

PREPARATION OF DESALINATION AGENT FROM CA-TYPE CLAY MINERALS

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ABSTRACT: The desalination technology of seawater is considered to secure water and food in recent years, and a new simple desalting material to decrease the high concentration of sodium chloride in seawater is desired. In this study, preparation of the desalting agent from two Ca-type clay minerals, natural zeolite and Ca-Fe type layered double hydroxide (LDH), attempted to desalinate seawater for agricultural water[1][2][5].

Natural zeolites used in this study were mordenite-type zeolite from Fukushima prefecture, Japan and clinoptilolite-type zeolite from Kagoshima prefecture, Japan, and raw and Ca-substituted zeolites were used for seawater desalination[1][2][3][4][5]. Regardless of zeolite type, desalination behaviors of Ca-substituted zeolite were almost same as those of raw zeolite. The salinity and pH of seawater were 3.46% and 8.0, respectively, while clinoptilolite decreased the salinity to 3.20%, mordenite decreased to 2.09%, above 5.0 g/L zeolite addition. As increasing the Calcined Ca-Fe LDH addition to seawater, the salinity decreased to 3.3%, and pH of the solution increased to pH 11.5, and then became almost constant above 2.0 g/L addition of Calcined Ca-Fe LDH. As increasing the mixing ratio of Calcined Ca-Fe LDH to raw mordenite, the salinity decreased to 0.8% (79.2% reduction) while pH of the solution was neutral (about 7.6~8.0). Radish sprouts could be harvested using the seawater treated with a mixture of raw mordenite-type natural zeolite and Calcined Ca-Fe LDH, although those could not be harvested using seawater, the seawater treated with natural zeolite or Calcined Ca-Fe LDH.

Keywords: Natural zeolite, Calcined Ca-Fe LDH, Desalination, Agricultural water

1. INTRODUCTION

The total amount of water resources on the earth is about 1.3 billion km³, but seawater is about 97.5% and freshwater is only about 2.5%, and the freshwater available to mankind is only about 0.01% of total water resources. About 70% of freshwater is used for the agricultural uses. In recent years, water demand has increased due to the increase in the world population, and the development of technology to obtain agricultural water from high salinity water, such as seawater, is considered in order to secure food. Multi-stage flash evaporation and reverse osmosis membrane are typical seawater desalination techniques and are often used for the securing of drinking and industrial water, which required high purity. Therefore, it is a high cost for the production of agricultural water and a simple new desalination method is desired.

In this study, we try to develop a new desalting material that reduces the high concentrations of sodium chloride in seawater causing salt damage to the level at which crops can grow [1][2]. In previous studies, we can prepare the cultivation solution, which can be used for radish sprout growth, from seawater by two-stage treatment of seawater with calcined hydrotalcite and mordenite natural zeolite [1]. Additionally, radish sprouts can be grown in the solution prepared from seawater treated by Ca-A

synthetic zeolite [3], and in calcined-layered double hydroxide (LDH), Ca-Fe LDH calcined at 500°C has high desalting ability [4].

In this study, a simple desalting material with high desalting ability was prepared using two Ca-type clay minerals, Ca type natural zeolite and calcined Ca-Fe LDH. We evaluated the desalting capacity of the new desalting material for two Ca-type clay minerals.

2. EXPERIMENTAL

Two types natural zeolites, clinoptilolite type natural zeolite obtained from Koriyama, Kagoshima prefecture, Japan, and mordenite type natural zeolite obtained from Iizaka, Fukushima prefecture, Japan, were used as natural zeolite sample in this study[5][6][7].

The following operations were performed to prepare Ca type natural zeolite. 5 g of natural zeolite was added to 100 mL of 5 mol/L CaCl₂ solution. Stirring (1000 rpm) was carried out at 80 °C for 1 hour and then filtered. The filtered solid was added into the fresh CaCl₂ solution and stirring was carried out again. This process was repeated 2 times. After that, the soiled was washed with 1 L of distilled water, dried in a drying oven to obtain Ca-type natural zeolite sample.

Calcined Ca-Fe LDH was prepared as follows. A mixed solution of Ca²⁺ and Fe³⁺ (Ca/Fe = 2) was

prepared from 0.2 M CaCl_2 solution and 0.1 M FeCl_3 solution, and dropped into a 0.3 M NaCl solution at 4 mL/min. Stirring was performed for 6 hours with bubbling nitrogen gas, and the pH of the NaCl solution was maintained at 12.5 by dropwise addition of NaOH during stirring. After stirring, the product was filtered and dried, and the resulting product was calcined at 500°C for 1 hour in electric furnace to obtain calcined Ca-Fe LDH[3][9].

2.1 Desalination Ability

Seawater was collected from the surface layer of Imari bay, Saga prefecture, Japan and filtered. Chemical composition, salinity and pH of seawater are shown in Table 1.

Table 1 Chemical composition, salinity and pH of seawater (mg/L)

	Sea Water
SO_4^{2-}	3137
Cl^-	26137
Na^+	9686
K^+	478
Mg^{2+}	1527
Ca^{2+}	471
Fe^{3+}	0.02
Salinity(%)	3.46
pH	8.0

The desalting ability was evaluated as follows. Raw and Ca-type natural zeolite, calcined Ca-Fe LDH, and the mixtures of natural zeolite and calcined Ca-Fe LDH with various mixing ratios was added to 20 mL of seawater, and shaken for a predetermined time. After shaking, the solution is filtered, and the pH of the filtrate is measured by pH meter (Horiba, F-72), salinity is measured by salinity meter (Mothertool, YK-31SA), the concentrations of Na^+ , K^+ , Mg^{2+} , Ca^{2+} , Cl^- , and SO_4^{2-} in the filtrate, were measured with an ion chromatograph (Tosho, IC-2010) and Fe^{3+} content in the filtrate was determined using an atomic absorption spectrophotometer (Perkin Elmer, AAnalyst 200). The reduction rate of each ion after treatment was calculated using equation (1).

$$R = (C_0 - C) / C_0 \times 100 \quad (1)$$

where R is reduction rate (%), C_0 is each ion concentration (mg/L) in initial solution, and C is each ion concentration (mg/L) in the solution after

desalination of the seawater.

Furthermore, the residue was dried, and the structure was confirmed by a powder X-ray diffraction apparatus (Rigaku, MiniFlex 600).

2.2 Growth Test

Radish sprouts (30 seeds) were used for 10 days growth Test. Seawater solution, seawater treated with mordenite type natural zeolite (10 g/ 20 mL), the seawater treated with Calcined Ca-Fe LDH (0.6 g/ 20mL) and the seawater treated with a mixture of mordenite type natural zeolite (10 g/ 20mL) and Calcined Ca-Fe LDH (8 g/ 20mL) was given by a spray every day, and germinations of radish sprouts were observed[2][9][10].

3. RESULT AND DISCUSSION

3.1 Seawater of Desalination with Zeolites

Fig. 1 shows the salinity and pH of seawater after treatment with natural zeolite. The white plots indicate clinoptilolite use and the black plots indicate mordenite use. For the raw and Ca-type clinoptilolite natural zeolite, when the addition amount increased to 1.0 g/ 20 mL, the salinity decreased to about 3.20% (about 5% reduction), and became constant above 1.0 g/ 20 mL. For the raw and Ca type mordenite natural zeolite, the salinity decreased to about 2.09% (about 38% reduction) when the addition amount increased to 10 g/ 20 mL. It was noted that the pH of the solution after desalination was 7.4 to 8.0 for all samples.

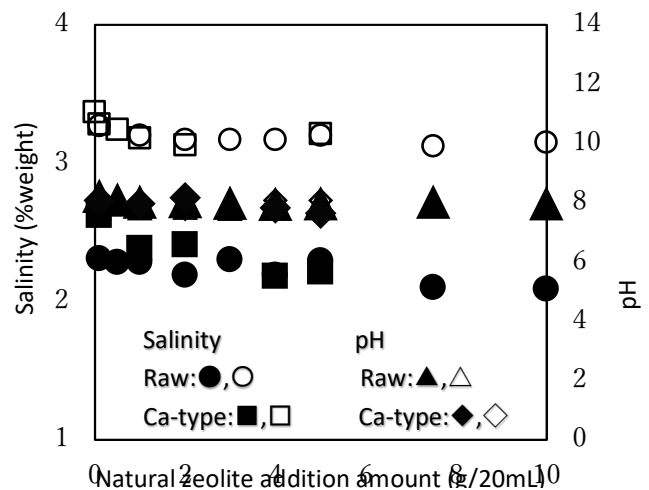


Fig. 1 Salinity and pH of seawater after treatment of natural zeolite

Fig. 2 shows the reduction of each ion in seawater after treatment with clinoptilolite zeolite. Fig. 3

shows the reduction of each ion in seawater after treatment with clinoptilolite zeolite and mordenite zeolite, respectively.

In clinoptilolite zeolite, the contents of Na^+ , Mg^{2+} , Cl^- and SO_4^{2-} in the solution treated with raw and Ca type natural zeolite are reduced (about 15~30%) when the addition amount is more than 1.0 g/ 20 mL. K^+ reduction is about 60~75% at more than 0.5 g/ 20 mL. In mordenite zeolite, the reduction of Na^+ and K^+ in the solution after zeolite treatment is about 65% when the addition amount is 10 g/ 20 mL, Mg^{2+} reduction was about 17~26% at more than 0.5 g/ 20 mL addition, and Cl^- and SO_4^{2-} reduction are about 31~51% at more than 0.1 g/ 20 mL.

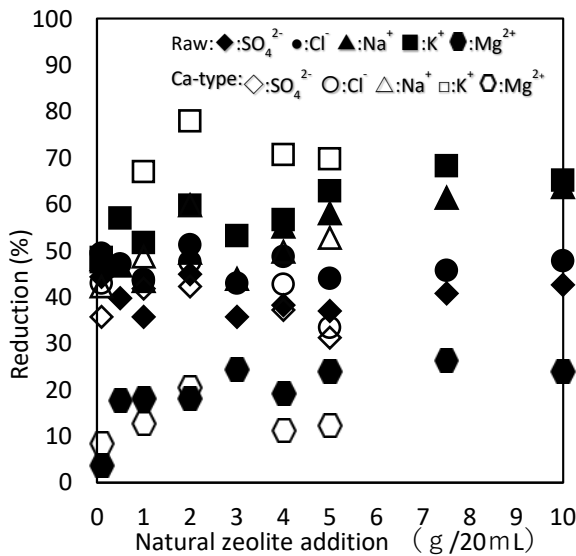


Fig. 2 Reduction of each ion in seawater after treatment of clinoptilolite natural

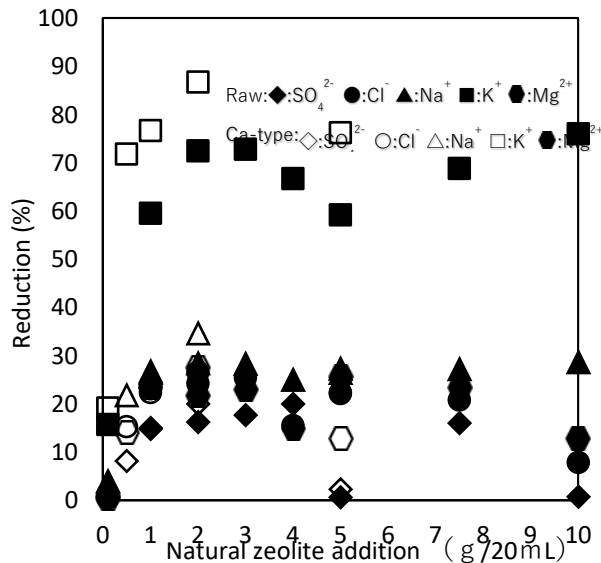


Fig. 3 Reduction of each ion in seawater after treatment of mordenite natural zeolite

From these results, it was found that the desalting ability of Ca-type substituted natural zeolites is the same as that of raw zeolites, and mordenite type natural zeolite has higher desalting ability than clinoptilolite type natural zeolite. The decrease of Na^+ , Mg^{2+} , Cl^- and SO_4^{2-} in seawater after treatment of mordenite-type natural zeolite is more than that of clinoptilolite type natural zeolite.

Fig. 4 shows the XRD patterns of clinoptilolite before and after desalination treatment. Fig. 5 shows the XRD patterns of mordenite before and after desalination treatment. It was confirmed that the peak intensity and pattern after treatment were the same for both raw and Ca-type natural zeolites.

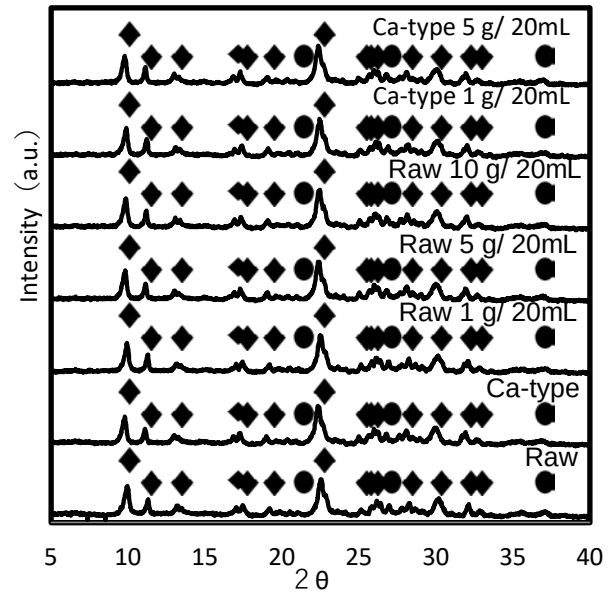


Fig. 4 XRD patterns of clinoptilolite type natural zeolite before and after desalination

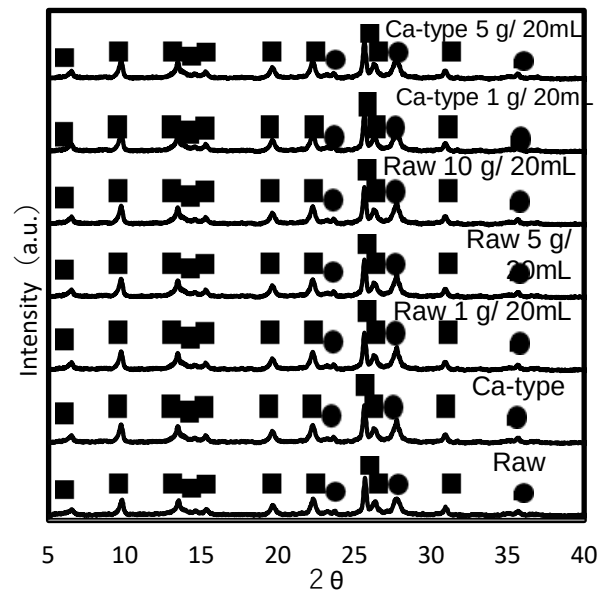


Fig. 5 XRD patterns of mordenite natural zeolite before and after desalination

◆: Clinoptilolite ■: Mordenite ●: Quartz

3.2 Seawater of Desalination with Calcined Ca-Fe LDH

Fig. 6 shows the salinity and pH of seawater after treatment with calcined Ca-Fe LDH. The salinity was reduced until 0.6 g/ 20 mL of calcined Ca-Fe LDH addition, and the salinity of seawater was reduced from about 3.55% to about 3.30% (about 6.5% reduction). The pH after desalination increased to about 11.0 ~ 11.5 when more than 0.4 g/ 20 mL of calcined Ca-Fe LDH was added because OH⁻ is released when calcined Ca-Fe LDH intercalates anions into layers by reconstruction of LDH structure [3].

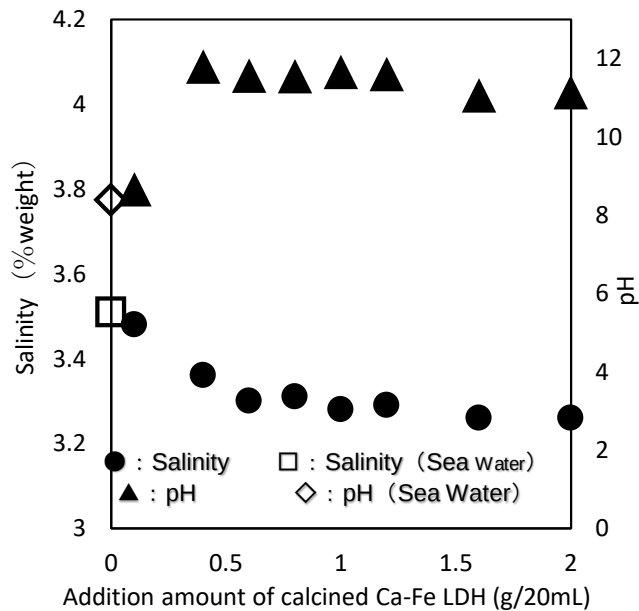


Fig. 6 Salinity and pH of seawater after desalination of calcined Ca-Fe LDH

Fig. 7 shows reduction of each ion concentration in seawater after treatment. The reduction of SO₄²⁻, Cl⁻, Na⁺ and K⁺ increased to 20 ~ 30% up to 0.6 g/ 20 mL of calcined Ca-Fe LDH. The reduction of Mg²⁺ was about 70 ~ 80% regardless of additional amount of calcined Ca-Fe LDH. It is considered that these decrease causes the decrease of salinity. It is noted that after the desalination of seawater, the concentration of Ca²⁺ and Fe³⁺ increased. Because the Ca²⁺ and Fe³⁺ would be released from calcined Ca-Fe LDH into the seawater.

The XRD of Ca-Fe LDH, calcined Ca-Fe LDH after seawater desalination are shown in Fig. 8. The peaks of Ca-Fe LDH were confirmed before calcination. After calcination, it was confirmed that no Ca-Fe LDH peak appeared. The peaks of LDH were confirmed in all the calcined Ca-Fe LDH after desalination of seawater. It is considered that desalination was occurred by the reconstruction of calcined LDH. It is noted that the formation of

calcium carbonate (CaCO₃) were confirmed in calcined Ca-Fe LDH after desalination.

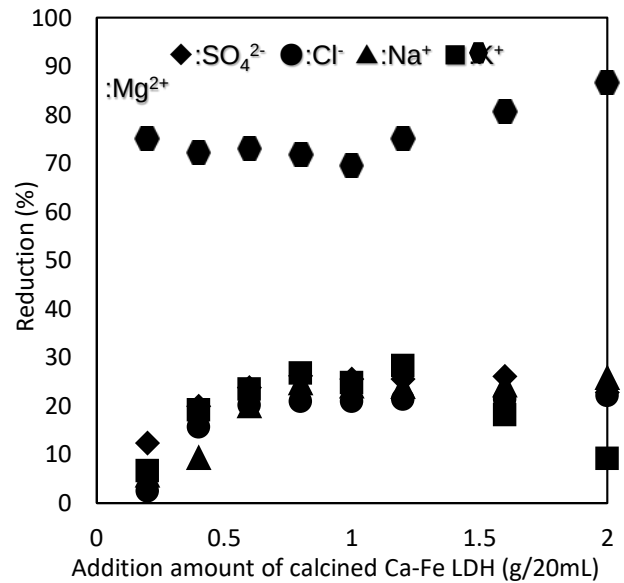


Fig. 7 Reduction of each ion concentration after seawater desalination using calcined Ca-Fe LDH

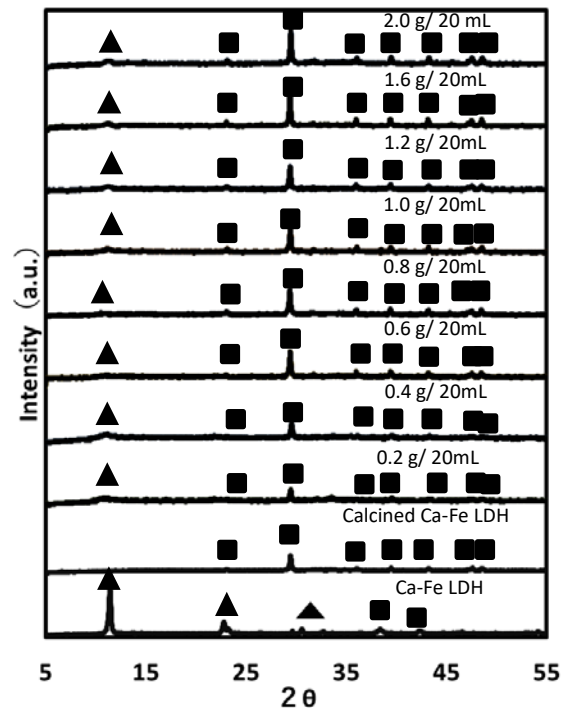


Fig. 8 XRD pattern of Ca-Fe LDH, calcined Ca-Fe LDH and the product after treatment with various Ca-Fe LDH

▲:Ca-Fe LDH ■:CaCO₃

3.3 Seawater of Desalination with a Mixture of Natural Zeolite and Calcined Ca-Fe LDH

In order to determine the optimum ratio for maximizing desalting ability of the mixture of

natural zeolite and calcined Ca-Fe LDH, 0 to 8.0 g of calcined Ca-Fe LDH is mixed with 10 g of raw mordenite zeolite, and the desalting ability was examined. Fig. 9 shows the salinity and pH of seawater obtained by treatment of the mixture of various amount of calcined Ca-Fe LDH and 10 g of raw mordenite type natural zeolite.

The salinity decreased to 0.70% when 8.0 g of calcined Ca-Fe LDH was added to 10 g of raw mordenite zeolite (about 79.2% reduction) and the pH after treatment was about 7.6 to 8.0.

Fig. 10 shows the reduction of each ion and Fig. 11 to 17 shows each ion concentration in seawater after treatment with a mixture of calcined Ca-Fe LDH and mordenite zeolite. It was confirmed that the concentration of Na^+ , K^+ , Mg^{2+} , Cl^- and SO_4^{2-} decreased. When 8.0 g of calcined Ca-Fe LDH is added to 10 g of raw mordenite zeolite, NaCl which causes salt damage is reduced, and 59% of Na^+ and 71% of Cl^- were removal by natural zeolite with cation exchange ability and calcined Ca-Fe LDH with anion removal ability, respectively. The decrease rate of each ion in seawater was SO_4^{2-} : about 87.7%, Mg^{2+} : 96.8%, and K^+ : about 64.0%. Ca^{2+} and Fe^{3+} increased with increase of the amount of calcined Ca-Fe LDH. It is considered that the increase in contents of Ca^{2+} and Fe^{3+} is released into seawater from mordenite zeolite and calcined Ca-Fe LDH.

From these result, it is considered that when the mixture of two clay minerals is used, the salinity decreases to the level that can be used for agriculture because more than 80% of SO_4^{2-} , Cl^- , Na^+ and Mg^{2+} decrease.

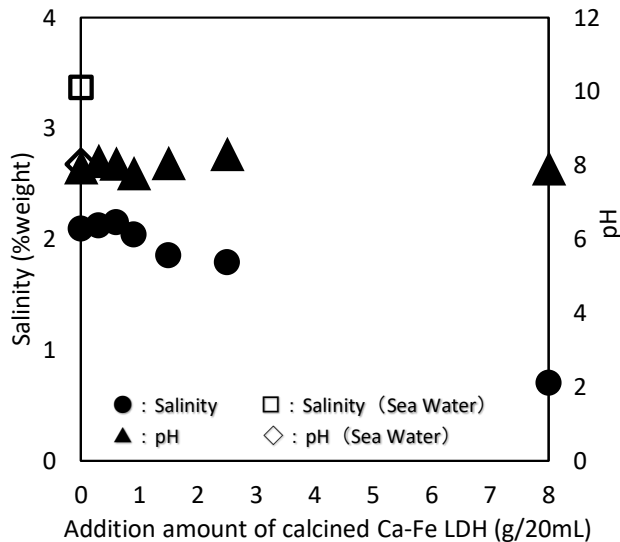


Fig. 9 Salinity and pH of seawater after treatment with mixtures of mordenite natural zeolite and calcined Ca-Fe LDH

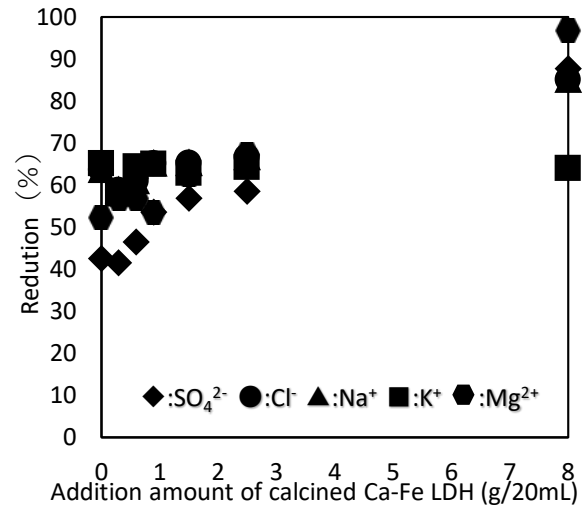


Fig. 10 Each ion reduction of seawater after treatment with a mixture of mordenite type natural zeolite and calcined Ca-Fe LDH

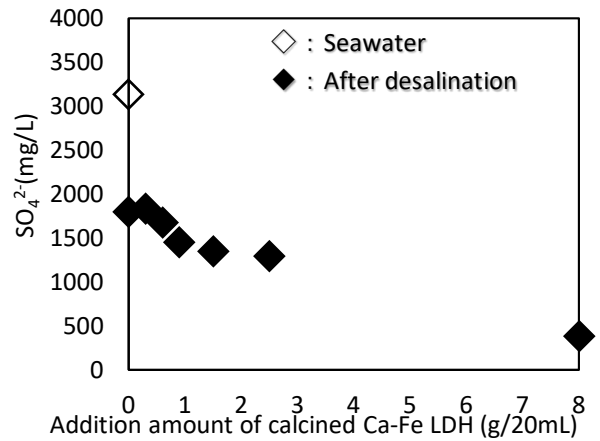


Fig. 11 SO_4^{2-} concentration of seawater after treatment with the mixture 10 g of mordenite type nature zeolite and various amounts of calcined Ca-Fe LDH

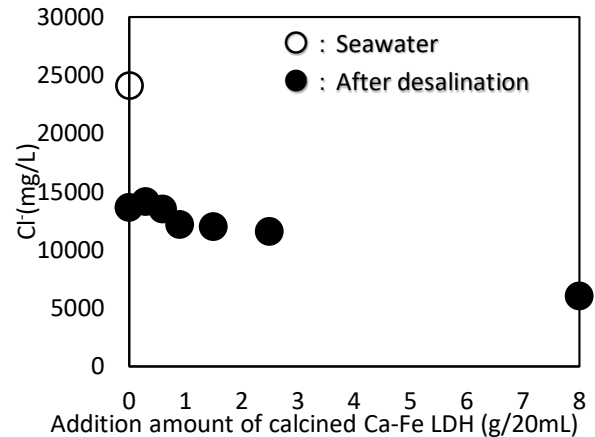


Fig.12 Cl^- concentration of seawater after treatment with the mixture 10 g of mordenite type nature zeolite and various amounts of calcined Ca-Fe LDH

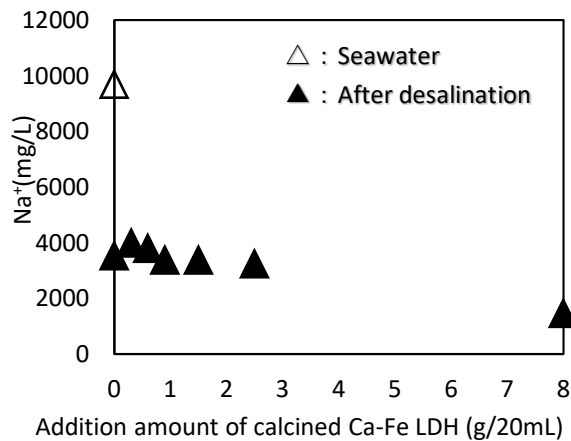


Fig.13 Na⁺ concentration of seawater after treatment with the mixture 10 g of mordenite type nature zeolite and various amounts of calcined Ca-Fe LDH

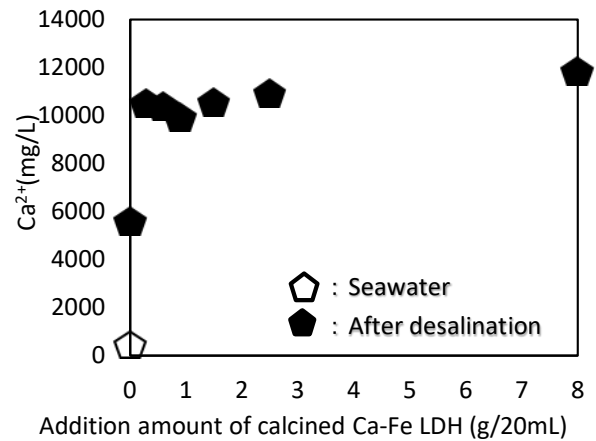


Fig.16 Ca²⁺ concentration of seawater after treatment with the mixture 10 g of mordenite type nature zeolite and various amounts of calcined Ca-Fe LDH

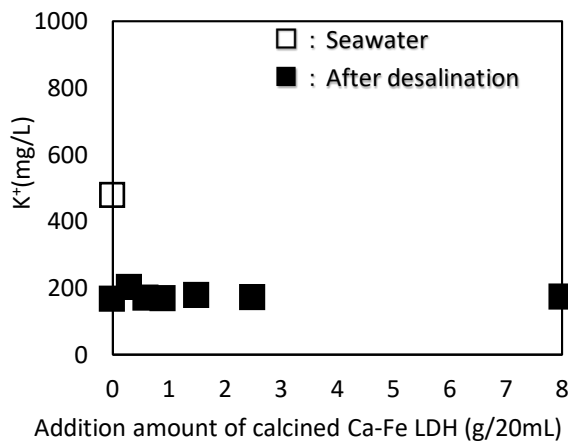


Fig.14 K⁺ concentration of seawater after treatment with the mixture 10 g of mordenite type nature zeolite and various amounts of calcined Ca-Fe LDH

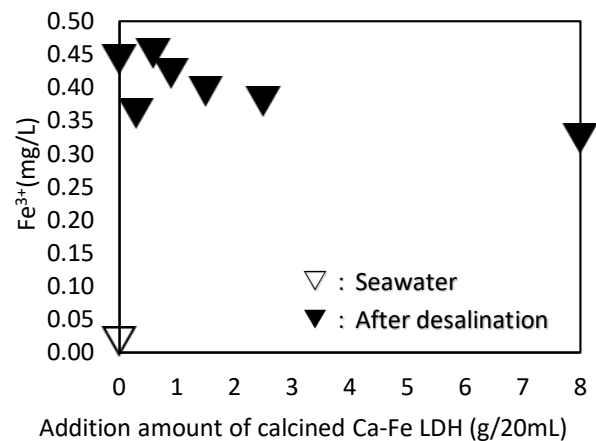


Fig.17 Fe³⁺ concentration of seawater after treatment with the mixture 10 g of mordenite type nature zeolite and various amounts of calcined Ca-Fe LDH

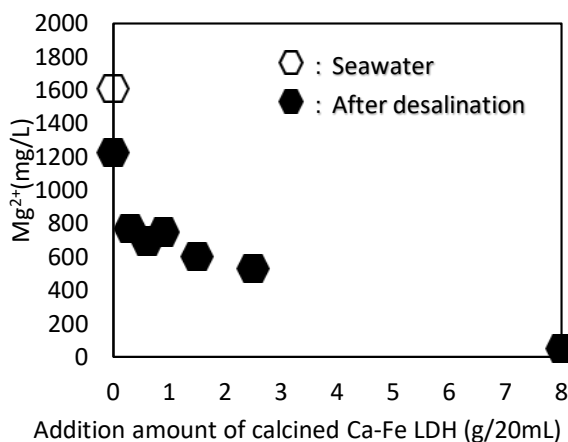


Fig.15 Mg²⁺ concentration of seawater after treatment with the mixture 10 g of mordenite type nature zeolite and various amounts of calcined Ca-Fe LDH

3.4 Cultivation of Radish Sprouts

Table 2 shows the concentration of each ion of (a)seawater, and the seawater treated with (b) raw mordenite zeolite (10 g/20 mL), (c) calcined Ca-Fe LDH (0.6 g), and (d) the mixture of raw mordenite zeolite (10 g) and calcined Ca-Fe LDH (8.0 g). When desalting seawater with natural zeolite, calcined Ca-Fe LDH, and a mixture of natural zeolite and calcined Ca-Fe LDH, the concentrations of Na⁺, K⁺, Mg²⁺, Cl⁻ and SO₄²⁻ decreased, and Ca²⁺ and Fe³⁺ increased.

The germination of radish sprouts was confirmed using seawater treated with a mixture of mordenite type natural zeolite and Calcined Ca-Fe LDH, while they can't germinate using seawater, the seawater treated with natural zeolite and that with Calcined Ca-Fe LDH (Fig. 18).

Table. 2 Each ion concentration of seawater and seawater after addition of desalination material (mg/L)

Sample	(a)	(b)	(c)	(d)
SO ₄ ²⁻	3137	1800	2391	386
Cl ⁻	26137	13646	20859	5997
Na ⁺	9686	3524	7758	1446
K ⁺	478	167	366	172
Mg ²⁺	1527	1225	431	51
Ca ²⁺	471	5644	2202	11860
Fe ³⁺	0.02	0.44	0.17	0.39
Salinity(%)	3.46	2.09	3.29	0.70
pH	8.0	7.83	11.6	7.80



Fig. 18 Observation of radish sprouts after 10 day growth using (a) seawater, and the seawater treated with (b) raw mordenite zeolite (10 g/20 mL), (c) calcined Ca-Fe LDH (0.6 g), and (d) the mixture of raw mordenite zeolite (10 g) and Calcined Ca-Fe LDH (8.0 g)

4. CONCLUSION

For the development of desalination material to obtain agriculturally usable freshwater from seawater for stable supply of water resources, two Ca types clay minerals, Ca type natural zeolite and calcined Ca-Fe LDH, were used for desalting from seawater.

When adding 10 g of mordenite zeolite, the salinity decreased to about 2.09% (about 38% reduction), and mordenite indicates higher desalting ability than the clinoptilolite zeolite. Reduction of the salinity using Calcined Ca-Fe LDH was about 6.5%, and pH rises to about 11-11.5 from about 8.0.

Seawater were treated with the mixture of raw

mordenite zeolite (10 g) and Calcined Ca-Fe LDH. With increasing the Calcined Ca-Fe LDH addition, the salinity decreased to 0.70% below the available salinity for agriculture (about 1.0%) and pH is neutral. When using desalting of seawater treated with a mixture of mordenite zeolite and Calcined Ca-Fe LDH, the germination of radish sprouts was confirmed.

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