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The Effect of $MgCl_2$ Solution Density on the Phases in Magnesia Cement Paste

KEYWORDS: Density, Setting time, Compressive strength, Durability, X-ray diffraction

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ABSTRACT *The effects of MgCl2 solution densities on phases and cementing properties of magnesia cement have been investigated. The results show that the increasing of MgCl2 density delayed the setting time of magnesia cement paste. The compressive strength, moisture resisting efficiency, durability and bonding characteristics are improved by increasing density of MgCl2 solution. Two main bonding crystalline phases; phase three (3Mg(OH)2.MgCl2.8H2O) and phase five (5Mg(OH)2.MgCl2.8H2O) are detected in X-ray diffraction patterns of magnesia cement. X-ray diffraction examination result also showed that formation of phase three becomes prominent on increasing density of MgCl2 solution.*

1. Introduction:

Magnesia cement has been attracted attention for many years due to their properties and potential applications. One type of magnesia cement is magnesium oxychloride cement (MOC). It is also known as Sorel cement [1]. It is a type of non-hydraulic cement formed by mixing powdered magnesium oxide (MgO) with a concentrated solution of magnesium chloride ($MgCl_2.6H_2O$).

The MOC cement has many superior properties compared to ordinary Portland cement. It has high fire resistance, low thermal conductivity and good resistance to abrasion and is unaffected by oil, grease and paints [2-6]. It is also distinguished by a high bonding, quick setting time and does not require humid curing [7]. This cement draws much research interest due to energy saving and environmental protection consideration. Production of lightly burnt MgO used in magnesium oxychloride cement requires much lower calcination temperatures compared to that for Portland cement. This reduces vast amount of energy consumption [8,9].

The major commercial and industrial applications of MOC cement are industrial flooring, fire protection, grinding wheel and light weight wall panels and also used for rendering wall insulation panels, interior plaster and decorative panels [2,10-11].

The setting and hardening of the MOC cement takes place in a through-solution reaction. [12]. Four main reaction phases in the ternary system are found; $2Mg(OH)_2.MgCl_2.4H_2O$ (phase 2), $3Mg(OH)_2.MgCl_2.8H_2O$ (phase 3), $5Mg(OH)_2.MgCl_2.8H_2O$ (phase 5) and $9Mg(OH)_2.MgCl_2.5H_2O$ (phase 9) out of which $3Mg(OH)_2.MgCl_2.8H_2O$ (phase 3) and $5Mg(OH)_2.MgCl_2.8H_2O$ (phase 5) is more prominent [13-16]. These phases exist as reinforced components in the ternary system at ambient temperature.

Magnesium oxychloride cement has many good engineering and mechanical properties, but it has a drawback that it becomes eroded when exposed to water for a long period of time thereby limiting its outdoor application. Consequently, many investigations on the water resistance of MOC cement have been carried out over the years [17-20].

This work aims to study the effects of $MgCl_2$ solution densities on phases and cementing properties (standard consistency, setting times, compressive strength, moisture resisting efficiency, durability and bonding characteristics) of hardened nagnesium oxychloride cement paste.

2. Materials and Methods

Materials: The raw materials used in the study were calcined magnesite (magnesia), magnesium chloride and dolomite powder.

Calcined magnesite: Commercial grade magnesia used in this study is of Salem origin having the following characteristics displayed in Table 1:

Table: 1 Chemical composition of calcined magnesite (in mass percentage)

MgO	SiO_2	CaO	Fe_2O_3	Al_2O_3	L O I
71.80%	10.18%	6.72%	0.19%	0.75%	9.82%

Magnesium chloride ($MgCl_2$.6H20): Magnesium chloride ($MgCl_2$.6$H_2$0) used in the study is IS grade 3 of IS:254-1973 with following characteristics: (i) colorless, crystalline, hygroscopic crystals (ii) highly soluble in water (iii) magnesium chloride minimum 94% (iv) magnesium sulphate, calcium sulphate and alkali chloride content < 5%.

Inert filler (dolomite): Dolomite dust was used as inert filler with following grading: (i) 100 % passing through 125 micron IS Sieve (ii) 50% retained on 250 micron IS Sieve. Its chemical composition is listed in Table 2. $CaCO_3$ - 55.50% ; $MgCO_3$ - 42.21%

Table: 2 Chemical composition of dolomite (in mass percentage)

SiO_2	CaO	MgO	Fe_2O_3	Al_2O_3	L O I
0.75 %	31.08 %	20.10 %	0.85 %	0.22 %	46.50%

Preparation of magnesium chloride solution: $MgCl_2$ solution was prepared in water. Flakes of magnesium chloride were transferred into plastic containers to which potable water was added to prepare concentrated solution. This solution was allowed to stand overnight so that insoluble impurities

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settle at the bottom. The supernatant concentrated solution was taken out in other plastic containers and well stirred after each dilution before determining the specific gravity. Density of the solution is expressed in terms of specific gravity on Baume scale (°Be).

Preparation of dry-mix composition: Dry-mixes were prepared by mixing equal amount of lightly calcined magnesite (magnesia) and dolomite (inert filler) in the ratio of 1:1 by their weight.

3. Experimental

The effect of $MgCl_2$ solution density on cementing properties and phases have been studied for 1:1 dry-mix composition of magnesia cement at 35°C of $MgCl_2$ solution. Following investigations have been carried out during the experimental works.

3.1 Determination of Standard consistency and setting times

Wet-mixes were prepared by $MgCl_2$ 1:1 dry-mix composition with different densities (20°Be, 24°Be, 28°Be & 32°Be) of $MgCl_2$ solution at 35°C temperature. The standard consistency, initial setting and final setting times were determined as per IS 10132-1982 using Vicat apparatus [21-23] at different densities of magnesium chloride solution. The observed results for standard consistency and setting time are summarized in Table 3.

Table.3 Effect of $MgCl_2$ solution density on standard consistency and setting time of magnesia cement

Temperature of $MgCl_2$ solution - 35°C | **1:1*(Dry mix)** | Humidity- 85 ± 5 %

S.No.	Density of $MgCl_2$ solution	Volume of MgCl2 solution (ml)	Setting time in Minutes Ist	Setting time in Minutes Fst
1.	20°Be	111	31	105
2.	24°Be	111.5	39	119
3.	28°Be	112	53	136
4.	32°Be	113	82	163
5.	35°Be	115	100	192

*One part by weight of magnesia and one part by weight of dolomite

3.2 Determination of soundness (Lechateier's test)

Lechatelier's test was conducted to find out the effect of density of $MgCl_2$ solution on soundness of the experimental product. Less is the expansion, great is the soundness. Tests were conducted as per standard procedure [24, 27]. Observed findings are summarized in Table 4.

Table.4 Effect of $MgCl_2$ solution density on soundness in the trial blocks of magnesia cement (Le-Chaterlier's test)

Temperature of MgCl2 solution - 35°C | 1:1*(Dry mix) | Humidity-85 ± 5%

S.No.	Observations	Concentration of $MgCl_2$ solution				
		20°Be	24°Be	28°Be	32°Be	35°Be
1.	Weight of cement composition (g)	38	38	38	38	38
	i. Magnesia	19	19	19	19	19
	ii.Dolomite	19	19	19	19	19
2.	Amount of $MgCl_2$ solution (in ml)	16	15.8	15	16	17
3.	Distance between two Pointers before starting (in m)	10	7	10	10	14
4.	Distance between two Pointers after 7 days before boiling(in mm)	12	12	13	14	21
5.	Distance between two Pointers after boiling (in mm)	14.6	14.4	15	15.1	21.5
6.	Expansion of cement (in mm)	**2.6**	**2.4**	**2.0**	**1.1**	**0.5**

*One part by weight of magnesia and one part by weight of dolomite

3.3 Determination of compressive strength

The effect of densities of $MgCl_2$ solution on compressive strength of the product was studied with the help of standard 70·6 mm^3 cubes, prepared for the I.S. consistency paste at various densities (20°Be, 24°Be, 28°Be & 32°Be) of $MgCl_2$ solution at 35°C. These cubes were allowed to be cured under identical conditions for one month and then subjected to compressions just sufficient for their rupture [21, 28-29]. Experimental findings are recorded in Table 5.

Table.5 Effect of $MgCl_2$ solution density on compressive strength of magnesia cement

Temperature of $MgCl_2$ solution - 35°C | **1:1*(Dry mix)** | Humidity- 85 ± 5 %

S.No.	Density of $MgCl_2$ solution	Compressive strength (In MPa)
1.	20°Be	52.156
2.	24°Be	54.162
3.	28°Be	58.172
4.	32°Be	60.180
5.	35°Be	50.150

*One part by weight of magnesia and one part by weight of dolomite

3.4 XRD Analysis

X- ray powder diffraction patterns provide phase, chemical and crystal structure information data that may afford greater understanding of cement property/performance relationships [30]. X-ray diffraction (XRD) technique was applied to identify the crystalline phases present in the magnesia cement pastes [31, 32]. The powdered method of X-ray diffraction was adopted in the present study. For this, Panalytical X'pert Powder with an X-ray source Cu-Kα radiation (λ = 1.54443) was used. The scan step size (2θ) was 0.02°, the collection time was 1S and the reflection angle (2θ) was 15° to 90°. The X-ray tube voltage and current were fixed at 45Kv and 30 mA respectively. Setting time blocks samples of each density of $MgCl_2$ solution were analyzed. First, setting time blocks were ruptured and then crushed into fine powder for XRD study. The obtained results are shown in the Figure 1 to 4.

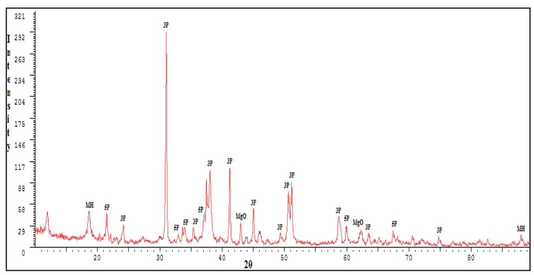

Fig.1 XRD pattern of magnesia cement prepared with 1:1dry-mix composition gauged by 20°Be density of $MgCl_2$ solution (35°C)

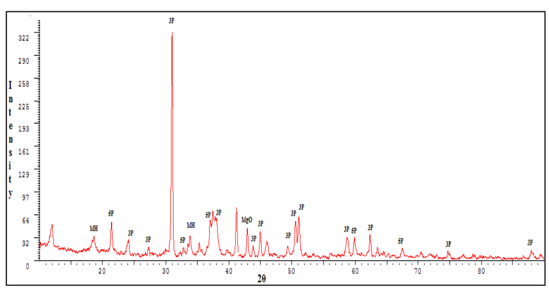

Fig.2 XRD pattern of magnesia cement prepared with 1:1dry-mix composition gauged by 24°Be density of $MgCl_2$ solution (35°C)

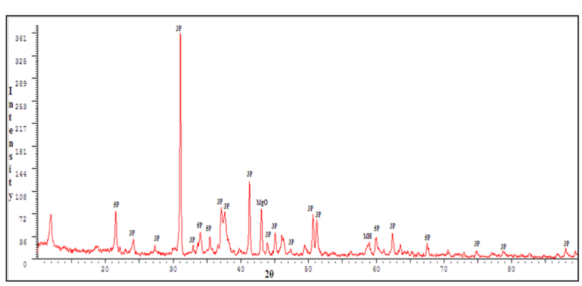

Fig.3 XRD pattern of magnesia cement prepared with 1:1dry-mix composition gauged by 28°Be density of $MgCl_2$ solution (35°C)

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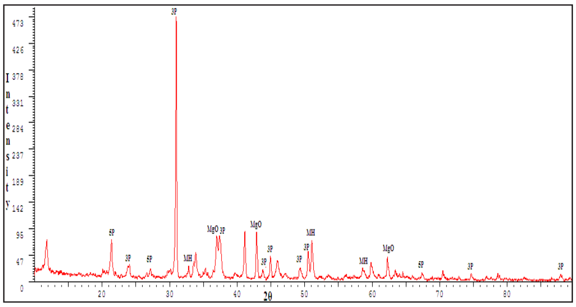

Fig.4 XRD pattern of magnesia cement prepared with 1:1dry-mix composition gauged by 32°Be density of $MgCl_2$ solution (35°C)

4. Result

Table 3 shows the amount of $MgCl_2$ solution of each density, required for Indian Standard (IS) consistency to gauge the dry-mix composition and setting times of magnesia cement paste. The amount of $MgCl_2$ solution used for IS consistency slightly increases as the density of solution increases from 20°Be to 32°Be. From the table, it is also clear that that initial as well as final setting time increases with increasing density of $MgCl_2$ solution. It is revealed, as the density of $MgCl_2$ increases, the mixes tend to become highly viscous and their initial setting time is found to increase. This is due to formation of strength giving 3 and 5 form phases which require more time to set. Similar trends are also observed in final setting.

$$MgO + MgCl_2 \cdot 6H_2O + Mg/CaCO_3 \text{ (Inert filler)} \rightarrow 5Mg(OH)_2 \cdot MgCl_2 \cdot 8H_2O \,/\, 3Mg(OH)_2 \cdot MgCl_2 \cdot 8H_2O + \text{Inert filler (Thermal shock absorber)} + \text{Heat (Exothermic)}$$

Table 4 shows the effect of density of $MgCl_2$ solution on soundness of 1:1 dry-mix of magnesia cement. The result reveals that soundness increases with increasing density of $MgCl_2$ solution. The expansion is quite less for high density (32°Be) of $MgCl_2$ solution. This may be attributed to fact that with concentrated $MgCl_2$ solution, magnesium chloride is available in more amounts for reaction with magnesia and its active lime content in the matrix. Consequently uncombined magnesia and its active lime are left in very small amount. Active lime and magnesia are more reactive than magnesia cement and react exothermically with moisture. This reaction is accompanied by expansion and favors water vapor transmission into the blocks. Hence, the increased soundness of the blocks is because of decrease amount of free magnesia in the blocks.

The observed result of compressive strength of the standard blocks of wet-mixes obtained by gauging 1:1 dry-mix with varying densities of $MgCl_2$ solution, are recorded in the table 5 Increasing trends in compressive strength of the product with increasing density of $MgCl_2$ solution from 20°Be to 32°Be of magnesia cement in the matrix are noticed. This is explicable by fact that comparatively increased availability of $MgCl_2$ per unit weight of magnesia in the wet-mixes and formation of perfect three dimensional network of interlacing crystals of strength giving forms (3 and 5 form phases) are increased relatively in the blocks. This contributes to increase in mechanical strength.

Figures 1 to 4 illustrate the XRD diffractogram for investigation of powdered MOC samples prepared with different densities of $MgCl_2$ solution having 35°C. The XRD data obtained in this study are in accord with the result reported in literature. The symbols on figure indicate the position and the peak intensities of the powdered diffractions are according with standard from ICDD database. Two main bonding crystalline phases; phase three and phase five are detected in XRD patterns of MOC. The MOC phase five ($5Mg(OH)_2 \cdot MgCl_2 \cdot 8H_2O$) indicated as 5P, phase three ($3Mg(OH)_2 \cdot MgCl_2 \cdot 8H_2O$) indicated as 3P and $Mg(OH)_2$ as MH in all XRD patterns. In each figure XRD analysis indicate a sharp peak at $2\theta \sim 31$ which is identified for phase three of MOC (PDF#76-1401). Some unidentified peaks may be presence of $CaCO_3$ and $MgCO_3$ in the matrix. From the figure1, it can be revealed that $Mg(OH)_2$ and phase five (5P) are equally prominent in MOC paste of 20°Be density of $MgCl_2$ solution. Phase three (3P) is next prominent phase with small peaks. Small peaks of MgO at $2\theta \sim 59.21$ (PDF# 30-0794) in XRD pattern of MOC paste is referred to as residual MgO phase in cement paste.

XRD pattern of MOC paste of 24°Be density of $MgCl_2$ solution (35°C) is shown in figure 2. It can be seen that phase three (3P) becomes prominent like as phase five (5P) while $Mg(OH)_2$ becomes minor phase. From Figure 3 and 4, it is cleared from XRD patterns that phase three (3P) is completely dominated over phase five (5P) at higher densities of $MgCl_2$ solution above 24°Be. $Mg(OH)_2$ is reported in traces with 2-3 peaks in XRD patterns.

Setting time result of different densities as observed in previous section can be explained with help of X-ray results. At lower densities (20°Be and 24°Be) the formation of phase five (5P) is promoted kinetically as per law of mass action. At the same time sufficient water is also available in the mix for the hydration of magnesia. Combined effect of both these factors causes an early setting of the wet-mix at these densities. At higher densities more $MgCl_2$ is available for reaction with magnesia. Also the decreased amount of water in the above situation reduces the chance of hydration of magnesia and hence its rate of hydration falls. Under these circumstances the setting is mainly due to the formation of 3 phase and 5 phase, having very slow rate of formation. Combined effects of all factors delayed the setting reaction. Thus, setting time is increased considerably at higher densities of $MgCl_2$. Presence of both crystalline phases in cement also fortified the result of compressive strength.

5. Conclusions: The following conclusion can be drawn from this study;

1. The cementing characteristics (strength, moisture resisting efficiency, durability and bonding characteristics) of magnesia cement improve with increasing density of gauging solution.
2. Formation of two crystalline phases (3 phase and 5 phase) increases with increase in concentration of gauging solution till saturation (XRD analysis).
3. Phase 3 and phase 5 in magnesia cement is responsible for high mechanical strength at higher density.

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