研 究

Effect of Ultrasonic Irradiation on Hydration of MgO Powder

Naoyo Enomoto, Masumi Katsumoto and Zenbe-e Nakagawa

Res. Lab. Eng. Mat., Tokyo Institute of Technology, 4259 Nagatsuta Midori-ku, Yokohama 227.

Received January 11, 1993

High-power ultrasound was applied during the hydration of MgO fine powders in order to see the effect of ultrasound in a heterogeneous fluid where the dissolution of MgO particles and the precipitation of $\text{Mg}(\text{OH})_2$ are included. The results obtained showed that the irradiation of ultrasound fairly promotes the dissolution of MgO, which is the rate-determining step in the reaction, and that it promotes the nucleation of $\text{Mg}(\text{OH})_2$, which has resulted in the reduction of crystallite sizes of the $\text{Mg}(\text{OH})_2$ precipitated.

1 Introduction

Sonochemistry, where the energy of ultrasonic waves is applied to a chemical system, is now being considered potential for the powder processings.¹⁻⁴⁾ It is known that a high-power ultrasound can promote/alter chemical reactions,^{5,6)} nucleation, and crystal growth.³⁾ It is then expected that the use of ultrasound may produce the powders with controlled sizes and homogeneities. We have reported so far on the sonochemical precipitation from homogeneous solution.²⁻⁴⁾ In such solutions that are precipitating, the powders/precipitates are "built up" from the reactions among ions and molecules. Action of ultrasound in these homogeneous systems should be on a few nm scale.

Chemical effects of ultrasound are in general attributed to cavitation, which means the formation and collapse of microbubbles in a solution subjected to the extreme pressure changes. There are numer-

ous factors affecting cavitation.⁷⁾ Especially, what can be an origin to nucleate a cavity is definitely influential on the intensity of cavitation; they are the species and the amount of the gases dissolved in the solution, the wall of the container, and solid particles or dust in the solution, etc.

In the present study, a high-power ultrasound was applied during the hydration of MgO fine powder in an aqueous solution. This system is considered heterogeneous in that the "observable" solid particles are already present in the ultrasonic-driven fluid, and the reaction here includes the dissolution of MgO (periclase) and the precipitation of $\text{Mg}(\text{OH})_2$ (brucite).

The aim of this study is to learn feasibilities of "sonochemical powder processing" in the heterogeneous system including the dissolution-precipitation processes.

2 Experimental

2.1 Samples Preparation

Ultrafine powder of MgO (Ube Chem.Ind., 20-80nm in diameter) was hydrated in distilled water at the mixing ratio of 1g MgO to 100cm³ H₂O. Hydration temperature was kept at 25°C through all the experiments in this study. In order to change the environment of hydration, the initial pH of H₂O was varied at 1.6, 5.9, and 11.9 by adding a suitable amount of H₂SO₄ or NaOH. The notations in this report for these three kinds of hydrating solutions are "A" for 1.6(acid), "N" for 5.9(neutral), and "B" for 11.9(base), respectively. The hydrating pH values of each solution, however, were altogether in basic region since the solution becomes basic as soon as MgO powders are added, as shown in Fig.1; that is, the "hydrating" pH values in practice are 9.8(A), 10.7(N), and 11.6(B). Hydration of MgO powders proceeded at these values in each solution.

Irradiation of ultrasound was executed by using ultrasonic homogenizer (Branson, model 450) at frequency of 20kHz and input power of 70W. Since the ultrasonica-

tion increases the temperature of the solution, external cooling was applied to keep it below 25°C. The notation in this study for the sample prepared with ultrasonic homogenizer is "USH", while that without ultrasonic treatment is "MS" (mechanical stirring).

After hydrated for fixed durations, the powders/precipitates were separated from the solution by sucking filtration or centrifugal separation at 3000rpm, washed by ethanol, and then dried in a 120°C oven for 2hours.

2.2 Evaluation

The progression of hydration was estimated by the following parameter,

$$\frac{B}{B+P} (\%) = \frac{\text{Brucite}[101]}{\text{Brucite}[101] + \text{Periclase}[200]}$$

, which was calculated from the peak area in X-ray diffraction patterns (XRD). Also, Crystallinity of the Mg(OH)₂ precipitated was estimated from the XRD patterns by measuring the peak broadness at half maximum (HPW; half peak width). Morphologies of the samples were observed by transmission electron microscope (TEM).

3 Results and Discussion

3.1 Effect of pH values in the MS-samples

Figure 2 shows the TE micrographs of the MgO raw powders, the sample A-MS, and the B-MS. Difference in pH values have resulted in the different morphology of Mg(OH)₂ precipitated; that is, needle-shaped particles with ≈10x150nm are observed in the sample A-MS, while, thicker columnar particles with ≈30x150nm are seen in the B-MS. The sample N-MS was similar to the A-MS. It is obvious that the crystallinity of Mg(OH)₂ is superior in the sample B-MS. The amount of Mg(OH)₂ precipitated increases with increasing time and decreases

Fig.1 Changes in pH values during hydration

Fig.2 TE micrographs of raw (i) and hydrated (ii,iii) MgO powders

ing hydrating pH, as shown in Fig.3. From these results, mechanisms for the hydration of MgO seem to be different in different pH's. Table 1 shows some equilibrium data for the hydrating solutions.

At lower pH, the dissolution of MgO must be accelerated but the degree of supersaturation of Mg(OH)_2 should be low since $[\text{OH}^-]$ is low. Thus, its crystallinity is poor. While at higher pH, the precipitates can grow larger but slower due to low solubility of MgO.

Fig.3 Hydration of MgO in different pH's.

Table 1 Equilibrium data for the hydration⁸⁾.

Solubility of MgO ; $1.5 \times 10^{-4} \text{ mol/kg H}_2\text{O}$
 Solubility Product of Mg(OH)_2 ; $K_{\text{sp}} = 1.2 \times 10^{-11}$

pH	$[\text{H}^+]$	$[\text{OH}^-]^2$	$[\text{Mg}^{2+}]$
9.8	1.6×10^{-10}	4.0×10^{-9}	$3.0 \times 10^{-3} \text{ mol/l}$
10.7	2.0×10^{-11}	2.5×10^{-7}	4.8×10^{-5}
11.6	2.5×10^{-12}	1.6×10^{-5}	7.5×10^{-7}

3.2 Effect of ultrasound on dissolution and precipitation

The separation of the USH-samples from solutions could not be executed by the sucking filtration since the ultrasound remarkably disperses the MgO powders into finer sizes than the channels in the filter papers. So, the centrifugal technique was employed to separate the USH samples. Figure 4 shows the result of the gravitation test, where ultrasonically dispersed MgO powders were settled quietly in a test tube and their sedimentation height was recorded as a function of time. Due to the nature of the interactions among MgO particles, they agglomerates in the solution A and the B. Therefore, the samples A-USH and the B-USH can be easily separated by centrifuge. Time required for the separation of the samples A-USH and the B-USH was about 20 minutes, which may be disre-

Fig. 4 Gravitation of MgO powders at different pH's.

garded in the samples hydrated for 160 minutes. On the other hand, the sample N-USH could not be separated by a 60 minutes' centrifuge. Followingly, the effect of ultrasound on the hydration is considered as for the A-USH and the B-USH samples which were hydrated for 160 minutes, as summarized in Table 2. It should be noted in Table 2 that the centrifuge separation process increases the formation of $\text{Mg}(\text{OH})_2$ compared to filtration but that it scarcely affect the peak broadness of $\text{Mg}(\text{OH})_2$.

Figure 5 illustrates the change in the HPW of $\text{Mg}(\text{OH})_2$ precipitated at different conditions. In the series "A", the apparent crystallinity of $\text{Mg}(\text{OH})_2$ curiously decreases as a function of time. Judging

from the TE micrograph in Fig. 2(ii), $\text{Mg}(\text{OH})_2$ particles in this series are defective. The HPW value of the sample A-MS increases to 3.05×10^{-2} at 220 min and decreases to 2.27×10^{-2} after 24 hours' treatment. Growth of the needle-shaped $\text{Mg}(\text{OH})_2$ crystals would include the dissolution of $\text{Mg}(\text{OH})_2$ as well as dissolution of MgO. Comparing the samples A-MS and the A-USH in Table 2, the effect of ultrasound in the series "A" is notable in that the formation of brucite is completed in the A-USH. It is inferred that ultrasound has promoted the dissolution of MgO, for the mass transfer in the solution would be remarkably increased and the surface area

Fig. 5 Changes in crystallinity of $\text{Mg}(\text{OH})_2$ precipitated at different pH's.

Table 2 Effect of ultrasound on hydration of MgO.

Sample name	A-USH	A-MS		B-USH	B-MS	
initial pH	1.6			11.9		
hydration pH	~9.8			~11.6		
separation method	cent.	cent.	filt.	cent.	cent.	filt.
B/(B+P) (%)	100	85.1	71.5	50.5	63.7	37.4
Mg(OH) ₂ HPW (x 0.01rad)	[101] 2.19 ----- [001]	2.68 -----	2.61 -----	1.35 1.30	0.85 1.03	0.86 0.98

of the MgO particles should be enhanced by effect of ultrasonic dispersion.

In the series "B", on the other hand, $\text{Mg}(\text{OH})_2$ crystals grow gradually in due course of time. Ultrasound apparently lowers the crystallinity of $\text{Mg}(\text{OH})_2$. In the presense of intense cavitation, collision among the $\text{Mg}(\text{OH})_2$ molecules which come out of supersaturated solution should be extremely promoted. Then, those $\text{Mg}(\text{OH})_2$ molecules would be consumed for nucleation rather than growth.³⁾ Consequently, the size of the crystals which precipitated in a ultrasonic field should be smaller and homogeneous.

Fig.6 TE micrographs of the ultrasonically-hydrated MgO powders.

TE micrographs in Fig.6 are consistent with the above discussion, for the sample A-USH contains larger needle-like particles than the A-MS; and the $\text{Mg}(\text{OH})_2$ particles in the sample B-MS appear to be rigider than the B-USH.

4 Summary

MgO ultrafine powders were hydrated in an ultrasonic-driven water at different pH's. In case of the hydration at higher pH, the ultrasonic treatment decreases the crystallite size of the $\text{Mg}(\text{OH})_2$ precipitated. This is due to the promotion of nucleation caused by ultrasonic waves. While at lower pH, ultrasonic waves have accelerated the dissolution of MgO and therefore have fastened the hydration processes.

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