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Formation Mechanism of Basic Magnesium Chlorides Whiskers

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The amorphous magnesium hydroxide [$Mg(OH)_2$], Mg^{2+}, Cl^- ions, H_2O and $[Mg(OH)_y]^{2-y}$ (y = 0,...6) anion coordination-polyhedras were proposed as the basic crystallization growth units to form the basic magnesium chlorides whiskers with the general composition $xMg(OH)_2 \cdot MgCl_2 \cdot yH_2O$ according to the experiment of the dissolution of MgO and $MgCl_2$ in water and the coordination reaction of Mg^{2+} and OH^- and the phase formation and transition reported in the literature can be easily predicted.

Key Words: Formation mechanism, Basic magnesium chlorides, Whiskers, $[Mg(OH)_y]^{2-y}$ anion coordination-polyhedras.

INTRODUCTION

The basic magnesium chlorides whiskers known as Sorel cement has been investigated in last few decades, The application development on function materials as flame retardants, fillers, polymer reinforcement agents and heat-insulting materials was being a hotspot by reason of its many superior properties such as high fire resistance, low thermal conductivity, high resistance to abrasion and high compressive and flexural strengths[1,2]. The general composition: $xMg(OH)_2 \cdot MgCl_2 \cdot yH_2O$ of the basic magnesium chlorides whiskers have been established by many authors since its discovery[2-5]. A number of phase stoichiometries can be found that most remain unconfirmed, the 2 (2-1-2 and 2-1-4) phase, 3 (3-1-1, 3-1-6 and 3-1-8) phase, 5 (5-1-3, 5-1-8 and 5-1-12) phase, 9 (9-1-4, 9-1-5 and 9-1-8) phase have been reported. The 3-1-8 phase with the formula $3Mg(OH)_2 \cdot MgCl_2 \cdot 8H_2O$ and the 5-1-8 phase with the formula $5Mg(OH)_2 \cdot MgCl_2 \cdot 8H_2O$ were two important and fundamental phase form which were extensive investigated[1,3,6-11] below 100 ºC and the basic magnesium chloride with the formulas 2-1-2, 2-1-4, 3-1-1, 9-1-4 and 9-1-5 phases were founded above 100 °C in the system $MgO\text{-}MgCl_2\text{-}H_2O$[1,4]. It was generally accepted that the crystal structure of the 3-1-8 phase and the 5-1-8 phase and the 9-1-4 phase in the system $MgO\text{-}MgCl_2\text{-}H_2O$ were a condensation of the MgO_6 octahedra with respect to the $Mg(OH)_2$ content and intercalated with chloride atoms/ions and water molecules[4,6,8,9]. The crystal structure of these can also be constructed by tetrahedrons of $[Mg(OH)_4]^{2-}$ and $[MgCl_4]^{2-}$ according to the theoretical model of anionic coordination polyhedron growth-units[5]. The formation of the 3-1-8 phaseand the 5-1-8 phase in the system $MgO\text{-}MgCl_2\text{-}H_2O$ mainly depends on the molar ratio of MgO, $MgCl_2$ and H_2O in the initial reactant, the 3-1-8 phase and the 5-1-8 phase are formed by the direct reaction between MgO or Mg^{2+} dissolved out from MgO and aqueous solution of $MgCl_2$ rather than $Mg(OH)_2$ produced by hydration of MgO and aqueous solution of $MgCl_2$[12]. The formation mechanism of the hydrates of magnesium oxychloride from Mg^{2+}, OH^-, Cl^- to the basic salts crystauines were the process of the hydrolysis-coordinating condensations of Mg^{2+} ions to form the polynuclear aquo-hydroxo magnesium complex ions[13].

The phase composition of the basic magnesium chloride whiskers in the system $MgO\text{-}MgCl_2\text{-}H_2O$ were complex and multiple. It is not only the difference of phase 2, 3, 5 and 9, but also the difference of the numbers of bounded water. the formation mechanism of the basic magnesium chloride whiskers in the system $MgO\text{-}MgCl_2\text{-}H_2O$ were uncertain and inconsistent and focus on the 3-1-8 phase, 5-1-8 phase, as well as 9-1-4 phase and the formation mechanism with regard to the others phase (especially as phase 2) and the bounding numbers of water were hardly any discussed. The initiation and growth process of the basic magnesium chloride whiskers in the system $MgO\text{-}MgCl_2\text{-}H_2O$ includes phase transformation, morphology evolution, growth mechanism and crystal orientation in whisker synthesis. The amorphous magnesium hydroxide $Mg\text{-}(OH)_2$, Mg^{2+} and Cl^- ions, $[Mg\text{-}(OH)y]^{2-y}$ (y = 0,…6) anion coordination-polyhedras[14] and H_2O were proposed as the basic units to form the basic magnesium chlorides whiskers $xMg(OH)_2 \cdot MgCl_2 \cdot yH_2O$ according to the experiment of the dissolution of MgO and $MgCl_2$ in water and the coordination reaction of Mg^{2+} ions and OH^-. the molar ratio of $MgO/MgCl_2$, the concentration of Mg^{2+} in the solution, the value of pH in the solution system and the reaction temperature are the most important factors to effect the phase form.

EXPERIMENTAL

In a typical method, appropriate amount of magnesium oxide powder was slowly added to 83 mL water in accordance with 0.6, 0.65, 0.7 and 0.75 MgO/H_2O, reaction time maintained for 1 h and the flask was placed in a constant-temperature bath at 60 °C and while the aqueous solution was stirred and change temperature from 30 to 80 °C while 0.7:1 MgO/H_2O and the mixture was fully stirred to dissolve the added magnesium oxide almost completely, then the heating was stopped, the pH was measured by pH acidy-meter (PHS-3C).

Magnesium chloride (203.3 g) was dissolved in 200 mL water at 60 °C for 0.5 h and the molar ratio of $MgCl_2/H_2O$ changed from 2 to 5 mol L^{-1}. 0.65:1, 0.7:1, 0.75:1, 0.8:1 and 0.85:1 molar ratio of $MgO/MgCl_2$, the temperature from 30 to 80 °C, under 0.7 molar ratio of $MgO/MgCl_2$ and the concentration of $MgCl_2$ changed from 2 to 5 mol L^{-1} were dissolved in water and the solution was left to stand at room temperature for 2 days. The resulting white precipitate was filtered off, washed with distilled water and absolute ethanol several times, respectively and then dried in an oven at 50 °C for 3 h to obtain the basic magnesium chloride whiskers.

RESULTS AND DISCUSSION

Process of activity magnesium oxide dissolved in water: Fig. 1 showed typical results obtained in dissolved experiments with the value of pH measured as a function of time. It can be seen in Fig. 1 that the pH decrease observed with time increase under certain molar ratio of MgO/H_2O, the pH slightly increase then decrease with low molar ratio of MgO/H_2O and the pH reach a constant after certain time. The pH increase before 0.75 molar ratio of MgO/H_2O and then decrease.

The predication of activity magnesium oxide reacts with water were the dissolution of activity magnesium oxide in water, a thixotropic suspension of hydration of magnesium oxide formed slightly[8] and then converted to an amorphous magnesium hydroxide $[Mg(OH)_2]$ as shown in eqn. 1. The amorphous magnesium hydroxide $[Mg(OH)_2$ huddled then form a gel $x[Mg(OH)_2$ as shown in eqn. 2. The dissociative ionization starts with the time increase in the solution, $[MgOH]^+$, even Mg^{2+} ions existed in the solution, therefore, the pH measured as a function of time in Fig. 1 increase as shown in eqns. 3 and 4. The OH^- concentration increases with time increase or the dissolution of activity magnesium oxide, the complexation of Mg^{2+} ions with the OH^- existed, then the pH decrease measured as a function of time (Fig. 1) as shown in eqns. 5 and 6. The above process included ionization equilibrium of weak electrolyte and dissociation equilibrium of complex ion in aqueous solution.

$$MgO+H_2O \rightarrow H_2O.MgO \rightarrow Mg(OH)_2 \rightarrow [Mg(OH)_2] \quad (1)$$

$$[Mg(OH)_2] + [Mg(OH)_2] + ... \leftrightarrow [Mg(OH)_2], x = 1,2, ... \quad (2)$$

$$x[Mg(OH)_2] \leftrightarrow x[MgOH]^+ + xOH^- \quad (3)$$

$$x[MgOH]^+ + xOH^- \leftrightarrow xMg^{2+} + (x+1)OH^- \quad (4)$$

$$Mg^{2+} + 2OH^- + OH^- + H^+ \leftrightarrow [MgOH]^+ + 2OH^- + H^+ \quad (5)$$

$$[MgOH]^+ + 2OH^- + H^+ \leftrightarrow [Mg(OH)_2 + OH^- + H^+ \quad (6)$$

The OH^- concentration increase assumed, the complexation of Mg^{2+} ions with the OH^- proceed. The stable $[Mg(OH)_6]^{4-}$ octahedra formed[15] at last as shown in eqns. 7 and 10. The general formula can be deducted as eqn. 11.

$$[Mg(OH)_2] + OH^- + H^+ \leftrightarrow [Mg(OH)_3]^- + H^+ \quad (7)$$

$$[Mg(OH)_2] + 2OH^- + 2H^+ \leftrightarrow [Mg(OH)_4]^{2-} + 2H^+ \quad (8)$$

$$[Mg(OH)_2] + 3OH^- + 3H^+ \leftrightarrow [Mg(OH)_5]^{3-} + 3H^+ \quad (9)$$

$$[Mg(OH)_2] + 4OH^- + 4H^+ \leftrightarrow [Mg(OH)_6]^{4-} + 4H^+ \quad (10)$$

$$[Mg(OH)_2] + (y-2)OH^- + (y-2)^{H+} \leftrightarrow [Mg(OH)_y]^{2-y} + (y-2)^{H+}, (0 \leqq y \leqq 6) \text{ or}$$
$$[Mg(OH)_2 + (y-2)\ H_2O \leftrightarrow [MgOH_y]^{2-y} + (y-2)^{H+}, (0 \leqq y \leqq 6) \quad (11)$$

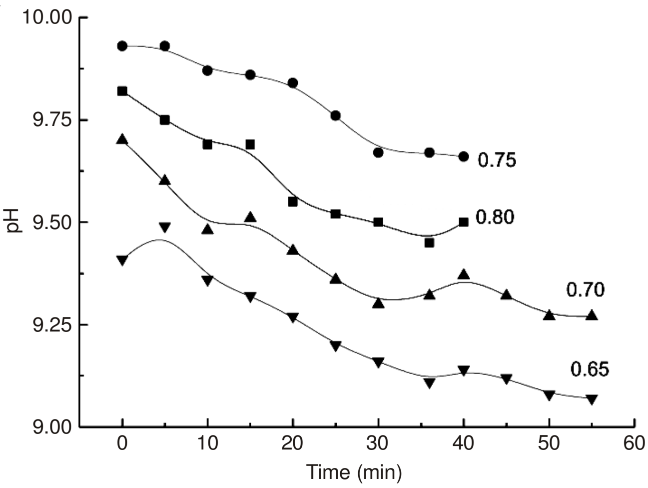

Fig. 1. The pH measured as a function of time with different molar ratio of MgO/H_2O

The process of activity magnesium oxide dissolved in water includes dissolution, hydration, transformation, aggregation, gelatination and disaggreagation. The pH of solution system increased in a relatively short time and then decreased as a result of complexation of Mg^{2+} ions with the OH^-. The stable form $[Mg(OH)_6]^{4-}$ octahedra formed at last under the hypothetical OH^- increase.

Fig. 2 showed that the pH slightly increase then decrease and the pH reach a constant after certain time below 50 °C, the pH decrease and the pH reach a constant after certain time above 60 °C and the pH increase at 50 °C then decrease under certain molar ratio of MgO/H_2O. The effect of the reaction temperature on the pH of the solution attributed to the change of solubility and convergent, the solubility of activity magnesium oxide increase with the temperature increase below 50 °C and the convergent and complexation of Mg^{2+} ions with the $^{\bullet}OH$ increase with the temperature increase above 60 °C (Fig. 2).

Known as above, the amorphous magnesium hydroxide $[Mg(OH)_2]$ as shown in eqn. 3 was the basic crystallization growth units and effect by the molar ratio of MgO/H_2O, or the concentration of Mg^{2+} ions, the pH of the solution system and the reaction temperature. The balance eqn. 3 will proceed towards the right with the increase of the molar ratio of MgO/H_2O or the concentration of Mg^{2+} ions and simultaneously, the amount of amorphous magnesium hydroxide $[Mg(OH)_2]$ will increase, Finally, the pH of the solution system presented alkalinity as seen in Fig. 1. The pH of the solution system reached the maximum with the reaction temperature increase from 30 to 50 °C and decrease after then due to the reversibility of the balance eqn. 3, that is the balance eqn. 3 will proceed towards the left after 50 °C (Fig. 2).

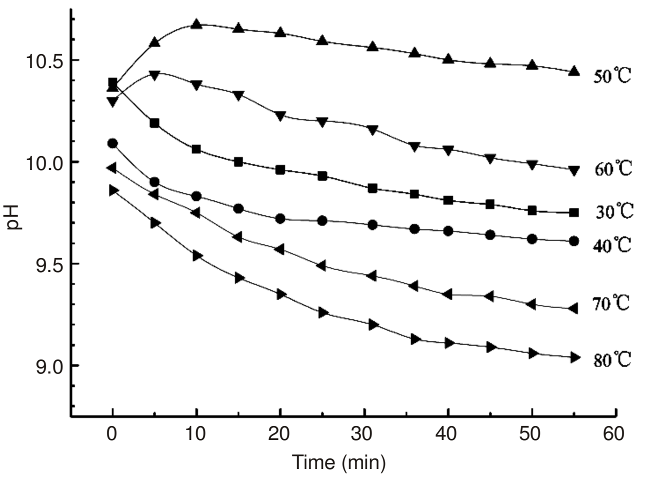

Fig. 2 The pH measured as a function of time with different reaction temperature

Process of magnesium chloride dissolved in water: Fig. 3 shows typical results obtained in dissolved experiments with the value of pH measured as a function of time. It can be seen in Fig. 3 that the pH suddenly decrease observed at the beginning, then increase with the time increase and constant in the end under certain molar ratio of $MgCl_2/H_2O$. The pH measured decrease with the increase molar ratio of $MgCl_2/H_2O$ (Fig. 4), the acidity of magnesium chloride in water plays an important part.

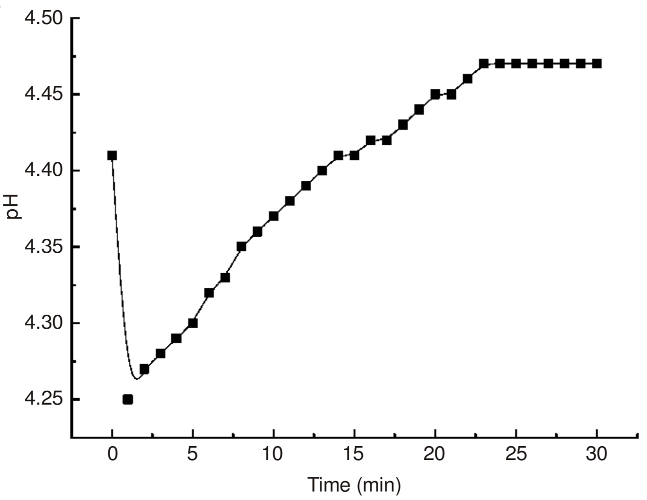

Fig. 3 The pH measured as a function of time under certain molar ratio of $MgCl_2/H_2O$

The dissolution of magnesium chloride in water were fast and easily, the acidity of strong acidic salt express out in a short time and the complexation of Mg^{2+} ions with the OH^- existed with the increase of reaction time under certain molar ratio of $MgCl_2/H_2O$ in eqns.12 and 13, as a result of the pH change (Fig. 3). Both of the concentration of Mg^{2+} ions and

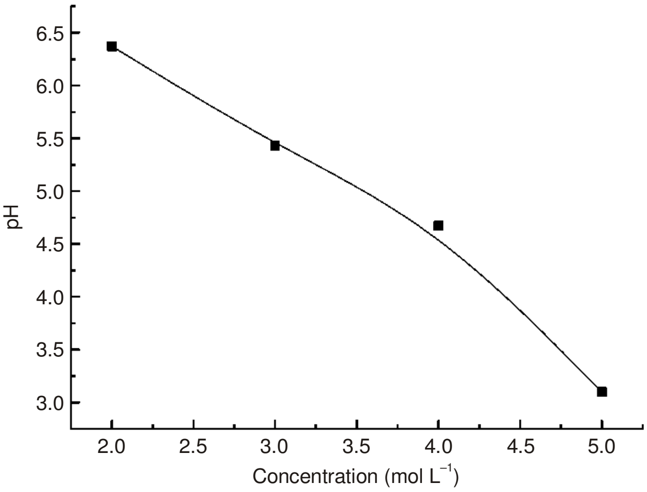

Fig. 4. The pH measured with different molar ratio of $MgCl_2/H_2O$

the neutralization of amorphous magnesium hydroxide $[Mg(OH)_2]$ with the increase molar ratio of $MgCl_2/H_2O$ make the eqn. 14 will proceed towards to right, what is more increase in eqn. 15 to 18 or a general expression in eqn. 19 (Fig. 4). It indicated that the crystallization growth units in the solution system of $MgCl_2/H_2O$ included Mg^{2+}, Cl^-, H_2O and $[Mg(OH)_y]^{2-y}$. The above process included the hydrolysis equilibrium of salts and dissociation equilibrium of complex ion in aqueous solution.

$$MgCl_2 + H_2O \rightarrow Mg^{2+} + 2Cl^- + OH^- + H^+ \quad (12)$$

$$Mg^{2+} + 2Cl^- + OH^- + H^+ \leftrightarrow [Mg(OH)]^+ + 2Cl^- + H^+ \quad (13)$$

$$Mg^{2+} + 2Cl^- + 2OH^- + 2H^+ \leftrightarrow Mg(OH)_2] + 2Cl^- + 2H^+ \quad (14)$$

$$Mg^{2+} + 2Cl^- + 3OH^- + 3H^+ \leftrightarrow [Mg(OH)_3]^- + 2Cl^- + 3H^+ \quad (15)$$

$$Mg^{2+} + 2Cl^- + 4OH^- + 4H^+ \leftrightarrow [Mg(OH)_4]^{2-} + 2Cl^- + 4H^+ \quad (16)$$

$$Mg^{2+} + 2Cl^- + 5OH^- + 5H^+ \leftrightarrow [Mg(OH)_5]^{3-} + 2Cl^- + 5H^+ \quad (17)$$

$$Mg^{2+} + 2Cl^- + 6OH^- + 6H^+ \leftrightarrow [Mg(OH)_6]^{4-} + 2Cl^- + 6H^+ \quad (18)$$

$$Mg^{2+} + 2Cl^- + yOH^- + yH^+ \leftrightarrow [Mg(OH)_y]^{2-y} + 2C^- + yH^+, (0 \leq y \leq 6) \quad \text{or}$$

$$Mg^{2+} + 2Cl^- + yH_2O \leftrightarrow [Mg(OH)_y]^{2-y} + 2Cl^- + y^{H+}, (0 \leq y \leq 6) \quad (19)$$

Process of activity magnesium oxide and magnesium chloride dissolved in water: Fig. 5 shows the pH measured as function of time with different molar ratio, 0.65, 0.7, 0.75, 0.8 and 0.85 of $Mg_2O/MgCl_2$, it can be seen that the pH increase in about ten minutes and then decrease slightly to constant in the end before 0.7 of the molar ratio of $Mg_2O/MgCl_2$, the solution system become a paste above 0.75 of the molar ratio of $Mg_2O/MgCl_2$ in a short time.

Fig. 6 shows the pH measured as function of time with different concentration of $MgCl_2$: 2 mol L^{-1}, 3 mol L^{-1}, 4 mol L^{-1} and 5 mol L^{-1} while reaction temperature at 60 °C and 0.7 of the molar ratio of $Mg_2O/MgCl_2$, it can be clearly seen that the pH change from alkalinity to acidity with the concentration of $MgCl_2$ from 2 mol L^{-1} to 5 mol L^{-1}. Fig. 7 shows the pH measured as function of time with different reaction temperature below 100 °C while the concentration of $MgCl_2$ is 4 mol/L

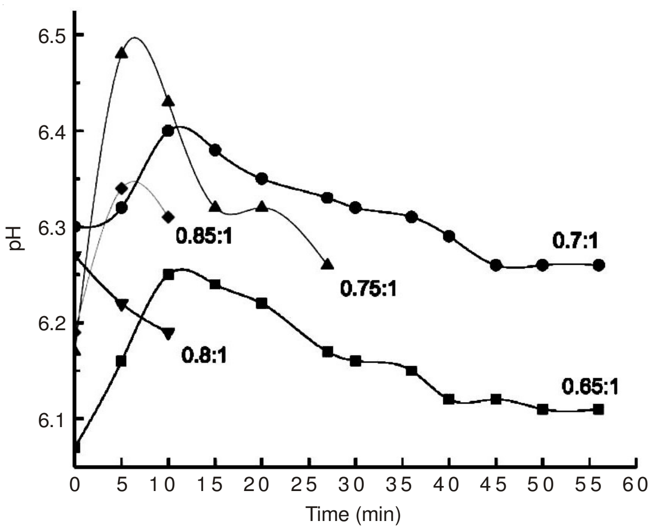

Fig. 5 The pH measured as function of time with different molar ratio

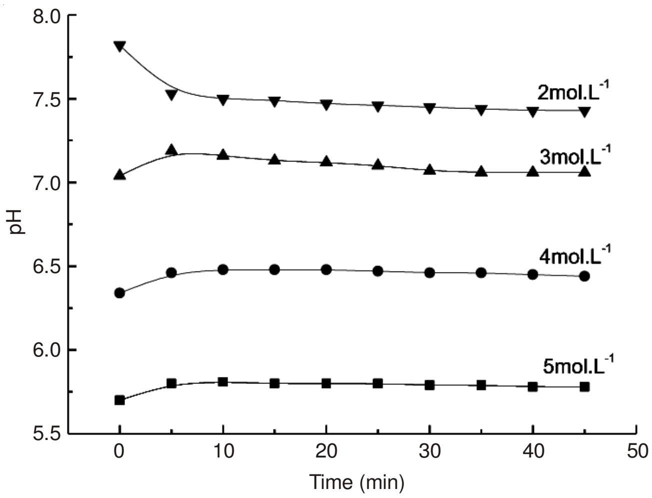

Fig. 6 The pH measured as function of time with different concentration of $MgCl_2$

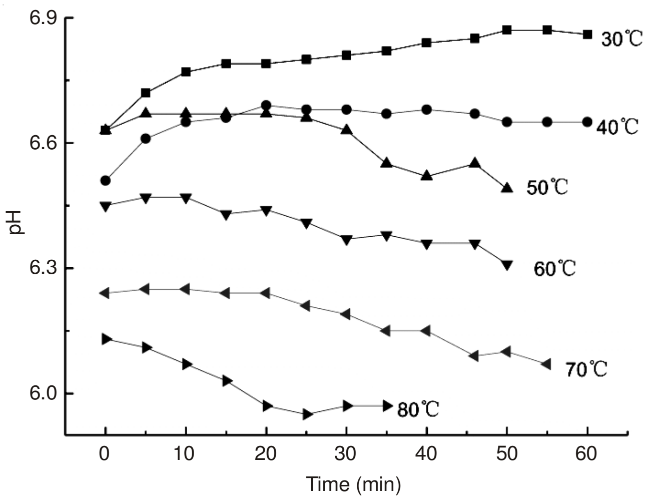

Fig. 7 The pH measured as function of time with different reaction temperature

and 0.7 of the molar ratio of $Mg_2O/MgCl_2$, it can be seen that the pH decreases with the increase of temperature.

Formation mechanism of basic magnesium chlorides whiskers: The equilibrium process included ionization of weak electrolyte, hydrolysis of salts and dissociation of complex ion existed in aqueous solution. The formation of the basic magnesium chlorides seriously depended on the molar ratio of $Mg_2O/MgCl_2$, or the pH and temperature. In other word, the form equations existed objectively and can be combined under appropriate conditions. The general formula in eqn. 20 can be obtained simply by combination of eqns. 3 and 19, thus it can be seen that the crystallization growth units includes $[Mg(OH)_2]$, $[Mg(OH)_y]^{2-y}$, Cl^-, $OH^-$and H^+, the formation of $xMg(OH)_2{\cdot}MgCl_2{\cdot}yH_2O$ depended on the molar ratio of $Mg_2O/MgCl_2$, the concentration of Mg^{2+} ions, the pH value in the solution system and the reaction temperature.

$$x[Mg(OH)]^+ + xOH^- + [Mg(OH)_y]^{2-y} + 2Cl^- + y^{H+} \rightarrow xMg(OH)_2{\cdot}MgCl_2{\cdot}yH_2O \quad \text{or}$$

$$x[Mg(OH)_2] + [Mg(OH)_y]^{2-y} + 2Cl^- + yH^+ \rightarrow xMg\ (OH)_2{\cdot}MgCl_2{\cdot}yH_2O \quad (20)$$

The phase form 2 (2-1-2and 2-1-4) as in eqn. 21 and eqn. 22 can be obtained while 2 times x and 2 or 4 times y decided in eqn. 20:

$$2[Mg(OH)]^+ + 2OH^- + [Mg(OH)_2] + 2Cl^- + 2H^+ \rightarrow 2Mg\ (OH)_2{\cdot}MgCl_2{\cdot}2H_2O \quad (21)$$

$$2\ [Mg(OH)]^+ + 2OH^- + [Mg(OH)_4]^{2-} + 2Cl^- + 4H^+ \rightarrow 2Mg(OH)_2{\cdot}MgCl_2{\cdot}4H_2O \quad (22)$$

The phase form 9 (9-1-4 and 9-1-5) as in eqn. 23 and eqn. 24 can be obtained while 9 times x and 4 or 5 times y decided in eqn. 20:

$$9[Mg(OH)_2] + [Mg(OH)_4]^{2-} + 2Cl^- + 4H^+ \rightarrow 9Mg(OH)_2{\cdot}MgCl_2{\cdot}4H_2O \quad (23)$$

$$9[Mg(OH)_2] + [Mg(OH)_5]^{3-} + 2Cl^- + 5H^+ \rightarrow 9Mg(OH)_2{\cdot}MgCl_2{\cdot}5H_2O \quad (24)$$

The deduction as eqn. 21 to 24 well proved that the solid phase changed from $Mg(OH)_2$, $Mg(OH)_2$ + 9-1-4 phase, 9-1-4 phase, 2-1-4 phase, to 2-1-2 phase with the change of molar ratio of $MgCl_2$ from 2 mol L^{-1}, 4 mol L^{-1}, 5 mol L^{-1} and to above. the 2-1-4 phase is replaced by the 2-1-2 phase above a solution concentration of about 7 mol of $MgCl_2$/kg H_2O, at low magnesium chloride concentrations brucite, $Mg(OH)_2$, is existent and can still be isolated from 3 mol of $MgCl_2$/kg H_2O as pure phase. brucite is metastable from approximately 2 mol of $MgCl_2$/kg H_2O up to higer concentrations with transition into the 9-1-4 phase in the table of the solubility data[7,8] in the system MgO-$MgCl_2$-H_2O at 120 °C. The pH measured indicate that the solution system display alkalinity below a solution concentration of about 3 mol of $MgCl_2$/kg H_2O and then transition to acidity from 4 to above in Fig. 6, as a result of the phase transition. The growth unit for 9-1-4 and 9-1-5 phase, $[Mg(OH)_2]$, $[Mg(OH)_4]^{2-}$ and $[Mg(OH)_5]^{3-}$ accordingly other than $[Mg(OH)_6]^{4-}$ octahedra existed in the solution at low concentration of below 3 mol of $MgCl_2$/kg H_2O, and the growth unit for 2-1-2 and 2-1-4 phase, $[Mg(OH)]^+$, $[Mg(OH)_2]$ and $[Mg(OH)_4]^{2-}$ accordingly existed in the solution at concentration of above 4 mol of $MgCl_2$/kg H_2O[3]. The transition from 9-1-4 and 9-1-5 phase just the temperature from 160 to 180 °C[3,5].

The phase form 3-1-8 and 5-1-8 as eqns. 25 and 26 can be obtained by combination of eqns. 9 and 18 and 5 times eqn. 6 and 15, respectively. Thus it can be seen that the growth unit for 3-1-8 and 5-1-8 phase, $[Mg(OH)_2$, $Mg(OH)_5]^{3-}$ and $[Mg(OH)_3]^{1-}$ accordingly other than $[Mg(OH)_6]^{4-}$ octahedra existed in the solution below 100 °C, the results were in excellent agreement with data reported in the isothermal section of the system MgO-$MgCl_2$-H_2O at 22 °C to 28 °C, And the phase form transition from Mg $(OH)_2$, Mg $(OH)_2$ + 5-1-8 phase, 5-1-8 phase, to 3-1-8 phase with the increase of the concentration of $MgCl_2$[4,7].

$$3[Mg(OH)_2] + 3OH^- + 3H^+ + [Mg(OH)_5]^{3-} + 2Cl^- + 5H^+ \rightarrow 3Mg(OH)_2{\cdot}MgCl_2{\cdot}8H_2O \quad (25)$$

$$5[Mg(OH)_2] + 5OH^- + 5H^+ + [Mg(OH)_3]^- + 2Cl^- + 3H^+ \rightarrow 5Mg(OH)_2{\cdot}MgCl_2{\cdot}8H_2O \quad (26)$$

The other unconfirmed form such as phase 3-1-6 and 5-1-3 can be obtained by combination of 3 times eqns. 3 and 18 and 5 times eqns. 3 and 15, as seen in eqns. 27 and 28, respectively.

$$3[Mg(OH)^+ + 3OH^- + [Mg(OH)_6]^{4-} + 2Cl^- + 6H^+ \rightarrow 3Mg(OH)_2{\cdot}MgCl_2{\cdot}6H_2O \quad (27)$$

$$5[Mg(OH)_2] + [MgOH_3]^- + 2Cl^- + 3H^+ \rightarrow 5Mg(OH)_2{\cdot}MgCl_2{\cdot}3H_2O \quad (28)$$

The form 9-1-8 can be obtained as seen in eqn. 29 to eqn. 34 by combination of 9 times eqn. 3, y decided from 1, 2, 3, to 6 in eqn. 20 and relatively H_2O were added respectively.

$$9[Mg(OH)_2] + 7OH^- + 7H^+ + [Mg(OH)]^+ + 2Cl^- + H^+ \rightarrow 9Mg(OH)_2{\cdot}MgCl_2{\cdot}8H_2 \quad (29)$$

$$9[Mg(OH)_2] + 6OH^- + 6H^+ + [Mg(OH)_2] + 2Cl^- + 2H^+ \rightarrow 9Mg(OH)_2{\cdot}MgCl_2{\cdot}8H_2O \quad (30)$$

$$9\ [Mg(OH)_2] + 5OH^- + 5H^+ + [Mg(OH)_3]^- + 2Cl^- + 3H^+ \rightarrow 9Mg(OH)_2{\cdot}MgCl_2{\cdot}8H_2O \quad (31)$$

$$9[Mg(OH)_2] + 4OH^- + 4H^+ + [Mg(OH)_4]^{2-} + 2Cl^- + 4H^+ \rightarrow 9Mg(OH)_2{\cdot}MgCl_2{\cdot}8H_2O \quad (32)$$

$$9[Mg(OH)_2] + 3OH^- + 3H^+ + [Mg(OH)_5]^{3-} + 2Cl^- + 5H^+ \rightarrow 9Mg(OH)_2{\cdot}MgCl_2{\cdot}8H_2O \quad (33)$$

$$9[Mg(OH)_2] + 2OH^- + 2H^+ + [Mg(OH)_6]^{4-} + 2Cl^- + 6H_+ \rightarrow 9Mg(OH)_2{\cdot}MgCl_2{\cdot}8H_2O \quad (34)$$

Conclusion

The concentration or molar ratio of $MgCl_2/H_2O$ and the reaction temperature in the system MgO-$MgCl_2$-H_2O seriously affect the form of the basic magnesium chlorides whiskers $xMg(OH)_2{\cdot}MgCl_2{\cdot}yH_2O$, the phase form transition from $Mg(OH)_2$, $Mg(OH)_2$ + 5-1-8 phase, 5-1-8 phase, to 3-1-8 phase with the increase of the concentration of $MgCl_2$ below 100 °C and decrease in accordance with reaction temperature. The phase change from $Mg(OH)_2$, $Mg(OH)_2$ + 9-1-4 phase, 9-1-4 phase, 2-1-4 phase, to 2-1-2 phase with the change of molar ratio of $MgCl_2$ above 100 °C and phase 9-1-4 trans to 9-1-5 while temperature from 160 to 180 °C.

The higher temperature and the pH value in the solution, the amorphous hydroxide $[Mg(OH)_2]$ was the mainly crystallization growth unit and $[Mg(OH)^+$, OH^- on the contrary. $[Mg(OH)_y]^{2-y}$ (y = 0,... 6) anion coordination-polyhedras was always the basic crystallization growth unit and change with the pH value of solution. In conclusion, the amorphous hydroxide $[Mg(OH)_2]$, $[Mg(OH)_y]^{2-y}$ (y = 0,...6) anion coordination-polyhedras, ions Mg^{2+}, Cl^- and H_2O/OH^- were the basic crystallization growth units in formation of the basic magnesium chlorides whiskers $xMg(OH)_2{\cdot}MgCl_2{\cdot}yH_2O$.

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REFERENCES

1. W.L. Fan, S.X. Sun, L.P. You, G.X. Cao, X.Y. Song, W.M. Zhang and H.Y. Yu, *J. Mater. Chem.*, **13**, 3062 (2003).
2. W.L. Fan, X.Y. Song, S.X. Sun and X. Zhao, *J. Cryst. Growth*, **305**, 167 (2007).
3. Z.Q. Yang, S. Cingarapu and K.J. Klabunde, *J. Sol-Gel Sci. Technol.*, **53**, 359 (2010).
4. R.E. Dinnebier, D. Freyer, S. Bette and M. Oestreich, *Inorg. Chem.*, **49**, 9770 (2010).
5. J.S. Wu, Y.K. Xiao, J.Y. Su, T.T. Deng, J.R. Feng, Y.Y. Mo and M. Zeng, *Sci. China Technol. Sci*., **54**, 682 (2011).
6. B. Tooper and L. Cartz, *Nature*, **211**, 64 (1966).
7. B. Matkovic and J.F. Young, *Phys. Sci*., **246**, 79 (1973).
8. C.A. Sorrell and C.R. Armastrong, *J. Am. Ceram. Soc*., **59**, 51 (1976).
9. Q. Wei and C.M. Lieber, *Mater. Res. Soc. Symp. Proc*., **581**, 3 (2000).
10. M. Altmaier, V. Metz, V. Neck, R. Muller and Th. Fanghänel, *Geochim. Cosmochim. Acta*, **67,** 3595 (2003).
11. Y.L. Xiong, H.R. Deng, M. Nemer and S. Johnsen, *Geochim. Cosmochim. Acta*, **74**, 4605 (2010).
12. Z.Y. Zhang, C.L. Dai, Q.C. Zhang, *et.al.*, *Sci. China* (*Series B*), **34,** 1501 (1991).
13. D.H. Deng and C.M. Zhang, *J. South China Constr. Univ*., **4**, 22 (1996) (in Chinese).
14. X.B. Li, E.W. Shi, Z.Z. Chen, *et. al.*, *J. Inorg. Mater.*, **23**, 238 (2008).
15. W.J. Li, E.W. Shi, W.Z. Zhong and Z.W. Yin, *J. Synth. Cryst*., **28**, 117 (1999).