Alkali Fusion of Waste Perlite Dust to Synthesize Faujasite Zeolite Using a Rotary Kiln

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***Abstract*—In this study, we attempted to continuously treat waste perlite dust by alkali fusion using a rotary kiln, to synthesize faujasite zeolite. A mixture of perlite dust and sodium hydroxide (NaOH) powder with three different mixture ratios (by weight) of 1:0.5, 1:0.8, and 1:1 was charged into a rotary kiln, and heated at 380 °C or 450 °C for 30 min. The resultant fused material was then converted into faujasite, a zeolite product, by heating it at 80 °C for 12 h followed by shaking for 24 h in distilled water at room temperature. It was confirmed that sodium silicate was formed using the rotary kiln, and the dissolution of Si and Al in the fused dust increased with increasing NaOH addition near the exit of the kiln. Faujasite could be synthesized for all fused conditions, and the cation exchange capacity (CEC) of the product increased with increasing NaOH addition, especially at close to the exit of the kiln. Varying amounts of the dust ranging from 0.1 to 1 g fused with NaOH (1:1) at 380 ℃ for 30 min using the rotary kiln were added to 2 mL of distilled water, shaken for 12 h at room temperature, and subsequently heated at 80 °C for 6 h to examine the effect of the solid/liquid ratio on the synthesis of zeolites from the fused dust. Regardless of the solid/liquid ratio, the amorphous material was formed after shaking at room temperature. Faujasite could be synthesized from the solution above a solid/liquid ratio of 0.25 g/mL, and the peaks of faujasite from the solution at 0.25 g/mL were higher than those at 0.5 g/mL.**

***Index Terms*—Alkali fusion, faujasite zeolite, rotary kiln, waste perlite dust.**

I. INTRODUCTION

In Japan, the exhaustion of natural resources has become a major concern, and effective utilization and recycling of unused resources has assumed great significance in recent times.

Perlite is a rhyolitic glass, primarily composed of silica (more than 70%) and alumina (13 %), and occurs in various types and forms in nature. Upon heating, perlite becomes a lightweight material, typically light gray to white in color, called “expanded perlite” [1]. Perlite is commercially low in price and is abundantly utilized in applications such as ceiling tiles, pipe insulation, gypsum wallboards, cryogenic insulation, and filter media [2]. However, expanded perlite waste (in subgrain form) is generated in various industrial production processes and is very difficult to store due to its high volatility. This perlite waste is a good source of reactive silica and therefore can be used in the synthesis of zeolites. Zeolites are a group of over 40 crystalline, hydrated aluminosilicate minerals with a structure based on a three-dimensional network of aluminum and silicon tetrahedra linked by shared oxygen atoms [3]. Due to their specific pore sizes and large surface areas, zeolites have potential for a wide range of applications such as molecular sieves, adsorbents, and catalysts.

In our previous studies, we succeeded in synthesizing highly functional faujasite-type zeolite by subjecting waste stone dust to alkali fusion [4]-[7]. However, an effective fusion process is necessary for the large amounts of stone dust generated annually. Therefore, in this study, we propose using a rotary kiln for facilitating the continuous alkali fusion of large amounts of waste perlite dust to synthesize zeolites.

II. EXPERIMENTAL

A. Waste Perlite Dust

Waste perlite dust was obtained from one of the plants in Japan. The chemical composition of raw perlite dust is shown in Table I, and the mineral composition, as measured by powder X-ray diffraction (XRD, Rigaku, MiniFlex600), is shown in Fig. 1. Waste perlite dust is primarily composed of SiO_2 (67.7 %) and Al_2O_3 (17.5 %) in amorphous phases, which is enough to synthesize zeolite. Some impurities such as CaO, K_2O, Fe_2O_3 and Cl, are also confirmed to be present in perlite dust.

TABLE I: CHEMICAL COMPOSITION OF WASTE PERLITE DUST

	SiO_2	Al_2O_3	CaO	K_2O	Fe_2O_3	Cl
Content (wt.%)	67.7	17.5	1.7	8.4	4.6	0.1

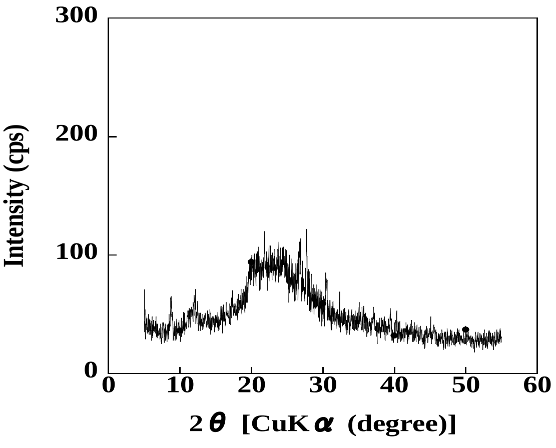

Fig. 1. XRD patterns of waste perlite dust.

B. Rotary Kiln

A rotary kiln was used for alkali fusion in this study. Fig. 2 shows the photographs of the rotary kiln and Table II lists the

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specifications for the same.

Fig. 2. Photographs of the rotary kiln used in the experiment.

TABLE II: SPECIFICATIONS OF THE ROTARY KILN

Raw material input		7 kg/h
Core tube dimensions	Core pipe length	1560 mm
	Inner diameter	150 mm
	Effective heating width	700 mm
Heat source		Electrical
Rotational speed		64 – 256 rpm
Angle of inclination		~ 5 °
Maximum temperature		1500 °C

C. Experimental Procedure

The following operations were carried out to as part of the current study:

The effect of NaOH addition on alkali fusion to synthesize zeolite was examined. Waste perlite dust and NaOH powder were mixed in weight ratios of 1: 0.5, 1:0.8, and 1:1 to prepare three different mixtures. Each of these mixtures was charged into the rotary kiln. The heating temperature of the rotary kiln was set at 380 ^{o}C, the inclination angle at 2^{o}, the rotational speed at 80 rpm, and the retention time in the kiln at 30 min.

The effect of the collection point in the rotary kiln on alkali fusion to synthesize zeolite was examined. The mixture with a mixing ratio of 1: 1 was charged into the rotary kiln at 450 ^{o}C, and after 30 min of operation, the fused dust was collected from three points in the rotary kiln, as shown in Fig. 3. The inclination angle, rotation speed, and retention time are the same as mentioned above.

The mineral composition of the collected samples was analyzed by XRD. The solubility of Si and Al in the fused sample was estimated by adding 0.1 g of the fused sample to 10 mL of 1 M HCl solution, and shaking it for 6 h. After shaking, the Si and Al concentrations in the filtrate were measured using an atomic absorption spectrophotometer (AAS, Perkin Elmer, AAnalyst200), and their solubility was calculated.

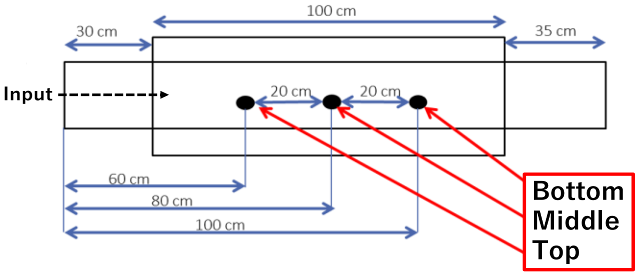

Fig. 3. Collection points in rotary kiln.

Next, to synthesize zeolite from the fused material, 0.5 g of the fused material was added to 20 mL of distilled water, and shaken for 24 h. After shaking, it was heated for 12 h at 80 °C in an oil bath, following which the solid was filtered and dried overnight in a drying oven at 60 °C to obtain the resulting product. The product was analyzed by XRD, and its CEC was measured by the method reported by Wajima *et al.* [8].

In addition, the effect of solid/liquid ratio, (i.e., the fused dust/distilled water ratio) on the synthesis of zeolite from the fused dust was examined. 0.1 to 1 g of the fused dust was added to 2 mL of distilled water, and shaken for 12 h to prepare the precursor of zeolite. After shaking, it was heated for 6 h at 80 °C in the oil bath. After heating, the solid was filtered and dried overnight in a drying oven at 60 °C to obtain the resulting product. The precursors and products were analyzed by XRD to examine the synthesis condition of the faujasite zeolites.

III. RESULTS AND DISCUSSION

Fig. 4 shows the photographs of raw perlite dust, alkali-fused dust, and the end product. Fig. 5 shows the photograph of the dust fused with NaOH (in 1:1 ratio) using the rotary kiln. While waste perlite is a fine powder in brown color as shown in Fig. 4(a), the alkali-fused dust, after passing through the kiln, turns into blue-colored grains, as shown in Fig. 4(b), and the end product after zeolite synthesis is the white-colored powder shown in Fig. 4(c). The dust fused with NaOH in the rotary kiln, shown in Fig. 5, is in the form of ball-like grains.

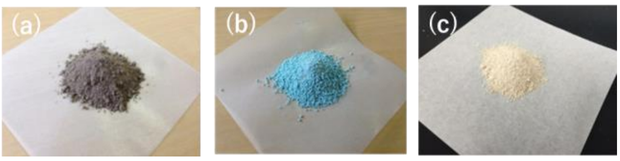

Fig. 4. Photographs of (a) raw perlite dust, (b) alkali-fused dust, and (c) end product (faujasite zeolite).

Fig. 5. Photograph of the dust fused with NaOH (1:1) using the rotary kiln.

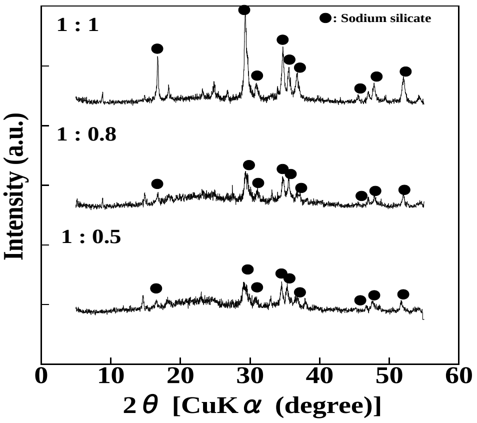

Fig. 6. XRD patterns of the alkali-fused dust with addition of different amounts of NaOH.

Fig. 6 shows the XRD pattern of the alkali fusion samples with different amounts of NaOH addition, and Table III shows the solubility of Si and Al in the fused samples. From Fig. 6, peaks of sodium silicates which have high solubility are confirmed for all mixture ratios, while those of NaOH cannot be confirmed in any of the XRD patterns. It may be inferred that all the added NaOH has reacted with silicate to form sodium silicate. Table III indicates that the amounts of dissolved Si and Al greatly increase as compared with raw dust (no NaOH). The amount of dissolution increases as the amount of added NaOH increases, due to the formation of sodium silicate.

TABLE III: SOLUBILITY OF SI AND AL IN THE ALKALI-FUSED DUST WITH DIFFERENT ADDITION OF NAOH

NaOH addition	Solubility (g/g)	
	Si	Al
Raw dust (1:0)	0.003	0.004
1:0.5	0.063	0.025
1:0.8	0.082	0.038
1:1	0.129	0.052

Fig. 7 shows the XRD pattern of the product synthesized from samples with different amounts of NaOH addition, and Table IV shows the CEC of the product. Peaks of faujasite-type zeolite are confirmed in all the samples. The peaks of faujasite and the CEC increase as the added amount of NaOH increases, due to the high solubility of the fused dust. Table IV also provides details for the commercially available faujasite-type zeolite, Molecular Sieves 13X, also known as MS-13X (Wako, Japan). The CEC of the product obtained from the fused dust with dust to NaOH in 1:1 ratio, is about half of the CEC of MS-13X zeolite.

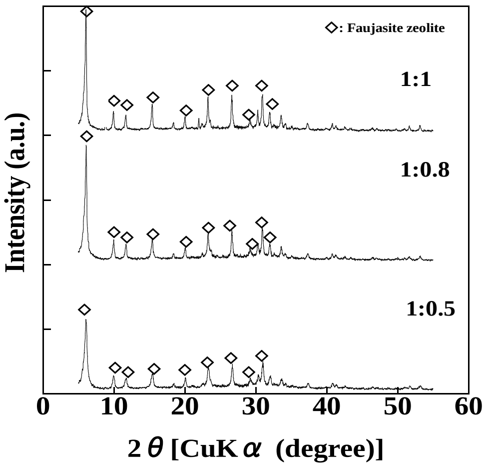

Fig. 7. XRD patterns of the product synthesized from alkali-fused dust with addition of different amounts of NaOH.

TABLE IV: CATION EXCHANGE CAPACITY OF THE PRODUCT SYNTHESIZED FROM THE ALKALI-FUSED DUST WITH ADDITION OF DIFFERENT AMOUNTS OF NAOH

NaOH addition	CEC (mmol/g)
Raw dust (1:0)	0.15
1:0.5	1.13
1:0.8	1.42
1:1	1.49
MS-13X	3.20

Fig. 8 shows the XRD pattern of the alkali fusion sample obtained at different positions of the rotary kiln, and Table V shows the solubility of Si and Al. Peaks of sodium silicate are also confirmed at all collection points. With increased retention time (from top to bottom), the solubility of Si and Al in the fused dust increases.

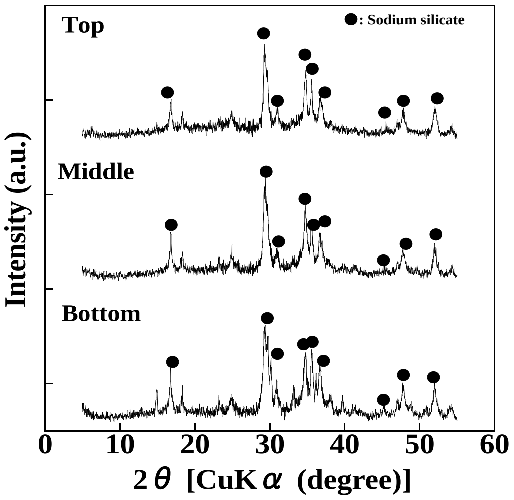

Fig. 8. XRD patterns of the alkali-fused dust at different points in rotary kiln.

TABLE V: SOLUBILITY OF SI AND AL IN THE ALKALI-FUSED DUST AT DIFFERENT PINTS IN ROTARY KILN

Position	Solubility (g/g)	
	Si	Al
Top	0.097	0.036
Middle	0.126	0.049
Bottom	0.127	0.051

Fig. 9 shows the XRD pattern of the product synthesized from the samples obtained at different positions of the rotary kiln, and Table VI shows the CEC of the products. Peaks of faujasite-type zeolite are confirmed for all the samples and are almost of the same magnitude. It may be further observed from Table IV that the CECs of the products obtained at the middle and bottom collection points are higher than that of the product obtained at the top collection point. It is considered that alkali fusion at points lower than the middle collection point is adequate to synthesize faujasite zeolite from the dust.

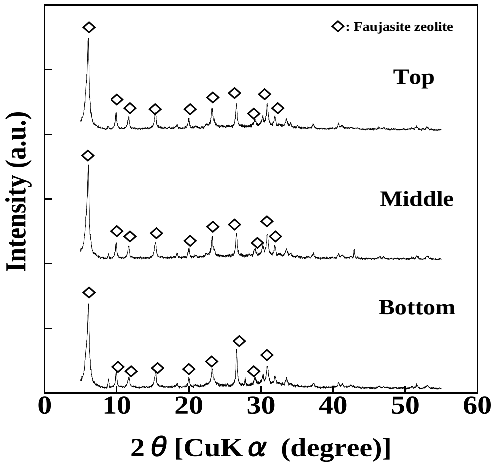

Fig. 9. XRD patterns of the product synthesized from alkali-fused dust at different points of collection of the rotary kiln.

TABLE VI: CATION EXCHANGE CAPACITY OF THE PRODUCT SYNTHESIZED FROM THE ALKALI-FUSED DUST AT DIFFERENT COLLECTION POINTS OF ROTARY KILN

Position	CEC (mmol/g)
Top	0.28
Middle	1.42
Bottom	1.45

Fig. 10 shows the XRD pattern of the precursors after shaking the fused salt in distilled water with the solid/liquid ratio of 0.05 to 0.5 g/mL, and Table VII shows the concentrations of Si and Al in the solution after shaking. Regardless of the solid/liquid ratios, the precursors are observed to be in the amorphous phase. With increasing solid/liquid ratio, concentrations of both Si and Al in the solution after shaking also increase, due to the increased amounts of soluble contents from the addition of fused dust.

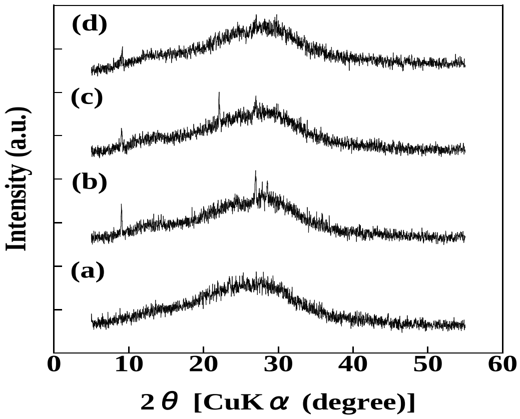

Fig. 10. XRD patterns of the precursor after 12 h-shaking of the fused dust in distilled water: (a)0.05 g/mL, (b)0.125 g/mL, (c) 0.25 g/mL, (d) 0.5 g/mL.

TABLE VII: CONCENTRATIONS OF SI AND AL IN THE SOLUTION AFTER SHAKING

Solid/Liquid (g/mL)	Concentration (mg/L)	
	Si	Al
0.05	2425	62
0.125	6085	175
0.25	12303	414
0.5	26540	883

Fig. 11 shows the XRD pattern of the product samples with solid/liquid ratios of 0.05 to 0.5 g/mL, and Table VIII shows the concentrations of Si and Al in the solution after zeolite synthesis. While there are no new peaks in the product with the solid/liquid ratios of 0.05 g/mL and 0.125 g/mL, peaks of faujasite appear in the product with a solid/liquid ratio of 0.25 g/mL. Further, in the product with a solid/liquid ratio of 0.5 g/mL, the presence of a mixture of faujasite and hydroxysodalite is confirmed. It is worth observing that the magnitude of the peaks of faujasite in the product with 0.25 g/mL is higher than that with 0.5 g/mL. It was reported in an earlier research [9] that high sodium content in the solution with 0.5 g/mL promotes the formation of hydroxysodalite . While the concentrations of both Si and Al in the solution after synthesis in the case of 0.05 g/mL and 0.125 g/mL are almost same as those after shaking, they reveal a different trend in the case of 0.25 g/mL and 0.5 g/mL. Compared to their respective counterparts after shaking, the Si concentrations are higher but the Al concentrations are lower. This can be attributed to the formation of zeolite crystals.

From these results, a solid/liquid ratio of 0.25 g/mL can be considered best for zeolite production from the fused dust.

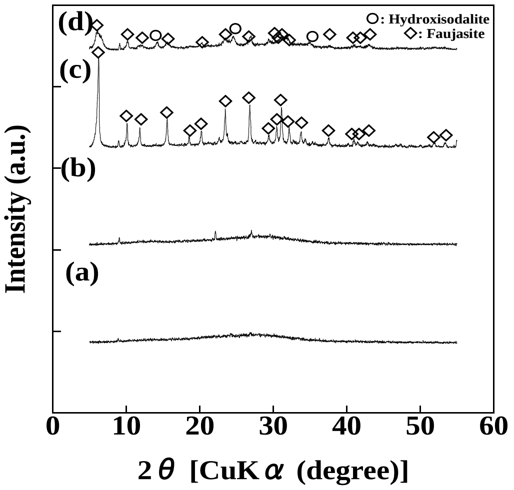

Fig. 11. XRD patterns of the product synthesized from alkali-fused dust: (a) 0.05 g/mL, (b) 0.125 g/mL, (c) 0.25 g/mL, (d) 0.5 g/mL.

TABLE VIII: CONCENTRATIONS OF SI AND AL IN THE SOLUTION AFTER ZEOLITE SYNTHESIS

Solid/Liquid (g/mL)	Concentration (mg/L)	
	Si	Al
0.05	2945	85
0.125	6160	194
0.25	13625	126
0.5	34380	161

IV. CONCLUSIONS

We have attempted to convert the waste perlite dust into soluble alkali-fused dust using a rotary kiln to synthesize faujasite zeolite. The rotary kiln facilitates continuous conversion of large amounts of perlite dust into fused materials with high solubility from which faujasite zeolite can be synthesized. This is because, the alkali fusion reaction occurs rapidly in a rotary kiln. Further, from our experiments, the fused dust/distilled water ratio of 0.25 g/mL is observed to be optimal for the synthesis of faujasite zeolite.

CONFLICT OF INTEREST

The authors have no conflicts of interest directly relevant to the content of this article.

AUTHOR CONTRIBUTIONS

T. Wajima conducted the research; S. Onishi analyzed the data; T. Wajima wrote the paper; all authors had approved the final version.

REFERENCES

[1] D. Shackley and M. J. Allen, “Perlite and the perlite industry: Minerals industry,” *Int. Inst. Min. Metall. Bull.*, vol. 1008, pp. 13-22, 1992.
[2] W. P. Bolen, “Perlite,” *Am. Ceram. Soc. Bull.*, vol. 73, pp. 117-118, 1994.
[3] R. M. Berrer, *Zeolites and Clay Minerals as Sorbents and Molecular Sieves*, London, U. K.: Academic Press, 1978.

[4] T. Wajima, “Synthesis of zeolite X from waste sandstone cake using alkali fusion method,” *Mater. Trans.*, vol. 49, pp. 612-618, 2007.
[5] T. Wajima, “Conversion of waste sandstone cake into crystalline zeolite X using alkali fusion,” *Mater. Trans.*, vol. 51, pp. 849-854, 2010.
[6] T. Wajima and Y. Ikegami, “Effect of a chelating agent on the synthesis of zeolitic materials from waste sandstone cake using alkali fusion,” *ARS Separatoria Acta*, vol. 5, pp. 76-87, 2007.
[7] T. Wajima, “Alkali fusion synthesis of zeolitic materials from waste dehydrated cake discharged from recycling of construction waste soil,” *Nat. Resour.*, vol. 8, pp. 300-305, 2017.
[8] T. Wajima, M. Haga, K. Kuzawa, H. Ishimoto, O. Tamada, K. Ito, T. Nishiyama, R. T. Downs, and J. F. Rakovan, “Zeolite synthesis from paper sludge ash at low temperature (90℃) with addition of diatomite,” *J. Hazard. Mater.*, vol. 132, pp. 244-252, 2006.
[9] D. W. Breck, *Zeolite Molecular Sieves*, New York: USA, 1984.

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