Desalination Properties of A Natural Zeolite and Calcined Hydrotalcite Mixture in Seawater

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Abstract—We attempted to prepare a desalination agent from natural zeolite and calcined hydrotalcite to reduce the salinity of seawater. Ion-exchanged natural zeolites, NH_4^+-, K^+-, Mg^{2+} and Ca^{2+}-zeolite, were prepared to remove Na^+ in a solution of seawater treated with calcined hydrotalcite (CHT), and the desalination property for the mixture of ion-exchanged natural zeolite and CHT in seawater was examined, in comparison with typical synthetic zeolites, zeolite-4A and zeolite-13X. A natural Japanese mordenite-type zeolite (Iizaka mine, Fukushima prefecture) was used in this study. The behaviors of Na^+ removal in solution treated with CHT (CHT-solution) using ion-exchanged zeolites is quite different from that for zeolites in seawater. Regardless of zeolite type, NH_4^+-zeolite can remove higher Na^+ content from the CHT-solution, and decrease the pH of the solution. Na^+ removal using natural zeolite is lower than that using synthetic zeolites. The mixture of NH_4^+-zeolite and CHT at the mixed weight ratio of 1:1 has better desalination properties than others because of the ion exchange with Na^+ and K^+ in aqueous solution by NH_4^+-zeolite and the removal of anions and Mg^{2+} and Ca^{2+} by CHT. The mixture of natural zeolite and CHT possesses slightly lower desalination properties than the mixture of synthetic zeolites and CHT.

Index Terms—Desalination, salinity, natural zeolite, calcined hydrotalcite.

I. INTRODUCTION

Production of a stable supply of food is essential to sustaining life. Securing agricultural water is one of the most important factors in food production. Recent environmental problems (e.g. soil desertification) are major contributors to the decline in water resources for crops, and an increasing number of regions are encountering difficulty in achieving a stable supply of food. During the twentieth century, the global human population increased fourfold, but the withdrawal of water from natural freshwater resources increased eightfold [1].

Seawater desalination is one of the important technologies for water utilization. Desalination technologies such as the multi stage flash (MSF) method and the reverse osmosis (RO) method are well known worldwide [2], [3], but these technologies are expensive for agricultural use. There are many rural areas with only saline water and saline soil all over the world. In addition, large areas of cultivated land in northeast Japan were damaged by tsunami, and became saline soil not suitable for agricultural use. Therefore, a simple and inexpensive technique is desirable for agricultural use to decrease the salinity of saline water or soil.

In earlier studies, a simple method to reduce NaCl concentration in seawater using natural zeolite treatment combining with calcined hydrotalcite (CHT) treatment was attempted, and radish sprouts were successfully grown in the resulting solution [4]-[6].

Hydrotalcite is a layered double hydroxide composed of a brucite-like positively charged layer due to the partial substitution of Mg^{2+} and Al^{3+}, which is compensated for by negatively charged interlayers containing anions and water [7]-[9], and can be synthesized from materials such as dolomite [10], aluminum dross [11], bittern [12]. Hydrotalcite calcined at 500–800 °C is transformed into Mg-Al oxide, which can adsorb anions from aqueous solutions through the reconstruction of their original structure [13]. Anion contaminants adsorbed from water solution or suspension by CHT have been reported and shown to have high removal capacity for acids [14]-[16], heavy metal ions [17], [18], pesticides [19]-[23], dyes [24]-[26], halogens [27], [28], phosphates [29]-[32], surfactants [33] and thiocyanate [34], and there are some reports for desalination treatments of seawater using CHT to reduce anions in seawater [35], [36].

Natural zeolite occurs in natural deposits, is generally associated with grassy volcanic rock, and is available in large quantities at low cost [37]. Based on their high ion-exchange capacity, absorption characteristics, water retention and low cost, natural zeolites have been used in agronomy, horticulture and industry [38]. There are some reports of Na^+ reduction in soil [39], [40], compost [41], or co-produced water from natural gas production [42], [43], using natural zeolite. Natural zeolite contains exchangeable cations such as Mg^{2+}, Ca^{2+}, K^+ and Na^+. When seawater is treated with natural zeolite, the Na^+ in seawater is exchanged with exchangeable cations in zeolite, and Na^+ can be removed from seawater and supply Mg^{2+}, Ca^{2+} and K^+ to the solution [44]. Therefore, natural zeolite has potential for use in reducing NaCl in saline water at low cost for agricultural use. In addition, Japan is volcanic country with abundant natural zeolite deposits, such as clinoptilolite, and mordenite, and development of natural zeolite utilization is an important issue for effective utilization of national resources [45].

In this study, we attempted to prepare the desalination agent by mixing natural zeolite and CHT. The two-step desalination process of seawater using natural zeolite following the treatment of CHT can produce the solution for using plant growth. Little information is available, however, on the one-step desalination process using the mixture of natural zeolite and CHT for the removal of NaCl from

seawater. The mixture's ability to remove Na^+ from seawater and the solution after treatment of seawater with CHT using the prepared ion-exchanged natural zeolite was examined, and the desalination properties of the mixture of natural zeolite and CHT were investigated and compared with those of synthetic zeolites to clarify its potential for application in the reduction of salinity in saline water or soil in cultivated lands.

II. EXPERIMENTAL

A. Samples

Three types of zeolite, natural zeolite, zeolite-4A and zeolite-13X, were used in this study. Natural zeolite (Nitto) is mordenite-type zeolite obtained from the deposit of Iizaka in Fukushima prefecture, Japan, and zeolite-4A (Molecular Sieves 4A) and zeolite-13X (Molecular Sieves 13X) were purchased from Wako chemical Co. Ltd. Zeolite samples were grounded by a mill, particles smaller than 500 μm were sorted, and heated at 60 ℃ overnight.

Commercial HT, KW-1000 (Kyowa Kagaku Kogyo Company Limited, Japan) was calcined at 500 ℃ for 3 h to use as calcined hydrotalcite (CHT) in this study.

Seawater was collected from the surface layer in Imari Bay, Saga Prefecture, Japan. The solution treated with CHT (CHT-solution) was prepared as follows. 100 grams of CHT was added to 1 L of seawater, and the slurry stirred for 18 h with a magnetic stirrer. After stirring, the solution was separated by filtration to obtain CHT-solution. The chemical compositions of main ions in seawater and CHT solution, and pH of seawater and CHT-solution are shown in Table I. Both seawater and CHT-solution contain high concentrations of Na^+ (10,400 mg/L and 11,693 mg/L) and K^+ (360 mg/L and 390 mg/L). While the contents of Mg^{2+} and Ca^{2+} in seawater are 1270 mg/L and 380 mg/L, respectively, those in CHT-solution are zero. The concentrations of Cl^- and SO_4^{2-} in CHT-solution (10,400 mg/L and 940 mg/L) are half of those in seawater (20,100 mg/L and 1880 mg/L). The pH of seawater is neutral (7.5), while that of CHT-solution is alkaline (13.6).

TABLE I: CHEMICAL COMPOSITIONS AND PHS OF SEAWATER AND CHT-TREATED SOLUTION

	Seawater	CHT-solution
Content (mg/L)		
Na^+	10400	11693
K^+	360	390
NH_4^+	0	0
Mg^{2+}	1270	0
Ca^{2+}	380	0
Cl^-	20100	10400
SO_4^{2-}	1880	940
pH	7.5	13.6

B. Ion Exchange of Zeolite Samples

For Na^+ removal, four different ion-exchanged zeolites, NH_4^+-, K^+-, Mg^{2+}- and Ca^{2+}-zeolite, were prepared using 1 M NH_4Cl, 1 M KCl, 0.5 M $MgCl_2$ and 0.5 M $CaCl_2$, respectively. One gram of zeolite sample was added into 40 mL of each

solution in 50 mL of centrifuge tube, and shaken with a reciprocal shaker for 1 h. After shaking, the tube was centrifuged at 3300 rpm for 10 min, and the supernatant was removed by decantation. Then, 40 mL of the fresh solution was put into the tube, and shaken again. This procedure was repeated 6 times, then the obtained solid was washed twice with 40 mL of 80 % EtOH, and dried at 60 ℃ for one day to obtain NH_4^+-, K^+-, Mg^{2+}- and Ca^{2+}-zeolite.

The amounts of exchangeable cations in each zeolite sample were examined as follows. 1 M KCl solution was used to extract NH_4^+ from NH_4^+-zeolite, and 1 M NH_4Cl solution was used to extract K^+, Mg^{2+} and Ca^{2+} from K^+-, Mg^{2+}- and Ca^{2+}-zeolites, respectively. Ion-exchanged zeolite (0.1 g) was added into 10 mL of the solution in a 50-mL tube, and shaken for 1 h to extract exchangeable cations in the zeolite sample. After shaking, the tube was centrifuged at 3300 rpm for 10 min, and the supernatant was collected by decantation. Then, 10 mL of the fresh solution put into the tube, and shaken again. This procedure was repeated 5 times, and then the concentration of NH_4^+ in the collected solution was measured using the timor blue method, and those of K^+, Mg^{2+} and Ca^{2+} were analyzed using inductively coupled plasma method (ICP) (ICPS-7500, Shimadzu).

C. Na^+ Removal of Ion-Exchanged Zeolites

Na^+ removal by ion-exchanged zeolites was examined. Ion-exchanged zeolite (0.3 g) was added into 3 mL of seawater or CHT-solution, and shaken for 2 h. After shaking, the tube was centrifuged at 3300 rpm for 10 min, and pH of the supernatant was measured with a pH meter (MA-130; Mettler, Toledo) and the concentration of Na^+ in the supernatant was determined using ICP.

D. Desalination of Seawater

The mixture of ion-exchanged zeolite and CHT was prepared to examine the seawater desalination properties. NH_4^+-zeolite (0–2 g) and CHT (0–2 g) were mixed to prepare the mixture with a total weight of 2 g. The mixture was then added into 10 mL of seawater in the tube, and shaken for 6 h. After shaking, the tube was centrifuged, and then pH and salinity of the supernatant were measured with a pH meter and salt concentration meter (YK–31SA, Lutron), respectively, and the concentrations of Na^+, K^+, NH_4^+, Mg^{2+}, Ca^{2+}, Cl^- and SO_4^{2-} in the supernatant were determined using ion chromatography (IC-2010, Tosoh).

III. RESULTS AND DISCUSSION

Fig. 1 shows the amounts of exchangeable cations in zeolites after ion-exchange treatment. Except for Mg^{2+}, regardless of exchangeable cation species, the amounts of exchangeable cations for natural zeolite, zeolite-4A and zeolite-13X are 150–200 cmol/kg, 350–450 cmol/kg and 300–400 cmol/kg, respectively, which means that almost every exchangeable site in these zeolites can be exchanged by NH_4^+, K^+, or Ca^{2+}, and synthetic zeolites, zeolite-4A and zeolite-13X, indicates higher amounts of exchangeable NH_4^+, K^+ and Ca^{2+} than in natural zeolite. Mg^{2+} can be exchanged in zeolite-13X, while it cannot be exchanged sufficiently in natural zeolite and zeolite-4A because of the larger hydration sphere of Mg^{2+} in aqueous solution.
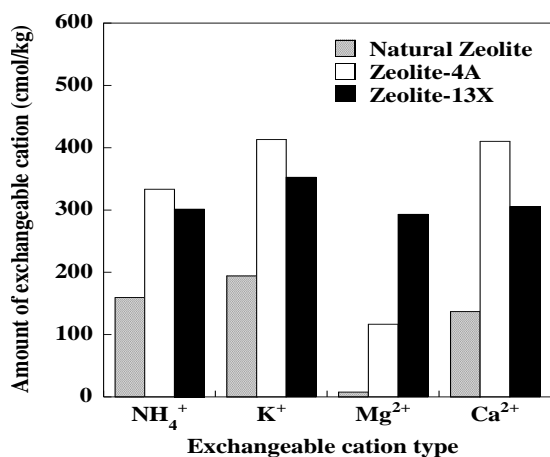
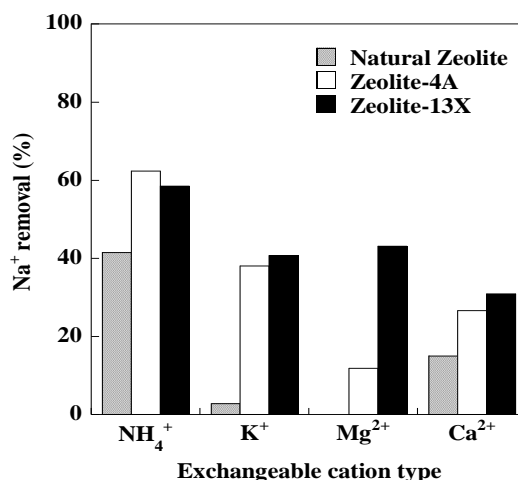Fig. 1. Amounts of exchangeable cations in zeolites after ion-exchange treatment.

Fig. 2. Na^+ removal from (a) seawater and (b) CHT-solution using various ion-exchanged zeolites.

Fig. 2 shows the Na^+ removal from (a) seawater and (b) CHT-solution using various ion-exchanged zeolites. In the case of seawater, natural zeolites with divalent ions, Mg^{2+} and Ca^{2+} indicate greater Na^+ removal than those with monovalent ions, NH_4^+ and K^+, while synthetic zeolites with monovalent ions indicate greater removal than those with divalent ions. The highest removal is approximately 40 % using NH_4^+- or K^+-zeolite 4A. In the case of CHT-solution, regardless of zeolite-types, NH_4^+-exchanged zeolites indicate greater Na^+ removal than others. The Na^+ removal of NH_4^+-natural zeolite is 40 % in CHT-solution, which is 4 times that in seawater, while the removal of NH_4^+-synthetic zeolites is about 60 %, which is 1.5–2.0 times those in seawater. This is likely caused by smaller amounts of Mg^{2+} and Ca^{2+} in CHT-solution.

Fig. 3 shows the pH of the solution after treatment of CHT-solution using various ion-exchanged zeolites. It is noted that pHs of the seawater samples were almost unchanged after zeolite treatment. Regardless of zeolite-type, NH_4^+-exchanged zeolite can reduce the pH of the solution, while others cannot. The pHs of the solutions after treatment with NH_4^+-natural zeolite and NH_4^+-synthetic zeolites are 11 and 10, respectively.

From these results, NH_4^+-exchanged zeolite is a better material for desalination by mixing with CHT, and synthetic zeolites have higher Na^+ removal ability than natural zeolite.
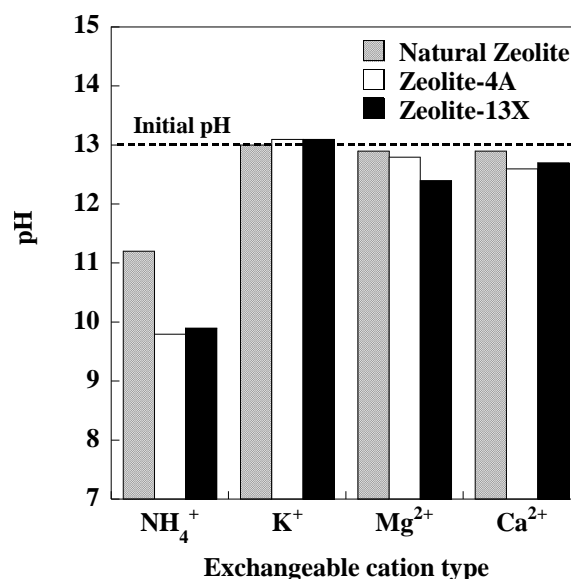
(a)

(b)

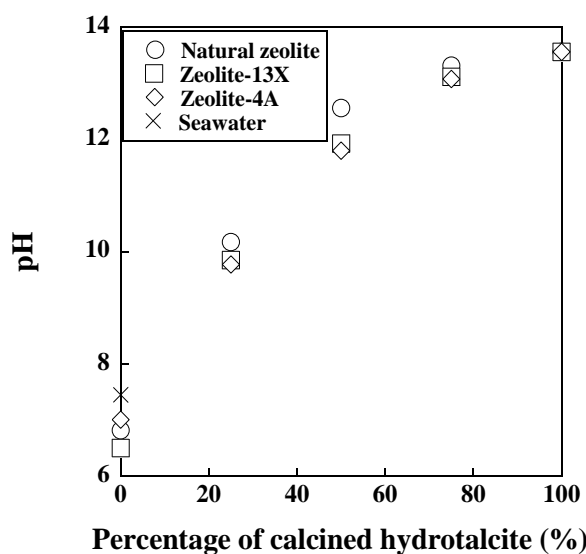Fig. 3. pH of the solution after treatment of seawater using various ion-exchanged zeolites.
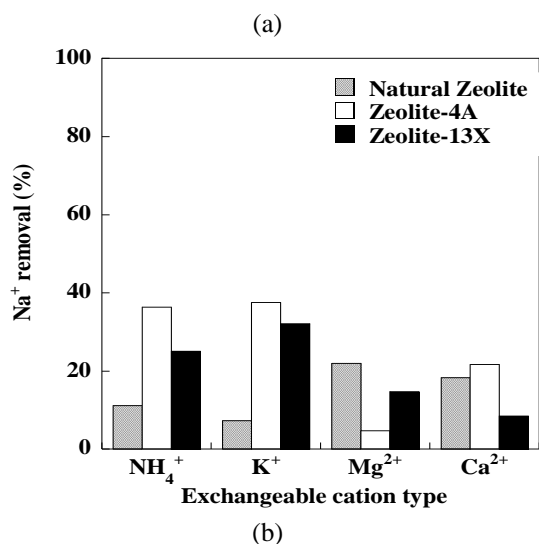

Fig. 4. pH of the solution after treatment of the mixture of NH_4^+-zeolites and CHT.

Fig. 4 shows the pH of the solution after treatment with the mixture of NH_4^+-zeolites and CHT. The pH of seawater is 7.5, and pHs of the solution after zeolite treatment was neutral

(6.5–7.0). The pH of the solution after treatment increases to alkaline with increasing percentage of CHT in the mixture, regardless of zeolite-type because CHT has the characteristics of fixing anions and releasing OH^-. It is noted that the pH of the solution treated with natural zeolite is slightly higher than those with synthetic zeolites.

Fig. 5 shows the salinity of the solution after treatment of the mixture of NH_4^+-zeolites and CHT. The salinity of seawater was 3.15%, and salinities of the solutions treated with zeolites were almost same, which means that the salinity of seawater cannot be decreased by only NH_4^+-zeolites. With the percentage of CHT in the mixture increased to 50 %, the salinity of the solution gradually decreases after treatment, and then steeply increases with CHT above 50% in the mixture, regardless of zeolite type. It is noted that the salinity of the solution treated with natural zeolite is slightly higher than those with synthetic zeolites.
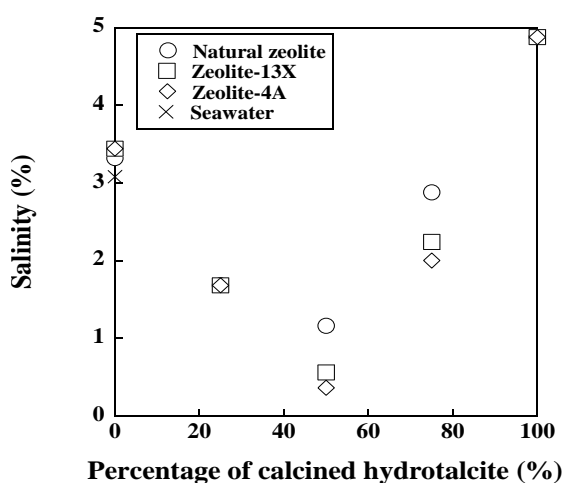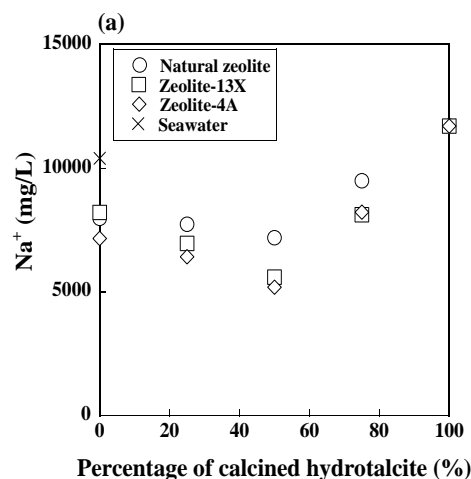

Fig. 5. Salinity of the solution after treatment of the mixture of NH_4^+-zeolites and CHT.

Fig. 6 shows the contents of (a) Na^+, (b) K^+, (c) NH_4^+, (d) Mg^{2+}, (e) Ca^{2+}, (f) Cl^- and (g) SO_4^{2-} in the solution after treatment of the mixture of NH_4^+-zeolites and CHT. In the case of Na^+, the Na^+ content in seawater is 10,400 mg/L, and ranges 7500–8000 mg/L in the solutions after treatment with only zeolites. With the percentage of CHT in the mixture increased to 50%, Na^+ content in the solution gradually decreases after treatment, and then steeply increases above 50 % CHT in the mixture, regardless of zeolite type. It is noted that Na^+ content in the solution treated with natural zeolite is slightly higher than in those with synthetic zeolites (Fig. 6(a)). The behavior of Na^+ content is almost identical to that of salinity, which means that salinity mostly depends on Na^+ content in the solution. In the case of K^+, K^+ content in seawater is 360 mg/L, about 100 mg/L in the solution treated with natural zeolite and zeolite-13X, and is zero solution treated with zeolite-4A. With the percentage of CHT in the mixture increased to 50 %, K^+ content gradually decreased in the solution after treatment with the mixture using natural zeolite or zeolite-13X, while K^+ content was zero in the solution after treatment with the mixture using zeolite-4A, and then steeply increases with CHT above 50 % in the mixture (Fig. 6(b)). The behavior of K^+ content using natural zeolite and zeolite-13X is also almost identical to that of salinity. In the case of NH_4^+, the behavior of NH_4^+ content is quite different from that of other monovalent ions, e.g., Na^+ and K^+. With the percentage of CHT in the mixture increased to 50 %, NH_4^+ content in the solution after treatment is almost constant, and then gradually decreases with CHT above 50 % in the mixture, regardless of zeolite-types. It is noted that NH_4^+ content in the solution treated with natural zeolite is slightly lower than those with synthetic zeolites (Fig. 6(c)). In the case of divalent cations, Mg^{2+} and Ca^{2+}, the contents of Mg^{2+} and Ca^{2+} in seawater are 1270 mg/L and 380 mg/L, respectively. Mg^{2+} content in the solution treated with only natural zeolite and zeolite-4A are almost same as that in seawater, while that with zeolite13X is 900 mg/L because of the large pore size to exchange with Mg^{2+} in aqueous solution. Ca^{2+} content in the solution treated with natural zeolite is almost same as that in seawater, while that in solutions with synthetic zeolites is approximately 50 mg/L. With the percentage of CHT in the mixture increased to 50 %, the contents of Mg^{2+} and Ca^{2+} in the solution after treatment decrease to zero, and are almost constant (zero) with CHT above 50 % in the mixture, regardless of zeolite type. It is noted that Ca^{2+} content in the solution treated with natural zeolite is slightly higher than in those treated with synthetic zeolites (Fig. 6 (d), (e)). The decrease of these divalent cations is likely caused by increasing pH to precipitate Mg^{2+} and Ca^{2+} [46]. In the case of anions, Cl^- and SO_4^{2-}, the contents of Cl^- and SO_4^{2-} in seawater are 20,100 mg/L and 1880 mg/L, respectively, and those in the solution treated with only zeolites are almost the same. For Cl^-, the percentage of CHT in the mixture increased to 50%, Cl^- content in the solution after treatment steeply decreases, and then gradually decreases with CHT in the mixture above 50 %, regardless of zeolite type. For SO_4^{2-}, with the percentage of CHT in the mixture increased to 25 %, SO_4^{2-} content in the solution after treatment steeply decreased, and then was almost constant (about 900 mg/L) with CHT above 25 % in the mixture, regardless of zeolite type. It is noted that the behavior of Cl^- and SO_4^{2-} using all zeolites was almost identical (Fig. 6 (f), (g)).

These results suggest that the desalination properties of the mixture of NH_4^+-zeolite and CHT with the mixed ratio of 1:1 are greater because of the ion exchange of monovalent cations by NH_4^+-zeolite and the removal of anion and divalent cations by CHT. Desalination using natural zeolite is slightly lower than with the use of synthetic zeolites.
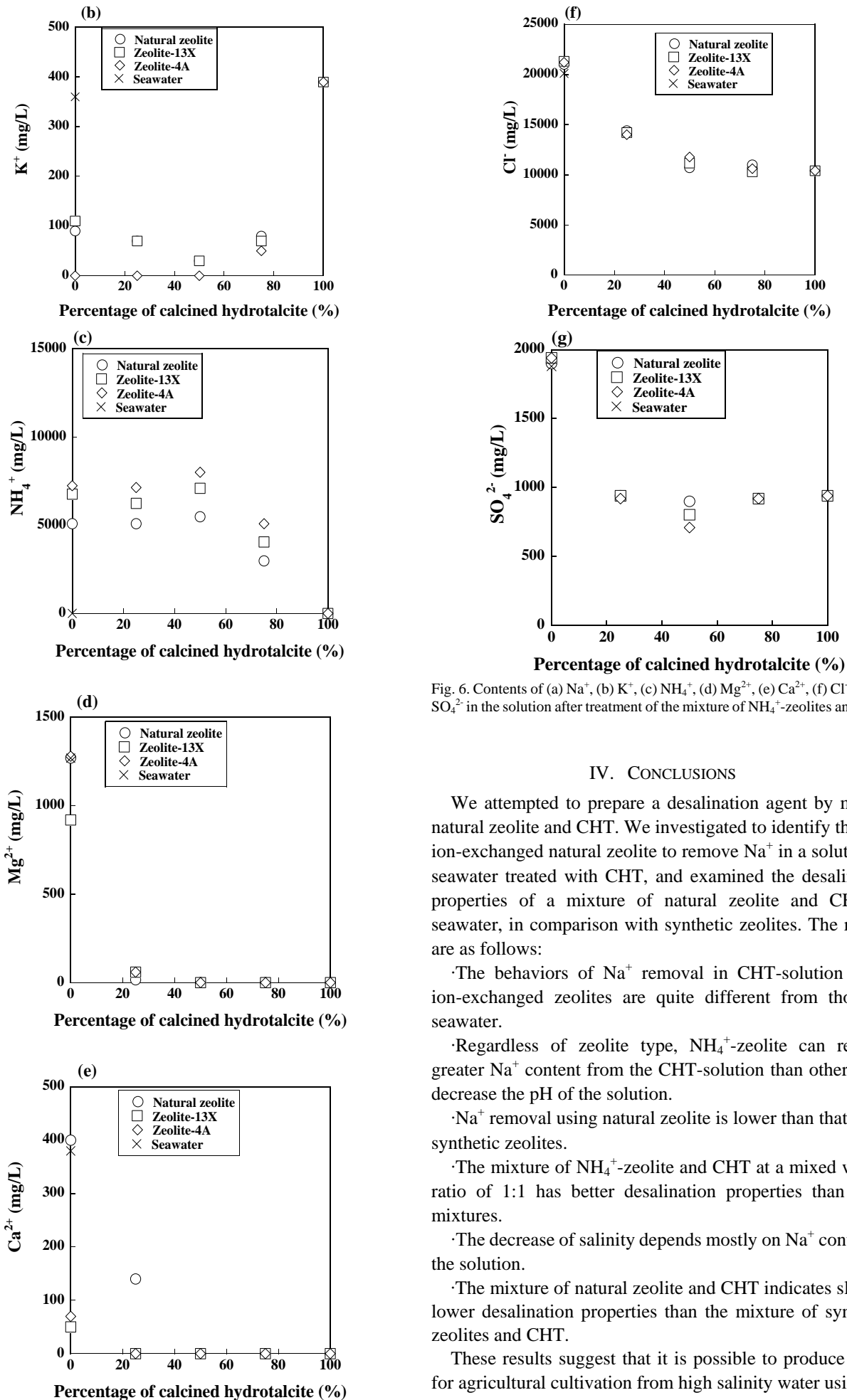

(a)

(b)

(f)

(c)

(g)

Fig. 6. Contents of (a) Na^+, (b) K^+, (c) NH_4^+, (d) Mg^{2+}, (e) Ca^{2+}, (f) Cl^- and (g) SO_4^{2-} in the solution after treatment of the mixture of NH_4^+-zeolites and CHT.

(d)

(e)

IV. CONCLUSIONS

We attempted to prepare a desalination agent by mixing natural zeolite and CHT. We investigated to identify the best ion-exchanged natural zeolite to remove Na^+ in a solution of seawater treated with CHT, and examined the desalination properties of a mixture of natural zeolite and CHT in seawater, in comparison with synthetic zeolites. The results are as follows:

·The behaviors of Na^+ removal in CHT-solution using ion-exchanged zeolites are quite different from those in seawater.

·Regardless of zeolite type, NH_4^+-zeolite can remove greater Na^+ content from the CHT-solution than others, and decrease the pH of the solution.

·Na^+ removal using natural zeolite is lower than that using synthetic zeolites.

·The mixture of NH_4^+-zeolite and CHT at a mixed weight ratio of 1:1 has better desalination properties than other mixtures.

·The decrease of salinity depends mostly on Na^+ content in the solution.

·The mixture of natural zeolite and CHT indicates slightly lower desalination properties than the mixture of synthetic zeolites and CHT.

These results suggest that it is possible to produce water for agricultural cultivation from high salinity water using the

mixture of natural zeolite and CHT.

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