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

Xiaojia Tang, Lin Guo, Chen Chen, Quan Liu, Tie Li, Yimin Zhu*

Institute of Environmental Remediation, Dalian Maritime University, China

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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.

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

* Correspondence to: Institute of Environmental Remediation, Dalian Maritime University, Dalian, Liaoning, 116026, China. Tel.: +86 411 847 26992.
E-mail address: ntp@dlmu.edu.cn (Y. Zhu).

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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 Cu$K\alpha$ 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 SAPPHIRE, Germany. Measuring range is 12–1,000,000 ×.

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_2O_3	1.44
Fe_2O_3	3.33
CaO	2.02
MnO	1.05
MgO	85.23
LOI	4.27
Total	99.80

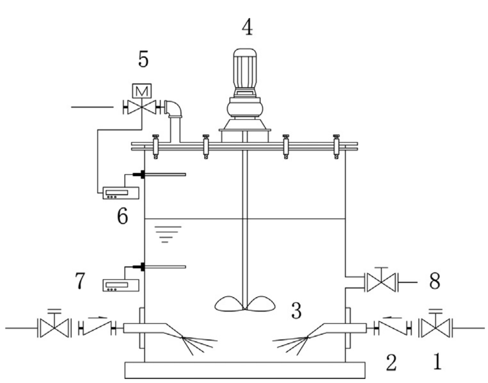

Fig. 1. The chat of hydration experiment for three-phase reaction system (1) Vapor pressure stabilization valve; (2) Check valve; (3) Steam nozzle; (4) Stirrer; (5) Magnetic valve; (6) Pressure sensor; (7) Temperature sensor; (8) Sample outlet.

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 μm diameter. The solid remaining in the filtering was thoroughly washed with ethanol, and then

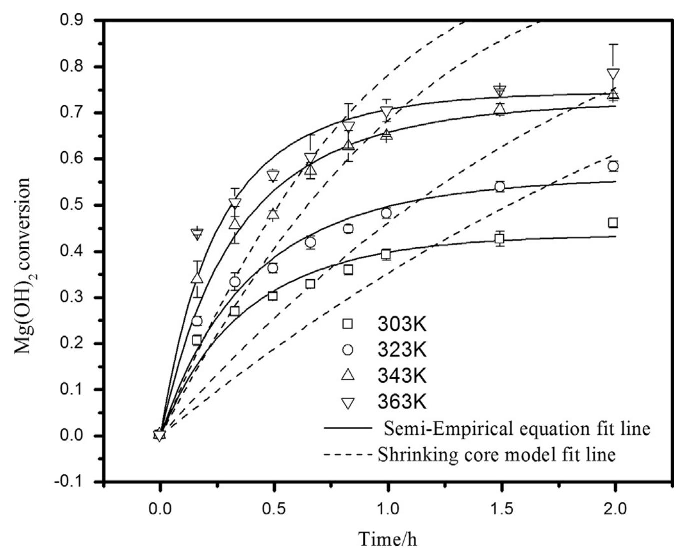

Fig. 2. Hydration rate of two-phase reaction system.

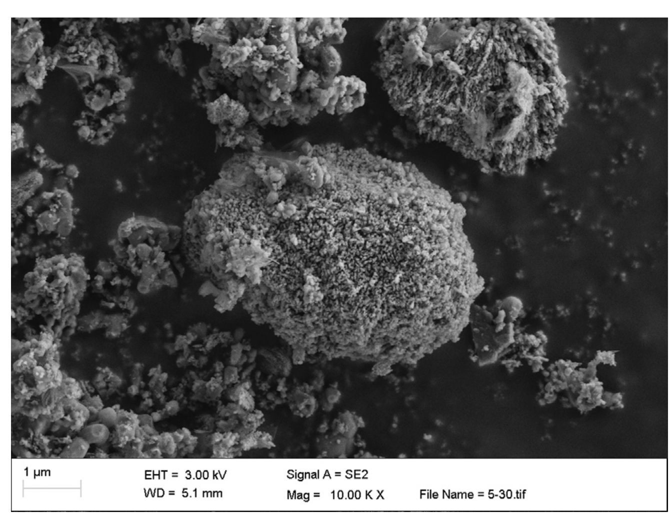

Fig. 3. SEM images of MgO.