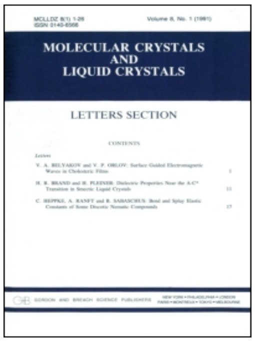

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Preparation of nano-magnesium oxide from seawater bittern using decarboxylation/precipitation method

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ABSTRACT
The nanoparticles of magnesium oxide used mainly for additives were synthesized through precipitation method in the presence of precipitants. The effects of preparation parameters, such as NaOH and $Ca(OH)_2$ concentrations, dilution rate, rotation speed on size and morphology of the nanoparticles were investigated. The magnesium oxide was produced from magnesium hydroxide in the waste-seawater bittern. The properties of the obtained nanoparticles were analyzed by XRD and SEM. The obtained magnesium oxide crystals showed a wide distribution of globular structure including sphere or cubic-like morphology. Also size and crystallinity of magnesium oxide crystals increased from 50 to 180 nm with increasing a rotation speed.

KEYWORDS
magnesium oxide; magnesium hydroxide; bittern; precipitation

Introduction

The precipitation of magnesium hydroxide is of great interest in the context of the manufacture of magnesium oxide (MgO) from magnesium chloride in seawater or natural brines [1]. Magnesium hydroxide ($Mg(OH)_2$) is one of the most important precursors of MgO [2]. ($Mg(OH)_2$), which is the intermediate of MgO, is used mainly in industries of pharmaceutical, flame retardant of rubber, plastic, fiber and resin, preparation of electronic material, wastewater treatment and desulphurization of fuel gases [3].

The preparation techniques of $Mg(OH)_2$ can be mainly classified by magnesite calcination/hydration method, pyrolysis method, and seawater bittern magnesium-deposition method [4]. In the bittern magnesium-deposition method, a chemical reaction between magnesium ions of bittern and an alkaline such as caustic soda, lime stone and ammonium hydroxide will result in the precipitated $Mg(OH)_{2,}$ as fellows;

$$Mg^{2+}+2NaOH \rightarrow Mg(OH)_2+2Na^+ \tag{1}$$

$$Mg^{2+}+Ca(OH)_2 \rightarrow Mg(OH)_2+Ca^{2+} \tag{2}$$

$$Mg^{2+}+2NH_4OH \rightarrow Mg(OH)_2+2NH_4^+ \tag{3}$$

Due to a low solubility of lime stone in water, $Mg(OH)_2$ caused a detrimental effect on product purity. The platelet-shaped superfine $Mg(OH)_2$ sample was prepared through ammonia

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Table 1. Composition of main elements in seawater bittern.

Ions (g/L)	Na^+	K^+	Mg^{2+}	Ca^{2+}
Bittern	29.39	34.02	35.34	11.91

magnesium-deposition method [5,6]. However, most of these approaches are costly, time-consuming and difficult to control the morphology of $Mg(OH)_2$ at room temperature. The conditions of the process need to be controlled in order to obtain nanocrystals with certain morphologies, particle sizes, agglomeration level, and crystallographic structures. Therefore, many studies were forced on the parameters of preparations, such as temperature, pressure and liquid jet streams, of nano-structured $Mg(OH)_2$ [6,7]. $Mg(OH)_2$ crystals with various morphologies, such as plates, lamellar, rod, disk, needle-like and so on, were synthesized by means of co-precipitation and hydrothermal methods [8]. The $Mg(OH)_2$ in the poly(acrylate) composite was converted to MgO nanoparticles by the heat treatment [9].

The nanoparticles of MgO were synthesized through decarboxylation/precipitation method in the presence of precipitants. The effects of operation parameters, such as NaOH and $Ca(OH)_2$ concentration, dilution rate, rotation speed on morphology of nanoparticle size were investigated. The properties of the nanoparticles have been characterized by X-ray diffraction (XRD) and scanning electron microscopy (SEM).

Experimental

Seawater bittern was discharged in the desalinization process of Hanju salt company. The composition of the main elements in seawater bittern is shown in Table 1. The Mg^{2+} concentration of the seawater bittern was 35.34 g/L (1.45 mol/L). The seawater bittern was diluted to 0.145 – 0.290 mol/L with deionized water.

The molar ratios of Mg^{2+}: Na^+ and Mg^{2+}: Ca^{2+} were the most essential factors during $Mg(OH)_2$ precipitation. Hence, batch experiments were carried out to investigate optimum Mg^{2+}: Na^+ and Mg^{2+}: Ca^{2+} molar ratio for synthesizing nano-MgO. NaOH and $Ca(OH)_2$ solutions were used as precipitants. NaOH, $Ca(OH)_2$ and H_2SO_4 were purchased from Sigma–Aldrich. All chemicals above were extra pure grade.

The synthetic procedure is illustrated in Figure 1. All the experiments were conducted in a 1 L glass beaker equipped with a stirrer and a temperature controller. Alkaline solution of NaOH or $Ca(OH)_2$ was added drop-wise by a burette to the glass beaker containing seawater bittern solution. 20 mL of NaOH or $Ca(OH)_2$ solutions (0.5 – 2.0 mol/L) was injected into 200 mL of the diluted seawater bittern solution under vigorous stirring for 1 hr at 30 °C. 1 mL (0.1 M) of sulfuric acid was added for decarboxylation. The mixed solution was homogenously stirred at 120 – 600 rpm for 2 hr.

The obtained mixtures were filtered under suction and then washed several times with deionized water to remove the residual impurities. The obtained samples were dried at 110 °C for 2 hr and then sintered at 500 °C for 4 hr in a muffle furnace to produce MgO powder.

X-Ray diffraction (XRD) patterns of the MgO crystals were recorded using a powder diffractometer (XRD: D8 Advance, Bruker AXS) with Cu Kα radiation ($\lambda = 1.54$ Å). The accelerating voltage and current used in this measurement were 40 kV and 40 mA, respectively. The diffractograms were recorded in the range of 10–80° in 0.02° steps (3 s per step) with a count time of 15 s at each measurement point. The morphologies of MgO crystals for the micro structural observation were analyzed using scanning electron microscopy (SEM, Hitachi S-4200). The samples were coated with a thin layer of platinum and mounted on a

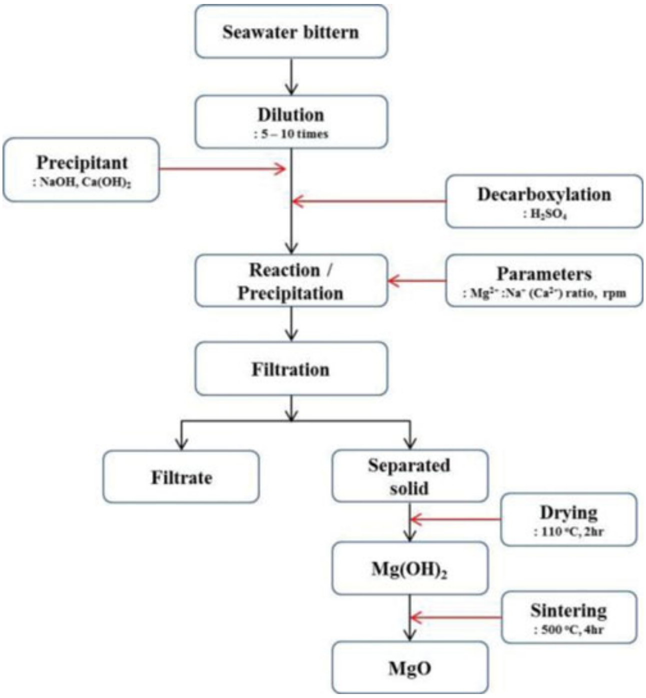

Figure 1. Process flow diagram of synthesis of MgO powder.

copper slab using double-sided tape for the SEM measurements. All ion concentrations of the filtrate were determined using inductively coupled–plasma atomic-emission spectrometry (ICP-AES, Perkin-Elmer 3000 XL).

Results and discussion

Figure 2 shows the effect of Mg^{2+}: Na^{+} and Mg^{2+}: Ca^{2+} ratio on the contents of the MgO produced from seawater bittern. The stirring speed and time to prepare MgO were fixed to 200 rpm and 2 hr, respectively, at 30 °C. After the precipitation, $Mg(OH)_2$ was converted to

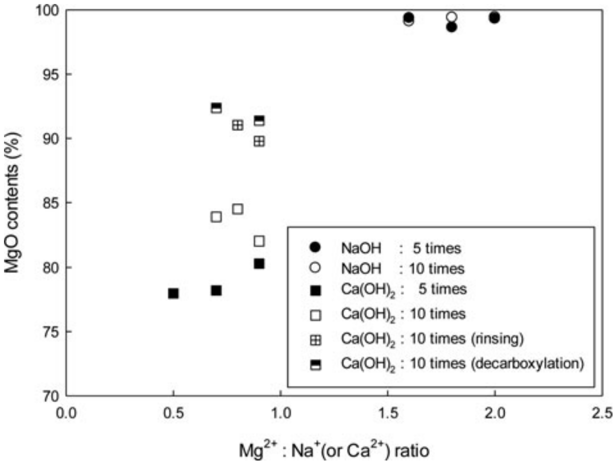

Figure 2. Effect of Mg^{2+}: Na^{+}(or Ca^{2+}) ratios on the contents of MgO.

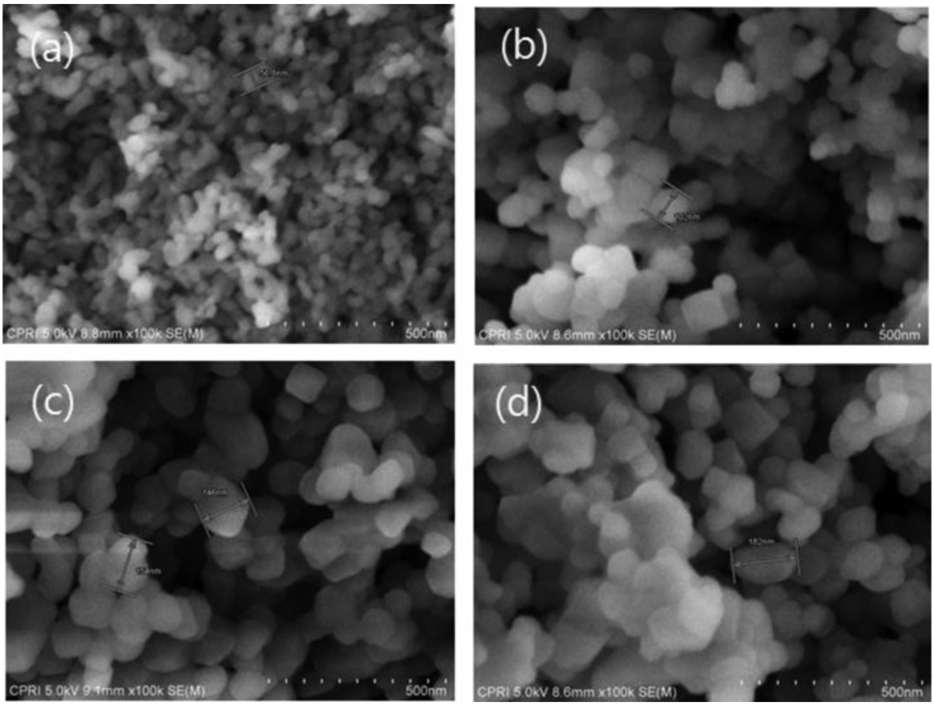

Figure 3. SEM micrographs of synthesized MgO samples at different rotation speeds. (a) 120 rpm; (b) 200 rpm; (c) 300 rpm; (d) 600 rpm.

MgO particles by sintering at 500 °C for 4 hr. Mantilaka et al.[9] reported that the $Mg(OH)_2$ in the composite was converted to MgO nanoparticles by the heat treatment at 500 °C for 3 hr. As dilution rate of seawater bittern solutions was changed to 5 and 10 times in the Mg^{2+}: Na^+ ratio of 1.6 – 2.0 with NaOH, the MgO contents in powder sustained to 98.6 – 99.4%. In the Mg^{2+}: Ca^{2+} ratio of 0.5 – 0.9 with $Ca(OH)_2$, the MgO contents (82.0 – 83.4%) at the dilution rate of 10 times were higher than at the dilution rate of 5 times (77.9 – 80.3%). At the dilution rate of 10 times, the MgO contents tended to increase to 89.8 – 91.0% with rinsing by deionized water. Moreover, during decarboxylation with sulfuric acid before injecting $Ca(OH)_2$, the MgO contents increased to 91.4 – 92.4%. NaOH is more effective than $Ca(OH)_2$ concerning the $Mg(OH)_2$ contents. NaOH was effective to raise the yield of $Mg(OH)_2$ nanoparticles from 75 to 98% more than ammonium hydroxide. The addition of a strong base into a metal salt solution made it difficult to generate monodispersed metal hydrous oxides [10]. Rabadzhieva et al. [11] desulfated natural brine using a $CaCl_2$ solution prior to the precipitation of $Mg(OH)_2$. However, the $Mg(OH)_2$ obtained had lots of the impure contents. Therefore, use of caustic soda as alkaline is more reasonable than lime when a highly pure product is desirable.

Figure 3 shows SEM micrographs of MgO particles synthesized from the diluted seawater bittern solution. Mg^{2+}: Na^+ ratio with NaOH was fixed at 1.6. The sample was made of MgO by the precipitation at 30 °C for 2 hr and sintered at 500 °C for 4 hr. SEM micrographs of MgO particles revealed definite difference in the morphologies and particle sizes according to rotation speeds. From Figure 3, all samples resulted in the formation of globular and cubic shapes with rounded edges, regardless of rotation speeds. It is interesting to note that when the rotation speed increased from 120 to 600 rpm, the morphology, the particle size and the

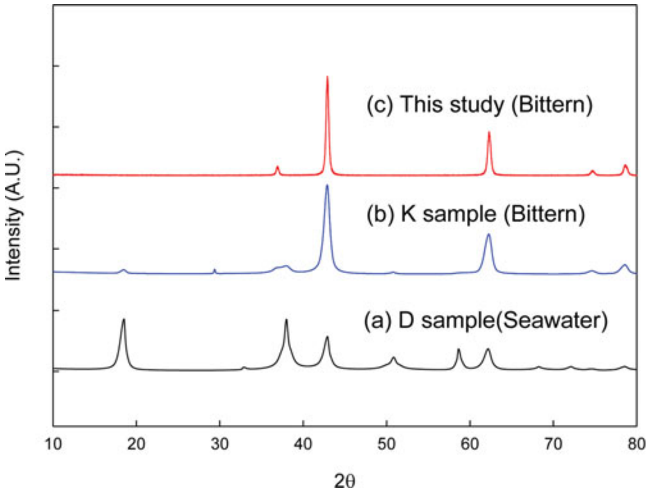

Figure 4. XRD patterns of three samples related to MgO. (a) D sample (Seawater); (b) K sample (Bittern); (c) This study (Bittern).

agglomeration level clearly increased. This globular structure can be explained by the aggregate of spherical units which have a diameter of ca 180 nm. $Mg(OH)_2$nanoparicles with the microstructure of the globular agglomerates, platelet-shaped particles or hexagonal lamellas have been synthesized by the precipitation of a magnesium salt with an alkaline solution [1]. Lü et al.[12] reported the precipitation of $Mg(OH)_2$ nanoparticles with three structural morphologies, needle-, lamellar- and rod-like in the presence of water-soluble dispersants. Xiong et al. [13] reported that $Mg(OH)_2$ on the SEM image exhibits a column-shaped superstructure, which can be attributed to the linkage of regular-hexagonal platelets with a diameter of 2 – 2.5 μm and a thickness of 150 – 200 nm.

Figure 4 shows the X-ray diffraction (XRD) patterns of two commercial products and the prepared sample. The sample was obtained by the decarboxylation/precipitation method at 200 rpm. Mg^{2+}: Na^{+} ratio with NaOH was fixed at 1.6. The D sample was made of MgO by precipitating at 30 °C for 2 hr and then sintering at 500 °C for 4 hr. The XRD pattern of the sample from seawater was composed of peaks at 18.6, 37.4, 42.9, 50.8, 58.6, and 62.3 of 2θ. The peaks at 37.4, 42.9 and 62.3 were assigned to the structure of MgO and the peaks at 18.6, 50.8 and 58.6 of 2θ seemed to be the structure of $Mg(OH)_2$ [9]. The XRD patterns of the samples synthesized from seawater bittern exhibited typical diffraction peaks at 37.4, 42.9 and 62.3 of 2θ which were assigned to the structure of MgO. In addition, no characteristic peaks of other impurities were observed in Figure 4c, which indicated that the prepared sample, Figure 4c, had a high purity. The XRD patterns (Figure 4c) reveals that the prepared nano-MgO are single crystalline and can be marked as cubic-phase magnesium oxide (JCPDS 89-7746). There are no peaks detected for other phases, indicating that a single phase of MgO with high purity has been prepared. Srivastava et al.[14] and Venkatesha et al.[15] suggested that the diffraction peaks matched with the face centered cubic structure of MgO. The sharp diffraction peaks of the sample indicated well-crystallized MgO crystals.

Figure 5 shows the SEM images of two commercial samples (Figures 4a and 4b) and the prepared sample (Figure 4c). D sample was different from the prepared sample (Figure 4c) and K sample differs (Figure 4b) on crystal and morphological structures according to raw materials. The prepared sample (Figure 4c) and K sample (Figure 4b) have different morphological structures even though they are similar in crystal structure from the XRD patterns.

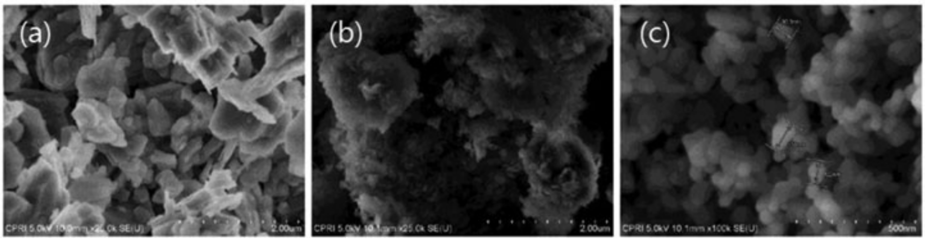

Figure 5. SEM micrographs of three samples related to MgO. (a) D sample (Seawater); (b) K sample (Bittern); (c) This study (Bittern).

Table 2. Compositions of main elements in MgO samples.

Contents		MgO samples	
	(a) D sample	(b) K sample	(c) This study
MgO	99.3	96.7	99.5
CaO	0.40	1.29	0.05
Cl	0.15	0.32	0.10
Other	0.15	1.39	0.35

D sample (Figure 5a) and K sample (Figure 5b) are rod or disk-like shape and amorphous in shape, respectively. The prepared sample (Figure 5c) is globular shape and cubic shape with rounded edges. The typical diameters of the prepared sample (Figure 4c) are 100 ± 30nm. Table 2 gives the chemical compositions of the two commercial samples and the prepared sample determined by XRF analysis. The XRF analysis indicated the MgO contents were 99.3% in (a) D sample, 96.7% in (b) K sample and 99.5% in (C) prepared sample.

Conclusions

This study has an objective to produce high purity and quality of MgO crystals with bittern discharged in the salt-making process. The MgO crystals were synthesized through solution decarboxylation/precipitation in the presence of precipitants. Morphology and particle size of nano- MgO particles synthesized in seawater bittern were studied.

It has been shown that the chemical nature of the base precipitant, NaOH and $Ca(OH)_2$, is of prime importance. When the Mg^{2+}: Ca^{2+} ratio of 1.6 with NaOH was synthesized, the MgO contents in powder sustained to 98.6 – 99.4%. In the Mg^{2+}: Ca^{2+} ratio of 0.5 – 0.9 with $Ca(OH)_2$, the contents of the MgO were 82.0 – 83.4%. The contents of the MgO tended to increase to 89.8 – 91.0% after rinsing with deionized water. Moreover, during decarboxylation with sulfuric acid before injecting $Ca(OH)_2$, the contents of $Mg(OH)_2$ increased to 91.4 – 92.4%. This result indicates that NaOH is more effective than $Ca(OH)_2$ for $Mg(OH)_2$ contents.

The MgO crystals with a wide distribution of globular structures with sphere or cubic-like needle and hexagonal disk-like morphology were obtained in the samples to be pretreated with decarboxylation. It has been shown that the increasing of rotation speeds improves the crystallinity of MgO particles. It was also possible to detect a relevant increase from 50 nm to 180 nm in MgO crystals with globular agglomerates in the samples obtained when the rotation speed increased from 120 to 600 rpm. This globular structure can be observed due to the aggregation of spherical and cubic shapes with rounded edges. This condition can also be applied to synthesize nano-MgO particles in an industrial plant of $Mg(OH)_2$ or MgO recovery using any other raw material.

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