AN EXPERIMENTAL STUDY EFFECT AND PERMISSIBLE LIMIT OF SULPHATES ($MgSO_4.7H_2O+FeSO_4.7H_2O$) IN MIXING WATER OF CEMENT

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Abstract

The study centered on the effect of different limits of sulphates in mixing water of cement and studies the properties of setting times, compressive strength and soundness of cement, In general, the sulphates encountered in soils and surface waters are Sodium sulphate (Na2So4), Calcium sulphates (CaSo4), Magnesium sulphate (Mgso4), Ammonium sulphate (NH4)2SO4 and Ferrous sulphate (FeSO4).The present experimental study evaluates the maximum permissible limit of sulphates in mixing water of cement. Cement mortar cubes were cast by using distilled water and sulphates [MgSO4+Na2SO4+feso4] spiked water for reference and test specimens respectively. The test samples, a significant increase in initial and final setting time. Tested specimens exhibit almost same performance in soundness. The permissible limit of sulphates in mixing water of cement has been reported but a particular combination of sulphates has not reported in various codes, indeed not enough work has been carried out on the limit of sulphates in mixing water of cement. Consequently a guide line on the permissible limit of a specific sulphate and a specific combination of sulphates in mixing water is needed.

Key words*: *distilled water, sulphates, setting times, compressive strength and soundness of cement

I. INTRODUCTION

Cement durability is one of the most important considerations in the design of new structures and when assessing the condition of existing structures. Cement construction is becoming increasingly complex and the importance of producing structures that are both cost effective and durable has never been higher. An understanding of cement durability is fundamental to establishing the service life of new or existing structures.

Sulphate attack has long been recognized as responsible for cement deterioration in a wide variety of structures. The main aim of this work is to study the deleterious effects of sulphates exposure to Portland cement and influence of water cement ratios that ensures durability of cement against exposure of sulphates salts. The influence of aggressive chemicals on the behavior of building materials is a topic of significant practical interest, as it affects the safety and durability of structures. The compressive strength of cement is considered one of the most important properties in the hardened state, and the design of cement structures is based primarily to resist compressive stresses. The ability of cement to resist weathering action, chemical attack, abrasion, or any other process of deterioration is called durability. In this project data on the effect of cement structure and hydration conditions on strength and strength development are analyzed. Emphasis is put on a critical analysis of models that describe the relationship between strength and influence of sulphates with curing age. Data on the progress of compressive strength with age and relevant properties of cement such as soundness and setting times are discussed in the presence of sulphates. the details of the chemicals formed during sulphate attack is mentioned below along with them details of some important sulphate forms are explained below, these are to be studied carefully and necessary investigations and researches are to be made in this area.

1.1 Calcium Sulphate

Calcium sulphate is generally believed to be the least aggressive of the three sulphates, mainly due to its lower solubility. The solubility of gypsum is approximately 1440 ppm, which is significantly less than that of sodium sulphate and magnesium sulphate. There are essentially two different schools of thought on the issue of gypsum solubility and its Impact on sulphate attack

1.2 Sodium Sulphate

Attack from sodium sulphate is more complex than attack from calcium sulphate because more phases are affected. Sodium sulphate may attack concrete in two different ways .The first form of attack involves sodium sulphate reacting with calcium hydroxide to form gypsum Once the calcium hydroxide is depleted , gypsum. Gypsum can then react with monosulfoaluminate to form ettrignite .Once the calcium hydroxide is depleted, gypsum formation will discontinue. Once the monosulfoaluminate becomes depleted, excess gypsum will form in the system and ettrignite formation will cease. The second form of attack involves sodium sulphate reacting with tricalcium aluminate to form ettrignite.

$CH+N2SH_{10} \rightarrow CSH_2+2NH+8H$

$C_3A\ (CS)\ H_{12}+2CSH_2+16H \rightarrow C_3A\ (CS)\ 3H_{32}$

$2C3AH_6+3N2SH_{10} \rightarrow C3A(CS)3H_{32}+2AH_3+6NH+5H$

1.3 Magnesium sulphate

Magnesium sulphate is the most complex of the three types of sulphates. It can be react with all hydrated cement products and is generally considered to be the most damaging form of sulphate. Magnesium sulphate will react with calcium silicate to form gypsum plus magnesium hydroxide and a silica gel, as shown in equation 2.6 This formation of magnesium hydroxide is known to form a barrier which may provide protection to the concrete and it also tends to internally affect pore solution PH. Brucite formation does have its downfall in that it needs a high amount of calcium hydroxide to form. Once the CH is deplted, the magnesium sulphate will seek more calcium. In this case, decalcification of the C-S-H will occur, due to a removal of calcium (Gollop and Taylor 1992).

$3CaO.2SiO2+MgSH7 \rightarrow 3\ (CSH2) + 3Mg\ (OH)2+2S$

1.4 Ferrous sulphate

Ferrous sulphate is obtained from the production of titanium dioxide. During the process ferrous

Sulphate crystallizes and is drawn off as so-called green salt. It is dried down to a residual Humidity content of about 4% by mass. The granulated salt with a content of ferrous sulphate of approximately 50% by mass contains 6 to 7 moles of crystallization water. In a further modification hexa-hepatahydrate is transformed in a second drying process under the influence of heat and vapor, into a powdery ferrous sulphate with 1 mole of crystallization water. This second modification, the monohydrate, has been developed in order to extend the storing time. As ferrous sulphate is a strong reducing agent, the presence of water and air always involves the risk of oxidation. This shall be avoided by the reduction of the crystallization water content.

II. Test Methods and Specifications

The materials used in the experimental investigation include:

- 53-Grade Ordinary Portland Cement (OPC)
- Fine Aggregate (Ennore sand)
- Distilled Water
- Sulphates($MgSO4.7H2O+Na2SO4+FeSO4.7H2O$)

2.1 Cement:

Initial experiments like initial setting time, final setting time, compressive strength and soundness test on mortar cubes were conducted on 53-grade cement. Oxides and their percentage of 53-grade OPC are presented in table

Table: 1

s.no	Oxides	Percentage of contents
1	Cao	65.49
2	SiO2	21.67
3	Al2O3	5.97
4	Fe2O3	3.85
5	SO3	1.66
6	MgO	0.78
7	K2O	0.46
8	Na2O	0.12

2.2 Sand:

The sand used throughout the experimental work was obtained from the ennore, near Chennai. The sand was obtained from Tamilnadu minerals limited, Chennai. It is only organization in India, approved by Indian Standard Institution to manufacture and supply of sand conforming to IS 650-1991. The sand used in the experimental work has the following practice size distribution.

- Passing through 2mm X retained in 1mm
- Passing through 1mm X retained in 0.5mm
- Passing through 0.5mm X retained in 0.09mm

Table: 2

SI. NO.	Properties	Units	Results
1	Specific gravity	-	2.64
2	Bulk density	KN/m3	15.54
3	Fineness modulus	-	2.72
4	Particle size variations	Mm	0.09 to 2.0
5	Colour	Hazan	Grayish white
6	Absorption in 24 hours	-	0.8%
7	Shape of grains	-	Sub angular

2.3 Distilled water

The characteristics of distilled water, to which various sulphates were spiked, are presented in the Table and the characteristics of distilled water were analyzed according to the standard methods for the examination of water and wastewater, (APHA 1994).

Characteristics of Distilled Water (except pH all values in mg/L)

Table: 3

S.No	Parameter	Distilled water
1	PH	7.1
2	TDS	5
3	Alkalinity	4
4	Acidity	1
5	Hardness	1
6	Sulphates	0.2
7	Chlorides	5

2.4 Test Methods

There exists a general lack of correlation between the performance of concrete subjected to standard test methods and concrete subjected to realistic field conditions (santhanam et al). Two current ASTM test methods for assessing sulphate attack are ASTM C 1012 and ASTM C452 for the potential expansion of portland cement mortars exposed to sulphate. The test involves casting mortar bars, typically containing a high C_3A cement and standard Ottawa sand, allowing the mixture to reach a minimums strength of 20Mpa and then immersing the specimens in 5% sodium sulphate solution for up to 18 months. This is the most common test method for determining sulphate resistance and is the test method chosen for equivalent testing in ACI 201.2R. One concentration with this test is that the PH of the pore solution. To minimize this PH effect, the sulphate solution is required to be replaced each time a measurement is conducted. However at interval of longer measurements periods, the ph may change considerably, there by the progression of sulphate attack. Mehta (1974) has proposed attest set-up that automatically adjusts the PH of the soaked solution to minimize this effect, but the complexity of this approach has hindered its use in standard test methods.

III. RESULTS AND DISCUSSIONS

3.1 Initial and Final Setting Time

The Figure shows the effect of distilled water and sulphates (MgSO4, Na2SO4, and FeSO4) spiked water on Initial and Final setting times. Both Initial and Final setting times had increased as the concentration of sulphates was increased. Effect of Distilled water on properties of cement

Table: 4: Effects of Sulphates on Setting times

S.No	Concentration	initial setting time	final setting time
1	1000ml	101	276
2	1500ml	103	282
3	2000ml	105	292
4	2500ml	107	305
5	3000ml	192	313
6	3500ml	204	329

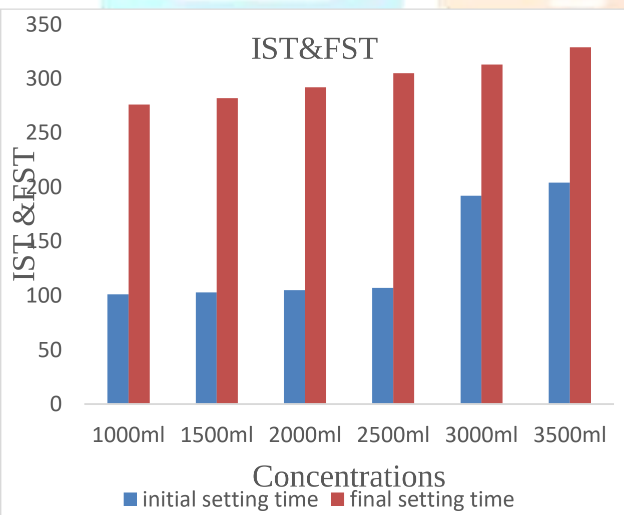

Fig 1

At the maximum concentrate of 3500mg/L, The test samples had a 204 min increase in initial setting time and a 329 min increase in the Final setting time, the reference specimens have Initial setting and Final setting times were 57 min and 210 min respectively. At the concentration of sulphates (MgSO4+Na2SO4+FeSO4).

3.2 Soundness

The Le-chatlier's test result as per IS: 5514-1969 for expansion in cement has an upper limit of 10 mm. The figure shows soundness test results on cement specimens made with distilled water and sulphates spiked water.

Table: 5: Effect of soundness

Sno	Concentration	Soundness (mm)
1	1000ml	2
2	1500ml	2
3	2000ml	2
4	2500ml	2.23
5	3000ml	2.27
6	3500ml	2.23

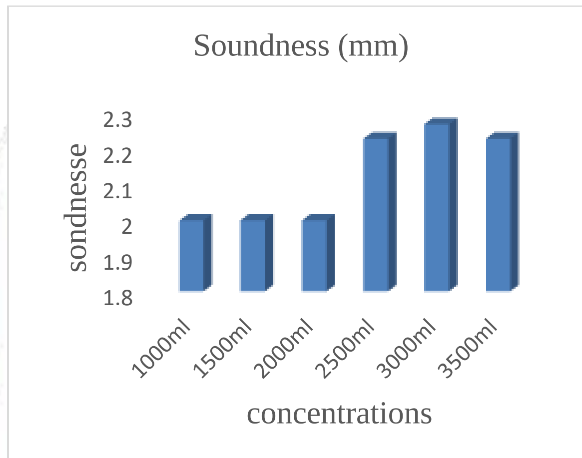

Fig 2

The expansions measured were 2, 2, 2, 2, 2.23, 2.27 and 2.33 at 0, 1000, 1500, 2000, 2500, 3000 and 3500 mg/L respectively. And the maximum soundness value is obtained at the concentration of 3000mg/L. As the measured values were less than 10 mm, all the samples passed in soundness test.

3.3 Compressive Strength

The change in compressive strength in test samples are shown from figure. The strength development in test specimens was higher as that of reference specimens but increase in strength development was decreased as the age progressed. At the age 3, 7 and 28 days, compressive strength of reference samples and test samples was 32.17, 48.14 and 60.42 MPa for 1500 mg/L concentration respectively. The corresponding difference in compressive strength were studies and show the variations of compressive strength with their respective concentrations.

Table: 6: compressive strengths for different concentrations

S. No	Sulphates Concentrations ($MgSO_4.7H_2O$+Na_2SO_4+$FeSO_4.7H_2O$) (mg/L)	Percentage change on compressive strength		
		3 Days	7 Days	28 Days
1	D.W	0	0	0
2	333+3333+333	33	5.08	0.313
3	500+500+500	28.5	8.21	3.67
4	667+667+667	33.57	13.25	2.65
5	834+834+834	35.71	10.26	2.29
6	1000+1000+1000	22.81	0.87	2.4
7	1167+1167+1167	15.04	5.96	2.47

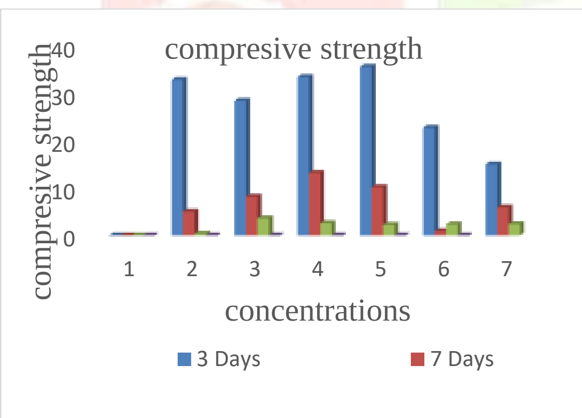

Fig 2

IV. CONCLUSIONS

1. Based on the results of this investigation, it can be concluded that sulphates spiked distilled water affects the setting times of cement. For the concentration of 1000 mg/L and above, 2500 mg/L and above, the initial and final setting times had significantly increased respectively.
2. The strength development in test specimens was higher as that of reference specimens but the increase in strength development was decreased as the age progressed.
3. For a maximum concentration of 3500mg/L, at an early age 3 and 7 days , compressive strength development was significant but at 28 days it was a little higher than reference specimen .
4. The presence of sulphates in cement matrix up to 3500mg/L appeared to positively influence engineering properties of cement.

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