

Improvement of Cation Exchange Capacity of Natural Zeolite with Alkali Treatments

Eko Hanudin¹, and Bambang Triyatmo²

¹Department of Soil Science, Faculty of Agriculture, Gadjah Mada University

²Department of Fisheries, Faculty of Agriculture Gadjah Mada University

Sekip Unit 1 Yogyakarta 55282, Telp. 0274-548814, Fax: 0274-563062

E-mail: eko@faperta.ugm.ac.id

ABSTRACT

The natural zeolite was treated with alkali (NaOH) solution and heating at 100 °C for 12 and 24 hours. The natural zeolite was collected from Gunungkidul, Jogjakarta, Indonesia. The series of NaOH solutions was 0.5, 1.0, 1.5, 2.5, 3.5 and 4.5 M. The final product of the reaction (precipitate) was designated as 'activated natural zeolite (ANZ)'. The cation exchange capacity (CEC) of the ANZ increased with increasing NaOH concentration up to 1.5-3.5 M. Treatment with NaOH 3.5 M and 12 hours in period of hydrothermal reaction resulted in a maximum CEC (395.6 cmol.kg⁻¹). The maximum CEC also observed for treatment with NaOH 1,5 M, but consumed a longer time (24 hours). The increase in the CEC of the ANZ about 300 % higher than the original one. The XRD (X-ray Diffraction) peaks of the ANZ appear at 2.7, 3.2, 4.1, 5.1, 7.2 Å, this indicated a new crystalline matters (possibility phillipsite) present. Electron micrograph showed that the ANZ has a large cubic/prismatic structure with a perfect form.

Keywords: Natural zeolite, cation exchange capacity (CEC), alkali treatment

INTRODUCTION

Natural zeolites in Indonesia were found widespread in Java, Sumatera, Sulawesi, Flores and Lombok islands. According to the geological point of view, potentially Indonesia may have abundant natural zeolite resources. The larger part of the region consists of volcanic rocks, including fine grained rhyolitic pyroclastic rocks, the parent material of zeolites (Husaini and Hardjatmo, 1996).

The zeolites are from a large family of aluminosilicates. In general the bulk composition of the zeolites tend to correlate with the parent rock-more aluminous zeolites are associated with rock deficient in silica and more siliceous zeolites are associated with rock high in silica. Some deposit can be primarily of one zeolite species and the deposits may contain little else than zeolites (Barrer, 1978).

Of five zeolites (Clinoptilolite, Modernite, Chabazite, Crionite and Phillipsite) which

are generally considered to be significant for industry, only Modernite and Clinoptilolite are found in Indonesia so far. The two mineral are found together in varied proportion. In general, Modernite is more dominant than Clinoptilolite, especially in Tasikmalaya and Malang which may contain to 84 % by weight and have CEC (Cation Exchange Capacity) more than 180 meq/100 g. The common associated minerals are quartz, cristobalite, feldspar, illite and smectite (Husaini and Hardjatmo, 1996).

The fundamental building units in natural zeolites are tetrahedra SiO₄ and AlO₄. Zeolite are tectosilicates, that is they are formed by the linking together of these tetrahedra to give three dimensional anionic networks in which each oxygen of a given tetrahedron is shared between this tetrahedron and one of four others. Thus there are no unshared oxygen's in the frameworks. This fact mean that in all tectosilicates (zeolites, feldspar and felspathoids) (Al+Si):O = 1:2. For every Si^{IV}

which is replaced in the framework by Al^{III} a negative charge is created which is neutralized by an electrochemical equivalent of cations (Barrer, 1978).

The three properties of zeolites which have industrial and agricultural potential are their capacities to sorb gases, vapors and liquids; catalyze reactions; and to act as cation exchanges (Barrer, 1978). Zeolite absorbents are useful for removal of NH₄⁺ from effluent, fish tank and reservoirs and for extraction of copper, lead, cadmium, zinc, barium, silver, iron and other metals from industrial effluent. As additive combined with fodders, zeolite can be used for feeding poultry and other animals, for deodorizing castle yards, for taking up colour in oil industrial, for scrubbing natural and industrial gases, for production of oxygen enriched air. Zeolite absorbents can be used as carrier in agriculture fixer of radioisotope (Setiadji, 1996).

Other applications of activated zeolite are as a solid support for the chromatographic and preparation of catalyst, as ion exchanger in water treatment, drying of gases and liquids, gas purifier on gas purification system, oxygen enrichment of air, deactivation of radioactive effluents. Filtration of drinking water and purification of effluents. Extraction of metals from complex solutions and industrial wastes. Zeolites are also as filler in the paper and rubber industries. Some further application in agriculture for protection of environmental has been developed (Setiadji, 1996).

Zeolite is routinely used in shrimp ponds in Taiwan to treat water when the water turbid and sticky. The mineral possesses unique properties due to its crystalline structure and resulting molecular-sized cavities. These cavities serve as a molecular sieve that absorbs particular gases, such as H₂S, SO₂, and CO₂ (Chaimberlain, 1988 cit. Chien, 1993). Zeolite is still widely used by shrimp farmers in Asia (included Indonesia). It appears that zeolite can adsorb suspended particles and clear the water. It is also said zeolite is favourable for the development of diatom population, probably because zeolite contains silicate (Chien, 1993).

The present study was concerned with an experiment to treat the natural zeolite with alkali (NaOH) solution for the purpose of transforming into materials having high cation exchange capacity. The final products of the reaction were designated as 'activated natural zeolites', which are useful in many industrial fields, agriculture, aquaculture and water quality management.

MATERIAL AND METHODS

1. Natural Zeolite

In this experiment, the natural zeolite (NZ) was collected from Gunungkidul, Jogjakarta, Indonesia. The NZ was ground and passed through a wire sieve with 100 meshes in diameter. The chemical composition of the NZ observed as follow: SiO₂ (69.5 %), Al₂O₃ (12.0 %), CaO (0.13 %), Fe₂O₃ (0.93 %), K₂O (0.6 %), Na₂O (2.22 %), MgO (0.86 %), MnO (0.01 %), P₂O₅ (0.05 %), H₂O (4.07 %) and TiO₂ (0.14 %).

2. Alkali (NaOH) Treatments

The natural zeolite was reacted with alkali (NaOH) solution. The series of NaOH solution were 0.5, 1.0, 1.5, 2.5, 3.5 and 4.5 M. Twenty gram of the sample reacted with 160 ml of NaOH solution, and poured into an Erlenmeyer flask (1 liter in capacity). The flask attached to a reflux condenser and heated at about 100 °C on the hot plates. Duration of the hydrothermal reaction was arranged for 12 and 24 hours. After finishing the treatment, the precipitate was separated from the colloid solution and washed with a distilled water to remove the excessive alkali. The precipitate was designated as 'activated natural zeolite (ANZ).

3. The Physical and Chemical Analysis

Cation exchange capacity (CEC) was determined by the method of Aomine and Harada (1971 cit. Henmi, 1987). The samples were saturated with Ca²⁺ (CaCl₂ 1 N), and the excessive CaCl₂ was washed with ethanol 80 %. The Ca²⁺ ions occupied the negative charge sites were replaced with NH₄Cl 1 N. The supernatant was brought to Atomic Absorption Spectrophotometer (AAS) to determine

Ca²⁺ content (Z-5000 Polarized Zeeman AAS, Hitachi).

X-ray diffraction pattern was taken by a Rigaku Geigerflex D/Max-A system using CoK α X-radiation at 30 kV and 10 mA. Application of a scanning speed at 2°/minute with interval of 0.01 ° in the range of 3 to 60 °.

The scanning electron micrograph was used to observe the samples (natural zeolite and hydrothermal products as 'activated natural zeolites'). Acetone and Au solution were used as medium to place the sample in the sample holder.

RESULTS AND DISCUSSION

1. Cation Exchange Capacity (CEC)

Improvement of Cation Exchange Capacity (CEC) of the natural zeolite after reaction with alkali (NaOH) solutions was shown at the Fig.1. Zeolite holds the position of tectosilicates in classification of mineralogy. Namely, the crystal structure of tectosilicates is built up of SiO₄ tetrahedra and AlO₄ tetrahedra of fundamental constituent units. The Al in 4-fold coordination, which exists in AlO₄ tetrahedral sites, gives rise to permanent negative charge of zeolite. Consequently, the mineral generally has high value of CEC which is independent on pH (Henmi, 1987).

The CEC of 'activated natural zeolite (ANZ)' was increased with increasing NaOH concentration up to 1.5-3.5 M.. Over 3.5 M (for 12 hours in heating duration) or 1.5 (for 24 hours in heating duration), the CEC decreased. This may correspond to dissolution of some silicates from the structure. Duration of the hydrothermal reaction also influenced in increasing the CEC of the ANZ. Treatment for 24 hours in the hydrothermal reaction resulted in the higher CEC than 12 hours. This was probably attributed to maturity of zeolization of the natural zeolites in which treated at longer period.

The CEC of original zeolite was 119.9 cmol_c.kg⁻¹. The maximum CEC of the ANZ was observed at 395.6 cmol_c.kg⁻¹ for treatment with NaOH 3.5 M and 12 hours in the period of the hydrothermal reaction.

Treatment with concentration of 1.5 M and 24 hours also found the maximum CEC of 391.7 cmol_c.kg⁻¹. Comparing with original one, the CEC of the ANZ increased by about 300 %.

The CEC of the treated natural zeolite is due to the formation of alumino silicate species possessing the framed structure of Si-O-Al (Fe) in hot alkaline solution (Ming and Mumpton, 1989 cit. Lee et al., 1998). The solubility of Si increases rapidly above pH 9 due to the ionization of monosilicic acid (Alexander et al., 1954 cit. Lee et al.,

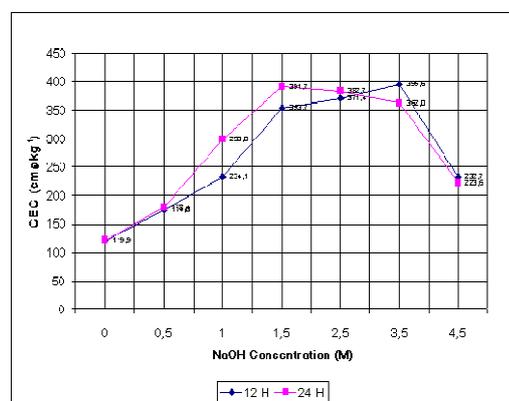


Fig.1. Effect of NaOH concentrations and periods of hydrothermal reaction on change in CEC of Zeolite

1998). Aluminium (Al) solubility increases above pH 8 where the Al(OH)₄⁻ ion predominates (Marion et al., 1976 cit. Lee et al., 1998) so substituted Al for Si increased with increasing pH above 8. The greater the substitution, the more alkaline or alkaline earth cations needed to maintain electrical neutrality, leading to the higher CEC (Lee et al., 1998).

Additionally in zeolites but not in feldspars or some feldspathoids the framework is sufficiently open to accommodate water molecules as well as cations. This openness imparts characteristic zeolite properties. The water molecules can move easily within the crystals and so can the cations. These ion there for undergo ready exchange with other cations, and the water molecule can be remove or replaced in a continuous manner and often reversible. Sorption isotherms do not normally show steps such as are found in crystallohydrates.

1. X-ray Diffraction Pattern

The mechanism of the increase in CEC of the zeolite, before and after alkali treatment was examined by the X-ray powder diffraction (XRD) analysis.

The original zeolite gave the pattern with four sharp diffraction peaks at 3.2, 3.5, 3.8, 4.0, 9.1 Å. These indicated that the natural zeolite contain some crystalline materials (Henmi, 1987). The crystalline materials were possibility feldspar and clinoptilolite. Essential components of the natural zeolite were SiO₂ (69.5 %) and Al₂O₃ (12.0 %). As minor components were CaO (0.13 %), Fe₂O₃ (0.93 %), K₂O (0.6 %), Na₂O (2.22 %), MgO (0.86 %), MnO (0.01 %), P₂O₅ (0.05 %), H₂O (4.07 %) and TiO₂ (0.14 %).

The XRD patterns of the zeolite after the alkali treatment for 12 and 24 hours were observed. Several sharp diffraction peaks were observed, indicating those crystalline matters which were not included in the natural zeolite before the treatment present in the treated zeolite.

The position (d spacing) and relative intensity of these diffraction peaks were identified by using Powder Diffraction File (ICDD, 1995) and XRD Powder Patterns for Zeolites (Treacy, et al., 1996). The XRD pattern of the ANZ indicated a new crystalline matters present. The new crystalline matters were possibility phillipsite (2.7, 3.2, 4.1, 5.1, 7.2 Å). The diffraction pattern of the ANZ which has the higher CEC is easier to be identified than the lower one.

5. Scanning Electron Micrograph

The hydrothermal alteration of glass depends on temperature, chemical composition and pH of the solution, chemical composition of starting material, the existence of an open or closed system during the alteration process (Holler and Wirsching, 1978 *cit. Lee et al.*, 1998). In hydrothermal reaction where aqueous bases were involved, the hydroxyl could be bonded to the aluminium in preference to the silicon atoms, the crystallization was also occurred by the copolymerization of the dissolved silicate and aluminate species. The rate of crystallization and the stability of the sodium zeolite phases were

optimum in the vicinity of 100 °C (Breck, 1974 *cit. Lee et al.*, 1998). The scanning electron micrograph of the natural zeolite showed imperfect shaped crystalline (a part non-crystalline and other some crystalline) (Warren and Dudas, 1984 *cit. Lee et al.*, 1998). Electron micrograph showed that the 'activated natural zeolite' has a large cubic/prismatic structure with perfect form.

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