

## 研究報告

# Utilization of Akita's Clinoptilolite Zeolite for the Production of Cation Exchangers and Geopolymers

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## Abstract

Natural zeolite, clinoptilolite, produced in Akita prefecture has a large potential for various practical usage. In this paper, we have tried to synthesize cation exchangers and geopolymers from the zeolite using sodium-silicate and sodium hydroxide as activator. We have varied some parameters like alkali concentration, particle size and curing time in order to improve the quality of cation exchanger and geopolymeric product. The  $\text{NH}_4^+$  retention capacity of the clinoptilolite is enhanced either by increasing alkaline metal cations content with chemical modification or by reducing particle size or increasing specific surface with mechanical modification. The geopolymer materials synthesized through mechanochemically treated clinoptilolite using NaOH and sodium silicate solutions showed increasing crushing strength up to around 25 MPa with increasing curing time.

## 1 Introduction

Natural zeolites, which are aluminosilicate minerals and found in volcanogenic sedimentary rocks, possess several important properties including adsorption, cation-exchange, dehydration-rehydration, and catalysis. These natural zeolites have broad range of applications in construction materials, soil improvements for water and nutrient retention, treatment of water and wastewater for removal of heavy metals and nutrients, dietary supplements for farm-raised animals, health care, and other beneficial uses<sup>(1)</sup>.

Clinoptilolite zeolites,  $(\text{Na}_3\text{K}_3)(\text{Al}_6\text{Si}_{30}\text{O}_{72})\cdot 24\text{H}_2\text{O}$ , are one of the naturally existing zeolites. The theoretical cation-exchange capacity (CEC) of Clinoptilolite is about 2.16 meq/g and is able to exchange ammonium-N with sodium and potassium<sup>(1)</sup>. This CEC has been utilized effectively for terrestrial agriculture, where clinoptilolites are first saturated with ammonium-N and then incorporated into crop soils. They act as a slow-release fertilizer, with plants able to extract the sequestered ammonia from the clinoptilolite<sup>(2)-(4)</sup>. Most of the manure-ammonia sequestered in the zeolite is unavailable to nitrifying bacteria because of the small (4-5 angstrom) pore size of the crystal lattice structure<sup>(1)</sup>. Furthermore, clinoptilolites

are also used for animal waste management, replacing clays in the cat litter market and are being used to create odorless, nitrogen-rich compost from farm livestock manures.

Geopolymers are a new fire-, blast- and acid-resistant group of building materials. They are ceramic-like, inorganic polymers produced at low temperatures and have the potential to transform the building products industry. The cost of using geopolymer-based building materials is similar to existing materials but these have greater technical and environmental benefits over the conventional cement type materials. These materials can help to cut back on damage done through industrial spills, improve long term performance, reduce capital or maintenance costs and further help to lower insurance costs. Besides these, geopolymer technology has the potential to reduce emission of carbon dioxide by 80% because high-temperature calcining is not needed while for every one tone of cement manufacturing, one tone of carbon dioxide is produced. Several types of waste product like fly ash, sludge, slag and zeolitic tuffs can be utilized for the production of cation exchangers and geopolymers.

The inorganic geopolymeric materials are normally synthesized using activating solutions of alkali metals as sodium and potassium. These metals are capable of forming highly concentrated aqueous solutions and solvate large amounts of silicon and aluminum. The aluminosilicate geopolymers consist of tetrahedral  $\text{AlO}_4$

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Received July 21, 2009

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and  $\text{SiO}_4$  units polycondensed at ambient temperatures under highly alkaline conditions into three-dimensional structures with charge stabilization provided by alkaline earth ions<sup>(5)</sup>.

Most of the studies on synthesis of geopolymers are carried out using kaolinite, metakaolinite, fly ash, high-calcium slags, blast furnace slag, etc. Several tones of zeolitic fine powder and small granules are thrown away as waste from industrial and agricultural sectors. These byproduct or waste portions of zeolites, which are rich source of alkali-alumino-silicates, can be mechanochemically modified to make them more effective raw materials for the production of cation exchangers and geopolymers.

In this paper, we have tried to synthesize cation exchangers and geopolymers from the granular byproduct of natural clinoptilolite zeolite, which are rich in  $\text{K}_2\text{O}$ ,  $\text{Al}_2\text{O}_3$  and  $\text{SiO}_2$  contents, with using sodium-silicate and sodium hydroxide as activator. We have varied some parameters like alkali concentration, particle size and curing time in order to improve the quality of cation exchanger and geopolymeric product.

## 2. Materials and Methods

### 2.1 Samples preparation and characterization

The natural granules of clinoptilolite zeolite used in this study were obtained from the Futatsui area, Akita, Japan. This granular form of zeolites was ground manually to obtain in powder form by using mortar and pestle. The powder was then modified in two ways: in first case the powder was modified chemically by treating with NaOH solution at room temperature. The solid sample was separated from solution by filtration and washed with distilled water for several times till the effluent became neutral to pH paper. Samples naming for thus obtained products were NZeo (natural zeolite) and Zeo-72 (zeolites treated with NaOH solution for 72 h).

In second case, the powder sample was subjected for mechanical modification by wet-milling in zirconia pot (80  $\text{cm}^3$ ) with zirconia balls (2 mm $\phi$ ) in planetary ball mill ((LA-PO.1, Ito Seisakusho Ltd., Japan) operating at 400 rpm for 24 h with using distilled water. After wet-milling, the slurry was filtered, washed and dried at 80°C for over night. The solid sample was designated as WM-50 (WM

for wet-milled followed by ball to powder mass ratio). The WM-50 sample was further treated with NaOH aqueous solution and then the slurry was filtered, washed and dried at 80°C for over night. This mechanochemically modified sample was designated as WM50-Na.

Powder X-ray diffraction (XRD) patterns were obtained using an X-ray diffractometer with monochromated Cu  $K\alpha$  radiation (JDX-3530, JEOL, Japan). The chemical compositions of the samples were analyzed by X-ray fluorescence (RIX2000, Rigaku, Japan). The specific surface area and texture of wet-milled samples were obtained by the BET method using a BELSORB-Mini instrument (BEL, Japan) and Scanning Electron Microscope (JSM-5900LV, JEOL, Japan), respectively.

### 2.2 $\text{NH}_4^+$ uptake experiment

The uptake of  $\text{NH}_4^+$  was performed with aqueous  $\text{NH}_4\text{Cl}$  solution (Wako, Japan) on NZeo, Zeo-72 and WM-50 under the following conditions: reaction temperature: 25°C, sample/solution ratio: 0.1 g/50  $\text{cm}^3$ , initial  $\text{NH}_4^+$  concentration: 28.22  $\text{mmol/dm}^3$ , reaction time: 24 h. The solution pH was measured just at the time of putting the sample into the solution (initial pH) and after the reaction (equilibrium pH).

After the uptake experiments, the samples were filtered and washed frequently with distilled water. The original  $\text{NH}_4^+$  solution (prior to uptake) and separated solutions (after uptake) were chemically analyzed for  $\text{NH}_4^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$  and  $\text{Ca}^{2+}$  ions by ion chromatograph (DX-120, DIONEX, USA).

### 2.3 Preparation of clinoptilolite based geopolymer

To synthesize clinoptilolite based geopolymer, several parameters such as NaOH concentration, ball to powder mass ratio of wet-milled samples, amount of sodium silicate solution and curing time were taken into account. In first case, WM-20 sample was blended manually for 2 min. using mortar and pestle with NaOH solution with varying concentrations separately. In second case, similar procedure was followed with WM-30, WM-50 and WM50-Na with using single NaOH concentration. In third case, WM-50 sample was blended with NaOH solution with varying the amount of sodium silicate solution (Wako, Japan; Assay: 52-57% and  $\text{SiO}_2/\text{Na}_2\text{O}$  molar ratio: 2.06-2.30). In fourth

case, similar procedure was followed with using WM50-Na sample, NaOH solution and sodium silicate solution with varying curing time.

The blended mixtures were separately placed in plastic moulds, sealed with thin plastic films and allowed to cure for 24 h (except the samples designated for curing time variation) at 40°C. After curing thin films were removed and samples were dried at 40°C. After demoulding, the samples were cut into finite sizes and crushed using an Autograph instrument (AGS-J, Shimadzu, Japan) with crosshead speed of 0.5 mm/min. The fragments from the crushing tests of few characteristic samples were powdered and examined by X-ray diffraction, X-ray fluorescence and scanning electron microscope.

### 3. Results and Discussion

#### 3.1 Sample characterization

The chemical compositions of natural and NaOH treated clinoptilolites are shown in Table 1. The XRD patterns of as-received-ground (NZeo), chemically, mechanically and mechanochemically modified clinoptilolite samples (Zeo-24, Zeo-72, WM-50 and WM50-Na) are shown in Fig. 1. The SEM micrographs of natural, mechanically and mechanochemically modified clinoptilolites are shown in Fig. 2.

There was no any appreciable change of the XRD patterns of natural clinoptilolite after NaOH treatment which indicates no any structural change with the incorporation of exchangeable sodium ions to the natural zeolite.

Almost complete amorphous form of clinoptilolite was obtained with mechanically/mechanochemically modified samples. This effect is attributed to the collision frequency which in turn leads to faster diffusion process<sup>(6)</sup>. When WM-50 sample was treated with NaOH solution, a broad peak at around  $2\theta = 26.5^\circ$  began to appear which is expected to be the formation of sodium-aluminum-

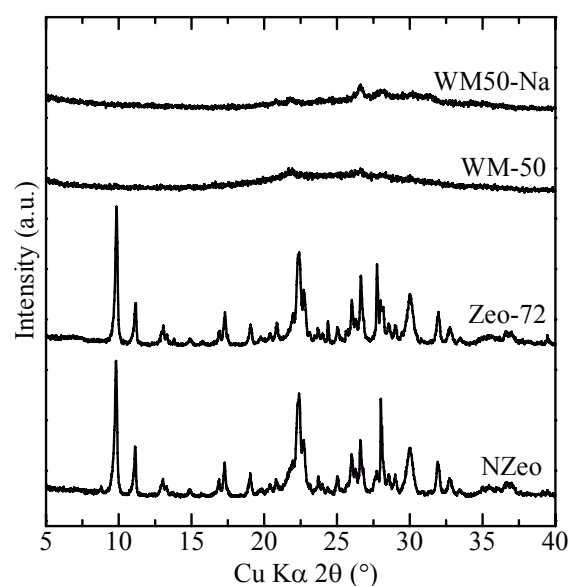


Fig. 1 XRD patterns of natural, chemically, mechanically and mechanochemically modified clinoptilolite zeolite samples.

silicate-hydrate (SASH) phase. The chemical composition data where large amount of Na<sub>2</sub>O was incorporated during the NaOH treatment also suggests the formation of such SASH phase. The beginning of the formation of crystallization can also be observed in the SEM micrograph shown in Fig. 2.

#### 3.2 NH<sub>4</sub><sup>+</sup> sorption

NH<sub>4</sub><sup>+</sup> uptake experiments with the variation of initial NH<sub>4</sub><sup>+</sup> concentration were performed on three samples namely NZeo, Zeo-72 and WM-50. The natural clinoptilolite (NZeo) was selected to obtain its NH<sub>4</sub><sup>+</sup> sorption capacity without any modification while Zeo-72 and WM-50 samples were selected to study the impact of its NH<sub>4</sub><sup>+</sup> sorption capacity by modifying its chemical composition and specific surface area (by changing from crystalline to amorphous form), respectively. The resulting sorption isotherms are shown in Fig. 3. The maximum

Table 1 The chemical compositions (mass %) of natural, chemically and mechanochemically modified clinoptilolites.

Sample	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	Na <sub>2</sub> O	CaO	MgO	K <sub>2</sub> O
NZeo	77.96	14.02	1.30	1.15	1.23	0.46	3.88
Zeo-72	73.74	14.78	1.62	4.03	1.74	1.15	2.94
WM50-Na	60.10	21.90	2.37	10.70	2.69	1.15	1.09

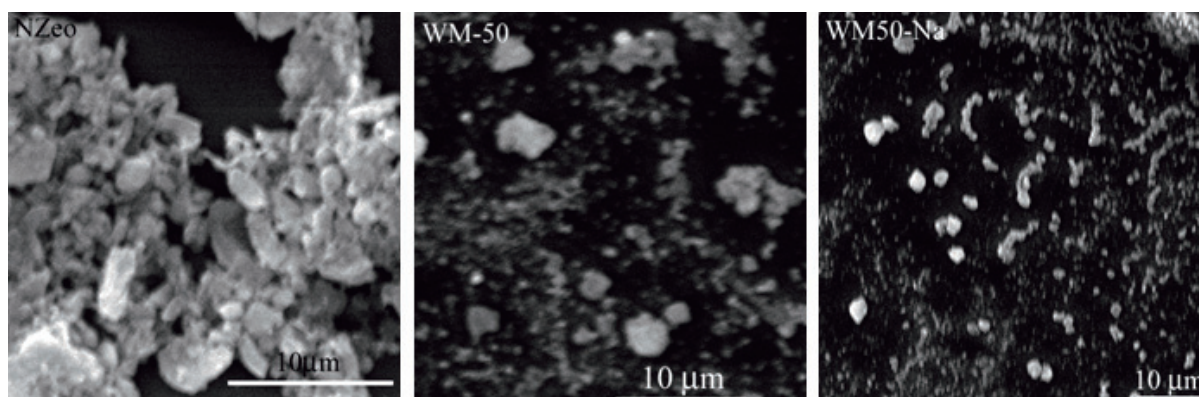


Fig. 2 SEM micrographs of natural, mechanically and mechanochemically modified clinoptilolite zeolite samples.

$\text{NH}_4^+$  sorption capacity ( $Q_{\text{max}}$ ) of natural zeolite (NZeo) is about 0.89 mmol/g while that of WM-50 is 1.39 mmol/g and the resulting  $Q_{\text{max}}$  values increase in the order  $\text{WM-50} > \text{Zeo-72} > \text{NZeo}$ . The  $\text{NH}_4^+$  sorption capacity of present natural clinoptilolite is relatively higher than previously reported for natural clinoptilolites. The variation in the  $\text{NH}_4^+$  sorption capacity of clinoptilolite from various resources is due to the difference in the relative content of alkaline metal cations and chemical-physical pretreatment techniques. The commercial clinoptilolites have much higher  $\text{NH}_4^+$  sorption capacity in comparison to present modified clinoptilolites. The possible reason for such a higher sorption capacity may be the clinoptilolite for the commercial market would probably be pre-screened and pre-treated to yield an optimal performance by removing inert components<sup>(7)</sup>.

### 3.3 Geopolymer and crushing strength

A production of good quality geopolymer with higher crushing strength depends on several parameters like concentration of alkali solution, appropriate starting material, use of sodium silicate solution, curing time and temperature.

The crushing strength is sharply increased with increasing NaOH concentration. The basic mechanism of such is the transformation of extremely reactive materials of alumino-silicates under alkaline condition and the dissolution process is initiated by the presence of hydroxyl ions. Higher amounts of hydroxyl ions facilitate the dissociation of silicate and aluminate species, which promote the polymerization<sup>(8)</sup>.

The amorphous nature of starting material is more preferable for geopolymer with better crushing strength.

This can be attributed to the enhanced dissolution of alumino-silicate particulates from amorphous material and thereby accelerated condensation of the monomer in presence of higher NaOH concentration. Furthermore, the process of geopolymerization involves dissolution, polymerization, condensation and hardening steps which are more favorable if the starting material is amorphous in nature.

The crushing strength was found initially increased and then decreased with increasing WM-50 to  $\text{Na}_2\text{SiO}_3$  mass ratio. This is expected to be due to excess silicate hinders water evaporation and structure formation<sup>(9)</sup>.

The crushing strength of geopolymers, obtained from WM50-Na with using sample to sodium silicate mass ratio of 2 and 5.0 M NaOH solution as a function of curing time

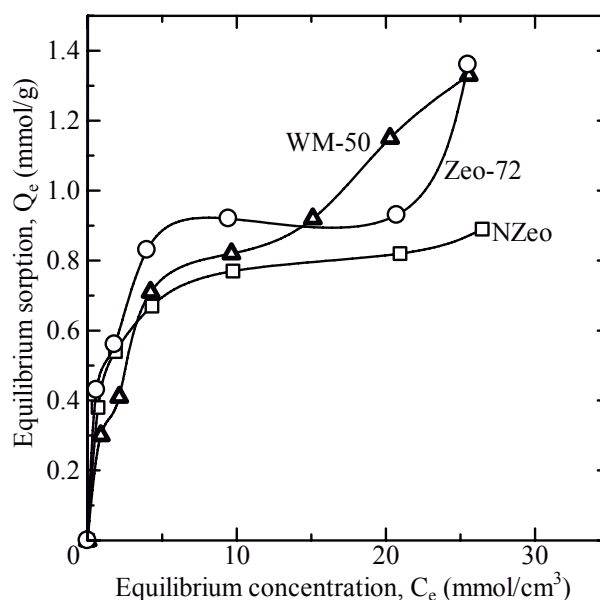


Fig. 3  $\text{NH}_4^+$  sorption isotherms of natural, chemically and mechanically modified clinoptilolites.



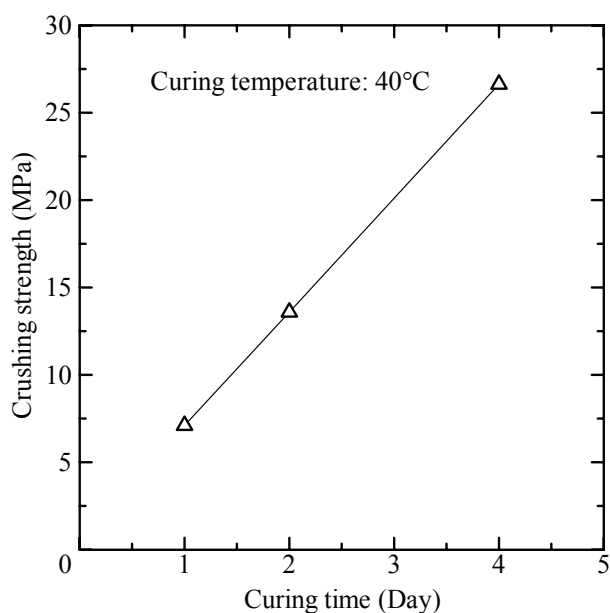


Fig. 4 The crushing strength of samples with the variation of curing time.

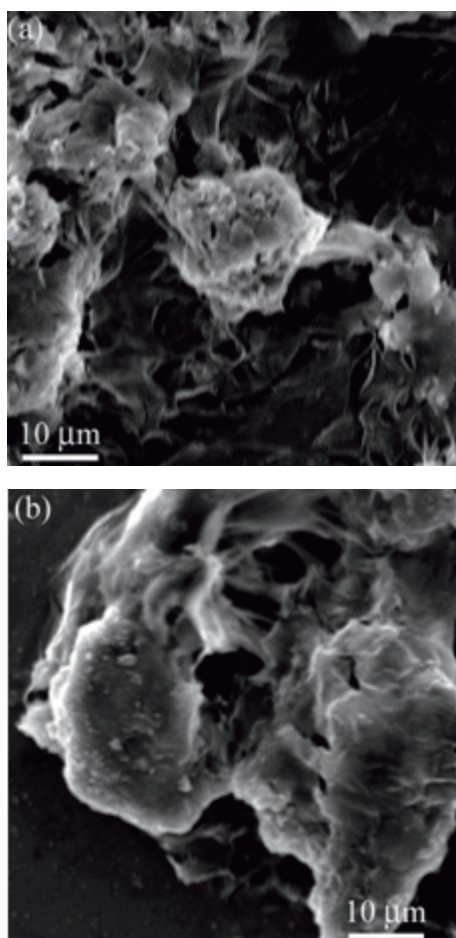


Fig. 5 SEM micrographs of geopolymers obtained from WM50-Na (a) without the use of sodium silicate solution and (b) with using sodium silicate solution and cured for 4 days.

is shown in Fig. 4. The crushing strength has found sharply increasing with curing time suggesting curing for longer period of time at low temperature is preferable which is in accordance with previous report<sup>(10)</sup>.

The chemical compositions and SEM micrographs of two types of geopolymer products obtained from WM50-Na starting material with and without using sodium silicate solution are shown in Table 1 and Fig. 5 respectively. The polymer phase together with crushing strength were found increased in the sample where sodium silicate was used and at the mean time  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio of this sample is higher than the sample where sodium silicate was not used. Thus, it can be said that higher  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio is responsible for the formation of polymer and increasing crushing strength of the product. Furthermore, higher  $\text{Al}_2\text{O}_3$  content may be suitable for the development of ceramic materials rather than geopolymer products<sup>(11)</sup>.

#### 4. Conclusion

The overall ammonium ion retention behavior of the clinoptilolite produced in Akita Prefecture, Japan is similar to that of clinoptilolite obtained from other resources. The present clinoptilolite has a high affinity for ammonium ion, which is observed across a range of ammonium ion concentrations of interest in the context of water treatment. The  $\text{NH}_4^+$  retention capacity of natural clinoptilolite is enhanced either by increasing alkaline metal cations content with chemical modification or by reducing particle size or increasing specific surface with mechanical modification.

The geopolymer materials synthesized through mechanochemically treated clinoptilolite using NaOH and sodium silicate solutions with the variations of types of starting material, NaOH concentration, amount of sodium silicate and curing time are mainly amorphous and contain absorbed atmospheric water. Present work will contribute to develop the possible pathway for the optimum utilization of natural resources as an alternative to cement in construction field.

#### Acknowledgements

We are thankful to Professor Dr. Osamu Yamamoto of Akita University, Center for Geo-Environmental Science for his help to measure the specific surface area and crushing strength of all the samples, to Dr. Yukio Enda of Industrial Technology Center of Akita Prefecture,

Environmental System Department for providing us ion chromatograph instrument to use and Dr. Yoshikazu Kameshima of Tokyo Institute of Technology, Department of Metallurgy and Ceramics Science for providing the chemical composition data of present samples.

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