International Research Journal of Natural and Applied Sciences
ISSN: (2349-4077)
Impact Factor 5.46 Volume 4, Issue 1, January 2017
Website- www.aarf.asia, **Email** : editor@aarf.asia , editoraarf@gmail.com

IMPROVEMENT IN WATER TIGHTNESS OF SOREL'S CEMENT BY ADDING POTASSIUM OXALATE

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ABSTRACT

Magnesium oxychloride cement known as Sorel's cement is very good binding material for insulation applications.The effect of potassium oxalate[$(COOK)_2.H_2O$] on Sorel's cement has been investigated by adding potassium oxalate to the gauging solution with a percentage of 0,5,10,15 and 20% by weight of Sorel's cement.Anionic part of this compound $(C_2O_4)^{-2}$ is awell-known sequestering ion for divalent and trivalent metal ions. Oxalates react with active lime and other harmful impurities and form aninsoluble precipitate of calcium oxalate.Similarly, magnesium ion forms an important case of post precipitation as magnesium oxalate under the conditions when calcium ion is precipitated in presence of magnesium ion as oxalate.The results revealed that the incorporation of potassium oxalate enhance the water tightness and increases setting period of magnesia cement.

Key words:Sorel's cement, Potassium oxalate,water tightness, setting period

INTRODUCTION

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 $5Mg(OH)_2.MgCl_2.8H_2O$. 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 potassium oxalate when added in Sorel's cement in various proportions.Anionic part $(C_2O_4)^{-2}$of potassium oxalate $[(COOK)_2.H_2O]$ has got capacity to react with active lime and other harmful impurities by converting them into insoluble inactive phase which is beneficial for the quality of magnesia cement.

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 INVESTIGATIONS

To evaluate potassium oxalate as an additive in magnesium oxychloride compositions following investigations have been carriedout.

***(i) Setting characteristics*:** In order to investigate the effect of saturated solution of potassium oxalate on setting characteristics of magnesia cement, it was mixed in varying 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 than gauged with magnesium chloride. solution of 23° Be the gauging solution was 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 uniform conditionsof temperature and humidity. Setting periods of these wet-mixes were found out with the help of Vicat needle apparatus as per IS specifications" and standard procedures. Experimental results are summarized in the table1.

Room Temperature: 28±1°CStrength 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 potassium oxalate (saturated solution) 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	200	300
3	10	66	230	305
4	15	69	240	315
5	20	71	300	335

g.s.= gauging solution

(ii)Weathering Investigations: All the setting time blocks with different proportions of saturated solution of potassium oxalate in varying amounts (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 ofpotassium oxalate (saturated solution) 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	267.82	261.85	259.70
3	10	272.84	267.85	265.42
4	15	277.04	268.48	265.09
5	20	278.02	268.00	264.02

(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 potassium oxalate (saturated solution) on Moisture IngressCharacteristics 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	NE
3	10	NE	NE	NE	NE	NE	NE
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 potassium oxalate (saturated solution)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 were 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 potassium oxalate (saturated solution)on Compressive Strength of Magnesia Cement.

S.No.	%Additive	Compressive Strength (Kg/Cm^2)
1	0	500
2	5	354
3	10	232
4	15	180
5	20	122

(v) Linear Change Investigations: The effect of saturated solution of potassium oxalate (saturated solution)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 potassium oxalate (saturated solution) on Linear Change Characteristics of Magnesia Cement.

S.No.	% Additive	Length of beams (mm)		Change in length (mm)
		Initial	Final	
1	0	200.00	200.29	0.29
2	5	200.00	201.19	1.19
3	10	200.00	200.80	0.80
4	15	200.00	200.57	0.57
5	20	200.00	200.54	0.54

DISCUSSIONS

Effect of potassium oxalate as an additive on setting characteristics of magnesia cement has been summarized in the table1. Observed data reveal that both initial as well as final setting periods increase gradually with increasing incorporations of potassium oxalate in the matrix. This may be attributed to the reactivity of oxalate ions towards calcium and magnesium ions present in the matrix. Calcium oxalate is precipitated first as an inactive solid crystalline phase because of its extremely low solubility product. Setting periods are found to increase as setting promoter, active lime, is inactivated. On further addition of potassium oxalate, chances of post- precipitation of magnesium ions as magnesium oxalate (inactive solid crystalline phase) increase. The rate of setting decreases slightly as available active amounts of magnesia and magnesium chloride reduce in the wet-mix.
Accordingly setting periods are found to increase with increasing proportions of potassium oxalate. Parallelly decreasing weights of the trial blocks with time are apparent from the data shown in the table 2. Even after final setting some uncombine or loosely combined water is left in the matrix which is given out gradually with lapse of time by way of evaporation. The effect of potassium oxalate on moisture ingress characteristics of magnesia cement is revealed from the table 3. It is found that water tightness of the trial blocks is increased remarkably due to the reactivity of oxalate ions towards harmful impurities like active lime etc. Excellent moisture sealing characteristics of potassium oxalate are expected as once these harmful di and trivalent metal cations have been converted into insoluble and inactive crystalline phases, water vapour transmission is almost sealed.

Effect of potassium oxalate as an additive on compressive strength of magnesia cement is revealed bytable 4. On increasing proportions of the additive, gradual decrease in the compressive strength is noticed. Plausible reason for this is that with increasing excess of oxalate ions formation of magnesium oxalate take place which results into decrease of active amounts of magnesia and magnesium chloride in the matrix. Consequently, chances of formation of strength giving compositions of magnesia cement also decrease parallelly.

The table 5 summarizes the effect of potassium oxalate on linear change characteristics of the trial beams. It appears that oxalates formed by incorporation of the potassium oxalate increase the crystal lattice gaps within the strength giving compositions. However, any excess of the additive causes' simultaneous formation of the said phases (cement and oxalates) separately. Thus, it is observed that initial incorporation of the additive contribute much more to the volume changes than the latterincorporations. The discussions mentioned above can be explained on the basis of following accompanying probable chemical changes during the setting.

$CaO/ MgO + HOH \rightarrow Ca(OH)2/Mg(OH)_2$

$Ca(OH)_2 + K_2C_2O_4 \rightarrow CaC_2O_4 + 2KOH$
(Active)(Inactive)

$Mg(OH)_2 + K_2C_2O_4 \rightarrow MgC_2O_4 + 2KOH$
(Active)(Inactive)

$2KOH + MgCl_2 \rightarrow Mg(OH)_2 + 2KCl$

$MgCl_2 + K_2C_2O_4 \rightarrow MgC_2O_4 + 2KCl$
(Active)(Inactive)

$CaCl_2 + K_2C_2O_4 \rightarrow CaC_2O_4 + 2KCI$
(Active)(Inactive)

$3Mg(OH)_2 + MgCl_2 + 8 H_2O \rightarrow 3 Mg(OH)_2.MgCl_2.8H_2O$

$5Mg(OH)_2 + MgCl_2 + 8 H_2O \rightarrow 5Mg(OH)_2.MgCl_2.8H_2O$
Strength giving compositions
(Sorel's cement)

CONCLUSIONS

1. Incorporation of potassium oxalate increases setting periods ofmagnesia cement.
2. Potassium oxalate improves water tightness of the product inall proportions within the experimental limits.

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