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Effect of Barium on High Performance Cement Mortar

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ABSTRACT: *The effect of Barium(Ba) present in mixing water for high performance cement mortar was experimentally evaluated. The properties investigated are setting times, soundness, compressive strength, and durability aspects like acid attack, alkaline attack, sulphate attack and chloride ion penetration. High performance cement mortar(HPCM) specimens were cast using deionised water and Barium(Ba) spiked deionized water for reference and the test specimens as mixing waters respectively. It is observed that on comparison with reference specimens, the initial and final setting of cement with test specimens got accelerated with increase of Barium concentration in deionised water. The increase in the initial setting time is insignificant at all concentrations of Barium whereas the increase in the final setting times are significant at 4000 mg/L and 5000mg/L concentrations of Barium. The change in expansion of cement mortar is insignificant at all concentrations of the Barium. The increase in compressive strength is almost constant up to concentration of 2000 mg/L and beyond that it decreases. The percent change in compressive strength is insignificant at all concentrations of Barium except for 5000 mg/L concentration at 28 days. 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 low.*

Keywords: *Barium(Ba), Deionized Water, High performance cement mortar(HPCM), Micro Silica, Super plasticizer (SP), setting times, compressive strength, soundness.*

1. Introduction

Industrialization, 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.

Non-potable water, such as treated industrial waste water, which contains heavy metals like Hg, Cu, Ni, Zn, Cr, Pb, Cd, and Fe was satisfactorily used in making cement mortar (Reddy Babu G., Sudarsana Rao H. and Reddy Ramana.I.V.,2009) [1]. Heavy metals like Pb, Zn, hg, Cu, Ni, Fe and Cr were friendly with cement mortar up to concentration of 600mg/L (Reddy Babu G., Sudarsana Rao H, and Reddy Ramana.I.V., 2007)[2]. Cadmium spiked deionized 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. (Reddy Babu G.1, Reddy B. Madhusudana2, Ramana N. Venkata3, Sashidhar C. 2011)[3]. The use of reclaimed wastewater for concrete cast did not have any detrimental effect on concrete. Concrete with improved initial compressive strength could be made with reclaimed wastewater used partially or totally for the mixing water (Tay J.H. and Yip W.K., 1987) [4]. Quality and quantity of mixing water in concrete and fresh cement mortar mix are important in determining properties of concrete and cement mortar [Neville, Adam 2000) [5]. Heavy metals such as Cu, Zn, Pb, caused a retardation of the early hydration and strength development of cement mortar (Tashiro C.,1980) [6]. It was suggested the term HPC for concrete mixtures that possess the following three properties: high strength, high workability, and high durability (Aitcin,2000) [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 (Darwin, et al) [8]. 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 (Per Fidjestol et al 2012) [9]. Biologically contaminated water has given inexplicit results both positive and negative on cement mortar (Reddy Ramana I.V., Reddy Prasad, N.R.S., Reddy Babu G., Kotaiah B. and Chiranjeevi P.,2006) [10]. It was investigated the effect of acid attack on concrete with fly ash and microsilica. 150 mm size concrete cubes which were cured for 28 days and immersed in water with 1 % of sulphuric acid for 45 day were tested and it was reported that the loss in weight of control concrete was 2.5% whereas the concrete with 15% flyash and 7.5% microsilica showed only 1.09% loss in weight (Natesan,2003) [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.

(Turkel S et al, 2007) [12]. Though reclaimed industrial wastewater are reported to be used in cement mortar for mixing, there is very small information available on the maximum permissible limit of heavy metals in mixing water and cement mortar made with metal spiked deionized water exposed to acid attack, alkaline attack and sulphate attack. Hence, this investigation was carried out to understand the effect of Barium (Ba) in mixing water on setting times, soundness, 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 (Deionized)
5. Super Plasticiser
6. Heavy Metal (Barium)
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
	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
Colour	Greyish 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 Corniche India (P) Ltd, Navi 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 property	Specific gravity	2.22
	Average particle size	0.1 microns
	Bulk density	224 kg/m^3

Table 6: Chemical Properties of Silica Fume

Chemical compound	Percent of total weight
SiO_2	95.75
Al_2O_3	0.35
Fe_2O_3	0.21
CaO	0.17
MgO	0.09
SO_3	0.42
Na_2O	0.51
Loss on ignition	1.44

2.4 Water

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

2.5 Superplasticizer

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

Barium (Ba) is a heavy metal with atomic number 56. It is readily soluble in water. Barium heavy metal introduced into the deionized water in predetermined concentrations such as 10, 50, 100, 500, 1000, 2000, 3000, 4000 and 5000mg/L. The physical properties of Barium are presented in the Table 8.

Table 8: Physical properties of Barium(Ba)

Physical properties	**Density**	**3.856 gm/cc**
	Melting point	962 °C
	Boiling point	1560 °C

2.7 Chemicals

2.7.1 Acids -Sulphuric acid of 2.5 % concentration mixed in de-ionised water and Hydrochloric acid of 2.5 % concentration mixed in de-ionised water.

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

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

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

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

2.8 Methods:

The experimental methods adopted were in accordance with the standard procedures laid down in Bureau of Indian standards. Barium was introduced into the deionized water in known concentrations such as 10, 50, 100,500, 1000, 2000, 3000, 4000, 5000mg/L. Based on the 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. 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

Nine series of specimens were cast for test, the test specimens were cast with (cement + 9% SF + 0.8% SP + Barium). Barium concentrations such as 10, 50, 100, 500, 1000, 2000, 3000, 4000, and 5000mg/L were introduced in deionised water as mixing water for test specimens. The quantities of cement, fine aggregate and mixing waters for each specimen were 200g, 600g and "(P/4) + 3" where 'P' denotes the percentage of mixing water required on combined weight of cement and fine aggregate to produce a paste of standard consistency. Initial and final setting times were found out by Vicat's apparatus. As per IS456-2000, 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 deioned 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 reference and test specimens were prepared using standard metallic cube mould of size 70.6 X 70.6 X 70.6 mm for compressive strength of cement mortar. The blend of cement to sand ratio is 1: 3 by weight throughout. The compressive strength of reference and test specimens was studied at different ages, i,e., 3, 7, 28, 90 and 180 days. The compacted specimens in mould were maintained at a controlled temperature of 27^0 c ± 2^0 c and at 90 percent relative humidity for 24 hours by keeping the moulds under gunny bags wetted by the de-ionized water. After de-molding, the specimens were cured in de-ionized water for further 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. The maximum Compressive strength was obtained at Barium concentration of 2000 mg/l. Hence the resistance to aggressive chemical nature was found at Barium concentration of 2000 mg/l.

In order to study the durability aspect, effects of acidic alkaline and sulfate were investigated. Solutions of Sulphuric acid, Hydrochloric acid, Sodium hydroxide and Magnesium sulphate were prepared with deionized water at 2.5% concentration in four nonabsorbent 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.

A specimen of size 100mm diameter and 50mm thickness was prepared from the cylinder 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. Then the concrete specimens were subjected to RCPT by infusing a 60V from a DC power source between the anode and cathode. Current is monitored up to '6' hours at an interval of '30' minutes. From the 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.

$$Q = 900\,(I_0 + 2I_{30} + 2I_{60} + 2I_{90} + \ldots\ldots\ldots\ldots + 2I_{300} + 2I_{330} + 2I_{360})$$

where,
Q = Charge passed (Coulombs)
I_0 = Current (amperes) immediately after voltage is applied,
I_t = Current (amperes) at 't' minutes after voltage is applied.

3 Results and Discussions:

Effect of Barium metal present in mixing water on the properties of High performance cement mortar are analysed 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 Barium present in different concentrations in the mixing water on setting times is represented graphically in Figure1. It is observed that the initial and final setting process of cement got accelerated with increase of Barium concentration in de-ionized water. The increase in the initial setting time is insignificant at all concentrations of Barium, but the increases in the final setting times are significant at 4000 mg/l and 5000mg/l concentrations of Barium. The increase in the initial setting time is below 30 minutes at all concentrations of barium and the increase in final setting time is 32 minutes at 4000 mg/L and 34 minutes at 5000 mg/L when compared with that of the test specimens made with deionised water, for all other concentrations it is less than 30 minutes.

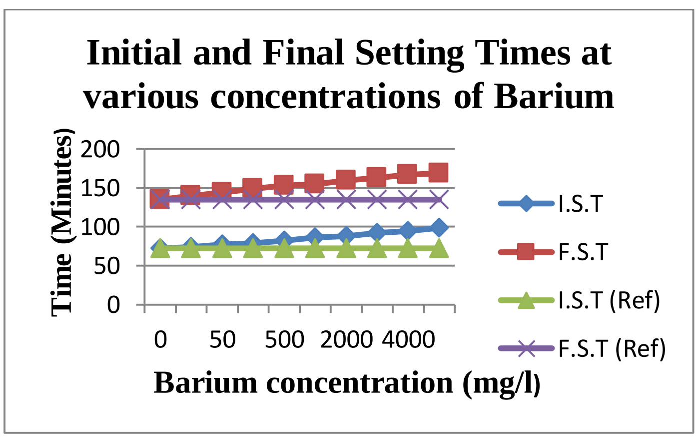

Figure 1: Variation of initial and final setting times of cement of various concentrations of Barium

Hence, the effect of Barium on an average over setting times is insignificant for all the specimens tested.

3.2 Effect on Soundness

The effect of Barium on soundness of blended cement mortar is represented graphically in Fig.2. The effect of Barium at all concentrations on soundness of the cement was studied. The expansion after soundness test obtained with de-ionized water is 1mm. The same was obtained as 1.13mm for 10mg/L Barium concentrated mixing water and 1.4mm at 5000 mg/L Barium concentrated mixing water. Expansion of cement mortar with all concentrations of Barium is well within the prescribed limits. Therefore, the effect of Barium metal present in mixing water for High performance cement mortar is insignificant.

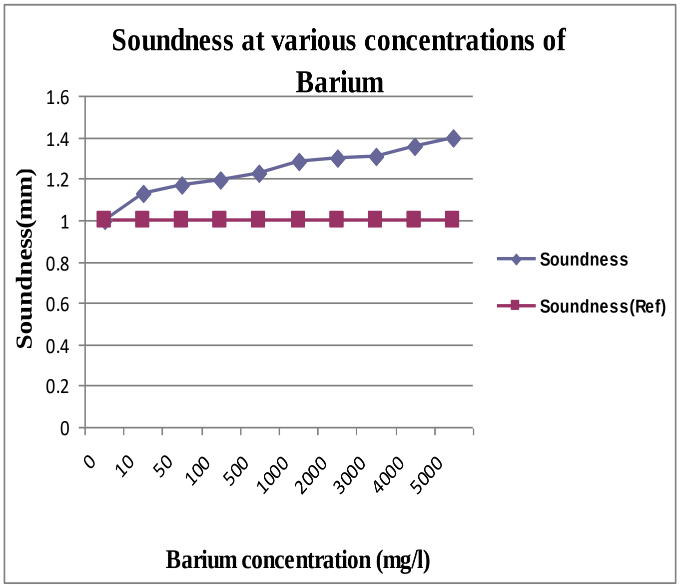

Figure 2: Soundness of specimens at various concentrations of Barium

3.3 Effect on Compressive Strength

The effect of Barium heavy metal present in mixing water at different concentrations on compressive strength of high performance cement mortar is graphically represented in Fig 3. Slight increase in the compressive strength was observed as the concentration of Barium increases up to 2000 mg/L. The rate of increase in the Compressive strength is found to be almost constant up to 2000 mg/L. Beyond 2000 mg/L the compressive strength decreases.

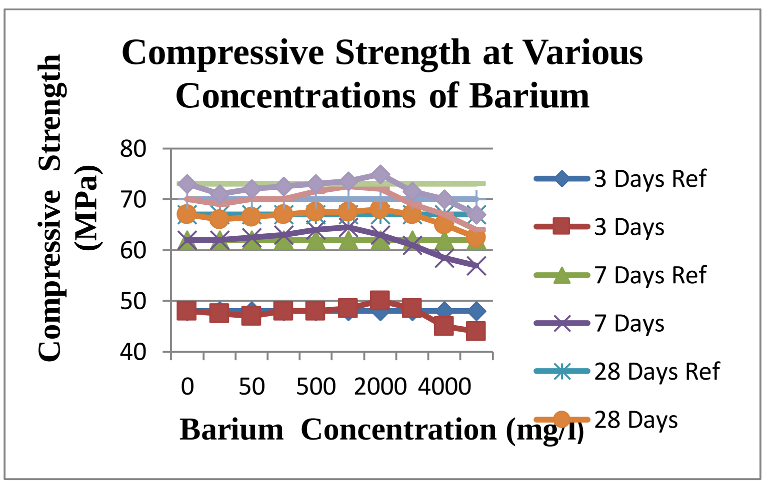

Figure 3: Compressive strengths of mortar cubes at various concentrations of Barium at different ages

The percent change in compressive strength of blended cement mortar cubes cast with different concentrations of Barium in de-ionized water was graphically represented in Fig 4. The percent change in compressive strength at all concentrations of Barium is below 10 percent except at 5000 mg/L at 28 days when compared with that of the compressive strength of blended cement mortar cubes cast with de-ionized water. Hence, the effect of Barium heavy metal on compressive strength up to 4000mg/L is insignificant.

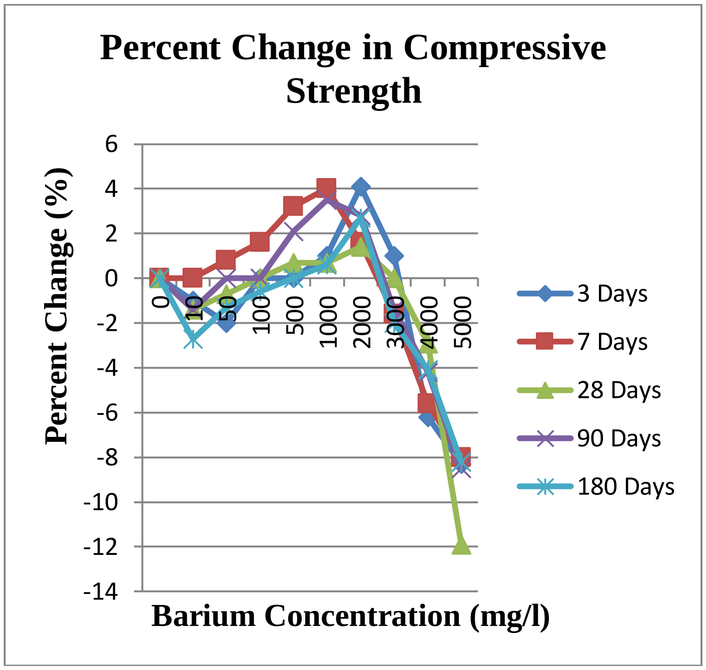

Figure 4: Percent change in compressive strengths at various concentrations of Barium at different Ages

3.4 Effect on Durability:

For conducting durability tests among the reference mix cubes made with deionised water, cement mortar cubes made with 2000mg/L Barium 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 deionised 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-ionised water and Barium spiked deionised 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 deionized water and Barium spiked deionised water are graphically represented in Figure 5 and Figure 6.

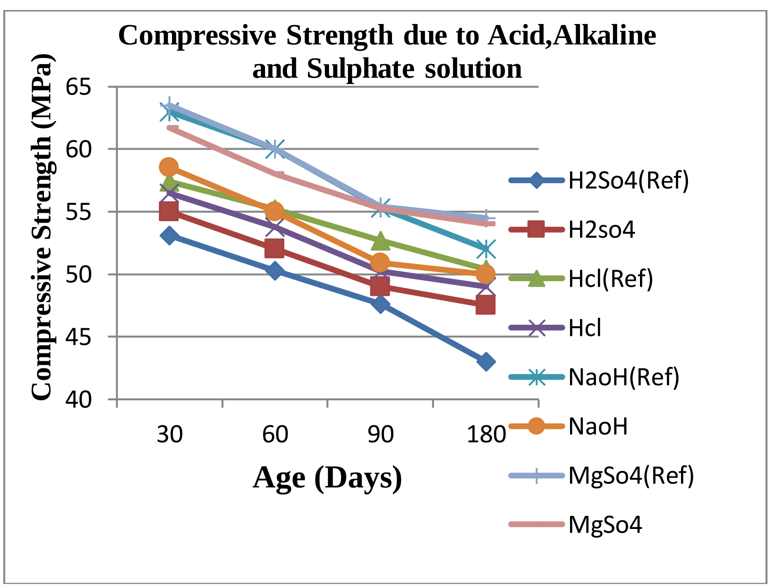

Figure 5: Compressive strength of control cement mortar cubes and that of cubes cast with Barium containing water immersed in different solutions.

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 Sulphuric 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. The change in the strength of the mortar cubes cast with Barium when compared with control mortar increases as the age increases. And as the age increases, the change in the compressive strength decreases, as shown in Figure 5. This is due to the reason that 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 19.1 % at 30 days exposure to 30.1 % at 180 days when exposure to Sulphuric acid. The percentage change in the compressive strength ranges from 16.9 % at 30 days exposure to 27.9 % at 180 days when exposure to Hydrochloric acid. The percentage change in the compressive strength ranges from 13.9 % at 30 days exposure to 26.4 % at 180 days when exposure to Alkaline media. The percentage change in the compressive strength ranges from 9.26 % at 30 days exposure to 20.5 % 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. 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.

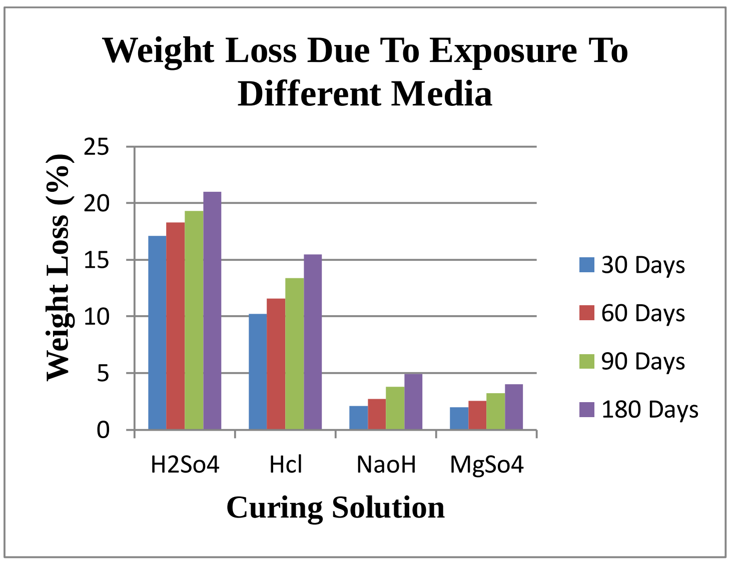

Figure 6: The graph showing the loss in weight of blended cement mortar cubes cast with water containing Barium immersed in different solutions

3.5 Rapid Chloride Permeability Test

The values of ion penetration of the cylinder specimens cast with deionized water and Barium spiked deionized water are graphically represented in Fig. 7. The charge passing is less for the cylinder specimen cast without metal. The charge passing through the cylinders cast with Barium 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 deionized water and Barium spiked deionized water is categorized as low.

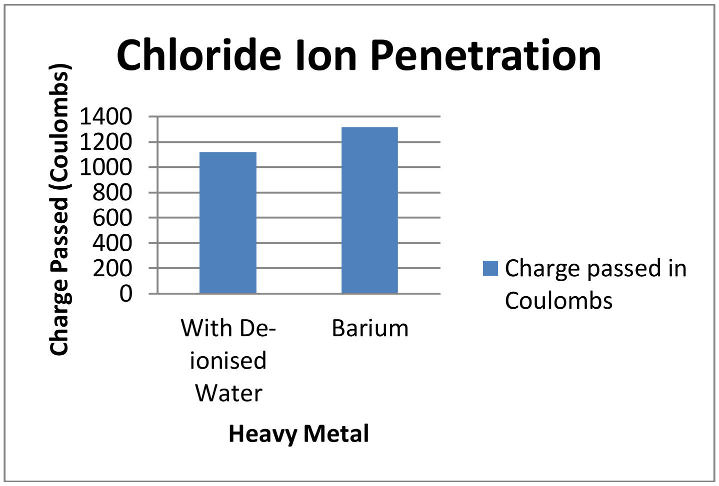

Figure 7: The graph showing the charge passed through the cement mortar specimens cast with Deionized water and Barium spiked Deionized water

Conclusions:

Based on the results of this investigation**,** the following conclusions may be drawn

- The initial and final setting times of blended cement got accelerated with increase of Barium concentration in de-ionized water. The increase in the initial setting time is insignificant at all concentrations of Barium.
- Expansion of blended cement spiked with Barium deionized water is well within limits at all concentrations.
- Increase in the compressive strength was observed as the concentration of Barium increases up to 2000 mg/L. The rate of increase in the Compressive strength is found to be almost constant up to 2000 mg/L. Beyond 2000 mg/L the compressive strength decreases. The percent change in compressive strength at all concentrations of Barium is insignificant except at 5000 mg/L of Barium concentration.
- The blended cement mortar cubes cast with Barium deionized water immersed in H_2So_4 solution showed less reduction in compressive strength than that of the controlled blended cement mortar. But Opposite trend is observed when the test cement mortar cubes exposed to HCl solution, NaOH solution and $MgSo_4$ solution. The reduction in compressive strength is significant at 30 days exposure to H_2So_4, HCl, NaOH solutions and is insignificant for exposure to $MgSo_4$ solution.
- Weight loss of the specimens is significant for the blended cement mortar cubes cast with Barium deionized water immersed in H_2So_4 and in HCl solutions. The same is insignificant when the specimens were exposed to NaOH and $MgSo_4$ solutions.
- Permeability of blended cement mortar specimens cast with Barium spiked deionized water is low.

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