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STUDY OF ZINC SULPHATE AS AN ADDITIVE IN MAGNESIA CEMENT

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ABSTRACT

Zinc sulphate in heptahydrate form gives good results when added in magnesium oxychloride cement (Sorel’s cement), in optimum proportions, on strength and durability of the product. Effect of its proportions on setting period, compressive strength and water tightness on the product it studied in detail. Its incorporation in the Matrix as an additive increase’s strength, durability and moisture sealing capacity of the product while zinc sulphate retards the setting process of magnesium cement within experimental limits.

Key words: Magnesium oxychloride cement, Setting period, Moisture Ingress, Compressive strength, Linear changes.

INTRODUCTION

Sorel's cement is a quick setting, high strength cement. It requires no humid curing. It is commonly used as a flooring material in Railway coaches and heavy-duty purposes due to its high early strength and low specific gravity. Magnesia cement may find varied applications and give better results than Portland cement in making sound quality terrazzo tiles, toys, statues, artificial marble/ ivory etc., calcined magnesite and partially calcined dolomite (from Rajasthan quarries) below 750° C have both been found good for these purposes. Various standards for the raw materials have been evolved and revised from time to time to meet the requirements of the users. The present investigations were undertaken as a trial to check the undesirable effects of zinc sulphate when added in Sorel's cement in various proportions.

Anionic part of zinc sulphate (SO_4^{-2}ion) has got capacity to react with active lime and other harmful impurities by converting them into insoluble inactive phase (calcium sulphate) which is beneficial for the quality of magnesia cement. As the cationic part of zinc sulphate (Zn^{+2}ion) belongs to second group, chemistry of Mg^{+2} and Zn^{+2} ions resemble closely. Ionic radii of Mg^{+2} and Zn^{+2} ions 0.65 angstrom and 0.69 angstrom respectively hence chances of formation of intercrossing crystals of zinc and magnesium oxychloride lattices increases the possibility of formation of a cross polymeric product with changed properties.

Magnesium oxychloride cement (magnesia cement), popularly known as Sorel's cement, is one of the strongest binders. It is obtained by reaction of magnesia with an aqueous solution of its salts, particularly halides and sulphates. A complex compound of definite composition $3MgO.MgCI_2.11H_2O$ is said to be formed with higher densities of gauging solution i.e., 20°Be or more, which is responsible for its setting and cementing action. This complex has been modified slightly as a mixture of $3Mg(OH)_2.MgCl_2.8H_2O$ and $5Mg(OH)_2.MgCl_2.8H_2O$.

MATERIALS USED

a. Commercially available lightly calcined magnesite of the following composition was used.
MgO: 90% (minimum)
CaO: 15% (maximum)
Ignition loss at 110 °C: 2.5±0.5% Bulk density: 0.85 Kg/lit.
Minimum 95% passing through 75 microns (200 IS sieve)
It was procured from M/S Shri, Hari Udyog Bharti, Alwar (Raj.)

b. Magnesium chloride used in the study was of IS grade III with following characteristics
Colourless, crystalline, hygroscopic crystals
$MgCl_2$: 95% (minimum)
$MgSO_4$, $CaSO_4$, and alkali chloride contents were less than 4%

c. Dolomite: It is a readily available inert filler. Locally available dolomite powder conforming to following grade was used.
MgO: 20.8%
Ca0: 28.7%
100% passing through 150 micron IS sieve.
50% retained on 75 micron IS sieve (minimum).

EXPERIMENTAL

To evaluate zinc sulphate as an additive in magnesium oxychloride compositions following investigations have been carried out.

(i) ***Setting Investigations:*** (i) Setting characteristics: The effect of saturated solution of zinc sulphate on setting characteristics of magnesia cement was studied by adding it in varying proportions (0%, 5%, 10%, 15%. 20%) by volume of gauging solution. Wet-mixes were prepared by gauging 1:2 dry mixes (by weight of magnesia and dolomite) with magnesium chloride solution of 23°Be containing saturated solution of zinc sulphate in specified proportions. The gauging solution used in an optimum amount just sufficient to obtain a plastic wet- mix of IS consistency. The wet-mixes so prepared were filled into vicat moulds and kept under identical conditions of temperature and relative humidity. Setting periods of wet-mixes were determined as per IS specifications and adopting standard procedure. Experimental findings are enumerated in the table 1.

Room Temperature: 28±1°C Strength of g.s: 23°Be
Relative humidity: above 90% Composition of dry-mix: 1:2(MgO:Dolomite)
Quantity of dry-mix: 225 gm.

Table 1: Effect of Zinc sulphate on Setting Characteristics of Magnesia Cement

S.No.	%Additive	Vol of g.s. (ml)	Setting time (min)	
			Initial	Final
1	0	54	140	225
2	5	64	220	285
3	10	66	190	250
4	15	69	190	250
5	20	71	190	250

g.s.= gauging solution

(ii) Weathering Investigations: All the setting time blocks with different proportions of saturated solution of zinc sulphate (0%, 5%, 10%, 15%, 20%) obtained from the above vicat moulds were cured under identical conditions of temperature and humidity. They were weighed on balance at different time intervals of 24 hrs, 7 days and 30 days. Weathering effects may be reflected by observing the change in weights with time as per standard procedure. Experimental results are recorded in the table2.

Room Temperature: 28±1°C Strength of g.s: 23°Be
Relative humidity: above 90% Composition of dry-mix: 1:2(MgO:Dolomite)
Quantity of dry-mix: 225 gm

Table 2: Effect of Zinc sulphate on Weathering Characteristics of Magnesia Cement.

S.No	%Additive	Weight of blocks (gm) after		
		24 hrs	7 days	30 days
1	0	256.52	252.20	249.70
2	5	255.90	249.02	246.07
3	10	261.25	255.25	251.24
4	15	252.90	245.20	242.29
5	20	249.75	241.35	237.83

(iii)Moisture Ingress Investigations: The above setting investigation blocks after studying weathering effects were subjected to steam test and exposed to boiling water in a water bath after at least 60 days of curing as per the standard procedure. These investigations are desirable in order to evaluate the relative moisture- ingress by the trial blocks. Observed results are summarized in the table 3.

Room Temperature: 28±1°C Strength of g.s: 23°Be
Relative humidity: above 90% Composition of dry-mix: 1:2 (MgO:Dolomite)
Quantity of dry-mix: 225 gm

Table 3: Effect of Zinc sulphate on Moisture Ingress Characteristics of Magnesia Cement.

S.No.	%Additive	Trial blocks kept in boiling water (in hrs)					
		0-5	5-10	10-15	15-20	20-25	25-30
1	0	NE	NE	NE	NE	C	-
2	5	NE	NE	NE	NE	NE	C
3	10	NE	NE	NE	NE	NE	C
4	15	NE	NE	NE	NE	NE	NE
5	20	NE	NE	NE	NE	NE	NE

NE= no effect; C=Cracked

(iv)Compressive Strength Investigations: In order to find out the effect of saturated solution of zinc sulphate on compressive strength of magnesia cement, it was incorporated in gauging solution in specified proportions (0%, 5%, 10%, 15%, 20%) by volume of gauging solution. Composition of dry-mix was kept uniformly as 1:2 by weight of magnesia and dolomite powder. Thoroughly mixed dry-mix was gauged with magnesium chloride solution of 23° Be having varying proportions of saturated solution of zinc sulphate, to obtain a plastic mass of IS consistency. The wet-mixes so prepared were filled into standard compressive strength testing moulds (70.6 mmx70.6mmx70.6mm) and kept under identical conditions of temperature and relative humidity for one month. Compressive strength of these blocks was determined as per standard procedure and IS specifications. Experimental results are recorded in the table 4.

Room Temperature: 28±1°C Strength of g.s: 23°Be
Relative humidity: above 90% Composition of dry-mix: 1:2 (MgO:Dolomite)
Quantity of dry-mix: 600 gm

Table 4: Effect of Zinc sulphate on Compressive Strength of Magnesia Cement.

S.No.	%Additive	Compressive Strength (Kg/Cm^2)
1	0	500
2	5	500
3	10	520
4	15	530
5	20	480

(v) Linear Change Investigations: The effect of saturated solution of zinc sulphate on linear change characteristics of magnesia cements was studied by its incorporation in gauging solution in varying proportions (0%, 5%, 10%, 15%, 20%) by volume of magnesium chloride. Composition of dry-mix was kept uniformly as 1:2 by weight of magnesia and dolomite powder. Dry-mixes were gauged with magnesium chloride solution of 23°Be having varying proportions of additive to obtain a plastic mass of IS consist- ency. Wet-mixes were then filled into standard sized moulds (200mmx25mmx25mm) and kept under identical conditions of relative humidity and temperature. Linear changes in the beams so formed were determined with the help of micro meter scale as per the IS specifications" and standard procedure. Results are summarized in the table 5.

Room Temperature: 28±1°C
Strength of g.s: 23°Be
Relative humidity: above 90%
Composition of dry-mix: 1:2 (MgO:Dolomite)
Quantity of dry-mix: 225 gm

Table 5: Effect of Zinc sulphate on Linear Change Characteristics of Magnesia Cement.

S.No	% Additive	Change in length (mm)	Length of beams (mm)	
			Initial	Final
1	0	0.29	200.00	200.29
2	5	0.01	200.00	200.01
3	10	0.02	200.00	200.02
4	15	0.03	200.00	200.03
5	20	0.04	200.00	200.04

DISCUSSIONS

The table 1 reveals the effect of saturated solution of zinc sulphate in the dry mix on setting characteristics of magnesia cement. On incorporation of saturated solution of zinc sulphate setting process is retarded by inactivating impurities like active lime present in commercial magnesia. It is interesting to note that on adding more of zinc sulphate solution in the gauging solution, setting process is found to be retarded. This abnormal trend in the setting period may be attributed to the increasing chances of formation of magnesium oxysulphide, zinc oxysulphide and zinc oxychloride competitively with magnesium oxychloride simultaneously. These processes as well as hydrolysis of zinc sulphate contribute to exothermicity of the setting process. As some uncombines or loosely bound moisture is left in the matrix even after final setting it is expected that weights of the blocks should decrease with time on account of natural vaporisation.

Zinc sulphate does not catalyse carbonation etc. The discussion is witnessed by the observations summarized in the table 2.

Table 3 records the influence of adding saturated solution of zinc sulphate on water vapour transmission tendencies of magnesia cement. As per the hypothesis proposed above, zinc sulphate interacts at various stages of the formation of magnesia cement. This results in the formation of a co-polymeric type of product with more compact lattice comprised of interlacing/crossing systems. This is witnessed by the fact that trial steam test samples having zinc sulphate could not be affected by boiling water under steam even after their exposure for more than 24 hrs.

Effect of the additive mixed in the matrix in varying proportion on compressive strength of the products is revealed from the table 4. Products having interlaced crystalline phases type structures or copolymeric type structures are known to have better strength than their individual components. Accordingly, it is found that incorporation of zinc sulphate improves compressive strength of the trial blocks up to an optimum value. Incorporation of zinc sulphate beyond this value results in the formation of less strength giving factors like oxysulphate and chloride of zinc in increasing amounts. Accordingly, it is observed that beyond optimum incorporation of zinc sulphate, strengths are found to be reduced to some extent Because of water tightness of the product formed on using zinc sulphate as an additive, as expected, strengths are more than the pure magnesium oxychloride blocks. It is also found that the trial beams do not show significant changes in the linear dimensions as apparent from the table 5.

The above discussions can be interpreted based on the following possible chemical changes.

$ZnSO_4 + MgCl_2 \rightarrow ZnCl_2 + MgSO_4$
$ZnSO_4 + MgO + H_2O \rightarrow Zn(OH)_2 + MgSO_4$
$ZnSO_4 + CaCl_2 + 2H_2O \rightarrow ZnCl_2 + CaSO_4.2H_2O$
$ZnSO_4 + CaO + 3H_2O \rightarrow CaSO_4.2H_2O + Zn(OH)_2$

$MgSO_4 + CaO + 3H_2O \rightarrow CaSO_4.2H_2O + Mg(OH)_2$
$ZnSO_4 + 2H_2O \rightarrow Zn(OH)_2 + H_2SO_4$
$3Mg(OH)_2 + MgSO_4 + 8H_2O \rightarrow 3Mg(OH)_2.MgSO_4.8H_2O$
$5Mg(OH)_2 + MgCl_2 + 8H_2O \rightarrow 5Mg(OH)_2.MgCl_2.8H_2O$
(Sorel's cement)

$xZn(OH)_2 + yZnCl_2 + zH_2O \rightarrow zZn(OH)_2.yZnCl_2.zH_2O$

(Strength giving compositions)

CONCLUSIONS

(i) Incorporation of zinc sulphate retards setting process of magnesia cement within experimental limits.

(ii) Up to an optimum amount, zinc sulphate is a good additive for strength, durability and moisture sealing capacity of the product.

(iii) Workability of wet mix is reduced on incorporation of zinc sulphate in large excess.

(iv) Zinc sulphate does not cause significant volume change of the product.

Based on above experimental findings zinc sulphate is a good additive if added in optimum proportions.

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