Available online at www.sciencedirect.com

SciVerse ScienceDirect

Ceramics International 38 (2012) 1741–1744

CERAMICS INTERNATIONAL

www.elsevier.com/locate/ceramint

Short communication

Material conversion from waste sandstone cake into cation exchanger using alkali fusion

Takaaki Wajima [*], Kenzo Munakata

Faculty of Engineering and Resource Sciences, Akita University, 1-1 Tegata-gakuen-cho, Akita 010-8502, Japan

Received 5 August 2011; received in revised form 13 September 2011; accepted 13 September 2011
Available online 17 September 2011

Abstract

An inorganic cation exchanger was synthesized from waste sandstone cake using the alkali fusion method. We used two starting materials: one was the original cake and the other was leached cake, which was prepared from the original cake by acid-leaching with 1 M HCl solution. Each starting material was mixed with NaOH powder (the weight ratio of NaOH/sandstone = 1.6) and then heated at 600 °C for 1 h to make a fused material. This fused material was then added to distilled water and agitated for one day, then heated at 80 °C, 120 °C, and 160 °C for 8 h in reaction bombs under autogenous pressure in order to synthesize the cation exchanger. From the original cake, a mixture of zeolite-X and hydroxysodalite was synthesized at 80 °C, hydroxysodalite alone was synthesized at 120 °C, and a mixture of hydroxysodalite and tobermorite was synthesized at 160 °C. From the leached cake, zeolite-X alone was synthesized at 80 °C, a mixture of zeolite-X and hydroxysodalite was synthesized at 120 °C, and the hydroxysodalite alone was synthesized at 160 °C. By increasing the synthesis temperature, the cation exchange capacity (CEC) of the product from both cakes decreased, and at each synthesis temperature the product from the leached cake had a higher CEC than did the original cake. The product with the highest CEC was the zeolite-X alone synthesized from the leached cake at 80 °C, which had a CEC of 230 cmol/kg.

Keywords: A. Powders: chemical preparation; C. Chemical properties; D. Clays; Inorganic cation exchanger

1. Introduction

Effective use and recycling of resources are important issues in the 21st century. During quarrying, waste stone cake is discharged as an industrial waste. The amount of cake is 50 million tons per year in Japan. Although part of the waste is used as an artificial aggregate or in some minor applications, a large part of it is dumped at landfills. In recent years, however, it has become more difficult to dispose of stone cake due to the lack of landfill sites. In Japan, furthermore, the Basic Law for Establishing a Recycling-Based Society and other laws to promote the effective use of resources have been established and improvements in recycling construction waste materials and by-products is required. Since the stone cake is viewed as construction sludge, or waste, research and development has been conducted on its utilization in civil engineering as a foundation improvement or riverbed material [1]. However, there have been no studies on its chemical conversion into functional materials.

In a previous study, we converted waste porcelain into a zeolitic material by the alkali fusion method and succeeded in synthesizing crystalline zeolite-13X with a high cation exchange capacity (CEC) [2]. By alkali fusion, most of the crystalline phases could be converted into soluble phases and transformed into zeolite crystals. This is a new way of converting the inorganic waste into functional materials. One of the waste stone cakes, sandstone cake, is mainly composed of quartz, feldspar, and calcite, having a high SiO_2 and Al_2O_3 content. However, since most types of SiO_2 and Al_2O_3 are in crystalline phases, it is difficult to dissolve them into an alkali solution by a hydrothermal reaction to be converted into functional inorganic materials such as zeolite.

In this study, we attempted to convert waste sandstone cake into inorganic materials with CEC using alkali fusion. The crystalline phases in the cake were converted into the precursor with soluble phases by alkali fusion, and were then used to synthesize an inorganic cation exchanger.

---

[*] Corresponding author. Tel.: +81 18 889 2748; fax: +81 18 889 2748.
E-mail address: wajima@gipc.akita-u.ac.jp (T. Wajima).

doi:10.1016/j.ceramint.2011.09.028

2. Materials and methods

2.1. Raw materials

The waste sandstone cake was obtained from a quarry in Kitakyushu, Fukuoka Prefecture, Japan. We used two starting materials: one was the original waste sandstone cake and the other was a leached cake. The original cake (25 g) was treated with 1 M HCl solution (100 mL) for 6 h, and then the solid was separated by filtration to obtain a leached cake with low Ca content. Before the experiment, both cakes were washed with distilled water and dried in an oven at 60 °C overnight.

The chemical compositions of the original and leached cakes determined by X-ray fluorescent spectrometry (XRF) (ZSX101e, Rigaku) are listed in Table 1, and the mineralogical components of the original and leached cakes determined by X-ray diffraction spectroscopy (XRD) (XRD-DSC-XII, Rigaku) are shown in Fig. 1. The original and leached cakes were mainly composed of SiO_2 and Al_2O_3 in the form of silicate and aluminosilicate minerals such as quartz, albite, muscovite, and clinochlore. The original cake also contained CaO and CO_2, thought to have originated in carbonate, mainly calcite, while the leached cake contained a slight amount of CaO and no CO_2 due to the removal of the calcite phase in the cake by acid-leaching, as shown in Fig. 1(b). It is noted that the contents of Si and Al in the leached cake were higher than those in the original cake.

2.2. Zeolite synthesis using alkali fusion

The experimental procedure is shown in Fig. 2. First, 10 g of both the original and leached cakes were mixed with 16 g of NaOH and ground to obtain a homogeneous mixture. This mixture was then heated in a nickel crucible, which is stable for alkali fusion in this experiment, in air at 600 °C for 1 h. The resultant fused mixture was cooled to room temperature and ground again. Then, 0.5 g of the mixture was added to 2 mL of distilled water in a 10 mL tube made of polymethylpentene. Aging was conducted with vigorous agitation by a reciprocal shaker at room temperature. After a 24 h agitation, the slurry was poured into reaction bombs and heated at 80 °C, 120 °C, and 160 °C for 8 h in an electric oven under autogenous pressure. After heating, the solid product was filtered, washed with distilled water, and dried in a drying oven at 60 °C overnight. The phases of the product were analyzed by XRD and the morphologies of the product were observed by a scanning electron microscope (SEM, SM-200, TOPCOM).

Table 1
Chemical composition of waste sandstone cake and the leached cake (mass%).

	Waste sandstone cake	Leached cake
SiO_2	38.9	65.3
Al_2O_3	12.2	19.1
CaO	6.9	0.4
MgO	2.7	4.7
Na_2O	1.4	2.0
K_2O	1.8	2.8
Fe_2O_3	3.1	4.8
CO_2	32.6	–
Total	99.6	99.1

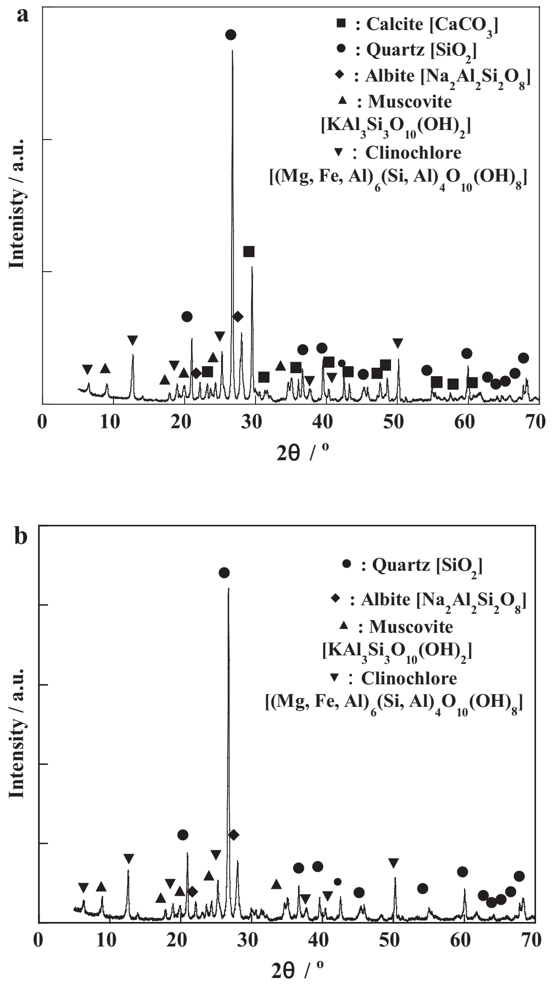

Fig. 1. Powder X-ray diffraction patterns of (a) waste sandstone cake and (b) leached cake.

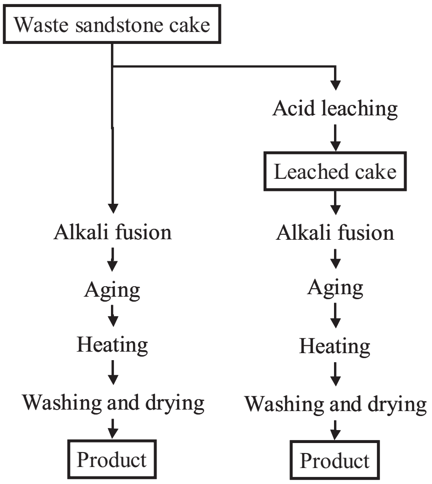

Fig. 2. Experimental procedure for material conversion from waste sandstone cake.

2.3. CEC of the product

The CEC of the product was measured by the modified Schörrenberg's method [3]. The exchangeable cations in the product were replaced by NH_4^+ using 1 M ammonium acetate solution.

This process was repeated for three times at 20 min per exchange. The sample was then washed with 80% EtOH solution to remove excess salt. The NH_4^+ was then replaced by K^+ using 10% KCl solution for 20 min. This process was also repeated for three times. Finally, the NH_4^+ in the KCl solution was analyzed by the method described by Koyama et al. [4] to determine the CEC of the sample.

3. Results and discussion

Fig. 3 shows the X-ray diffraction patterns of the product synthesized from the original cake at (a) 80 °C, (b) 120 °C, and (c) 160 °C. It was confirmed that no mineral phases, including the original cake, were present in any of the obtained products, and zeolite-X, hydroxysodalite, and tobermorite were synthesized. This means that all mineral phases in the original cake can be converted into the zeolite and tobermorite phases through alkali fusion treatment. Different phases in the product were confirmed at each reaction temperature. The mixture of zeolite-X and hydroxysodalite was synthesized at 80 °C, hydroxysodalite alone was synthesized at 120 °C, and a mixture of hydroxysodalite and tobermorite was synthesized at 160 °C.

Fig. 4 shows the X-ray diffraction patterns of the product synthesized from the leached cake at (a) 80 °C, (b) 120 °C, and (c) 160 °C. It was confirmed that no mineral phases, including the leached cake, were present in any of the obtained products, and zeolite-X and hydroxysodalite were synthesized, which also means that all mineral phases in the leached cake can also be converted into the zeolite phase through alkali fusion treatment. Different phases in the product from the leached cake were confirmed at each reaction temperature, in comparison with those from the original cake. Zeolite-X alone was synthesized at 80 °C, the mixture of zeolite-X and hydroxysodalite was synthesized at 120 °C, and hydroxysodalite alone was synthesized at 160 °C. It is noted that tobermorite was not synthesized from leached cake at 160 °C due to the lower Ca content of the leached cake to create a tobermorite Ca–Si structure. Furthermore, single crystalline zeolite-X can be synthesized from leached ash at 80 °C. It has been reported that Ca ions have a higher affinity for silicate species than do Al ions to disturb the dissolution of Si into the alkali solution [5]. It may be considered that a higher Si content could be dissolved from the leached ash into the solution than it could with the original ash, to create single crystalline zeolite-X.

Fig. 5 shows the SEM photographs of the typical products synthesized from the original cake at (a) 80 °C, (b) 120 °C, and (c) 160 °C. Different morphologies of each product were observed. In the case of the product synthesized at 80 °C,

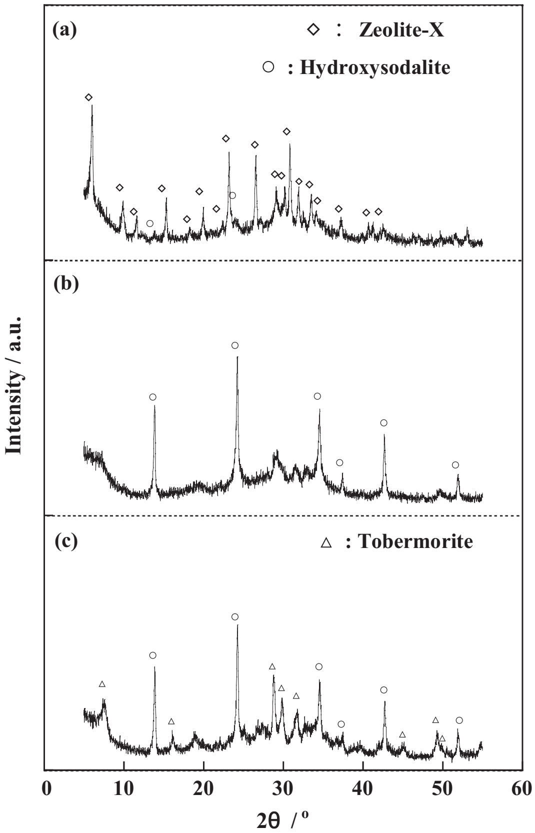

Fig. 3. Powder X-ray diffraction patterns of the product from original cake at (a) 80 °C, (b) 120 °C, and (c) 160 °C.

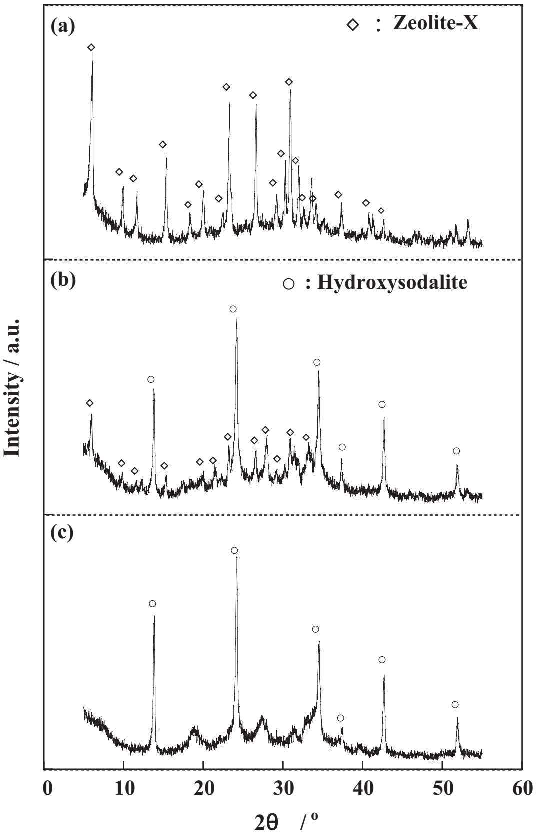

Fig. 4. Powder X-ray diffraction patterns of the product from leached cake at (a) 80 °C, (b) 120 °C, and (c) 160 °C.

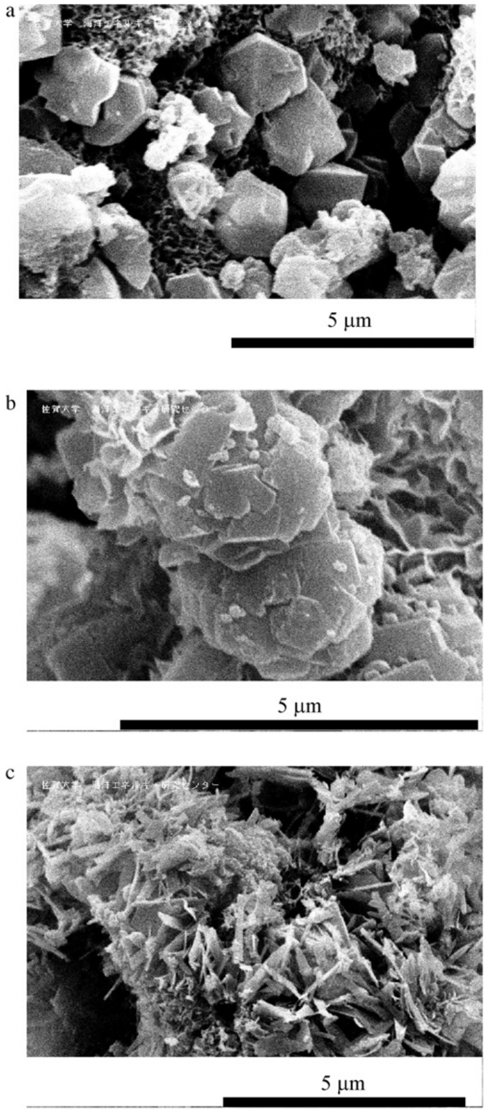

Fig. 5. Scanning electron photomicrographs of the typical product, which were synthesized from original cake at (a) 80 °C, (b) 120 °C, and (c) 160 °C.

octahedral crystals of zeolite-X can be observed in the product, as shown in Fig. 4(a). In the cases of the product synthesized at 120 °C and 160 °C, aggregate, hydroxysodalite, and plate-like tobermorite can be observed at 120 °C and 160 °C, respectively. Since zeolite-X was the metastable phase, zeolite-X was easily transformed into hydroxysodalite and tobermorite at temperatures higher than 100 °C.

Fig. 6 shows the cation exchange capacity of the product synthesized from the original and leached cake at 80–160 °C. The CEC of the product decreased with the increase in heating temperature, and the product of the leached cake was higher in CEC than that of the original cake. Hydroxysodalite has a lower CEC than zeolite-X and is easily synthesized due to the increase of heating temperature and Ca content. The product with the highest CEC was synthesized from the leached cake at 80 °C, and the CEC was 230 cmol/kg. It is noted that the CEC of commercial zeolite-13X (Wako) is 284 mmol/g, which is 1.23 times greater than that of the obtained product.

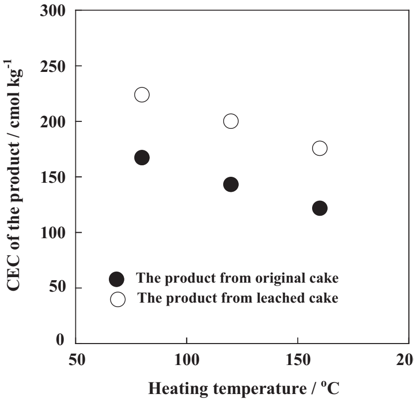

Fig. 6. Cation exchange capacity of the product synthesized from original and leached cake at 80–160 °C.

4. Conclusions

An inorganic cation exchanger can be synthesized from waste sandstone cake using the alkali fusion method. Zeolite-X, hydroxysodalite, and tobermorite were synthesized. For the original cake, the mixture of zeolite-X and hydroxysodalite was synthesized at 80 °C, hydroxysodalite alone was synthesized at 120 °C, and a mixture of hydroxysodalite and tobermorite was synthesized at 160 °C. For the leached cake, zeolite-X alone was synthesized at 80 °C, a mixture of zeolite-X and hydroxysodalite were synthesized at 120 °C, and hydroxysodalite alone was synthesized at 160 °C. Tobermorite was not synthesized from the leached cake at 160 °C, due to the removal of Ca content from the cake. The CEC of the product decreased with an increase in heating temperature, and the product of the leached cake was higher in CEC than that of the original cake because hydroxysodalite has a lower CEC than zeolite-X and is easily synthesized due to the increase of heating temperature and Ca content. The product with the highest CEC (230 cmol/kg) was zeolite-X alone, synthesized from the leached cake at 80 °C.

Acknowledgments

This study was supported by the TOSTEM Foundation for Construction Materials Industry Promotion and Mukai Science and Technology Foundation, for which we would like to express our gratitude.

References

[1] H. Tanaka, Recycle of surplus soil issued from road repairing and crushed stone plant, Inorg. Mater. 4 (1997) 475–482.

[2] T. Wajima, Y. Ikegami, Synthesis of crystalline zeolite-13X from waste porcelain using alkali fusion, Ceram. Int. 35 (2009) 2983–2986.

[3] Development of New Utilization of Materials, Natural Zeolite and its Utilization, No. 111 Committee, Japan Society for the Promotion of Science, Tokyo, 1994, pp. 318–325.

[4] M. Koyama, T. Hori, Y. Kitayama, IARC report, Kyoto University, vol. 2, 1976, 11–14.

[5] P. Catalfamo, G. Patane, P. Primerano, S.D. Pasquale, F. Corigliano, The presence of calcium in the hydrothermal conversion of amorphous aluminosilicates into zeolites: interference and removal, Mater. Eng. 5 (1994) 159–173.