



The analysis of magnesium oxide hydration in three-phase reaction system



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ABSTRACT

In order to investigate the magnesium oxide hydration process in gas–liquid–solid (three-phase) reaction system, magnesium hydroxide was prepared by magnesium oxide hydration in liquid–solid (two-phase) and three-phase reaction systems. A semi-empirical model and the classical shrinking core model were used to fit the experimental data. The fitting result shows that both models describe well the hydration process of three-phase system, while only the semi-empirical model right for the hydration process of two-phase system. The characterization of the hydration product using X-Ray diffraction (XRD) and scanning electron microscope (SEM) was performed. The XRD and SEM show hydration process in the two-phase system follows common dissolution/precipitation mechanism. While in the three-phase system, the hydration process undergo MgO dissolution, Mg(OH)₂ precipitation, Mg(OH)₂ peeling off from MgO particle and leaving behind fresh MgO surface.

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1. Introduction

Magnesium hydroxide (Mg(OH)₂), a versatile material, is widely used in the field of fire protection and environmental protection [1,2]. One of the most common ways of producing Mg(OH)₂ is hydration of magnesium oxide (MgO) which has been studied since the 1960s. The kinetics of vapor-phase hydration of magnesium oxide was studied by Layden and Brindley et al. [3]. According to the results of their research, hydration of MgO by water vapor seemed to involve two distinct steps: (1) sorption of water on the MgO surface followed by (2) chemical reaction between the solid and the absorbed water. A kinetic study of developing an MgO/water chemical heat pump was performed by Yukitaka Kato et al. [4]. It was assumed that the reactant MgO has four reaction regimes for water, i.e. regimes of (1) containment of water as fixed structural water, (2) physical adsorption of water, (3) chemical reaction with water producing Mg(OH)₂, and (4) inert portion to water. As conclude in Rocha's study [5], magnesia hydration was considered not to be affected by particles of different sizes. The mechanism consists of the following steps: (1) water adsorbs at the surface and diffuses inside porous MgO particles simultaneously; (2) oxide dissolution occurs within particles, changing porosity with time; (3) creation of supersaturation, nucleation and growth of Mg(OH)₂ at the surface of magnesia. Van der Merwe et al. [6] suggested a dissolution/precipitation process for hydration. It

consists of two distinct processes during hydration stage depending on the temperature. At high temperatures, the hydration seems to be initially governed by the dissolution of MgO (chemical control); however, as the reaction progresses, both the surface and the pores of the MgO particles are progressively covered by the Mg(OH)₂ produced. As a result, the diffusion of water is hindered inside the particles, which reduces the overall reaction rate (diffusion controlled). At low temperatures, the hydration is purely chemical controlled due to the relatively low conversion efficiency. In order to promote the hydration rate, hydrating agents (acetic acid, magnesium acetate, magnesium chloride, etc) are added into the aqueous solution. The behavior of MgO hydration in hydrating agent solution (liquid–solid) has been studied [7–10].

At present, research related to magnesia hydration mainly focuses on gas–solid or liquid–solid reaction system. In addition, more academics tend to use liquid–solid (two-phase) reaction system, because it is more close to the conventional manufacturing technology of Mg(OH)₂. To date, few studies on the gas–liquid–solid (three-phase) hydration behavior have been reported. Thus, this study was conducted to compare the hydration efficiency of the two-phase with three-phase reaction system, analyze the hydration product, and discuss the hydration process in three-phase reaction.

2. Experiment system

2.1. Materials

MgO: The light yellow powder with particle size distribution of 50–70 μm was produced through calcining magnesium carbonate

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from Yinkou, China. The Chemical composition of the powder is shown in Table 1.

Citric acid (AR) was purchased from Bo di Corporation (Tianjin, China) with the purity 99.5%.

2.2. Instrumentation

X-ray power diffraction (XRD) analyses was conducted on an automated RIGAKU D/MAX-Ultima⁺, Japan and monochromated CuK α radiation. The powdered samples were pressed into the holder using a glass slide.

Scanning electron microscope (SEM) analyses was conducted on an automated ZEISS SUPRA 55 SAPHIRE, Germany. Measuring range is 12–1,000,000 \times .

2.3. Citric acid reactivity test

The citric acid method of determination of powder reactivity was conducted before hydration experiment. In this method, a 0.07 mol/L citric acid solution was prepared, and slurry of 1.50 g of powdered MgO, in the among of 100 ml and 0.07 mol/L citric acid solution was shaken, with phenolphthalein as indicator, until the color changed from white to pink. The time it takes for the slurry to change color is then reported as the citric acid reactivity [11,12].

Table 1
Chemical composition of the raw material.

Element	Mass(%)
SiO ₂	2.46
Al ₂ O ₃	1.44
Fe ₂ O ₃	3.33
CaO	2.02
MnO	1.05
MgO	85.23
LOI	4.27
Total	99.80

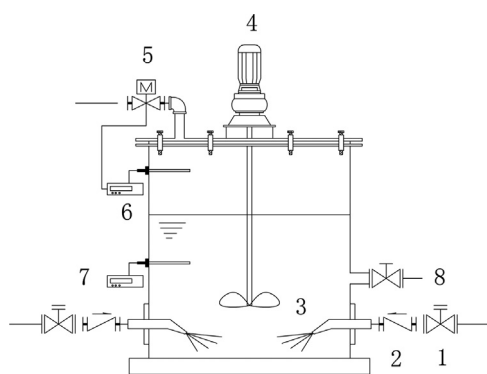


Fig. 1. The chat of hydration experiment for three-phase reaction system (1) Vapor pressure stabilization valve; (2) Check valve; (3) Steam nozzle; (4) Stirrer; (5) Magnetic valve; (6) Pressure sensor; (7) Temperature sensor; (8) Sample outlet.

Table 2
The results of citric acid reactivity test.

MgO(g)	Citric acid(ml)	Color changing time(s)
1.5012	100 (313 K)	48
1.5023	100 (313 K)	50
1.5015	100 (313 K)	43

2.4. Hydration procedure

The experiments of two-phase reaction system were carried out in a glass conical flask of 250 ml, stirred at a constant rate of 900 rpm in a magnetic stirring water bath pot (ZNCL-S, Yuezhong, Shanghai). The top of the glass conical flask was connected to a reflux tank to prevent the evaporation of water. In this method, 10 g powdered MgO and 90 ml deionized water were added to the glass conical flask at the specified temperature and the slurry was kept under constant agitation for a specified period of time.

The experiments of three-phase reaction system were carried out in an independent design self-made pressure vessel. The reaction equipment was shown in Fig. 1. In this method, 1000 mL slurry of 10% (w/w) MgO and deionized water was injected into the vessel, then the vapor was injected into vessel, and finally the stirring rate was set at 900 rpm. In order to stabilize the inlet vapor pressure at 0.25 MPa and the pressure in the container at 0.2 MPa, the linkage of pressure sensor and Magnetic valve was installed. The reaction temperature was gained from the temperature sensor.

Both approaches adopted timing sampling method. After sampling, the pulp was then immediately vacuum filtered through a membrane with pores of 0.8 μ m diameter. The solid remaining in the filtering was thoroughly washed with ethanol, and then

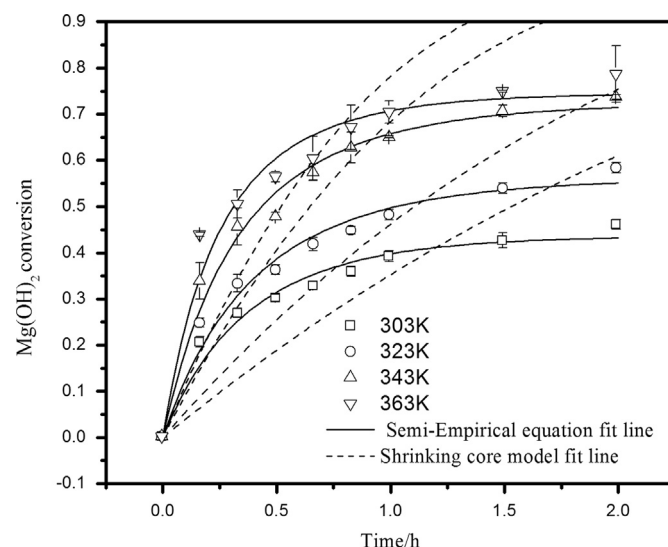


Fig. 2. Hydration rate of two-phase reaction system.

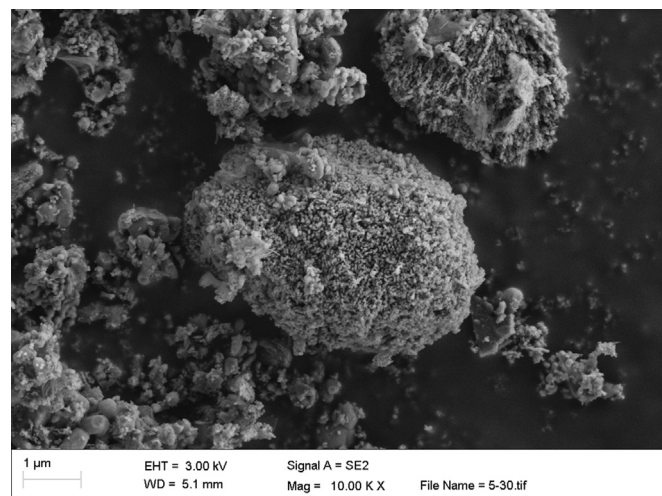


Fig. 3. SEM images of MgO.

filtered again. The sample was dried at 378 K for 2 h to eliminate water not chemically bonded and then weighed. After that it was transferred to the muffle furnace drying at 873 K for 2 h and then weighed. The conversion of this reaction (α) was based on Eq. (1):

$$\alpha = \frac{m_2 - m_3}{m_3 - m_1} \times \frac{M_1}{M_2} \times f \quad (1)$$

where m_1 is the mass of the crucible, g; m_2 is the mass of the samples after drying 378 K, g; m_3 is the mass of the samples after drying 873 K, g; M_1 is the molar mass of water, g/mol; M_2 is the molar mass of magnesium oxide, g/mol; f is a correction factor which accounts for the presence of impurities in the magnesite and is equal to 1.176 ($f = 1/0.85$) [7].

Table 3
Fitted parameters a and b from experimental data of liquid–solid reaction system.

$T(K)$	a	Standard error	b	Standard error	R^2
303	−2.16	0.33	1.24	0.13	0.96
323	−1.80	0.29	1.48	0.15	0.97
343	−1.78	0.27	2.29	0.21	0.98
363	−3.28	0.62	3.10	0.46	0.96

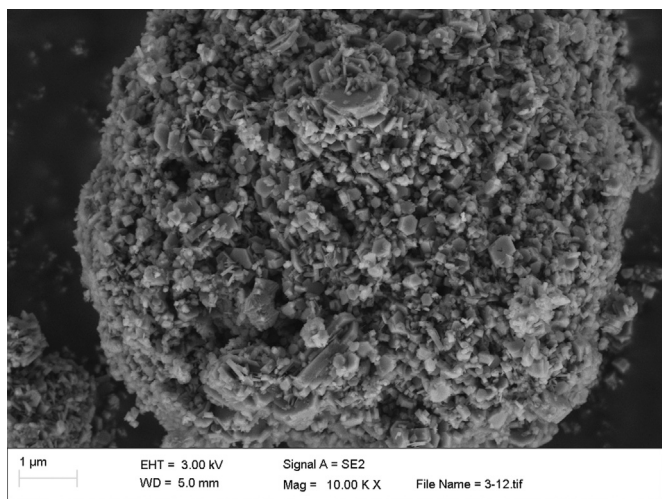


Fig. 4. SEM images of the hydration products of two-phase reaction system.

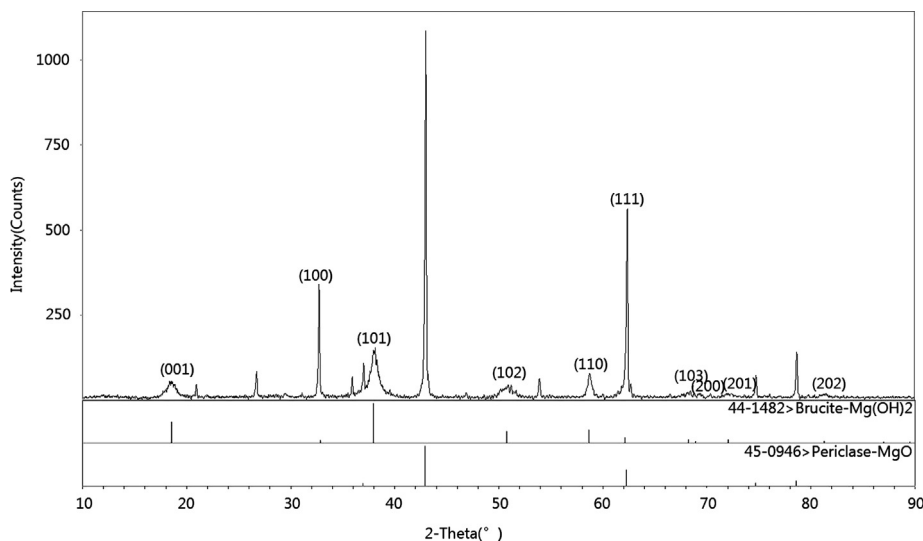


Fig. 5. XRD spectrogram of the hydration products of liquid–solid reaction system.

3. Results and discussion

3.1. Results of citric acid reactivity test

The reactivity of MgO was measured through the citric acid test in which the time needed for the MgO sample to neutralize the citric acid solution was measured. Industry uses values of less than 60 s for highly reactive (soft burnt) MgO. Medium reactive MgO gives a measurement between 180 and 300 s, while a low reactivity MgO (hard burnt) gives a value of more than 600 s and dead-burnt MgO approximately 900 s [13]. The reactivity of the MgO used in the experiments was highly reactivity light-burnt powder (Table 2).

3.2. Liquid–solid reaction system

Fig. 2 depicts the hydration rate of two-phase reaction system in different hydration temperatures. The graph shows that hydration rate grows faster in the first 0.5 h. But the hydration rate starts to level off after 1 h. The hydration rate rises with the increase of hydration temperature.

Smithson and Bakhshi [14] proposed the shrinking core model under the liquid–solid system. According to their model, the reaction happens on the surface of the MgO particles. As the reaction progresses, MgO particles begin shrinking. The classical shrinking core model equation is calculated according to the following equation:

$$kt = 1 - (1 - \alpha)^{1/3} \quad (2)$$

In Eq. (2) α is the extent of conversion, t is the reaction time (h) and k is the apparent reaction constant (h^{-1}).

The shrinking core model assumes that MgO is spherical particle, on whose surface the reaction happens. But MgO particles are porous structure (Fig. 3). The reaction of MgO with water occurs at the whole external surface and inside the pores of the particles. The porosity changes with time showing a non-linear relationship. Birchall et al. [15] introduced two empirical parameters a and b to describe porosity changing with time. A semi-empirical equation based on Arrhenius formula was as follows:

$$C_2(t) = C_1 - C_1 \exp\left[\frac{b}{a}(1 - e^{at})\right] \quad (3)$$

where C_1 is the initial concentration of MgO, C_2 is the concentration of $\text{Mg}(\text{OH})_2$. The conversion can be obtained through the

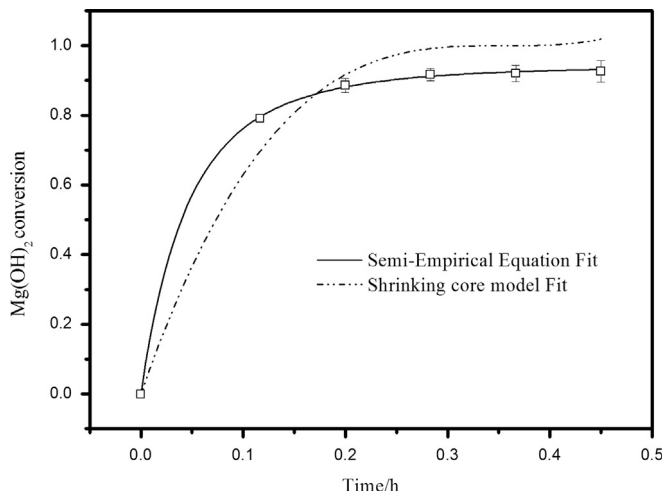


Fig. 6. Hydration rate of three-phase reaction system.

Table 4

Fitted parameters from experimental data of gas–liquid–solid reaction system.

Semi-empirical model	a	Error	b	Error	R^2
	−7.22	0.35	20.14	0.60	0.99
Classical shrinking core model	k			Error	R^2
	2.82			0.35	0.96

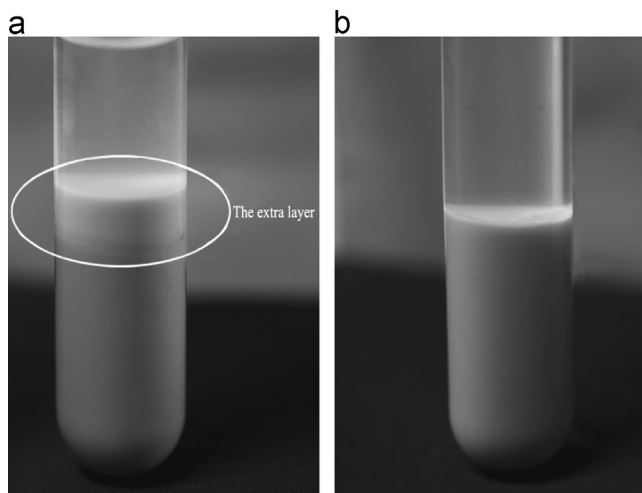


Fig. 7. Comparison of the hydration products of the two systems (a) three-phase reaction system (b) two-phase reaction system.

following equation:

$$\alpha = 1 - \exp\left(\frac{b}{a}(1 - e^{at})\right) \quad (4)$$

According to Fig. 2, the classical shrinking core model was found to be inadequate to describe the hydration of MgO with high standard error. According to the values of R^2 (Table 3), the semi-empirical model well described the experimental data which was obtained in the present work.

From the SEM images of the hydration products of two-phase reaction system (Fig. 4), it can be found that both the surface and the pores of magnesia particles are covered by the hexagonal hydroxide. Obviously the main components of the products (Fig. 5) are MgO and $\text{Mg}(\text{OH})_2$.

The dissolution/precipitation mechanism is well accepted in the literature. At higher temperature, both MgO dissolution and $\text{Mg}(\text{OH})_2$ precipitation are promoted. Thus, the hydration rate rises with the increase of hydration temperature. But as the reaction progresses, both the surface and the pores of the MgO particles are progressively covered by the $\text{Mg}(\text{OH})_2$ produced. As a result, the diffusion of water is hindered inside the particles thus reducing the overall reaction rate. Therefore, the hydration rate grew faster at first, and then tended to level off. This viewpoint is also verified in the experiment. Therefore, it can be concluded that the hydration process of two-phase reaction system follows common dissolution/precipitation mechanism. Because the surface of MgO particle is porosity and there was no evidence of shrinking process, the shrinking core model was found to be inadequate to describe the hydration process with a relatively great deviation, whereas the semi-empirical model properly described the experimental data by considering the porosity change.

3.3. Gas–liquid–solid reaction system

Fig. 6 depicts the curve of three-phase reaction system hydration rate changing with time. At the beginning of the experiment, the water temperature was 293 K. After 7 min the temperature

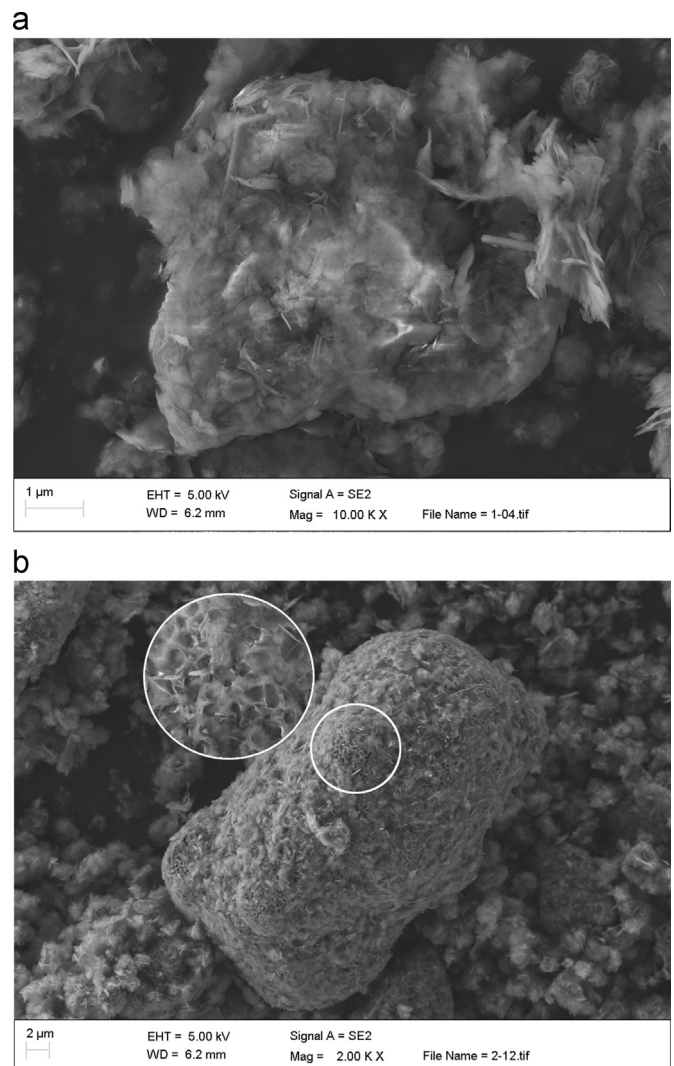


Fig. 8. SEM images of the hydration products of three-phase reaction system (a) SEM images of the supernatant layer products (b) SEM images of the underlying products.

sensor showed 363 K, then remained in the range of 363–366 K. As shown in Fig. 6, hydration rate grows faster in the first 0.2 h. It starts to level off after 0.2 h, remaining over 0.9. Both the hydration rate and the efficiency are more substantially promoted than two-phase reaction system.

Experimental data was fitted by both the classical shrinking core model and the semi-empirical model. According to the values of R^2 shown in Table 4, the semi-empirical model and the classical shrinking core model both well described the experimental data which was obtained in the present work. It can be concluded that the hydration behavior in three-phase reaction system is well fitted for the hypothesis of the classical shrinking core model and the semi-empirical model.

Fig. 7 shows the images of the hydration products in the two reaction systems. According to the images, it is obvious that there exist two layers of precipitate (Fig. 7(a)) in hydration products of the three-phase reaction system. However, the hydration products (Fig. 7(b)) are not layered in the two-phase reaction system. The distinct difference could indicate that different hydration behaviors occurred in the two systems, respectively.

The supernatant layer products of three-phase reaction system are amorphous substance (Fig. 8(a)), packing together loosely. According to Fig. 8(b), the surfaces of MgO particles are partially covered by hydroxide, revealing some pits. Some of the products are hexagonal sheets; others are not fixed shape but with fuzzy outline. According to Fig. 9, the supernatant layer products are Mg(OH)₂ and the underlying products are a mixture of MgO and Mg(OH)₂. Combining Figs. 8 and 9, it could be obtained that the supernatant layer products are loose packing of Mg(OH)₂, Mg(OH)₂ which peel off from the surface of MgO. Because of the loose packing and relative less density, the flocs float on the surface of the underlying products. The pits in the underlying products are the fresh oxide surfaces left by the peeling-off Mg(OH)₂.

The peeling-off mechanism was first put forward by Nakanishi [16]. In his study, there were three phases in the process of hydration in magnesium acetate aqueous: In the initial stage, MgO dissolution followed by Mg(OH)₂ forms and covers each magnesia particle; In second process stage, the hydroxide layer starts cracking and peeling off from the mother magnesia particle; In the last process stage, all small magnesia particles are totally

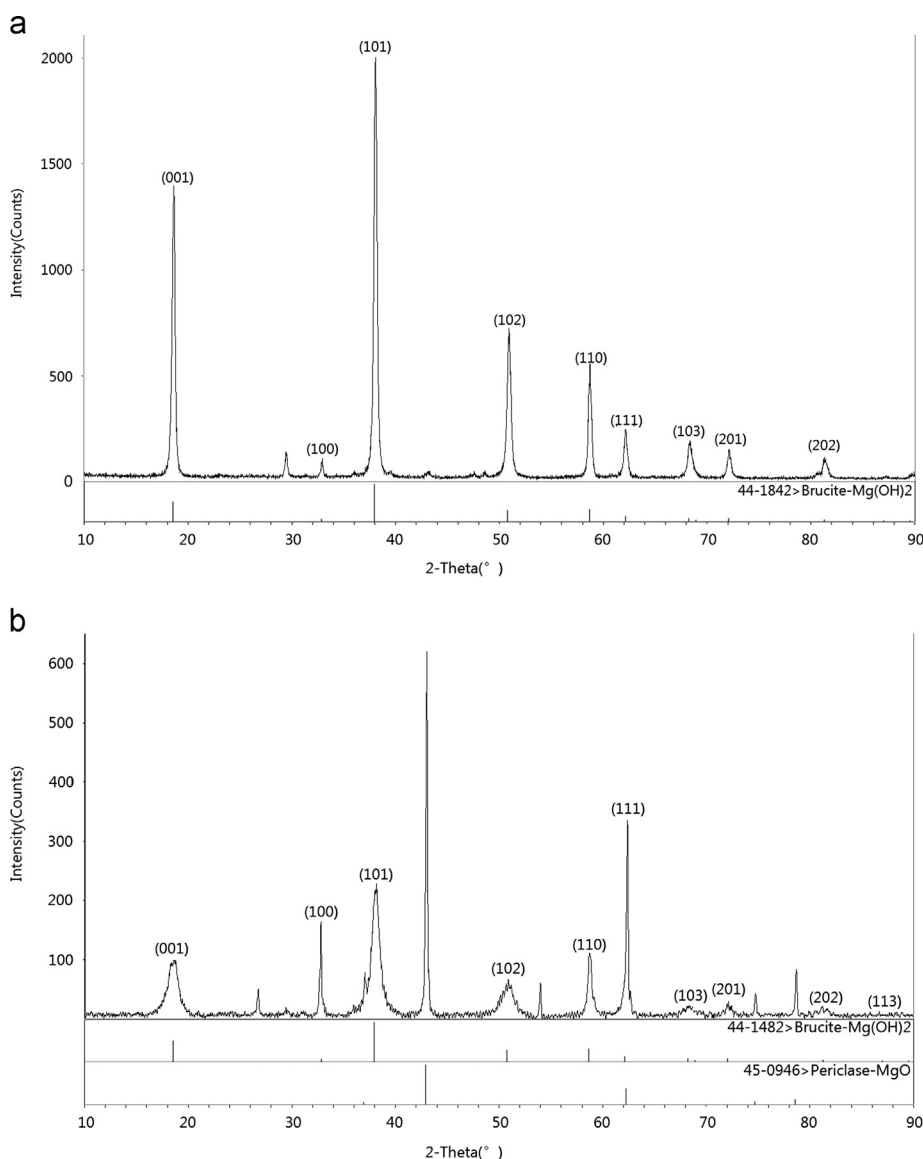


Fig. 9. XRD spectrogram of the hydration products of three-phase reaction system (a) XRD spectrogram of the supernatant layer products (b) XRD spectrogram of the underlying products.

converted to magnesium hydroxide, while the few relatively large magnesia particles continue to hydrate very slowly. Filippou denied the existence peeling-off process in his study, because the marked particles of magnesia were not found in the partially hydrated solid samples [7]. But in present experiment, according to the images of three-phase reaction system, there exist some pits in the surface of magnesium oxide particles. In addition, it is obvious that there exist two layers of precipitate in hydration products of the three-phase reaction system. From the SEM and XRD images, it can be obtained that the supernatant layer products are loose packing of $\text{Mg}(\text{OH})_2$, which peel off from the surface of MgO. And the underlying products are a mixture of MgO and $\text{Mg}(\text{OH})_2$.

Therefore, it can be concluded that there exists a peeling-off process in the three-phase system. Unlike Nakanishi's research, the solution used in the present experiment was deionized water rather than magnesium acetate solution. So the peeling-off process should be a physical process. In the three-phase reaction system, the high pressure steam was directly injected into water. Water directly contacted with high pressure steam and quickly overheated, with the impact similar to the "microexplosion" phenomenon. The strong impact forced the magnesium hydroxide to peel off (physical) from the surface of the MgO particles, leaving behind a fresh oxide surface to be attacked by water again. This phenomenon is quite similar to the hypothesis of shrinking core model that the diameter of the particles progressively decreases. Therefore, the shrinking core model can fit the hydration of three-phase reaction system. It becomes more and more difficult to peel off the $\text{Mg}(\text{OH})_2$ as the MgO particle size decreases consistently. Meanwhile it is more difficult to peel off the $\text{Mg}(\text{OH})_2$ in the pores, thereby causing the porosity of MgO to reduce. Accordingly, the semi-empirical model can properly describe the experimental data.

Therefore, the MgO hydration process of three-phase reaction system based on the dissolution/precipitation mechanism can be concluded as follows: (1) MgO dissolution; (2) $\text{Mg}(\text{OH})_2$ precipitation; (3) $\text{Mg}(\text{OH})_2$ layer covers surfaces and pores of MgO particles; (4) $\text{Mg}(\text{OH})_2$ layer cracks and peels off (physical) from MgO particle; (5) Another dissolution/precipitation process.

4. Conclusions

In summary, as reported in the previous study, the hydration process of two-phase reaction system follows common dissolution/precipitation mechanism. While in the three-phase reaction system, there exists a peeling-off process. In the initial stage, just

like the dissolution/precipitation process, $\text{Mg}(\text{OH})_2$ forms and covers the surface and pores of the MgO particles. Then, the layer starts cracking and peeling off from the mother magnesia particles by the impact of steam. Finally, the fresh MgO surface which left behind by peeling-off $\text{Mg}(\text{OH})_2$ is attacked by water again. It can be concluded that the peeling-off process exclusively causes the higher hydration rate and efficiency.

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