Desalination and Water Treatment
www.deswater.com

doi: 10.5004/dwt.2019.23791

157 (2019) 324–331
July

Determination of optimal conditions for magnesium recovery process from seawater desalination brine using paper sludge ash, sulfuric acid, and ethanol

Hye-Rim Na[a], Myoung-Jin Kim[b,*]

[a]*Department of Convergence Study on the Ocean Science and Technology, Korea Maritime and Ocean University, Busan, Korea, email: jangmi7020@naver.com*
[b]*Department of Environmental Engineering, Korea Maritime and Ocean University, Busan Korea, Tel./Fax: +82 51 410 4433; email: kimmj@kmou.ac.kr*

Received 9 October 2018; Accepted 10 January 2019

ABSTRACT

The release of seawater desalination brine with a salt concentration about two times that of seawater without any treatment may cause serious environmental problems. Moreover, because of the higher concentration of dissolved salts present, the amount of recoverable resources is greater, but the impurities become more difficult to control. In this study, we conducted a three-step process to recover Mg resources from seawater desalination brine with Mg concentration of 2,340 mg/L, and determined the optimal conditions for minimizing the impurities and maximizing Mg recovery efficiency at each step. The process was as follows: (1) pre-precipitation of Mg using paper sludge ash (PSA) (PSA:brine = 1:40) (g:mL), (2) dissolution of Mg using 1.0 M sulfuric acid (H_2SO_4) corresponding to one-fifth of the brine volume, and (3) precipitation of magnesium sulfate ($MgSO_4$) using ethanol (solution:ethanol = 1:1) (mL:mL). Under the optimal conditions, the reaction efficiencies of the three steps were determined to be 98%, 70.8%, and 88%, respectively, and the overall efficiency of recovering Mg from the seawater desalination brine was 61.1%. The $MgSO_4$ obtained in this study contained no impurities other than Ca, comprising as much as 6.7% of the precipitate.

Keywords: Seawater desalination brine; Mg; Recovery; Paper sludge ash

---

1. Introduction

Seawater desalination is a straightforward technique for pure water production, but it also results in brine with higher salinity and temperature than seawater. Almost 41% of the total volume of seawater desalination brine is discharged into the sea without undergoing treatment processes [1], which may cause hazardous environmental problems [2].

To solve these problems, many studies have been conducted on the management of brine through safe disposal or reuse of brine [3]. The recovery of minerals from seawater desalination brine has been widely studied because it is an environmentally friendly and economic method that reduces the discharge of brine and produces valuable resources [4]. Many resources that are dissolved in seawater desalination brine have been the targets of extraction, such as Mg [5–13], Li [14–16], Ca [17], K [18], and Cl [19]. An evaluation of the profitability of each element recovered from seawater desalination brine via its concentration and market price implies that Mg is worth extracting from seawater desalination brine because of economic aspects, which highly depend on the purity of the final Mg product (Fig. 1) [20].

Many novel methods for recovering Mg from seawater desalination brine have been presented, including membrane separation [10], ion exchange [11], biocrystallization [5], and chemical processes [5–7,21]. Zahedi and Mohamad Ghasemi [10] recovered 97% of the Mg contained in seawater desalination brine using a bulk liquid membrane in 2.5 h. Pérez-González et al. [11] used an ion-exchange resin

---

[*] Corresponding author.

Presented at the EDS conference on Desalination for the Environment: Clean Water and Energy, 3–6 September 2018, Athens, Greece

1944-3994/1944-3986 © 2019 Desalination Publications. All rights reserved.

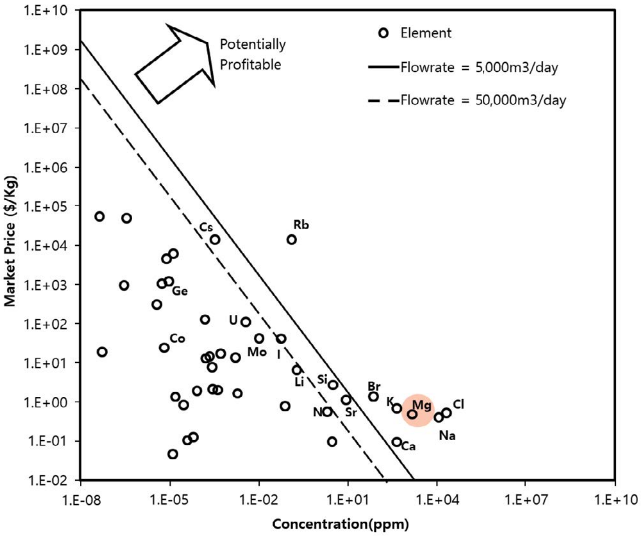

Fig. 1. Log-log plot showing concentration and market price of each mineral in the seawater desalination brine [20].

to extract Mg from seawater desalination brine along with Ca. Wan et al. [22] performed biomineralization experiments that precipitated the Mg of the brine in the form of a granular microstructure over 16 d.

However, currently commercialized methods for recovering Mg from brine or seawater are simple chemical precipitation methods that use lime or dolomite [20]. Alkali precipitants, such as sodium hydroxide (NaOH), ammonium hydroxide (NH_4OH), or sodium carbonate (Na_2CO_3), have been used in many studies [5–7,21]. The form of recovered Mg salts depends on the components of the precipitant, and its purity is determined either by the amount of impurities derived from the brine (such as Ca or B) or precipitant. Casas et al. [5] obtained magnesium hydroxide ($Mg(OH)_2$) by using NaOH as a precipitant, which has a purity of approximately 52%–57% and contains approximately 3%–26% calcium carbonate ($CaCO_3$) along with a small amount of K and B. Sorour et al. [6] recovered Mg in the form of magnesium carbonates and magnesium phosphates using Na_2CO_3 and $Na_3PO_4 \cdot 12H_2O$ as Mg precipitants in seawater desalination brine, but large amounts of Ca was also precipitated in the process. Dong et al. [7] added NH_4OH to brine for precipitating $Mg(OH)_2$ with a purity of approximately 75.6%–98%. $CaCO_3$ was the major impurity detected, which comprised approximately 2%–24.4% of the Mg precipitate. Lehmann et al. [9] used calcium oxide (CaO) as a Mg precipitant. In order to improve the precipitation efficiency of $Mg(OH)_2$, micro magnesite particles were added to a $Mg(OH)_2$ slurry and subsequently dissolved in acid (sulfuric acid [H_2SO_4], hydrochloric acid [HCl], and carbonic acid [H_2CO_3]). The purity of the Mg solution obtained was greater than 97%, and the impurities contained trace amounts of B and Fe.

Instead of the expensive alkali precipitants, such as NaOH and NH_4OH, used in previous studies, we used paper sludge ash as an alkali industrial by-product. In addition, we eliminated the impurities, such as B or Ca, to increase the purity of the final Mg product. In this study, we conducted a continuous three-step process for recovering Mg from seawater desalination brine: pre-precipitation of Mg using alkaline industrial by-products, dissolution of Mg using H_2SO_4, and precipitation of $MgSO_4$ using ethanol. The aim of this study was to derive optimal conditions not only to maximize the recovery efficiency of Mg from the brine, but also to minimize the content of impurities.

2. Materials and methods

The seawater desalination brine was taken from the 'A' desalination plant in Busan, South Korea and stored in a refrigerator. Paper sludge ash (PSA), which is an alkali industrial by-product, was used as the Mg precipitant and supplied by a paper mill in South Korea. H_2SO_4 (95%) and ethanol (99%) from Junsei Company (Japan) was used. X-ray diffraction (XRD, Optima 8300, Shimadzu, Japan), X-ray fluorescence (XRF, Shimadzu, XRF-1700, Shimadzu, Japan), and scanning electron microscopy (SEM, MIRA-3, Tescan, Czech Republic) were used to determine the constituents and contents of the solids and the crystal form of $MgSO_4$. A laser scattering particle size analyzer (HELOS, Sympatec, Germany) was used to measure the size of the PSA. Inductively coupled plasma-optical emission spectrometry (Optima 8300, Perkin Elmer, USA) was used to determine the concentrations of Mg, Ca, Al, Fe, Si, and B, and the pH was measured using a pH meter (Orion Star 211, Thermo, USA).

The process of recovering Mg from the seawater desalination brine in the form of $MgSO_4$ was conducted in three successive steps (Fig. 2). The first step was pre-precipitation of Mg, in which a mixture of PSA and brine was prepared to precipitate the Mg ion of the brine into $Mg(OH)_2$. The second step was dissolution of Mg, wherein a mixture of PSA and $Mg(OH)_2$ was added to H_2SO_4 in order to elute Mg. The third step was precipitation of $MgSO_4$, in which ethanol was added to the eluent to precipitate $MgSO_4$. In this study, the following experiments were conducted to derive the optimum conditions at each step.

2.1. Pre-precipitation of Mg

We used the PSA to precipitate the Mg of the seawater desalination brine. A certain amount of PSA was mixed with 100 mL of brine and then stirred at 250 rpm for 1 h. The solid to liquid ratio of PSA and brine was controlled at ratios of 1:25 and 1:100. After filtering the suspension through a 0.45 μm membrane, the concentrations of Mg, Ca, and B and the pH of the filtrate were measured. By varying the ratios of PSA to brine, the minimum amount of PSA needed to precipitate all the Mg of the brine as the optimum condition was determined.

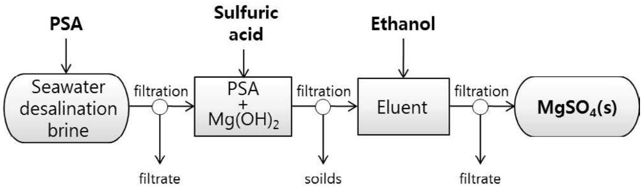

Fig. 2. Three-step process for recovering Mg from seawater desalination brine.

2.2. Dissolution of Mg

2.5 g of PSA was mixed with 100 mL of brine based on the optimum conditions derived from Section 3.1, and the solid was collected after the precipitation of the mixture. Eight solid samples were prepared using the same method. Each solid sample was added to 20 mL of H_2SO_4 and sufficiently stirred at 250 rpm for 1 h. Here, the concentration of H_2SO_4 was varied from 0.3 M to 4.0 M. After filtering the suspension through a 0.45 μm membrane, we measured the pH and the concentrations of Mg, Ca, Al, Si, Fe, and B in the filtrate. The components of the solids were also analyzed. The optimum condition of H_2SO_4 as the minimum concentration needed to dissolve the Mg as much as possible was determined.

2.3. Precipitation of $MgSO_4$

Twelve solid samples, which were obtained by mixing 2.5 g of PSA and 100 mL of brine and filtering the mixture, were prepared. Among these samples, six solid samples were mixed with 20 mL of 1.0 M H_2SO_4 and the others were mixed with 20 mL of 1.5 M H_2SO_4. Each mixture was stirred at 250 rpm for 1 h and then filtered through a 0.45 μm membrane to obtain the filtrate, which had a volume of about 20 mL and was called eluent. Ethanol was injected into each eluent by controlling the amount of ethanol in the range of approximately 4–40 mL, which corresponded to the volume ratio of eluent to ethanol of approximately 1:0.2–1:2.0. The mixture of the eluent and ethanol stood for at least 6 h at room temperature, the solid was filtered, and the pH and the concentrations of Mg, Ca, Al, Si, Fe, and B of the filtrate were measured. The solids obtained when the volume ratio of the eluent to ethanol was 1:1 were analyzed using XRD, XRF, and SEM.

3. Results and discussion

3.1. Materials analysis

Table 1 shows the results of the analysis of the brine. The concentrations of Mg and Ca were 2,340 and 664 mg/L, respectively, and the pH was 7.8.

Table 2 shows the components of the PSA measured using XRF. The main components of the PSA were 67% Ca and some Si, Al, Mg, and Fe. The average particle size of the PSA was 24.5 μm (Fig. 3).

Table 1
Concentrations of Mg, Ca, and B in the seawater desalination brine used in this study

Component	Concentration (mg/L)
Mg	2,340
Ca	664
B	6.6

Table 2
X-ray fluorescence analyses of the paper sludge ash

Component	Content (%)
CaO	67.21
SiO_2	15.02
Al_2O_3	6.62
MgO	4.37
Fe_2O_3	1.77
SO_3	2.72
P_2O_5	0.53

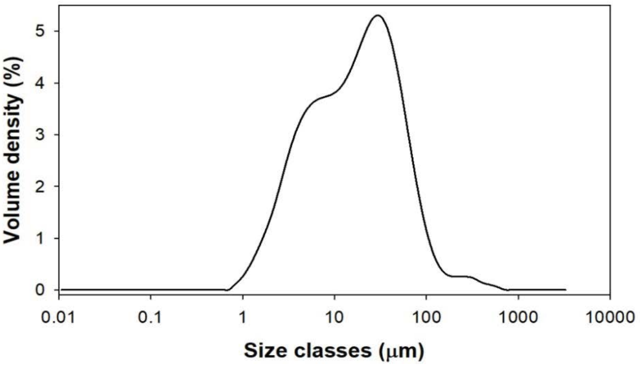

Fig. 3. Particle size distribution of PSA.

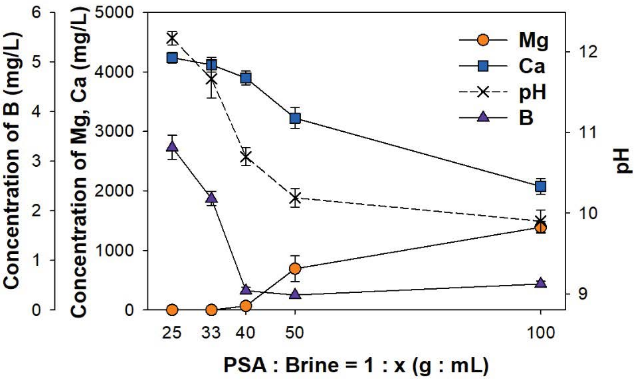

Fig. 4. Concentrations of Mg, Ca, and B and the pH of the filtrate depending on the ratio of paper sludge ash (PSA) to brine.

3.2. Pre-precipitation of Mg

Fig. 4 shows the concentrations of Mg, Ca, and B and the pH of the filtrate depending on the solid to liquid ratio of PSA and brine. As the ratio of PSA to brine increased, the pH and the concentration of Ca gradually increased while the concentration of Mg decreased. When the ratio was 1:40, the concentration of Mg was 46 mg/L, which was close to zero compared with the initial Mg concentration of 2,340 mg/L, and the pH was 10.8. This was because the Mg ion in the brine precipitated in the form of $Mg(OH)_2$ [5,7,21]. Therefore, the optimum ratio of PSA to brine required for precipitating the Mg of the brine was decided to be 1:40 (g:mL; PSA:brine), and the Mg precipitation efficiency was 98%.

Figs. 5a and b show the XRD results of the raw PSA and the solid obtained after filtering the mixture of PSA

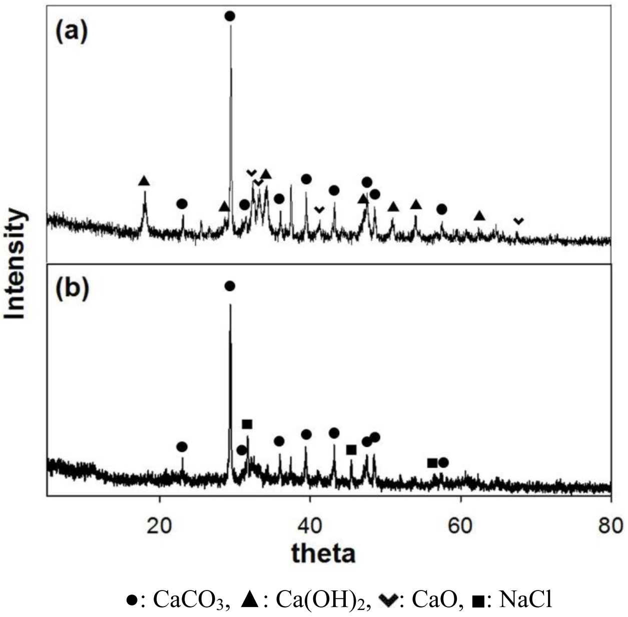

Fig. 5. X-ray diffraction results: (a) raw paper sludge ash (PSA) and (b) solid obtained after filtering the mixture of PSA and brine when the ratio was 1:40.

and brine when the ratio was 1:40, respectively. In Fig. 5a peaks of calcium hydroxide ($Ca(OH)_2$), CaO, and $CaCO_3$ were mainly observed, whereas in Fig. 5b only $CaCO_3$ remained. By the reaction of PSA and brine, the CaO of the PSA was hydrated to $Ca(OH)_2$, which dissolved easily in the form of Ca^{2+} and OH^-. This OH^- reacted with the Mg^{2+} of the brine to precipitate $Mg(OH)_2$. These mechanisms have already been widely used in common Mg precipitation methods [9,23].

$$CaO + H_2O \rightarrow Ca(OH)_2 \tag{1}$$

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

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

It was difficult to find the peaks of $Mg(OH)_2$ in Fig. 5b owing to the poor crystallization characteristics of $Mg(OH)_2$ [24,25].

The species that most influenced the pH in the suspension where the PSA and brine coexisted was the $Ca(OH)_2$ of the PSA. When a relatively small amount of PSA was added to the brine, the PSA to brine ratio was lower than 1:40, and most of the OH^- dissolved from $Ca(OH)_2$ was used to react with the Mg ion; thus, the pH remained lower than 10.8 (Fig. 4). In addition, this reaction boosted the formation of $Mg(OH)_2$ and dissolution of Ca from the PSA. On the other hand, if more PSA than required was added to precipitate the Mg of the brine, then the PSA to brine ratio was higher than 1:40, and the extra OH^- rapidly increased the pH to higher than 10.8.

Meanwhile, the B concentration was almost 0 mg/L when the ratio of PSA to brine was 1:40, which implied that most of the B in the brine precipitated as a solid phase (Fig. 4). Therefore, B was eluted along with the Mg as H_2SO_4 was added to the mixture of PSA and $Mg(OH)_2$ during the subsequent dissolution step.

3.3. Dissolution of Mg

In many previous studies, acid solvents, such as HCl or acetic acid, were used to dissolve Mg from the solid phase [26–28]. H_2SO_4 was used to dissolve the Mg from the mixture of $Mg(OH)_2$ and PSA. The reason for using H_2SO_4 was that the Mg of $Mg(OH)_2$ was eluted in the form of Mg^{2+} while the Ca of the PSA was converted into solid calcium sulfate ($CaSO_4(s)$), so a large amount of Ca would not be eluted into the solution [29]. Mg was concentrated using H_2SO_4 with a volume that corresponded to one-fifth of the volume of the brine used in the previous step.

As shown in Fig. 6, as the concentration of H_2SO_4 increased, the concentration of Mg in the eluent at first increased proportionally, and then became constant. When the concentration of H_2SO_4 was higher than 1.0 M, the concentration of Mg in the eluent was approximately 8,500–10,000 mg/L, which was 3.5–4 times higher than that of the raw brine (2,340 mg/L). The efficiency of the Mg dissolution was approximately 72.6%–85.5%.

The concentrations of Al, Si, and Fe showed similar trends, and they all originated from the PSA (Fig. 6). When the concentration of H_2SO_4 was lower than 1.0 M, the concentrations of Al, Si, and Fe were almost 0 mg/L, and when the concentration of H_2SO_4 increased to higher than 1.5 M, they suddenly increased.

Changes in the concentrations of Mg, Al, Si, and Fe were closely related to the change in pH of the eluent. At a relatively low concentration of H_2SO_4 (lower than 1.0 M), the pH of the eluent was as high as approximately 8–9, while the pH decreased rapidly to lower than 1 when the concentration of H_2SO_4 was higher than 1.5 M. Therefore, when the concentration of H_2SO_4 was lower than 1.0 M, only Mg dissolved out from the mixture of $Mg(OH)_2$ and PSA [24,30]. As the concentration of H_2SO_4 increased to higher than 1.5 M, the pH rapidly decreased and Al, Si, and Fe were eluted together.

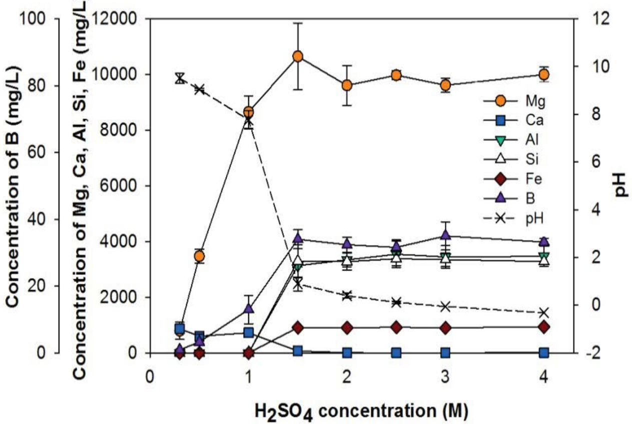

Fig. 6. Concentrations of Mg, Ca, Al, Si, Fe, and B and the pH of the eluent depending on the concentration of H_2SO_4.

Fig. 7 shows the XRD results of the remaining solids after the eluent was prepared using H_2SO_4 with different concentrations of approximately 0.3–1.5 M. In the XRD results using 0.3 M H_2SO_4 and 0.5 M H_2SO_4, the peaks of $CaCO_3$ and $CaSO_4{\cdot}2H_2O$ coexisted, whereas only $CaSO_4$ peaks were observed when using 1.0 M H_2SO_4 and 1.5 M H_2SO_4. This indicated that when the concentration of H_2SO_4 was higher than 1.0 M, $CaCO_3$ was dissolved by excessive H_2SO_4 and $CaSO_4$ was produced.

It was found that at least 1.0 M H_2SO_4 should be used in order for the Mg concentration to be sufficiently high and to accelerate the precipitation reaction of $MgSO_4$ in the following step. The pH and the concentrations of components in each eluent obtained using 1.0 M H_2SO_4 and 1.5 M H_2SO_4 are shown in Table 3. With 1.0 M H_2SO_4, a small amount of Ca and B were retained in the eluent with no other impurities, which was advantageous to obtain $MgSO_4$ with high purity. Meanwhile, with 1.5 M H_2SO_4, impurities such as Fe, Al, Si, B, and Ca were eluted, but the maximum amount of Mg was eluted, so a large amount of $MgSO_4$ could be precipitated. In the subsequent experiments using 1.0 M H_2SO_4 and 1.5 M H_2SO_4, the effect of H_2SO_4 concentration on the purity of precipitated $MgSO_4$ was observed and the efficiency of Mg precipitation was compared.

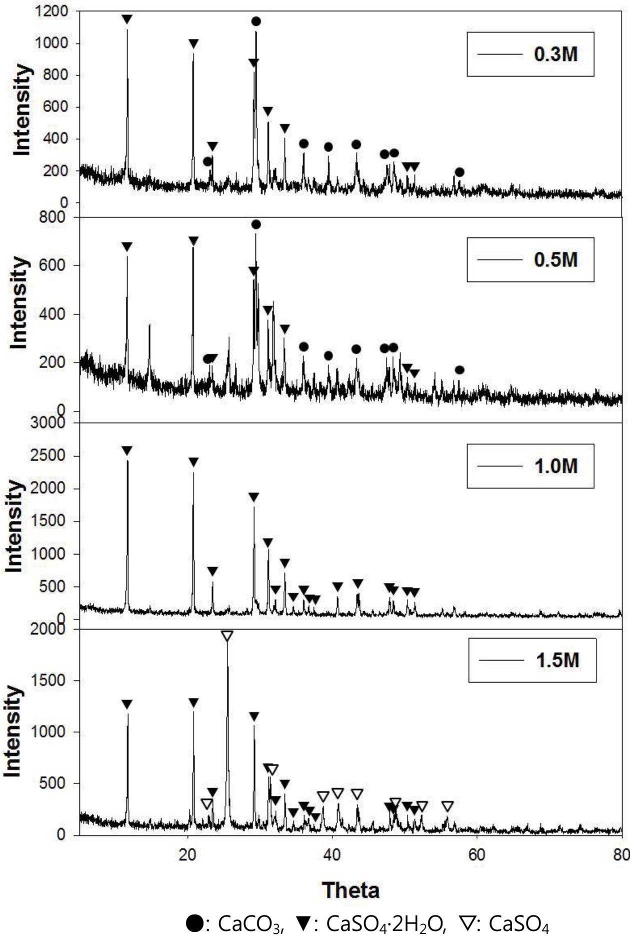

Fig. 7. X-ray diffraction results of solids remaining after dissolving Mg with 0.3–1.5 M H_2SO_4.

3.4. Precipitation of $MgSO_4$

In this process, ethanol was added to the eluent to precipitate $MgSO_4$ as a solid. It was based on the characteristics of $MgSO_4$, which is rarely soluble in organic solvents [29]. The amount of ethanol injected was expressed as the volume ratio of eluent to ethanol. The eluent prepared using 1.0 M H_2SO_4 and 1.5 M H_2SO_4 was called as 1.0 M eluent and 1.5 M eluent, respectively.

Fig. 8 shows the change in Mg precipitation efficiency according to the volume ratio of eluent to ethanol. When the volume ratio was lower than 1:1, the Mg precipitation efficiency from the 1.5 M eluent was higher than that of the 1.0 M eluent, and the highest Mg precipitation efficiency was 94% and 88%, respectively.

The Mg precipitation efficiency tended to increase as the amount of injected ethanol increased, in the form of an *S*-curve (Fig. 8). This pattern was observed in both eluents; in other words, it was not relevant to the characteristics of the eluent, such as pH or the concentrations of its components. The precipitation reaction of $MgSO_4$ was closely related to the solubility of the $MgSO_4$ in the ethanol–water–$MgSO_4$ system. Zafarani-Moattar and Salabat measured the solubility of $MgSO_4$ in a mixed solution of water and ethanol at 25°C [31]. As the portion of the ethanol increased in the mixture of water and ethanol, the solubility of the $MgSO_4$ decreased. Notably, the solubility of the $MgSO_4$ was almost 0 when the mass percentage of the ethanol was greater than 43.2, which corresponded to the volume ratio of water to ethanol of 1:1.03 when considering the ethanol density of 0.789. Thus, as shown in Fig. 8, the Mg precipitation efficiency reached its maximum when the volume ratio approached 1:1. The precipitation reaction occurred was observed, and at a volume ratio of approximately 1:0.6–1:0.8, the mixture of eluent and ethanol turned turbid with some suspended solids, which did not contain specific crystals, whereas at a volume ratio greater than 1:1.0, the solution rapidly crystallized and separated itself into the precipitate and supernatant. Therefore, in order to obtain $MgSO_4$ crystals and achieve high Mg precipitation efficiency, ethanol should

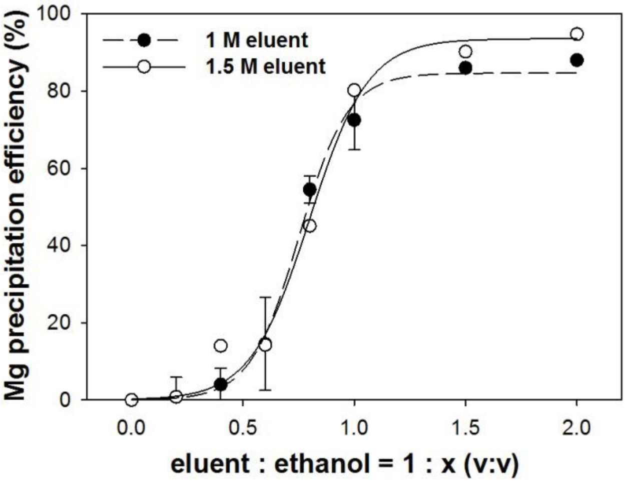

Fig. 8. Change in Mg precipitation efficiency according to the volume ratio of eluent to ethanol.

be added to the eluent so that the volume ratio of eluent to ethanol is at least 1:1.0.

Fig. 9a shows the amount of components remaining in the filtrate after $MgSO_4$ precipitation with a volume ratio of 1.0 M eluent to ethanol. The 1.0 M eluent contained a small amount of Ca and B as impurities (Table 3). As shown in Fig. 9a, the amount of B in the filtrate did not change with the eluent:ethanol ratio, but the amount of Ca changed. The amount of Ca decreased when a small amount of ethanol (volume ratio of 1:0.4 or less) was injected into the eluent. Therefore, if ethanol was added in a ratio higher than 1:1, then the precipitated $MgSO_4$ would contain Ca as an impurity. Components such as Al and Fe were not present in the precipitated $MgSO_4$ because they were not present in the 1.0 M eluent (Table 3).

Fig. 9b shows the amount of components remaining in the filtrate after $MgSO_4$ precipitation using 1.5 M eluent and ethanol. The amount of Al and Fe in the filtrate decreased when the volume ratio was approximately 1:0.6–1:1.0. The Al and Fe ions would have precipitated in the form of aluminum sulfate ($Al_2(SO_4)_3$) and iron(III) sulfate ($Fe_2(SO_4)_3$), respectively, which are insoluble in ethanol [29]. The color of the $MgSO_4$ recovered from the 1.5 M eluent was yellow because Fe was co-precipitated as $Fe_2(SO_4)_3$. There was no change in the amount of B and Si in the filtrate, thereby indicating that B and Si were not precipitated as impurities of $MgSO_4$.

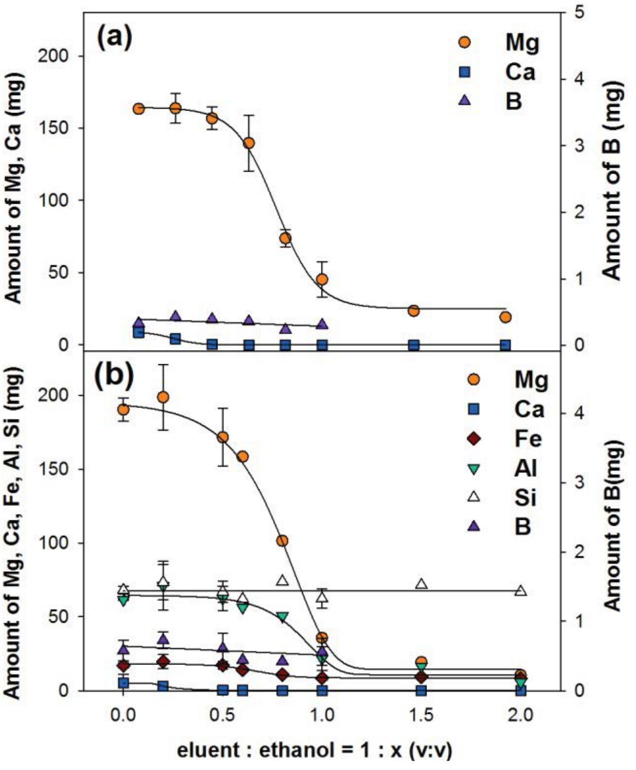

Fig. 9. Amount of components remaining in the filtrate after $MgSO_4$ precipitation depending on the volume ratio of eluent to ethanol (a) 1.0 M eluent and (b) 1.5 M eluent.

Table 3
pH and concentrations of the components of each eluent obtained using 1.0 M H_2SO_4 and 1.5 M H_2SO_4

H_2SO_4 (M)	Concentration (mg/L)						pH
	Mg	Ca	Al	Si	Fe	B	
1.0	8,600	725	0	0	0	13	7.5
1.5	10,600	70	3,100	3,300	910	30	<1

The purity of the $MgSO_4$ recovered from the 1.0 M eluent was compared with the 1.5 M eluent (Table 4). The $MgSO_4$ solids used in the comparison were recovered when the volume ratio of eluent to ethanol was equal to 1:1. The purity of $MgSO_4$ was 89.6% for the 1.0 M eluent and 84.9% for the 1.5 M eluent. In the case of $MgSO_4$ obtained from the 1.0 M eluent, only Ca was present as an impurity. If the salt (NaCl) was removed by adding an NaCl washing process, then the purity of $MgSO_4$ increased up to 93%. On the other hand, the $MgSO_4$ from the 1.5 M eluent contained Ca, Al, and Fe as major impurities.

As shown in Fig. 10, the peak of $MgSO_4{\cdot}7H_2O$ was mainly observed in the precipitated solid when the ratio of eluent to ethanol was 1:1. The $MgSO_4$ recovered from the

Table 4
X-ray fluorescence results of $MgSO_4$ precipitated using 1.0 M eluent and 1.5 M eluent

H_2SO_4(M)	1.0	1.5
S	68.5	65.9
Mg	21.1	19.0
Ca	6.7	4.8
Al	–	4.3
Fe	–	3.3
Si	–	–
Na	0.6	1.2
Cl	3.0	–
K	–	0.5

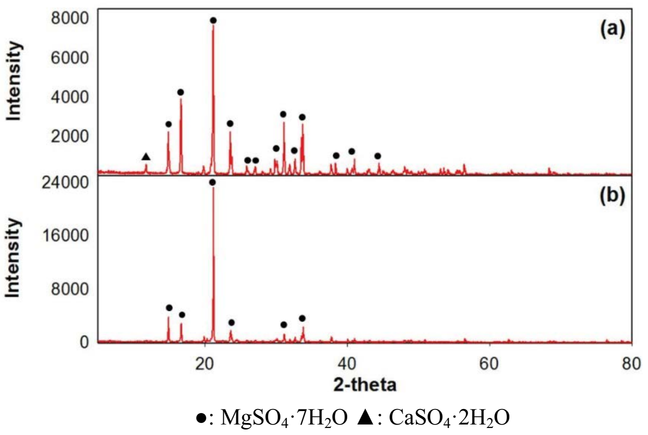

Fig. 10. X-ray diffraction results of the precipitated $MgSO_4$ when the ratio of eluent to ethanol was 1:1: (a) 1.0 M eluent and (b) 1.5 M eluent.

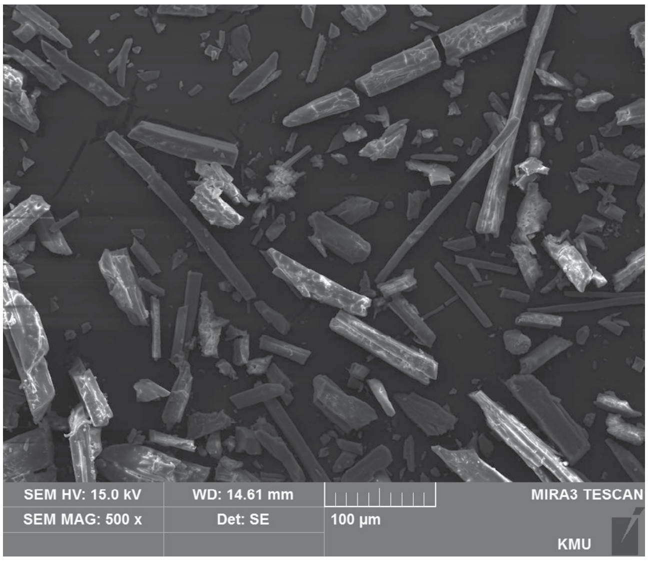

Fig. 11. Scanning electron microscope (SEM) image of the precipitated $MgSO_4$ using 1.0 M eluent when the ratio of eluent to ethanol was 1:1.

1.0 M eluent contained some $CaSO_4$ (Fig. 10(a)). In the case of the 1.5 M eluent, no peaks corresponded to impurities, which was because the intensity of the characteristic peak of $MgSO_4·7H_2O$ was so high that the peaks of the other compounds had a relatively low peak height and were difficult to distinguish in the graph.

Fig. 11 shows the SEM image of the $MgSO_4$ obtained from the 1.0 M eluent when the ratio of eluent to ethanol was 1:1. The precipitated $MgSO_4$ was square pillar-shaped, which corresponded with a previous result stating that the $MgSO_4$ crystal structure is monoclinic [32].

4. Conclusion

In this study, we determined the optimum conditions of a three-step process to recover Mg from seawater desalination brine using an alkali industrial by-product, H_2SO_4, and ethanol. In the first step, involving the pre-precipitation of Mg, the optimum ratio of PSA to brine to precipitate all the Mg from the brine was 1:40 (g:mL). The Mg was precipitated in the form of $Mg(OH)_2$ and the use of PSA facilitated the filtration of the $Mg(OH)_2$. During the dissolution of Mg, an eluent with concentrated Mg was produced by adding a mixture of PSA and $Mg(OH)_2$ to H_2SO_4 in a volume one-fifth of that of brine. We determined that the optimum concentration of H_2SO_4 was 1.0 M when the Mg dissolution efficiency was greater than 70% and no impurities were eluted, except for Ca. Finally, the precipitation of $MgSO_4$ led to the recovery of Mg in the form of $MgSO_4·7H_2O$ by adding ethanol in a ratio of 1:1. This was the ratio that used the minimum amount of ethanol to maximize the $MgSO_4$ precipitation efficiency.

This technology is more economical than other existing technologies for recovering magnesium from seawater desalination brine for the two following representative reasons. First, the alkali industrial by-product was used instead of the existing expensive alkali precipitants. Second, ethanol and H_2SO_4 could be recovered and then reused in the process.

In future studies, it was planned to improve the purity of $MgSO_4$ by removing Ca before precipitating $MgSO_4$. It is assumed that the seawater desalination brine and PSA used in this study for the three-step process could be replaced by seawater or bittern and other alkali by-products. The optimal conditions could be derived in the same way as that proposed here, but the specific values of the optimal conditions may be different from the results of this study.

Acknowledgments

This work was supported by a National Research Foundation (NRF) of Korea grant funded by the Korean government (NRF-2017R1A2B4008114) and by the Open Laboratory Operational Business Developing and Diffusing the Regional Specialization Technology funded by the Busan Institute of S&T Evaluation and Planning (BISTEP).

References

[1] N. Ahmad, R.E. Baddour, A review of sources, effects, disposal methods, and regulations of brine into marine environments, Ocean Coast. Manage., 87 (2014) 1–7.

[2] T.M. Missimer, R.G. Maliva, Environmental issues in seawater reverse osmosis desalination: intakes and outfalls, Desalination, 434 (2018) 198–215.

[3] A. Giwa, V. Dufour, F. Al Marzooqi, M. Al Kaabi, S.W. Hasan, Brine management methods: recent innovations and current status, Desalination, 407 (2017) 1–23.

[4] T. Jeppesen, L. Shu, G. Keir, V. Jegatheesan, Metal recovery from reverse osmosis concentrate, J. Clean. Prod., 17 (2009) 703–707.

[5] S. Casas, C. Aladjem, E. Larrotcha, O. Gibert, C. Valderrama, J.L. Cortina, Valorisation of Ca and Mg by-products from mining and seawater desalination brines for water treatment applications, J. Chem. Technol. Biotechnol., 89 (2014) 872–883.

[6] M.H. Sorour, H.A. Hani, H.F. Shaalan, G.A. Al-Bazedi, Schemes for salt recovery from seawater and RO brines using chemical precipitation, Desal. Wat. Treat., 55 (2014) 2398–2407.

[7] H. Dong, E.H. Yang, C. Unluer, F. Jin, A. Al-Tabbaa, Investigation of the properties of MgO recovered from reject brine obtained from desalination plants, J. Clean. Prod., 196 (2018) 100–108.

[8] H. Dong, C. Unluer, E.H. Yang, A. Al-Tabbaa, Synthesis of reactive MgO from reject brine via the addition of NH_4OH, Hydrometallurgy, 169 (2017) 165–172.

[9] O. Lehmann, O. Nir, M. Kuflik, O. Lahav, Recovery of high-purity magnesium solutions from RO brines by adsorption of $Mg(OH)_2(s)$ on Fe_3O_4 micro-particles and magnetic solids separation, Chem. Eng. J., 235 (2014) 37–45.

[10] M.M. Zahedi, S. Mohamad Ghasemi, Separation study of Mg^{+2} from seawater and RO brine through a facilitated bulk liquid membrane transport using 18-Crown-6, J. Water Reuse Desal., 7 (2017) 468–475.

[11] A. Pérez-González, R. Ibáñez, P. Gómez, A.M. Urtiaga, I. Ortiz, J.A. Irabien, Recovery of desalination brines: separation of calcium, magnesium and sulfate as a pre-treatment step, Desal. Wat. Treat., 56 (2014) 3617–3625.

[12] A. Cipollina, M. Bevacqua, P. Dolcimascolo, A. Tamburini, A. Brucato, H. Glade, L. Buether, G. Micale, Reactive crystallisation process for magnesium recovery from concentrated brines, Desal. Wat. Treat., 55 (2014) 2377–2388.

[13] A. Cipollina, A. Misseri, G.D.A. Staiti, A. Galia, G. Micale, O. Scialdone, Integrated production of fresh water, sea salt and magnesium from sea water, Desal. Wat. Treat., 49 (2012) 390–403.

[14] M.J. Park, G.M. Nisola, A.B. Beltran, R.E.C. Torrejos, J.G. Seo, S.P. Lee, H. Kim, W.J. Chung, Recyclable composite nanofiber adsorbent for Li^+ recovery from seawater desalination retentate, Chem. Eng. J., 254 (2014) 73–81.

[15] M. Peterková, C. Valderrama, O. Gibert, J.L. Cortina, Extraction of valuable metal ions (Cs, Rb, Li, U) from reverse osmosis concentrate using selective sorbents, Desalination, 286 (2012) 316–323.
[16] T. Hoshino, Innovative lithium recovery technique from seawater by using world-first dialysis with a lithium ionic superconductor, Desalination, 359 (2015) 59–63.
[17] Y. Choi, G. Naidu, S. Jeong, S. Lee, S. Vigneswaran, Effect of chemical and physical factors on the crystallization of calcium sulfate in seawater reverse osmosis brine, Desalination, 426 (2018) 78–87.
[18] F. Mohammadesmaeili, M.K. Badr, M. Abbaszadegan, P. Fox, Mineral recovery from inland reverse osmosis concentrate using isothermal evaporation, Water Res., 44 (2010) 6021–6030.
[19] N. Melián-Martel, J.J. Sadhwani, S. Ovidio Pérez Báez, Saline waste disposal reuse for desalination plants for the chlor-alkali industry, Desalination, 281 (2011) 35–41.
[20] A. Shahmansouri, J. Min, L. Jin, C. Bellona, Feasibility of extracting valuable minerals from desalination concentrate: a comprehensive literature review, J. Clean. Prod., 100 (2015) 4–16.
[21] H. Dong, C. Unluer, E.H. Yang, A. Al-Tabbaa, Recovery of reactive MgO from reject brine via the addition of NaOH, Desalination, 429 (2018) 88–95.
[22] A.-M. Wan, B. Mansoor, F. Ahmad, Magnesium recovery from brines using exopolymeric substances of sulfate-reducing bacteria, Desal. Wat. Treat., 57 (2016) 25747–25756.
[23] R.H. Dave, P.K. Ghosh, Enrichment of bromine in sea-bittern with recovery of other marine chemicals, Ind. Eng. Chem. Res., 44 (2005) 2903–2907.
[24] A. Smith, P.E. Heckelman, S. Budavari, The Merck Index: An Encyclopedia of Chemicals, Drugs, and Biologicals, Wiley, New Jersey, 2001.
[25] D. Barba, V. Brandani, G. Di Giacomo, P.U. Foscolo, Magnesium oxide production from concentrated brines, Desalination, 33 (1980) 241–250.
[26] B. Dönmez, F. Demir, O. Laçin, Leaching kinetics of calcined magnesite in acetic acid solutions, J. Ind. Eng. Chem., 15 (2009) 865–869.
[27] S. Teir, H. Revitzer, S. Eloneva, C.J. Fogelholm, R. Zevenhoven, Dissolution of natural serpentinite in mineral and organic acids, Int. J. Miner. Process., 83 (2007) 36–46.
[28] M. Özdemir, D. Çakır, İ. Kıpçak, Magnesium recovery from magnesite tailings by acid leaching and production of magnesium chloride hexahydrate from leaching solution by evaporation, Int. J. Miner. Process., 93 (2009) 209–212.
[29] D.R. Lide, CRC Handbook of Chemistry and Physics, 83rd ed., Taylor & Francis, Boca Raton, 2002.
[30] O.S. Pokrovsky, J. Schott, Experimental study of brucite dissolution and precipitation in aqueous solutions: surface speciation and chemical affinity control, Geochim. Cosmochim. Acta, 68 (2004) 31–45.
[31] M.T. Zafarani-Moattar, A. Salabat, Phase diagrams of aliphatic alcohols + magnesium sulfate + water, J. Chem. Eng. Data, 42 (1997) 1241–1243.
[32] N.A. Clontz, R.T. Johnson, W.L. McCabe, R.W. Rousseau, Growth of magnesium sulfate heptahydrate crystals from solution, Ind. Eng. Chem. Fund., 11 (1972) 368–373.