Effect of Admixing Sodium Oxalate on the Properties of Magnesium Oxysulphate Cement

Ritu Mathur [1*], Garima Khandelwal [1#] and M. P. S. Chandrawat [2]

[1] *Department of Chemistry, R. R. Govt. College, Alwar – 301 001 (Rajasthan) India.*

[2] *Eternal University, Baru Sahib – 173 101 (Himachal Pradesh) India.*

Abstract: Magnesium Oxysulphate Cement (MOS) is one of the most important kind of cement that was first prepared by S. T. Sorel in 1867 and therefore it is also named as Sorel's cement. It is generally suitable for the flooring and internal decorative plasters due to its good acoustical and adaptable properties and attractive marble-like appearance. It is developed by the chemical reaction of Magnesium Sulphate ($MgSO_4$), Magnesium Oxide (MgO; Magnesia) and Dolomite. Sodium Oxalate is an important admixture which can play an imperative role to modify the properties of MOS cement by nullifying the harmful effects of the impurities present in the matrix. Sodium Oxalate improves the Watertightness and Compressive Strength of the product. Slight increase in length of the linear beams with in the experimental limits are noticed with passage of time. It is suitable for artificial stone cast, flooring and light weight insulating panels.

Keywords: Magnesium Oxysulphate Cement; Sodium Oxalate; Watertightness; Compressive Strength; Linear Beams.

INTRODUCTION

Cement is one of the most important and valuable binding, hardening and setting material that has been used for human civilization throughout the world. It is usually a mixture of inorganic chemical substances (chemical binders) and is based on lime or calcium silicate which is calcined in furnaces at high temperatures. The major inorganic chemical components of most of the cements usually belong to silica, iron, alumina, calcium and sulphate resources (Saleh and

Rahman, 2018). Chemical binders are the chemical substances which can be used directly or indirectly for the binding and adhesive purposes (Mathur and Sharma, 2003). Sorel Cement is a non-hydraulic oxysalt cement, one of the most important cements that was first prepared by French chemist S. T. Sorel in 1867 (George, 2002; Sorel, 1867; Walling and Provis, 2016). Sorel's cement is of two types - Magnesium Oxysulphate (MOS) or Magnesium Oxychloride (MOC) Cement (Walling and Provis, 2016). This new type of cement is a strong and flexible in comparison to normal Portland cement. The resistance of MOS is about 1 to 5 times to that of Portland cement (Singh *et al.*, 1997). MOS is suitable material for fire proofing, insulating and nuclear applications (Wu *et al.*, 2015; Wilson and Nicholoson, 2009). There are five known types of MOS cements. The most common composition of MOS generally found is $Mg(OH)_2.MgSO_4.8H_2O$.

$$MgO + H_2O \longrightarrow Mg(OH)_2 \quad \text{.................................} \quad (i)$$

$$3Mg(OH)_2 + MgSO_4.7H_2O \xrightarrow{H_2O} 3Mg(OH)_2.MgSO_4.8H_2O \quad \text{............} \quad (ii)$$

$$5Mg(OH)_2 + MgSO_4.7H_2O \xrightarrow{H_2O} 5Mg(OH)_2.MgSO_4.8H_2O \quad \text{............} \quad (iii)$$

MOS is generally used as binders in flooring materials. It is manufactured by mixing of MgO powder with solution of $MgSO_4$ in appropriate ratio (Newman, 1964). Dolomite is used as an inner filler in the matrix to absorb the heat evolved during the formation of MOS Cement (Mathur, 2009). Therefore, MOS is an eco-friendly cement (Hu *et al.*, 2020; Li *et al.*, 2022; Walling and Provis, 2016; Wilson and Nicholoson, 2009).

In this research work, Sodium Oxalate is used as a chemical additive. Chemical additives can alter the properties of MOS and their optimum concentration in the MOS can nullify the destructive outcome of impurities present in the matrix. Sodium Oxalate is added in MOS matrix to improve the properties of eco-friendly magnesia cement. The molecular formula of Sodium Oxalate is $Na_2C_2O_4$. It is mixed in the proportion of 0% to 20% in MOS matrix . The objective of this study is to determine the effect of mixing Sodium Oxalate in MOS cement on strength and durability of the product.

Effect of $Na_2C_2O_4$ on the following characteristics of MOS cement was studied by incorporating it in different amounts in dry mix [1: 2 dry mix was prepared by weight of Magnesia and Dolomite].

1. Setting Time Investigation
2. Weathering Effect
3. Moisture Ingress
4. Compressive Strength
5. Linear Changes

MATERIALS AND METHODS

A. Materials: In this research work, MgO, $MgSO_4$ and Dolomite are used as basic raw materials. The materials used in this study are:

1. **Magnesia or Magnesium Oxide (MgO):** In the study, commercial grade magnesia is used and the chemical composition of magnesia is MgO (86.50%), SiO_2 (4.03%), CaO (1.68%), Fe_2O_3 (0.49%) and Al_2O_3 (1.50%). The loss of Ignition (LOI), brightness and whiteness of magnesia is 5.38%, 75.10% and 79.20%, respectively.
2. **Magnesium Sulphate ($MgSO_4$):** In the study, technical grade $MgSO_4$ is used and the chemical composition of $MgSO_4$ is $MgSO_4$ (58.25%), CaO (0.33%) Fe_2O_3 (0.03%), and Al_2O_3 (0.07%). The brightness and whiteness of $MgSO_4$ is 75.10% and 79.20%, respectively.
3. **Dolomite:** In the study, commercial grade Dolomite is used and the chemical composition of Dolomite is $CaCO_3$ (54.20%), $MgCO_3$ (41.37%), CaO (30.35%), MgO (19.70%), SiO_2 (3.10%), Fe_2O_3 (0.65%) and Al_2O_3 (0.31%). The loss of Ignition (LOI), brightness and whiteness of Dolomite is 45.50%, 92.60% and 95.00%, respectively.

B. Methods and Characterizations: The experiments were conducted to investigate the influence of Sodium Oxalate on MOS cement (IS 10132 - 1982).

1. **Setting Time Investigation:** In this study, powdered $Na_2C_2O_4$ was mixed with Magnesia in varying proportions. The concentration of additive was calculated on the basis of weight of Magnesia. Wet mixes were was prepared by gauging 1: 2 dry mix of Magnesia and Dolomite with different proportions of $Na_2C_2O_4$

additive and gauging Magnesium sulphate solution of 25°Be. The volume of gauging solution was kept constant for each set of trial. Standard procedures were adopted according to Indian Standard (IS) specifications to determine Standard Consistency, Initial and final Setting time using **Vicat Needle Apparatus** (IS 10132 - 1982). Results are summarized in **Table 1**.

2. **Weathering Effect:** Standard blocks prepared for setting time investigations were used in the study. Weight of blocks were measured with passage of time (24 hours, 7 days, 30 days and 45 days) using analytical balance. Different weathering effects may increase or decrease the weight of the MOS blocks with passage of time. The experimental findings are summarized in **Table 2**.

3. **Moisture Ingress Test:** The effect of $Na_2C_2O_4$ on soundness of MOS Cement was studied by performing Moisture Ingress Test for all these setting time blocks. This test was performed under identical condition of temperature and humidity blocks were exposed to boiling water for at least 30 hours in a closed steam bath. The relative moisture ingress efficacies were studied as a function of time. Moisture ingress and soundness are inversely proportional to each other. The experimental outcomes are concised in **Table 3**.

4. **Compressive Strength:** Effect of $Na_2C_2O_4$ on compressive strength of MOS Cement was also investigated. The standard 50 cm^2 cubes (70.6 mm x 70.6 mm x 70.6 mm) were prepared through the standard consistency pastes having $Na_2C_2O_4$ in different proportions. The cubes were tested on compressive strength testing machine after 30 days of curing period under identical condition as per standard procedure (IS 10132 - 1982; Beaudoin and Ramachandran, 1975). The experimental results are summarized in **Table 4**.

5. **Linear Change:** The effect of $Na_2C_2O_4$ on linear changes of MOS Cement was investigated. The standard sized beams (200 mm x 25 mm x 25 mm) were set having varying concentrations of $Na_2C_2O_4$ in order to study of effect on linear changes of MOS Cement. Trial beams were measured after 24 hours of setting using in micro meter scale. The blocks were tested for final length of the beams after 28 days of curing under identical condition. Trial beams were kept under 90% humidity and about 30±2°C temperature. The experimental results are summarized in **Table 5**.

RESULTS AND DISCUSSION

The results of this study showed that the addition of $Na_2C_2O_4$ can significantly improve the physical and mechanical properties of MOS. **Table 1** represents the effect of mixing $Na_2C_2O_4$ in varying ratios (0% to 20%) in the MOS matrix on initial and final Setting Times. Initial setting periods decrease with increasing quantities of additive. It may be due to the prompt reactions of oxalate ions with Ca^{+2} and Mg^{+2} ions of the matrix. Such reactions result in the formation of insoluble solid phases of metal oxalates [**Eq. (iii)-(iv)**], which resists the initial setting needle touching the base plate of Vicat mould. Hence gradual decrease in initial setting periods is noticed. An increase in final setting periods is noticed with increasing amount of additive due to inactivation of active lime (setting accelerators) and other harmful impurities. Addition of the additive increase the chances of post precipitation of the Magnesium ions of gauging solution as Magnesium oxalate, which is inactive solid crystalline phase and hence reduces the amount of gauging solution. Sodium Oxalate also reacts with Magnesium Sulphate [**Eq. (iii)-(ix)**] and hence reduces its availability for cementation. Increasing setting periods are thus obvious. Sodium Oxalate converts Magnesium Hydroxide into inactive Magnesium Oxalate [**Eq. (iv)**], consumes MgO, reduces the chances of formation of MOS and hence contributes to increase in setting periods by retarding in setting process.

Table 1: Effect of sodium oxalate ($Na_2C_2O_4$) on setting characteristics of MOS.

S.No.	Additive Concentration (%)	initial Setting Time (min)	Final Setting Time (min)
1.	0%	37	145
2.	5%	35	200
3.	10%	30	250
4.	15%	26	295
5.	20%	24	340

Note: Concentration of gauging solution = 25°Be; dry mix composition ratio = (1: 2); temperature = 30±2°C; quantity of dry mix = 200 g; and relative humidity = above 90%; volume of gauging solution= 55 mL

Table 2 represents the results of the Weathering Effect Investigations of the MOS cement blocks with different proportions of Sodium Oxalate (0% to 20%). The weight of Sodium Oxalate incorporated MOS cement blocks show decreasing trends with increasing curing period from 24 hours to 45 days. Oxalate ions have a tendency to inactive gross moisture absorbing constituents like Ca^{+2}, unreacted Mg^{+2}, hence decrease in weights is obvious. The loss in weights is also attributable to the loss of moisture from the MOS cement blocks with passage of time. Retarding setting process makes the entire process sluggish and hence a lot of moisture is left unreacted even after final setting in the matrix .This excess moisture evaporates with time as is witnessed by the decreasing weights of blocks.

Table 2: Effect of sodium oxalate ($Na_2C_2O_4$) on weathering characteristics of MOS.

S.No.	Additive Concentration (%)	Weight (g) of Blocks After			
		24 hours	7 days	30 days	45 days
1.	0%	260.213	258.198	260.543	250.876
2.	5%	261.395	258.465	255.274	253.278
3.	10%	246.245	240.315	239 115	238.315
4.	15%	255.145	240.134	234.675	242.108
5.	20%	258.175	254.145	250.345	244.345

Note: Concentration of gauging solution = 25°Be; volume of gauging solution = 55 mL; dry mix composition ratio = (1: 2); quantity of dry mix = 200 g; and relative humidity = above 90%.

Table 3 represents the effect of $Na_2C_2O_4$ on Moisture Ingress Characteristics of MOS. $Na_2C_2O_4$ reacts with Mg^{2+} of hydrated Magnesia or of gauging Magnesium Sulphate solution and form Magnesium Oxalate which is insoluble and crystalline in nature [**Eq. (iv)**].These insoluble phases from intercrossing systems with MOS and make the structure watertight, tough and less porous. Watertightness may also be improved by the inactivation of active lime and other harmful impurities which are responsible for moisture ingress.

Table 3: Effect of sodium oxalate ($Na_2C_2O_4$) on moisture ingress characteristics of MOS.

S.No.	Additive Concentration (%)	Trial Blocks in Boiling Water after					
		0-5 hours	5-10 hours	10-15 hours	15-20 hours	20-25 hours	25-30 hours
1.	0%	NE	NE	NE	NE	NE	NE
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

Note: Concentration of gauging solution = 25°Be; dry mix composition ratio = (1: 2); temperature = 30±2°C; quantity of dry mix = 200 g; relative humidity = above 90%; and NE = No effect.

Table 4 represents the results of Compressive Strength investigations of the MOS cement blocks with different proportions of Sodium Oxalate (0% to 20%). The maximum Compressive Strength of MOS cement blocks was observed with 5% Sodium Oxalate and thereafter decreased with increasing additive amount .Initial incorporation of the additive improves the Compressive Strength of the cement (about 5%) due to the inactivation of the active lime [**Eq. (i)**]. Decreasing trends in the strength data on further addition of the additive is noticed. The reason is that quantities of Magnesia, which is main component of MOS cement, decrease with increasing quantities of additive. This results in the decreasing chances of formation of main strength giving component i.e. Magnesium Oxysulphate [**Eq. (ix)**]. That is why decreasing trends of strength data are observed.

Table 4: Effect of sodium oxalate ($Na_2C_2O_4$) on compressive strength of MOS.

S.No.	Additive Concentration	Compressive Strength (kg/cm^2)
1.	0%	280
2.	5%	350
3.	10%	290
4.	15%	265
5.	20%	255

Note: Concentration of gauging solution = 25°Be; dry mix composition ratio = (1: 2); temperature = 30±2°C; quantity of dry mix = 565 g; and relative humidity = above 90%.

Table 5 represents the results of the Linear Changes investigation of the MOS cement beam with different proportion of Sodium Oxalate (0% to 20%). Oxalates formed by the initial incorporation of Sodium Oxalate increase the crystal lattice gaps in the matrix, so slight increase in the volume within the experimental limits are observed.

Table 5: Effect of sodium oxalate ($Na_2C_2O_4$) on linear changes of MOS.

S.No. y	Additive Concentration (%)	Length of Beams (mm)		Change in Length (mm)
		Initial	Final	

1.	0%	200.00	199.980	0.020
2.	5%	200.00	200.030	0.030
3.	10%	200.00	200.076	0.076
4.	15%	200.00	200.036	0.036
5.	20%	200.00	200.074	0.074

Note: Concentration of gauging solution = 25°Be; dry mix composition ratio = (1: 2); temperature = 30±2°C; quantity of dry mix = 200 g; and relative humidity = above 90%.

The above discussion can be interpreted on the basis of the following chemical changes:

$$CaO + H_2O \longrightarrow Ca(OH)_2 \quad \text{.................................} \quad (iv)$$

$$MgO + H_2O \longrightarrow Mg(OH)_2 \quad \text{.................................} \quad (v)$$

$$Ca(OH)_2 + ZnCO_3 \longrightarrow CaCO_3 + Zn(OH)_2 \quad \text{.....................} \quad (vi)$$

(Inactive)

$$Mg(OH)_2 + ZnCO_3 \longrightarrow MgCO_3 + Zn(OH)_2 \quad \text{...................} \quad (vii)$$

(Inactive)

$$MgSO_4 + Zn(OH)_2 \longrightarrow Mg(OH)_2 + ZnSO_4 \quad \text{....................} \quad (viii)$$

$$MO + H_3O/CO_3 \longrightarrow M(OH)_2/CO_2 \quad \text{.............................} \quad (ix)$$

$$xMg(OH)_2 + yMgCO_3 + zH_2O \longrightarrow xMg(OH)_2.yMgCO_3.zH_2O \quad \text{..........} \quad (viii)$$

Basic Magnesium Carbonate

(Solid phase non setting)

$$5Mg(OH)_2 + MgCO_3 + 8H_2O \longrightarrow 5Mg(OH)_2.MgCO_3.8H_2O \quad \text{...............} \quad (ix)$$

Magnesium Oxysulphate Cement

(Strength giving composition)

CONCLUSION

It was concluded that

1. Sodium Oxalate incorporated MOS blocks showed lower initial and higher

final setting Time as compared to additive free MOS cement blocks.

2. Improved Watertightness is observed by incorporation of additive.
3. Compressive Strength is improved by the addition of $Na_2C_2O_4$ up to 5% ratio.
4. Insignificant volume changes (slight increase) within the experimental limits are noticed on adding the additive in the matrix.

ACKNOWLEDGEMENT

The authors are thankful to Principal, Government R. R. College, Alwar (Rajasthan, India) and HOD, Department of Chemistry, Government R. R. College, Alwar (Rajasthan, India) for providing over all financial support and the necessary laboratory facilities to fulfill the present research work.

REFERENCES

Beaudoin, J. J., and Ramachandran, V. S. (**1975**). Strength development in magnesium oxychloride and other cements. *Cement and Concrete Research*, vol. 5(6), pp. 617-630.

Brady, G. S., Clauser, H. H., and Vaccari, J. A. (**2002**). Materials Hand Book: An Encyclopedia for Managers, Technical Professionals, Purchasing and Production Managers, Technicians, and Supervisors (15th edition). McGraw Hill, ISBN: 9780071360760.

Hu, Z., Guan, Y., Chang, J., Bi, W., and Zhang, T. (**2020**). Effect of carbonation on the water resistance of steel slag—Magnesium oxysulfate (MOS) cement blends. *Materials*, vol. 13, article no.: 5006.

IS 10132 - 1982 (**1982**). Method of test for materials for use in the preparation of magnesium oxychloride flooring compositions. Flooring and Plastering Sectional Committee, BDC 5, New Delhi (India).

Li, Q., Su, A., and Gao, X. (**2022**). Preparation of durable magnesium oxysulfate cement with the incorporation of mineral admixtures and sequestration of carbon dioxide. *Science of the Total Environment*, vol. 809, article no.: 152127.

.

Mathur, R. (**2009**). Effect on setting, strength, water tightness and linear changes of Magnesium Oxysulphate Cement on mixing Sodium Silicate as an additive. *Journal of Chemical and Pharmaceutical Sciences*, vol. 2(2), pp. 132-135.

Mathur, R., and Sharma, S. K. (**2003**). Magnesium Oxysulphate Cement: Change in properties of admixing Sodium bicarbonates as an additive. *Rasayan J. Chem.*, vol. 1(3), pp. 620-630.

Newman, E. S. (**1964**). Preparation and heat of formation of a magnesium oxysulphate cements. *Journal of Research of the National Bureau of Standards. Section A, Physics and Chemistry*, vol. 68A(6), pp. 645-650.

Saleh, H. M., and Rahman, R. O. A. (**2018**). Chapter-1: Properties and Applications of Cement-based Materials. In: Cement based Materials (Ed.: H. Saleh), IntechOpen.

Singh, D., Wagh, A. S., Cunnane, T. C., and Mayberry, J. L. (**1997**). Chemically bonded phosphate ceramics for low-level mixed-waste stabilization. *Journal of Environmental Science and Health. Part A: Environmental Science and Engineering and Toxicology*, vol. 32(2), pp. 527-541.

Sorel, S. T. (**1867**). Sur un nouveau ciment magnesien. *C. R. Hebd. Seances Acad. Sci., Paris*, vol. 65, pp. 102-104.

Walling, S. A., and Provis, J. L. (**2016**). Magnesia-Based Cements: A Journey of 150 Years, and Cements for the Future?. *Chemical Reviews*, vol. 116, pp. 4170-4204.

Wilson, A. Q., and Nicholson, J. W. (**2009**). Acid base cement: their biomedical and industrial application. Cambridge University Press, pp. 283-302.

Wu, C., Yu, H., Zhang, H., Dong, J., Wen, J. and Tan, Y. (**2015**). Effects of phosphoric acid and phosphates on magnesium oxysulfate cement. *Materials and Structures*, vol. 48(4), pp. 907-917.