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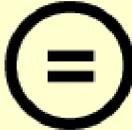
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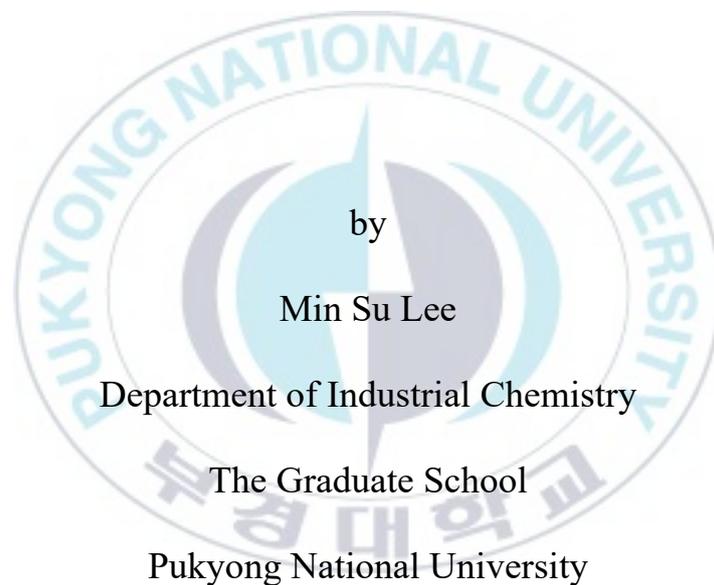
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Thesis for the Degree of Master of Engineering

A study for Ca/Mg separation efficiency  
improvement in the preparation of high purity  
magnesium carbonate from seawater



by

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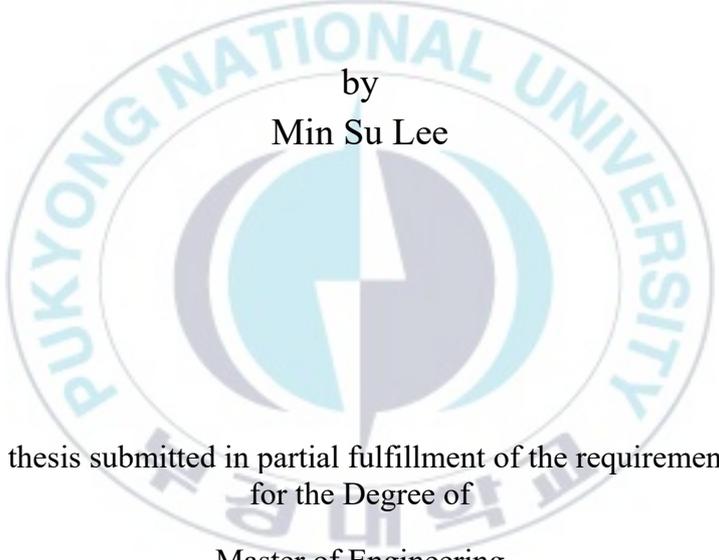
August 2019

# A study for Ca/Mg separation efficiency improvement in the preparation of high purity magnesium carbonate from seawater

해수로부터 고순도 탄산마그네슘 제조 시  
Ca/Mg 분리효율 개선에 관한 연구

Advisor: Prof. Seong Soo Park

by  
Min Su Lee

The logo of Pukyong National University is a circular emblem. It features a central stylized design with a blue and grey color scheme, possibly representing a compass or a similar navigational instrument. The words "PUKYONG NATIONAL UNIVERSITY" are written in a light blue, sans-serif font around the perimeter of the circle. Below the circle, the Korean name "북양대학교" is also visible in a similar font.

A thesis submitted in partial fulfillment of the requirements  
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Pukyong National University

August 2019

A study for Ca/Mg separation efficiency improvement  
in the preparation of high purity magnesium carbonate  
from seawater

A dissertation

by

Min Su Lee

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August 2019

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# 해수로부터 고순도 탄산마그네슘 제조 시 Ca/Mg 분리효율 개선에 관한 연구

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## 요 약

해수로부터 추출 가능한 마그네슘, 칼슘, 나트륨과 같은 양이온 및 화력발전소에서 발생하는 이산화탄소를 활용한 다양한 탄산염의 제조가 많은 관심을 받고 있다. 풍부한 자원의 활용과 지구온난화를 발생시키는 물질을 제거하는 관점에서 경제적이고 친환경적인 요인을 제공해준다. 탄산염의 제조는 이 방법을 통하여 CCUS (Carbon capture storage and utilization)로 적극 활용되어 왔다. 칼슘 및 마그네슘의 분리는 해수를 사용하여 고순도의 마그네슘염을 제조하는데 중요한 부분이다. 탄산마그네슘염 제조과정에서 중간단계인 수산화마그네슘 제조 단계에서 문제가 발생한다. 알칼리 첨가를 통해 pH=10-12 조건에서 해수에 녹아있는 마그네슘이온은 수산화마그네슘으로 침전되는데, 동시에 탄산칼슘의 침전이 발생한다. 수산화마그네슘 제조 시 탄산칼슘의 공침을 억제하기 위해서는 높은 Ca/Mg 분리효율에 의한 주의 깊은 제어가 요구된다. 산 및 열처리, 나트륨옥살레이트와 같은 화학시료 첨가 등의 다양한 방법들이 사용된다. 본 연구에서는 고순도의 수산화마그네슘 및 탄산마그네슘염 제조에 대하여 체계적인 실험을 진행하였다. XRD(X-ray diffraction analysis)와 ICP(Inductively coupled plasma)는 마그네슘, 칼슘의 순도 및 해수에 잔류하는 염의 농도를 확인하기 위해 사용하였고, 생성물의 미세구조는 SEM(Scanning electron microscope)을 통해 관찰하였다. 첫 단계에서 칼슘의 공침을 최소화 시킨 마그네슘 분리 공정을 통해 해수로부터 순도 높은 수산화마그네슘 염 제조가 가능하였으며, 이 공정은 이후 추가적인 탄산칼슘, 탄산나트륨 제조 및 해수 담수화 공정을 위한 중요한 단계임을 보여준다.

# Chapter I. Introduction

## I-1. Purpose of the study in terms of CCS & CCU<sup>1-3</sup>

According to the International Energy Agency (IEA), most of the world's greenhouse gases are generated by more than 68 % of the energy sector (thermal power plants, cogeneration plants, steel mills, etc.). Among them, carbon dioxide (90 %) is much higher than methane gas (9 %) and nitrous oxide (1 %). The annual average CO<sub>2</sub> concentration in the atmosphere of the world in 2016 is 403.3 ppm, an increase of 3.3 ppm year-on-year, and a 45 % increase from pre-industrial (278 ppm in 1750).<sup>1</sup> At the 21<sup>st</sup> General Conference of the United Nations Framework Convention on Climate Change (COP21) in 2015, the need to reduce greenhouse gas (CO<sub>2</sub>) emissions has been emphasized by signing the Paris Agreement to combat global warming.<sup>2</sup> Current energy use efficiency of industry is at the maximum level, so excessive CO<sub>2</sub> reduction may lead to weakening of industrial economy. Therefore, in addition to efforts to reduce carbon dioxide emissions, it is required to directly reduce carbon dioxide through storage and utilization as a technical alternative. Carbon dioxide capture, storage and utilization include technologies to capture gas from industrial facilities and store them in the ground, as well as to convert them into valuable resource materials

with high added value. Developed countries such as USA, Europe, and Japan are promoting next-generation technology for mass demonstration and cost reduction for CCS (carbon dioxide capture and storage) commercialization. Some of the technologies in Korea are at the global level but lack experience of storage and large-scale demonstration. The weak point of the CO<sub>2</sub> immobilization technology currently applied domestically and abroad is that it does not utilize the excess emission process in the capture of CO<sub>2</sub> and it is aimed at conversion without using the multistage separation process system in the inorganic separation process.<sup>3</sup> The resulting composite carbonates have low utility and added value. In this study, to overcome these weaknesses, a system to positively utilize the CO<sub>2</sub> overflow process is constructed and the collection cost is zeroed. In addition, through stepwise processes, it is intended to add value by converting into a single carbonate form (such as magnesium and calcium carbonate) rather than a complex carbonate form.

### **I-1-1. Trends for CCUS utilization of national institutions<sup>4-5</sup>**

Capture, storage, conversion, and usage of carbon dioxide have attracted much attention due to its potential applications to solve the environmental problems of global warming by reducing carbon dioxide in atmosphere. The developed countries are planning to actively utilize the next generation Carbon Capture Storage (CCS) and Carbon Capture Utilization (CCU) technologies to solve

global problems.<sup>4</sup> In the United States, the National Carbon Capture Center (NCCC) was established under the Department of Energy. The EU, Australia, and Netherlands are looking for ways to save carbon dioxide while at the same time minimizing carbon dioxide emissions from thermal power plants. Korea Carbon Capture and Sequestration R&D center (KCRC) has been organized at 2010 and started to build foundation and to develop CCS technology.<sup>5</sup>

### **I-1-2. Advantage of seawater for CCUS<sup>6-10</sup>**

The utilization of CO<sub>2</sub> has been studied in the areas of chemical fixation of CO<sub>2</sub>, which is conversion of CO<sub>2</sub> into fuels, polymeric materials, and fine/pharmaceutical chemicals.<sup>6</sup> Survey of global carbon reservoirs suggests that the most stable, long-term storage mechanism for atmospheric CO<sub>2</sub> is the formation of carbonate minerals such as calcite, dolomite and magnesite.<sup>7</sup> As one of promising carbon dioxide storage technology, carbon dioxide may be injected into deep underground rock formation, often at depths of one kilometer or more, however there is growing concern about the stability of CO<sub>2</sub> storage underground.<sup>7</sup> It may be converted to useful chemical compounds including CO<sub>2</sub> as either organic or inorganic compounds. The storage of CO<sub>2</sub> as carbonates has been studied as stable storage of CO<sub>2</sub> by making use of cation rich sources of fly ash from power plant, slag from steel making or seawater.<sup>7</sup> The mineral carbonation has been studied that the formation of carbonates follows several

elementary steps of dissolution of CO<sub>2</sub> in water, alkaline solid dissolution, and precipitation of carbonates.<sup>8</sup> Therefore, liquid waste including Ca and Mg is preferable as a carbonate reservoir of CO<sub>2</sub>, so that the use of seawater for CO<sub>2</sub> mineralization is promising and has been investigated.<sup>8-10</sup>

### **I-1-3. Carbon dioxide storage using salts in seawater<sup>6, 8-11</sup>**

The carbonate formation process from seawater may make use of cations of magnesium, calcium, and sodium of saline water. 1m<sup>3</sup> of sea water may store 14.1 kg of CO<sub>2</sub> as carbonates, that is 2.12 kg, 0.48 kg, and 11.48 kg of CO<sub>2</sub> as magnesium carbonate, calcium carbonate, and sodium carbonate, however, the utilization is not as complete as theoretical expectation, since the materials in replica brine solution with coexisting Mg and Ca are found that the carbonate precipitation is not readily occurs. Magnesium carbonate is not completely precipitated in the seawater, compared with calcium carbonates.<sup>9</sup> The solubility product of magnesium carbonate is relatively higher than calcium carbonate. Furthermore, the calcium carbonate precipitation is also limited by ions in brine so that the residual calcium ions in brine remain are un-precipitated until the concentration of 18 times higher than solubility of CaCO<sub>3</sub>.<sup>11</sup> The CO<sub>2</sub> mineralization cycles from seawater concentration from desalination process has been studied, which is composed of pH increase, followed by CO<sub>2</sub> bubbling, and

filtration.<sup>6</sup> It is reported that the repeated cycles may reduce concentration of Ca and Mg, finally precipitated 99 % of Ca and 86 % of Mg from the brine.<sup>9</sup> The separation of Mg ion as magnesium hydroxide from simulate concentrated seawater by membrane electrolysis has been reported that over 99 % of the Ca<sup>2+</sup> ion and Mg<sup>2+</sup> ions are converted into pure calcium carbonate and magnesium carbonate hydroxide.<sup>8</sup>

#### **I-1-4. Seawater desalination through stepwise carbonization**

There have been only reported CO<sub>2</sub> mineralization by using of Ca<sup>2+</sup> and Mg<sup>2+</sup> ions from seawater and the residual water is effluent, however, we are proposing the complete usage of cations in seawater for CO<sub>2</sub> mineralization, which have been industrialized in the sense of unit reactions, however the complete stepwise carbonation reactions of Mg<sup>2+</sup>, Ca<sup>2+</sup>, and Na<sup>+</sup> in seawater for the CO<sub>2</sub> mineralization are the first report to the best of our knowledge. The process may be useful not only it stores the CO<sub>2</sub> as carbonates but also the residual fresh water could be considered as a result of stepwise desalination of sea water. We have proposed stepwise carbonization of cations originated from seawater, consisting of 6 unit reactions at Table I-1. In order to produce the high-purity carbonate through unit 6 reactions, the Ca/Mg separation efficiency in unit 1 should be high. Therefore, we conducted experiments on extraction processes of calcium or magnesium in unit 1 and found an optimized method.

**Table I-1.** Six stepwise unit reactions in the process of separation of ions originated from seawater for CO<sub>2</sub> storage

No	Originated from Seawater	Addition	Product	Variables
1	Na <sup>+</sup> <sub>(aq)</sub> , Mg <sup>++</sup> <sub>(aq)</sub> , Ca <sup>++</sup> <sub>(aq)</sub>	CaO Ca(OH) <sub>2</sub> NaOH	Mg(OH) <sub>2</sub>	Alkali source and amount, T
2	Mg(OH) <sub>2(s)</sub>	CO <sub>2</sub>	MgCO <sub>3</sub>	CO <sub>2</sub> concentration and flow rate, reaction time, T, bubble size and distribution
3	Na <sup>+</sup> <sub>(aq)</sub> , Ca <sup>++</sup> <sub>(aq)</sub>	NaOH	Ca(OH) <sub>2</sub>	NaOH amount and T
4	Ca(OH) <sub>2(s)</sub>	CO <sub>2</sub>	CaCO <sub>3</sub>	CO <sub>2</sub> concentration and flow rate, reaction time, T, bubble size and distribution
5	Na <sup>+</sup> <sub>(aq)</sub>	-	NaOH <sub>(aq)</sub> , HCl <sub>(aq)</sub>	Electrolysis (Electrode type and size, distance, current and voltage, etc.)
6	NaOH <sub>(aq)</sub>	CO <sub>2</sub>	Na <sub>2</sub> CO <sub>3</sub>	CO <sub>2</sub> concentration and flow rate, T

## **I-2. Utilization of salts originated from seawater<sup>12-15</sup>**

Generally seawater of 1 L contains salts of 35 g, the major components are such as sodium ( $\text{Na}^+$ ), magnesium ( $\text{Mg}^{2+}$ ), calcium ( $\text{Ca}^{2+}$ ), potassium ( $\text{K}^+$ ), chlorine ( $\text{Cl}^-$ ), sulfate ( $\text{SO}_4^{2-}$ ) and carbonate ion ( $\text{HCO}_3^-$ ,  $\text{CO}_3^{2-}$ ).<sup>12</sup> According to the Oceanographic Survey of the National Fisheries Research and Development institute, there may be differences in the concentration of salts on location and season, but the ratio of salts contained per surface unit volume is constant. The concentration of chemical ion in the average seawater and samchonpo seawater can be seen in Table I-2. Magnesium and calcium can be founded not only in dolomite of complex carbonate type but also in seawater and brine water.<sup>13-15</sup> Based on Table I-2, magnesium (1,290 ~ 1,360 ppm) is the second abundant element after sodium in seawater, so extraction and utilization of it is a promising method. It is possible to produce complex carbonate through mineralization of magnesium and calcium ion in seawater, and it may be more valuable separate to respectively high-purity magnesium carbonate and calcium carbonate through the stepwise separation process. In this study, we explain the process of increasing the Ca/Mg separation efficiency to utilization the two ions more efficiently.

**Table I-2.** Ion concentration of seawater<sup>12</sup>

Chemical ion	Concentration (g/L)	
	Average seawater	*Samchonpo seawater
Sodium (Na <sup>+</sup> )	10.752	11.330
Magnesium (Mg <sup>2+</sup> )	1.295	1.360
Calcium (Ca <sup>2+</sup> )	0.416	0.400
Potassium (K <sup>+</sup> )	0.390	0.383
Chloride (Cl <sup>-</sup> )	19.345	.
Sulfate (SO <sub>4</sub> <sup>2-</sup> )	2.701	.

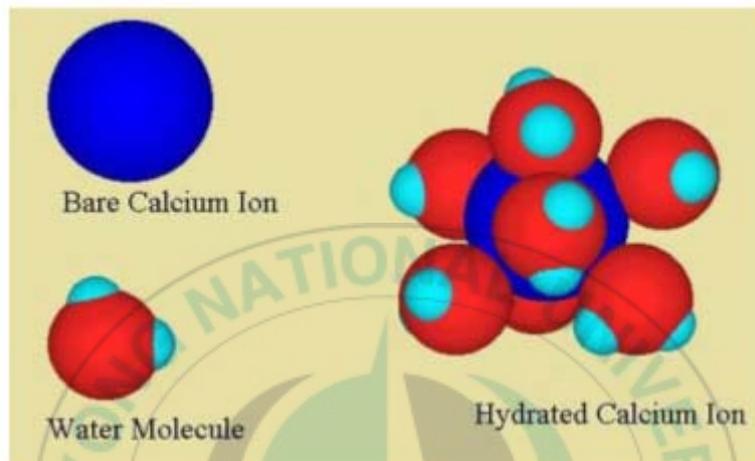
\* The ICP used in this analysis is perkin elmer ICP 8300

### **I-3. The chemical state of calcium ion in seawater<sup>16</sup>**

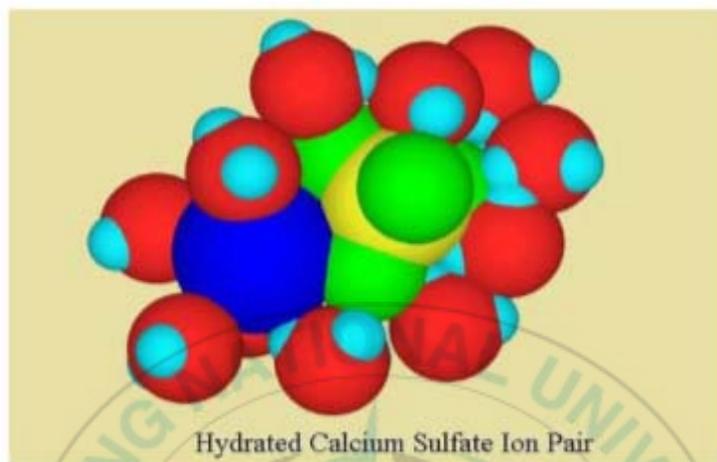
In fresh water below  $\text{pH} = 10$  or so, calcium ions are essentially free. That is, they are not strongly attached to anything else except water and move about independently of all other ions in the solution (exceptions being if the water has certain calcium-complexing agents in it, such as phosphate or certain organics). Figure I-1 shows a calcium ion hydrated with water molecules. This hydration sphere is quite strongly attached to the ion in water, with about 6 ~ 7 water molecules in a looser arrangement, and beyond that, all of the other things in solution. All these water molecules around the ion are very rapidly exchanging, but those closest to the ion exchange more slowly and move with it as it moves through the solution. In seawater, the situation is slightly more complicated. While the majority of calcium ions are still free, some (about 10 ~ 15 %) are present as an ion pair with sulfate, forming the neutral ion pair  $\text{CaSO}_4$  (Figure I-2). These types of soluble ion pairs are short lived, forming and breaking apart quite rapidly. Nevertheless, they can have significant impact on the properties of seawater. This pair is in turn hydrated with water molecules, as shown in Figure I-2. Calcium similarly forms ion pairs with carbonate and bicarbonate. While these comprise a small fraction of the total calcium, the calcium carbonate ion pair comprises a fairly large portion of the total carbonate (together with magnesium, about 2/3 of the carbonate). These ion pairs consequently tend to lower the free concentration of carbonate, and thereby help to inhibit precipitation of calcium

carbonate, and consequently increase its solubility. Finally, calcium forms ion pairs with fluoride, hydroxide, borate, the various forms of phosphate, and other ions to smaller extents that are unimportant to the free calcium concentration, but may impact the free concentrations of these other ions. In almost all cases, however, the effect of calcium is smaller than the effect of magnesium on these ions, both because the concentration of magnesium is higher, and because in some cases it actually more strongly.





**Figure I-1.** A hydrated calcium ion showing its inner sphere of hydrating water molecules. Calcium is shown in dark blue, oxygen in red, and hydrogen in light blue.<sup>16</sup>



**Figure I-2.** A calcium/sulfate ion pair showing its inner sphere of hydrating water molecules. The colors are the same as Figure I-1 except that the sulfur is shown in yellow, and the sulfate oxygen atoms are shown in green to make them stand out from the water molecules. Water molecules have been removed from the top to permit better visualization of the calcium and the sulfate.<sup>16</sup>

#### I-4. Calcium carbonate in seawater<sup>17</sup>

One very important aspect of calcium is that, in seawater, it is actually supersaturated. What supersaturation means in this context is that given the right circumstances, it will precipitate as solid calcium carbonate.

The equilibrium constant expression for the dissolution of calcium carbonate is shown below.

$$K = [\text{Ca}^{2+}] [\text{CO}_3^{2-}] \dots\dots\dots (1)$$

When  $K = K_{sp}^*$  (the solubility product constant in seawater at any given temperature, pressure and salinity), then the solution is said to be exactly saturated (equation 2).

$$K_{sp}^* = [\text{Ca}^{2+}] [\text{CO}_3^{2-}] \text{ (saturation)} \dots\dots\dots (2)$$

When the product of the concentration of calcium and carbonate exceeds the  $K_{sp}^*$ , the solution is said to be supersaturated, and there is “too much” calcium and carbonate in solution (equation 3).

$$K_{sp}^* < [\text{Ca}^{2+}] [\text{CO}_3^{2-}] \text{ (supersaturation)} \dots\dots\dots (3)$$

When the product of the concentration of calcium and carbonate is less than the

$K_{sp}^*$ , the solution is said to be undersaturation, and calcium carbonate can dissolve if put into the solution (equation 4).

$$K_{sp}^* > [Ca^{2+}] [CO_3^{2-}] \text{ (undersaturation) } \dots\dots\dots (4)$$

In normal seawater, equation 3 holds (supersaturation). Consequently, calcium carbonate is poised to precipitate from seawater, given the opportunity.



## **I-5. Cause of calcium carbonate precipitation in alkali condition<sup>18</sup>**

As shown in Figure I-3, Magnesium dissolved in seawater precipitate as magnesium hydroxide under the condition of the pH = 10 ~ 12 by the addition of alkali. It is difficult to obtain high purity magnesium hydroxide due to co-precipitation of calcium carbonate in this region. The reasons is explained by effect of various salts in seawater and the behavior of carbonate ion according to pH.

### **I-5-1. Influence of various salts (Na<sup>+</sup>, Mg<sup>2+</sup>, Cl<sup>-</sup>, etc.) in seawater**

In the case of distilled water (under 50 uS/cm), the solubility of calcium carbonate is low ( $K_{sp} = 5.61 \times 10^{-12}$ ) and most of it is sedimented. However, in seawater, the calcium ion is present in a supersaturated state even though the concentration of calcium ion is 4 to 6 times higher than the saturation concentration. The reason is that various ions such as Na<sup>+</sup>, Mg<sup>2+</sup>, Cl<sup>-</sup> and SO<sub>4</sub><sup>2-</sup> dissolved in seawater interfere with the nucleation of calcium carbonate.<sup>4,16-17</sup> Firstly, magnesium and sodium ions hold onto carbonate ions and reduce their free concentration, thereby reducing the likelihood of precipitation onto calcium carbonate surfaces. Secondly, these ions (Na<sup>+</sup>, Mg<sup>2+</sup>) get onto the growing surface of the crystal, essentially poisoning it for future precipitation of calcium carbonate. Note that while both of these processes inhibit precipitation of calcium carbonate, the first actually increases the solubility, whereas the second does not.

It is worth noting that the solubility of calcium carbonate in seawater is about 18 times higher than in freshwater at the same temperature, and this first effect of magnesium and sodium is one of the reasons. In a sense, it inhibits the pathway between soluble calcium and carbonate ions, and the solid calcium carbonate that would form.

### **I-5-2. Influence of carbonate ion in seawater<sup>18</sup>**

When the pH of the seawater is at pH = 8.0 ~ 8.5, CO<sub>2</sub> dissolved in the seawater is mostly present as HCO<sub>3</sub><sup>-</sup> (more than 129 ppm, 90.2 mol %), which is a mono-anionic state. At condition of pH = 10 or higher after addition of the alkali, carbonate ion exists mostly in CO<sub>3</sub><sup>2-</sup> (more than 132 ppm, 92.4 mol %), which is a divalent anion state as shown in Table I-3. At the point calcium carbonate may precipitate by reacting with supersaturated Ca ion and divalent carbonate ion in seawater.<sup>18</sup> So, it is difficult to inhibit the co-precipitation of calcium carbonate during precipitation of magnesium hydroxide in seawater.

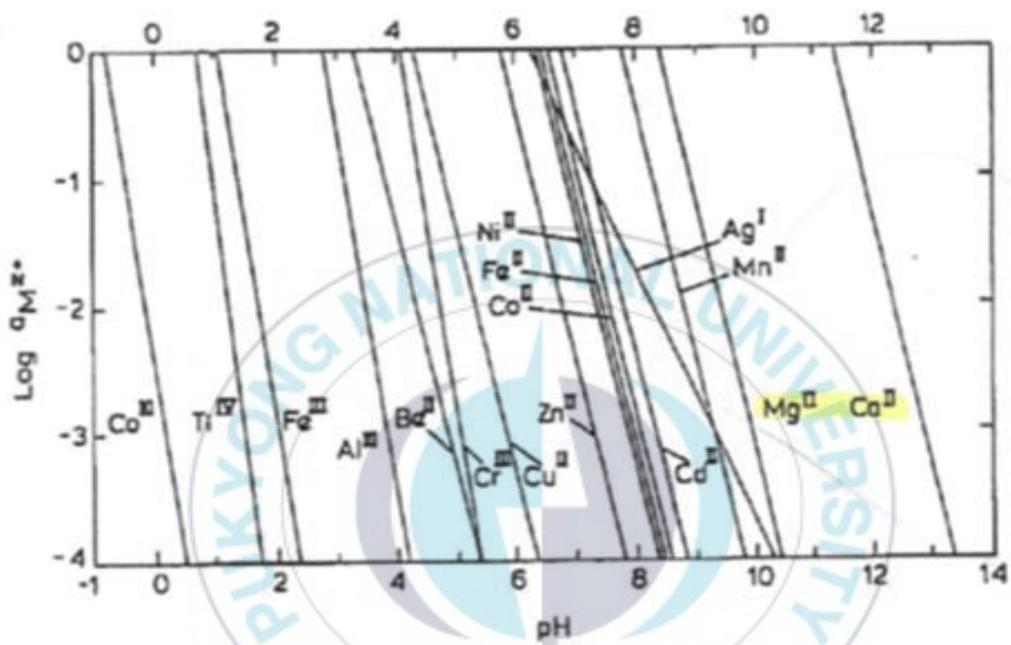


Figure I-3. The metal precipitate of diagram.<sup>18</sup>

**Table I-3.** Total dissolved inorganic carbon in seawater<sup>18</sup>

Total dissolved inorganic carbon (g/L) in seawater							
pH		4.3 (HCl)		8.5 (Seawater)		11.0 (Alkali)	
CO <sub>2</sub>	(ppm, mol%)	141.03	98.9	0.59	0.57	0.44	0.31
HCO <sub>3</sub> <sup>-</sup>	(ppm, mol%)	2.28	1.06	129	90.2	11.25	7.89
CO <sub>3</sub> <sup>2-</sup>	(ppm, mol%)	0	0.00	13	9.23	131.8	92.4

## **I-6. Method of Ca/Mg separation in seawater**

There are two methods for increasing the purity of magnesium hydroxide. The first method is to remove carbonate ion dissolved in the seawater by de-carbonation process such as acid and heat treatment. The second one is to remove calcium ion dissolved in the seawater in the form of insoluble salt such as calcium oxalate by addition sodium oxalate, a chelate salt, before magnesium hydroxide production.

### **I-6-1. Carbonate ion removal through de-carbonation process**

When the pH of the seawater is lowered to 4.5 or less by the addition of acid, most of the carbonate ion exists in the form of dissolved  $\text{CO}_2$  (more than 141 ppm, 98.9 mol %) and can be released into the air through additional heat treatment as shown in Table I-3.<sup>10</sup> The concentration of Ca ion to precipitate  $\text{CaCO}_3$  in the seawater is 4 to 6 times or more, but if the dissolved carbonate ion is removed, the co-precipitation of calcium carbonate can be suppressed under alkaline conditions of pH = 10 or more.

### **I-6-2. Calcium ion removal through chelate salt precipitation**

Calcium ion can be removed from seawater by the difference in solubility of calcium and magnesium oxalate through the addition of sodium oxalate, a chelate

slat, at  $\text{pH} = 10$  or lower. When sodium oxalate is added, it is possible to effectively extract Ca ion while maintaining the  $\text{pH} = 8.0 \sim 8.5$  of seawater.<sup>19-21</sup> Table I-4 and Figure I-4 shown solubility and precipitation periods of oxalate salts. The solubility of magnesium oxalate is respectively high, but the solubility of calcium oxalate is low at  $\text{pH} = 4 \sim 11$  so selective separation is possible.



**Table I-4.** Solubility products of hydroxides, carbonates and oxalates at 25°C

Hydroxides/Carbonates/Oxalate	Solubility (g/L)	K <sub>sp</sub>
Mg(OH) <sub>2</sub>	0.00096	1.5 × 10 <sup>-11</sup>
MgCO <sub>3</sub>	0.039	4.0 × 10 <sup>-5</sup>
Mg <sub>5</sub> (CO <sub>3</sub> ) <sub>4</sub> (OH) <sub>2</sub> ·4H <sub>2</sub> O	.	1.2 × 10 <sup>-5</sup>
MgC <sub>2</sub> O <sub>4</sub>	0.104	8.6 × 10 <sup>-6</sup>
Ca(OH) <sub>2</sub>	0.173	7.9 × 10 <sup>-6</sup>
CaCO <sub>3</sub>	0.00062	3.8 × 10 <sup>-9</sup>
CaC <sub>2</sub> O <sub>4</sub>	0.00067	2.3 × 10 <sup>-9</sup>

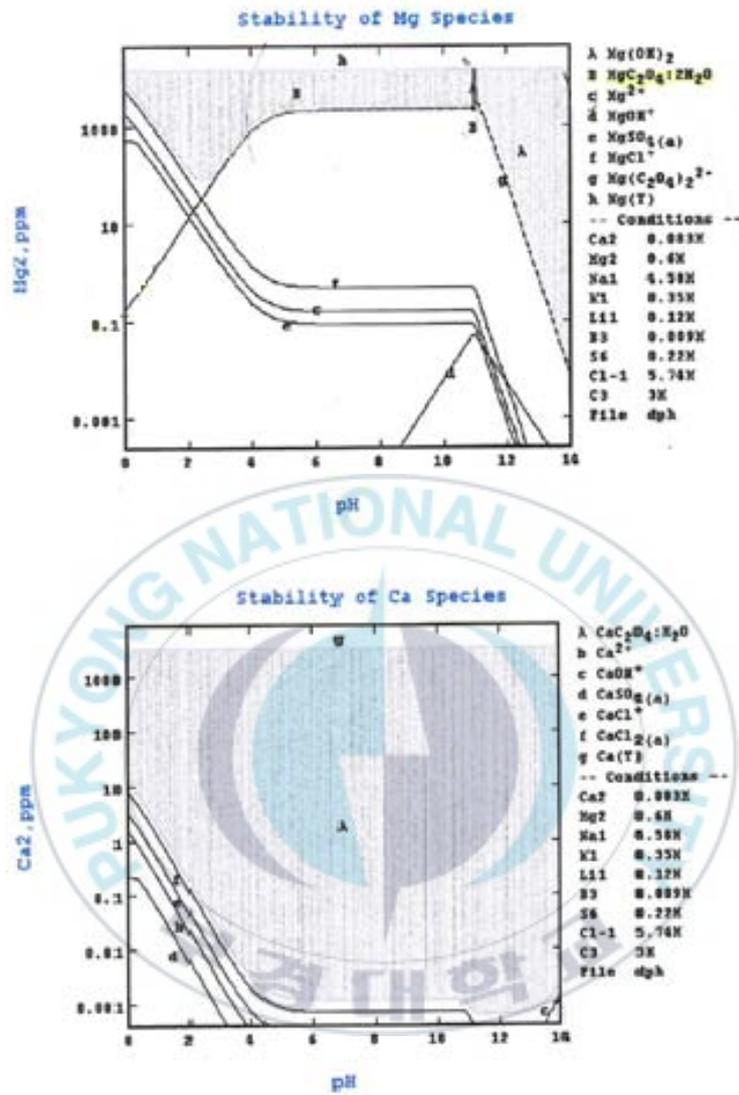


Figure I-4. Precipitation diagram of calcium and magnesium species.<sup>19-21</sup>

## Chapter II. Experimental

### II-1. Materials and reagents

The seawater sample was sampled nearby Samchonpo Power Plant located in Gosung, Gyeongsangnamdo province, Korea. It brought to laboratory at KICET(Korea Institute of Ceramic Engineering & Technology). The suspended materials and impurities in seawater were removed by 2  $\mu\text{m}$  housing filter. Chemical composition of sample was measured by inductively coupled plasma atomic emission spectroscopy (ICP-OES 8300, Perkin elmer) and was listed in Table I-2. The pH (pH meter, HI5221, HANNA) and ion conductivity (Conductivity meter, HI2030, HANNA) of the seawater were 8.5 and 48.0 mS/cm, respectively. Sodium hydroxide (99 %, DAEJUNG) and sodium oxalate (99 %, DAEJUNG) were used in this study as chemical reagents to improve Ca/Mg separation efficiency.

### II-2. Experimental methods

Experiments were divided into two types: Effect of acid and heat treatment and addition of chemical reagent ( $\text{Na}_2\text{C}_2\text{O}_4$ ). Experiments to improve Ca/Mg separation efficiency and magnesium hydroxide production are shown in Figure II-1.

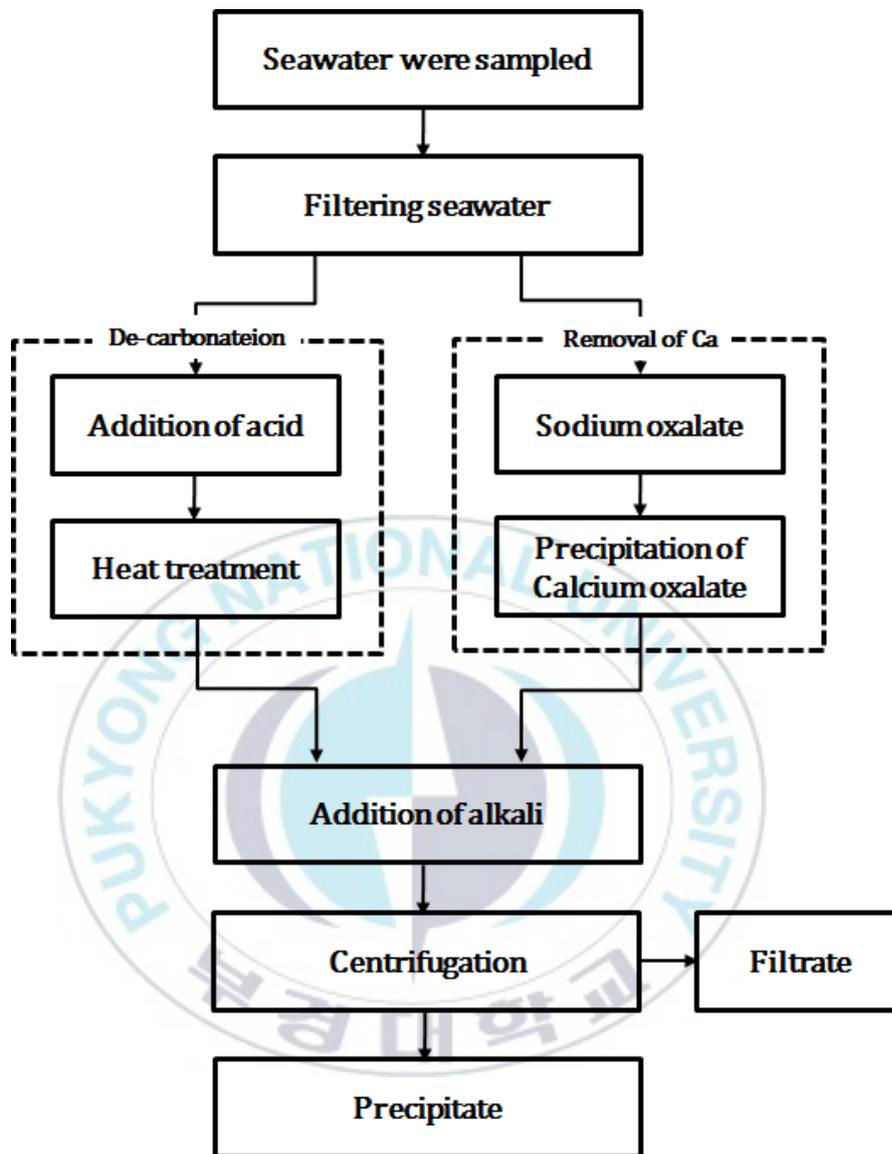


Figure II-1. Process of magnesium hydroxide production.

### **II-2-1. Acid and heat treatment experiment**

Acid and heat treatment experiment were carried out with reference to Table I-3 which shows carbonate ion behavior in solution according to pH.<sup>10</sup> The volume of 0.1 N HCl added to seawater was 15, 30, and 45 ml, while the feed seawater sample was kept constant at 1.0 L. As the amount of acid added to seawater increased, the pH of the seawater gradually decreased until pH = 2.5. Most of carbonate ion was insoluble in acid conditions, more than 141 ppm, 98.9 mol % in dissolved carbon dioxide, and removed it in solution by evaporation at 70 °C for 30 min. Then seawater of 1.0 L was stirred for 30 min with addition of alkali, equivalent molar amount with Mg ion concentration, that is 0.056 mol/L, 4.41 g NaOH. The transparent seawater became turbid by addition of alkali. The precipitate was separated from the liquid phase by centrifugation (8,000 rpm, 15 min, 25 °C). The water soluble salt such as Na<sup>+</sup>, K<sup>+</sup>, Cl<sup>-</sup> and SO<sub>4</sub><sup>2-</sup> were removed from precipitate by washing with the second distilled water five times. The purity of precipitate and residual seawater were checked by inductively coupled plasma atomic emission spectroscopy (ICP-OES).

### **II-2-2. Addition of chemical reagent experiment**

Addition of chemical reagent (Na<sub>2</sub>C<sub>2</sub>O<sub>4</sub>) experiment is calcium ion extraction method using the difference in solubility of magnesium and calcium oxalate salts.

Oxalic acid can be used to selectively extract Ca ion in the form of calcium oxalate in seawater and brine.<sup>14-15,19</sup> However, acidic conditions require not only delicate pH control but also environmental regulation. In this study, experiments were carried out using sodium oxalate which can improve Ca/Mg separation efficiency without changing pH = 8.0 ~ 8.5 of seawater. Seawater of 1.0 L was stirred for 30 min with sodium oxalate, 1.0, 1.5, and 2.0 times of equivalent molar amount with Ca ion concentration, that is 1.34, 2.01, and 2.68 g Na<sub>2</sub>C<sub>2</sub>O<sub>4</sub>. The precipitate after the reaction (addition of sodium oxalate) filtrated to separate the precipitation and filtrate. The precipitate was analyzed by SEM to know the morphology and XRD to find its phase. Filtrate was analyzed by ICP-OES to get concentration of ion in seawater. The seawater eliminated Ca ion was followed by treatment with sodium hydroxide (NaOH) to precipitate magnesium hydroxide. Experiments were carried out under the same conditions (amount of NaOH added, reaction time, centrifugation conditions, amount of washes, etc.) as in the magnesium hydroxide production experiment that was previously conducted after de-carbonation. At the point the powder products was analyzed in terms of crystal structure, purity and morphology by x-ray diffraction (XRD; D/MAX-2200/PC, Rigaku), ICP-OES and scanning electron microscope (SEM; SM-300, TOPCON). The residual seawater after process was checked for confirmation of proper separation of magnesium and calcium ions from sea water by ICP-OES.

### **II-2-3. Magnesium carbonate production by reaction with CO<sub>2</sub>**

The unit 2 process is magnesium carbonate formation reaction starting from the precipitate (5 % (w/v)) produced through each process (untreated, de-carbonation and addition of sodium oxalate). The precipitates dispersed in slurry form were stirred with CO<sub>2</sub> (99.9 %, 0.5 L/min) bubbling in 500 ml beaker. The XRD and ICP analyzes were carried out to confirm the purity of magnesium carbonate.



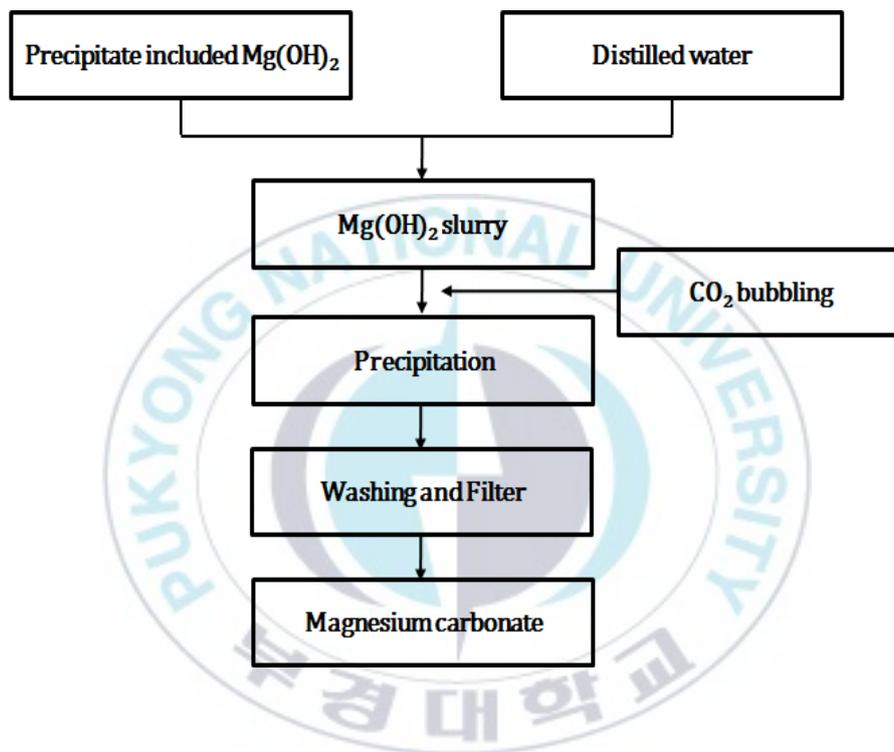


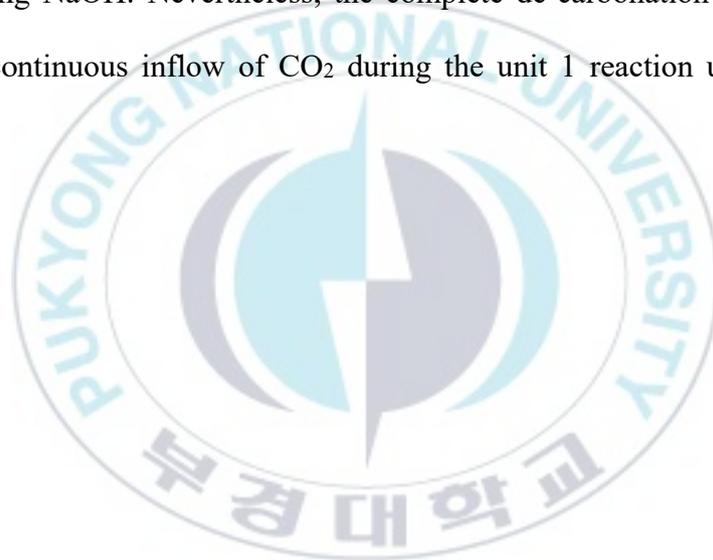
Figure II-2. Process of magnesium carbonate production.

## Chapter III. Results and Discussion

### III-1. Effect of acid and heat treatment

It was summarized in Table III-1 about the effect of de-carbonization process on the purity of magnesium hydroxide. The elimination of soluble carbonate ion ( $\text{HCO}_3^-$ ,  $\text{CO}_3^{2-}$ ) was done by acidification to reduce solubility of  $\text{CO}_2$  and boiling to remove dissolved  $\text{CO}_2$ . Then sodium hydroxide was added to precipitate magnesium ion in the form of magnesium hydroxide. The crystalline phase of the products was identified as magnesium hydroxide and calcium carbonate and their phase ratio was further analyzed by JADE program of XRD and ICP. The XRD and ICP results showed that the phase ratio of magnesium hydroxide to calcium carbonate was 81.2 (m/m %) and 83.5 (m/m %), respectively without de-carbonation, and after de-carbonation of acid and heat treatment, the precipitation (denoted to sample 'B~D-AH' in Table III-1) obtained with NaOH addition in the first unit reaction shown that the phase ratio of magnesium hydroxide was 87.4 ~ 97.5 (m/m %) and 89.2 ~ 98.3 (m/m %), respectively. The amount of Ca ion precipitated in the sedimentation of magnesium hydroxide was a double checked from the result of ICP which confirmed the amount of calcium ion in the filtrate after unit 1 reaction. 400 ppm of calcium ion in the initial seawater were present at 321 ~ 380 ppm (A-N: 198 ppm, B-AH: 321 ppm, C-AH: 360 ppm, D-AH: 380

ppm) in the filtrate. As the amount of acid added increased, the conversion to dissolved CO<sub>2</sub> and the removal of carbonate ion in seawater were effective. As the result, the purity of magnesium hydroxide produced through the de-carbonation process increased by 15 % compared with magnesium hydroxide in the non-treatment (A-N: 83.5 (m/m %), D-AH: 98.3 (m/m %)). Before the reaction of unit 1 (precipitation of magnesium carbonate by alkali addition), the efficiency of Ca/Mg separation was improved by acid and heat treatment. Then, the concentration of Mg ion present in seawater was maintained at 0.5 ppm or less by adding NaOH. Nevertheless, the complete de-carbonation was not easy due to the continuous inflow of CO<sub>2</sub> during the unit 1 reaction under alkaline conditions.



**Table III-1.** XRD and ICP analysis of product and residual seawater produced by alkali addition after de-carbonation

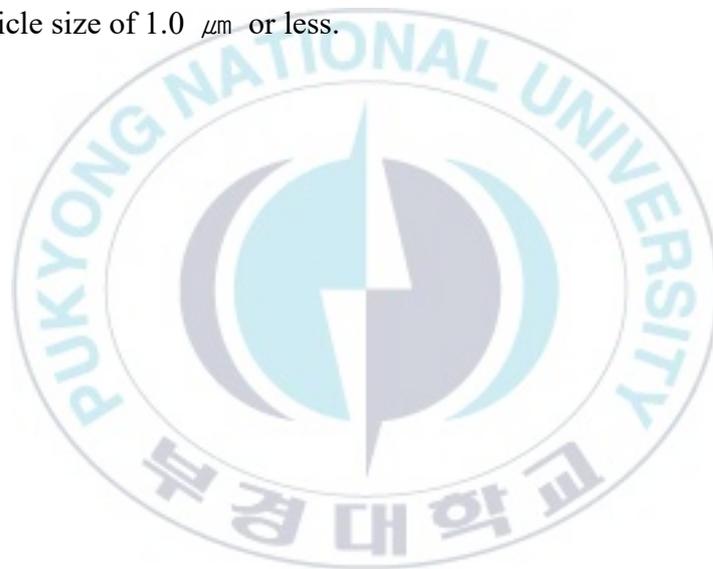
Sample	Volume of acid (ml)	pH after acid addition	Product(%) by XRD		Product(%) by ICP		Residual seawater(mg/L) by ICP	
			CaCO <sub>3</sub>	Mg(OH) <sub>2</sub>	CaCO <sub>3</sub>	Mg(OH) <sub>2</sub>	Ca <sup>2+</sup>	Mg <sup>2+</sup>
A-N	0	8.5	18.8	81.2	16.5	83.5	198	<0.5
B-AH*	15	5.5	12.6	87.4	10.8	89.2	321	<0.5
C-AH*	30	3.2	4.5	95.5	5.3	94.7	360	<0.5
D-AH*	45	2.5	2.5	97.5	1.7	98.3	380	<0.5

\*The sample-AH applied acid and heat treatment to remove carbonate ion in seawater

### III-2. Effect of addition of chemical reagent

It was summarized in Table III-2 about the effect of amount of sodium oxalate added in seawater on the purity of magnesium hydroxide. As the amount of reagent ( $\text{Na}_2\text{C}_2\text{O}_4$ ) increased, the amount of calcium oxalate salt precipitated increased. The concentrations of Ca and Mg ion remaining in seawater after precipitation of calcium oxalate were confirmed by ICP-OES analysis. Concentrations of Ca and Mg ion were 36 ppm and 1,310 ppm in the A-SO filtrate, 23 ppm and 1,280 ppm in the B-SO filtrate, and 8 ppm and 1,230 ppm in the C-SO filtrate, respectively. After checking the effect of addition of chemical reagent, sodium hydroxide was added to precipitate magnesium ion in seawater to magnesium hydroxide. The crystalline phase of the products was identified as magnesium hydroxide and calcium carbonate and their phase ratio was further analyzed by ICP. The ICP results showed that the phase ratio of magnesium hydroxide to calcium carbonate was 99.4 ~ 99.8 (m/m %) (donated to sample 'A~C-SO' in Table III-2) and the concentration of Ca and Mg ion in the filtrate after the unit1 reaction was in 0.5 ppm or less. The smaller the concentration of calcium ion in the filtrate was, the less the probability that Ca was contained as an impurity in the production of magnesium hydroxide under alkaline conditions. In the case of sample C-SO in which calcium ion was most effectively removed before unit 1, the purity of magnesium hydroxide was the highest at 99.8 (m/m%). Compare to the de-carbonation process, the sodium oxalate addition process

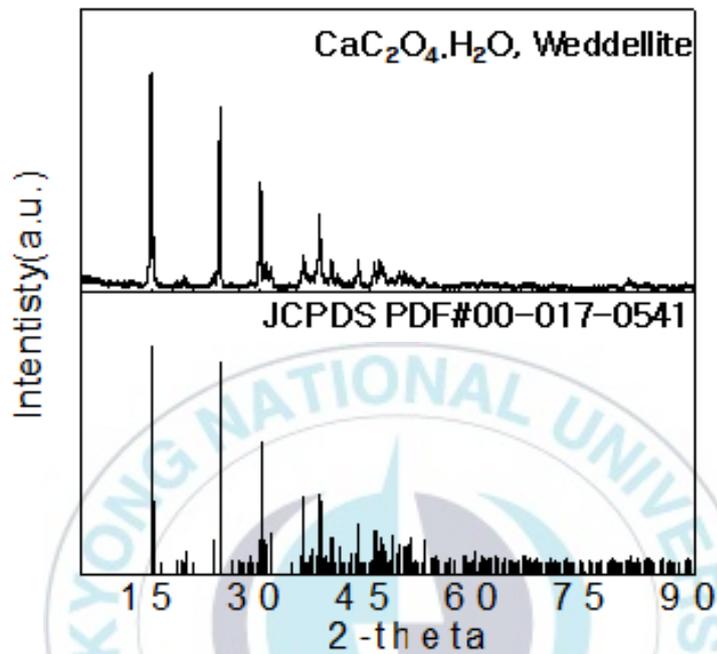
significantly improved the purity of magnesium hydroxide. Primary product before the unit 1 reaction was analyzed in terms of crystal structure, morphology by XRD and SEM. As shown in the Figure III-1, XRD analysis with  $2\theta = 5 \sim 90^\circ$  was done in this study and crystal phase identified calcium oxalate with a tetragonal lattice structure. As the result of the analysis using the XRD JADE program, co-precipitation of  $\text{Mg}(\text{OH})_2$  was not detected but confirmed by ICP-OES. As shown in the Figure III-2, the calcium oxalate produced through the reaction of  $\text{Ca}^{2+}$  ion and  $\text{C}_2\text{O}_4^{2-}$  ion had an irregular structure with an average primary particle size of  $1.0 \mu\text{m}$  or less.



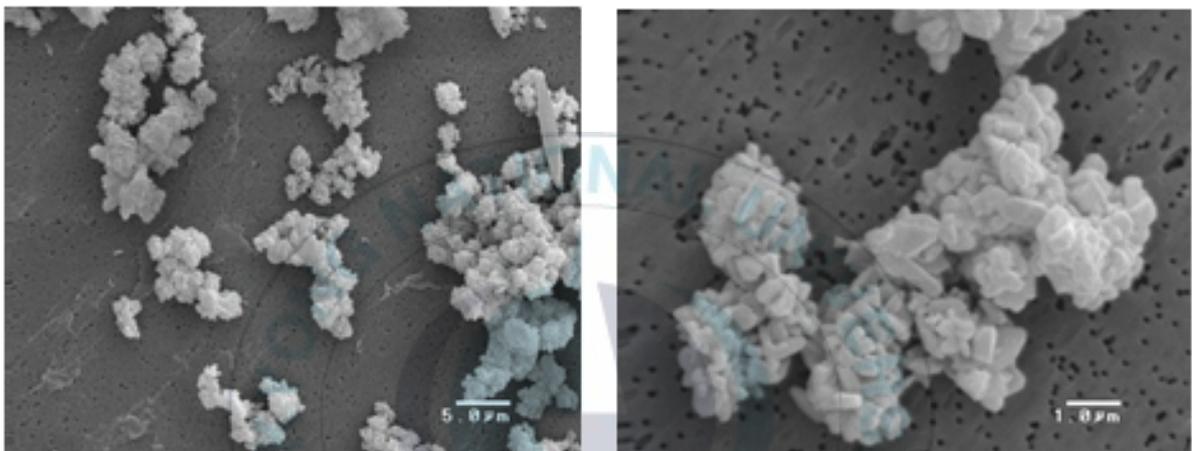
**Table III-2.** XRD and ICP analysis of product and residual seawater produced by alkali addition after calcium ion removal via sodium oxalate

Sample	Amount of $\text{Na}_2\text{C}_2\text{O}_4$ (g)	After production of calcium oxide				After production of magnesium hydroxide			
		Product(%) by ICP		Residual seawater(mg/L) by ICP		Product(%) by ICP		Residual seawater(mg/L) by ICP	
		$\text{CaC}_2\text{O}_4$	MgO	$\text{Ca}^{2+}$	$\text{Mg}^{2+}$	$\text{CaCO}_3$	$\text{Mg}(\text{OH})_2$	$\text{Ca}^{2+}$	$\text{Mg}^{2+}$
A-SO*	1.34	99.8	0.2	35	1,310	0.6	99.4	<0.5	<0.5
B-SO*	2.01	99.7	0.3	23	1,280	0.4	99.6	<0.5	<0.5
C-SO*	2.68	99.3	0.7	8	1,230	0.2	99.8	<0.5	<0.5

\* The sample-SO use sodium oxalate to remove calcium ion in seawater

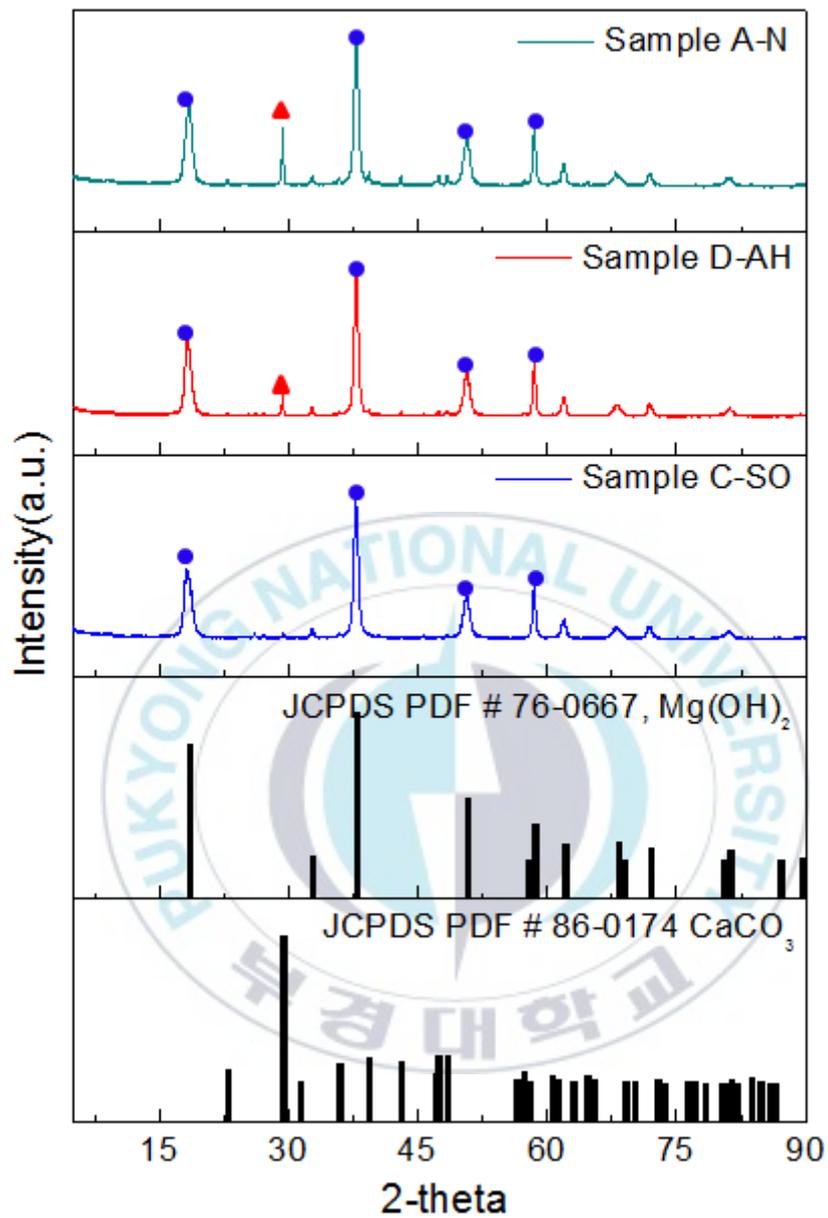


**Figure III-1.** XRD pattern of precipitate obtained through addition of sodium oxalate.

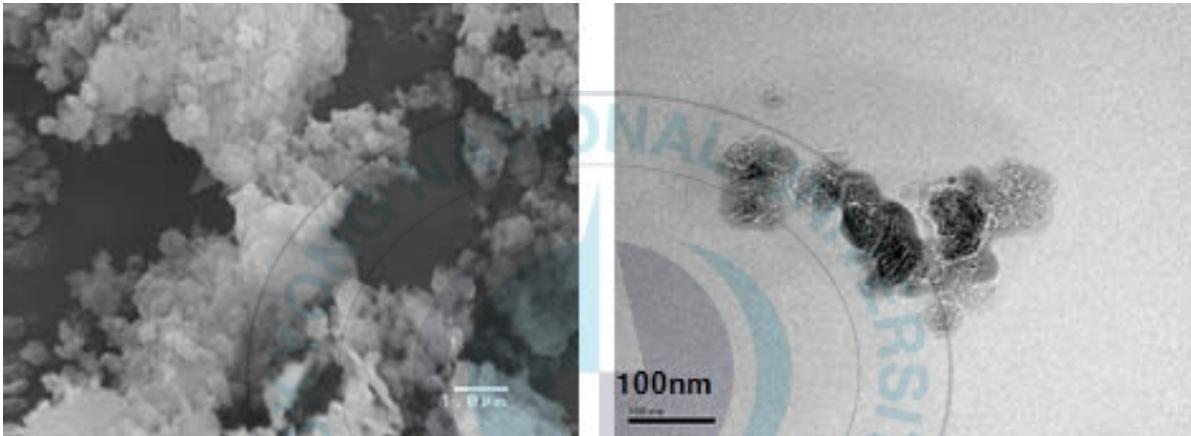


**Figure III-2.** SEM images of calcium oxalate obtained from sodium oxalate before unit 1 reaction.

Figure III-3 shows the XRD patterns of magnesium hydroxide produced by the untreated (A-N), de-carbonation (D-AH), and calcium removal treatment(C-SO) process. In the case of the A-N sample, magnesium hydroxide was produced under no-treatment before unit 1, so the amount of calcium carbonate co-precipitated was the greatest. As a result of ICP, the phase ratio of magnesium hydroxide to calcium carbonate was 83.5 (m/m %). Both samples (D-AH, C-SO) were the highest purity of the magnesium hydroxide produced through each process (de-carbonation and addition of sodium oxalate). In the D-AH sample, the phase ratio of magnesium hydroxide to calcium carbonate was 98.3 (m/m %). In the C-SO sample, the phase ratio of magnesium hydroxide to calcium carbonate was 99.8 (m/m %). Secondary product in the unit 1 reaction was analyzed in terms of crystal structure, morphology by XRD and SEM. As shown in the Figure III-3, X-ray diffraction (XRD) analysis with  $2\theta = 5 \sim 90^\circ$  was done in this study and crystal phase identified magnesium hydroxide with a hexagonal lattice structure. As the result of the analysis using the XRD JADE program, co-precipitation of  $\text{CaCO}_3$  (Calcite) with a hexagonal lattice structure was detected. As shown in the Figure III-4, the magnesium hydroxide produced through the reaction of  $\text{Mg}^{2+}$  ion and  $\text{OH}^-$  ion had an spherical structure with an average primary particle size of  $0.5 \mu\text{m}$  or less.



**Figure III-3.** XRD patterns of magnesium hydroxide obtained from the untreated (A-N), de-carbonation (D-AH), and calcium removal treatment(C-SO) process.



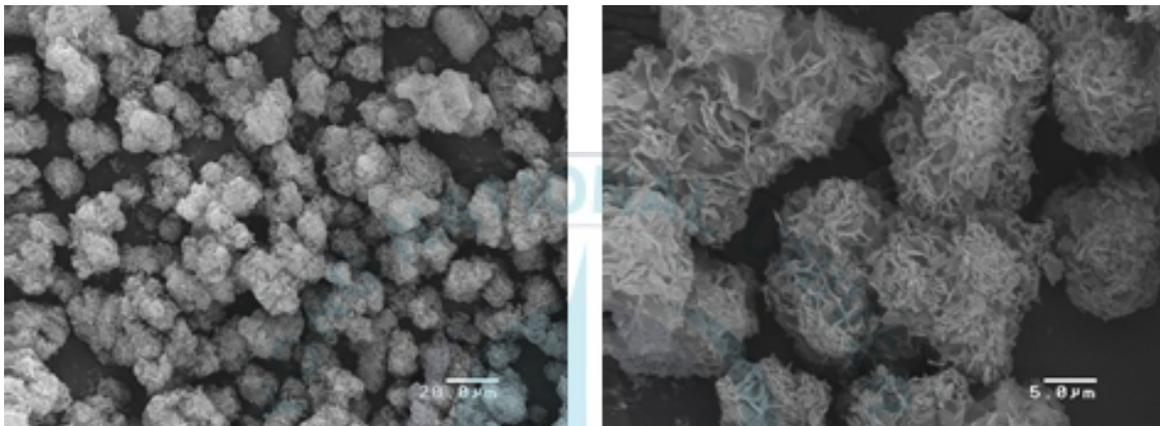
**Figure III-4.** SEM and TEM images of magnesium hydroxide in unit 1 reaction.

### **III-3. Effect of Ca/Mg separation on the purity of magnesium carbonate**

Magnesium carbonate was produced by reaction carbon dioxide with three kinds of magnesium hydroxide (A-N, D-AH, C-SO) having different purity generated through the steps (untreated, de-carbonate, sodium oxalate addition). Table III-3 summarized the effect of Ca/Mg separation methods on the purity of magnesium carbonate. As a result of ICP, the phase ratio of magnesium carbonate was 84.2 (m/m %) in A-N sample. Both samples (D-AH, C-SO) were the highest purity of the magnesium hydroxide produced through each process (de-carbonation and addition of sodium oxalate). In the D-AH sample, the phase ratio of magnesium carbonate was 97.2 (m/m %). In the C-SO sample, the phase ratio of magnesium carbonate was 99.2 (m/m %). As shown in the above results, calcium carbonate contained in magnesium carbonate was mostly originated from calcium ion in seawater.

**Table III-3.** XRD and ICP analysis of product prepared by reaction of magnesium hydroxide with carbon dioxide after the unit 1 reaction

Sample	Product(%) by XRD		Product(%) by ICP	
	CaCO <sub>3</sub>	Mg carbonate	CaCO <sub>3</sub>	Mg carbonate
A-N	18.2	81.8	15.8	84.2
D-AH	3.6	96.4	2.8	97.2
C-SO	0.6	99.4	0.8	99.2



**Figure III-5.** SEM images of magnesium carbonate produced by reaction of carbon dioxide with magnesium hydroxide produced unit 1 reaction.

## Chapter IV. Conclusions

Studies on the improvement of the purity of carbonates ( $\text{MgCO}_3$ ,  $\text{CaCO}_3$ ,  $\text{Na}_2\text{CO}_3$ ) carried out by using selective Ca/Mg separation method such as de-carbonation and addition of reagent process. The de-carbonation process through acid and heat treatment was a method for removing carbonate ion in seawater, and the sodium oxalate addition process was a method for eliminating calcium ion in seawater. Both of them was methods for inhibiting the co-precipitation of calcium carbonate in the production of magnesium hydroxide by addition of alkali. After the de-carbonate step, magnesium hydroxide with a purity of 98.3 (m/m %), and magnesium carbonate with a purity 97.2 (m/m %) were produced through addition of alkali and  $\text{CO}_2$  bubbling in the sample D-AH. However, it spent a lot of time and energy because of heat treatment. In addition, the complete de-carbonation was not easy due to the continuous inflow of  $\text{CO}_2$  during the reaction under alkaline conditions. After calcium ion removal through the addition of reagent ( $\text{Na}_2\text{C}_2\text{O}_4$ ) step, magnesium hydroxide with a purity of 99.8 (m/m %), and magnesium carbonate with a purity 99.2 (m/m %) were produced in the sample C-SO. The pH of seawater was not changed regardless of addition of sodium oxalate. It was possible to remove Ca ions from seawater without further processing such as acid and heat treatment, and the Ca ions after the

reaction was 8 ppm. Considering that the Ca ion was 400 ppm in the initial seawater, the concentration reduction effect was over 40 times, and thus the purity of magnesium hydroxide produced was improved. Through these experiments, we have searched for an optimal solution for improving the purity of magnesium carbonate. As a result, it was possible to produce magnesium carbonate having a purity of 99.8 (m/m %) or more when sodium oxalate, 2.0 times of equivalent molar amount with Ca ion concentration was added. In order to prepared each high purity carbonate, the calcium and magnesium should be well separated. The purity of magnesium hydroxide was improved by decarbonation process and addition of sodium oxalate before the unit 1 reaction. Also, the concentration of calcium and magnesium ions in the filtrate after the unit 1 reaction was found to be 0.5 ppm or less by ICP analysis. Excess sodium ions were presented in the filtrate with minimal calcium and magnesium concentrations, and it produced high purity sodium carbonate or sodium bicarbonate through electrolysis and reaction with carbon dioxide. Through stepwise reactions, it was possible to produce seawater desalination as well as to produce various high-purity carbonates.

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## 감사의 글

모교인 부경대학교에서 공학도로서 연구하지는 않았지만 한국세라믹기술원이라는 연구기관에서 과제를 진행하게 도와주신 지도교수 박성수 교수님께 진심으로 감사의 말씀드립니다. 그리고 석사가 되기 이전 학부생으로서 지식을 쌓을 수 있게 도와주신 이근대 교수님, 진영읍 교수님, 박진환 교수님, 문명준 교수님, 장동욱 교수님, 손민영 교수님 그리고 박치영 교수님 정말 감사합니다. 그리고 2년 동안 부족함 많은 저의 연구를 지켜봐 주시고 지도해 주신 임형미 박사님께 진심으로 감사의 말씀드립니다. 타지에 올라와 석사생으로 생활하는 동안 하나의 팀으로 함께 일해온 고현석박사, 소윤누나, 희선누나, 임주형, 경우, 그리고 사무실에서 도움을 주신 영준이형, 우성이형, 진욱이, 석훈이 모두 감사합니다. 길면 길고 짧으면 짧은 2년이라는 시간 동안 한없이 부족한 저를 모든 분들께서 믿음 하나로 성장하게 도와주셨습니다. 여전히 부족함 많고 배울 부분이 많은 저이지만 좀 더 넓은 세상에서 스스로 일어설 수 있는 기회를 주셔서 잘 마무리하게 되었습니다. 이 세상은 보이지 않는 끈으로 연결되어 있으며 제가 지난 2년동안 더듬으며 찾아온 짧은 세라믹기술원에서의 삶이라는 끈의 끝부분이 보입니다. 지난 모든 시간들과 사람들의 추억이 앞으로 나아갈 밑거름이 되었다는 것을 믿어 의심치 않습니다. 석사 생활 동안 저를 지지해주고 도와주신 모든 분들께 다시 한번 감사의 말씀을 드립니다. 감사합니다.