Geology, Characterization, Quality improvement and Recommended Utilization of Natural Zeolite (Zeolitic Tuff) Deposits from Gunung Kidul, Yogyakarta Special Teritory, Indonesia

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Abstract: - The natural zeolite (zeolitic tuff) in Gunung Kidul regency-Yogyakarta, Indonesia is the most promising deposit to be ranked as the most prominent commodity. Lithologically, the areas are occupied by interbedding green stone breccia, zeolitic tuff and sandstone tuff layers. Zeolitic tuff is characterised by green in colour, coarse – fine sand grain sized, with a variably thickness of up to 15 m. Zeolite minerals consist of clinoptilolite and mordenite with a range of 3.52-7.17 and 6.29-18.47 wt. %, respectively. Mordenite (Na-rich zeolite) is more abundant than clinoptilolite (K-rich zeolite). This agrees well with the bulk-geochemical composition of the rocks, where Na2O content (1.06-1.51 wt. %) is relatively higher than K2O (0.71-0.98 wt. %). Initial (un-activated) CEC of the zeolitic tuffs vary from 39.41 to 67.84 mg Na2O/100 gr zeolite. The measured resources of zeolitic tuffs in the studied areas are 451,248 tonnes. If the average percentage of zeolite minerals (clinoptilolite and mordenite) is 18.14 wt. %, the total amount of zeolite minerals within the rocks are 81,856 tonnes. The quality of zeolites (in term of CEC) was improved by thermal activation. The optimum operating condition was achieved at temperatures of 250 °C during 1 hour heating, which is indicated by an increase of CEC from 67.37 to 88.26 mg Na2O/100 gr zeolite. The Gunung Kidul natural zeolites are recommended to be an additive material for a slow release fertilizer.

Key-Words: - Deposit geology, natural zeolite, characterization, quality improvement, slow release fertilizer.

1 Introduction

Industrial minerals are abundant in the Gunung Kidul Regency, Yogyakarta, Indonesia, and are potentially can be a major income for the region. Among these industrial minerals, the natural zeolite is the most promising deposit to be ranked as the most prominent commodity. The development of zeolite resources will support the development of the local zeolite-based industry. In turn, this will stimulate the development of the economy growth of the local community.

This research deals with the deposit geology and characterization of the natural zeolite deposit (in term of mineralogy, geochemistry and physical properties), quality and quantity (resources), conducting research on applications of zeolites for additive fertilizer materials for the small local enterprises as a pilot project for designated application.

2 Research Area

Preliminary studies e.g. [1], [2], [3] and [4] revealed that the quality of natural zeolites from Gunung Kidul regency, Yogyakarta, is among the highest rank compared to other deposits have been developed in Indonesia (in term of cation exchange capacity). Therefore, in this project, we proposed four areas to be investigated including Serut, Sidomulyo, Hargomulyo and Jatirejo, which are situated in Gunung Kidul regency, Yogyakarta (Fig. 1).

3 Regional Geology

Regionally, the studied area is situated in the northwestern part of the Southern Mountain. It is comprised of Oligocene-Miocene volcano-clastic sediments, which have the dips of layers relatively to south [5]. The regional stratigraphy of the Southern Mountain (from the oldest to the youngest) consists of the Kebobutak Formation, Semilir Formation, Nglanggran Formation, Sambipitu Formation, Wonosari Formation, Kepek Formation and Quartenary alluvium.

The zeolitic tuff, in the research area, is a member of the Kebobutak Formation. The Kebobutak formation is covered conformably by the Semilir Formation, which is characterised by
dacitic breccia, dacitic pumice tuffaceous and white tuff [6]. The Kebobutak Formation is composed of interbedding sandstone, vitricose tuff and zeolitic green stone layers, which is Late Oligocene – Lower Miocene in age [7].

5 Results and Discussion
5.1 Deposit geology

In general, the studied areas, including Serut, Sidomulyo, Hargomulyo and Jatirejo are occupied by interbedding green stone breccia, zeolitic tuff and sandstone tuff layers. The greenstone breccia is comprised of angular fragments derived from zeolitic tuffs, which are megascopically green in colour, granular-sand grain sized with matrix of tuff. Zeolitic tuff is characterised by green in colour, coarse – fine sand grain sized, with a thickness of 0.1 – 3.00 m. Sandstone tuff is typified by light grey in colour and coarse – fine sand grain sized. Serut prospect situated in the north-western part of the studied area has two layers of zeolitic tuffs (TZ-1 and TZ-2) with a thickness of 1.3 and 15 m, respectively. Four layers of zeolitic tuffs are recognised in Sidomulyo (Fig. 2).

Fig. 1 Location map of research area, which is situated in Gunung Kidul regency, Yogyakarta Special Territory, Indonesia.

4 Analytical Methods

A total of 20 natural zeolites (zeolitic tuff) samples taken from Gunung Kidul regency, Yogyakarta, were analysed in term of mineralogy, geochemistry and physical properties. For mineralogical characterization, petrographical, XRD (X-ray Diffraction) and SEM (Scanning Electron Microscope) analyses were performed. Geochemical characterization was conducted by analysing 20 zeolitic tuff samples by means of XRF (X-ray Fluorescence) for major oxides and minor elements. Physical properties, including water absorption, specific gravity, pH, and Cation Exchange Capacity (CEC) were also analysed.

The geology of deposit was mapped out on a detailed scale (1:500). Core drilling was conducted for 4 points with a total depth of 24 meters. Based on the geological maps and drilling data, the measured resources (quantity) of the natural zeolites could be estimated by applying a section method. To improve the quality (in term of CEC) of the natural zeolites, a thermal activation process was also performed.

Fig. 2 Geological map and cross-sections of natural zeolites (zeolitic tuffs) of Sidomulyo prospect, Gunung Kidul, Yogyakarta, Indonesia.

The zeolitic tuffs are megascopically characterised by light green – pale green in color, clastic texture and silt – fine sand in grain size with a thickness ranging from 1.5 to 4 m
(thickness is calculated on the basis of geological reconstruction and core drilling). Some layers show a normal gradational structure from fine sand to silt size. Hargomulyo located in the south-eastern part of Sidomulyo prospect has four layers of zeolitic tuffs with a thickness ranging from 1.6 to 3.8 m (Fig. 3). Jatirejo situated in south-eastern part of research area consists of two zeolitic tuff layers, with a thickness of 10 and 12 m. Detailed mapping exhibits that structural geology developed in the studied area is uncomplex and only manifested by the presence of normal fault in Serut. The research area is interpreted as a flank of fold, which is indicated by the general trend of layer dips towards south-east and south-west.

5.2 Characteristics of natural zeolites

The petrographical analysis indicates that the rock is typified by a clastic texture, composed of volcanic glass (44.3-61.3 vol.%), quartz (4.1-11.0 vol.%), plagioclase (2.0-12.0 vol.%), orthoclase (0.2-3.4 vol.%), chlorite (1.3-5.7 vol.%), magnetite (1.9-3.7 vol.%), serisite (1.0-1.5 vol.%) and altered minerals from volcanic glass, which is interpreted as zeolite minerals (15.7-27.1 vol.%). The X-ray Diffraction (XRD) analysis of the zeolite samples show the peaks of diffraction are belong to clinoptilolite and mordenite (zeolite minerals), also the other minerals including montmorilonite, plagioclase and quartz (Fig. 4). The samples are predominantly composed of mordenite, compared to clinoptilolite. The presences of mordenite and clinoptilolite are also well recognised by scanning electron micrograph (SEM analysis), illustrated by Fig. 5A and B, respectively. Mordenite is mostly characterised by needles/fibers structures (Fig. 5A), whereas clinoptilolite occurred in monoclinic symmetry of blades/tabular and laths (Fig. 5B). Webby structure of montmorilonite and volcanic glass (precursor of zeolite minerals) are also identified.

Fig. 4 Representative XRD analysis of zeolitic tuff from Gunung Kidul regency, Yogyakarta, showing the presence of mineral phases, including zeolite minerals, clinoptilolite (Cpt) and mordenite (Mor).

Fig. 5 Scanning electron micrograph of (A) mordenite needles/fibers [Mor], and (B) clinoptilolite [Cpt] with a monoclinic symmetry of blades and laths in zeolitic tuff from Gunung Kidul regency, Yogyakarta, Indonesia
Bulk-geochemistry of Gunung Kidul zeolitic tuffs are characterised by major oxides SiO$_2$ (72 wt. %), Al$_2$O$_3$ (9-11 wt. %), FeO (1.6 wt. %), MgO (0.8-1.2 wt. %), CaO (3.3 – 4.5 wt. %), Na$_2$O (1.1-1.5 wt. %), K$_2$O (0.7-1 wt. %) and H$_2$O (8 wt. %). The normative calculation indicates the presence of ilmenite (0.46-0.68 wt. %), magnetite (1.72-3.66 wt. %), K-feldspar (1.66-2.95 wt. %), chlorite (0.99-2.41 wt. %), albite (0.25-2.65 wt. %), anortite (0.91 – 2.95 wt. %), montmorillonite (0.72 – 7.16 wt. %), illite (2.66 – 4.21 wt. %) and quartz (6.45 – 16.86 wt.%). Zeolite minerals consisting of clinoptilolite and mordenite are also detected in a moderate amount with a range of 3.52-7.17 and 6.29-18.47 wt. %, respectively. Volcanic glass was interpreted as a predominant phase with amount of 45.52-54.79 wt. %. Mordenite (Na-rich zeolite) is more abundant than clinoptilolite (K-rich zeolite). This agrees well with the bulk-geochemical composition of the rocks, where Na$_2$O content is relatively higher than K$_2$O.

The physical properties of zeolitic tuffs are represented by Cation Exchange Capacity (CEC), acidity (pH), water absorption and density. Initial (un-activated) CEC of Gunung Kidul natural zeolitic tuffs vary from 39.41 to 67.84 mg Na$_2$O/100 gr zeolite. The acidities (pH values) of zeolitic tuffs are slight alkali with pH ranging from 7.3 to 8.3. Water absorption analysis revealed a wide range of values, varying from 13.42 to 27.60%. Density of the zeolitic tuffs are relatively low (1.34 – 1.74 gr/cm$^3$). Density data is useful for estimation of measured resources (quantity) of the natural zeolite deposits in the studied areas.

Zeolite deposits in the four studied areas were mapped out on a detailed scale (1:500). By using this scale of deposit maps, the measured resources of the deposits enable to be estimated by applying a section method and verified by core drilling data. The estimation of zeolitic tuff in the areas indicates the total of measured resources of 451,248 tonnes. If the average percentage of zeolite minerals (clinoptilolite and mordenite) is 18.14 wt.%, the total amount of zeolite minerals within the rocks are 81,856 tonnes.

5.3 Quality improvement

The quality of zeolites (in term of Cation Exchange Capacity, CEC) was improved by thermal activation. Measurement result on CEC of the activated natural zeolite is presented in Fig. 6. Comparing the data presented on the graph (Fig. 6) with those belong to unactivated zeolite (at zero hour of activation), one can conclude that the activation process can increase the cation exchange capacity of the zeolite. As seen on the graph, both temperature and duration of heating of the activation process affect the cation exchange capacity. High temperature and long heating period gives high CEC value. However, the temperature can not be set too high as it could change the zeolite structure resulting in lower CEC value (see CEC value at 250 °C and 300 °C). Data on the graph suggests the optimum condition for activation process is at the heating temperature of 250 °C and duration of 1 hour.

Fig. 6 Relationship between duration of thermal activation (hours) and CEC of representative zeolitic tuff from, Gunung Kidul Regency, Yogyakarta, Indonesia. Notes: CEC at zero hour of activation is unactivated CEC of the sample.

5.4 Utilization

Zeolite is a very useful industrial mineral that can be utilized by different types of industries such as agriculture, animal husbandry, water treatment and additive fertilizer materials. Based on the mineralogical, geochemical and physical characteristics, optimum duration and temperature conditions of activation as well as CEC (Cation Exchange Capacity), the natural zeolites (zeolitic tuffs) in the studied areas are recommended to be used for additive materials for fertilizer. Unfortunately, there is no quality standard found in literatures for zeolitic tuffs required in this application. However, previous experimental study conducted by Widiasmoro et al. (2000) revealed that the zeolitic tuffs from this region are suitable to be used as an additive material for fertilizer. Additionally, the reason of choosing the application of the natural zeolites for additive fertilizer materials, due to: (1) the surrounding areas where the natural zeolites occurred are predominantly as agriculture and animal husbandry region, (2) the treatments of the natural...
zeolites to be additive fertilizer materials are relatively uncomplicated and easily-used for the local small-medium enterprises in the region, and (3) the use of zeolite is an environmentally fertilizer as it allows nutrients to be released to the root in a slow plant root demand-driven fashion.

6 Conclusion

The natural zeolite (zeolitic tuff) in Gunung Kidul regency, Yogyakarta Special Territory, Indonesia is the most promising deposit to be ranked as the most prominent commodity. Lithologically, the areas are occupied by interbedding green stone breccia, zeolitic tuff and sandstone tuff layers. Zeolite tuff is characterised by green in colour, coarse – fine sand grain sized, with a variably thickness of up to 15 m. Study on characterization indicates that zeolite minerals consist of clinoptilolite and mordenite in a moderate amount ranging from 3.52 to 18.47 wt. %. Mordenite (Na-rich zeolite) is more abundant than clinoptilolite (K-rich zeolite). This agrees with the geochemical composition of the rocks, where Na content is relatively higher than K. Initial (unactivated) CEC of the zeolitic tuffs vary from 39.41 to 67.84 mg Na\(^2\)/100 gr zeolite with slight alkali acidities (pH of 7.3-8.3). Water absorption shows a wide range of values (13.42-27.60 %). Density of the zeolitic tuffs are relatively low (1.34 – 1.74 gr/cm\(^3\)). Based on the detailed deposit maps (scale 1:500) and core drilling data, measured resources of zeolitic tuffs in four studied areas are 451,248 tonnes. The quality of zeolites (in term of CEC) was improved by thermal activation. The optimum operating condition was achieved at temperatures of 250 \(^\circ\)C during 1 hour heating, which is indicated by an increase of CEC from 67.37 to 88.26 mg Na\(^2\)/100gr zeolite. Based on social-economic condition of the local community (as agriculture and animal husbandry region) as well as the mineralogical, geochemical, physical characteristics and an increase of CEC of the Gunung Kidul zeolitic tuffs, the best utilization of the deposit is to be an additive material for a slow release enviromental-friendly fertilizer.

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