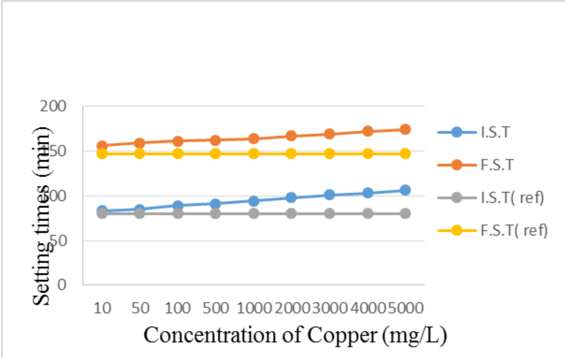


Percentage change in compressive strength of high strength cement mortar cubes at various concentrations of Mercury at different ages.

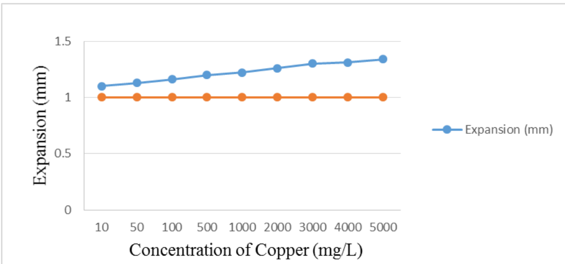
The maximum % change in compressive strength is observed at the concentration of 2000 mg/L. But the same is insignificant.

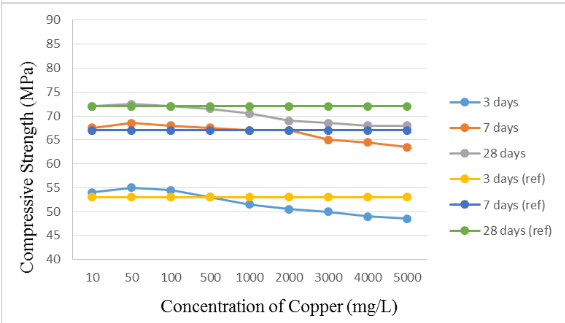
COPPER:

Setting times and Soundness of high performance cement at various concentrations of Copper

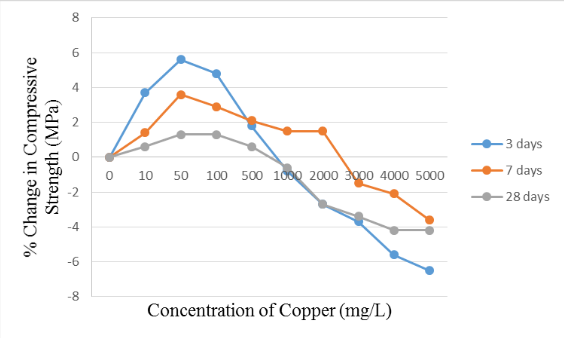


INFLUENCE ON SOUNDNESS



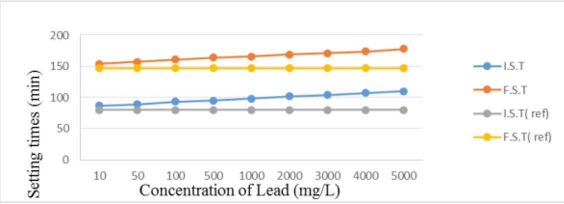


Compressive strength of high strength cement mortar cubes at various concentrations of Copper at different ages



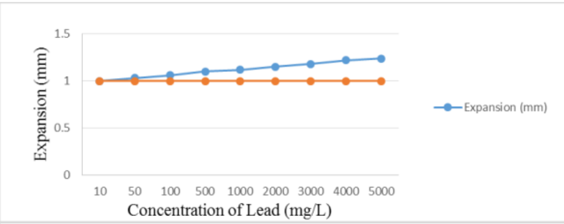
Percentage change in compressive strength of high strength cement mortar cubes at various concentrations of Copper at different ages

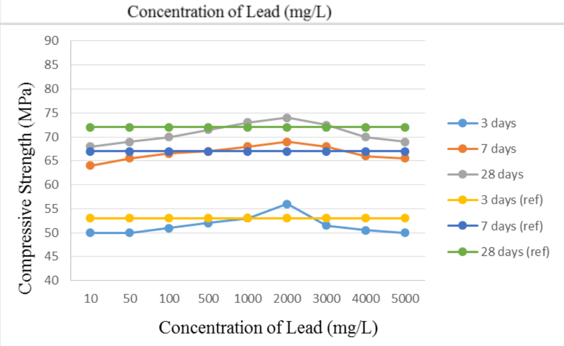
From the maximum % change in compressive strength is observed at the concentration of 50 mg/L. But the same is insignificant



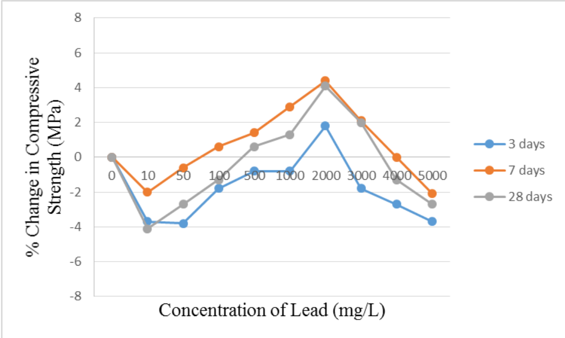
Variation of initial and final setting times of high strength cement using different concentrations of Lead Metal

INFLUENCE ON SOUNDNESS





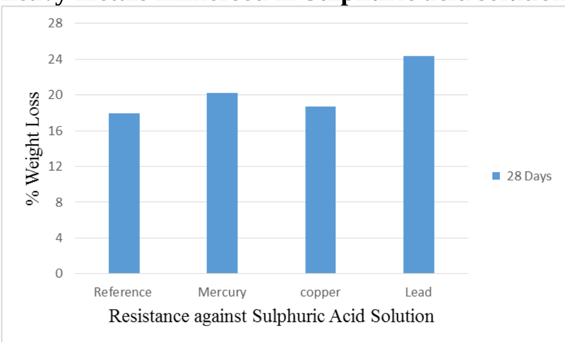
Compressive strength of high strength cement mortar cubes at various concentrations of Lead at different ages



Percentage change in compressive strength of high strength cement mortar cubes at various concentrations of Lead at different ages.

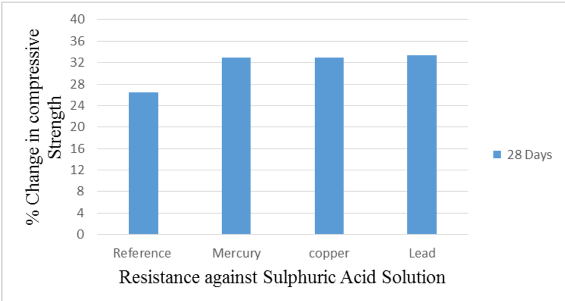
From the above graph the maximum % change in compressive strength is observed at the concentration of 2000 mg/L. But the same is insignificant

Loss of percentage in weight of high strength cement mortar cubes casted with reference and heavy metals immersed in Sulphuric acid solution



Percentage change in compressive strength of high strength cement mortar cubes casted with reference and heavy metals immersed in Sulphuric acid solution

% change in compressive strength due to immersion in H_2SO_4 solution	28 Days
Reference	26.44
Mercury	32.98
copper	32.98
Lead	33.33



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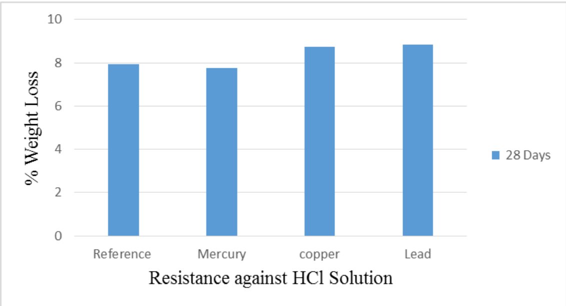
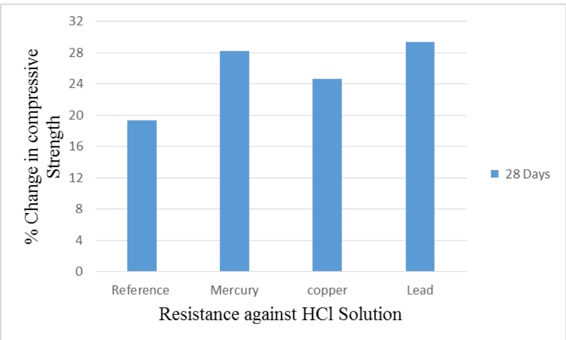
Loss of percentage in weight due to immersion in HCl solution	**28 Days**
Reference	7.94
Mercury	7.75
copper	8.73
Lead	8.86

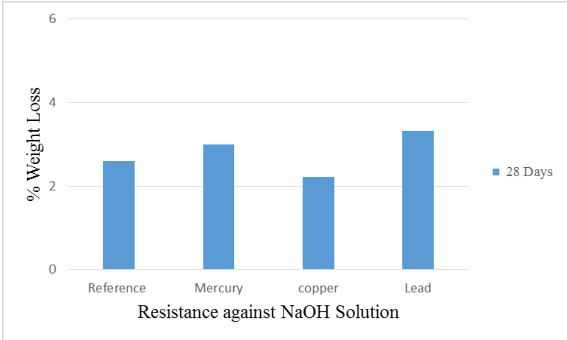


Percentage change in compressive strength of high strength cement mortar cubes casted with reference and heavy metals immersed in Hydrochloric acid solution

% change in compressive strength due to immersion in HCl solution	**28 Days**
Reference	19.40
Mercury	28.22
copper	24.71
Lead	29.35

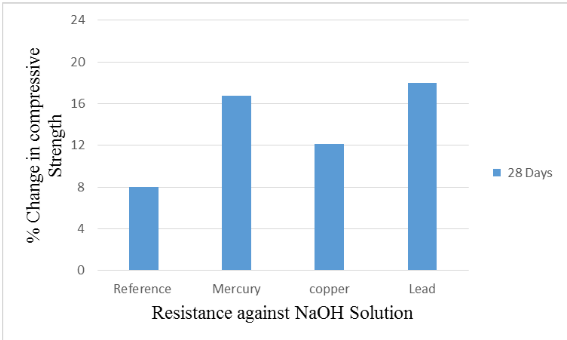


Loss of percentage in weight due to immersion in NaOH solution	**28 Days**
Reference	2.60
Mercury	3.00
copper	2.22
Lead	3.33



Percentage change in compressive strength of high strength cement mortar cubes casted with reference and heavy metals immersed in Sodium Hydroxide solution

% change in compressive strength due to immersion in NaOH solution	**28 Days**
Reference	8.00
Mercury	16.76
copper	12.10
Lead	18.00



IV. CONCLUSIONS

Based on the results obtained in the present investigation in chapter 5, the following conclusions are drawn

(i) For 53 grade OPC, the maximum compressive strength was obtained at silica fume replacement of 9.0% by weight of cement and 0.8% superplasticizer by weight of cement.

(ii) When Mercury metal is mixed in de-ionized water, it accelerates the setting times, soundness at various concentrations up to 5000 mg/L but not significant.

(iii) The effect of Mercury on Compressive strength of high strength cement mortar at various concentrations up to 5000 mg/L is insignificant

(iv) When Copper metal is mixed in de-ionized water, it accelerates the setting times, soundness at various concentrations up to 5000 mg/L but not significant.

(v) The effect of Copper on Compressive strength of high strength cement mortar at various concentrations up to 5000 mg/L is insignificant

(vi) When Lead metal is mixed in de-ionized water, it accelerates the setting times up to the concentration of 4000 mg/L is insignificant; and soundness at various concentrations up to 5000 mg/L is insignificant.

(vii) The effect of Lead in Compressive strength of high strength cement mortar at various concentrations up to 5000 mg/L is insignificant at different ages.

(viii) The decrease in compressive strength observed due to acidic, alkaline and sulphate attack, for all the metals. But the decrease in strength for Lead metal is more when compared to other metals and reference.

(ix) The rapid Chloride Permeability test results shows that,

(a) High strength cement mortar has very low permeability.

(b) High strength cement mortar with Mercury has low Permeability.

(c) High strength cement mortar with Copper has Low Permeability.

(d) High strength cement mortar with Lead has low Permeability.

do not replicate the abstract as the conclusion. A conclusion might elaborate on the importance of the work or suggest applications and extensions.

SCOPE FOR FURTHER STUDY:

In the present study, the effect of heavy metals contained in waste water from the electroplating industry is used to find the properties of the High Strength Cement Mortar. In the same way, the effect of heavy metals contained in the other waste waters emerging from other industris like bewerages, textiles, etc. can be used to find the properties of the High Strength Cement Mortar.

Further the similar study can be carried, not only over the effect of single heavy metal, but also the combination of the heavy metals present in the waste water.

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