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工學碩士 學位論文

산업부산물(CKD, PSA)을 이용하여  
해수로부터 마그네슘을 회수하는 방법

Method for recovering magnesium from seawater using  
industrial by-products (CKD, PSA)



指導教授 金明珍  
共同指導教授 李熙俊

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韓國海洋대학교 海洋科學技術專門大學院

海洋科學技術融合學科

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위원장 고 성 철 (인)

위 원 김 명 진 (인)

이 희 준 (인)

2016년 7월

한국해양대학교 해양과학기술전문대학원

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# 산업부산물(CKD, PSA)을 이용하여 해수로부터 마그네슘을 회수하는 방법

Cho, Taeyeon

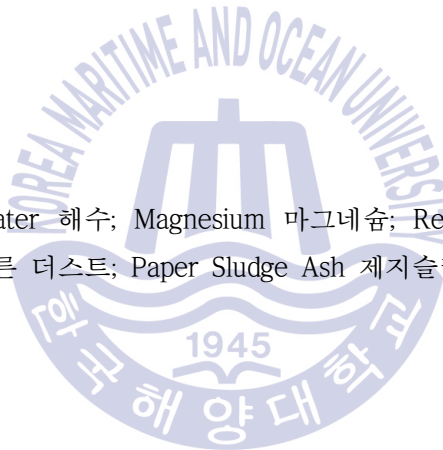
Department of Convergence Study on the Ocean Science and  
Technology  
Graduate School of Korea Maritime and Ocean University

## Abstract

본 연구에서는 해수에 용존되어 있는 마그네슘을 회수하기 위하여 3 가지 단계를 진행하였다. 해수에 산업부산물을 주입하여 마그네슘을 침전시키는 단계, 산을 주입하여 침전된 마그네슘을 용출시키는 단계, 산에 용출된 마그네슘에 아세톤을 주입하여 마그네슘을 석출하는 단계로 진행하였다. 해수로부터 마그네슘을 농축하기 위하여 세 가지 침전제(NaOH, 시멘트 킬른 더스트, 제지슬러지소각재)를 이용하여 마그네슘을 침전시키고, 황산을 이용하여 마그네슘을 용출하는 실험을 진행하였다. 세 가지 침전제의 침전반응 효율은 100 %에 가까웠으며, 용출반응 효율은 77~89 %였다. 침전반응과 용출반응을 통해 해수의 마그네슘이 약 3.8~4.4배 농축되었으며 그 때 마그네슘 농도는 4975~5775 mg/L이었다. 본 연구에서 침전제로 사용한 산업부산물의 반응효율은 거의 100 %로

기존의 고가 침전제와 비슷하였다. 해수의 마그네슘이 4배 이상 농축된 용액에 아세톤을 첨가하여 황산마그네슘을 석출하였다. 용액의 pH가 높을수록, 그리고 아세톤의 비율이 높을수록 고체 황산마그네슘의 생성 효율이 높아졌다. 용액의 pH가 1.0~1.5이고, 용액:아세톤=1:1.5(v:v)일 때 거의 100 %의 마그네슘이 황산마그네슘 수화물( $MgSO_4 \cdot 6H_2O$ )로 석출되었다. 석출 공정에 사용한 아세톤은 분별증류에 의해 100 % 회수되었다. 해수의 마그네슘 농도가 1300 mg/L 이므로, 해수 1 톤으로부터 황산마그네슘( $MgSO_4 \cdot 6H_2O$  기준) 12.3 kg을 회수할 수 있다.

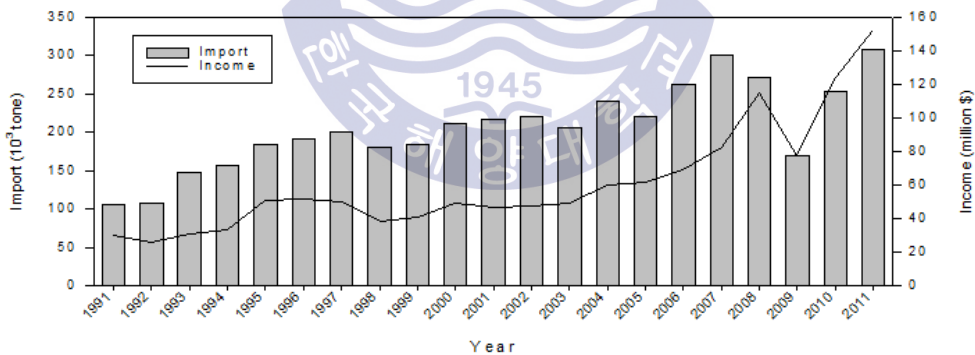
**KEY WORDS:** Seawater 해수; Magnesium 마그네슘; Recovery 회수; Cement Kiln Dust 시멘트 킬른 더스트; Paper Sludge Ash 제지슬러지소각재.



# Chapter 1. Introduction

## 1. Background

Magnesium is as strong as steel, 40 % lighter than aluminum. Because of the high strength, durability, impact resistance and the structural properties of the magnesium, it has been used in a variety applications (Shim & Lee, 2011). It is used as important raw material at domestic industries such as electronic, automobile and iron. In the future it is expected that the demand of magnesium for produce high quality and light products will be increased (Park & Knag, 2011). Now the consuming of magnesium in the Korea relies on import, Table. 1 shows import and income of magnesium during annual.



**Fig. 1** Annual domestic magnesium import and income

(Data source: Korea International Trade Association)

Identified world land reserves of magnesium totaled 3.6 billion tones. The magnesium exists the formation of magnesite, dolomite, serpentine and brucite. The concentration of magnesium at seawater is 1300 mg/L

and considering the whole seawater, the magnesium quantity is  $1.84 \times 10^{15}$  tons which are 500,000 time bigger than land reserves. Since South Korea is surrounded by the sea, the magnesium recovery from seawater is expected to improve our country's national competitiveness and economic effects of the industrial markets.

When recovering the magnesium from mineral, the first step is extracting the magnesium using acid and second step is precipitating the magnesium injecting the alkaline substance (Elsner & Rothon, 1998; Ozdemir et al., 2009). Elsner and Rothon (1998) recovered the precipitated magnesium hydroxide by drying at the high temperature. Ozdemir et al. (2009) conducted the experiment that hydrochloric acid was added to magnesite, then extracted the magnesium and boiled the solution to precipitated and recovered the magnesium chloride. Mainly used precipitant were lime, dolomite, NaOH, KOH,  $\text{NH}_4\text{OH}$  and etc, and before precipitating the magnesium, the calcium was removed first (Ju et al., 2001; Henrist et al., 2003; Lee & Lim 2007; Lehmann et al., 2014). Ju et al. (2001) recovered the magnesium by adding the NaOH to the bittern where the magnesium concentration is 100 % higher than the normal seawater. They were first to proceed with the decarboxylation process at the bittern to prevent carbonate produced. And seeding process was done in order to increase the particle of magnesium hydroxide. Finally, approximately 95 % of precipitated magnesium hydroxide was extracted by using an organic extraction agent. Also Lee and Lim (2007) recovered the magnesium from bittern using NaOH. First, they put the sulfuric acid to remove the calcium in the brine, and the carboxy methyl cellulose was added to precipitate the magnesium hydroxide which was produced by adding NaOH. The average particle size of magnesium hydroxide was  $0.5 \mu\text{m}$  and purity was 99.5 %.

Technology extracting magnesium from seawater to produce magnesium (magnesium oxide) is already commercially available in the world, but it is not easy to secure economic efficiency. And the development of a high efficiency and economic recovery techniques are still required. When we recovered the magnesium using conventional precipitant, an alkali, the biggest problems are precipitating and filtering the magnesium hydroxide. In addition, the economic costs related to the alkaline precipitant such as NaOH and  $\text{NH}_4\text{OH}$  can be described as the main problems with practical use. Among the many ways to solve this problem, it is an alternative to find out the replacing cheap precipitant is an alternative. For example, industrial by-products such as paper sludge ash (PSA), cement kiln dust (CKD), slag, and fly ash can be used a replaced precipitant.

## 2. Objective

In this study, we suggested an effective method for recovery the magnesium from seawater. In chapter 2, the experiments were performed to find out the optimum condition of the precipitant which could precipitate the magnesium. And precipitated magnesium was extracted by sulfuric acid. In chapter 3, acetone was used to precipitated the magnesium sulfate. Magnesium sulfate is insoluble at the acetone, using this character, the acetone was added to the solution which dissolved the magnesium sulfate and precipitated the magnesium sulfate. At each step the precipitation efficiency, extraction efficiency and the final precipitation efficiency were calculated.

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## Chapter 2. Production of concentrated magnesium solution from seawater using industrial by-products



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## 1. Introduction

Magnesium is as strong as steel, 40 % lighter than aluminum. And magnesium has been used in a variety of applications due to the high strength-weight ratio properties, durability, impact resistance and structural properties (Shim & Lee, 2011). Magnesium is used in very important raw material at major domestic industry, such as electronics, automotive and steel industry. In the future, demand of magnesium will be increased to produce light weight and high quality products (Park & Kang, 2011). Furthermore the use of magnesium compound in a variety of industries including the pharmaceutical, agriculture and the building is very large. Consumption of magnesium in domestic relies on import currently.

The amount of world's magnesium land reserves is estimated at about 36 million tons and the reserves exist in the mineral like magnesite, dolomite, serpentine and brucite. The magnesium concentration of seawater is about 1300 mg/L and in the whole seawater quantity, the magnesium amounts in seawater is  $1.85 \times 10^{15}$  tons (500,000 times of land reserves).

The methods of recovering the magnesium are divided with two methods, the one is from the mineral and the other is from the seawater (include brine and bittern). When recovering the magnesium from the mineral, the first step is extracting the magnesium using acid and the second step is to precipitate the magnesium injecting the alkaline substance (Elsner & Rother, 1998; Ozdemir et al., 2009). Methods for recovering magnesium from seawater are precipitation using alkaline substance (Ju et al., 2001; Henrist et al., 2003; Lee & Lim, 2007; Lehmann et al., 2014), ion exchange resin (Lee & Bauman, 1980;

Khamizov et al., 1998; Muraviev et al., 1996), solvent extraction (Grinstead & Davis, 1970; Anil & Syamal, 1974) and etc.

There were many researches recovering the magnesium from seawater using alkaline precipitant. Lime, dolomite, NaOH, KOH and  $\text{NH}_4\text{OH}$  were mainly used as precipitant and most cases they removed the calcium before precipitating the magnesium (Ju et al., 2001; Henrist et al., 2003; Lee & Lim, 2007; Lehmann et al., 2014). Ju et al. (2001) recovered the magnesium by injecting the NaOH to the bittern which has the concentration of magnesium 100 times higher than the seawater does. First they conducted decarboxylation process at the bittern to prevent the carbonate produced, seeding process to large the making magnesium hydroxide and injecting NaOH to precipitate magnesium effectively. Finally, they extracted 95 % precipitated magnesium using organic extracts. Also Lee and Lim (2007) recovered the magnesium from bittern using NaOH. First they removed the calcium by adding the sulfuric acid to the bittern, and added carboxy methyl cellulose to precipitated resulting magnesium hydroxide using NaOH. The average particle size of recovered magnesium hydroxide was  $0.5 \mu\text{m}$  and the purity was 99.5 %.

Recently there were many tries to recover the magnesium from brine (Lehmann et al., 2014; Atashi et al., 2010; Tran et al., 2013). Atashi et al. (2010) recovered the magnesium by vaporizing the brine. First they precipitated calcium in the brine using  $\text{Na}_2\text{SO}_4$ , extracted NaCl and KCl, respectively by vaporizing the filtrate and extracting the magnesium by  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ . At this time the recovery rate was 75 % and purity was 98 %. Also Tran et al. (2013) recovered the 95 % magnesium to the form of Magnesium oxalate by adding oxalic acid and NaOH. Before precipitating the magnesium they removed calcium by modulating the pH and oxalate/Ca mole ratio. Lehmann et al. (2014) added micro size

synthetic magnetite to the brine and produced magnesium hydroxide, which allowed to precipitate magnetite surface by the addition of KOH. And they extracted the magnesium by adding the acid, at this time the purity of this magnesium solution was 97 %. pH was adjusted from 4 to 6 to prevent not melting magnetite. Due to the magnet, the filtration of magnesium hydroxide was very easy.

The filtration of magnesium hydroxide is the biggest difficulty of using alkaline precipitant when recovering the magnesium. Because the magnesium hydroxide is not only very fine particles but also low crystallization properties (Henrist et al., 2003; Baird et al., 1988). To solve magnesium hydroxide particle problem, Alamdari et al. (2008) added the 5~40  $\mu\text{m}$  magnesium hydroxide seed as the magnesium hydroxide was made and recovered the 50~60  $\mu\text{m}$  sized magnesium hydroxide.

The technology by extracting magnesium from seawater to produce magnesia (magnesium oxide) is already commercially available in the world. But it is no easy to secure economic efficiency and it still requires the development of highly efficiency and economic extraction techniques. In particular, the economic costs related to the alkaline precipitation agent, such as NaOH,  $\text{NH}_4\text{OH}$  can be described as the main problems with practical use. Among the many ways to solve this problem, the search of cheap precipitating agent is an alternative. For example the alkaline industrial by-products such as paper sludge ash (PSA), cement kiln dust (CKD), slag and fly ash can be used as precipitant. There was few research using industrial by-products as precipitant. Kang et al. (2012) just conducted the research recovering the magnesium with magnesium hydroxide formation by adding the coal and NaOH to the seawater.

At this study, we found out the optimum condition that the process which recovering the magnesium from seawater by enriching the high concentration. At first, magnesium from seawater was precipitated using three precipitant (NaOH, CKD, PSA). The precipitated magnesium hydroxide was extracted by sulfuric acid, derived the optimal conditions for precipitation and extraction reaction of three precipitating agent and compared the reaction efficiency. In this study, it is possible to significantly lower the magnesium production cost using industrial by-products as the precipitant. Also the magnesium concentration of seawater is lower than the former study's brine or bittern and the seawater have advantage of stably supplying the magnesium without depletion.

## **2. Materials and Methods**

### **2.1 Materials and analyses**

Seawater was gathered near the Busan port and filtered with 0.45  $\mu\text{m}$  filter before the experiment. CKD and PSA, used in this study, was supplied each in domestic 'D' and 'G' company. We used NaOH (97 %) and  $\text{H}_2\text{SO}_4$  (95 %) reagent from Junsei company. To find out the particle size of CKD and PSA, laser diffraction particle size analyses (Beckman coulter, LS 13320) was used. To analyze CKD and PSA composition, the X-ray diffraction (XRD, Shimadzu, Optima 8300) and X-ray fluorescence analyzer (Shimadzu, XRF-1700) was used. The pH of CKD and PSA was measured in the following way. Each industrial by-product and distilled water was mixed with 1:5 (g:mL) ratio and pH was measured after filtration (Lee et al., 2011). AAS (Perkin Elmer, AA200) was used to measure the calcium and magnesium concentration,

pH meter (Thermo, Orion star 211) was used to measure the pH.

## 2.2 Methods

Experiment was performed as Fig. 1. The magnesium from seawater was precipitated to magnesium hydroxide by adding alkaline substance to seawater and magnesium was extracted using a small amount of acid and made high concentration of magnesium solution.

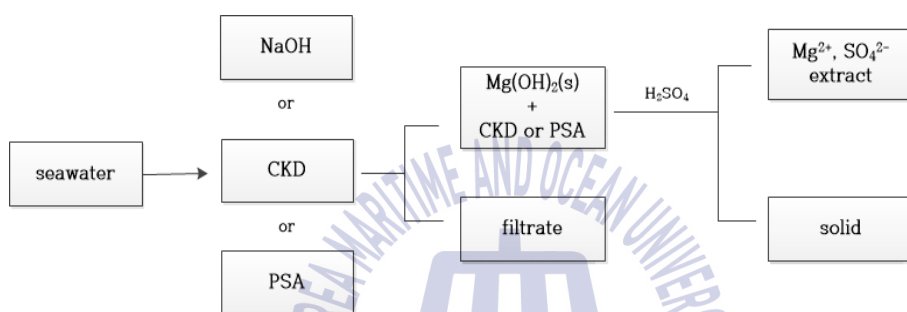


Fig. 1 Schematic diagram for concentrating the magnesium in seawater

### 2.2.1 Magnesium precipitation

Three kinds of alkaline substance (NaOH, CKD, PSA) were used to precipitate the magnesium at seawater. Following experiments were conducted to find out the optimum condition of each precipitant.

#### 2.2.1.1 NaOH

The magnesium was precipitated when 4 M NaOH solution was added to 100 mL seawater. We controlled the volume of 4 M NaOH solution (0.5~5.0 mL) and in accordance with the concentration was 2.0~20.0 mmol. 4 M NaOH with seawater was mixed at 250 rpm during 30 min and the suspension was filtered with 0.45  $\mu\text{m}$  filter. pH of filtrate was measured and calcium and magnesium concentration was measured with

AAS. The filtered solid was dried at 105 °C during 12 hours and used XRD analyze.

### **2.2.1.2 CKD, PSA**

0.5~3.5 g of CKD was added to 100 mL seawater and mixed with 250 rpm for 30 min. The suspension was stored at the 3 °C refrigerator during 24 hours and filtered with 0.45 µm membrane filter. The concentration of calcium and magnesium of filtration was measured using AAS and pH was also measured. The filtered solid was dried at 105 °C during 12 hours and used XRD analyze. Same experiment was conducted with PSA instead CKD.

### **2.2.2 Magnesium extraction**

Magnesium was precipitated with a formation of magnesium hydroxide using three kinds of precipitant and the sulfuric acid was used to extract this magnesium. To decide the optimum sulfuric acid concentration, a variety of concentration of sulfuric acid was used. Before the magnesium extraction experiment, solid sample was prepared with the method of “2.2.1 Magnesium precipitation” and the precipitant amount to the seawater was added more than optimum condition.

#### **2.2.2.1 NaOH**

4 M NaOH 29 mL was added to 1 L seawater and synthesized solid was dried. Dried solid was crashed and divided into 5 samples equally and used to extraction experiments. Total dried solid was 3.65 g and each sample amount was 0.73 g. The sulfuric acid (0.1, 0.3, 0.5, 1.0, 2.0,



M) 40 mL was added to each 10 solid sample and mixed with 250 rpm during 30 min. Suspension was filtered with 0.45  $\mu\text{m}$  membrane filter. Filtrate's pH was measured and filtrates' calcium and magnesium concentration was measured by AAS. Filtered solid was measured XRD after dried at 105  $^{\circ}\text{C}$  for 12 hours.

### **2.2.2.2 CKD**

15 g of CKD was added to 1 L seawater and obtained solid was dried. Dried solid was crashed and divided into 10 samples equally and used to extraction experiments. Total dried solid was 8.0 g and each sample amount was 0.8 g. The sulfuric acid (0.1, 0.3, 0.5, 1.0, 1.5, 2.0, 2.5, 3.0, 3.5, 4.0 M) was added to each 10 solid sample and mixed with 250 rpm during 30 min. The next step was same with "2.2.2.1 NaOH"

### **2.2.2.3 PSA**

PSA 20 g was added to 1 L seawater and synthesized solid was dried. The following step was same with "2.2.2 CKD" . but the total dried solid which reacted to seawater with PSA was 27.0 g and was divided into 2.7 g 10 sample.

## **3. Results and Discussion**

### **3.1 Seawater and material analyses**

The pH of seawater of this study was 8.3, and calcium and magnesium concentration was 443 and 1300 mg/L. This value was similar with reference average value (Table 1). Here, pre-treatment such as smash or crush was not needed because the average particle size of CKD and

PSA was 23.6  $\mu\text{m}$  and 126.9  $\mu\text{m}$ . The each pH of CKD and PSA was 13.1 and 12.9.

**Table 1** Concentrations of Mg and Ca in seawater

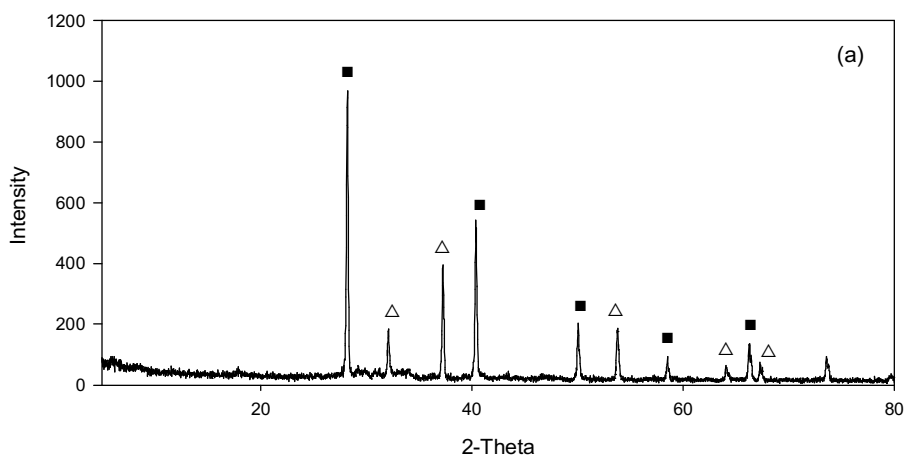
|                       | Concentration (mg/L) |     |
|-----------------------|----------------------|-----|
|                       | Mg                   | Ca  |
| this study            | 1,300                | 443 |
| Leggett and Rao, 2015 | 1,290                | 411 |

Table 2 was the XRF analyses of CKD and PSA. Main component of these two kinds of industrial by-products was calcium. CKD contains 42.7 % calcium and PSA contains more calcium in 42.7 %. Also CKD and PSA contains magnesium 2.8 % and 4.4 %, respectively. Magnesium was also contained more in the PSA.

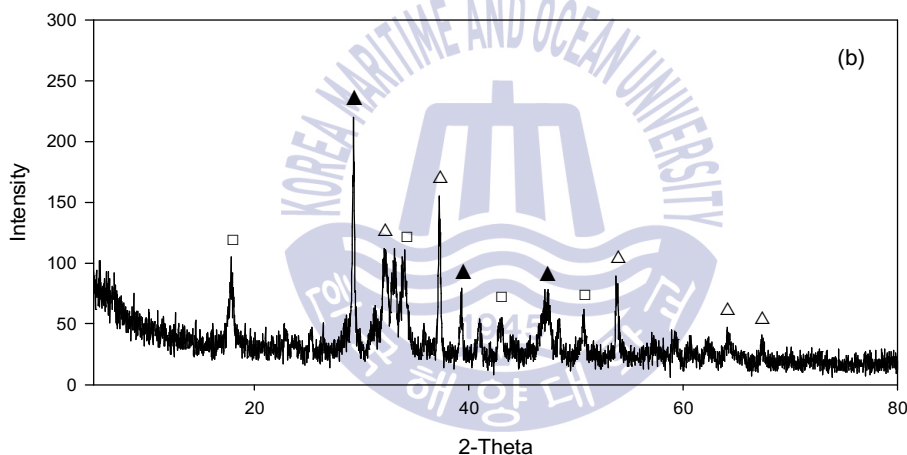
**Table 2** XRF analyses of CKD and PSA

|                       | Concentration (mg/L) |     |
|-----------------------|----------------------|-----|
|                       | Mg                   | Ca  |
| this study            | 1,300                | 443 |
| Leggett and Rao, 2015 | 1,290                | 411 |

Fig. 2 was the XRD analyses of CKD and PSA. The main compositions of CKD were sylvine (KCl) and lime (CaO), most of calcium existed in the simple and soluble formation. In the meanwhile, the main composition of PSA was portlandite [ $\text{Ca}(\text{OH})_2$ ], lime (CaO) and calcite ( $\text{CaCO}_3$ ), most calcium existed in the formation which is hard to dissolve in water.



■: Sylvine (KCl), △: Lime(CaO)



□: Portlandite [Ca(OH)<sub>2</sub>], △: Lime (CaO), ▲: Calcite (CaCO<sub>3</sub>)

Fig. 2 XRD diagrams: (a) CKD, (b) PSA

### 3.2 Magnesium precipitation

The magnesium in seawater precipitated by alkaline precipitant like Eq. (1) and its equilibrium constant (K) was very high as  $1.78 \times 10^{11}$ . On the other hand, the solubility product ( $K_{sp}$ ) of the magnesium hydroxide for the reverse reaction of Eq. (1) is very small as  $5.61 \times 10^{-12}$ , which

means that the precipitated magnesium hydroxide was insoluble matter. Also the calcium in seawater could be precipitated to the calcium hydroxide by alkaline precipitant like Eq. (2). However solubility product ( $K_{sp}$ ) of calcium hydroxide was  $5.02 \times 10^{-6}$ , which was higher than the magnesium hydroxide.



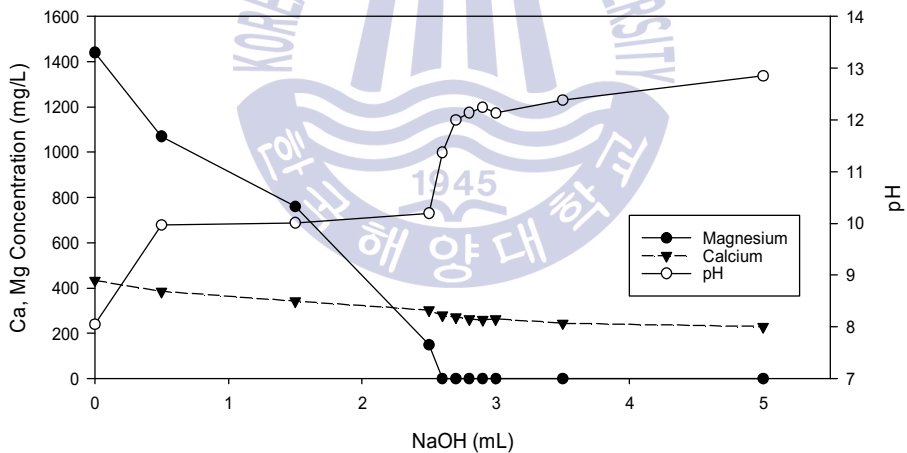
At this study, the magnesium in seawater was precipitated effectively in the formation of magnesium hydroxide by three kinds of precipitant and each precipitant was derived by the optimum condition of the experiment.

### 3.2.1 NaOH

The white solid was created as injecting the 4 M NaOH to the seawater. There were many difficulties to filtrate because magnesium hydroxide has characteristics of floating and hard to coagulation (Henrist et al., 2003; Baird et al., 1988). The amounts of solid were increased and became constant as the 4 M NaOH addition. pH of filtrate and magnesium and calcium concentration per 4 M NaOH volume was seen at Fig. 3. The magnesium concentration was decreased rapidly as the 4 M NaOH injection volume was increased. And the magnesium concentration of filtrate became 0 mg/L when the NaOH injection volume was 2.6 mL (10.4 mmol). This means most of magnesium in seawater was precipitated to solid and pH was 11.4. Also the calcium concentration was decreased slowly as the NaOH volume was increased. This tendency appears because the solubility of calcium hydroxide was relatively large. Magnesium concentration and pH change have opposite

tendency to each other as shown in Fig. 3. Fig. 4 is a result of the precipitated solid XRD analyses. It was confirmed that only the peak of magnesium hydroxide.

The magnesium concentration of seawater is 1300 mg/L and at 100 mL seawater has 5.35 mmol magnesium. To precipitate the magnesium hydroxide, magnesium reacted with two times of hydroxide ions as shown at Eq. (1). In this way to precipitate the magnesium in seawater we need 10.70 mmol hydroxide ions. This value is very consistent with this study's optimum condition of NaOH, 10.4 mmol. The minimum volume of 4 M NaOH to precipitate all of magnesium from 100 mL seawater was 2.6 mL (10.4 mmol).



**Fig. 3** Variations of the magnesium and calcium concentrations and pH in the filtrate obtained after the precipitation with the 4 M NaOH volume

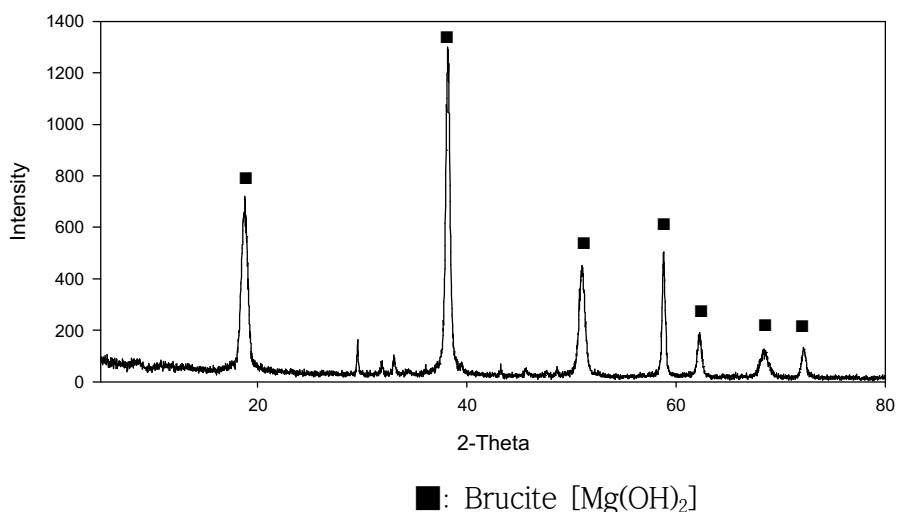


Fig. 4 XRD diagram of solid obtained after the precipitation reaction between seawater and NaOH

### 3.2.2 CKD

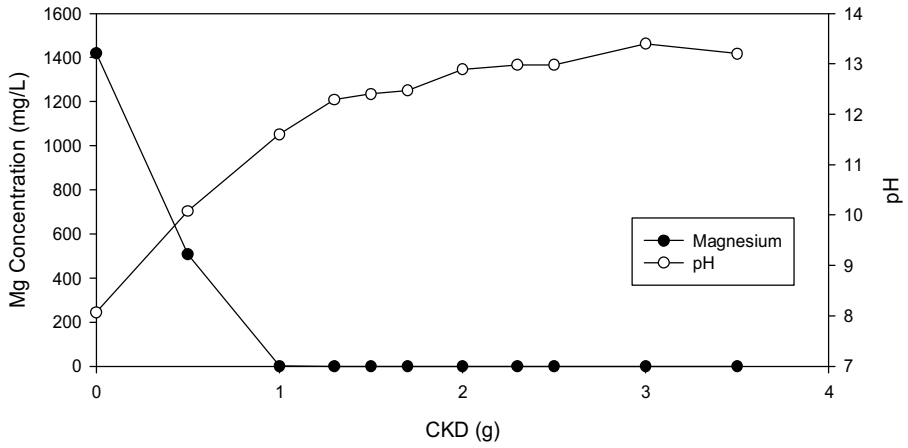
When using CKD and PSA as a precipitant, it was much easier to filtrate than using NaOH. The reason was thought because the particles of magnesium hydroxide was rarely coagulation and precipitated with industrial by-products. This was the advantages of industrial by-products as a precipitant (Ju et al., 2001; Lee & Lim, 2007; Alamdari et al., 2008).

When the CKD was added varying amounts (0.5~3.5 g) to the 100 mL seawater, magnesium concentration and pH of filtrate was shown at Fig. 5. As the CKD amount was increased, the pH was also increased rapidly and later increased gradually. The maximum pH value was 13.4. However the magnesium concentration was decreased sharply and became to 0 mg/L. It means whole magnesium in seawater was

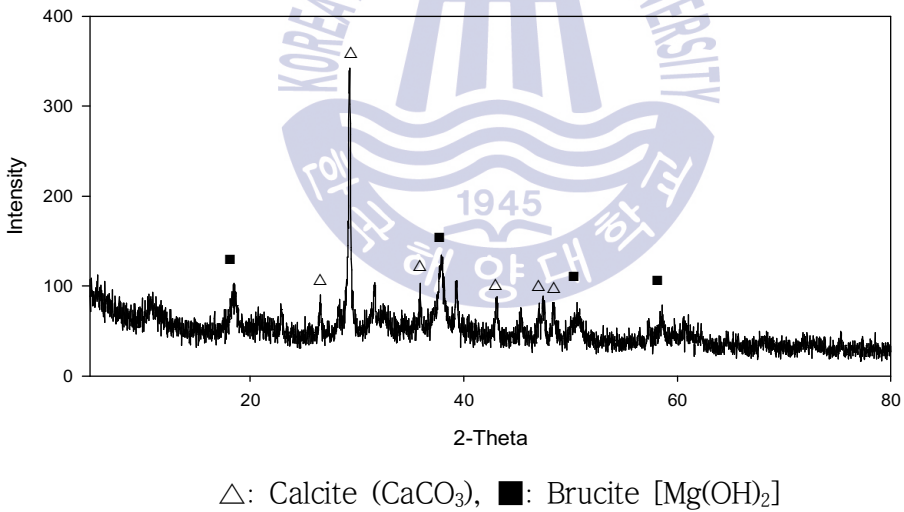
precipitated to magnesium hydroxide. Fig. 6 was the results of XRD analyses which the solid after the reaction which CKD and seawater. The main peak was magnesium hydroxide and this presence was the reason of precipitated the magnesium hydroxide. The minimum CKD amount to precipitated the magnesium in 100 mL seawater is 1.0 g and at this time the pH was 11.8.

Meanwhile as the CKD amount was increased, the calcium concentration of filtrate was increased and became steady. The calcium concentration was increased from 443 mg/L to 3700 mg/L because the calcium oxide and calcium hydroxide from CKD was dissolved to the water [Eq. (3), (4)]. According to this reaction the pH of seawater, 8.3, was increased to 13.4. The optimum condition of CKD was decided to seawater:CKD=100:1 (mL:g).





**Fig. 5** Variations of the magnesium concentration and pH in the filtrate obtained after the precipitation with the CKD amount

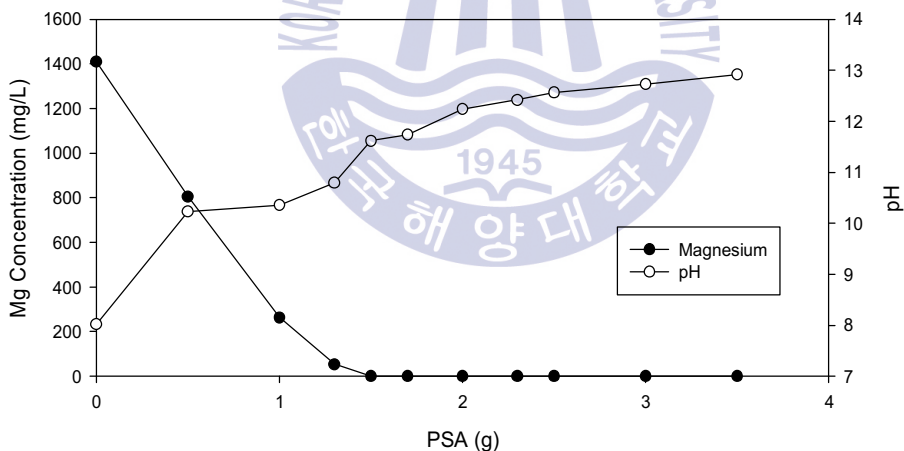


**Fig. 6** XRD diagram of solid obtained after the precipitation reaction between seawater and CKD

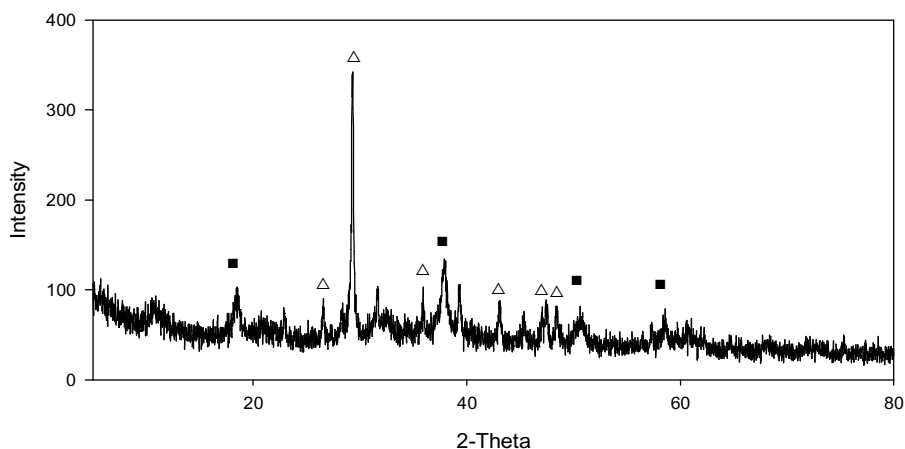


### 3.2.3 PSA

When the PSA 0.5~3.5 g was injected to 100 mL seawater, magnesium concentration and pH change was shown at Fig. 7. This results were similar with the precipitation reaction using CKD. As the PSA amounts which dosage to 100 mL seawater was increased, the pH was also increased to 12.9. The minimum PSA amounts was 1.5 g in precipitated the magnesium from seawater and at that point, the pH value was 11.6. Also as the PSA was injected to seawater, the calcium concentration was increased to 3100 mg/L. Fig. 8 was the results which analysed the solid using XRD. The main peak was just calcite, and magnesium oxide peak was not observed. In precipitated the magnesium in 100 mL seawater, PSA should be injected 1.5 times than CKD.



**Fig. 7** Variations of the magnesium concentration and pH in the filtrate obtained after the precipitation with the PSA amount



△: Calcite (CaCO<sub>3</sub>)

**Fig. 8** XRD diagram of solid obtained after the precipitation reaction between seawater and PSA

### 3.3 Magnesium extraction

The results shown at “3.2 Magnesium precipitation”, magnesium in seawater was precipitated to magnesium hydroxide effectively using three kinds of precipitant. However the magnesium hydroxide was easily suspended and hard to coagulate so the filtration was very hard (Henrist et al., 2003; Baird et al., 1988). Furthermore, because the magnesium hydroxide was mixed with industrial by-products, it is hard to divide physically. Then the precipitated magnesium hydroxide was extracted using sulfuric acid. Among the other acids, sulfuric acid could be solidified in the calcium which interfered magnesium recovery. As shown at Eq. (5), calcium reacted to sulfuric acid, and then made calcium sulfate solid (Haynes & Lide, 2010).



### 3.3.1 NaOH

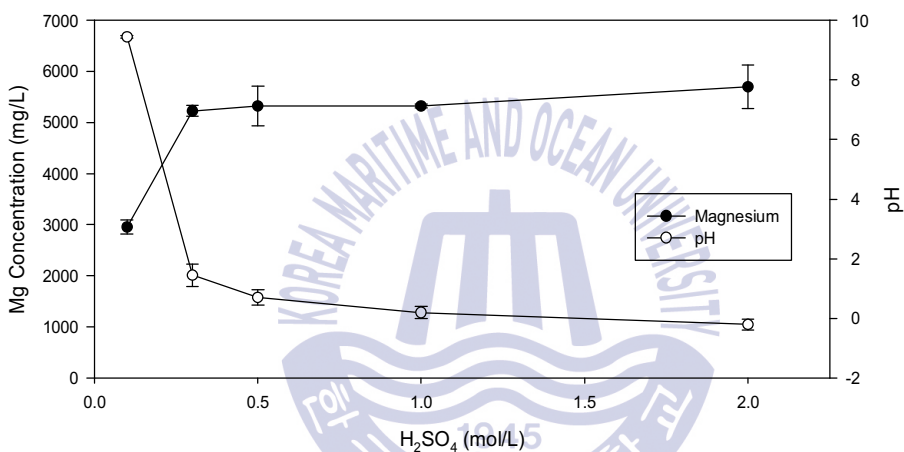
As explaining “2.2.2.1 NaOH” , NaOH was injected to the seawater to create the magnesium hydroxide solid, and this solid was used to extracting experiments. 116 mmol NaOH was added to 1 L seawater, and this was 11 % excess of the optimum condition, which was the way to precipitate the magnesium in seawater completely. After the precipitation reaction, the filtrate pH was 11.7. The solids was divided into 5 parts and used extraction experiments. One sample could be made based on the seawater 200 mL. Sulfuric acid volume was fixed to 40 mL and controlled the sulfuric acid concentration from 0.1 to 2.0 mol/L. Magnesium concentration in seawater was 1300 mg/L and through this, precipitated magnesium hydroxide mole at the 200 mL seawater was 10.70 mmol and the acid which extracting the magnesium hydroxide was 10.70 mmol too. As shown Eq. (6), magnesium hydroxide and sulfuric acid react ratio was 1:1. Containing this ratio, sulfuric acid concentration range was determined.



Fig. 9 showed pH and magnesium concentration changes per the change of sulfuric acid concentration. Filtrate magnesium concentration was increased and pH was decreased rapidly according to sulfuric acid concentration that was increased until 0.3 M. When 0.3 M sulfuric acid 40 mL added to solids, the magnesium concentration of filtrate was 5225 mg/L and pH was 1.45. However the concentration of sulfuric acid was higher than 0.3 M, and the magnesium concentration and pH was steady. This means that the optimum condition of sulfuric acid was 0.3 M and 40 mL to extract the magnesium from 200 mL seawater. 0.3 M sulfuric acid 40 mL was 12.00 mole and this was similar with theoretically

calculate dosage, 10.70 mmol. At the optimum condition, the magnesium concentration of filtrate was 5225 mg/L and the 40 mL filtrate has 209 mg of magnesium. From the precipitated magnesium amount, 260 mg, and this value, 209 mg, the magnesium extraction efficiency was 80.4 % (Eq. 7).

$$\text{Extract efficiency}(\%) = \frac{\text{magnesium in 40mL extrats}(mg)}{\text{precipitated magnesium in 200mL seawater}(mg)} \times 100 \quad (7)$$



**Fig. 9** Variations of the magnesium concentration and pH in the extract with the H<sub>2</sub>SO<sub>4</sub> concentration. Here, the volume of H<sub>2</sub>SO<sub>4</sub> is fixed at 40 mL and NaOH is used as a precipitant

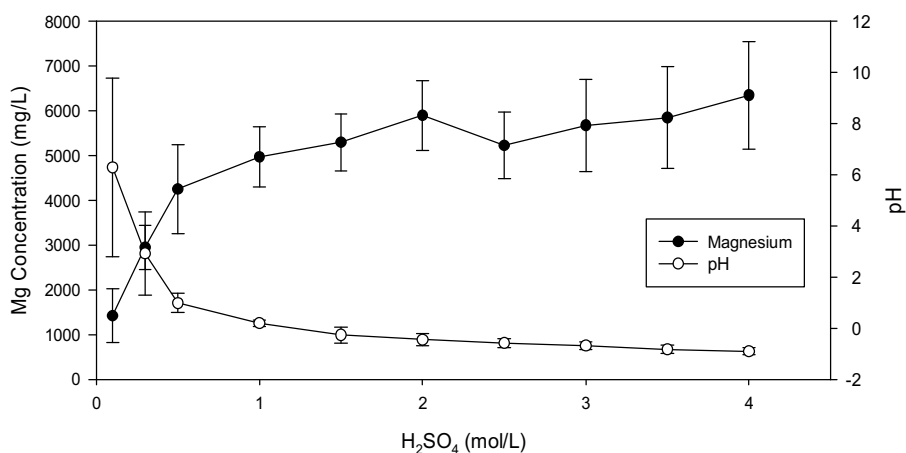
### 3.3.2 CKD

To prepare the solid sample for extraction examples, magnesium was precipitated by 15 g CKD when it was added to 1 L seawater. After the magnesium hydroxide with CKD was dried, the total amounts of solid were 8.2 g. Despite of formation the magnesium hydroxide, the CKD amounts were less than the first dosage. According to Fig. 2(a), CKD included lots of KCl and this KCl dissolved the seawater as well as the

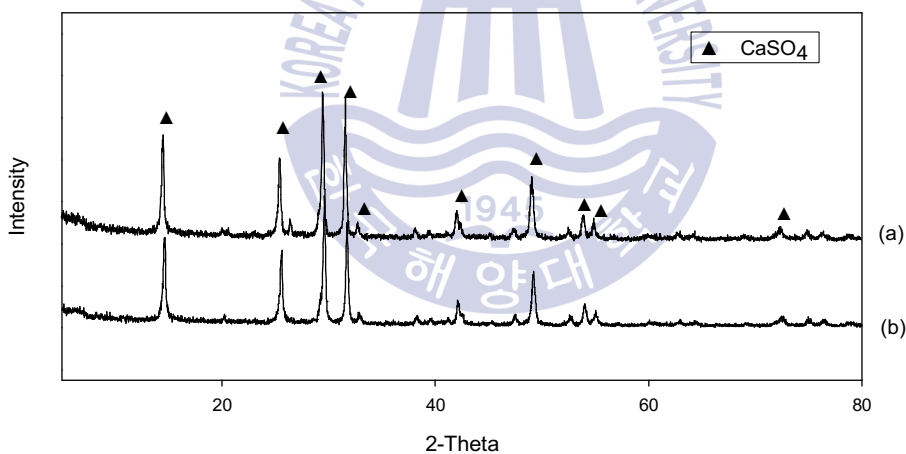
calcium oxide and calcium hydroxide dissolve the water too.

After the precipitation, the pH of filtrate was 12.3. To find out the optimum condition based on 100 mL seawater, sulfuric acid volume was fixed at 20 mL and the concentration was changed from 0.1 to 4.0 M. The results were shown at Fig. 10. Until the sulfuric acid concentration was 1.0 M, the pH was decreased as magnesium concentration was increased. The magnesium concentration of filtrate was 4975 mg/L and pH was 0.20 when the sulfuric acid concentration was up to 1.0 M. However when the sulfuric acid concentration exceeded 1.0 M, the magnesium concentration and pH changes were little. Based on 100 mL seawater, the optimum condition to extract the magnesium precipitated by CKD was 1.0 M sulfuric acid 20 mL. At the optimum condition, the magnesium concentration was 4975 mg/L and calculated magnesium recovery efficiency was 76.5 % (Eq. 7).

Regardless of sulfuric acid concentration, the calcium concentration was measured 13~50 mg/L. Considering the calcium contents of CKD, this value was very low. Because the sulfuric ion reacted to calcium, it created the insoluble solid and calcium sulfate. Fig. 11 showed the XRD results of dried solid after extracting the magnesium with sulfuric acid. Main peaks were not magnesium hydroxide but calcium sulfate.



**Fig. 10** Variations of the magnesium concentration and pH in the extract with the H<sub>2</sub>SO<sub>4</sub> concentration. Here, the volume of H<sub>2</sub>SO<sub>4</sub> is fixed at 20 mL and CKD is used as a precipitant



**Fig. 11** VXRD diagrams of solids to remain after the magnesium extraction using H<sub>2</sub>SO<sub>4</sub> : (a) CKD, (b) PSA

### 3.3.3 PSA

To prepare the solid sample for extraction examples, magnesium was precipitated by 20 g PSA, which was added to 1 L seawater. After the

magnesium hydroxide with CKD was dried, the total amounts of solid were 27 g. After the precipitating reaction, dried solid was increased unlike the CKD results. It seemed that the precipitated magnesium from seawater increased the weight.

To find out the optimum condition based on 100 mL seawater, sulfuric acid volume was fixed at 20 mL and the concentration was changed from 0.1 to 4.0 M. The results were shown at Fig. 12. Until the sulfuric acid concentration was 1.5 M the pH was decreased along with magnesium concentration was increased. The magnesium concentration of filtrate was 5775 mg/L and pH was 0.56 when the sulfuric acid concentration was up to 1.5 M. The magnesium concentration was increased gradually and pH was decreased gradually as the sulfuric acid solution was from 1.5 M to 4.0 M. Based on 100 mL seawater, the optimum condition was decided to 1.5 M sulfuric acid 20 mL. Through this value, the extraction efficiency was 88.8 % (Eq. 7). Calcium concentration of filtrate was 0.6~6 mg/L which were much more lower than CKD.

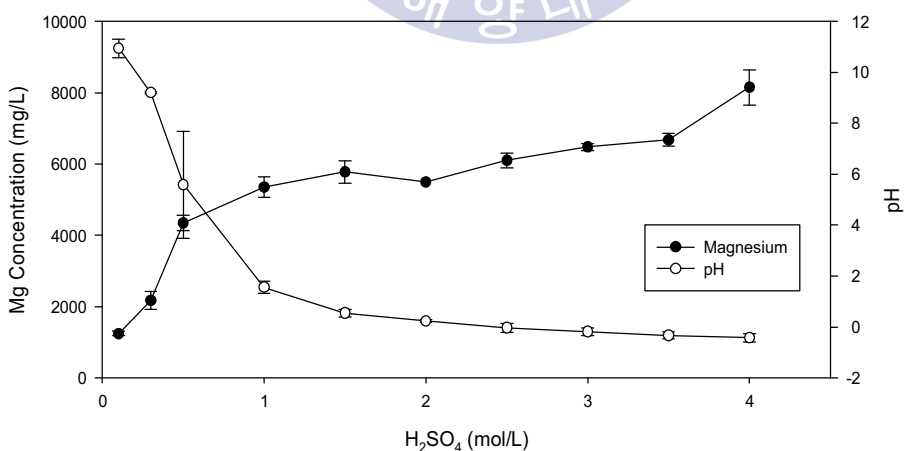


Fig. 12 Variations of the magnesium concentration and pH in the extract

with the  $\text{H}_2\text{SO}_4$  concentration. Here, the volume of  $\text{H}_2\text{SO}_4$  is fixed at 20 mL and PSA is used as a precipitant

#### 4. Conclusions

At this study, three kinds of precipitant (NaOH, CKD, PSA) were used to precipitate the magnesium from seawater to magnesium hydroxide. And using sulfuric acid, magnesium was extracted to high concentrate magnesium solution.

The react efficiency of precipitation using three kinds of precipitant was almost 100 %. The minimum volume to precipitate the magnesium from seawater was : 4 M NaOH 2,6 mL (10.4 mmol), CKD 1.0 g, PSA 1.5 g. Each optimum precipitant was added to seawater, the pH was 11.4~11.8. If we wanted to precipitate the magnesium in seawater, the final pH would exceed to 11.4. Using CKD and PSA, filtration was much easier than using NaOH because particle magnesium hydroxide was precipitated with industrial by-products.

Based on 100 mL seawater, magnesium was precipitated by the precipitant and the optimum condition of 20 mL sulfuric acid was 0.3 M, 1.0 M, 1.5 M. When using the CKD and PSA it includes more components which was dissolved by acid than using NaOH so higher acid concentration was need. At the optimum condition the magnesium extraction efficiency was 77~89 %. When the precipitant was NaOH, CKD and PSA, the magnesium concentration of extracts was 5225, 4975, 5775 mg/L and pH was 1.4, 0.20, 0.56. Despite difference of precipitant and sulfuric acid dosage, the magnesium concentration and pH didn't make a big difference. This proposes that the CKD and PSA could be alternative precipitant of NaOH.



At the results of this study, we could make the magnesium solution which concentration was concentrated 3.8~4.4 times higher than the seawater magnesium (about 1300 mg/L). When recovering the magnesium from seawater, the biggest problem was economic problem. Through this study we look forward to being solved by using industrial by-products such as CKD and PSA.



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### Chapter 3. Precipitation of magnesium sulfate from concentrated magnesium solution for recovery of magnesium in seawater



This chapter has been submitted as : Cho, T. Y. and Kim, M. J.,  
Submitted : Precipitation of magnesium sulfate from concentrated  
magnesium solution for recovery of magnesium in seawater.

## 1. Introduction

The properties of magnesium have white silver color and light metal, and they exist in the formation of magnesite, dolomite, carnalite and etc. This element is the seventh abundant at the earth's crust and the third abundant element in the seawater (Haynes & Lide, 2010). The magnesium concentration of seawater is 1300 mg/L and considering the whole seawater amounts, the magnesium quantity is estimated about  $1.84 \times 10^{15}$  tons.

The magnesium alloys used as a mixture as aluminum, zinc and etc because it is hard and has low density. And this is used for very important raw material at the domestic industry like automobile, steel and digital industry (Shim & Lee, 2011). It is expected to greatly increase the demand for magnesium for a lightweight and high-quality production of the product in the future (Park & Kang, 2011). Currently, South Korea is relying on imports for most of the magnesium. If we develop the way to recover the magnesium from the seawater economically, it is expected to make not only economically effect to domestic industry but also competitiveness of South Korea.

Mostly the magnesium is recovered from mineral or seawater (include bitter and brine). When recovering the magnesium from mineral, researchers extract the magnesium using the acid and solidify the magnesium by precipitation using alkaline substance (Elsner & Rother, 1998; Ozdemir et al., 2009). Elsner and Rother (1998) recovered the magnesium by drying the precipitated magnesium hydroxide at high temperature, Ozdemir et al., (2009) and extracted the magnesium by adding the hydrochloric acid to magnesite and recovered the magnesium

with the formation of magnesium chloride solid by heating the solution.

“Dow Chemical” is well known for recovering the magnesium from seawater and detail of its process as following (Wulandari et al., 2010). Lime was added to seawater to precipitate the magnesium from seawater by the formation of magnesium hydroxide and extracted the magnesium by injecting the hydrochloric acid. Next they precipitated the magnesium chloride solid to concentrate the acid solution and made magnesium metal through the electrolysis the magnesium chloride solid. The used hydrochloric acid was recovered for reuse. Through this method, Dow Chemical’s Texas plant produced 90000~100000 tons of magnesium per year from 50 million gallons of seawater per day (Mutaz & Wagialia, 1990). Meanwhile domestic company, “Posco chemtech”, exports magnesia (magnesium oxide) which was made by seawater and lime (Son et al., 2008).

Magnesium compounds most commonly used in the industry are the magnesium chloride ( $\text{MgCl}_2$ ), magnesium hydroxide [ $\text{Mg}(\text{OH})_2$ ], magnesium sulfate ( $\text{MgSO}_4$ ) and etc.  $\text{MgSO}_4$  was recovered from mineral or artificial synthetic and produced. Magnesium sulfate is very soluble in water. For example, water temperature at 20 °C and 40 °C, 71 g and 91 g  $\text{MgSO}_4$  is dissolved, respectively. But  $\text{MgSO}_4$  is hardly soluble in alcohol and insoluble in acetone (Weast, 1979; O’ Neil, 2006).  $\text{MgSO}_4$  exists in various forms of hydrate along the temperature ( $\text{MgSO}_4 \cdot x\text{H}_2\text{O}$ ,  $x=1\sim7$ ). And heptahydrate is the most normal forms. It is used as paper, fertilizer and medicine.

In our laboratory, we conducted these three process continuously to recover the magnesium from seawater: 1) magnesium precipitation using industrial by-products, 2) magnesium extraction using sulfuric acid, 3) precipitate the magnesium sulfate powder using acetone (Fig. 1).

Through the advanced research cement kiln dust (CKD) and paper sludge ash (PSA) made magnesium in seawater to precipitate 100 % magnesium hydroxide, and magnesium was extracted over the 90 % using sulfuric acid (Cho & Kim, 2016). In this study, acetone was added to precipitate the magnesium dissolved in the sulfuric acid, and the experiments were performed by dividing into two groups: 1) The precipitation experiment was conducted by adjusting the pH and the percentage of acetone at artificial magnesium solution. Through this condition, we decided the optimum condition which magnesium precipitation, and 2) adjusted to the seawater using the optimum condition from artificial magnesium solution.

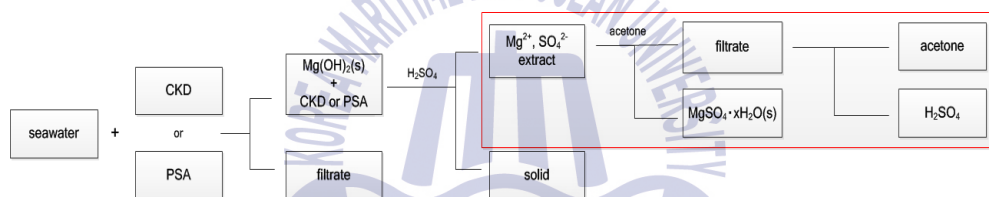


Fig. 1 Schematic diagram for recovering the magnesium from seawater

## 2. Experiment

### 2.1 Materials and analyses

Seawater was attained near the Busan port and filtration was done using 0.45  $\mu\text{m}$  filter before the experiment. Industrial by-product, CKD and PSA, was supplied domestic “D” cement company and “G” paper company, respectively. 97 % NaOH, 95 %  $\text{H}_2\text{SO}_4$  and 99.8 % acetone of Junsei company was used. Particle size of CKD and PSA was measured by laser diffraction particle size analyses (Beckman coulter, LS



13320). To find out the components and contents of solids which CKD, PSA and precipitated magnesium, x-ray diffraction analyses (Shimadzu, Optima 8300) and x-ray fluorescence analyses (Shimadzu, XRF-1700) was used. AAS (perkin Elmer, AA200) was used to measure the calcium and magnesium concentration. pH meter (Thermo, Orion star 211) was used to measure the pH. GC-MS (Shimadzu, Qp-2010 Ultra) was used to qualitative analyses and quantitative analyses of acetone.

## **2.2 Methods**

### **2.2.1 Recovering the magnesium sulfate from the magnesium artificial solution**

Former study of our laboratory, the magnesium concentration after the precipitation and extraction experiments using seawater was 4975~5775 mg/L and pH was 0.20~0.56. Considering this value, artificial solution was manufactured for 10000 mg/L magnesium concentration and -0.26~1.20 pH.

Six kinds of artificial solution's magnesium concentration were 10000 mg/L and pH was different (-0.26, 0.13, 0.30, 0.56, 0.97, 1.20). To make this artificial solution, distilled water, 95 % sulfuric acid 11.75 mL and magnesium hydroxide solid 12.10 g were put into six kinds of 500 mL volumetric flask. And finally 95 % sulfuric acid was put into the flask again but the volume of sulfuric acid were 3, 4.5, 11, 14, 20, 36 mL. Each six flasks had different pH and each 50 mL was taken to 6 kinds of 250 mL erlenmeyer flasks. And acetone (25, 37.5, 50, 62.5, 75, 100 mL) was added each erlenmeyer flask. In other words, each one pH had different acetone ratio (1:0.5, 1:0.75, 1:1, 1:1.25, 1:1.5, 1:2 (v:v)) and

made 36 samples totally. 36 samples were sealed and kept in refrigerator (3 °C) during 24 hours. The filtration was done with 1 µm paper filter, and the filtrate solid was dried and analysed XRD and XRF. The filtrate's pH, volume and magnesium concentration was also measured.

## **2.2.2 Recovering the magnesium sulfate from the seawater**

The process of recovering the magnesium from seawater was divided into three step (pre-precipitant, extract and precipitant). The sample was prepared to experiment the last step, precipitant, and added the acetone to the sample to precipitate the magnesium sulfate powder. Following steps are the method of making sample. CKD 15 g was added to 1 L seawater and mixed at 250 rpm during 30 min. The suspension was kept in refrigerator (3 °C) for 24 hours and filtration was done with 0.45 µm membrane filter. The solids were dried and divided into 5 sample equally. The total weight of dried solids were 9.32 g and each divided sample weight was 1.82 g. 0.5 M and 1.0 M sulfuric acid 40 mL was injected to each two sample and mixed 250 rpm for 30 minutes. Suspension was filtered using 0.45 µm membrane filter. pH and magnesium concentration of filtrate was measured.

The acetone was added to filtrate of 1:1 and 1:1.5 (v:v) ratio, and the filtrate was made by using 0.5 M and 1.0 M sulfuric acid. The acetone mixing ratio was decided through “2.2.1 Recovery the magnesium sulfate from the magnesium artificial solution”. And this solution was kept in refrigerator (3 °C) for 24 hours. The solid was filtered with 1 µm paper filter and dried with 100 °C. XRD, XRF and the weight was also measured. pH and magnesium concentration of filtrate was measured.

In the same way, the precipitation experiments were done with PSA instead of CKD. There were some differences. The PSA amounts were 20 g at 1 L seawater, the sulfuric acid concentration was 1.0 M and 1.5 M and the ratio of extracts and acetone was 1:1.5 and 1:2 (v:v).

### **2.2.3 Collecting the used acetone**

After the experiment of “2.2.2 Recovering the magnesium sulfate from the seawater”, the final filtrate (120~160 mL) was taken into round bottom flask and connected with fractionating column and cooler. When the solution were into water bath with 60~70 °C, some portion was divided. Divided solution was measured with GC-MS.

## **3. Results and Discussion**

### **3.1 material analyses**

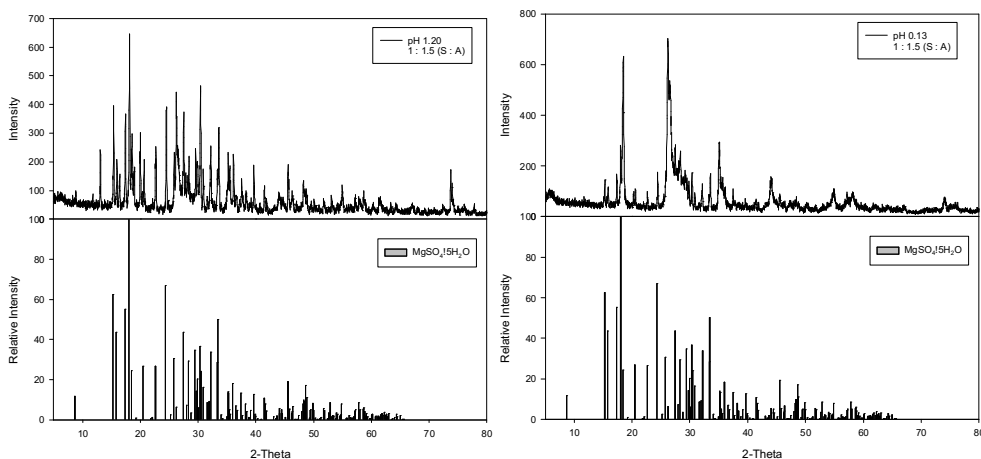
The pH of seawater was 8.3 and the seawater concentration of magnesium and calcium was 1300 and 443, respectively. This value was similar with references value, 1290 and 411 mg/L (Leggett & Rao, 2015). After the sieve with 425 µm sieve, a particle size of CKD and PSA was 23.6 µm and 126.9 µm. pH of CKD and PSA was 13.1 and 12.9. From the XRF results, calcium contents of CKD and PSA was 46.4 % and 69.5 % and magnesium contents was 1.3 % and 3.9 % (Table 1). The main portion of two kinds of industrial by-products was calcium. CKD had more calcium and magnesium portion than PSA did. Through the XRD results, main components of CKD were lime (CaO) and sylvine (KCl), PSA were portlandite [Ca(OH)<sub>2</sub>], lime (CaO) and calcite (CaCO<sub>3</sub>).

**Table 1** XRF analyses of CKD and PSA

| Components                     | Content (%) |       |
|--------------------------------|-------------|-------|
|                                | CKD         | PSA   |
| CaO                            | 46.41       | 69.54 |
| SiO <sub>2</sub>               | 6.42        | 13.94 |
| Al <sub>2</sub> O <sub>3</sub> | 2.32        | 6.35  |
| K <sub>2</sub> O               | 21.02       | -     |
| MgO                            | 1.27        | 3.85  |
| Fe <sub>2</sub> O <sub>3</sub> | 1.39        | 2.04  |
| SO <sub>3</sub>                | 3.65        | 2.19  |
| P <sub>2</sub> O <sub>5</sub>  | -           | 0.55  |

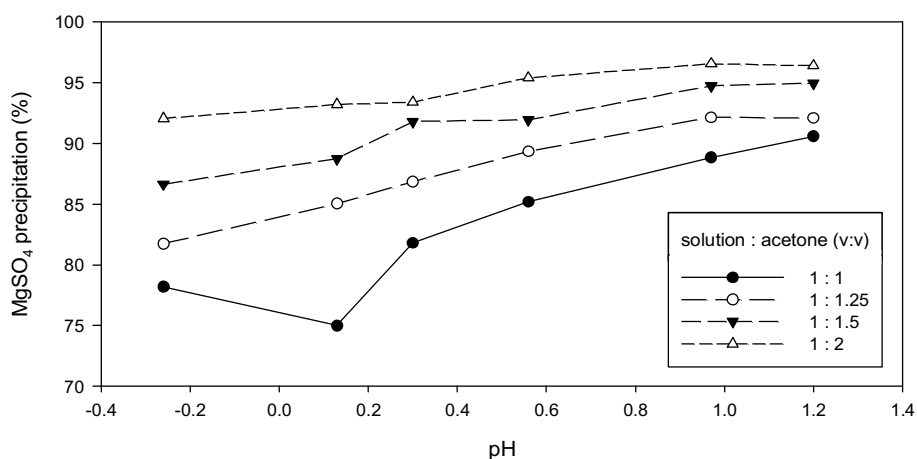
### 3.2 Recovering the magnesium sulfate from the magnesium artificial solution

The solid was not precipitated at the mixing ratio of artificial solution:acetone 1:0.5 and 1:0.75. Meanwhile the other solutions of the acetone adding to artificial solution, the solution was temporarily murky and precipitated to the solid later. Depending on the sample, some samples created the solid at the room temperature within an hour, but the solution was kept in refrigerator (3 °C) for 24 hours to give enough time and condition. After the 24 hours, all samples (24 erlenmeyer flask) created the white solid. XRD analyses results of this solid was shown at Fig. 2. Magnesium was existed the formation of magnesium sulfate pentahydrate ( $\text{MgSO}_4 \cdot 5\text{H}_2\text{O}$ ). The filtrate pH was 0.4~2.13 and all of that were higher than the first.



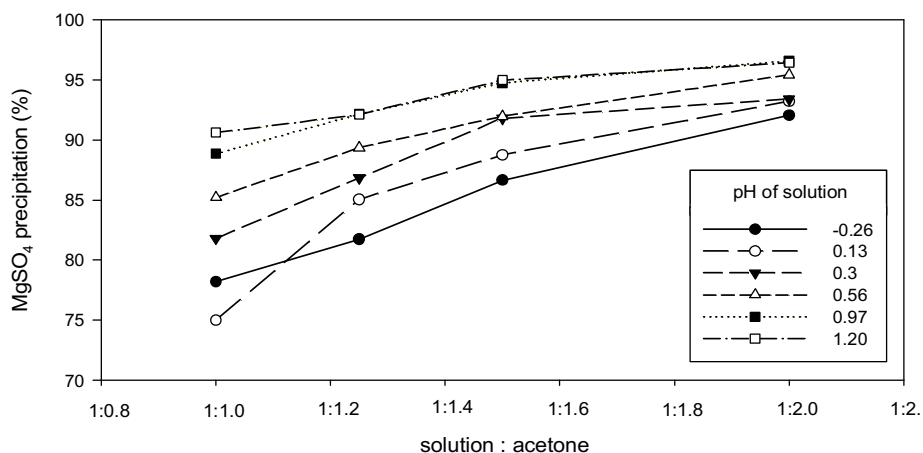
**Fig. 2** XRD diagrams of the solids precipitated in artificial magnesium solutions (10000 mg/L) by adding acetone into the solutions

Variations of the magnesium sulfate precipitation efficiency with pH of the artificial magnesium solution were shown at Fig. 3. The precipitation efficiency of solid magnesium sulfate changed per acetone ratio and pH, and the efficiency range was 75~95 %. In the steady state rate, precipitation efficiency of magnesium sulfate was increased as the pH was high. However as the acetone ratio was high (acetone added in excess) the change of solid precipitation efficiency along pH change was low. For example, when the mixing ration is 1:2 (artificial solution and acetone), even though the pH was changed, solid precipitation efficiency was 92~97 % constantly.



**Fig. 3** Variations of the MgSO<sub>4</sub> precipitation efficiency with pH of the artificial magnesium solution

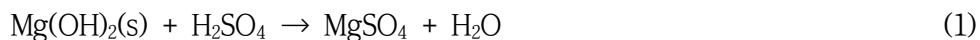
Variations of the magnesium sulfate precipitation efficiency with the volume ratio of acetone to the solution are shown at Fig. 4. At the steady pH, the more acetone ratio, magnesium sulfate precipitation efficiency was increased. However pH was higher, but the variations of the magnesium precipitation efficiency by acetone ratio are lower. For instance, when the pH was 1.20, precipitation efficiency was 91~96 % even though the acetone ration was changed.



**Fig. 4** Variations of the MgSO<sub>4</sub> precipitation efficiency with the volume ratio of acetone to the solution

The higher the pH of artificial solution and acetone ratio was, the larger the amounts of precipitated magnesium sulfate was large. Among these conditions when the pH was 1.20 and the ratio was artificial solution:acetone=1:2 (v:v), the quantity of magnesium sulfate was the largest and efficiency was 96.40 %.

The artificial solution was made by mixing the magnesium hydroxide and sulfuric acid, dissolved magnesium hydroxide by following reaction (Eq. 1)



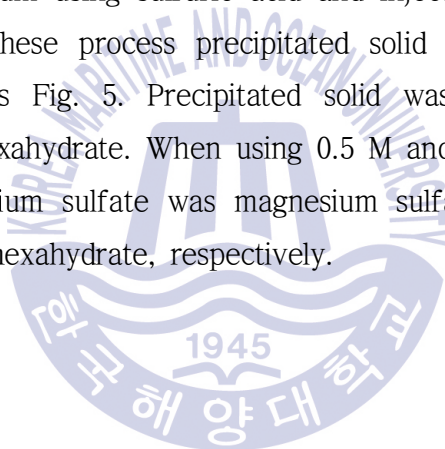
Magnesium sulfate is very soluble in water and if the temperature is high, the solubility will be high. Solubility in acid solution is thought to be much larger than in water. Magnesium sulfate is hardly soluble in alcohol and insoluble in acetone (Weast, 1979; O' Neil, 2006). Since the

chemical properties of acetone was mixed well with the water which does not dissolve the magnesium completely, if the acetone was added to the sulfuric acid which contained magnesium sulfate, the magnesium sulfate could be precipitated.

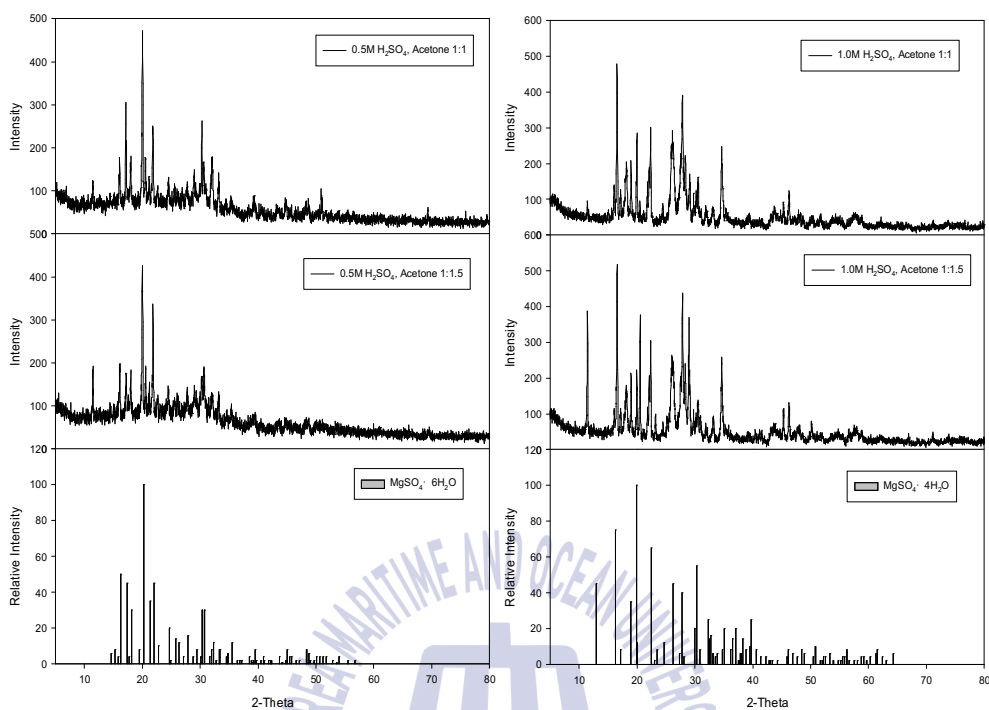
### **3.3 Recovering the magnesium sulfate from the seawater**

#### **3.3.1 Using CKD as a precipitant of magnesium**

CKD was used to pre-precipitate the magnesium from seawater, extract the magnesium using sulfuric acid and inject the acetone to the extracts. Through these process precipitated solid was measured using XRD and shown as Fig. 5. Precipitated solid was magnesium sulfate tetrahydrate and hexahydrate. When using 0.5 M and 1.0 M sulfuric acid, precipitated magnesium sulfate was magnesium sulfate tetrahydrate and magnesium sulfate hexahydrate, respectively.







**Fig. 5** XRD diagrams of the solids precipitated by adding acetone into extracts. Here, the extracts are obtained through the precipitation of dissolved magnesium in seawater using CKD and the extraction of the magnesium using  $\text{H}_2\text{SO}_4$

Table 2. showed the results which are changes of magnesium concentration and pH (sulfuric acid concentration) by adding acetone into extracts. Before injecting the acetone to four kinds of filtrate, magnesium concentration was changed from 6650~7800 mg/L of filtrate to 26.5~1395 mg/L that after the solid was precipitated. Precipitation efficiency of magnesium sulfate was very high, maximum 99.6 %. Precipitated magnesium sulfate weight was 1.01~1.79 g. The pH of

filtrate was higher and the acetone ratio is higher, and efficiency of magnesium sulfate was changed. This tendency was same as using artificial results. For example when the pH was 1.48 and the ratio is 1:1.5 then the efficiency was 99.6 %. At the same time, pH was 0.01 and ratio was 1:1, and efficiency was just 82.1 %.

**Table 2** Changes of Mg concentration and pH by adding acetone into extracts. Here, the extracts are obtained through the precipitation of dissolved magnesium in seawater using CKD and the extraction of the magnesium using H<sub>2</sub>SO<sub>4</sub>

| H <sub>2</sub> SO <sub>4</sub><br>(mol/L) | after acidification |      | extract:acetone<br>(v:v) | after acetone addition |      |
|---|---------------------|------|--------------------------|------------------------|------|
|   | Mg (mg/L)           | pH   |                          | Mg (mg/L)              | pH   |
| 0.5                                       | 7,050               | 1.65 | 1:1                      | 347.5                  | 2.32 |
| 0.5                                       | 6,650               | 1.48 | 1:1.5                    | 26.5                   | 2.17 |
| 1.0                                       | 7,800               | 0.01 | 1:1                      | 1,395                  | 1.95 |
| 1.0                                       | 7,425               | 0.08 | 1:1.5                    | 337.5                  | 1.65 |

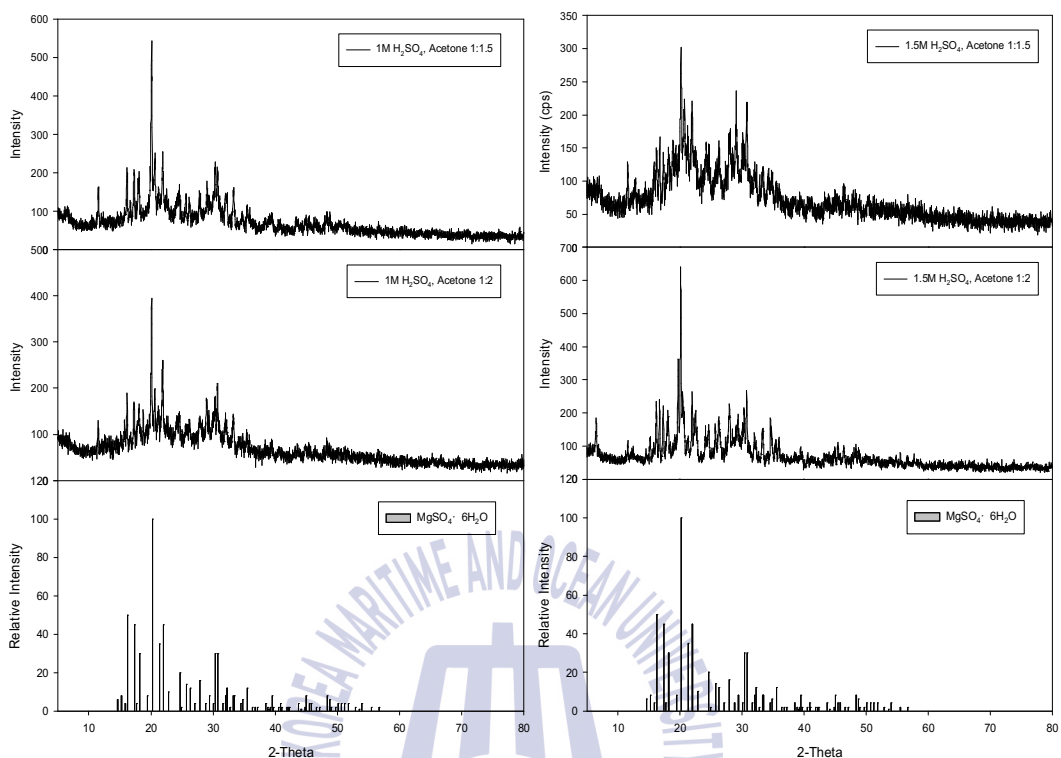
There was a change in pH. Before added the acetone, the pH was 0.01~1.65. After adding the acetone, the pH was increased to 1.65~2.32. At first, the volume was 69~90 mL. After the precipitate the magnesium sulfate, the final volume was 54~73, decreased about 20 %. Table 3. was the XRF results of the precipitated solid. Magnesium sulfate purity was 91.8~95.8 %, and impurities included calcium (1.8~5.9 %) and some aluminum (about 2.9 %).

**Table 3** XRF analyses of the solids precipitated by adding acetone into extracts. Here, the extracts are obtained through the precipitation of dissolved magnesium in seawater using CKD and the extraction of the magnesium using H<sub>2</sub>SO<sub>4</sub>

| H <sub>2</sub> SO <sub>4</sub> (M) | H <sub>2</sub> SO <sub>4</sub> :<br>acetone (v:v) | SO <sub>3</sub>   | MgO              | CaO  | Al <sub>2</sub> O <sub>3</sub> | Fe <sub>2</sub> O <sub>3</sub> | K <sub>2</sub> O |
|------------------------------------|---|-------------------|------------------|------|--------------------------------|--------------------------------|------------------|
| 0.5                                | 1:1   | 66.71             | 25.07            | 2.97 | 2.91                           | 0.86                           | 0.70             |
| 0.5                                | 1:1.5   | 67.61             | 25.96            | 1.76 | 2.92                           | 0.83                           | 0.55             |
| 1.0                                | 1:1   | 66.62             | 29.17            | 2.27 | 0.74                           | 0.26                           | 0.35             |
| 1.0                                | 1:1.5   | 66.39             | 26.73            | 5.94 | 0.30                           | 0.10                           | 0.08             |
| H <sub>2</sub> SO <sub>4</sub> (M) | H <sub>2</sub> SO <sub>4</sub> :<br>acetone (v:v) | Na <sub>2</sub> O | SiO <sub>2</sub> | ZnO  | MnO                            | CuO                            |                  |
| 0.5                                | 1:1   | 0.35              | 0.14             | 0.14 | 0.07                           | 0.07                           |                  |
| 0.5                                | 1:1.5   | -                 | 0.12             | 0.12 | 0.08                           | 0.06                           |                  |
| 1.0                                | 1:1   | -                 | 0.31             | 0.15 | 0.07                           | 0.06                           |                  |
| 1.0                                | 1:1.5   | -                 | 0.23             | 0.14 | 0.05                           | 0.04                           |                  |

### 3.3.2 Using PSA as a precipitant of magnesium

XRD diagrams of the solids precipitated by adding acetone into extracts using PSA as precipitant were shown at Fig. 6. The solids from four kinds of conditions were magnesium sulfate hexahydrate.



**Fig. 6** XRD diagrams of the solids precipitated by adding acetone into extracts. Here, the extracts are obtained through the precipitation of dissolved magnesium in seawater using PSA and the extraction of the magnesium using  $\text{H}_2\text{SO}_4$

The results of changes of magnesium concentration and pH by adding acetone into extracts were shown at Table 4. Filtrate magnesium concentration was 5500~6600 mg/L and then it was changed to 2.8~5.8 mg/L after precipitated the magnesium solids. Regardless of the condition, the efficiency was almost 100 %. There was no relationship between pH and acetone ratio with magnesium sulfate efficiency. The weight of precipitated magnesium sulfate solid was 1.66~3.06 g

Before injecting the acetone, pH was 0.09~1.52 and after the injecting the acetone, pH was 0.99~1.30. And the first volume of filtrate and acetone was 78~93 mL, after the filtrate which precipitated the solid, the volume was 61~80 mL. Alike the results of “3.3.1 Using CKD as a precipitant of magnesium” the volume of solution was decreased into 14~23 %.

**Table 4** Changes of Mg concentration and pH by adding acetone into extracts. Here, the extracts are obtained through the precipitation of dissolved magnesium in seawater using PSA and the extraction of the magnesium using H<sub>2</sub>SO<sub>4</sub>

| H <sub>2</sub> SO <sub>4</sub><br>(mol/L) | after acidification |      | extract:acetone<br>(v:v) | after acetone addition |      |
|---|---------------------|------|--------------------------|------------------------|------|
|   | Mg (mg/L)           | pH   |                          | Mg (mg/L)              | pH   |
| 1.0                                       | 5,800               | 1.07 | 1:1.5                    | 5.1                    | 1.22 |
| 1.0                                       | 5,500               | 1.52 | 1:2.0                    | 2.8                    | 0.99 |
| 1.5                                       | 6,100               | 0.09 | 1:1.5                    | 5.8                    | 1.30 |
| 1.5                                       | 6,600               | 0.47 | 1:2.0                    | 3.6                    | 1.21 |

Table 5. was the results that XRF analyses of magnesium sulfate solid. The purity of magnesium sulfate was 85.2~90.1 %, was lower than using CKD. Impurity included Ca, Al, Fe and the contents of this was 2.1~3.6 %, 5.2~9.0 %, 1.2~1.6 %, respectively.

**Table 5** XRF analyses of the solids precipitated by adding acetone into extracts. Here, the extracts are obtained through the precipitation of dissolved magnesium in seawater using PSA and the extraction of the magnesium using H<sub>2</sub>SO<sub>4</sub>

| H <sub>2</sub> SO <sub>4</sub><br>(M) | H <sub>2</sub> SO <sub>4</sub> :<br>acetone (v:v) | SO <sub>3</sub>  | MgO   | CaO  | Al <sub>2</sub> O <sub>3</sub> | Fe <sub>2</sub> O <sub>3</sub> | K <sub>2</sub> O | Na <sub>2</sub> O |
|---------------------------------------|---|------------------|-------|------|--------------------------------|--------------------------------|------------------|-------------------|
| 1.0                                   | 1:1.5   | 67.09            | 20.30 | 3.58 | 6.54                           | 1.43                           | 0.08             | -                 |
| 1.0                                   | 1:2   | 67.51            | 22.63 | 2.49 | 5.21                           | 1.20                           | 0.07             | -                 |
| 1.5                                   | 1:1.5   | 66.97            | 22.58 | 2.25 | 5.16                           | 1.59                           | 0.10             | 0.27              |
| 1.5                                   | 1:2   | 69.02            | 16.21 | 2.07 | 8.96                           | 1.51                           | 0.10             | -                 |
| H <sub>2</sub> SO <sub>4</sub><br>(M) | H <sub>2</sub> SO <sub>4</sub> :<br>acetone (v:v) | SiO <sub>2</sub> | ZnO   | MnO  | CuO                            | P <sub>2</sub> O <sub>5</sub>  | TiO <sub>2</sub> |                   |
| 1.0                                   | 1:1.5   | 0.24             | 0.11  | -    | 0.08                           | 0.39                           | 0.16             |                   |
| 1.0                                   | 1:2   | 0.19             | 0.11  | -    | -                              | 0.41                           | 0.18             |                   |
| 1.5                                   | 1:1.5   | 0.20             | 0.10  | -    | 0.04                           | 0.53                           | 0.20             |                   |
| 1.5                                   | 1:2   | 1.05             | 0.10  | 0.05 | -                              | 0.66                           | 0.27             |                   |

### 3.4 Collecting the used acetone

After the reaction the solution (120~160 mL) was divided by the fractional distillation. When the water bath temperature was 60~70 °C, some parts of solution (60~90 mL) was divided with vaporizing. Through the GC-MS results, all of divided solution were acetone (Fig. 7). If acetone was recovered and reused at the precipitated process, it would be expected to improve the economic improvement.

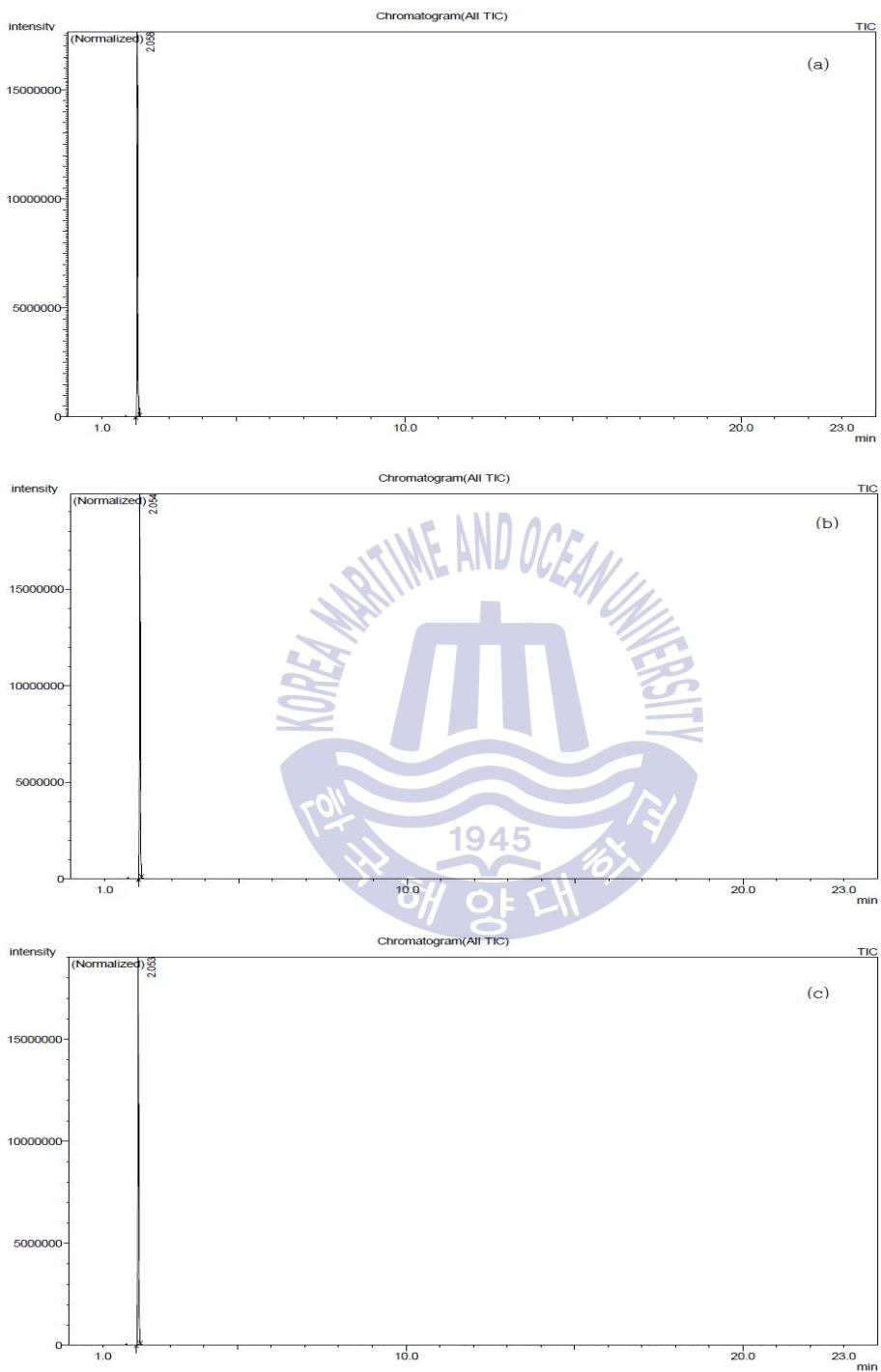


Fig. 7 GC-MS analyses of (a) acetone, (b) and (c) solutions obtained

after the fractional distillation when CKD and PSA are used as precipitants, respectively

#### **4. Conclusions**

At this study, the last step of the experiments was conducted to recovery the magnesium from seawater. First using artificial solution, it was found that optimum conditions affect the precipitation efficiency and through this results, the condition was adapted to seawater to precipitate the magnesium from seawater. The pH was higher, the acetone ratio was higher and increased the efficiency of precipitated magnesium sulfate. After the magnesium sulfate precipitating, acetone was collected 100 % from filtrate using fractional distillation.

At this study, to recover the magnesium from seawater these following three steps were conducted; 1) magnesium from the seawater was precipitated the formation of magnesium hydroxide using industrial by-product such as CKD and PSA, 2) the magnesium was extracted using sulfuric acid, and 3) the sulfuric magnesium solid was precipitated by injecting the acetone. Since the magnesium concentration was 1300 mg/L, it could recover the magnesium sulfate hexahydrate 12.3 kg from the seawater 1 tone. The biggest problem of this technologies for the recovery of magnesium in seawater is economy. If the industrial by-product which didn't require the material cost, it was used as precipitant and recovered the acetone to reuse, it would be possible to recover the magnesium economically.



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