

MAKING A SYNTHETIC ZEOLITE FROM A RESIDUE OF BAUXITE WASHING

PEMBUATAN ZEOLIT SINTETIK DARI SISA HASIL PENCUCIAN BAUKSIT

KUKUH N. HIDAYAT¹, AGUS WAHYUDI¹ and HUSAINI²

¹ Research and Development Centre for Mineral and Coal Technology
Jalan Jenderal Sudirman 623 Bandung 40211
Telp. (+6222) 6030483, Fax. (+6222) 6003378
e-mail: kukuhnoer@gmail.com

² Laman Mining, Ltd.
Treasury Tower, 12th Floor, Unit L-M, District 8, SCBD, Lot. 28, Jakarta

ABSTRACT

A zeolite synthetic of NaA type is generally prepared by mixing the alumina and silicate-containing materials (alkali alumino hydro-silicates). The used raw materials include the amorphous solids such as metakaolin, siliceous earth, coal ash, kimberlite waste, alumina trihydrate $[\text{Al}(\text{OH})_3]$, bauxite, and aluminum metal. Residue of bauxite washing retains a fine texture and contains significant alumina and silica content, namely 30-36% Al_2O_3 and 10-15% SiO_2 . Both components are required for making the zeolite NaA. In this research, the zeolite NaA was made by extracting the alumina from residue of bauxite washing with caustic soda, and followed by reacting it with a water glass after through the flushing and washing process. The composition of zeolite NaA is as follows: 33.87% SiO_2 , 27.63% Al_2O_3 , 16.31% Na_2O , and 22.18% H_2O with $\text{Na}_{96}\text{Al}_{96}\text{Si}_{96}\text{O}_{384} \cdot 216\text{H}_2\text{O}$ or $\text{Na}_{12}(\text{AlO}_2)_{12}(\text{SiO}_2)_{12} \cdot 27\text{H}_2\text{O}$ as its mineral composition.

Keywords: alumina, bauxite, reactive silica, waste washing bauxite, zeolite NaA.

ABSTRAK

Zeolit sintetik jenis NaA umumnya dibuat dengan mencampurkan bahan yang mengandung senyawa aluminat dan silikat (alkali alumino hydro-silicates). Bahan baku yang sudah digunakan antara lain padatan amorf seperti metakaolin, mineral silikat (siliceous earth), abu batubara, limbah kimberlit, alumina trihidrat $[\text{Al}(\text{OH})_3]$, bauksit, dan logam aluminium. Sisa hasil pencucian bauksit memiliki tekstur halus dan kandungan alumina serta silika reaktif cukup signifikan (30-36% Al_2O_3 dan 10-15% SiO_2). Kedua komponen tersebut diperlukan untuk pembuatan zeolit A. Pada penelitian ini, zeolit NaA dibuat dengan mengekstraksi alumina limbah pencucian bauksit dengan soda kostik, kemudian direaksikan dengan water glass sehingga menghasilkan zeolit A setelah melalui proses pembilasan dan pencucian. Produk zeolit NaA yang dihasilkan memiliki komposisi kimia 33,87% SiO_2 , 27,63% Al_2O_3 , 16,31% Na_2O , dan 22,18% H_2O dengan komposisi mineral $\text{Na}_{96}\text{Al}_{96}\text{Si}_{96}\text{O}_{384} \cdot 216\text{H}_2\text{O}$ atau $\text{Na}_{12}(\text{AlO}_2)_{12}(\text{SiO}_2)_{12} \cdot 27\text{H}_2\text{O}$.

Kata kunci: alumina, bauksit, silika reaktif, sisa hasil pencucian bauksit, zeolit NaA.

INTRODUCTION

Zeolite is a group of minerals produced from hydrothermal processes in igneous rock (Zozulya *et al.*, 2018). The mineral is usually found to fill the gaps or fractures from the rock (Saputra, 2006). Normally, the zeolite from mines must be processed prior to use it directly. The steps of zeolite processing include crushing, grinding, sifting and

activation (Zulkarnain *et al.*, 2010). Zeolite is a multipurpose industrial mineral due to its physical and chemical properties as absorbent, ion exchange, molecular filter and catalyst (Kusdarto, 2008; Aidha, 2013).

Zeolites are divided into two types based on their origin, namely the natural and synthetic zeolites (Sugiarti, Charlena and Aflakhah, 2017). The synthetic zeolites is commonly

used for commercial purposes than the natural zeolite. Due to its particle size uniformity and high level purity. Synthetic zeolites are used for catalyst in the petrochemical industry, hazardous waste treatment and radioactive waste (Goenadi, 2004). Another advantage is that the synthetic zeolite structure is flexible to utilize (Sugiarti, Charlena and Aflakhah, 2017).

One type of synthetic zeolite is the NaA zeolites which develops to overcome the disadvantage of natural zeolites that have non-uniform pore sizes (Saraswati, 2015). e NaA zeolite, or hydrated aluminum silicate is a white powder-shaped material with a cube-shaped crystal structure, and has density about 0.40 to 0.48 g/ml with chemical formula $\text{NaAlSi}_2\text{O}_6 \cdot \text{H}_2\text{O}$ (Selim *et al.*, 2017). If hydrolyzed in water, it can provide an alkaline pH condition ($\text{pH}=10.1-11.4$ for 1% zeolite Na suspended in water). As the Na zeolite is a mineral, its chemical composition varies, with the average as follows: 17% Na_2O , 28% Al_2O_3 , 33% SiO_2 and 22% H_2O .

The structure of NaA zeolite is isometric trapezohedron which contains relatively large central cavity that allows large ions or other molecules to enter or stay within the crystal frame. (Figure 1). So, it can function as a molecular coating (chemical sieve). One of very important uses is for detergent, where the NaA zeolite replaces the sodium tripolyphosphate in detergent as a water softener. Phosphate in detergent can cause a rapid growth of algae in waste water. The NaA zeolite acts as a media for ion exchange while the calcium cation in the water is exchanged by sodium ions in zeolite. The NaA zeolite is also used as a catalyst for crude oil cracking, drying agent and absorbent, stabilizer (if added to PVC, it can prevent the damage of water pipe).

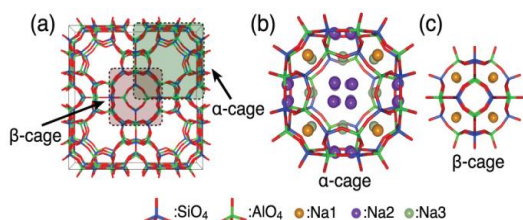


Figure 1. Structure of NaA zeolite

Preparing the synthetic zeolite requires two main raw materials, that is aluminum and silica. The aluminum hydrate is one of aluminum sources, usually in the form of $\text{Al}_2(\text{SO}_4)_3$ or $\text{Al}(\text{NO}_3)_3$ salt while as sources of silica usually uses sodium silica (Aziz, 2010). The aluminum hydrate can be obtained by digesting the bauxite with NaOH which will produce sodium aluminate and then is purified into aluminum hydrate (Husaini *et al.*, 2015).

This research used raw material from the residue of bauxite washing which still contains significant alumina and silica (30-36% Al_2O_3 and 10-15% SiO_2). Several studies on the making of synthetic zeolite can be prepared from low-cost materials, such as low-grade natural zeolite and coal fly ash (Mustain *et al.*, 2014; Kurniawan and Widiastuti, 2017). Those materials can be synthesized into the NaA zeolite by melting method at the temperature of 750°C , followed by a hydrothermal process at temperature of 100°C for 12 hours to extract Al and Si which requires a long process and high temperature compared to this study. The purpose of this research is to exploit the potential of processing Indonesia's waste washing bauxite for making the NaA zeolite.

METHOD

Equipment and Materials

The equipment used in this study comprises rotary drum scrubber, ball mill, hydrocyclone, reactor, filter press, and storage tank for producing NaA zeolite. The materials used include waste washing bauxite, caustic soda (NaOH), sodium silicate (water glass) and water. The instrumentals used for sample characterization are XRD (x-ray diffraction) for mineralogy analysis (Al, Na and Si) and XRF (x-ray fluorescence) for chemical composition analysis. The data from raw material characterization are then used as a reference in the process of digesting with autoclave to determine the amount of NaOH solution used.

Preparation of NaA Zeolite

Figure 2 shows the flow diagram of preparing synthetic NaA zeolite from waste washing bauxite. Beneficiation process of the waste and autoclaving process were conducted in pilot scale, while synthesize process of

zeolite was conducted in lab scale. The waste washing bauxite was produced from the *rotary drum scrubber* (RSD) and then pumped into a hydro-cyclone to separate the fine particles (*over flow*) and the coarse ones (*under flow*). The fine particles (< 100 mesh) were reacted with caustic soda (concentration of 100-400 g/L) using the heat from a hot steam in boiler at 100 °C and 1 atm to produce temperature of 60 °C in autoclave in terms of obtaining sodium silicate and sodium aluminate. Reaction process in autoclave followed by raising the temperature between 120-160 °C to obtain a higher concentration of sodium aluminate, which still mixed with sodium silicate and red mud. Sodium aluminate from autoclave process then is put into a stirred tank for cooling and/or for dilution, and then filtered by filter press.

The mixture of sodium silicate and sodium aluminate were diluted with water in the reactor-to get the concentration of aqueous sodium aluminate about 0.5-0.6% as an Al_2O_3 and sodium silicate about 0.01-0.02% as a SiO_2 , with the comparison in composition between solution:water about 1:10-20. The solution of concentrated sodium silicate (water glass) with concentration of 7.37% Na_2O and 23.89%

SiO_2 was mixed into aqueous sodium silicate solution in reactor and stirred until homogenous and pre-heating at initial temperature of 80 °C for 30-60 minutes to produce solution in gel form. Then a higher concentration of sodium aluminate about 6-7.5% was added and heated to 70 °C for 30-60 minutes and stirred until it become homogenous to get the initial formation of synthetic zeolite crystal core. The variations of ratio water glass used, aqueous sodium aluminate and concentrated sodium aluminate are summarized in Table 1.

The next step was adding the crystal core or seed to solution at 87 °C for 30-60 minutes and stirred until homogenous and obtained the synthetic zeolites in the form of pulp/slurry. This synthetic zeolite slurry was filtered using a vacuum filter to produce a cake synthetic zeolite, then washed and rinsed with clean water to clean up the contaminants, such as silica. The synthetic zeolite was then dried at 100-110 °C in order to obtain the final product of dry synthetic zeolite according to the desired specification. Then the dry synthetic zeolite was mashed up by pulverizer until reached a certain smoothness (-150 mesh).

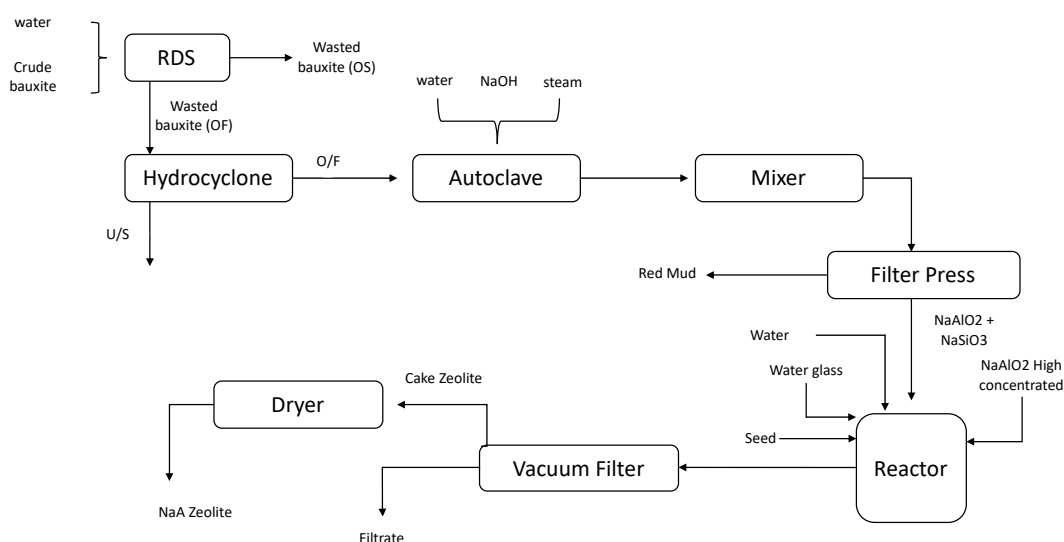


Figure 2. Flow diagram of preparing synthetic NaA zeolite (O/F: Over Flow, U/F: Under Flow, O/S: Over Size and U/S: Under Size)

Table 1. Variations of ratio water glass, aqueous sodium aluminate and concentrated sodium aluminate in the synthesize of NaA zeolite

| No. | (a) Water glass | | (b) Aqueous Na-aluminate | | (c) Concentrated Na-aluminate | |
|-----|-----------------|------------|--------------------------|------------|-------------------------------|------------|
| | Water glass (g) | Water (mL) | Na-AlO ₂ (g) | Water (mL) | Na-AlO ₂ (g) | Water (mL) |
| 1 | 25 | 55.61 | 2.276 | 61.8 | 97.72 | 121.76 |
| 2 | 50 | 55.61 | 2.276 | 61.8 | 97.72 | 121.76 |
| 3 | 52.24 | 55.61 | 2.276 | 61.8 | 97.72 | 121.76 |
| 4 | 60 | 55.61 | 2.276 | 61.8 | 97.72 | 121.76 |
| 5 | 70 | 55.61 | 2.276 | 61.8 | 97.72 | 121.76 |
| 6 | 80 | 55.61 | 2.276 | 61.8 | 97.72 | 121.76 |
| 7 | 90 | 55.61 | 2.276 | 61.8 | 97.72 | 121.76 |

RESULTS AND DISCUSSION

The characterization of washing bauxite residue and product of NaA zeolite is carried out with XRD and XRF. The X-ray diffractogram can be seen in Figure 3 and 4 respectively.

Figure 3 shows the diffractogram of minerals content in washing bauxite residue, such as kaolinite [Al₂Si₂O₅(OH)₄], hematite (Fe₂O₃), quartz (SiO₂), gibbsite Al(OH)₃, and goethite [Fe₃O(OH)]. While the analysis of chemical

composition using XRF can be seen in Table 2.

Table 2. Major chemical composition of waste washing bauxite

| Compounds | Wt. % |
|--------------------------------|-------|
| SiO ₂ | 34.80 |
| Al ₂ O ₃ | 33.21 |
| Fe ₂ O ₃ | 11.52 |
| TiO ₂ | 1.55 |

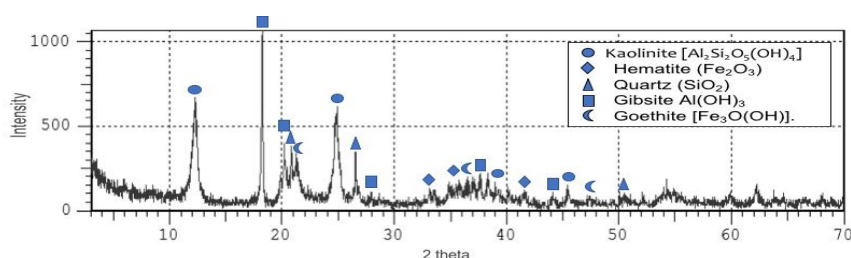


Figure 3. X-ray diffractogram of waste washing bauxite

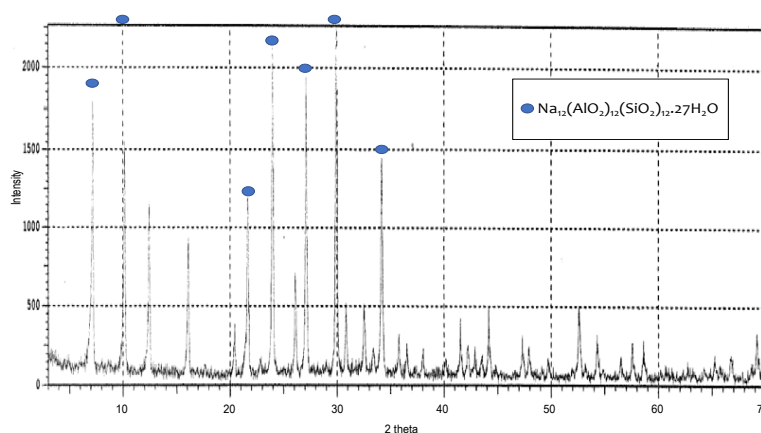


Figure 4. X-ray diffractogram of the prepared NaA synthetic zeolite from washing bauxite residue

According to the XRD and XRF analysis of the washing bauxite residue, the dominant compounds are alumina and silica. The alumina comes from gibbsite, typical alumina source in Indonesian bauxite, and the silica from quartz. Besides, iron oxide is still available in the waste shown by the typical red color of iron oxide minerals.

The process explained in Figure 2 aims to extract the alumina and silica from the washing bauxite residue using sodium hydroxide by autoclaving process. The extracted materials, sodium aluminate and sodium silicate, are the raw materials for preparing NaA zeolite.

Table 1 shows a series of experiments with variation of amount of water glass (25-90 g), while the amount of dilute sodium aluminate (2.276 g) and concentrated sodium aluminate (97.72 g) is the same. Its aim is to see how much the role of water glass in synthesizing zeolite from waste washing bauxite.

Water glass is a silica source and has been widely used to increase the ratio of silica/alumina for obtaining proper ratio to synthesis NaA zeolite. Selim *et al.* (2017) used commercial sodium silicate (water glass) to synthesis NaA zeolite from aluminum scrub. Aluminum scrub was used as alumina source and then mixed with commercial sodium silicate to produce NaA zeolite. The NaA zeolite then is successfully used as an adsorbent for cadmium removal from water.

Mustain *et al.* (2014) did not use the water glass to synthesize the NaA zeolite from natural zeolites, since the silica content in natural zeolites is already high. They used commercial sodium aluminate to increase the alumina content. By alkaline fusion hydrothermal method, they successfully converted high impurities natural zeolite with silica/alumina ratio of 8.21 to zeolite NaA with silica/alumina ratio of 1.93 and less CaO impurities.

Based on the XRF analysis, chemical composition of the synthesized zeolite can be seen in Table 3.

Table 3. Chemical composition of the prepared synthetic zeolite

| Number of experiment | Composition of A zeolite product (crystal water level adjustment) | | | |
|----------------------|-------------------------------------------------------------------|------------------------------------|-----------------------|----------------------|
| | SiO ₂ (%) | Al ₂ O ₃ (%) | Na ₂ O (%) | H ₂ O (%) |
| 1 | 40.00 | 23.41 | 14.40 | 22.18 |
| 2 | 36.30 | 24.34 | 17.18 | 22.18 |
| 3 | 38.75 | 24.47 | 14.59 | 22.18 |
| 4 | 37.34 | 25.75 | 14.73 | 22.18 |
| 5 | 33.87 | 27.63 | 16.31 | 22.18 |
| 6 | 35.31 | 18.58 | 23.93 | 22.18 |
| 7 | 40.27 | 21.20 | 16.35 | 22.18 |

Experiment number 5 has a chemical composition close to the standard and commercial NaA Zeolite. It means that the right composition of water glass, dilute sodium aluminate and concentrated sodium aluminate is 70 g, 2.266 g and 97.72 g, respectively to produce high quality of NaA zeolite. Chemical composition of the NaA zeolite of this work compare to the standard can be seen in Table 4.

Table 4. Chemical composition of standard NaA zeolite and the prepared zeolite of this work

| Compound | Standard* (Wt. %) | This work (Wt. %) |
|--------------------------------|-------------------|-------------------|
| SiO ₂ | 33 | 33.87 |
| Al ₂ O ₃ | 28 | 27.63 |
| Na ₂ O | 17 | 16.31 |
| H ₂ O | 22 | 22.18 |

Source: Rulli (2004)

The XRD result supports the analysis (Figure 4). It clearly shows that the product of the synthesized zeolite in this work belongs to the zeolite NaA or Na₁₂(AlO₂)₁₂(SiO₂)₁₂·27H₂O as indicated by the position of the peak patterns (2 theta= 7.18°, 10.16°, 21.65°, 23.97°, 27.09°, 29.92°, 34.16°). This result confirms with the NaA synthetic zeolite that has been conducted by previous researchers (Mustain *et al.*, 2014; Zhang, Chen and Yang, 2016).

CONCLUSION

High quality NaA synthetic zeolite was produced successfully by preparing low-cost material, washing bauxite residue. Chemical composition of synthesized NaA zeolite of this work is 33.87% SiO₂, 27.63% Al₂O₃, 16.31% Na₂O, and 22.18% H₂O. The chemical and mineralogical properties of the product had met the quality of commercial and standard NaA zeolite.

ACKNOWLEDGEMENT

The authors would like to send gratitude to the Ministry of Energy and Mineral Resources, Republic of Indonesia, for the funding to the research.

REFERENCES

- Aidha, N. N. (2013) "Aktivasi zeolit secara fisika dan kimia untuk menurunkan kadar kesadahan (Ca dan Mg) dalam air tanah," *Jurnal Kimia dan Kemasan*, 35(1), pp. 58–64. doi: 10.24817/jkk.v35i1.1874.
- Aziz, M. (2010) "Ekstraksi alumina dari residu bauksit untuk bahan baku zeolit sintetis dengan produk samping konsentrat besi," *Jurnal Zeolit Indonesia*, 9(2), pp. 54–60.
- Goenadi, D. H. (2004) "Teknologi pengolahan zeolit menjadi bahan yang memiliki nilai ekonomi tinggi," *Jurnal Zeolit Indonesia*, 3(1), pp. 42–49.
- Husaini *et al.* (2015) *Persiapan pembangunan demo plant rotary drum scrubber 50 ton/jam dan optimalisasi PAC dan tawas dari tailing washed bauksit*. Bandung: Puslitbang tekMIRA.
- Kurniawan, R. Y. and Widiastuti, N. (2017) "Sintesis zeolit-A dari abu dasar batubara dengan pemisahan Fe dan Ca," *Jurnal Teknik ITS*, 6(1), pp. C-17-C–20.
- Kusdarto (2008) "Potensi zeolit di Indonesia," *Jurnal Zeolit Indonesia*, 7(2), pp. 78–87. Available at: <https://izindo.files.wordpress.com/2014/12/jzi-vol-7-no-2-2008.pdf>.
- Mustain, A., Wibawa, G., Nais, M. F. and Falah, M. (2014) "Synthesis of zeolite NaA from low grade (high impurities) Indonesian natural zeolite," *Indonesian Journal of Chemistry*, 14(2), pp. 138–142. doi: 10.22146/ijc.21250.
- Rulli, C. (2004) *Sodium zeolite, Chemistry 503 Molecule Report*. Available at: <https://www.sas.upenn.edu/~crulli/Zeolite.htm>.
- Saputra, R. (2006) "Pemanfaatan zeolit sintetis sebagai alternatif pengolahan limbah industri," *Jurnal Hibah Bersaing*, 3, pp. 1–8.
- Saraswati, I. (2015) "Zeolite-A synthesis from glass," *Jurnal Sains dan Matematika*, 23(4), pp. 112–115.
- Selim, M. M., EL-Mekkawi, D. M., Aboelenin, R. M. M., Sayed Ahmed, S. A. and Mohamed, G. M. (2017) "Preparation and characterization of Na-A zeolite from aluminum scrub and commercial sodium silicate for the removal of Cd 2+ from water," *Journal of the Association of Arab Universities for Basic and Applied Sciences*, 24(1), pp. 19–25. doi: 10.1016/j.jaubas.2017.05.002.
- Sugiarti, S., Charlena and Aflakhah, N. A. (2017) "Zeolit Sintetis terfungsionalisasi 3-(trimetoksisilil)-1-propantol sebagai adsorben kation Cu(II) dan biru metilena," *Jurnal Kimia VALENSI*, 3(1), pp. 11–19.
- Zhang, X., Chen, C. and Yang, R. (2016) "Synthesis of small crystals zeolite NaA by a two-step growth approach," *Digest Journal of Nanomaterials and Biostructures*, 11(4), pp. 1271–1275.
- Zozulya, D., Kullerud, K., Ravna, E., Savchenko, Y., Selivanova, E. and Timofeeva, M. (2018) "Mineralogical and geochemical constraints on magma evolution and late-stage crystallization history of the Breivikbotn silicocarbonatite, Seiland Igneous Province in Northern Norway: Prerequisites for zeolite deposits in carbonatite complexes," *Minerals*, 8(11), p. 537. doi: 10.3390/min8110537.
- Zulkarnain, Husaini, Syukri, S., Iriansyah, R., Sudirman, A., Supriatna, J. and Wijaya, K. (2010) *Proses pengolahan zeolit dan bentonit skala pilot*. Bandung: Puslitbang Teknologi Mineral dan Batubara.