INVESTIGATION OF BLUE VITRIOL *(COPPER SULPHATE PENTAHYDRON)* AS AN ADMIXTURE ON THE PROPERTIES OF MAGNESIA CEMENT: AN ECO-FRIENDLY APPROACH

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ABSTRACT
Incorporation of the copper sulphate in magnesia cement, increase the setting periods and water tightness. It is an eco-friendly approach, because it does not require any heat or light for its setting.Howevere excessive use of the copper sulphate reduces the mechanical strength of the product.
Key Words : *Blue vitriol, magnesia cement, soundness.*

INTRODUCTION
Magnesia cement (Magnesium oxychloride cement, MOC), discovered by S.T. Sorel in 1867, has many superior properties to those of Portland cement. as observed by several researcher.[1-8] it is eco-friendly and does not require any heat, light or energy source for its setting.The Major Reaction Product of MOC Paste (magnesium oxychloride cement) (MgO-$MgCl_2$-H_2O system) has long been revealed to be four crystalline phases : $5Mg(OH)_2$. $MgCl_2$. $8H_2O$ (5 phase) ; $3Mg(OH)_2$. $MgCl_2$. $8H_2O$ (3 phase) ; $2Mg(OH)_2$. $MgCl_2$. $8H_2O$ (2 phase) and $9Mg(OH)_2$. $MgCl_2$. $8H_2O$ (9 phase). All of the phases are the basic salts whose formal formula can be written as $Mg(OH)_y$.Cl.nH_2O. It has been find out that soluble phosphates increase the water resistance of the MOC.[9-13] A parametric study has been conducted to investigate the influence of the molar ratio of $MgO/MgCl_2$ and $H_2O/MgCl_2$ on the properties of (MOC) magnesium oxychloride cement.[14] It has been reported that undesirable effects of active lime in Sorel's cement are reduced by addition of copper powder (approx 10% by weight of magnesia) in the dry-mix.[15,16] However, copper sulphate is not readily available and its use is uneconomical. The authors therefore thought to investigate copper sulphate as an alternative for the following reasons. (i) it is easily available and serves as a light greenish blue pigment. (ii) such products inhibit growth of micro organizations and moulds *i.e*. they are more hyenice[17,18]. (iii) its incorporation transforms active lime into inactive calcium sulphate.
The experimental investigations with copper sulphate (Power and saturated solution) as an admixture were therefore carried out in order to find out its effect on strength and durability of magnesia cement.

EXPERIMENTAL
The following materials were used in this investigation :
Magnesia : Magnesia used in the this study was of Salem (Chennai). It had the following characteristics – (i) Bulk density 0.85 Kg/I (ii) 95% passing through 75 micron (200 IS sieve) (iii) Magnesium oxide 90% (iv) Ca0 < 1.5% (v) Ignition loss at 100^0C – 2.5 +- 0.5%.
Inert filler (dolomite): Dolomite with following grading was used : (i) 100% passing through 150 micron IS Sieve (ii) 50% retained on 75 micron IS Sieve (iii) Ca0 28.7% (iv) Mg0 20.8% (v) Insoluble and other sesquioxide contents were less than 1.0%
Magnesium chloride ($MgCl_2.6H_20$): used in the study was IS Grade 3 of IS : 254 – 1973 with following characteristics: (i) Colourless, crystalline, hygroscopic crystals. (ii) Highly soluble in water. (iii) Magnesium chloride minimum and 95% (iv) magnesium sulphate, Calcium sulphate and alkali chlorides (NaC1) contents were less than 4%.

Effect of copper sulphate (powder and saturated solution) on setting and strength of magnesia cement was studied after incorporation it is different proportions in the wet-mix, on the basis of the following investigations.

Setting time test:

Experiments pertaining to the consistency, initial and final setting periods were performed as per standard procedures mentioned in the I.S. specifications with the help of Vicat needle apparatus.[18-21] Separate investigations were carried out with the dry-mix, containing powdered copper sulphate and the gauging solution containing saturated, copper sulphate in different proportions. The observed results are summarized in table 1.

Weathering effects:

Investigation were made by recording the variation in weights of the setting time blocks (as taken from the vicat moulds) with time after 24 h, 7 and 30 days respectively. Weight of the test blocks may increase or decrease with time due to different weathering effects promoted by the admixture[8,19,22]. The experiential findings are recorded in table 2.

Moisture ingress test (Steam tests) :

To find out the effect of copper sulphate (powder and saturated solution) on moisture ingress in magnesia cement, standards setting time blocks were used. These were subjected to steam tests after one month air curing under identical conditions to estimate their relative moisture sealing efficiencies according to the standard procedure[19,20,23,24]. The observed results are summarized in the table 3.

Compressive strength test :

The effect of copper sulphate (powder in dry-mix and saturated solution in gauging solution) on compressive strength of the magnesia cement was determined with the help of compressive strength testing machine as per the standard procedures. [18,24,25] The practical results are recorded in the table 4.

Soundness tests (Le-Chaterlier's test) :

This test was carried out with the Le-chatelier's test apparatus which consists of small split cylinder forming a mould and two glass plates to cover each side of the cylinder. Two parallel indicating arms with pointed ends are attached on either side. The wet-mix which is to be tested for soundness of the products is placed into the mould resting on a glass plate and then covered with another glass plate. The wet-mix is than allowed to set for the one week. Then difference (x) between pointed ends of the indicating arms is measured. Now the mould is immersed in water at 27^0 to 32^0 C for 48 hours. Again the distance (x) between pointed ends of the indicating arms is measured. Then the mould is immersed in a beaker of boiling water for 1 h, cooled and again the distance (y) measured. The difference (y-x) measures the soundness or expansion of the product. The value of (y-x) should not be more than 5 mm for a good product[19,20,22]. The results of the investigation are summarized in the table 5.

RESULTS AND DISCUSSION

Table 1 summarizes the effect of copper sulphate (power and saturated solution) on setting properties of magnesia cement. The volume of gauging solution decreases with increasing amounts of the copper sulphate. The plausible reason for this may be the tendency of copper sulphate to reduces the rate of hydration of magnesia cement formation. Thus, the activity of magnesia is reduced. Decreasing volume of the gauging solution with increasing amounts of copper sulphate is thus expected. Further, it is noteworthy that copper sulphate is an acidic salt of weak base $Cu(OH)_2$ and strong acid, H_2SO_4. Hence, some side reactions start simultaneously with the formation of magnesia cement hindering the normal setting process. Accordingly, it is noted that initial as well as final setting periods in the table is found to increase with increasing amount of the admixture. It may be noted that reactions of copper sulphate with active lime (calcium oxide or calcium chloride) occurs in the matrix because of theirs presence as impurities to some extent in commercial magnesia and magnesium chloride respectively.

$$CuSO_4 + MgCl_2 \rightarrow CuCl_2 + MgSO_4 \quad \text{(i)}$$

$$CuSO_4 + MgO + H_2O \rightarrow Cu(OH)_2 + MgSO_4 \quad \text{(ii)}$$

$MgSO_4 + CaO + 2H_2O \rightarrow Mg(OH)_2 + CaSO_4$ (ppt..) (iii)

$MgSO_4 + CaCl_2 \rightarrow MgCl_2 + CaSO_4$ (ppt..) (iv)

$CuSO_4 + CaCl_2 \rightarrow CuCl_2 + CaSO_4$ (ppt..) (v)

$CuSO_4 + CaO + H_2O \rightarrow Cu(OH)_2 + CaSO_4$ (vi)

$CuCl_2 + 3\,Cu(OH)_2 \xrightarrow{\text{slow}} 3Cu(OH)_2 . CuCl_2$ (vii)
(Atacaite)

$MgSO_4 + 5Mg(OH)_2 + 8H_2O \xrightarrow{\text{slow}} 5Mg(OH)_2 . MgSO_4 . 8H_2O$ (viii)
(Magnesium oxysulphate cement)

$MgCl_2 + 5Mg(OH)_2 + 8H_2O \xrightarrow{\text{Slow}} 5Mg(OH)_2 . MgCl_2 . 8H_2O$ (ix)
(Magnesia cement)

The reactions (iii - vi) inactivate active lime and thus minimize its harmful expansive effects. Therefore, volume changes are found to the insignificant and the surface texture of the products is glossy. Weathering effects of copper sulphate (powder in dry-mix and saturated solution in the gauging solution) on magnesia cement are recorded in the table 2. Gravimetric studies of the trail blocks in questions reveals a uniform decrease in their weights with time almost in every case. This is partly due to inactivation of active lime and partly to the retarding effect of copper sulphate on setting process of magnesia cement. Thus, entire amount of the uncombined water is not given out during setting periods. Loss in weight with time is thus expected.

From the above reactions and discussions, it is obvious that incorporation of copper sulphate inactivates active lime (iii - iv) responsible for fast moisture ingress and causes the formation of watertight compositions like copper oxychloride and magnesium oxysulphate (viii - ix). Combine effects of these factors made the product almost watertight. Experimental findings of the table 3 relating the effects of copper sulphate powder and solution as an admixtures on moisture ingress in trial blocks witness this fact beyond an shade of doubt.

Effects of copper sulphate as an admixture (powder in the dry-mix and saturated solution in the gauging solution) on compressive strength of magnesia cement are summarizes in table 4. Initial incorporation of copper sulphate (up to 5%) in small amounts causes gain in the strength. This may be due to inactivation of harmful impurities like active lime, which make the products unsound. However, with further additions of copper sulphate, strength are found to decrease constantly. This may be due to the increasing proportions of cupric oxychloride and magnesium oxysulphate (vii and viii) in that way. Both of these composition are not as strength giving as magnesium oxychloride. Such a effect is much more pronounced with saturated solution as an admixture, because the gauging solutions become increasingly poorer in magnesium chloride amounts. Such a situation reduces much more the formation of the strength giving magnesium oxychloride composition.

The discussion and the hypothesis proposed above are strongly supported by the Le-Chaterlier's tests pertaining to the influence of copper sulphate (powder in the dry-mix and saturated solution in the gauging solution) as admixture on soundness of magnesia cement (table 5). As argued earlier copper sulphate inactivates like active lime responsible for expansion and contribution to water tightness (formation of atacaite). It is noted that volume changes in both the cases are almost absent.

CONCLUSIONS

1. Copper sulphate as an admixture increase setting periods and water tightness of magnesia cement.
2. Excessive use of copper sulphate reduces the mechanical strength of the product.
3. It controls the volume change of magnesia cement. Hence, it is an excellent admixture for flooring compositions particularly in hot seasons or in case of caustic magnesia as the raw material.

Table-1: Effect of Copper Sulphate (Powder and saturated solution) on setting characterizations of Magnesia Cement
Gauging Solution: 22^0Be; Temperature: 29^0C ;
Dry-mix Composition: 1:2* (Inter Filler) ; Humidity: 75%

S.No.	Observation	Composition of Dry-mix (% additive w/w)					Composition of Dry-mix (% additive v/v)				
		0	5	10	15	20	0	5	10	15	20
1	Volume of gauging Solution (ml)	60	52	52	49	46	60	54	52	59	44
2	Initial setting time (min)	130	195	230	260	375	130	135	180	240	300
3	Final Setting time (min)	245	245	350	410	435	245	370	410	455	480
4	Nature of Blocks										
	i.Glossiness	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes
	ii.Volume Change	Insignificant					Insignificant				

*One part by weight of magnesia and two parts by weight of dolomite.

Table-2: Effect of Copper Sulphate (Powder and saturated solution) on Weathering of Magnesia Cement
Gauging Solution: 20^0Be; Temperature: 29^0C ;
Dry-mix Composition: 1:2* (Inter Filler) ; Curing: Air Drying

S.No.	Observation	Composition of Dry-mix (% additive w/w)					Composition of Dry-mix (% additive v/v)				
		0	5	10	15	20	0	5	10	15	20
1	Weight after 24h. (g)	260	257	258	256	253	385	250	264	264	270
2	Weight after 7 Days (g)	245	250	250	247	243	384	236	256	255	262
3	Weight after 30 Days (g)	240	250	250	246	240	280	235	248	252	260

*One part by weight of magnesia and two parts by weight of dolomite.

Table-3: Effect of Copper Sulphate (Powder and saturated solution) on on moisture ingress (steam test) in the trial blocks
Gauging Solution: 22^0Be; Dry-mix Composition: 1:2* (Inter Filler)

S.No.	Observation	Composition of Dry-mix (% additive w/w)					Composition of Dry-mix (% additive v/v)				
		0	5	10	15	20	0	5	10	15	20
1	10h	N.E.	N.E.	N.E.	N.E.	N.E.	60	54	52	59	44
2	15h	N.E.	N.E.	N.E.	N.E.	N.E.	130	135	180	240	300
3	20h	N.E.	N.E.	N.E.	N.E.	N.E.	245	370	410	455	480
4	25h	N.E.	N.E.	N.E.	N.E.	N.E.	Yes	Yes	Yes	Yes	Yes
5	30h	C	N.E.	N.E.	N.E.	N.E.	C	N.E.	N.E.	N.E.	N.E.
6	35h	-	N.E.	N.E.	N.E.	N.E.	-	N.E.	N.E.	N.E.	N.E.
7	40h	-	N.E.	N.E.	N.E.	N.E.	-	N.E.	N.E.	N.E.	N.E.
8	45h	-	+	+	+	+	-	+	+	+	+

*One part by weight of magnesia and two parts by weight of dolomite.
(N.E.= No Effect, C=Cracked , += Moisture ingress but not cracked)

Table-4: Effect of Copper Sulphate (Powder and saturated solution) on Compressive Strength of Magnesia Cement
Gauging Solution: 24^0Be; Dry-mix Composition: 1:2* (Inter Filler)

Observation	% Additive (w/w of magnesia)					% Additive (v/v of gauging solution)				
	0	5	10	15	20	0	5	10	15	20
Compressive Strength (Kg/Cm^2)	480	580	540	525	520	480	540	480	440	410

*One part by weight of magnesia and two parts by weight of dolomite.

Table-5: Effect of Copper Sulphate (Powder and saturated solution) on soundness of Magnesia Cement (Le-Chatelier's Test)
Gauging Solution: 24^0Be; Dry-mix Composition: 1:2* (Inter Filler)

S.No.	Observation	Composition of Dry-mix (w/w % additive of magnesia)					Composition of Dry-mix (v/v % additive of gauging solution)			
		0	5	10	15	20	5	10	15	20
1	Weight of Cement composition (g) i. Magnesia ii.Dolomite iiiAdditive	13 26 -	13 24.7 1.3	13 23.4 2.6	13 22.1 3.9	13 20.8 5.2	13 26 0.5	13 26 1	13 26 1.5	13 26 2
2	Use of MgCl2 solution (ml)	11.5	10	10	10	10	9.5	9	8.5	8
3	Distance between two pointers before starting (cm)	1.8	1.1	1.4	1.4	3.0	1.1	1.2	1.6	2.0
4	Distance between two pointers after 7 days(cm)	2.0	1.2	1.5	1.4	2.1	1.1	1.3	1.6	2.0
5	Time in water at 27^0C to 32^0C (h)	48	48	48	48	48	48	48	48	48
6	Distance between two pointers before boiling (cm)	2.0	1.2	1.6	1.5	2.1	1.1	1.3	1.6	2.0
7	Distance between two pointers after boiling (cm)	2.3	1.2	1.6	1.5	2.1	1.1	1.3	1.6	2.0
8	Expansion of Cement (cm)	0.1	0	0	0	0	0	0	0	0

*One part by weight of magnesia and two parts by weight of dolomite.

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