

Ion Exchange Properties of Japanese Natural Zeolites in Seawater

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Ion exchange properties of five different Japanese natural zeolites in seawater were examined. Sodium ions could be reduced by all zeolites, although anions, Cl^- and SO_4^{2-} , in seawater showed barely changes. Natural zeolite desalination treatment mainly depends on the ion exchange between Na^+ , K^+ and Mg^{2+} in seawater and Ca^{2+} in natural zeolite. This study found that mordenite is superior to clinoptilolite for use in Na^+ reduction. Mordenite with high cation exchange capacity containing Ca^{2+} resulted in the highest Na^+ reduction from seawater.

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Introduction

Seawater desalination is an important technology for water utilization. Desalination technologies such as the multi stage flash (MSF) method, reverse osmosis (RO) method and electrodialysis, are well known,¹⁻³ but these technologies have a large footprint and are expensive for agricultural use. There are many rural areas all over the world that only have access to saline water and salted soil. Cultivated lands in northeast Japan have also been damaged by tsunamis, resulting in salted soil that is not suitable for use in agriculture. For agricultural purposes, there is a great need for simple and inexpensive techniques for decreasing the salinity of saline water or salted soil.

Natural zeolites occur in natural deposits, generally associated with grassy volcanic rock, and are available in large quantities at low cost.⁴⁻⁶ Because of their high ion-exchange capacity, absorptivity, water retention and low cost, natural zeolites have been used in agronomy, horticulture and various other industries.⁷⁻¹² In earlier studies, a simple method to reduce NaCl concentration in seawater using natural zeolite treatment combined with calcined hydrotalcite treatment was attempted, and radish sprouts were grown in the resulting solution.¹³⁻¹⁷ Therefore, natural zeolites have the potential to reduce the NaCl in saline water at low cost for agricultural use. Japan is a volcanic country with abundant natural zeolite deposits, such as clinoptilolite and mordenite, and the development of natural zeolite utilization is an important issue for effective utilization of natural resources.⁶ However, there has been little research published on the treatment of saline water with Japanese natural zeolites.

In this study, the desalination properties of five natural zeolites on seawater were examined to clarify the possibility of reducing salt in saline waters or salted soil in cultivated lands.

Experimental

Seawater and samples

Seawater used in this study was collected from the surface of Imari Bay, Saga Prefecture, Japan (Fig. S1 (Supporting Information)). The chemical composition and pH of the seawater are shown in Table 1. The seawater contained high concentrations of Na^+ (453.1 mM) and Cl^- (498 mM), and was pH neutral (8.0).

Five kinds of Japanese natural zeolites; Iizaka-zeolite (IZ), Tenkawachi-zeolite (TZ), Koriyama-zeolite (KZ), Futatsui-zeolite (FZ) and Niki-zeolite (NZ) were used in zeolite treatment. The occurrences and X-ray diffraction patterns of these natural zeolites are shown in Figs. S1 and S2 (Supporting Information), respectively. IZ and TZ were mordenite-type zeolites, and KZ, FZ and NZ were clinoptilolite-type zeolites. These natural zeolites were typical of natural zeolite structures found all over the world.

Natural zeolite treatment

Natural zeolite samples used in this study were crushed, ground, sieved under 500 μm , and dried at 80°C for one day before use in experiments. A 20-g amount of natural zeolite was added to 200 mL of seawater, and stirred for 2 h with a magnetic stirrer. After stirring, the slurry was filtered, and fresh natural zeolite was added to the filtrate. This procedure was repeated 10 times, and the pH of the filtrate and Na^+ , K^+ , Mg^{2+} , Ca^{2+} , Cl^- and SO_4^{2-} concentrations in the filtrate were determined after each zeolite treatment. This experiment was performed in triplicate to confirm reproducibility.

Table 1 Chemical compositions and pH of seawater

Chemical composition/mM						pH
Na^+	K^+	Mg^{2+}	Ca^{2+}	Cl^-	SO_4^{2-}	
453.1	9.6	51.9	9.4	498.0	27.0	8.0

Table 2 Exchangeable cations and cation exchange capacity of natural zeolites

Sample	Type of crystal ^a	Exchangeable cation/mmol g ⁻¹				CEC/ mmol g ⁻¹
		Na ⁺	K ⁺	Mg ²⁺	Ca ²⁺	
IZ	Mor.	0.56	0.21	0.03	0.44	1.67
TZ	Mor.	0.70	0.11	0.06	0.24	1.27
KZ	Cli.	0.58	0.28	0.02	0.40	1.51
NZ	Cli.	0.88	0.20	0.02	0.23	1.27
FZ	Cli.	0.84	0.71	0.02	0.07	1.67

a. Mor., Mordenite-type zeolite; Cli., clinoptilolite-type zeolite.

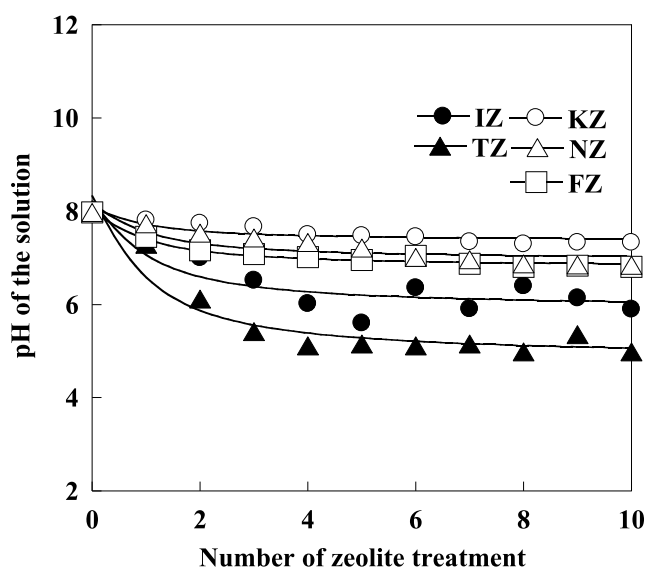


Fig. 1 pH of the solution treated with various natural zeolites as a function of the number of natural zeolite treatments.

Characterization

The pH of the filtrate was measured with a pH meter (MA-130, Mettler-Toledo), and the concentrations of Na⁺, K⁺, Mg²⁺, Ca²⁺, Cl⁻ and SO₄²⁻ in the solution were determined using ion chromatography (DX-120, Japan Dionex). Exchangeable cations and cation exchange capacities of natural zeolites were measured by the modified Schorrenberg's method.⁶

Results and Discussion

Table 2 shows the exchangeable cations and cation exchange capacity (CEC) of natural zeolites. The CEC and composition of exchangeable cations of IZ and KZ were very similar. In addition, the CEC and composition of exchangeable cations of TZ and NZ were also similar. The CEC of IZ and KZ were higher than those of TZ and NZ. FZ had a high CEC, which was almost the same as IZ and KZ, but had a high content of exchangeable K⁺, which differed from IZ and KZ.

Figure 1 shows the pH of the solution as a function of the number of zeolite treatments. The pH curves of the five samples were similar throughout treatment. The pH of the solution initially decreased for the first four treatments, and then remained constant after this point. After 10 treatment repetitions, the pH of all solutions were in the range of 5–8, which is a feasible standard for agricultural use. Using mordenite-type

samples, the solution pH decreased more noticeably than when using clinoptilolite-type samples.

Figure 2 shows the change in concentration of (a) Na⁺, (b) K⁺, (c) Mg²⁺, (d) Ca²⁺, (e) Cl⁻ and (f) SO₄²⁻ in the solution as a function of the number of natural zeolite treatments. Na⁺ concentration in seawater could be reduced by natural zeolite treatment, while the concentration of Cl⁻ and SO₄²⁻ ions barely changed, because zeolite is a cation exchanger. The solution treated with IZ and KZ indicate higher Na⁺ reduction than those with TZ and NZ, because IZ and KZ have a higher CEC than TZ and NZ. IZ (mordenite-type zeolite) resulted in higher reduction of Na⁺ ions than KZ (clinoptilolite-type zeolite). TZ (mordenite-type zeolite) also resulted in greater reduction of Na⁺ ions than NZ (clinoptilolite-type zeolite). These reductions correlated closely with an increase in Ca²⁺ ions. The clinoptilolite-type zeolite indicated a higher reduction of K⁺ and Mg²⁺ than mordenite-type zeolite. From these results, it is considered that the reduction of Na⁺ mainly occurs by ion exchange between Na⁺, K⁺ and Mg²⁺ in seawater and exchangeable Ca²⁺ in zeolite, with mordenite-type zeolites having higher selectivity of Na⁺ than clinoptilolite-type zeolites. FZ has a high CEC, but the reduction of Na⁺ is the worst among the five zeolite samples used. It is reported that the clinoptilolite has four cationic sites (M1, M2, M3 and M4) where ion exchange occurs, and M1, M2, M3 and M4 sites preferably occupy Na⁺, K⁺, Ca²⁺ and Mg²⁺, respectively.^{18,19} The preferential order of cation selectivity for clinoptilolites is K⁺ > NH₄⁺ > Na⁺ >> Ca²⁺ > Mg²⁺.²⁰ It is considered that the exchangeable sites to reduce Na⁺ (M1, M2 and M3) in FZ were occupied by K⁺ before zeolite treatment, hence the amount of exchangeable sites available to reduce Na⁺ in seawater was limited, although the CEC (number of exchangeable sites) of FZ is high. Additionally, for Mg²⁺ reduction, ion exchange between Mg²⁺ in seawater and K⁺ at the exchangeable M4 site of the clinoptilolite competes with Ca²⁺ at the exchangeable M4 site. These results suggested that the best natural zeolite for the reduction of Na⁺ in seawater is IZ, which is a mordenite-type zeolite with high CEC and exchangeable cation sites mainly occupied by Ca²⁺ available to exchange with Na⁺ in seawater. It is noted that the Ca²⁺ released into seawater was not equal to the total reduction of Na²⁺, K⁺ and Mg²⁺. It is unclear why there was a difference between the released amount of Ca²⁺ and the total reduced amount of cations in seawater. In this study, only main elements in seawater, Na⁺, K⁺, Mg²⁺, Ca²⁺, Cl⁻ and SO₄²⁻, were determined. However, other elements, such as H⁺, Br⁻, CO₃²⁻ etc., also exist in seawater. It may be considered that subsidiary reactions occur during the ion exchange process using natural zeolite.

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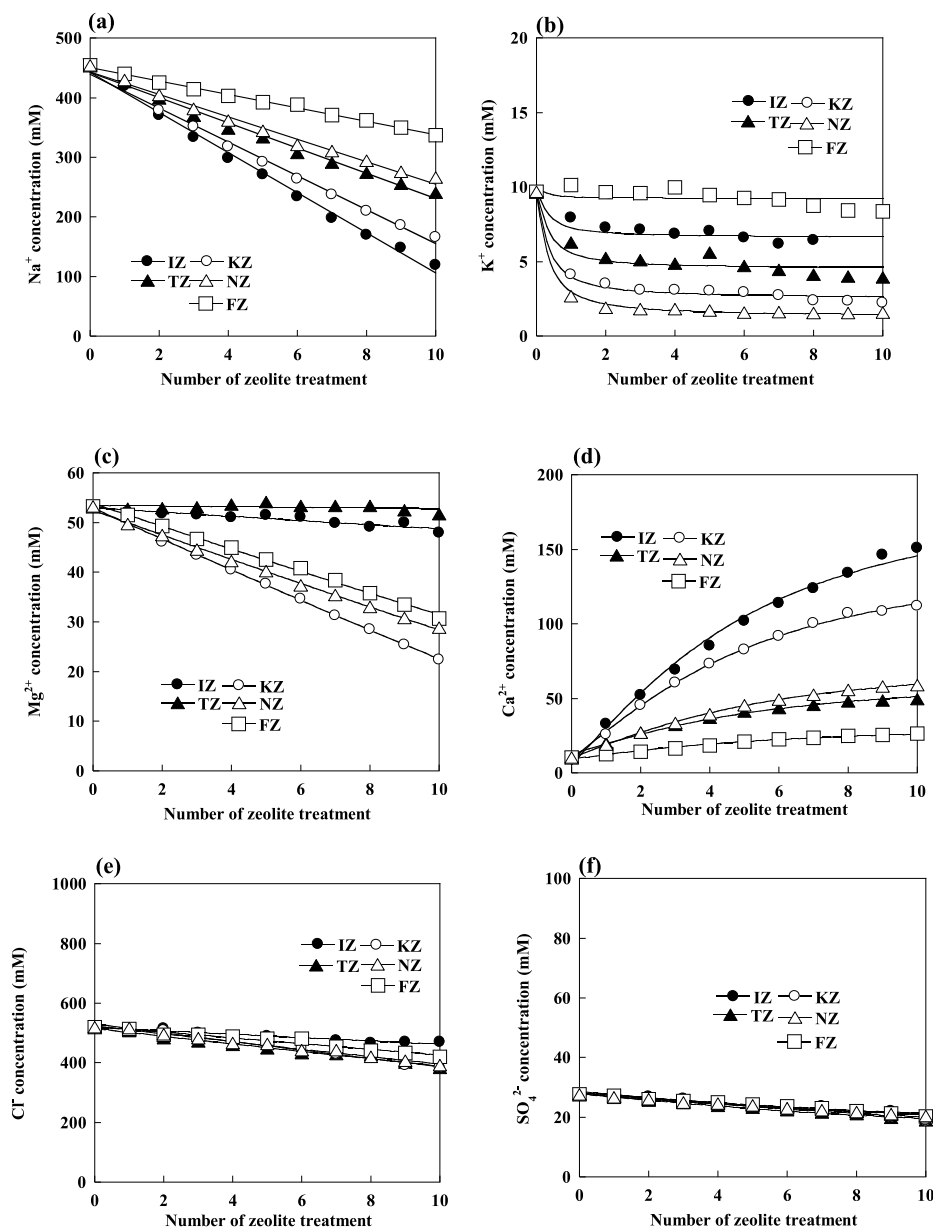


Fig. 2 Concentrations of (a) Na^+ , (b) K^+ , (c) Mg^{2+} , (d) Ca^{2+} , (e) Cl^- and (f) SO_4^{2-} in the solution treated with various natural zeolites as a function of the number of zeolite treatments.

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