Precipitation Rate Investigation on Precipitated Magnesium Carbonate by Ultrasonic of Magnesium Bicarbonate

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Abstract. Indonesia has a lot of dolomite reserves. Magnesium carbonate can be synthesized from dolomite. One of the main steps that requires a lot of energy are magnesium bicarbonate thermal decomposition. Magnesium bicarbonate solution are heated to make magnesium carbonate as precipitate. One of the ways to improve this process are by using ultrasonic waves as energy carrier. The purpose of this study is to find the effect of ultrasonic waves heating (sonochemistry) to thermal decomposition of magnesium bicarbonate. In this work, the author conducted ultrasonic heating with the amplitude of the waves varied around 20 µm and 30 µm for 35 minutes. Conventional heating using heat plate was also conducted and compared with ultrasonic heating. Higher decomposition ratio was reached on samples heated using ultrasonic waves with the value of 85.70% compared to conventional heating with decomposition ratio of only 50.08%. Amplitude effect on decomposition ratio were also observed. Higher amplitude made decomposition rate faster.

1. Introduction
Magnesium carbonate are naturally recurring compound and mainly extracted from minerals such as limestones and dolomites. Magnesium carbonate are widely used as fireproofing and fire-extinguisher composition, neoprene rubber reinforcing agent, drying agent and color retention in foods, and in cosmetics industry[1]. Magnesium Carbonate also recognized as a safe material by the American Food and Drug Administration (FDA) and have the possibility to be useful in pharmaceutical fields[2]. With the widespread of Pidgeon process, dolomite also has become an important material for magnesium production[3]. Magnesium has a lot of application such as for automotive industry[4], [5] and implant for medical application[6].

Indonesia has very abundant dolomite reserves[7]. Dolomite is a double salts of magnesium and calcium carbonate [CaMg(CO₃)₂][8]. Indonesia largest reserves of dolomite are located in East Java Province[7], [9]. Magnesium carbonate could be extracted from dolomite by calcining dolomites to obtain a mixture of calcium carbonate and magnesium oxide. The mixture was wet-grounded to hydrate the magnesium oxide. The slurry product was then subjected to carbonation and filtered. The filtered cake is mainly consisted of calcium carbonate and the filtrate are rich in magnesium bicarbonate. Magnesium carbonate were precipitated by thermal decomposition of magnesium bicarbonate solution[10].
Thermal decomposition of magnesium bicarbonate solution is an important step to obtain high purity of magnesium carbonate because it stands as one of the energy intensive step in the process. Approximately 60% of energy consumption of MgO production process is in the thermal decomposition process[11]. Sheila and Khangaonkar studied thermal decomposition of magnesium bicarbonate solution by heating the solution in a thermostatic bath[12]. Zhao and Zhu study its kinetics and mechanism[11]. Li et al. study the effect of temperature on magnesium bicarbonate decomposition[13]. One of the methods of increasing effectiveness in thermal decomposition of magnesium bicarbonate is using ultrasonic waves to deliver the energy into the solution. New process using sonochemistry were investigated to improve the magnesium carbonate precipitation. The purpose of this study is to compare the amount and the characteristic between magnesium carbonate precipitated traditionally and by using ultrasonic waves.

2. Methods

Previous research was already conducted to obtain magnesium bicarbonate rich solution which contain 1446.42 ppm of magnesium. The solution obtained from dolomite processing, which consist of calcining the dolomite, dissolving calcined dolomite in water, carbonation the slurry, and filtration of the slurry. The solution was processed by giving ultrasonic waves with the frequency of 20 kHz. The amplitude was varied at around 20 µm and 30 µm to see the effect of amplitude on the process. Time was also varied between 10 to 35 minutes with the increment of 5 minute. To compare the result of samples processed using ultrasonic waves, magnesium bicarbonate rich solution was also heated using heating plate set to reach the maximum temperature of 90°C for 30 minutes. All sample heated using ultrasonic waves and heating plate are stirred using magnetic stirrer with the speed of 50 rpm. After going through heating process the solution was filtered to separate between the precipitated magnesium carbonate and the remaining solution. The remaining solutions were analyzed using ICP-OES and the precipitates were analyzed using XRD to see its phase, XRF to see its composition, and SEM to see its morphology. Diagram of the experiment is shown in figure 1.

3. Results

Magnesium bicarbonate solution was heated using two different ways, using ultrasonic waves and heat plate. Both ways are applied to convert the magnesium bicarbonate in the solution into magnesium
carbonate. Thermal decomposition of magnesium bicarbonate proposed by Zhao and Zhu [11] follow several steps of reaction which are Mg(HCO₃)₂ ionization reaction which consist of reaction (1), (2), (3) and (4); reaction of Mg²⁺ with CO₃²⁻ and OH⁻ which consist of equation (5) and (6); and basic magnesium carbonate formation with equation (7). The overall reaction of magnesium bicarbonate decomposition can be seen in equation (8).

\[
\begin{align*}
Mg(HCO_3)_2 \leftrightarrow M + 2HCO_3^- \\
HCO_3^- \leftrightarrow H^+ + CO_3^{2-} \\
HCO_3^- \leftrightarrow CO_3^{2-} + H_2O \\
CO_3^{2-} + H^+ \rightarrow H_2CO_3 \\
MgCO_3 \rightarrow MgCO_3 \downarrow \\
MgCO_3 \rightarrow MgCO_3 + CO_2 \downarrow \\
(x + y)MgCO_3 \rightarrow xM + y(MgCO_3) \rightarrow zH_2O \rightarrow (x + y)MgCO_3 \rightarrow zH_2O \\
(x + y)MgCO_3 \rightarrow xM + y(MgCO_3) \rightarrow zH_2O \
\end{align*}
\]

(8)

The effect of ultrasonic heating at amplitude of around 20 and 30 µm on magnesium concentration can be seen in figure 2. The effect of time of ultrasonic heating effect on the Mg concentration tend to follow a straight line because the decomposition rate of magnesium bicarbonate is relatively constant. Decomposition ratio of magnesium bicarbonate can be calculated using equation (9). \(N_0\) is defined as precipitate formed at time \(t\), while \(N_1\) is initial precipitate formed at time \(t_1\). This indicates that the reaction controlled only by one mechanism and follow zero-order mechanism.

\[
\eta = \frac{N_0 - N_1}{N_0} 
\]

(9)

Figure 2. Mg concentration changes during ultrasonic heating at amplitude of around 20 µm and 30 µm.

Ultrasonic wave creates physical effect when applied to a liquid such as micro-steaming, agitation, turbulence, micro-jetting, and shock waves [14]. Since the reaction series of thermal decomposition of magnesium bicarbonate involves gas, liquid, and solid phase, those physical effects of ultrasonic wave
make diffusion resistance on the reaction become minimum. The turbulence effect also makes reactant particles in motion and increase the chance of collision.

Amplitude of ultrasonic waves influence the intensity of the waves. Higher amplitude of a wave gives higher intensity and energy. This effect can be seen in figure 3b, where on amplitude 30 µm the temperature of the solution rises faster and higher. This explain why decomposition ratio on samples treated with ultrasonic waves with 30 µm amplitude is slightly higher than those with 20 µm amplitude (figure 3a). Maximum decomposition ratio was reached on sampled treated with amplitude 30 µm with the value of 85.70%, while only slightly lower on amplitude 20 µm sample with the value of 79.18%.

![Figure 3. Decomposition ratio during ultrasonic heating (a) and temperature of magnesium bicarbonate solution during ultrasonic heating (b).](image)

To compare the results of ultrasonic wave heating, samples also heated using conventional heat plate for 30 minutes. The results can be seen in table 1. Samples treated with ultrasonic waves reach significantly higher degradation ratio compared to sample treated with heating plate. This could happen not only because of physical effect created by ultrasonic waves, but also because its chemical effect. The extreme conditions created by ultrasonic waves are also increasing the formation of highly radical species such as H\(^-\) and OH\(^-\) from water. This radical species generation can initiate secondary reaction [15]. This result means that ultrasonic heating is much more effective compared to conventional heating.

| Heat Treatment Types | Heat Plate | Ultrasonic Waves |
|---------------------|------------|------------------|
| Amplitude 20%       | 50.08%     | 79.18%           |
| Amplitude 30%       | 82.59%     |                  |

3.1. **Product characterization**

Table 2 show XRF analysis result of precipitated salts. XRF analysis was conducted using Bruker S2 Puma and was able to see the concentration of element starting from sodium. It can be seen that magnesium are the main constituent of precipitate followed by calcium. This co-precipitation of calcium was expected since the magnesium bicarbonate solution used as raw material was obtained from dolomite processing from previous experiment. Ratio between magnesium and calcium was very small with the value of 63.03. Dolomite was processed using calcination, dissolving it with water, and carbonation to obtain magnesium bicarbonate solution. Figure 4 show XRD pattern of the precipitate. Three main peaks of the pattern are at 2θ = 15.2005, 36.7605, and 21.1488. Analysis conducted using
Jade 1.6 and Linus Pauling File (LPF) No. 2080021 confirm that the precipitate main phase is $\text{Mg}_5(\text{CO}_3)_4(\text{OH})_2(\text{H}_2\text{O})_4$.

Table 2. Chemical composition of precipitated product from ultrasonic heating.

| Component | Mass (%) |
|-----------|----------|
| Mg        | 58.74    |
| O         | 39.45    |
| Ca        | 0.93     |
| Na        | 0.53     |
| Si        | 0.10     |
| Others    | 0.26     |

SEM-EDX analysis was conducted to see the precipitate morphology and chemical composition. The equipment used for this analysis was JEOL JSM-6390A with 20kV voltage. The results of SEM can be seen in figure 5. SEM results show that the particle in the precipitate are homogenous in the form of soft crystal. The particle size range are 280 – 650 nm.

Figure 4. XRD pattern of precipitate.
Figure 5. SEM results of precipitate from ultrasonic heating with 30% amplitude.

4. Conclusion
Based on this study, ultrasonic heating is more efficient compared to hotplate heating in the thermal decomposition of magnesium bicarbonate process. Maximum decomposition ratio of 85.70% was reached on ultrasonic heating with amplitude of 30 µm. Higher amplitude delivers more energy which made decomposition of magnesium bicarbonate faster. The optimum condition of ultrasonic heating in this study is at 30 µm amplitude and 35 minutes heating time. Precipitate obtained was mainly composed of Mg₅(CO₃)₄(OH)₂(H₂O)₄.

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