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Effect of magnesium chloride concentrations on the properties of magnesium oxychloride cement for nano SiC composite purposes

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Abstract

Different magnesium oxychloride cements (MOCs) were studied with a fixed 13 moles of magnesite and 12 moles of water with different moles of magnesium chloride, $MgCl_2{\cdot}6H_2O$ from 0.5 to 1.9. Cold crushing strength, initial and final setting times, and dissolution in water were all increased with an increase in magnesium chloride. 1.5 moles of magnesium chloride showed the highest compressive strength. X-ray diffraction analysis (XRD) studies showed a gradual decrease in hydrated magnesia, $Mg(OH)_2$ and a gradual increase in phase 5, $5Mg(OH)_2{\cdot}MgCl_2{\cdot}6H_2O$. Scanning electron microscopy (SEM) studies indicated that needle shaped crystals of phase 5 are responsible for the reinforcement of the matrix of these Sorel cements. The highest strength sample was used to develop a nano composite with nano particles of SiC. This composite does not require melting or firing for sintering, and there is no risk of grain growth. High content of needle shaped reinforcing crystals of phase 5 in the matrix with an increase in magnesium chloride, together with nano sizes aggregate particles of SiC provided a promising nano composite.

Keywords: B. Nano composite; C. Strength; Magnesium oxychloride cement; Needle shaped crystal

1. Introduction

Magnesium oxychloride (MOC), known as Sorel Cement, was discovered in 1867 [1]. Due to having high strength and abrasion resistance over other cements, Sorel cement has been used as a binding agent for many years [2]. The superior performances of the MOC cement are: high strength, proper adhesion, rapid setting, bonding ability to various amounts of fillers and aggregates such as SiC and SiO_2, high fire resistance, low thermal conductivity and good resistance to abrasion [3]. The major commercial applications of Sorel cement are grinding stone, industrial flooring and fire protection. Sorel cement is the product of complex reactions of magnesium oxide, magnesium chloride and water with specific molar ratios. 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)

$9Mg(OH)_2{\cdot}MgCl_2{\cdot}5H_2O$(Phase 9)

Phases 3 and 5 exist at room temperature, and phases 2 and 9 are stable only at temperatures above 100 °C [4–7]. Scroll-tubular whiskers of phase 5 are responsible for high strength of this cement [8,9]. Excess amount of magnesium oxide and water are suggested to be used, to ensure the formation of phase 5 [1]. Researches showed that, for MOC cement possessing phase 5 crystals, the molar ratios of $MgO/MgCl_2$ of 11–17 and $H_2O/MgCl_2$ of 12–18 are to be the most proper ranges for design purposes [10]. Using 13 moles of magnesium oxide instead of 5 moles caused variations in physical and strength behavior of cement; and unreacted MgO particles can be treated as fillers [10]. Beside this, if the concentrations of magnesium chloride are selected incorrectly, and not to be sufficient for the mixture, MgO will react with water and form $Mg(OH)_2$. This phase is not a proper cement phase. On the other hand, if the concentration of the magnesium chloride is more than enough,

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Table 1
Composition of the different MOC pastes with mole changes of magnesium chloride.

Sample number	Mole 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

the existence of surpluses of chloride ions will cause corrosion problems [11,12].

In this paper, a thorough study of magnesium oxychloride cement is conducted to investigate the influences of various concentrations of magnesium oxychloride on the compressive strength, setting time and water resistance. Microstructural examinations of MOC cement with different concentrations of magnesium chloride provide great information about the crystal structure of different reaction phases. MOC cements were prepared by mixing magnesia and water in the ratio of 13:12, and were mixed with different mole changes of magnesium chloride to the saturation limit in water, in ranges of 0.5–1.9 moles.

2. Experimental and materials

Magnesium oxide, magnesium chloride and water are the primary materials of Sorel cement. Magnesium oxide powder used in this study was calcined magnesite powder with an averaged particle size of about 37 μm, and a purity of 96% from Iranian Magnesite Company. The magnesium chloride was hygroscopic hexahydrate, $MgCl_2{\cdot}6H_2O$, crystals with a purity of 97% from India. The amounts of magnesia and water are kept constant in this study, 13 moles of magnesia and 12 moles of water.

Magnesium chloride was first dissolved in water and mixed for about 1 min and then magnesium oxide powder was added to the solution and mixed again for about a few minutes to produce MOC cement. The composition of magnesium oxychloride cement with a wide range of magnesium chloride is shown in Table 1.

The most upper limit of solution of magnesium chloride in cold water is 1.9 moles under the condition of this study.

For each mixture described in Table 1, cubic specimens with a size of 50 mm × 50 mm × 50 mm were cast in steel moulds. The samples were cured at room temperature of 25 ± 3 °C for 20 days.

The compressive strength (CCS) of the samples was measured after 20 days, and the crushed parts of the samples were powdered and prepared for X-ray diffractions measurement (Philips XL 30 series, using Cu-Kά radiation) to identify the crystalline and to strengthen phases in the mixtures. The X-ray powder diffraction data were collected for each sample from 5° to 105° (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 scanning electron microscopy (SEM) in the secondary electron (SE) mode on fractured surface.

The setting time of the mixtures was determined by a Vicat apparatus at room temperature. The initial setting time was defined as when a Vicat needle would penetrate the sample to a point of 25 mm. The final setting time was defined when a Vicat needle would leave no visible mark on the surface of the samples.

Water dissolution of the samples was determined through the equation below:Water dissolution $= 100\left(\frac{W_1-W_2}{W_1}\right)$

Dry weight of the samples was measured (W_1) and was suspended in water for 10 days, then the weight of the samples was measured again (W_2). Reduction in weight was considered as water dissolution.

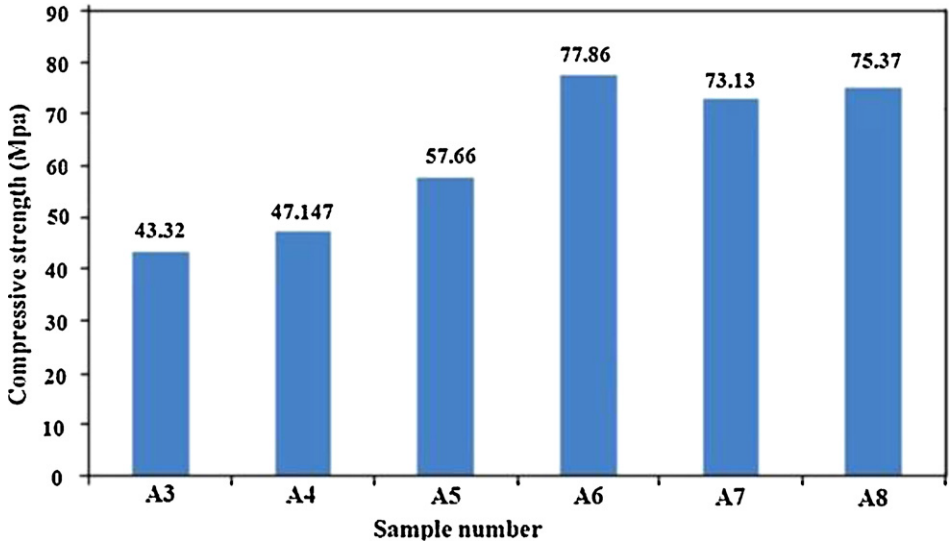


Fig. 1. Compressive strengths of different mixtures after air curing of 20 days.

3. Results

3.1. Effect of mole changes of magnesium chloride in the compressive strength

Cold crushing strength is one of the important parameters to identify the properties of the cement and concrete. The compressive strength of different mixtures after air curing of 20 days is plotted in Fig. 1, as shown in Table 1, A1 and A8 compositions have minimal and maximal amounts of magnesium chloride in solutions, respectively. Due to having high ratio of powder to water, A1 did not form cement composition properly; and A2 also formed high concentrated paste so that it was not possible to mix and produce proper cement paste. With an increase in the amount of magnesium chloride in the composition of A3–A8, the fluidity of slurry increased. As shown in Fig. 1, A6 composition has the highest CCS strength after air curing of 20 days. Existence of proper magnesium chloride in solutions caused the proper reactions of MgO with $MgCl_2$, so that after curing, an amorphous phase was converted to crystallize phases.

The formation mechanisms of the hydrated phases in magnesium oxychloride cement are as below [4]:

The dissociation of $MgCl_2$ crystals in water:

$$MgCl_2 \cdot 6H_2O \xrightarrow{H_2O} [Mg(H_2O)_6]^{2+}_{(aq)} + 2Cl^-_{(aq)} \quad (1)$$

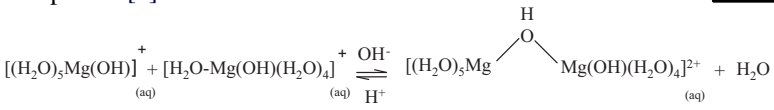
$$[Mg(H_2O)_6]^{2+}_{(aq)} \underset{H^+}{\overset{OH^-}{\rightleftharpoons}} [Mg(H_2O)_5(OH)]^+_{(aq)} + H^+_{(aq)} \quad (2)$$

The reactions of MgO in $MgCl_2$ solutions [4]:

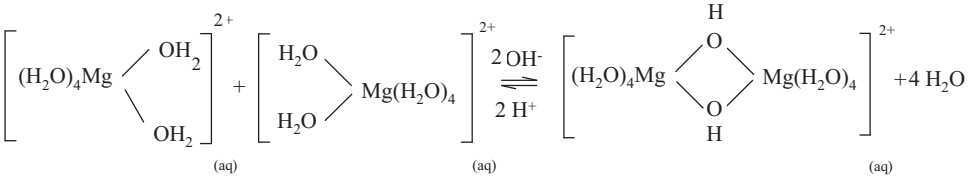
$$MgO + 2H^+_{(aq)} + 6H_2O \rightarrow [Mg(H_2O)_6]^{2+}_{(aq)} \quad (3)$$

$$MgO + H^+_{(aq)} + 5H_2O \rightarrow [Mg(H_2O)_5(OH)]^+_{(aq)} \quad (4)$$

The hydrolyzing-bridging reaction of the mononuclear complexes [4]:



(5)



(6)

$$xMg^{2+}_{(aq)} + (z+y)\,H_2O \underset{H^+}{\overset{OH^-}{\rightleftharpoons}} [Mg_x(OH)_y(H_2O)_z]^{2x-y}_{(aq)} + y\,H^+_{(aq)} \quad (7)$$

This process involving a series of the hydrolyzing-bridging reactions can be written as in Eq. (8) [4]:

$$[Mg_x(OH)_y(H_2O)_z]^{2x-y}_{(aq)} + Cl^-_{(aq)} + H_2O \rightarrow [Mg_3(OH)_5(H_2O)_m] \cdot Cl \cdot (4-m)H_2O \quad (8)$$

Gelation quickly occurs and an amorphous gel phase rapidly forms within several hours. Then, the crystal-line hydrate phase is converted from the amorphous gel phase over several days or weeks. These crystallizations can be represented as shown in Eqs. (9) and (10) [4]:

$$[Mg_x(OH)_y(H_2O)_z]^{2x-y}_{(aq)} + Cl^-_{aq} + H_2O \rightarrow [Mg_2(OH)_3(H_2O)_3] \cdot Cl \cdot H_2O \quad (9)$$

$$[Mg_x(OH)_y(H_2O)_z]^{2x-y} + Cl^- + H_2O \rightarrow [Mg_2(OH)_3(H_2O)_3]^+ Cl^- H_2O \quad (10)$$

Corresponding to the above equations, it is concluded that the existence of chloride ions is a very important factor in the formation of hydrated crystalline phases. On the other hand, optimum formation of phase 5 crystals in the magnesium oxychloride cement is desirable. The intergrowth of the needle shaped crystals of phase 5 can be the reason for the strength development of Sorel cement. In A7 and A8, because of the large amount of magnesium chloride and structural molecular water, the amount of total water in the system is increased so that the increase in the amount of water causes a lot of pores in the cement system, and decreases strength. It is probable that by the increase in phase 5 and increase in hardness, micro-cracks would initiate in the matrix and the CCS would slightly drop to lower values (sample A7 and A8); because of this, sample A6 with the highest CCS value was selected for further studies.

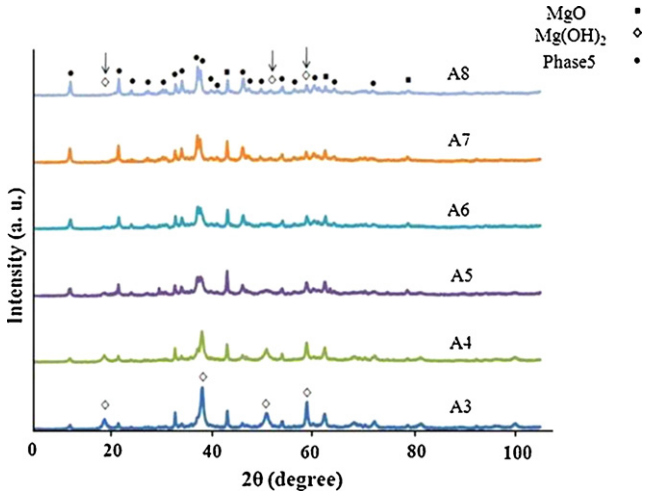


Fig. 2. XRD spectrograms of the mixtures (from bottom to top A3 to A8).

3.2. X-ray diffraction (XRD) analysis

To investigate the influences of the mole changes of the magnesium chloride on the properties of MOC cement, the X-ray diffractograms of mixtures A3, A4, A5, A6, A7, A8 is shown in Fig. 2. It shows that Mg $(OH)_2$ is a dominant phase in A3 composition with excess MgO; so, it can be concluded that the amount of magnesium chloride is low. By increasing the mole of magnesium chloride, the amount of phase 5 is increased and that of Mg $(OH)_2$ is decreased. A6 composition contains phase 5 and excess MgO. Existence of phase MgO shows that excess MgO acts as filler and has the potential to produce more of phase 5 if more of magnesium chloride is available. So, it is believed that by increasing the mole of magnesium chloride, the amount of phase 5 increases and that of $Mg(OH)_2$ decreases in samples A6, A7 and A8. Fig. 3 shows the X-ray diffractograms of A6 composition in 10, 20, 30 days, the amount of phase 5 in A6 composition increases with an increase in life time.

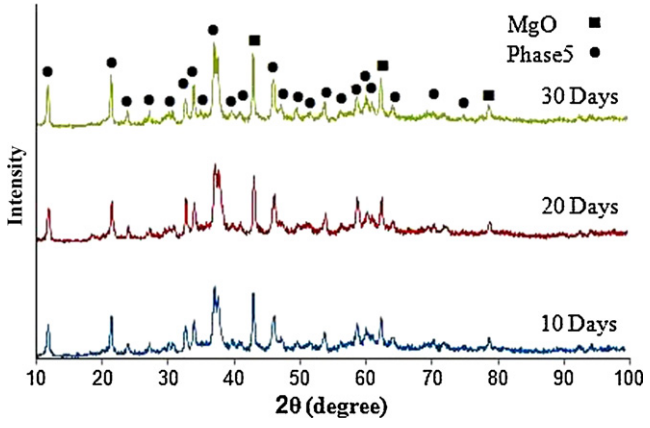


Fig. 3. XRD spectrograms of the mixture A6 at different life times (from bottom to top, 10, 20, 30 days respectively).

Table 2
Effect of different compositions on setting characteristics of oxychloride cement.

Sample number	Initial setting time (min)	Final setting time (min)
A3	90	220
A4	110	240
A5	150	265
A6	210	330
A7	300	390
A8	305	400

3.3. Effect of mole changes of magnesium chloride on the setting time characteristics of MOC cement

Setting test of the samples was measured by Vicat apparatus, and the results of the experiments are listed in Table 2. It shows that initial and final setting periods systemically increase with an increase in the amount of magnesium chloride. It is due to the required time for total formation of crystals of phase 5, are gradually increased by the increase of $MgCl_2{\cdot}6H_2O$ content and large amounts of total water in the system.

3.4. Effect of mole changes of magnesium chloride in water dissolution

Water dissolution of the samples is determined as shown in Table 3. Due to an increase in the moles of magnesium chloride, structural water increases and causes free water which forms more pores in the matrix, more diffusion of water into the samples, more area of interface between water and the matrix, and more dissolution of the sample in water.

3.5. Microstructure of the MOC phases

The morphology of the fractured surfaces of mixtures A3, A4, A5, A6, A7 and A8 is shown in Fig. 4. It can be seen that the crystals of mixtures A3 and A4 are slightly different from the needle shaped crystals of phase 5 in sample A6. It is more probable that the other phase is developed in combination with some amount of phase 5 and $Mg(OH)_2$. This is due to the highest concentration of MgO with respect to magnesium chloride in these samples.

The concentration of this phase seems to be small in XRD analysis and the peaks are in the fluctuation of the background. This is especially due to the fact that crystal structure with low symmetry produces weak peaks in XRD studies. It is required

Table 3
Water dissolution of different mixtures.

Sample number	Water dissolution (%)
A3	14.65
A4	19.83
A5	23.32
A6	23.78
A7	29.32
A8	32.57

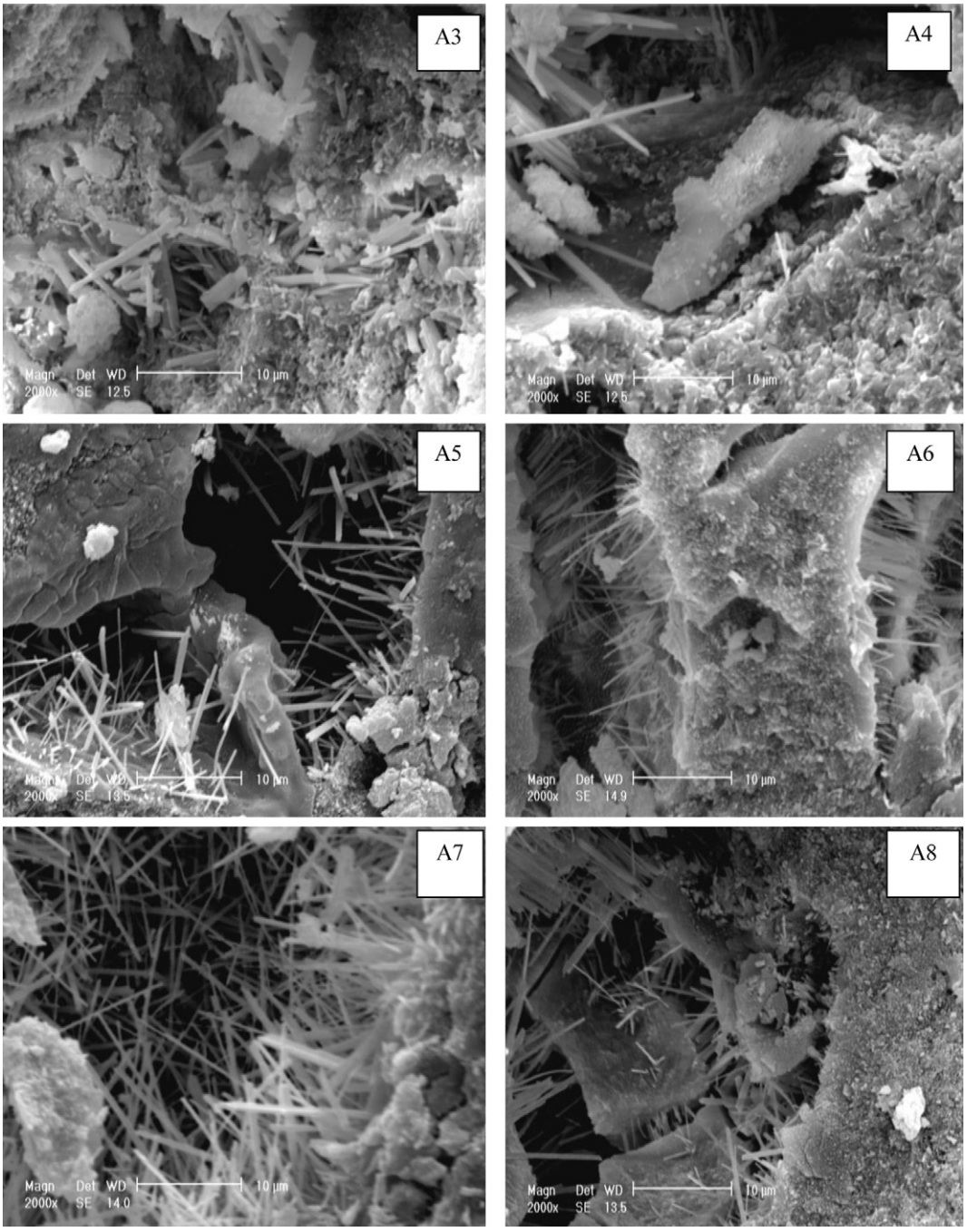


Fig. 4. Microstructural crystals of different mixtures (a) A3, (b) A4, (c) A5, (d) A6, (e) A7 and (f) A8 all at a comparable magnification of 2000x.

that in future quantitative XRD studies be performed on the system by one of the quantitative XRD methods [13,14].

The formation of the needle shaped crystals of phase 5 is observable in A5, A6, A7 and A8. The amount of crystals of phase 5 increases in mixtures by increasing the mole amount of magnesium chloride, and the sizes of the crystals are also slightly coarsened. It might be concluded that in composition A6, homogenous needle shaped crystallites of phase 5 are responsible for strength in this composition, but the values of strength, as well as the presence of crystalline 5 phase are comparable in samples A6, A7, A8. Generally speaking, the increase in $MgCl_2{\cdot}6H_2O$ has moved to be beneficial from the point of view of mechanical properties.

Fig. 5 shows the development of phase 5 from the matrix in sample A6. These needle shaped crystals are responsible for the reinforcement of the matrix and the strength increase in specimen with high concentration of $MgCl_2{\cdot}6H_2O$.

3.6. Formation of nano composite with SiC

One of the major applications of this cement is in grinding and marble stones. The aggregates to the cement matrix are

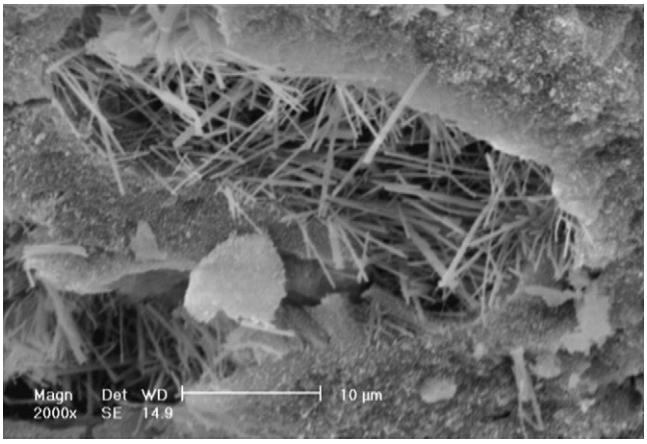


Fig. 5. Microstructure of needle shaped crystals of phase 5 developed from the matrix in sample A6.

abrasive silicon carbide of different mesh numbers. The proper binding of SiC with matrix of Sorel cement has proved to provide a suitable ceramic matrix composite (CMC).

After getting the best mechanical properties of this cement by 1.5 moles of magnesium chloride, 13 moles of magnesium oxide and 12 moles of water, which is the subject of this paper, the addition of different amounts and particle sizes of SiC to sample A6 was performed, which is the subject of the subsequent paper.

The particles size of SiC used was from coarse size of 24 meshes to nano size. The nano size SiC was a product of China. The composite of nano size particle of SiC with high mechanical strength Sorel cement (sample A6) was very promising. The performance of nanocomposite of SiC-samples comes from the fact that no heat treatment is required and that there is no grain growth of nano SiC.

In many nano composites of metal matrix (MMC), ceramic matrix (CMC) or polymer matrix (PMC), melting or firing for sintering is required that might increase the nano size in agglomeration of particles dispensed in the matrix. By increasing the needle shaped reinforcement crystals of phase 5 in Sorel cement and by using nano sized aggregates of SiC, a suitable nano composite is produced.

4. Conclusions

1. Increasing the moles of magnesium chloride developed compressive strength of the samples.
2. By increasing the magnesium chloride moles, setting time and water dissolution and amount of needle shaped crystals of phase 5 of the cement is increased.
3. 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.
4. A nano composite of sample A6 with nano particles of SiC is produced with promising results. This composite does not require melting or firing for sintering, and there is no risk of grain growth.

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