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The formation mechanism of the hydrate phases in magnesium oxychloride cement[1]

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Abstract

The formation mechanism of the hydrate phases in magnesium oxychloride cement (MOC) pastes is discussed. The major reaction products of MOC pastes (MgO-$MgCl_2$-H_2O system) has long been revealed to be four crystalline phases: $5Mg(OH)_2 \cdot MgCl_2 \cdot 8H_2O$ (5 phase); $3Mg(OH)_2 \cdot MgCl_2 \cdot 8H_2O$ (3 phase); $2Mg(OH)_2 \cdot MgCl_2 \cdot 4H_2O$ (2 phase); and $9Mg(OH)_2 \cdot MgCl_2 \cdot 5H_2O$ (9 phase). All of the phases are the basic salts whose formal formula can be written as: $Mg_x(OH)_y \cdot Cl \cdot nH_2O$. It can be considered that the formation of these phases occurs neither through $Mg(OH)_2$ and $MgCl_2$, nor through simple ions Mg^{2+}, Cl^- and OH^-, etc. It was suggested that the formation of these phases probably occurs through the polynuclear complexes $[Mg_x(OH)_y(H_2O)_z]^{2x-y}$ and Cl^-, OH^- ions. The hydrolyzing experiments for the system Mg^{2+}-OH^--H_2O show that the hydrolysis of Mg^{2+} in $MgCl_2$ solutions with a certain concentration can yield $[Mg_x(OH)_y(H_2O)_z]^{2x-y}$. In the system MgO-$MgCl_2$-H_2O, the action of MgO is to increase the concentrations of Mg^{2+} and OH^- ions that induce and promote the hydrolysis of Mg^{2+}. It can be concluded that the formation of the hydrate phases in MOC pastes involves the neutralization and dissolution of MgO powder; the hydrolyzing-bridging of Mg^{2+} ions in $MgCl_2$ solutions to form a number of polynuclear complexes $[Mg_x(OH)_y$-$(H_2O)_z]^{2x-y}$ with uncertain composition; and the conversion of the amorphous hydrogel consisting of $[Mg_x(OH)_y(H_2O)_z]^{2x-y}$ complexes, Cl− and OH− ions and H_2O to the crystalline hydrate phases.

Keywords: Oxychloride cement; MgO; Hydration products

1. Introduction

Magnesium oxychloride cement (MOC) was discovered not long after portland cement. MOC pastes are the mixtures of MgO powder or calcined magnesite powder (in which the major component is MgO) and $MgCl_2$ solutions of a certain concentration (MgO-$MgCl_2$-H_2O system). It is known that two hydrate phases $5Mg(OH)_2 \cdot MgCl_2 \cdot 8H_2O$ (5 phase) and $3Mg(OH)_2 \cdot MgCl_2 \cdot 8H_2O$ (3 phase) are the major reaction products responsible for hardening and the strength of MOC. How these phases are formed has not been completely resolved. Ved et al. [1] proposed that the formation of these products is by a polymerization process and concluded that the formation of these phases does not occur through $Mg(OH)_2$ and $MgCl_2$ but through $[HO$-Mg-$O]^-$, $[Mg(H_2O)_{6-1} \cdot Cl]^+$, $[Mg(H_2O)_{6-x} \cdot OH]^+$, OH^-, Cl^-, H^+, and $[MgOH]^+$, etc. ions. Bilinski and his coworkers [2] considered that the mechanism of these phase formations was not necessarily as complicated as suggested by Ved et al. By the comparison of the systems MgO-$MgCl_2$-H_2O and the $NaOH$-$MgCl_2$-H_2O, they proposed that these phases were formed from Mg^{2+},Cl^- and OH^- etc. simple ions. By the thermodynamic analysis of several possible reactions in the system MgO-$MgCl_2$-H_2O, Zhang Zhenyu and his coworkers [3] also concluded that the 5 phase and 3 phase were not produced by the reaction of $Mg(OH)_2$ and $MgCl_2$ solutions, but by the reaction of MgO or Mg^{2+} and $MgCl_2$ solutions.

Both the 5 phase and 3 phase occur as well-crystallized needles that have been described as scroll-tubular whiskers. Many studies have shown that the needles first appear a few hours after mixing the pastes. Urwongse and Sorrell [4] observed the important fact that the initial set of the neat cement pastes takes place prior to observable crystallization of either the 5 phase or 3 phase. This fact indicates quite clearly that there is a process of some medium-gel formations between the simple ions Mg^{2+}, OH^-, Cl^-, and the crystalline phases that is responsible for the initial set of MOC phases. To explain the mechanisms of the formations

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of the phases, the formation process and the composition of the medium-gel that causes MOC pastes to be initially set must be clear. This is important to understand MOC and other inorganic cements.

The objective of the present paper is to relate the formation of the medium-gel phase as well as to propose the mechanisms of both the formation of these phases and the setting and hardening of MOC pastes.

2. The process of the phase formations

The hydrates (both 5 phase and 3 phase) are basic salts of Mg^{2+} ions. Their chemical formulas can be written as $Mg_3(OH)_5 \cdot Cl^- \cdot 4H_2O$ and $Mg_2(OH)_3 \cdot Cl \cdot 4H_2O$, respectively. Based on the investigation of Wolff and Walter-Levy [5], the crystal structure of the 3 phase consists of puckered layers of infinite double chains of "MgO_6" octahedra parallel to 100 and extending in the b-direction. Both OH^- ions and H_2O molecules provide the sharing oxygen atoms that form the corners of the octahedra. Other H_2O molecules alternate with an equal number of Cl^- ions to form rows parallel to and between the layers. Thus, its structure formula can be written as $[Mg_2(OH)_3(H_2O)_3]^+$. $Cl^- \cdot H_2O$. Also, the structure formula of the 5 phase is probably represented by analogy with the 3 phase as $[Mg_3(OH)_5(H_2O)_m]^+ \cdot Cl^- \cdot (4\text{-m})H_2O$. From these chemical structures, it can not be thought that Cl^- ions are directly bonded with the Mg^{2+} ions filled in the centers of the octahedra. The Cl^- ions lying between the layers are neutralized with the valent charges of the infinite double chains of the octahedra, in which the repeating structure units are the complex ion species $[Mg_2(OH)_3(H_2O)_3]^+$ or $[Mg_3(OH)_5(H_2O)_m]^+$ for 3 phase and 5 phase, respectively. If it is assumed that the formation of the hydrates 5 phase and 3 phase occur through Cl^- ions and some species $[Mg_x(OH)_y(H_2O)_z]^{2x-y}$ with positive charges, then the formation of the species $[Mg_x(OH)_y(H_2O)_z]^{2x-y}$ should take place prior to the crystallization of the hydrate phases. This can be supported by the studies of Urwongse and Sorrell [6] on the system $MgO\text{-}MgCl_2\text{-}H_2O$. They observed that the initial set of the neat cement pastes takes place prior to the observable crystallization of the phases. This is to say that before the production of the phases, some chemical reaction have occurred in the system and yielded some products combined with many H_2O molecules that are responsible for the initial set of MOC pastes. Thus, these products should be some of the complex species $[Mg_x(OH)_y(H_2O)_z]^{2x-y}$ with uncertain compositions. Because there are a lot of the ligand H_2O molecules and OH^- ions formed by the ionization of H_2O in the formula $[Mg_x(OH)_y(H_2O)_z]^{2x-y}$ (termed polynuclear aquohydroxoco magnesium complex ions, abbreviated to "polynuclear complexes"). Their solubility is decreased with the increase of the values of x and y, thus these polynuclear complexes together with other ions and H_2O can constitute metastable saltlike hydrogels with a solid feature in which a number of the amorphous colloidal particles somehow set up a coherent continuous structure in MOC pastes.

It appears that the formation of the polynuclear complexes $[Mg_x(OH)_y(H_2O)_z]^{2x-y}$ takes place prior to the formation of the hydrate phases. Chemically, the polynuclear complexes $[Mg_x(OH)_y(H_2O)_z]^{2x-y}$ can form through the hydrolysis of metal ions Mg^{2+} in the solutions of some salts. In fact, a basic salt can be produced simply through the hydrolysis of a salt in water. Consequently, the formation of the basic magnesium chlorides 5 phase and 3 phase would occur through the polynuclear complexes formed by the hydrolysis of Mg^{2+} ions in the $MgCl_2$ solutions. Then, the following steps can be proposed for the formation of the hydrate phases in the ternary system $MgO\text{-}MgCl_2\text{-}H_2O$.

2.1. The dissociation of $MgCl_2$ crystals in water

When $MgCl_2 \cdot 6H_2O$ is dissolved in water, $MgCl_2$ molecules could be dissociated to yield Cl^- ions and aquo magnesium ions $[Mg(H_2O)_6]^+$; and because of the polarization of Mg^{2+} ions, some $[Mg(H_2O)_6]^{2+}$ can be slightly hydrolysed. See Eq. (1) and Eq. (2).

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

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

This hydrolysis yields free H^+ ions that make the $MgCl_2$ solution acidic and mononuclear aquo hydroxoco magnesium complex ions $[Mg(OH)(H_2O)_5]^+$ (abbreviated to "mononuclear complexes").

2.2. The reactions of MgO in $MgCl_2$ solutions

When MgO is mixed with $MgCl_2$ solutions, the possible reactions shown in Eq. (3) and Eq. (4) occur:

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

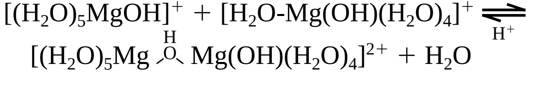
or

$$MgO + H^+(aq) + 5H_2O \Rightarrow [Mg(OH)(H_2O)_5]^+(aq) \quad (4)$$

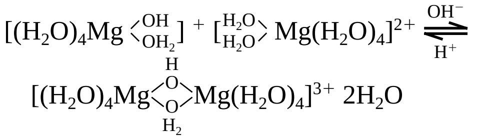
These are the neutralizations of MgO and H^+ ions formed by the hydrolysis in Eq. (2) in $MgCl_2$ solutions that result in the dissolution of MgO powder and the increase of the pH value in $MgCl_2$ solutions.

2.3. The hydrolysing-bridging reaction of the mononuclear complexes

The dissolution of MgO and the increase of pH value in the $MgCl_2$ solutions not only causes the mononuclear complexes to be formed, but also induces the mononuclear complexes to bridge with each other by sharing the ligands (OH^- ions or H_2O molecules) between two Mg^{2+} ions to form some polynuclear complexes with uncertain composition, as shown in Eq. (5) and Eq. (6):

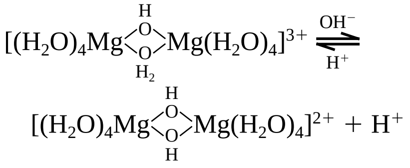


$$[(H_2O)_5MgOH]^+ + [H_2O\text{-}Mg(OH)(H_2O)_4]^+ \underset{H^+}{\overset{OH^-}{\rightleftharpoons}} [(H_2O)_5Mg \overset{H}{O} Mg(OH)(H_2O)_4]^{2+} + H_2O \quad (5)$$



$$[(H_2O)_4Mg\langle^{OH}_{OH_2}] + [^{H_2O}_{H_2O}\rangle Mg(H_2O)_4]^{2+} \underset{H^+}{\overset{OH^-}{\rightleftharpoons}} [(H_2O)_4Mg\langle^{\overset{H}{O}}_{\underset{H_2}{O}}\rangle Mg(H_2O)_4]^{3+}\ 2H_2O \qquad (6)$$

The bridging reactions yield binuclear, trinuclear and polynuclear complexes with the higher charges. They are also hydrolyzed further to reduce their charges and release free H^+ ions, as in Eq. (7):



$$[(H_2O)_4Mg\langle^{\overset{H}{O}}_{\underset{H_2}{O}}\rangle Mg(H_2O)_4]^{3+} \underset{H^+}{\overset{OH^-}{\rightleftharpoons}} [(H_2O)_4Mg\langle^{\overset{H}{O}}_{\underset{H}{O}}\rangle Mg(H_2O)_4]^{2+} + H^+ \qquad (7)$$

These hydrolyzing and bridging reactions occur alternatively and continuously with the dissolution of MgO in $MgCl_2$ solutions. This induces the formation of polynuclear complexes with uncertain compositions. So, this process involving series of the hydrolyzing-bridging reactions can be written as in Eq. (8):

$$xMg^{2+}(aq) + (z + y)H_2O \underset{H^+}{\overset{OH^-}{\rightleftharpoons}} [Mg_x(OH)_y(H_2O)_z]^{2x-y} + yH^+ \qquad (8)$$

2.4. The crystallization of the hydrate phases

The hydrolyzing reactions yield free H^+ ions, required by the neutralizations in Eq. (3) and Eq. (4), that promote dissolving of MgO powder and cause the hydrolytic species (mononuclear and polynuclear complexes) to be further hydrolyzed and bridged. Thus. at the early age, the amount of MgO is decreased and the number of the hydrolytic species with uncertain compositions is increased in MOC pastes.

The formation of the hydrolytic species with the lower solubility implies a decrease in water content in MOC pastes. Gelation quickly occurs and the amorphous gel phase rapidly forms within several hours. Then, the crystalline hydrate phase is converted from the amorphous gel phase over several days or weeks. These crystallizations can be represented as shown in Eq. (9) and Eq. (10):

$$[Mg_x(OH)_y(H_2O)_z]^{2x-y} + Cl^- + H_2O \rightarrow [Mg_3(OH)_5(H_2O)_m]^+Cl^-(4\text{-m})H_2O \qquad (9)$$

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

Therefore, the formation process of the hydrate phases in MOC pastes can be summarized as "the dissolution of MgO powder by the neutralization; the hydrolysing-bridging of Mg^{2+} ions to form $[Mg_x(OH)_y(H_2O)_z]^{2x-y}$, that results in the formation of amorphous gel phases and the initial set of MOC pastes; then the conversion of parent compounds in the amorphous form into the crystalline hydrate phases."

3. Analysis and discussion

3.1. The acidity of $MgCl_2$ solutions

The pH values of the $MgCl_2$ solutions with the different concentrations were measured by the Px-215 ion meter (Shanghai Analytic Instrument Co. Shanghai, P.R. China). The results are shown in Fig. 1. It can be seen that all the pH values of these solutions are the <7 and decrease with the increase of their concentrations. This confirms that these $MgCl_2$ solutions are slightly acidic. It is believed that their acidity is due to the hydrolysis of Mg^{2+} ions.

3.2. The reactions of MgO in $MgCl_2$ solutions

When MgO powder is mixed with $MgCl_2$ solutions, besides the neutralizing reaction in Eq. (3), the hydration reaction in Eq. (11) possibly occurs:

$$MgO + H_2O \Rightarrow Mg(OH)_2 \downarrow \qquad (11)$$

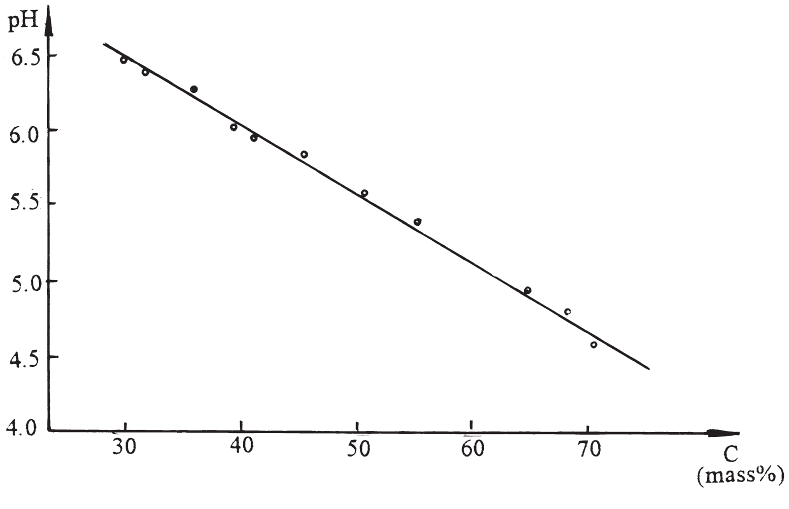


Fig. 1. The curve of pH versus the concentrations (mass percent) of $MgCl_2$ solutions.

Thermodynamically, the standard enthalpies of the neutralizing reaction in Eq. (3) ($\Delta G^0_{(3)}$) and the hydration reaction in Eq. (11) ($\Delta G^0_{(11)}$) are -123.62 kJ/mol and -27 kJ/mol, respectively. Thus, the former reaction is the more favorable than the latter one.

Dynamically, both neutralizing and hydrating reactions are heterogeneous reactions. The rates of the two reactions are to a large extent dependent on the surface area ratio and the size of crystalline grains of MgO powder (the reactivity of MgO powder). The higher the reactivity of MgO powder, the higher the rates. However, the products formed by the neutralizing reaction are easily dissolved into the liquid, which causes new surfaces on MgO grains to be available. This helps the neutralizing reaction to be continuously carried out. The product $Mg(OH)_2$ formed by the hydration reaction is not over-soluble. It precipitates and covers on the surface of MgO grains, hindering the next step reactions. It can be thought that the neutralizing reaction is also superior to the hydrating reaction.

The neutralizing reaction needs free H^+ ions. Thus, when the concentration of $MgCl_2$ solution is the higher and its pH value is the smaller, the neutralizing reaction is the more favorable reaction. Under this condition, only the neutralizing reaction can occur in practice. This has been confirmed by the results of X-ray diffraction analysis in the reaction process of neat MOC pastes. As shown in Fig. 2, when the molar ratio $MgCl_2/H_2O$ in the $MgCl_2$ solution is 1/13 and the molar ratio $MgO/MgCl_2$ is 8, no matter what the days are, only 5 phase and MgO can be observed, and no $Mg(OH)_2$ can be detected in the hardened MOC paste. This result shows that the reaction of MgO in the $MgCl_2$ solutions with the higher concentrations is merely the neutralization. If the concentrations of $MgCl_2$ solutions are the lower value and the activity of MgO powder is the higher value, the hydrating reaction of MgO in the $MgCl_2$ solutions possibly occurs. This had been shown by Bilinski and his coworkers [2]. Under this condition, $Mg(OH)_2$ forms first, but the 5 phase and 3 phase are not abundant. The system $MgO\text{-}MgCl_2\text{-}H_2O$ cannot become a good cementious material, because the $Mg(OH)_2$ does not react with the $MgCl_2$ solutions to form the hydrate phases.

Therefore, during the setting and hardening of neat MOC pastes, the reaction of MgO in $MgCl_2$ solution must be the

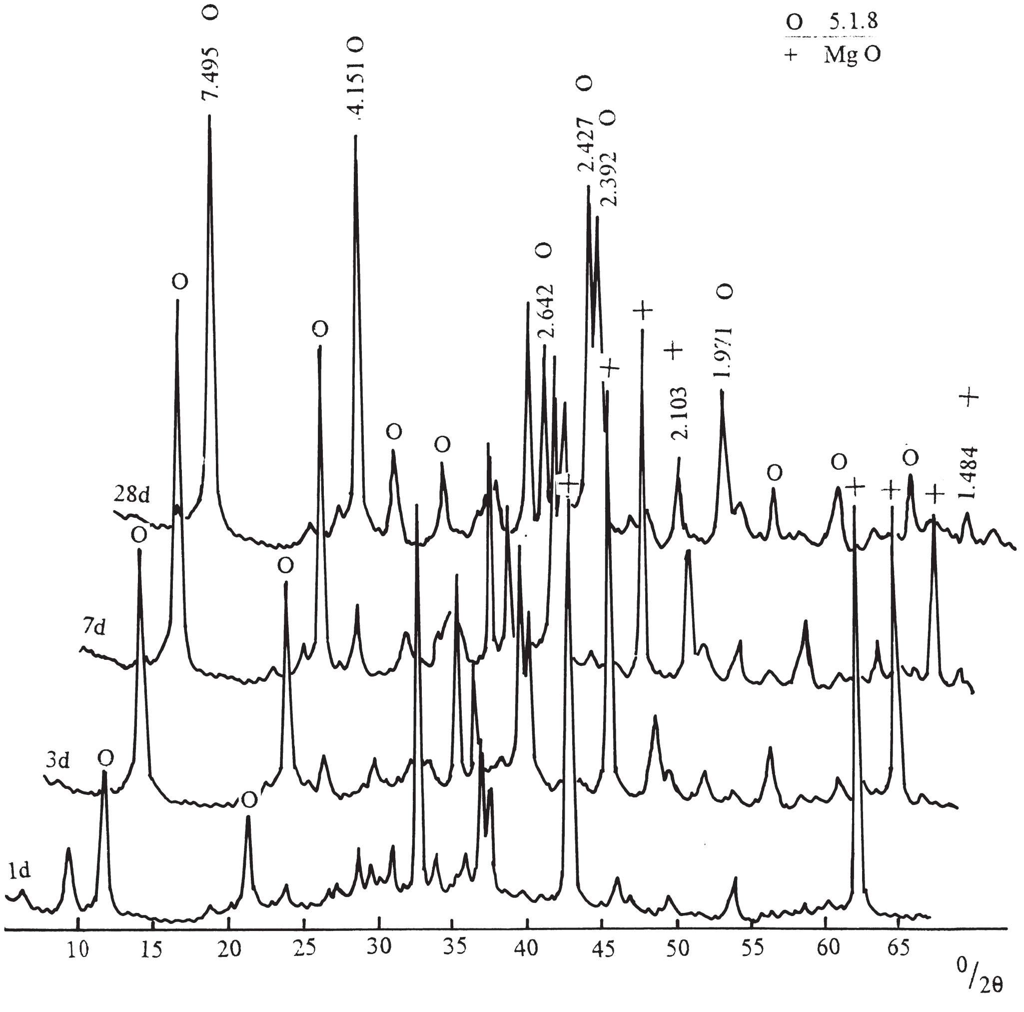


Fig. 2. The X-ray diffraction patterns of the phases in MOC paste at different ages.

neutralizing reaction, because only the neutralizing reaction can induce the hydrate phases to form when the dissolution of MgO can increase the concentration of Mg^{2+} and pH value.

3.3. The presence of polynuclear complex species $[Mg_x(OH)_yH_2O_z]^{2x-y}$ in the $MgCl_2$ solutions

Bilinski and his coworkers [2] have shown that the hydrate phases 5 and 3 can be generated not only in the system MgO-$MgCl_2$-H_2O, but also in the system $NaOH$-$MgCl_2$-H_2O (i.e., OH^--$MgCl_2$-H_2O system). This fact illustrates that addition of OH^- into $MgCl_2$ solutions can cause the 5 phase and 3 phase to be formed. Thus, for the hypothesis mentioned above to be confirmed, it should be determined whether the hydrolysis of Mg^{2+} in the Mg^{2+}-OH^--H_2O system can or cannot yield the polynuclear complex $[Mg_x(OH)_y(H_2O)_z]^{2x-y}$ ($x > 1$).

There is very limited data in the literature about the hydrolysis of Mg^{2+}, especially the hydrolysis of Mg^{2+} in concentrated solutions. Lewis [6] studied the hydrolysis of Mg^{2+} in the $MgCl_2$ solutions with 1.5, 1.25, and 1.0 M concentrations at 25°C. He concluded that two polynuclear complex species, $[Mg_2(OH)]^{3+}$ and $[Mg_4(OH)_4]^{4+}$ (ligands H_2O being omitted here), could be formed. But the stability constants of the two complex species are very small. The reason for this can be due to too lower values of the concentrations of $MgCl_2$ solutions used by them. The products formed by the hydrolysis of a metal ion are closely related to the concentration of the metal ion in solution. Only when the concentration of a solution is above the limit which is dependent on the characteristics of the metal ion can polynuclear complex species be formed by the hydrolysis of the metal ion. When the concentrations of the metal ion are below the limit, only mononuclear complex species can be formed. The study of Mazuranic and his coworkers [7] had confirmed that the lowest limit of $MgCl_2$ solution in which the 5 or 3 phase can be formed is 1.96 M. Generally, the concentrations of $MgCl_2$ solutions used for MOC pastes are much higher than 1.96 M. Because the hydrolysing reaction of Mg^{2+} ion in concentrated solutions is complicated and controlled by various effects, it is very difficult to measure and analyse the hydrolysis of Mg^{2+} ions in concentrated solutions by the methods analogous those of Lewis [6]. However, it is fortunate that the rough analysis of the Mg^{2+}-OH^--H_2O system can be carried out by means of pH-potentiometric titrations at 25°C to qualitatively confirm whether polynuclear complexes exist in the system.

For the hydrolysis reaction of Mg^{2+} as shown in Eq. (8), if the H_2O ligands are omitted, the formation function ñ and the stability constant β_{xy} of polynuclear complex species $[Mg_x(OH)_y]^{2x-y}$ can be represented respectively as Eq. (12):

$$\tilde{n} = (T_L - [OH^-])/T_M \tag{12}$$

and Eq. (13).

$$\beta_{xy} = [Mg_x(OH)_y]^{2x-y}/[Mg^{2+}]^{x.}[OH^-]^y \tag{13}$$

where $[OH^-]$ is the concentration of free OH^- ions in solution and T_M is the total concentration of Mg^{2+} ions in solution, which can be written by Eq. (14):

$$T_M = [Mg^{2+}] + \sum_{x=1}^{x}\sum_{y=1}^{y} x\beta_{xy}[Mg^{2+}]^x[OH^-]^y \tag{14}$$

T_L is the total concentration of OH^- ions in solution, which can be written by Eq. (15):

$$T_L = [OH^-] + \sum_{x=1}^{x}\sum_{y=1}^{y} Y\beta_{xy}[Mg^{2+}]^x[OH^-]^y \tag{15}$$

If the complex species formed by the hydrolysis as in Eq. (8), Mg^{2+} are only mononuclear species $[Mg(OH)_y]^{2-y}$, (i.e., $x = 1$), the formation function ñ becomes what is shown in Eq. (16):

$$\tilde{n} = \sum_{y=1}^{y} y\cdot\beta_{1y}[OH^-]^y \Big/ \left(1 + \sum_{y=1}^{y} y\cdot\beta_{1y}[OH^-]^y\right) \tag{16}$$

It can be seen that ñ is only related to the concentration of OH^- ions. If the complex species formed by the hydrolysis of Mg^{2+} are polynuclear species $[Mg_x(OH)_y(H_2O)_z]^{2x-y}$ (i.e., $x > 1$), then ñ becomes what is shown in Eq. (17):

$$\tilde{n} = \sum_{x=1}^{x}\sum_{y=1}^{y} y\cdot\beta_{xy}[Mg^{2+}]^{x.}[OH^-]^y \Big/ \left([Mg^{2+}] + \sum_{x=1}^{x}\sum_{y=1}^{y} x\cdot\beta_{xy}[Mg^{2+}]^{x.}[OH^-]^y\right) \tag{17}$$

Thus, ñ is related to not only the concentration of OH^- ions, $[OH]^-$, but also to the concentration of Mg^{2+}, $[Mg^{2+}]$. This experimental investigation involves a series of pH-potentiometric titrations at 25°C for some Mg^{2+}-OH^--H_2O systems with different $T_{Mg}{}^{2+}$ and $T_{OH}{}^{-}$. First, ten $MgCl_2$ solutions with the different concentrations were prepared. Then, one of these solutions was divided into eight glass bottles. There are 50 mL $MgCl_2$ solutions in every bottle, to which are added slightly different amount of 10 M NaOH solutions to form eight systems Mg^{2+}-OH^--H_2O, respectively. If the volumes of 10 M NaOH solutions added are neglected for every system, the total concentrations of Mg^{2+} ions, $T_{Mg}{}^{2+}$ in these systems are same and are just the molar concentration of this $MgCl_2$ solutions. The molar numbers of the NaOH solutions added are divided by the total volume of the each system to get the total concentrations of OH^- ions, $T_{OH}{}^{-}$. At same time the pH value of the each Mg^{2+}-OH^--H_2O system is measured using a pX-215 Ionic Metre (Shanghai Analytic Instrument Co., Shanghai, P.R. China). The molar concentration of the free H^+ ions, $[H^+]$, that can be exchanged into concentration of the free OH^- ions, $[OH]^-$, by the ion product of H^+ and OH^- under this condition is determined. Thus, the formation functions ñ can be calculated by Eq. (12) for these Mg^{2+}-OH^--H_2O systems

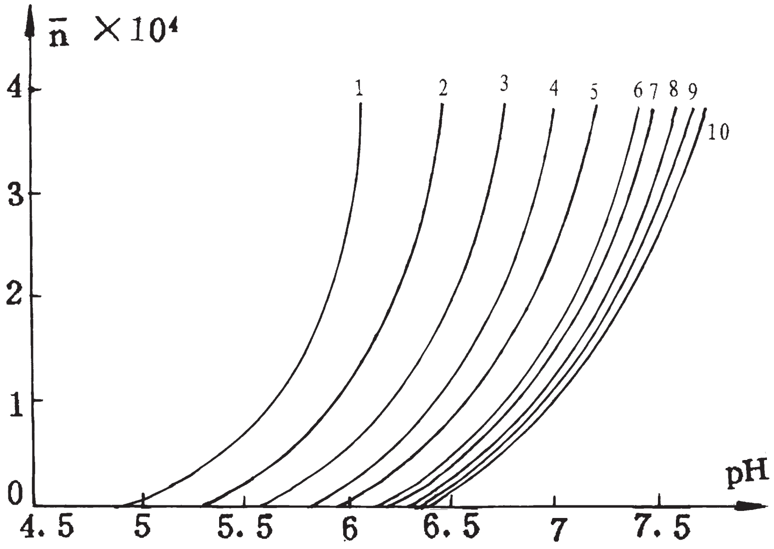


Fig. 3. The plots of ñ versus pH of the systems Mg^{2}+-OH−-H_2O (see Table 1).

with the same $T_{mg}{}^{2+}$ and the different T_{OH}-. Then, the plot of ñ versus pH ($[OH]^-$) can be made for the Mg^{2+}-OH^--H_2O systems at this same concentration of Mg^{2+} ions. The plots of ñ versus pH for the Mg^{2+}-OH^--H_2O at other concentrations of Mg^{2+} ions can be made in the same way; the results are shown in Fig. 3 and Table 1. Obviously, when $T_{[Mg]}{}^{2+}$ are the same, the plots of ñ versus pH increase progressively. When $T_{[Mg]}{}^{2+}$ are different, the plots of ñ versus pH are not coincident. This clearly illustrates that the formation function ñ is related to not only $T_{OH}{}^-$, but also $T_{Mg}{}^{2+}$ for the Mg^+-OH^--H_2O system. Therefore, the hydrolysis of Mg^{2+} in the $MgCl_2$ solutions can yield some stable polynuclear complex species $[Mg_x(OH)_y(H_2O)_z]^{2x-y}$. It is also seen that the differences between two neighbouring plots of ñ versus pH are smaller, and are nearly coincident with the decrease of Mg^{2+} ion concentrations. It implies that when Mg^{2+} ion concentration is the lower, ñ may not be related to the concentration of Mg^{2+} ions. This is to say that any polynuclear complex species cannot be readily formed in Mg^{2+}-OH^--H_2O systems with the lower concentration of Mg^{2+} ions.

At the same time, this experimental investigation also proved that if the amount of 10 M NaOH solution added is increased to a certain extent, the concentrated $MgCl_2$ solutions can be become the stable gels; the more dilute $MgCl_2$ solutions can yield only the precipitate of $Mg(OH)_2$.

There is much evidence to show that when the concentrated solutions of $MgCl_2$ are used, the hydrates 5 phase or 3 phase can be easily formed in either MgO-$MgCl_2$-H_2O systems or $NaOH$-$MgCl_2$-H_2O systems. When more dilute solutions of $MgCl_2$ are used, the phases do not easily form, especially at an early age. As shown above, in the concentrated solutions of $MgCl_2$, the hydrolysis of Mg^{2+} induced by the addition of OH^- ions could yield some stable polynuclear complexes $[Mg_x(OH)_y(H_2O)_z]^{2x-y}$; but in more dilute solutions of $MgCl_2$, the hydrolysis of Mg^{2+} induced by the addition of OH^- ions yields mainly mononuclear complexes $[Mg(OH)_y(H_2O)_z]^{2-y}$ or $Mg(OH)_2$ precipitation.

According to the rule named "the least difference between the static electricity powers" suggested by Baes and Masmer [8], the most stable polynuclear complexes produced by the hydrolysis in Eq. (8) of Mg^{2+} ions are $[Mg_3(OH)_3(H_2O)]^{3+}$ and $[Mg_6(OH)_8(H_2O)]^{4+}$, because the differences between the static electricity powers of the reactants and products in Eq. (8) are zero for these two polynuclear complexes. While the repeat structure unit of 5 phase crystalline is $[Mg_3(OH)_5\text{-}(H_2O)_m]^+.Cl^- \cdot (4\text{-}m)H_2O$. It is apparent that the number of Mg^{2+} ions involved in both the stable polynuclear complexes and the repeat structure units of the 5 phase crystalline are identical or double. It is noted that the crystalline phase that first emerges in MOC pastes is the 5 phase, no matter whether the initial molar ratios of $MgO/MgCl_2$ are over or below 5. This is an accidental or inevitable result which has yet to be studied. These facts are enough to illustrate that the formation of the hydrate phases

Table 1
Apparent density (g/ml) of each MgO_2/H_2O solution

No	$MgCl_2/H_2O$ (Molar ratio)	Density
1	1:11	1.2972
2	1:13	1.2568
3	1:15	1.2280
4	1:17	1.2048
5	1:19	1.1868
6	1:22	1.1628
7	1:23	1.1560
8	1:25	1.1452
9	1:27	—
10	1:29	—

5 or 3 are closely related to the stable polynuclear complexes $[Mg_x(OH)_y(H_2O)_z]^{2-y}$ produced by the hydrolysis of Mg^{2+} ions.

In summary, in MOC pastes(MgO-$MgCl_2$-H_2O system), MgO is neutralized with free H^+ ions in the $MgCl_2$ solution with a certain concentration that increases the concentration of Mg^{2+} in the solution and provides free OH^- ions for the hydrolysis of Mg^{2+} ions. Thus, this neutralization promotes the hydrolyzing-bridging of Mg^{2+} ions to yield a number of polynuclear complexes $[Mg_x(OH)_y(H_2O)_z]^{2x-y}$. Then, these polynuclear complexes of uncertain composition can combine with the salt base ions Cl^- and H_2O to form amorphous phase gels. These can almost be quantitatively converted to the crystalline basic salts, 5 phase or 3 phase. This is the formation mechanism of the hydrate phases in MOC pastes (the system MgO-$MgCl_2$-H_2O). According to the mechanism, the effects of the reactivity of MgO and the concentration of $MgCl_2$ solutions on the formation of the phases can be explained; the fast and slow setting of MOC pastes, the stability and conversion of the phases, and the effects of some additives and a few impurities on the phases can also be explained.

4. Conclusions

1. The hydrate phases $Mg_3(OH)_5 \cdot Cl \cdot 4H_2O$ (5 phase) and $Mg_2(OH)_3 \cdot Cl \cdot 4H_2O$ (3 phase) formed in MOC pastes (the system MgO-$MgCl_2$-H_2O) are basic salts. It can be considered that these phases are not directly crystallized from the supersaturated solutions of the simple ions Mg^{2+}, OH^-, Cl^-, etc., but are converted from an amorphous phase (hydrogel consisting of some polynuclear complexes $[Mg_x(OH)_y(H_2O)_z]^{2x-y}$ with uncertain composition yielded by the hydrolysis of Mg^{2+} ions, Cl^- ions, and H_2O molecules).
2. The three steps forming process of the phases in MOC pastes may be summarized as: neutralizing-hydrolyzing-crystallizing. First, MgO powder is neutralized by free H^+ ions in the concentrated solution of $MgCl_2$ and dissolved into the solution. This increases the concentration of Mg^{2+} and OH^- ions in the solution. Second, the hydrolyzing-bridging reaction of Mg^{2+} ions is promoted by the dissolution of MgO to yield some polynuclear complexes $[Mg_x(OH)_y(H_2O)_z]^{2x-y}$; these two steps promote each other and alternatively yield a number of the polynuclear complexes. Then, these complexes and Cl^- ions, H_2O, are absorbed and then condensed to form a continuous amorphous phase (the hydrogel, which is subsequently converted to the crystalline phases).
3. The formation of a significant amount of the complexes $[Mg_x(OH)_y(H_2O)_z]^{2x-y}$ makes available a large number of free H_2O molecules in MOC pastes. This causes the pastes to be changed into midstable hydrogels without mobility (initial setting of the paste). Then, with the quantitative conversion of the hydrogel to the crystalline phases, a micro and continuous network consisting of the fibric hydrate crystals can form (hardening of the paste). This is the mechanisms responsible for the setting and hardening of MOC pastes.

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