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INVESTIGATIONS ON THE PROPERTIES OF MAGNESIUM OXYCHLORIDE CEMENT PRODUCED BY IN SITU AND CLASSIC METHODS

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ABSTRACT

In this research, magnesium oxychloride cement was produced by two methods, one with a classic method by using $MgCl_2$ in MgO- $MgCl_2$- H_2O system and the other one with in situ method by using HCl in ternary system of MgO- HCl- H_2O. The compressive strength of the cements was measured after the 10th day. The comparison of the mechanical properties of the cements showed that the cement which was produced by the classic method, MgO- $MgCl_2$- H_2O, had low strength properties with respect to the in situ cement, MgO- HCl- H_2O, with the same composition. In situ production of magnesium oxychloride cement was significantly related to the heat reaction of MgO with HCl and setting time of the cement. The strength development of the cement which was produced by in situ method was due to the optimum formation of the needle shaped crystals of phase $5MgO{\cdot}MgCl_2{\cdot}8H_2O$ in cement system. The morphology and microstructure of the phases were characterized by using scanning electron microscope (SEM). Bulk densities were also measured. X-Ray diffraction (XRD) of matrix phases was investigated.

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KEY WORDS: Magnesium oxychloride cement; Needle shaped crystal; In situ; Setting time; Strength

1. INTRODUCTION

Magnesium oxychloride (MOC), known as Sorel Cement, is one type of magnesia cement [1]. Sorel cement has been used as a bonding agent for many years due to its excellent properties [2].The superior performances of the MOC cement are: rapid hardening rate, very high strength, proper adhesion, shaping conveniences, excellent fire-proofing, bonding ability to various amounts of fillers and aggregates such as SiC and SiO_2, good resistance to abrasion, low thermal conductivity and ability to resist high temperature conditions [3,4]. Sorel cement is used in industrial floorings, ship decks, grinding stone and fire protection industries [5]. The cement is the product of reactions of magnesium oxide, magnesium chloride and water with specific molar ratios. The four crystalline phases in Sorel cement are:

$2Mg(OH)_2{\cdot}MgCl_2{\cdot}4H_2O$ (Phase2), $3Mg(OH)_2{\cdot}MgCl_2{\cdot}8H_2O$ (Phase3), $5Mg(OH)_2{\cdot}MgCl_2{\cdot}8H_2O$ (Phase5), $9Mg(OH)_2{\cdot}MgCl_2{\cdot}5H_2O$ (Phase9). It is known that two hydrated phases, $3Mg(OH)_2{\cdot}MgCl_2{\cdot}8H_2O$ (phase 3) and $5MgO{\cdot}MgCl_2{\cdot}8H_2O$ (phase 5) exist at room temperature are the main reaction products [6-9]. The formation of phase 5 in this cement is desirable because the scroll-tubular whiskers of phase 5 are responsible for the high strength of this cement [10].

In this paper, a thorough study of magnesium oxychloride cement properties produced by classic method (using $MgCl_2$ solution) and in situ method (using HCl) has been conducted. Microstructural examinations and X-ray characterization of MOC cement provide excellent information about the crystal structure and different reaction phases of classic and in situ methods.

2. EXPERIMENTS

2.1. Raw Materials

Magnesium oxide, magnesium chloride and water are the starting materials of Sorel cement. Magnesium oxide powder used in this study was calcined magnesite powder with an average 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. Hydrochloric acid (HCl, 37 wt %) with a purity of 99.99 % from Merck company was used.

2.2. Preparation of the Magnesium Oxychloride Cement with by In situ and Classic Methods

Theoretically, phase 5 can be obtained from a molar ratio of $MgO/MgCl_2$ with 5 and 13 moles of water. Indeed, 5 moles of MgO, 1 mole of $MgCl_2 \cdot 6H_2O$ and 7 moles of water were mixed as shown by the equation below by classic method:

$$5\ MgO + 1\ MgCl_2 + 13\ H_2O = 5MgO \cdot MgCl_2 \cdot 8H_2O \quad (1)$$

Magnesium chloride was first dissolved in water and stirred for about 1 minute and then magnesium oxide powder was added to the solution and mixed again for a few minutes to produce MOC cement.

For in situ production of the same mixture of the cement produced by classic method, one mole of magnesium oxide should be reacted with two moles of hydrochloride acid to create one mole magnesium chloride in the reaction mixture. The equation is written as follows:

$$MgO + 2HCl = MgCl_2 + H_2O \quad (2)$$

Hydrochloride acid is added to the calculated amount of water. Subsequently, magnesium oxide is added slowly to the mixture and mixed for a

few minutes and then cast into the steel mold. For the in situ method, the exact mole amount of HCl which produced stoichiometric amounts of magnesium chloride in the system was not clear; therefore, the effect of different moles of hydrochloride acid in the system was investigated. The mole amount of hydrochloride acid solution (37%Wt) is shown as Table 1. Sample S1 was produced by classic method in MgO- $MgCl_2$- H_2O system and samples S2 to S5 were produced by in situ method in ternary system of MgO- HCl- H_2O.

For each mixture described, cubic specimens with a size of 50×50×50 mm^3 were cast in steel moulds. The samples were cured at room temperature of 25±3ºC for different curing days.

The compressive strength (CCS) of the samples according to ASTM C0133-97R03 was measured, and the crushed parts of the samples were powdered and prepared for X-ray diffractograms measurement (Philips Xl30series, using Cu-Kά radiation) to identify the crystalline and strengthen phases in the mixtures. The X-ray powder diffraction data were collected for each sample from 10-100º (2θ) with a step size of 0.05 and 1 sec 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 bulk density and water absorption of samples were measured according to Archimedes equations (ASTM C0020-00R05).

3. RESULTS

In order to evaluate the accurate stoichiometry of the chloride ions in the system the varied amount of the hydrochloric acid, by a step of 5ml from 67.97 to 82.97 ml , 1.74 to 2.12 mole, was studied. Mole ratio of powder to cement is kept constant in all mixtures. As given in Table 1, using more than 82.97 ml hydrochloric acid creates surplus ion chloride in the system which causes corrosion problems and less than 67.97 ml hydrochloric acid causes the viscosity

of the cement slurry to decrease. The compressive strength of the samples is shown in Figure 1. Bulk density measurements of the samples are shown in Figure 2. It can be seen that all the samples prepared by in situ method have high strength, density and low water absorption with respect to the classic sample.

The result of XRD analysis of the cement prepared by in situ and classic methods is shown in Figure 3. According to the XRD results, phase 5, MgO and phase 3 are the dominant phases of sample S1, but two phases in the cement S2, phase 5 and MgO exist.

Microstructural observations provide critical information about the crystal phases of the cements. The morphology of the fracture surfaces of sample S1 and S2 is shown in Figure 4. It can be seen that the needle shaped crystals of S1 are slightly different from those in sample S2. Both phases 3 and 5 are identified in microstructure of cement S1, but only crystals of phase 5 which is desirable phase are identified in sample S2.

4. DISCUSSIONS

It can be seen that all the samples prepared by in situ reaction (S2 to S5) have higher strength than the sample prepared by classic method (S1). Sample S2 with 67.97 ml hydrochloric acid solution has the highest strength among the other samples. The highest strength of in situ samples is as a result of the complete reaction of starting materials (MgO- HCl- H_2O). There are so many factors such as particle size, solvent volume, powder density, reaction temperature and condition of the mixing which can influence the final properties of the product in classic method. But, in in situ method reaction of the MgO with HCl creates a homogeneous mixture. In this way, phases are created quickly, and all areas of the cement sample become homogeneous. First, due to the reaction of the surface parts of the magnesia powders with acid, the particle sizes of the magnesia powders decrease and hydration process is done completely. One of the important factors to form hydrated phases is particle sizes of magnesia

powder. In fact, by decreasing the particle sizes of powders due to the quick reaction of surface parts of magnesium oxide powders with acid the hydrated reaction products form speedily. Second, the presence of chloride ions in in situ method affects strongly the dissolution process of Mg^{2+} in mixture and the formation of the hydrated phases. In fact, chloride ions are very important factors in the formation of the phase 5 and final compressive strength. Third, using hydrochloric acid decreases the setting time of the cement. Thus, it can be concluded that by decreasing the setting time of the cement the in situ method provides high kinetic reaction and quick hydration process with respect to the classic method with the same mixture. As shown in Figure 2, the densities of the cement prepared by in situ method are higher than that of classic cement and increases slightly. It is well known that usually porosity (P) and strength (S) are related as:

$S = s_0 \exp(-bP)$ in which b and s_0 are constants for a given system. Beside this, by increasing the hydrochloride acid solution amount in the system the total amount of water increases; so, the viscosity of the cement slurry increases and air bubbles exit easily by mixing the slurry.

According to the results of XRD analysis and SEM observations, due to the high kinetic reaction in in situ cement, desirable phase 5 forms quickly. In order to form the compact and needle shaped structure, optimum formation of the needle shaped crystals of phase 5 in the Sorel cement is fundamental. In fact, these crystals are responsible for 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 the Sorel cement. Therefore, in in situ method by using HCl in ternary system of (MgO- HCl- H_2O) the strength of the cement increases.

5. CONCLUSIONS

One of the most important factors of in situ method that influences the reaction product is the heat of reaction of magnesia with acid which controls the kinetic of the reaction. The results showed that the properties of the cement produced by two different methods, in situ and classic, mainly depend on kinetic of the reaction and setting time of the cement. The in situ production of cement (MgO- HCl- H_2O) showed high strength properties and dense microstructure with respect to the classic system. Indeed, in situ method provides high kinetic reaction and optimum formation of the needle shaped crystals of phase 5.

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CAPTIONS

Fig.1. The compressive strength of the samples prepared by classic and in situ method after air curing of 10 days

Fig.2. Bulk density and water absorption measurement of the samples

Fig.3. The XRD pattern of samples S1 and S2

Fig.4. Microstructural crystals of different mixtures a) S1 b) S2

Table1. Mole amount of the hydrochloride acid solution

Table 1 : Mole amount of the hydrochloride acid solution

Sample number	*Mole amount of HCl*	*Amount of HCl (ml)*
**S1*	*0*	*0*
S2	*1.74*	*67.97*
S3	*1.87*	*72.97*
S4	*2*	*77.97*
S5	*2.12*	*82.97*

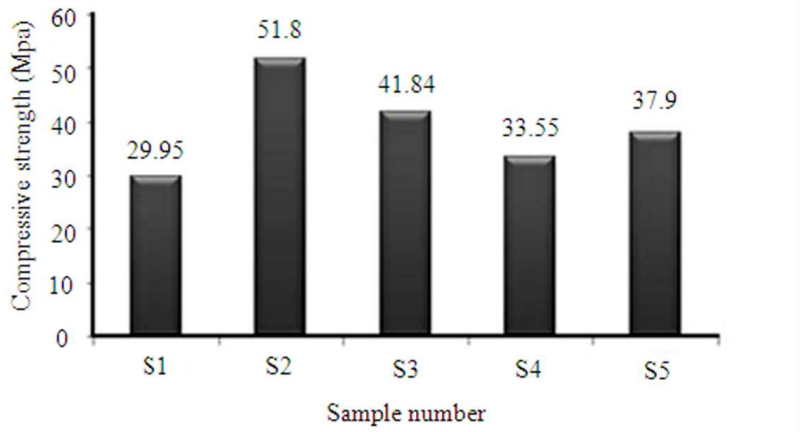

Fig. 1

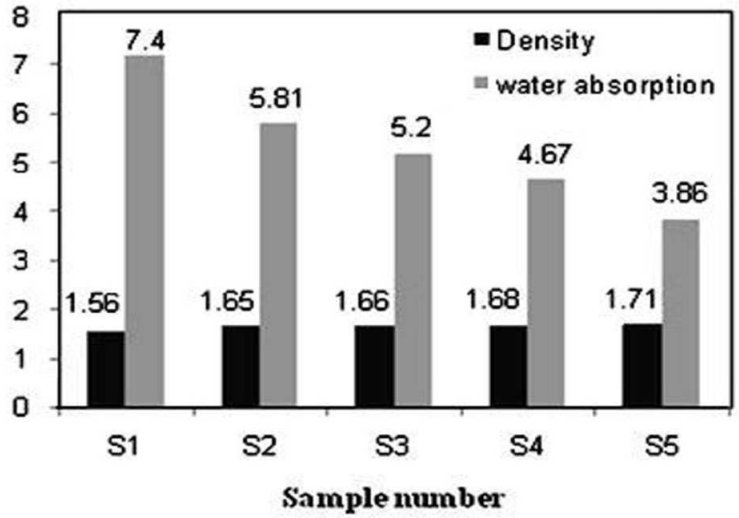
8
7
6
5
4
3
2
1
0
7.4
5.81
5.2
4.67
3.86
1.56
1.65
1.66
1.68
1.71
Density
water absorption
S1
S2
S3
S4
S5
Sample number

Fig. 2

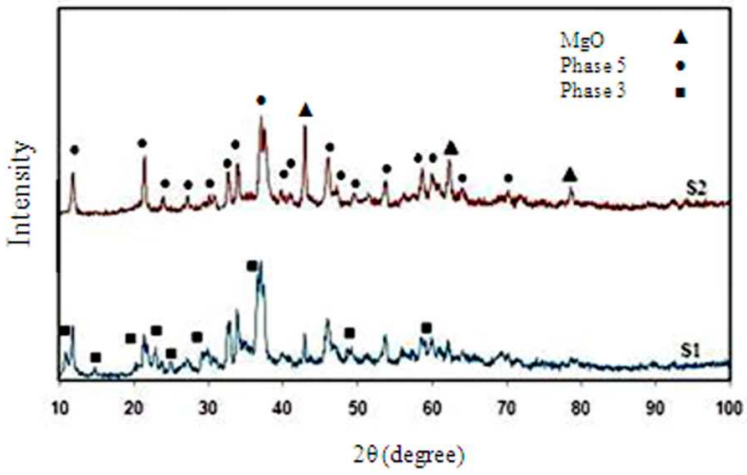
MgO
Phase 5
Phase 3
S2
S1
Intensity
10
20
30
40
50
60
70
80
90
100
2θ (degree)

Fig. 3

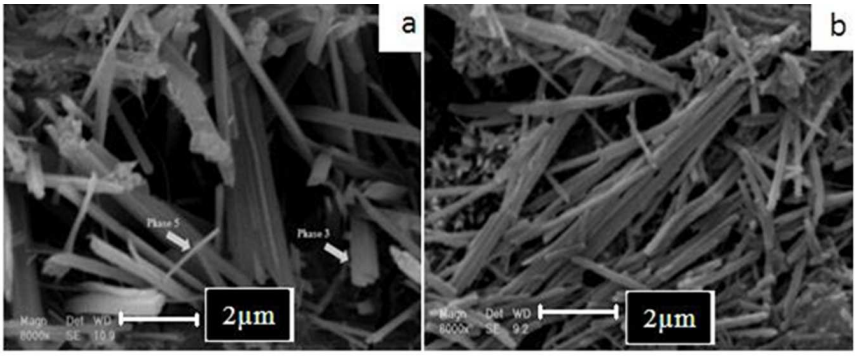

Fig. 4