

Impurities Removal in Seawater to Optimize the Magnesium Extraction

N C Natasha¹, F Firdiyono¹ and E Sulistiyono¹

¹Research Center of Metallurgy and Materials, LIPI, Puspiptek Gedung 470, Indonesia

E-mail: nadia_natasha90@yahoo.com

Abstract. Magnesium extraction from seawater is promising way because magnesium is the second abundant element in seawater and Indonesia has the second longest coastline in the world. To optimize the magnesium extraction, the impurities in seawater need to be eliminated. Evaporation and dissolving process were used in this research to remove the impurities especially calcium in seawater. Seawater which has been evaporated from 100 ml to 50 ml was dissolved with variations solution such as oxalic acid and ammonium bicarbonate. The solution concentration is 100 g/l and it variations are 2 ml, 4 ml, 6 ml, 8 ml, 10 ml, 20 ml, 30 ml, 40 ml and 50 ml. This step will produce precipitate and filtrate then it will be analysed to find out the result of this process. The precipitate was analysed by X-ray Diffraction (XRD) and Scanning Electron Microscope (SEM) but the filtrate was analysed by Inductively Coupled Plasma (ICP). XRD analysis shows that calcium oxalate and calcium carbonate were formed and ICP analysis shows that the remaining calcium in seawater using oxalic acid is about 0.01% and sodium 0.14% but when using ammonium bicarbonate the remaining calcium is 2.5% and sodium still more than 90%. The results show that both oxalic acid and ammonium bicarbonate can remove the impurities but when using oxalic acid, not only the impurities but also magnesium was precipitated. The conclusion of this research is the best solution to remove the impurities in seawater without precipitate the magnesium is using ammonium bicarbonate.

1. Introduction

Magnesium is an alkaline earth metal and highly abundant in the earth's crust that has many functions in automotive, aerospace, medical, electronic and etcetera [1]. To improve its properties, magnesium needs to be designed and alloyed with other metals [2]. Magnesium can be found not only in dolomite, magnesite but also in seawater and brine water [3]. Seawater is a solution that contain of many elements and organisms. The most abundant of chemical dissolved in seawater can be seen on Table 1.

Table 1. Chemical dissolved in seawater [4]

Chemical ion	Concentrations (parts per thousand)	Proportion of total salinity
Sodium	10.752	55.03
Magnesium	1.295	3.68
Calcium	0.416	1.18
Potassium	0.390	1.11
Chloride	19.345	55.03
Sulfate	2.701	7.68

¹ To whom any correspondence should be addressed.



Based on table 1, magnesium is the second abundant element in seawater after sodium so that magnesium extraction from seawater is promising way. Unfortunately, there are many impurities in seawater such as sodium, calcium, and potassium so that the removal impurities needed to be done. Magnesium extraction was done by many researchers such as Robinson in 1943 gave patent about recovering magnesium as $Mg(OH)_2$ from seawater [5], Yildirim in 2010 extracted the MgO from dolomite ore by removing the calcium first as carbonates [6], Khuyen Thi Tran in 2013 extracted magnesium oxalate from Uyuni Salar brine by removing the impurities such as calcium, potassium and lithium [3] and Khuyen Thi Tran in 2015 extracted the magnesium from Uni Salar brine as magnesium carbonate by removing the calcium first using oxalic acid then use NaOH and Na_2CO_3 solution [1].

From previous works, authors conclude that to optimize magnesium extraction, the impurities especially calcium in seawater needed to be eliminated. Calcium needed to be eliminated because it can reduce the magnesium purity in the process of magnesium extraction [3]. The effect of oxalic acid and ammonium bicarbonate addition to calcium removal in seawater from local area Indonesia was studied. This study was done to know the best solution to remove the impurities without remove the magnesium.

2. Experimental

2.1. Materials and reagents

Seawater from beach in Tangerang was taken and brought to laboratory at Research Center of Metallurgy and Materials. Chemical composition of seawater was analysed first using Inductively Coupled Plasma (ICP). Oxalic acid and ammonium bicarbonate were used in this study as reagents to remove the impurities.

2.2. Experimental Methods

Seawater was filtered to remove the dirt and analysed by ICP to know its initial composition. Seawater was heated with the ratio 1 : 2 of seawater evaporated then analysed with ICP. The concentration of oxalic acid and ammonium bicarbonate is 100 g/l. Volume variations of oxalic acid and ammonium bicarbonate were done from 2 ml, 4 ml, 6 ml, 8 ml, 10 ml, 20 ml, 30 ml, 40 ml and 50 ml. Dissolution of oxalic acid and ammonium bicarbonate in seawater was done at ambient temperature for 24 hours without stirring. The precipitate from this step filtered to separate the precipitation and filtrate. Precipitation was analysed by SEM to know the morphology and XRD to find its phase. Filtrate was analysed by ICP to get the final concentration of seawater.

3. Results and discussion

3.1. Filtrate

Before doing the experiment, ICP analysis was done to know the initial concentration of seawater. ICP analysis shows that seawater consisted of sodium (10129.3 ppm), magnesium (1672.09 ppm) and calcium (553.21 ppm). It tells that sodium dominates and magnesium is the second abundant element in sample. Heating the seawater until 50% of sample evaporated can affect the concentration of seawater either it will be increased or decreased. ICP analysis was done to find the effect of heating process. Analysis results in filtrate are sodium (20175.5 ppm), magnesium (1576.2 ppm) and calcium (826.204 ppm). It indicates that heating process effect the seawater more saline because the concentration of sodium and calcium increased.

This filtrate then added with two different solutions that are 100 g/l oxalic acid and 100 g/l ammonium bicarbonate. Volume variations were done to find the optimum volume to remove the impurities. This process produced liquid residue and precipitate. Liquid residue was analysed with ICP to find the final concentration of seawater. The analysis can be seen at Table 2.

Table 2. ICP analysis of seawater with 100 g/l oxalic acid and 100 g/l ammonium bicarbonate

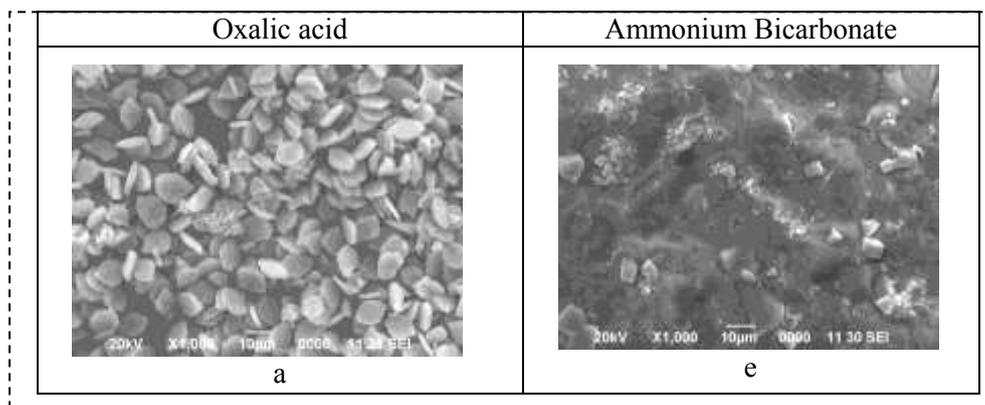
Volume (ml)	Sodium (%)		Magnesium (%)		Calcium (%)	
	Oxalic Acid	Ammonium Bicarbonate	Oxalic Acid	Ammonium Bicarbonate	Oxalic Acid	Ammonium Bicarbonate
2	10.98	103.35	14.04	102.76	21.11	31.13
4	11.93	102.24	15.36	104.91	2.62	5.61
6	3.63	98.14	15.51	104.13	2.21	4.46
8	10.52	92.98	16.02	105.74	2.40	4.08
10	3.69	96.93	18.02	108.13	0.65	3.38
20	21.1	101.80	15.24	113.78	2.34	2.98
30	16.11	98.35	22.45	120.44	3.66	2.50
40	0.92	102.65	7.84	122.95	0.20	3.29
50	0.14	100.08	0.00	131.39	-0.01	3.56

Table 2 shows that by using oxalic acid the content of sodium and calcium are reduced until 0.14% and 0.01% remained while using ammonium bicarbonate only calcium that reduced rapidly until 2.5% remained but sodium only 2% removed from seawater. Unfortunately, more than 90% magnesium in seawater also reduced when using oxalic acid. Calcium with oxalic acid will react and form white precipitation as calcium oxalates. Calcium oxalates will be produced immediately in concentrated solution but in aqueous solution it will be produced slowly [7] so that calcium can be eliminated from seawater using oxalic acid. According to Khuyen Thi Tran, magnesium in oxalic acid will be precipitated at $\text{pH} > 1$. Oxalic acid solution in this experiment is an aqueous solution with the concentration less than 1 M. Thus, magnesium in seawater was removed.

Magnesium in mixture of seawater and ammonium bicarbonate was not removed. It can be seen at Table 2 that more than 90% of magnesium in seawater using ammonium bicarbonate still exist. Calcium with hydrogen carbonate solution will give white precipitation but this precipitation has high solubility in water and the precipitation will dissolve in water [7]. So that if calcium in oxalic acid was compared with calcium in ammonium bicarbonate, the calcium concentration in ammonium bicarbonate higher than calcium concentration in oxalic acid. It caused by the precipitate re-dissolved in seawater. Magnesium with ammonium bicarbonate will not produce a white precipitate. It caused by ammonium (NH_4^+) effect the equilibrium reaction and hydrogen carbonate ion produced [7].

3.2. Precipitate

Reaction between oxalic acid and ammonium bicarbonate produced a precipitate. The precipitate was analysed by SEM to know the morphology of precipitate and XRD to confirm the phase that formed from this experiment.



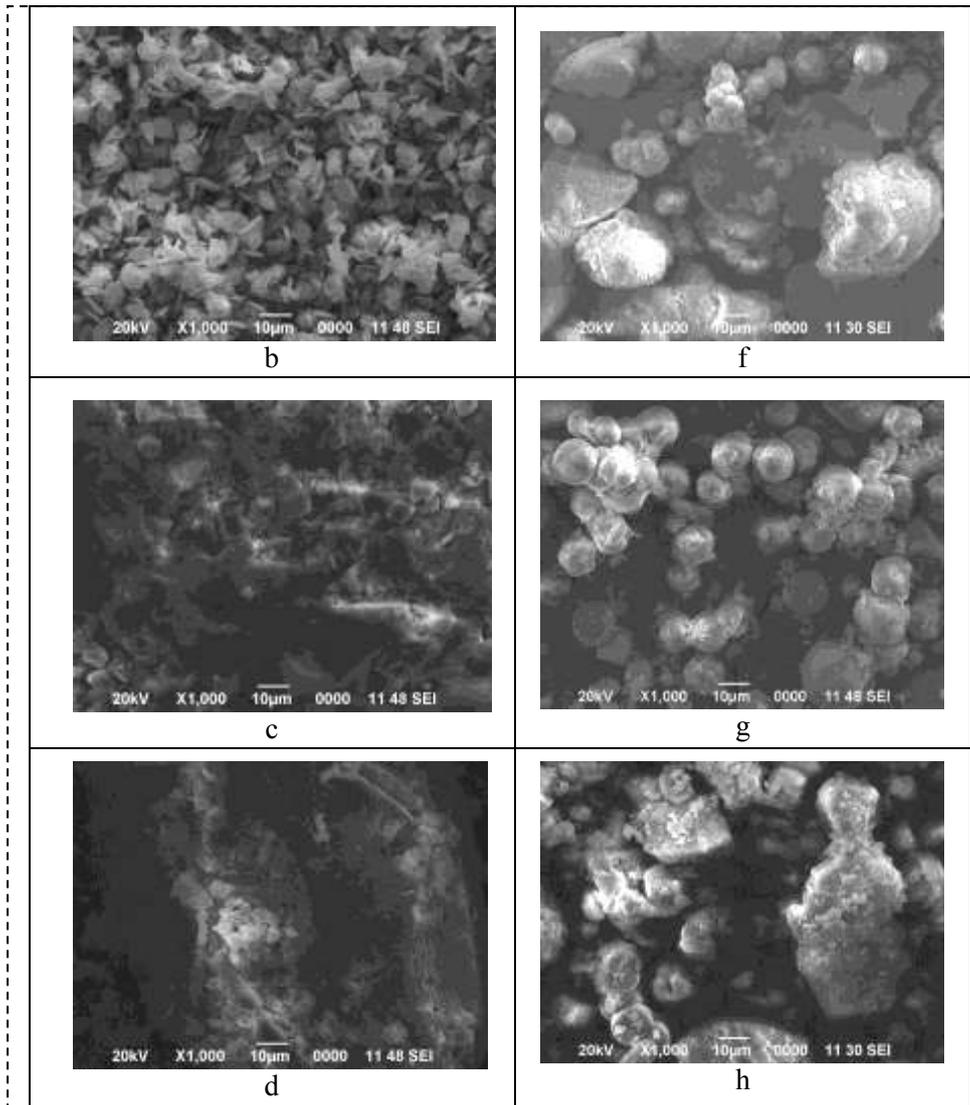
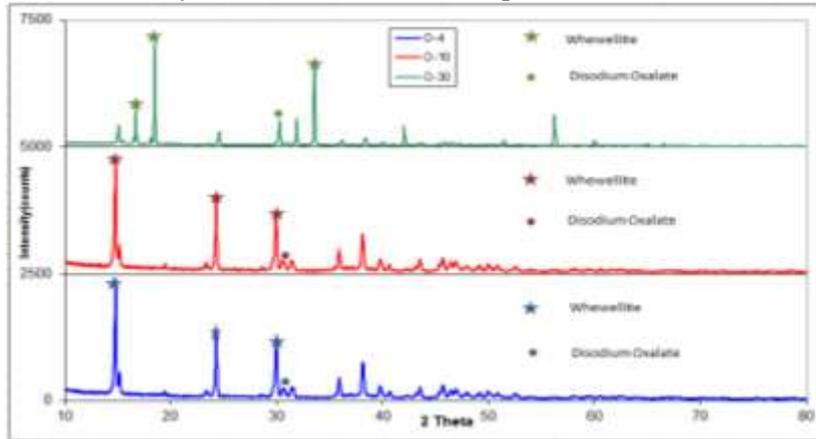


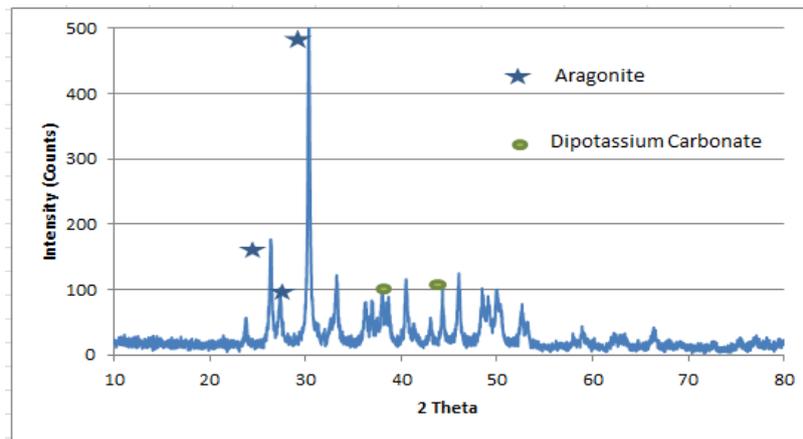
Figure 1. SEM image of precipitation in 1000x magnification using oxalic acid and ammonium bicarbonate. a) 2 ml oxalic acid in seawater b) 10 ml oxalic acid in seawater c) 30 ml oxalic acid in seawater d) 40 ml oxalic acid in seawater e) 2 ml ammonium bicarbonate in seawater f) 10 ml ammonium bicarbonate in seawater g) 30 ml ammonium bicarbonate in seawater h) 40 ml ammonium bicarbonate in seawater

Figures 1a – 1d are precipitate result from seawater with oxalic acid addition whereas Figures 2e – 2h are precipitate result from seawater with ammonium bicarbonate addition. Figure 1a – 1b shows that monoclinic and prismatic crystal system appeared clearly. It indicates that calcium oxalates monohydrated was formed in this experiment [8]. Figures 1c – 1d show that monoclinic and prismatic crystal appeared in small amounts and dominate with other forms. It indicates that not only calcium oxalate formed in this experiment but also other oxalates. While in figures 2e – 2h show that the rounded crystal dominated and become extended when the ammonium bicarbonate increased. It indicates that calcium carbonate was formed from this reaction.

To confirm the phase of the precipitate that produced from oxalic acid and ammonium bicarbonate addition in seawater, XRD analysis was done on these samples.



a



b

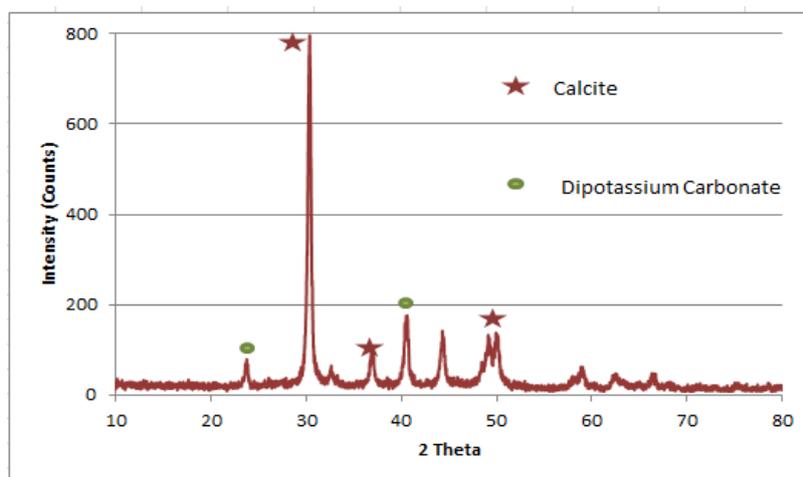


Figure 2. XRD analysis of precipitate from oxalic acid and ammonium bicarbonate addition. a) seawater with 4 ml oxalic acid, 10 ml oxalic acid and 30 ml oxalic acid. b) seawater with 10 ml ammonium bicarbonate. c) seawater with 40 ml ammonium bicarbonate

X-ray diffraction (XRD) analysis with 2 Theta 10° - 80° was done in this study. Figures 2a showed that whewellite ($\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$) and disodium oxalate monoperhydrate ($\text{Na}_2\text{C}_2\text{H}_2\text{O}_6$) formed when 10 ml oxalate was added into sea water while whewellite and sodium hydrogenoxalate hydrate formed when 30 ml oxalate was added into seawater. Figures 2b – 2c showed ammonium bicarbonate in seawater addition caused aragonite (CaCO_3) and dipotassium carbonate (K_2CO_3) formed. Figures 2a – 2c show that the intensity of oxalic acid addition is higher than ammonium carbonate addition in seawater. It can be seen that the intensity of oxalic acid addition reached 7000 while the intensity of ammonium carbonate addition only reached 800.

This analysis also tells that both whewellite and disodium oxalate monoperhydrate have a monoclinic crystal system but sodium hydrogen oxalate hydrate has anorthic crystal system. While aragonite has orthorhombic crystal system and others have hexagonal crystal system. The analysis results confirmed that both oxalic acid and ammonium bicarbonate are able to eliminate the impurities in seawater but the best solution to eliminate the impurities without remove the magnesium is ammonium bicarbonate.

4. Conclusion

Oxalic acid and ammonium bicarbonate can remove the impurities in seawater from Tangerang, Indonesia that consisted of sodium (10129.3 ppm), magnesium (1672.09 ppm) and calcium (553.21 ppm) in order to extract the magnesium. Oxalic acid able to remove sodium and calcium until 0.14% and 0.01% remained while using ammonium bicarbonate only calcium that reduced rapidly until 2.5% remained but sodium only 2% removed from seawater. This experiment shows that oxalic acid also can remove the magnesium but ammonium bicarbonate only can remove calcium so that the best solution to remove the impurities without remove the magnesium is ammonium bicarbonate. Variations in solution concentration need to be done to know whether oxalic acid can eliminate the impurities without remove the magnesium.

References

- [1] Khuyen T T, Kyu S H, Su J K, Myong J K, Tam T 2016 *hydrometallurgy* **160** pp 106 – 114
- [2] Anonymous <http://www.intlmag.org/magnesiumresources/process.cfm> International Magnesium Association akses 22 september 2016
- [3] Khuyen T T, Tri V L, Jeon-Woong A, Dong-Jun K, Myong-Jun K, Tam T 2013 *hydrometallurgy* **138** pp 93 – 99
- [4] Genny A 2008 Seawater Composition <http://www.marinebio.net/marinescience/02ocean/swcomposition.htm> akses 22 september 2016
- [5] Robinson, H.A., Friedrich, R.E., Spencer, R.S 1943 *Magnesium hydroxide from seawater. US Patent 2,405,055* (30 June 1943).
- [6] Yildirim, M., Akarsu, H 2010 *Physicochem. Probl. Miner. Process* pp 257–272
- [7] Ir. L. Setiono, Dr. A. Hadyana Pudjaatmaka. 1990. *Vogel Buku Teks Analisis Anorganik Kualitatif Makro dan Semimikro Bagian I*. Jakarta.
- [8] Emel A, Mualla O 2014 *J. Cryst. Growth* **401** pp 260 – 265