

Investigations on the mechanical and hydration properties of sorel cement by changing the concentration of magnesium chloride

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The effect of concentration changes of magnesium chloride on the mechanical and hydration properties of magnesium oxychloride (Sorel) cement was investigated. The results demonstrated that a concentration change of $MgCl_2$ can strongly affect the properties of the Sorel cement. The amount of magnesium chloride was varied from 0.5 to 1.9 moles and the cold crushing strength (CCS) of each sample was measured after 2, 4, 10, and 20 days. The bulk density and porosity were also measured. X-Ray diffraction (XRD) of the matrix phases was investigated. The morphology and microstructure of the phases were characterized using a scanning electron microscope (SEM). The micrographs showed a vast formation of needle shaped crystallites of $5MgO \cdot MgCl_2 \cdot 8H_2O$ (phase 5). The behavior arising from evaporation of water from the surface of the cement and the nature of hydration products were investigated. It was shown that a molar ratio of $MgO/H_2O = 13 : 12$ with 1.5 moles of $MgCl_2 \cdot 6H_2O$ can produce a promising matrix composition for a proper design.

Key words: Magnesium oxychloride cement, Sorel, Magnesia, Magnesium chloride, Hydration process, Needle shaped crystal.

Introduction

Magnesium oxychloride (MOC), known as Sorel cement, is one type of magnesia cement. This type of cement has superior performance such as a high strength, proper adhesion, rapid setting, bonding ability to the various amounts of fillers, high fire resistance, low thermal conductivity and good resistance to abrasion [1, 2]. It has a low coefficient of thermal expansion and insignificant volume change during the setting operation. Magnesium oxychloride cement has a particular application in the production of abrasive tools that are used for grinding [3]. The cement is a complex reaction product of calcined magnesium oxide, magnesium chloride, and water, which is admixed in specific proportions and allowed to be hardened [4]. The four crystalline phases in Sorel cement are: $2Mg(OH)_2 \cdot MgCl_2 \cdot 4H_2O$ (phase 2), $3Mg(OH)_2 \cdot MgCl_2 \cdot 8H_2O$ (phase 3), $5Mg(OH)_2 \cdot MgCl_2 \cdot 8H_2O$ (phase 5), and $9Mg(OH)_2 \cdot MgCl_2 \cdot 5H_2O$ (phase 9). Phases 3 and 5 exist at room temperature, whereas phases 2 and 9 are stable only at temperatures above $100^\circ C$. Both of the 5 and 3 phases are crystallized as needle shapes [5-8]. The three steps of phase formation in MOC cement may be summarized as: 1) neutralizing 2) hydrolyzing and 3) crystallizing [4]. At first, MgO powder is neutralized by free H^+ ions in the concentrated solution of $MgCl_2$ and consequently dissolved in the water [4]. This phenomenon increases the concentration of Mg^{2+} and OH^- ions in the solution. In the second

step, the hydrolyzing-bridging reaction of Mg^{2+} ions is promoted by the dissolution of MgO to produce some polynuclear complexes $[Mg_x-(OH)_y(H_2O)_z]^{2x-y}$. The two mentioned steps promote each other and yield a number of polynuclear complexes [4]. Finally, the polynuclear complexes, Cl^- ions and H_2O , are accumulated, and then condensed to form a continuous amorphous phase. Then, the hydrogel is converted to the crystalline phases [4].

Researchers have shown that the six waters of hydration associated with magnesium chloride are not enough for the chemical bond, and the amount of magnesium oxide should be more than 5 moles in cementitious compositions to ensure the formation of the crystallized hydrated phase 5. The magnesium chloride concentrations are one of the important factors for the final strength of the cement [9-12]. Li [10] previously showed that, for MOC cement having phase 5 crystals, the molar ratios of $H_2O/MgCl_2 = 12-18$ and $MgO/MgCl_2 = 11-17$ are to be the most proper ranges for design purposes. Li [10] also concluded among the different molar ratios of MgO and H_2O with 1 mole of $MgCl_2$, the molar ratio of $MgO/H_2O = 13 : 12$ has the highest strength [10].

The objective of the present paper is to set the molar ratio of MgO/H_2O to $13 : 12$ and investigate the effect of different concentrations of magnesium chloride on the strength and viscous properties of the Sorel cement. The compressive strengths of the different mixtures after air curing for 2, 4, 10, and 20 days were compared with each other and the least square method was used for the analysis of the variance of the slope of each curve. The hydration process of the different mixtures and different microstructure of the composition

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of the cement with the various amounts of magnesium chloride were also studied.

Materials and Experimental

Magnesium oxide powder (MgO) used in this study was calcined magnesite powder with an average particle size of about $37\ \mu\text{m}$, and a purity of 96%, from the Iranian Magnesite Company. The magnesium chloride was the hygroscopic hexahydrate crystal, $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, with a purity of 97% from India.

As shown in Table 1, 13 moles of magnesium oxide, 12 moles of water and a wide range of concentration of magnesium chloride were used. With respect to the experimental conditions, the maximum solubility of magnesium chloride in cold water is 1.9 moles.

Magnesium chloride crystals were first dissolved in water and mixed for about 1 minute. To the solution was then added magnesium oxide powder and the reaction mixture was stirred continuously for a few minutes to produce Sorel cement.

The slurry of the cement was cast into a cubic mould ($50 \times 50 \times 50\ \text{mm}^3$) and vibrated slightly to release the air bubbles from the cement. The samples were cured at room temperature ($25 \pm 3\ ^\circ\text{C}$) for different periods of time.

The bulk density and apparent porosity of 20-days samples (A3 to A8) were measured according to Archimedes equations by the standard ASTM C0020-00R05.

The compressive strength (CCS) of the samples was measured after 2, 4, 10, and 20 days according to ASTM C0133-97R03, and the crushed parts of the samples were powdered for X-ray diffraction measurements (Philips X130 series, using $\text{Cu-K}\alpha$ radiation) to identify the crystalline and strengthening phases in each mixture. The X-ray powder diffraction data were collected for each sample from 10° to 100° (2θ) with a step size of 0.05 and 1 s time per step. The morphology and microstructure of the reaction products were characterized by SEM (Phillips XL 30: Eindhoven, The Netherlands) in the secondary electron (SE) mode on the fracture surfaces. Three specimens have been used for the determination of each compressive strength and other test values.

Table 1. Composition of the different MOC pastes by changing the mole ratio of magnesium chloride

Sample number	Moles of Magnesium chloride of sample
A1	0.5
A2	0.7
A3	0.9
A4	1.1
A5	1.3
A6	1.5
A7	1.7
A8	1.9

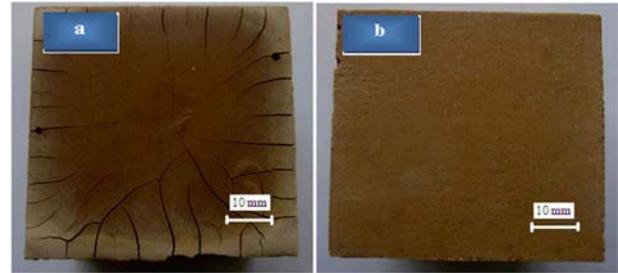


Fig. 1. Images of the sample A6 after removing from the moulds a) appearance of the cracks in sample without using the paraffin film b) a complete elimination of the cracks by using a layer of paraffin film.

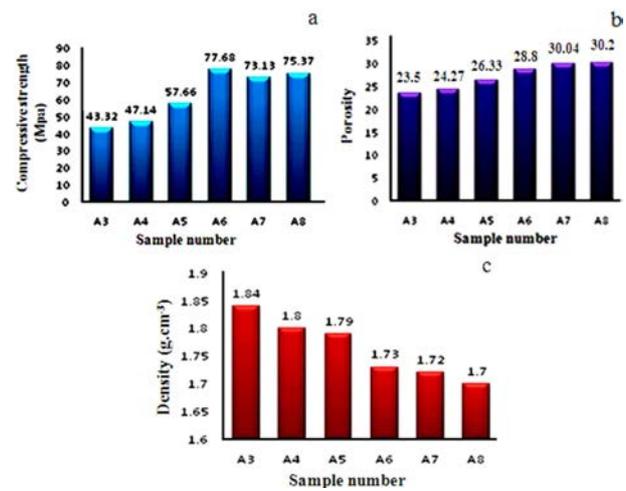


Fig. 2. Compressive strength, bulk density and porosity of different mixtures.

Results

The problem of crack formation

During air curing of the cement in the atmosphere, inhomogeneous and fast evaporation of water from the upper face of the cubic cement sample, too many cracks were created on the surface of the cement, because only one side of the cement is exposed to the air in a cubic mould. The appearance of cracks decreases the compressive strength of the cement. To control the evaporation of water and prevent crack formation on the surface of the cement, the upper face of each cubic sample was covered by a layer of paraffin film. Fig. 1 shows the surface of the sample A6, before and after using a layer of paraffin film. As can be clearly seen, the problem of crack formation is entirely eliminated after using the paraffin film.

Effect of magnesium chloride concentration on the compressive strength

In order to form the compact and needle shaped structure, an optimum formation of the needle shaped crystals of phase 5 in the Sorel cement is fundamental. In fact, these crystals are responsible for the high compressive strength. The mechanical locking and the intergrowth of the needle shaped crystals of phase 5 can

be the reason of the strength development of Sorel cement.

The presence of chloride ions affects the dissolution process of Mg^{2+} in the mixture and finally the formation of the hydrated phases. Therefore, chloride ions are very important factors in the formation of the phase 5 and final compressive strength. Fig. (2a) shows the compressive strength of the cements by changing the concentration of magnesium chloride.

As shown in Fig. (2a), A6 composition with 1.5 moles of magnesium chloride has the highest CCS after air curing for 20 days. It is obvious that in samples A3 to A6, increasing the chloride ion concentration provides the proper reaction of MgO with $MgCl_2 \cdot 6H_2O$. The values of strength, as well as the presence of the crystalline phase 5 are comparable in sample A6, A7, and A8. In the compositions A7 and A8, it is more probable that by increasing the phase 5 and hardness in the sample, microcracks would initiate in the matrix and the CCS would drop to lower values. Beside this, due to the high concentration of magnesium chloride in the solution (close to the upper saturation limit of salt in the water), the excess amount of magnesium chloride would deposit through the mould and some white precipitates would form on the surfaces of the sample. These precipitates lead to a decrease in the strength of the cement due to the inhomogeneous composition of the cements. Additionally, these white precipitates increase the water absorption and decrease the strength. Both samples, A7 and A8, are not desirable. Therefore, there is an optimum amount of the magnesium chloride in the system, and A6 composition has the proper rheological and mechanical properties among the other compositions.

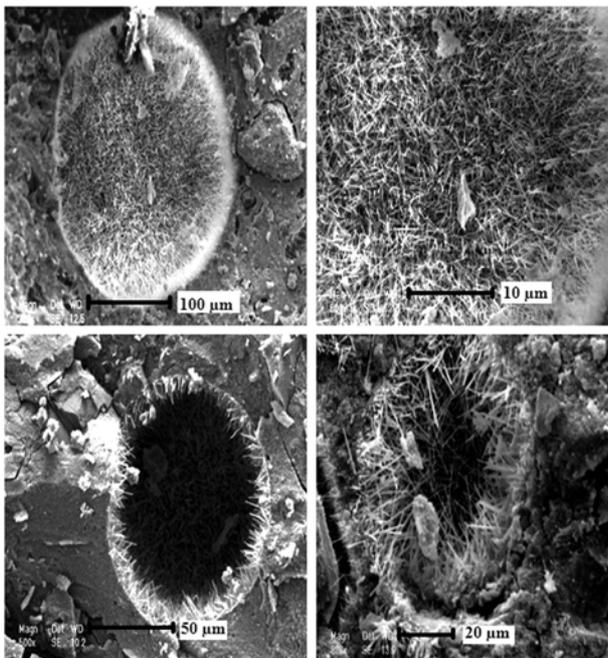


Fig. 3. The growth of needle shaped crystals of phase 5 from the porosities in sample A6.

Fig. 2 (a, b and c) shows the increase of CCS from A3 to A8, associated with the increase of porosity and decrease of density. It is well known that usually porosity (P) and strength (S) are related as:

$$S = s_0 \exp (-bP) \tag{1}$$

In which b and s_0 are constants for a given system. This means that CCS must decrease with an increase of porosity. It was concluded that this controversy is due to the formation of phase 5 in sample with an increase of porosity. In fact, the porosities from evaporation of excess water provide internal space area of pores with high surface energy which are suitable for the nucleation of phase 5 and also provide space area for the growth of needle shaped crystals of phase 5, as observed in Fig. 3.

Compressive strength development of the samples after different air curing

In order to investigate the complete cement reaction and formation of the hydrated phases, different air curing times for the samples were studied and shown as strength changes by time. Fig. 4 shows the strength changes of the cements after different air curing times for 2, 4, 10, and 20 days.

The least squares method can be applied to the values that satisfy the linear equation as closely as possible. In this way, choosing the highest slope of the diagram and

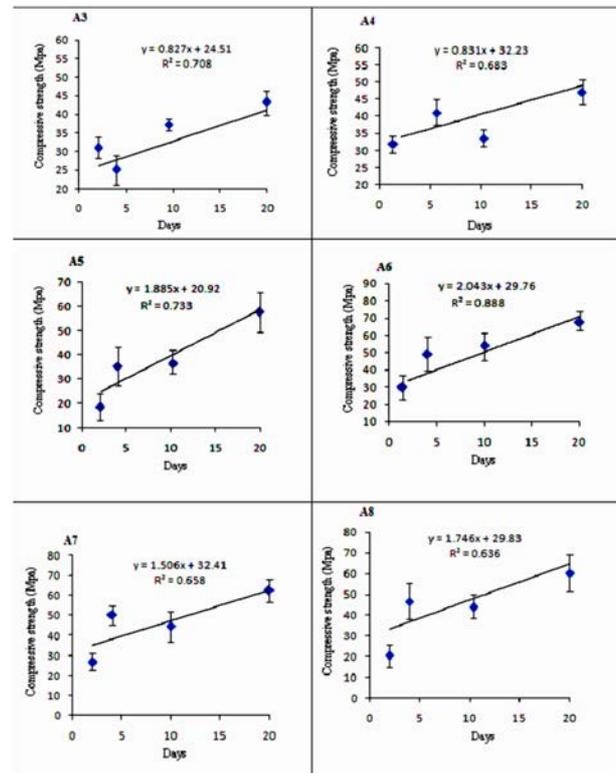


Fig. 4. Compressive strength of different mixtures after air curing for 2, 4, 10, and 20 days.

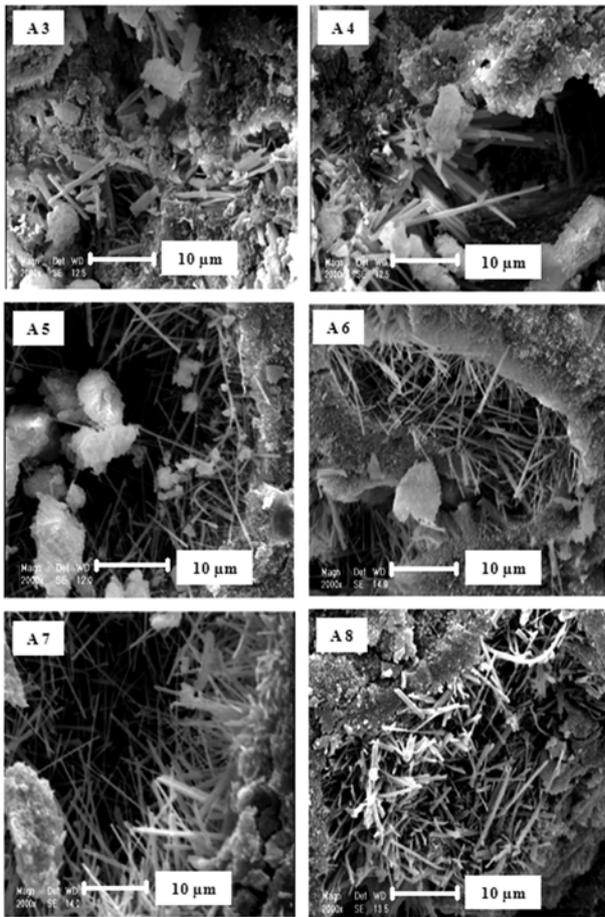


Fig. 5. Microstructure of different phases in A3 to A8 samples (from top to bottom).

the more compatibility of the data to the suggested equation will be practical. The slopes of the curves show the variation of the strength with time, as shown in Fig. 4, A6 composition has the highest slope compared with the other cements, and the compatibility between the A6 data (R^2) is also better than the other samples.

Microstructure of crystal phases in the different mixtures

Microstructural observations provide important information about the crystal phases of the cement. Changing the concentration of magnesium chloride causes different reaction phases. As mentioned before, the presence of the needle shaped crystals of phase 5 develops the compressive strength in cement samples.

Fig. 5 shows the morphology of the fracture surfaces of the mixtures A3, A4, A5, A6, A7 and A8. The formation of the needle shaped crystals in samples A5 to A8 is obvious and it can be seen that by increasing the magnesium chloride concentration, the amount of needle shaped phases increases and creates more dense structures. In sample A8, these crystals are large in size, and it can be one of the reasons for decreasing of the strength of the A8 mixture.

The crystal structure of the mixtures A3 and A4 are

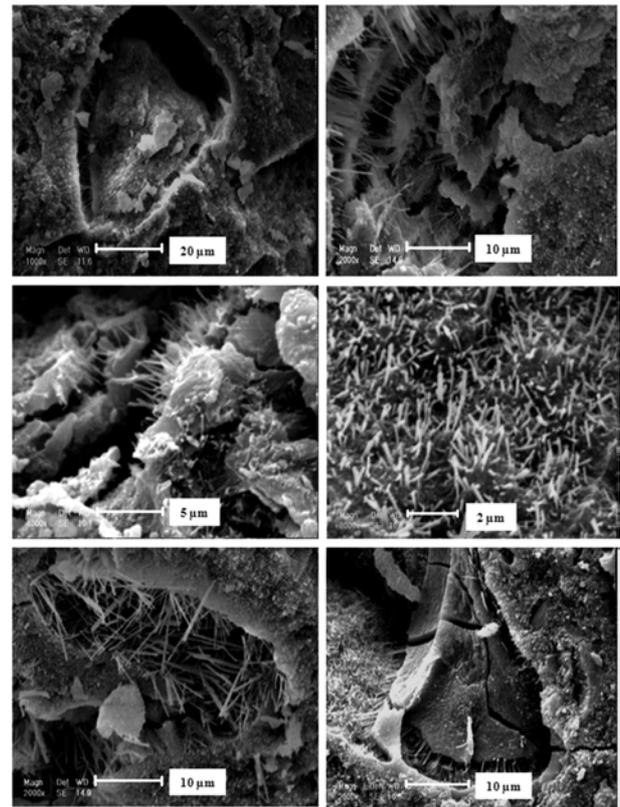


Fig. 6. Development of phase 5 in sample A6.

different. Because of the existence of plate shaped crystals in these samples, it is probable that, these phases are $Mg(OH)_2$. This is due to the higher concentration of MgO with respect to magnesium chloride in these samples and the possible reaction of magnesia with water to form $Mg(OH)_2$. Development of needle shaped crystal of phase 5 in all area of cement A6 is shown in Fig. 6.

Phase identification

Changing the concentration of magnesium chloride and reaction phases were investigated by X-ray diffraction (XRD) analysis. Fig. 7 shows the X-ray diffractograms of the mixtures A3, A4, A5, A6, A7 and A8.

$Mg(OH)_2$ is the major reaction product of MgO with H_2O , where there is not enough magnesium chloride in the system, excess MgO will react with H_2O and produce $Mg(OH)_2$. The formation of $Mg(OH)_2$ is obvious in the X-ray diffractograms of sample A3 and A4.

By increasing the amount of magnesium chloride in system, it can be seen that the $Mg(OH)_2$ phase disappears. One of the major reasons for a decrease of the strength of A3 and A4 is the formation of $Mg(OH)_2$, because this phase is not a proper phase for cement bonding.

In samples A6 to A8, the amount of the MgO phase decreases and this is due to the reaction of MgO and $MgCl_2$ in the system. Dominant phases in cement A6 are phase 5 and MgO . The existence of the MgO phase

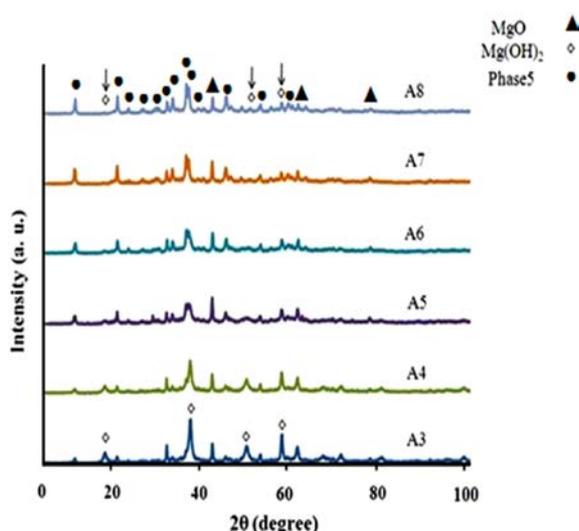


Fig. 7. The X-ray diffraction pattern of the phases (from bottom to top A3 to A8).

shows that excess MgO is treated as a filler and has the potential to produce more phase 5 if more magnesium chloride would be available. So it is believed that by increasing the concentration of magnesium chloride, the amount of phase 5 increases and the amount of Mg(OH)₂ decreases in samples A6, A7 and A8 and causes strength development.

Conclusions

1) Because of the different reaction phases, changing the concentration of magnesium chloride influences the

mechanical properties of Sorel cement. Increasing the concentration of the magnesium chloride develops compressive strength.

2) By using 1.5 moles of magnesium chloride, 13 moles of magnesium oxide and 12 moles of water, the strength of the cement increased to 77.86 MPa after 20 days of curing at room temperature. The strength development of the samples after different curing times shows the highest slope and best result for the A6 composition by using the least squares method.

3) Homogeneous evaporation of water in the system can be performed by covering the mould by a layer of paraffin film.

4) SEM photographs show that phase 5 is a needle shaped crystallize phase that reinforces the matrix and develops strength.

References

1. Ji. Yunsong, J. Mater. Let. 56 (2002) 353-363.
2. A. Misra, J. Mater. Sci. 30 (2007) 239-246.
3. G. Li, Y. Yu, Cem. Concr. Res. 33 (2003) 1663-1668.
4. D. Deng, C. Zhang, Cem. Concr. Res. 29 (1999) 1365-1371.
5. H. Bilinski, B. Matkovic, J. Am. Ceram. Soc. 67 (1984) 266-269.
6. I. Kanesaka, J. Raman. Spectrosc. 32 (2001) 361-367.
7. W. Cole, T. Demediuk, Aust. J. Chem. 8 (1955) 234-251.
8. C. Chau, J. Mater. Struc. 41 (2008) 853-862.
9. B. Tooper, L. Cartz, Nat. Phys. Sci. 211 (1966) 64-66.
10. Z. Li, Cem. Concr. Res. 37 (2007) 866-870.
11. M. Chandrawat, R. Yadav, J. Mater. Sci. 23 (2000) 69-72.
12. J. Beaudoin, Cem. Concr. Res. 5 (1975) 617-630.