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Investigations on the Effect of Non Aqueous Effluent Wastes From Paint Industry as Additive on Different Properties of Magnesium Oxysulphate Cement.

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ABSTRACT

Oxysalt cements were first prepared by Sorel S.T., a French chemist, in 1867. Magnesium oxysulphate cement is a combination of magnesium oxide, magnesium sulphate solution and inert filler dolomite in definite ratio. Its cementing properties are superior to that of calcareous Portland cement. When paint is added in the matrix as an additive, very encouraging results are observed. Initial incorporation of paint in the matrix accelerates the setting process. Remarkable increase in the strength and watertightness of the cement is noticed with increasing quantities of the additive. Minor contractions, within the experimental limits, are also noticed in the linear beams with the passage of time. Weathering effects of the trial block are also very encouraging.

Keywords: magnesium oxysulphate cement, compressive strength, watertightness, setting periods, weathering effects, linear changes.

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INTRODUCTION

Binders are the materials which can be exploited directly or indirectly for fastening, adhering or binding substances due to their polymerization tendencies or interlocking crystal habits. Cement term is used for inorganic binders [1]. In 1867 a French Chemist Sorel S.T. observed that plastic wet mixes of cement like characteristics are observed by gauging magnesium oxide with aqueous solutions of its salts, particularly halides and sulphates. These wet mixes (Sorel's cement) form rock like masses after being allowed to set under proper conditions [2-5]. Magnesium oxysulphate cement is obtained by the interaction between lightly calcined magnetite (loss on ignition 2 – 4 %) and aqueous solution of magnesium sulphate of suitable density at room temperature [6-8]. Inert filler dolomite is added to absorb the excess heat evolved during the exothermic formations of magnesium oxysulphate cement. The compositions of magnesium oxysulphate cement are 3, 1, 8 and 5, 1, 8 although some other compositions are also known (3, 1, 11; 6, 1, 3; 5, 1, 13 etc). Interlocking crystals of $5Mg(OH)_2.MgSO_4.8H_2O$ composition are actually responsible for the cementing characteristics of the product.

$$Mg + H_2O \text{ -- } Mg(OH)_2$$
$$3Mg(OH)_2 + MgSO_4.7H_2O + H_2O \text{ -- } 3Mg(OH)_2.MgSO_4.8H_2O$$
$$5Mg(OH)_2 + MgSO_4.7H_2O + H_2O \text{ -- } 5Mg(OH)_2.MgSO_4.8H_2O$$

Sorel's cement shows high fire resistance, low thermal conductivity, high abrasion resistance, high transverse and crushing strength and does not require wet curing. It is also suitable for nuclear applications [9-11].

Additives may alter the properties of the cement to a great extent as they can nullify the harmful effects of the impurities present in the raw materials. Paint industry in associated with the discharge and deposition of non-aqueous effluent waste. Utilization of industrial waste is the need of the hour as it is beneficial for the environment, mankind, and society as well as for the industry itself. Hence the authors tried to extract paint from the waste and used it as additive for magnesium oxysulphate cement. For this purpose the non-aqueous effluent waste is concentrated and distilled. Then the residual tari material (paint) is used as additive. Paint is a pigmented liquid composition which is converted to an opaque solid film after application as a thin layer [12]. It is a uniformly dispersed medium having a viscosity ranging from a thin liquid to a semisolid paste. The important ingredients of paint and the functions are as follows.

S.No.	INGREDIENTS	FUNCTIONS
(I)	Film forming material-A drying oil or binder. It is a blend of unsaturated higher fatty oil (e.g. linseed oil, soybean oil, dehydrated castor oil, linseed oil emulsions, sucrose esters etc.)	To form the protective film through oxidation and polymerization of the unsaturated constituents of the drying oil.
(ii)	Thinner- This may be of two types : (a) Aliphatic hydrocarbons Mixed sprit, naphtha, petroleum fractions, turpentine etc. (b) Aromatic hydrocarbons - Toluol, xylol, methylated naphthalene etc. Note : Binder and thinner are collectively called vehicle	To suspend pigments, dissolve film forming materials and to thin concentrated paints for better handling.

(iii)	Driers-Metal salts e.g. Co, Mn, Pb, Zn, naphthenates resinates, octoates, linoleates, tallates etc.	To accelerate the drying of the film through oxidation and polymerization.
(iv)	Antiskinning agents - Polyhydroxyl phenols.	To prevent gelling and skinning of the finished product before applications.
(v)	Plasticizer- Some oils.	To give elasticity to film thus minimizing or preventing cracking.
(vi)	Pigments - Inorganic and Organic (Toner)	To protect the film by reflecting the destructive U.V. light, to strengthen the film and to impart an aesthetic appeal. Pigment should possess the following properties - opacity and good covering power, mixing ability with oil, chemical inertness, nontoxicity or low toxicity, reasonable cost.
(vii)	Extenders or inerts - e.g. Gypsum, China clay, mica, asbestos, silica, metal sterates etc.	To reduce the pigment cost and in many cases to increase the covering and weathering power of pigment by complementing pigment particle size, thus improving consistency levelling and setting.

On the basis of the above mentioned details it is expected that these compositions are likely to form polymeric water impervious resinous products which should contribute to strength and durability of magnesium oxysulphate cement.

MATERIALS AND METHODS

RAW MATERIALS: In the present study, the basic raw materials used for the preparation of magnesium oxysulphate cement are commercial grade magnesium oxide, magnesium sulphate (Epsom salt) and inert filler dolomite [13]. The specifications of these materials are given below:

(a) **Magnesium oxide** : Magnesium oxide of Salem origin is used in the present study having the following characteristics : MgO 90%, LOI 2 1 %, active lime in traces, Si2O3 Al2O3 0.2 – 0.4%, Fe2O3 1.4%, bulk density 0.85 kg/l, 95% passing through 75 micron sieve [14].

(b) **Epsom Salt (Magnesium sulphate) $MgSO_4.7H_2O$**: Magnesium sulphate (technical grade) used for Sorel's cement was strictly according to IS specifications having the following characteristics: Magnesium sulphate 98%, Chlorides (as Cl), lead (as Pb), Arsenic (as As_2O_3), Iron (as Fe), Zinc and matter insoluble in water in traces [15].

(c) **Dolomite (Inert filler)**: Inert filler absorbs the heat evolved during the exothermic formation of Sorel's cement and thus reduces thermal shocks in the matrix. Uncalcined dolomite powder is used in the study passing through 150 micron sieve and retained 50% on 75 micron sieve. It contains CaO 28.7%, MgO, 20.8% insoluble and other sesquioxide contents < 1%, LOI 50% [16].

EXPERIMENTAL

In order to study the effect of paint on the properties of the cement following experiments were carried out as per IS specifications [17]

(a) Setting Time Investigations: Paint is mixed in the dry mix in varying proportions (0%, 5%, 10%, 15%, and 20%) so as to study its effect on setting characteristics of the cement. The quantity of the additive was calculated by weight of magnesia. 1:2 dry mixes (by weight of magnesia and dolomite) having different quantities of the additive were gauged with magnesium sulphate solution (25°Be) to obtain wet mixes. The volume of the gauging solution was kept constant for each lot of dry mix. Initial and final setting periods were determined using Vicat Apparatus as per the standard procedure. Experimental findings are reported in Table :1 [18-22].

(b) Weathering Effects : All the setting time blocks with different quantities of paint, prepared as above, were cured under identical conditions of temperature and humidity. These blocks were weighed on chemical balance at different time intervals. Weathering effect may be reflected by observing the change in weights with time. Experimental findings are summarized in Table : 2 [18-22].

(c) Moisture Ingress Investigations: Setting time blocks were cured for 60 days under standard conditions and then exposed to boiling water for 30 hrs in a steam bath. These investigations are desirable in order to evaluate the relative moisture sealing efficacies of the blocks. Relative water vapour transmission has been expressed as a function of time. Results are tabulized in Table: 3 [18-22].

(d) Compressive Strength Investigations: Paint may alter the compressive strength of the cement, so it was added in different proportions in the matrix. Standard sized trial blocks (70.6mm× 70.6mm× 70.6mm) were prepared by gauging dry mixes (one part by weight of magnesia and two parts by weight of dolomite) having varying quantities of paint with constant volume of magnesium sulphate solution (25°Be). Compressive strength of each block was determined as per the standard procedure. Table: 4 shows the experimental findings [18-22].

(e) Linear Change Investigations: Standard sized beams (200 mm× 200 mm× 200 mm) were prepared by wet mixes having different quantities of the additive. These beams were kept under 90% relative humidity and 30 ± 2° C temperature for 24 hrs. Length of each beam was measured after 24 hrs and then after 28 days using micrometer scale. Difference between initial and final length shows the linear change. Lesser the linear change, the greater will be the quality of the product. Observations are enumerated in Table: 5 [18-22].

Table 1 : Effect of Paint on Setting Characteristics of Oxysulphate Cement

Conc. Of g.s = 25^{O} Be
Volume of g.s. = 70 ml
Temperature … 30 ± 2^{O}C
Relative humidity…above 90%

Dry –mix composition …… 1:2
(a) One part by weight of magnesia
(b) Two parts by weight of dolomite + additive
Quantity of dry mix … 200 gm

S.No	Dry Mix Composition (% additive)	Setting Time	
		Initial (Min)	Final (Min)
1	0%	30	133
2	5%	18	113
3	10%	23	118
4	15%	24	122
5	20%	28	128

g.s. = gauging solution

Table 2 : Effect of Paint on Weathering Characteristics of Oxysulphate Cement

Conc. Of g.s = 25^{O} Be
Volume of g.s. = 70 ml
Temperature … 30 ± 2^{O}C
Relative humidity…above 90%

Dry –mix composition …… 1:2
(a) One part by weight of magnesia
(b) Two parts by weight of dolomite + additive
Quantity of dry mix … 200 gm

S	Dry Mix Composition (% additive)	Weight of Blocks in gm after			
		24 hr	7 day	30 days	45 days
1	0%	258.870	251.163	243.322	241.440
2	5%	252.600	243.850	238.250	237.360
3	10%	238.770	229.470	224.730	224.060
4	15%	237.200	227.380	221.920	221.070
5	20%	235.090	224.980	219.500	218.970

g.s. = gauging solution

Table 3 : Effect of Paint on Moisturing Ingress Characteristics of Oxysulphate Cement

Conc. Of g.s = 25^{O} Be
Volume of g.s. = 70 ml
Temperature … 30 ± 2^{O}C
Relative humidity…above 90%

Dry –mix composition …… 1:2
(a) One part by weight of magnesia
(b) Two parts by weight of dolomite + additive
Quantity of dry mix … 200 gm

	Dry Mix Composition (% additive)	Trial blocks kept in boiling water for					
		0-5 hrs	5-10 H	10-15 hrs	15-20 Hrs	20-25 Hrs	25-30 hrs
1	0%	N.E.	N.E.	N.E.	N.E.	C	----
2	5%	N.E.	N.E.	N.E.	N.E.	N.E.	C
3	10%	N.E.	N.E.	N.E.	N.E.	N.E.	N.E.
4	15%	N.E.	N.E.	N.E.	N.E.	N.E.	N.E.
5	20%	N.E.	N.E.	N.E.	N.E.	N.E.	N.E.

g.s. = gauging solution, N.E. = No effect, C = Cracked

Table 4 : Effect of Paint on Compressive Strength of Oxysulphate Cement

Conc. Of g.s = 25^{O} Be

Dry –mix composition …… 1:2

Volume of g.s. = 200 ml
Temperature ... 30 ± 2^{O}C
Relative humidity...above 90%

(a) One part by weight of magnesia
(b) Two parts by weight of dolomite + additive
Quantity of dry mix ... 565 gm

Dry Mix Composition	0%	5%	10%	15%	20%
Compressive Strength (kg/cm^2)	275	260	290	320	360

g.s. = gauging solution

Table 5 : Effect of Paint on Linear Changes of Oxysulphate Cement

Conc. Of g.s = 25^{O} Be
Volume of g.s. = 105 ml
Temperature ... 30 ± 2^{O}C
Relative humidity...above 90%

Dry –mix composition 1:2
(a) One part by weight of magnesia
(b) Two parts by weight of dolomite + additive
Quantity of dry mix ... 300 gm

S.No	Dry Mix Composition (% additive)	Length of Beams (mm)		Change in Length (mm)
		Initial	Final	
1	0%	200.00	200.02	0.02
2	5%	200.00	199.47	0.53
3	10%	200.00	199.51	0.49
4	15%	200.00	199.55	0.45
5	20%	200.00	199.59	0.41

g.s. = gauging solution

RESULTS AND DISCUSSION

Table: 1 reflects the effect of paint on setting characteristics of magnesium oxysulphate cement. Co- polymerization of paint composition and cement composition becomes complementary and co-operative (eq ......vi). This causes earlier setting of the trial blocks. However, with increasing quantities of paint, its hydrophobic nature hampers cementing process on account of the low chances of interaction of magnesium sulphate and water with magnesium oxide, as there is a barrier of paint layer around magnesia particles. Thus, it is observed that setting periods (initial as well as final) decrease on mixing paint in the matrix and then increase gradually with increasing proportions of the additive.

Weights of trial blocks of varying compositions decrease gradually with passage of time as shown in Table: 2. Loss of moisture of the cementing composition and thinners of the painting composition and little chances of weathering are the major reasons of loss of weight with lapse of time.

The effect of paint on watertightness of oxysulphate cement is shown in Table :3. It is observed that incorporation of paint in the matrix makes the product more watertight.

Entanglement of individual inorganic polymer (of cement composition) and organic polymer (of paint composition) and co polymerization of cement composition and paint composition are responsible for improved water tightness of the product. (eq....v, vi).

Compressive strength of oxysulphate cement increases with increasing proportions of paint in the matrix as is evident from the data shown in Table: 4. increasing entanglement of individual inorganic and organic polymers and also increasing co -polymerization of cement composition and paint composition is responsible for increase in strength data with increasing additive quantities (eq .... v, vi)

Table: 5 summarizes the effect of paint on volume changes of oxysulphate cement. Almost insignificant contractions are noticed in each case. Volatilizations of thinner solvent and moisture with passage of time are the major factors responsible for the compaction of the structure.

The following probable chemical changes can explain the above discussion.

$MgO + H_2O \longrightarrow Mg(OH)_2$ .... (i)

$CaO + H_2O \longrightarrow Ca(OH)_2$ .... (ii)

$xMgO + yMgSO_4 + zH_2O + nPaint \longrightarrow$ Magnesium Oxysulphate + Painting Composition + Copolymers of Magnesia cement and of resin ....(iii)

$Ca(OH)_2 + MgSO_4 \longrightarrow CaSO_4 + Mg(OH)_2$ .... (iv)

nA $\longrightarrow$ - A - A - A - A - A - (Paint Polymer)

mB $\longrightarrow$ - B - B - B - B - B - (cement Polymer)

Paint Polymer + Cement Polymer $\longrightarrow$ Entanglement ....(v)

A = Paint B = Magnesium oxysulphate cement

Paint composition (A) + Cement Composition (B) $\xrightarrow{\text{Coptymerization}}$ -- B - B - B - B - A - B - B - B - A - B - B - B- B - A -B – ....(vi)

$5Mg(OH)_2 + MgSO_4 + 8H_2O \longrightarrow 5Mg(OH)_2 . MgSO_4 . 8H_2O$ ....(vii)

Oxysulphate cement (Strength giving composition)

CONCLUSIONS

(i) Initial incorporation of paint in the matrix accelerates the setting process but further increase in the quantities of the additive hampers the process.

(ii) Incorporation of paint in the matrix contributes to strength and durability of the product.

(iii) Insignificant contraction in the trial beams is noticed on mixing paint in the dry mix.

REFERENCES

[1] Brady G S. Materials Hand Book. Mc Graw Hill, 15th Edition, 2002, PP. 17.

[2] Wollff P M De, Walter L L. Acta Cryst. 1953; 6: 40.

[3] Sorel S T. J Comp. Rend. 1867; 63: 102-105.

[4] Kalaitzaki P, Maravelaki G, Moraitov. *Cement & Concrete Res* 1999; 29(12): 1929-1935.

[5] British Cement Association: Different Types of Cements, www.azobuild.com, article id 7959, 2006.

[6] Kacker K P, Shrivastava R S. Chemical Age of India 1970: 21.

[7] Rai M. Research and Industry 1983: 28.

[8] Mathur R, Chandrawat M P S, Nagpal K C, Research and Industry 1984; 29: 195-201.

[9] Beaudoin J J, Vangipuram S R, Feldman R F. *American Ceramic Society Bulletin* 1977: 424.

[10] Vangipuram S R, Ralph M P, Baeudoin J, Delgado A H. Handbook of Thermal Analysis of Construction Materials. William Adrew Inc, 2002 PP. 359.

[11] Ramchandran V S, Feldman R F. *Cem. And Concrete Research* 1973; 3: 729.

[12] ASTM Standards: Paint Testing Manual Part 20 and 21, Philadelphia 1972; 13: 53-164.

[13] Prakash S, Madan R D. Modern Inorganic Chemistry. S.Chand, 2005 PP. 906.

[14] Indian Standard: 657 (1982).

[15] Indian Standard: 2730 (1977).

[16] Indian Standard: 1760 (1962).

[17] Indian Standard: 10132 (1982).

[18] Chandrawat M P S, Yadav R N, Mathur *R. Res & Ind* 1994; 39: 18-21.

[19] Gupta Y K, Chandrawat M P S, Yadav R N. *Res & Ind* 1990; 35: 191-193.

[20] Mathur R, Chandrawat M P S, Sharma S K. Material Science Research India 2008; 5(2): 313-320.

[21] Mathur R, Chandrawat M P S, Sharma S K. E-Journal of Chemistry 2009; 6(2): 412-418.

[22] Mathur R, Chandrawat M P S. Pelagia Research library / der chemica sinica 2010; 1(3): 1 169-175.