

# Desalination Property of Various Calcined Layered Double Hydroxides from Seawater

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**Abstract**— Now, approximately 20% of farmland in the world becomes salt damage soil with unsuitable properties for agriculture. In general, salt was removed from soil by flushing out with rain water due to the improvement of soil permeability using gypsum and so on. However, there are arid and semi-arid areas with an insufficient supply amount of rain water to remove salts from soil. In this study, a novel method to capture salt in soil using various calcined layered double hydroxides (LDHs) as a desalination agent was attempted to estimate desalination property from seawater. 4 kinds of LDH with the different  $M^{2+}/M^{3+}$  ratios are prepared using 2 kinds of  $Mg^{2+}$  and  $Ca^{2+}$  as  $M^{2+}$  and 2 kinds of  $Al^{3+}$  and  $Fe^{3+}$  as  $M^{3+}$ . The desalination ability of these calcined LDHs was investigated using seawater. As a result, the decrease of salinity was confirmed using all samples. Among these samples, the calcined Mg-Al LDH with  $Mg/Al = 3.45$  and Ca-Fe LDH with  $Ca/Fe = 2.35$  indicated the highest desalination property, due to the decrease of  $Cl^-$  and  $SO_4^{2-}$  from seawater, by reconstruction reaction. Ca-Fe LDH was calcined at various temperatures and the desalination ability at different calcined temperatures was also evaluated. It was found that the desalination ability of calcined LDH depends on the calcination temperatures and Ca-Fe LDH calcined at 500 °C indicated the highest desalination ability.

**Keywords**— Seawater, Desalination agent, Calcined LDH,  $M^{2+}/M^{3+}$  composition, Calcination temperature.

## I. INTRODUCTION

In the 21st century, global environmental issues are very serious, and effective utilization of energy and mineral resource and the securing of food and water are urgent problems.

Now, there are about 1/5 of salt-damaged soils in the world farmland. The demand for food is increasing due to the global population growth, and production of a stable supply of food is essential to sustain human life. Securing farmland is one of the most important factors in food production. Furthermore, in 2011, great earthquake occurred in Tohoku area of Japan and farmland in Tohoku was damaged by Tsunami. A lot of farmlands are damaged by salt, and it is desired to improve the salt-damaged soil into plantable soil.

There are some desalination methods, such as leaching, elution, disposal of outer layer soil, and salt absorption due to the halotolerant plant. Now, leaching method, which makes farmlands good water permeability and flush out salt with water, is a popular desalination method to improve salt-damaged farmlands. However, the method needs a long time to improve the salt damaged soil completely, and depends on weather. There are some studies to improve salt-damaged soil rapidly. For example, electrodialysis desalination was studied, but this technology is expensive and needs a large space.

In this study, we develop a new salt-damaged soil improving agent prepared from calcined layered double hydroxide (LDH). Chemical formula of LDH expresses as  $[M^{2+}_{1-x}M^{3+}_x(OH)_2][A^{n-}_{x/n} \cdot mH_2O]$  ( $M^{2+}$ : divalent metal ions,  $M^{3+}$ : trivalent metal ions,  $A^{n-}$ : anionic species,  $x = 0 - 1$ ), and composed of metal complex hydroxide known as inorganic anion exchangers [1]. Hydrotalcite is well known for Mg/Al type LDH, and the uptake of anions onto hydrotalcites from aqueous solution was occurred by two mechanisms: (1) intercalation by anion exchange; (2) intercalation by reformation of calcined samples [2]. Intercalation by anion exchange was used for the removal of the anion or oxi-anions, such as  $H_3AsO_4$ , from water solution [3]. Intercalation by reformation of calcined LDH was also used for anion removal, e.g. adsorption of  $VO_4^{3-}$  or  $NO_3^-$  [4]. In our previous study, calcined hydrotalcite could desalinate seawater and the solution could use for plant growth by combination with natural zeolite treatment [5]. However, little information can be available on desalination property of calcined LDH. The objective of this study was to investigate the desalination properties of various calcined LDH from seawater.

## II. MATERIAL AND METHOD

### 2.1 Preparation of various calcined LDH

Four kinds of LDH are prepared with the different  $M^{2+}/M^{3+}$  ratios ( $M^{2+} : M^{3+} = 1-6$ ) using two kinds of  $Mg^{2+}$  and  $Ca^{2+}$  as  $M^{2+}$  and two kinds of  $Al^{3+}$  and  $Fe^{3+}$  as  $M^{3+}$ , as follow. The mixed solution of  $M^{2+}$  (0.1 - 0.6 mol) and  $M^{3+}$  (0.1 mol) was prepared using  $M^{2+}(NO_3)_2$  and  $M^{3+}(NO_3)_3$  to synthesize the product with  $M^{2+}/M^{3+}$  molar ratio of 1 - 6. The  $M^{2+}/M^{3+}$  mixed solution was quantitatively added to 0.3 M  $NaNO_3$  solution at pH 12.5 under stirring at 50 °C with  $N_2$  bubbling. In order to maintain pH of the solution (12.5),  $NaOH$  solution was slowly dropped in the stirring solution. The mixed solution was stirred for 6 hours, and then solids were obtained by a vacuum filtration method. The filtrated solid washed with distilled water and then dried at 50 °C overnight to obtain the LDH with various  $M^{2+}/M^{3+}$  ratio. The calcined LDH was obtained by heating each LDH at 450 °C for an hour in an electric furnace [6, 7]. To estimate calcined LDH with the highest desalination ability for Ca-Fe LDH, the Ca-Fe LDH was calcined at 100-900°C.

Identification of crystal structure of the products and calcined products were carried out with a X-ray diffraction (XRD) equipment (Rigaku, MiniFlex 600).  $M^{2+}/M^{3+}$  ratio in the structure were investigated as follow. 0.1 g of samples were dissolved in 10 mL of 1 M HCl solution by shaking for 24 hours with Recipro Shaker SR-1 (TAITEC), and then the contents of Mg, Ca, Al and Fe in the solution were analyzed using atomic absorption spectrometry (AAS) (Perkin Elmer, Analyst 200) to calculate the  $M^{2+}/M^{3+}$  molar ratio of the samples.

### 2.2 Desalination property

The desalination abilities of each calcined LDH were investigated using seawater obtained from the surface of Imari bay, Saga prefecture, Japan. The chemical composition, pH and salinity of seawater used in this study is shown in Table 1.

TABLE 1  
CHEMICAL COMPOSITION, PH AND SALINITY OF SEAWATER.

Concentration (mg/L)						pH	Salinity (%)
$SO_4^{2-}$	$Cl^-$	$Na^+$	$K^+$	$Mg^{2+}$	$Ca^{2+}$		
2850	22742	11026	384	1451	377	8.3	3.36

0.1 g of each calcined product was put into 5 mL of seawater in 50 mL of centrifuged tube and shaken for 5 hours. After shaking, salinity of seawater treated with calcined LDH were measured by salinity concentration meter (Lutron, YK-31SA). pH were measured by pH meter (HORIBA, LAQUA). The samples after the experiment were collected by filtration and analyzed by XRD equipment. The chemical composition of seawater after experiment were measured by ion chromatograph (Tosoh, IC-2010), and the amount of each ions removed by calcined LDH,  $q$  (mmol/g), was calculated using the following equation (1):

$$q = ((C_0 - C) \cdot V)/w \quad (1)$$

where  $C_0$  and  $C$  are the concentrations (mmol/L) of each ion in the initial solution and the measured solution, respectively.  $V$  is the volume (L) of the solution, and  $w$  is the weight (g) of the sample added to the solution.

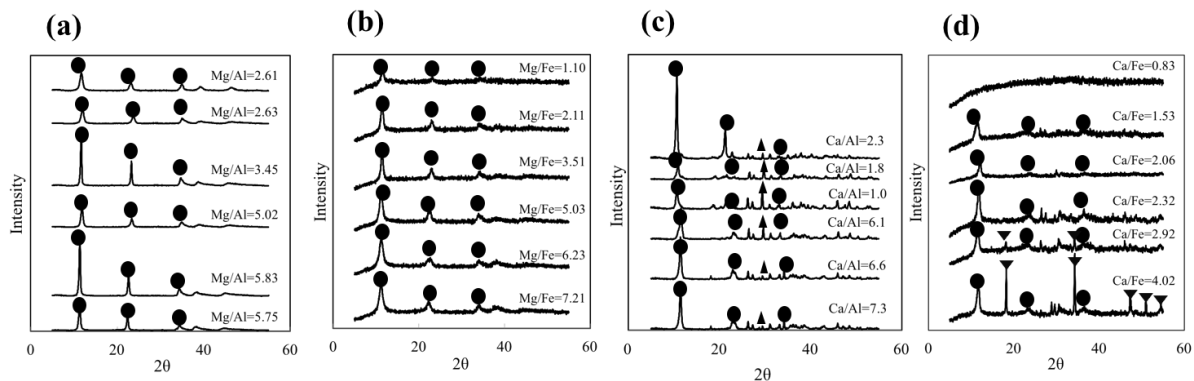
The removal percent of salt after treating seawater with each calcined product,  $R$  (%), was calculated using the following equation (2):

$$R = (C_0 - C)/C_0 \times 100 \quad (2)$$

## III. RESULTS AND DISCUSSION

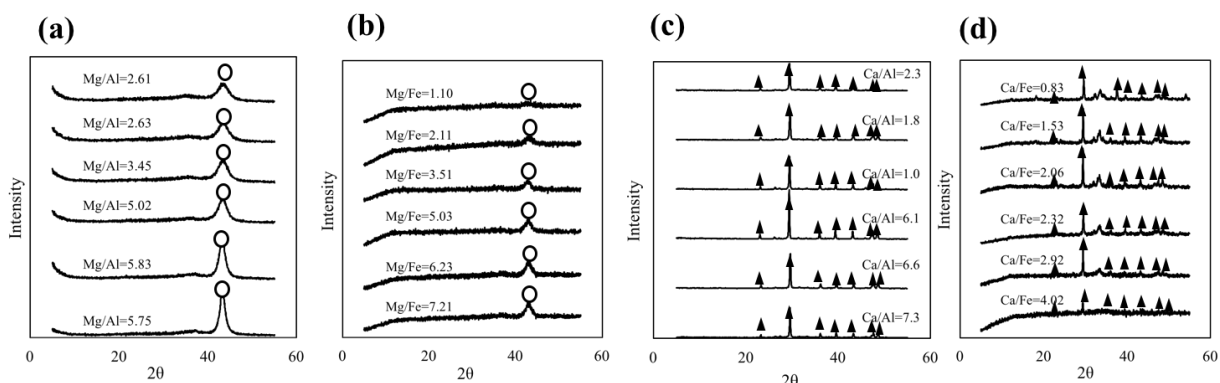
### 3.1 Preparation of various calcined LDH

The XRD patterns of the obtained LDH are shown in Fig. 1. It is noted that  $M^{2+}/M^{3+}$  molar ratio of each LDH indicates in Fig. 1. In all products, LDH peaks were confirmed, and we succeed to prepare various LDHs with different  $M^{2+}/M^{3+}$  molar ratio. Al-LDH peaks were clearer than Fe-LDH peaks. In Ca-LDH,  $CaCO_3$  peaks were confirmed in Ca-Al LDH and  $Ca(OH)_2$  peaks were confirmed in Ca-Fe LDH.



**FIGURE 1. XRD Pattern Of the LDHs : (a) Mg-Al LDH, (b) Mg-Fe LDH, (c) Ca-Al LDH, (d) Ca-Fe LDH**  
 ●: LDH, ▲: CaCO<sub>3</sub>, ▼: Ca(OH)<sub>2</sub>

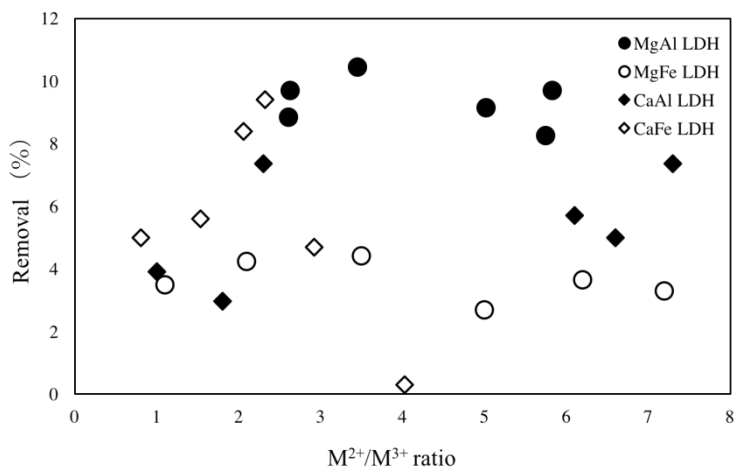
The XRD patterns of calcined LDH are shown in Fig. 2. In calcined Mg-Al and Mg-Fe LDHs, Mg oxide, Mg-Al oxide or Mg-Fe oxide peaks were confirmed and peak intensity increases with increasing M<sup>2+</sup>/M<sup>3+</sup> ratio of calcined LDH, regardless of the peak intensity of LDH before calcination, because the peaks of obtained oxide mainly depends on those of Mg oxide. In calcined Ca-Al or Ca-Fe LDH, CaCO<sub>3</sub> peaks were mainly confirmed.



**FIGURE 2. XRD Pattern Of the LDHs After Calcination: (a) Mg-Al LDH, (b) Mg-Fe LDH, (c) Ca-Al LDH, (d) Ca-Fe LDH.** ○: Mg oxide, Mg-Al oxide or Mg-Fe oxide, ▲: CaCO<sub>3</sub>

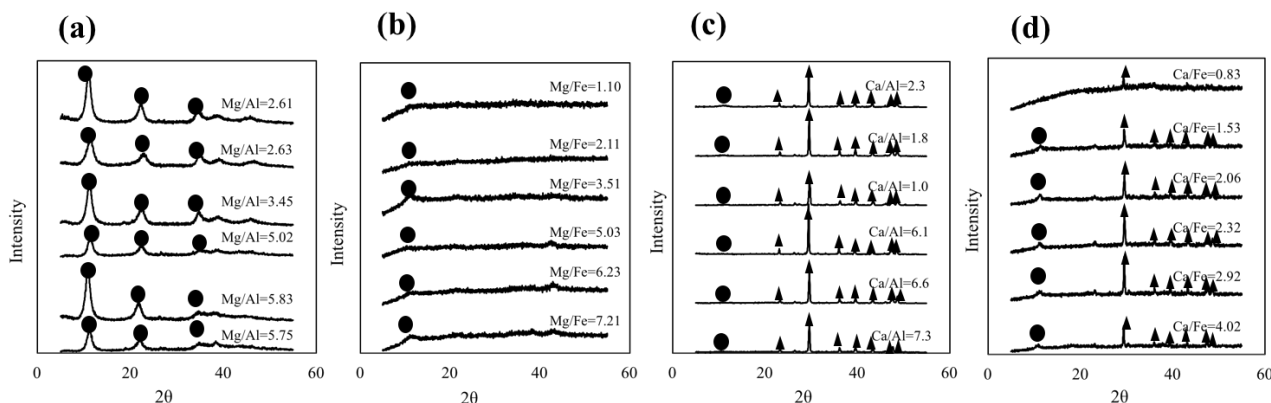
**3.2 Desalination ability of calcined products**

The removal percent of salt after treating seawater with all calcined products are shown in Fig. 3. The salinity decreased in all seawater after treatment with calcined LDH. Desalination ability of Mg-Al, Mg-Fe, and Ca-Al LDH are almost constant regardless of M<sup>2+</sup>/M<sup>3+</sup>, while desalination ability of Ca-Fe LDH increases with increasing Ca/Fe to about 2.0 and then decreases.



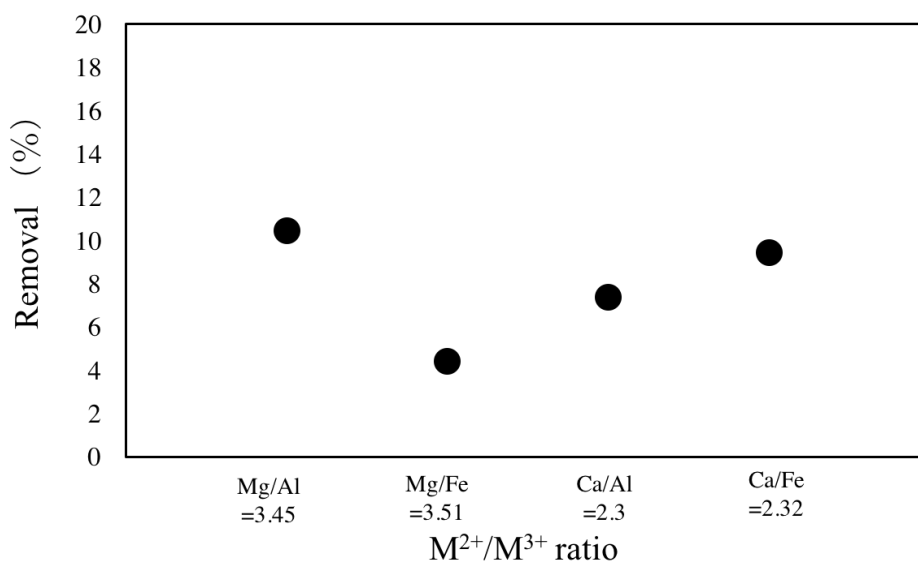
**FIGURE 3. Removal of Seawater Treated With All Calcined LDHs**

XRD patterns of the product after desalination tests are shown in Fig. 4. The structure of calcined LDH returned to that of LDH by reformation reaction. It was confirmed that all products remove salts in seawater by reformation reaction. It is noted that CaCO<sub>3</sub> was confirmed in Ca-LDH after desalination test.



**FIGURE 4. XRD Pattern Of the Calcined LDHs After Desalination Test: (a) Mg-Al LDH, (b) Mg-Fe LDH, (c) Ca-Al LDH, (d) Ca-Fe LDH. ●: LDH, ▲: CaCO<sub>3</sub>**

The highest removal of seawater treated with each M<sup>2+</sup>/M<sup>3+</sup> products after calcination are shown in Fig. 5. The calcined LDHs with about M<sup>2+</sup>/M<sup>3+</sup> = 3.5 have high desalination ability in Mg-LDHs, while there with about M<sup>2+</sup>/M<sup>3+</sup> = 2.3 have high ability in Ca-LDH. The highest removal of salt from seawater is approximately 10% using the Mg-Al LDH with Mg/Al = 3.45 and Ca-Fe LDH with Ca/Fe = 2.32.



**FIGURE 5. Removal of Seawater Treated With the Highest Each Calcined LDH**

Removal amounts of each element in seawater by calcined LDHs are shown in Fig. 6. It is noted that pHs of the seawater after desalination test was about 10 using there calcined LDHs, are shown in Fig. 7. For Mg-Al LDH, Cl<sup>-</sup> and Mg<sup>2+</sup> mainly decrease, and for Mg-Fe LDH, Cl<sup>-</sup> and Na<sup>+</sup> mainly decrease. For Ca- LDH, Cl<sup>-</sup>, Na<sup>+</sup> and Mg<sup>2+</sup> mainly decrease. The decreases of salinity using calcined LDHs are due to the removal of Na<sup>+</sup>, Cl<sup>-</sup> and Mg<sup>2+</sup> from seawater. It may be considered that removal of Cl<sup>-</sup> was caused by LDH reformation reaction and removal of Na<sup>+</sup> and Mg<sup>2+</sup> were caused by increasing pH of the seawater. The removal amounts of Cl<sup>-</sup>, Na<sup>+</sup> and Mg<sup>2+</sup> in seawater using Ca-LDH were higher than those using Mg-LDH, while desalination ability of Ca-LDH is lower than that of Mg-LDH. It may be caused by increasing Ca<sup>2+</sup> in the seawater after desalination test.

These results suggest that calcined LDH can decrease salinity of seawater due to the removal of Cl<sup>-</sup>, Na<sup>+</sup> and Mg<sup>2+</sup> from seawater.

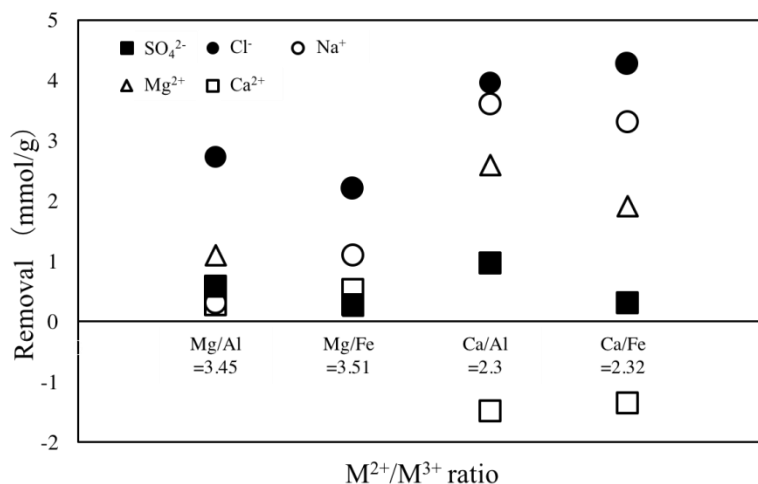


FIGURE 6. Removal Amounts of Each Element in Seawater by Calcined LDH

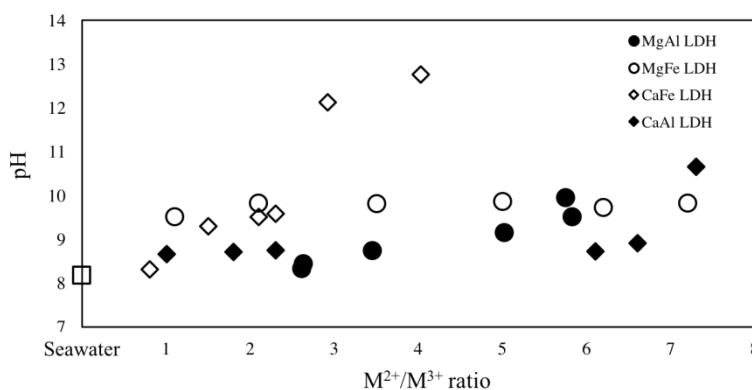


FIGURE 7. PH Of Seawater after Desalination Test

3.3 Desalination ability of Ca-Fe LDH calcined at various temperatures

Because Ca<sup>2+</sup> and Fe<sup>3+</sup> are cheaper than Mg<sup>2+</sup> and Al<sup>3+</sup>, we select Ca-Fe LDH (Ca/Fe = 2.32) for the best desalination product in this experiment.

The XRD patterns of Ca-Fe LDH calcined at various temperatures are shown in Fig. 8. For calcination at 100 and 300°C, LDH peaks were confirmed and peak intensity decreases as the calcination temperature rises. For calcination temperature over 500°C, LDH peaks were disappeared above 500°C and Ca<sub>2</sub>Fe<sub>2</sub>O<sub>5</sub> and CaO appeared at 700 and 900°C.

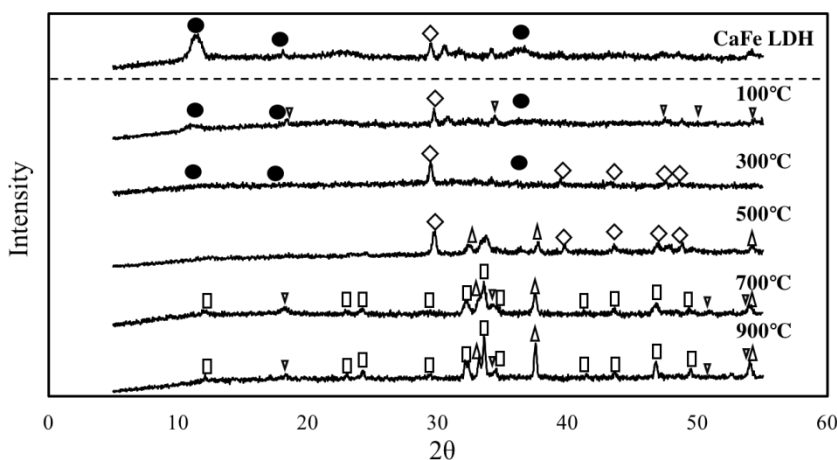
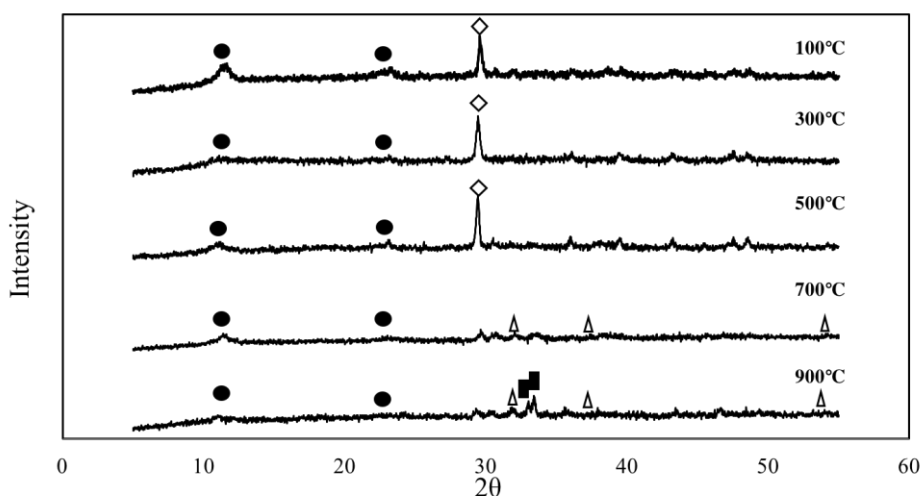


FIGURE 8. XRD Pattern of the Products after Calcination at Various Temperatures

●: LDH, ◇ : CaCO<sub>3</sub>, ▽ : Ca(OH)<sub>2</sub>, □ : Ca<sub>2</sub>Fe<sub>2</sub>O<sub>5</sub>, △ : CaO

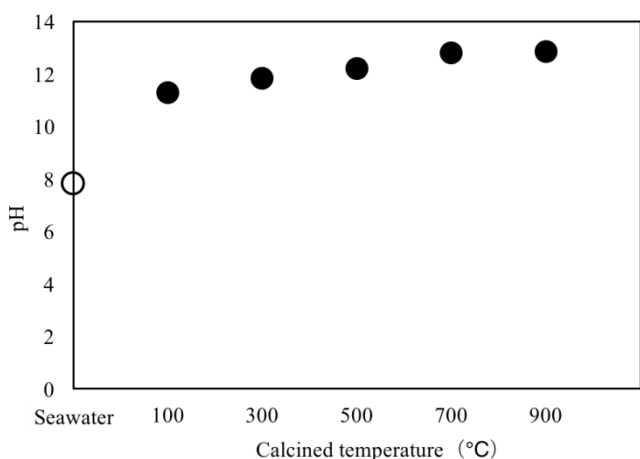
XRD patterns of the calcined products after desalination tests are shown in Fig. 9. The structure of calcined LDH returned to that of LDH by reformation reaction. It was confirmed that all products remove salts in seawater by reformation reaction. For LDHs calcined at 100, 300 and 500°C, CaCO<sub>3</sub> was confirmed, and for LDHs calcined at 700°C and 900°C, CaFe<sub>2</sub>O<sub>4</sub> and CaO were confirmed.



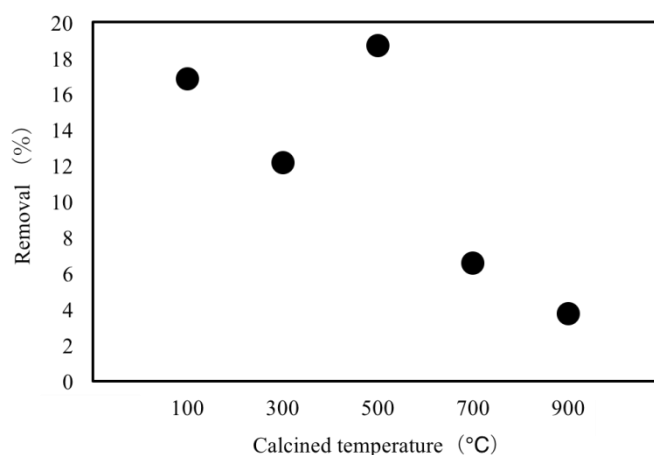
**FIGURE 9. XRD Pattern of the Products after Desalination Tests ●: LDH, ◇: CaCO<sub>3</sub>, △: CaO, ■: CaFe<sub>2</sub>O<sub>4</sub>**

The pHs of seawater after desalination test are shown in Fig. 10. For all calcined LDH, the pH increased to 12-13 after desalination tests.

The removal percent of salt after treating seawater with all calcined LDHs are shown in Fig. 11. The salinity decreased in seawater after treatment with all calcined LDHs. The highest removal of salt from seawater is approximately 20% using the Ca-Fe LDH calcined at 500°C.



**FIGURE 10. PH of Seawater after Desalination Test**

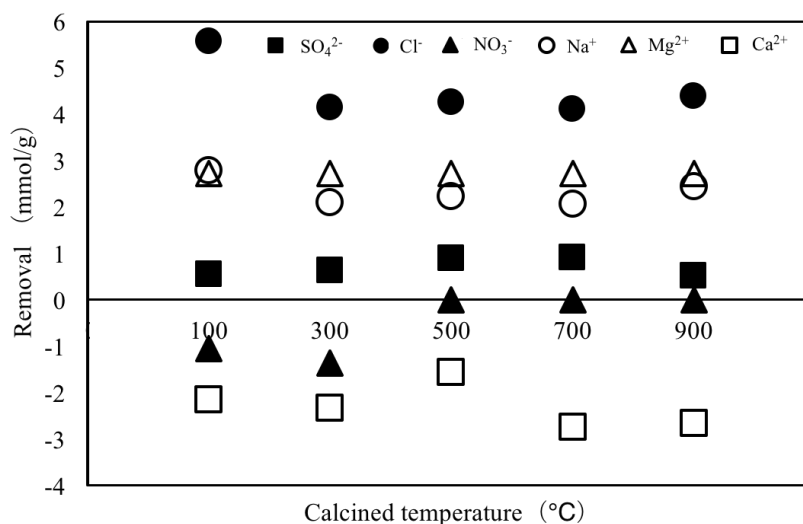


**FIGURE 11. Removal of Seawater Treated with Ca-Fe LDH after Calcination at Various Temperatures**

Removal amounts of each element in seawater by calcined LDH are shown in Fig. 12. For all calcined LDHs, Cl<sup>-</sup>, Na<sup>+</sup> and Mg<sup>2+</sup> mainly decrease and Ca<sup>2+</sup> increase. The decreases of salinity are due to the removal of Cl<sup>-</sup>, Na<sup>+</sup>, and Mg<sup>2+</sup> from seawater. For LDHs calcined at 100 and 300°C, NO<sub>3</sub><sup>-</sup> increased because of NO<sub>3</sub><sup>-</sup> release with ion exchange of Ca-Fe LDH. For LDHs calcined at 500, 700 and 900°C, became NO<sub>3</sub><sup>-</sup> were not detected in the solution. Removal of Cl<sup>-</sup> and SO<sub>4</sub><sup>2-</sup> were caused by LDH reconstruct and removal of Na<sup>+</sup> and Mg<sup>2+</sup> were caused by increasing pH of the seawater.

These results also suggest that calcined LDH can decrease salinity of seawater due to the removal of Cl<sup>-</sup>, Na<sup>+</sup> and Mg<sup>2+</sup> from seawater.

From these results, Ca-Fe LDH calcined at 500°C indicated the highest desalination ability.



**FIGURE 12. Removal Amounts of Each Element in Seawater by Calcined LDHs**

#### IV. CONCLUSION

In this study, we investigated the desalination properties of calcined LDH. As a result, Mg-Al oxide and Mg-Fe oxide peaks confirmed in calcined Mg-LDH and peak intensity of Mg-Al oxide and Mg-Fe oxide increased with increasing  $Mg^{2+}/M^{3+}$  ratio of the LDH. In calcined Ca-LDH, calcite peaks were mainly confirmed. After desalination test, for all calcined LDHs, the structure of calcined LDH returned to that of LDH by reformation reaction. In calcined Ca-LDH, calcite was confirmed in the LDHs after desalination test. The salinity decreases in all seawater after treatment with calcined LDH. The highest desalination from seawater were treated with the calcined Mg-Al LDH with  $Mg/Al = 3.45$  and calcined Ca-Fe LDH with  $Ca/Fe = 2.32$ , because the structure of calcined LDH can remove high amounts of  $Cl^-$ ,  $Na^+$  and  $Mg^{2+}$  from seawater. The removal amounts of  $Cl^-$ ,  $Na^+$  and  $Mg^{2+}$  in seawater treated with calcined Ca-LDH were more than Mg-LDH. Because  $Ca^{2+}$  and  $Fe^{3+}$  are cheaper than  $Mg^{2+}$  and  $Al^{3+}$ , it would be considered that Ca-Fe LDH ( $Ca/Fe = 2.32$ ) is the best desalination product for desalination in this experiment. For Ca-Fe LDH calcined at various temperatures, salinity decreased in seawater after treatment with all calcined LDHs. The highest removal of salt from seawater is approximately 20% using the Ca-Fe LDH with  $Ca/Fe = 2.32$  calcined at 500°C.

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#### REFERENCES

- [1] T. Kameda, T. Yoshioka, Y. Umezumi, and A. Okuwaki, "Application to water environmental conservation, purification of hydrotalcite," *The Chemical Times*, 195, pp. 10-16, 2005.
- [2] F. Cavani, F. Trifiro, "A hydrotalcite-type anionic clays: preparation, properties and applications", *Catalysis Today*, 11, pp. 173-301, 1991.
- [3] G. P. Gillman, "A simple technology for removal from drinking water using hydrotalcite," *Science of the total environment*, 366, pp. 926-931, 2006.
- [4] T. Wang, Z. Cheng, B. Wang, and W. Ma, W., "The influence of vanadate in calcined Mg/Al hydrotalcite synthesis on adsorption of vanadium (V) from aqueous solution," *Chemical Engineering Journal*, 181-182, pp. 182-188, 2011.
- [5] T. Wajima, "Desalination behavior of calcined hydrotalcite from seawater for preparation of agricultural cultivation solution using natural zeolite," *Energy and Environment Research*, 4, pp. 3-10, 2014.
- [6] T. Wajima, "Removal of boron from geothermal water using hydrotalcite", *Toxicological & Environmental Chemistry*, 92(5), 879-884, 2010.
- [7] T. Wajima, "Removal of bromide from desalinated water using hydrotalcite", *International Journal of Environmental Science and Development*, 5(2), 202-206, 2014.