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Synthesis of zeolitic materials from waste porcelain at low temperature via a two-step alkali conversion

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Abstract

An attempt was made to convert waste porcelain into zeolitic materials using a two-step alkali conversion. During the first step, under optimum conditions for both high Si extraction from the waste and residue with high cation exchange capacity (CEC), the concentration of Si extracted from the waste was ca. 26,000 mg/L, and the residue contained zeolitic (Na–P1, and hydroxysodalite) materials and residual phases (quartz, and mullite), which had high CEC (170 cmol/kg). In the second step, Na–A, Na–X, and Na–P1 zeolites were synthesized from the extracted solution during the first step, with addition of aluminate solution. With increasing Si/Al molar ratio of the solution, the product phase changed from Na–A → Na–X → Na–P1, and the Si content increased in the solution.

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1. Introduction

Unsold fired products from the ceramic industry are discharged as waste ceramics. A part of these are used as an artificial aggregate, cement production or other minor applications [1]. The remaining part of the waste ceramics is deposited at landfills. The limited capacity of the landfills causes social and environmental problems. An effective utilization would be to convert the waste into zeolitic materials.

Zeolites have gained a great deal of attention from the chemical industry. Zeolites are a group of over 40 crystalline, hydrate aluminosilicate minerals with a structure based on a three-dimensional network of an aluminum and silicon tetrahedral, linked by sharing oxygen atoms. Due to specific pore sizes and large surface areas, zeolites have the potential in a wide range of applications such as molecular sieves, adsorbents, and catalysts [2].

Zeolites occur in natural deposits, generally associated with the alternation of glassy volcanic rocks, or are synthesized from a wide variety of high Si and Al starting materials. Many researchers reported the synthesis of zeolites from kaolin, high silica bauxite, halloysite, interstratified illite-smectite, montmorillonite, bentnite, and incinerated ash [3–10].

Waste porcelain contains mainly SiO_2 and Al_2O_3 (>90%), which form crystalline substances (quartz and mullite) and amorphous glass, and has potential in the conversion to zeolitic material.

This study attempted to convert waste porcelain into useful zeolitic materials using a two-step alkali conversion at a low temperature (80 °C). The first step is the alkali conversion of powdered waste porcelain into a zeolitic material, and extraction of the Si content from waste porcelain into a NaOH solution at 80 °C. The second step is the synthesis of pure zeolites from the extracted Si with addition of an Al source. We determined the optimum condition for production of zeolitic material with high cation exchange capacity (CEC), and high Si extraction from waste porcelain, by varying alkali concentrations, the ratios of sample weight to volume of the alkali solution (*S*/*L*), and reaction time during the first step. Pure zeolite crystal was then synthesized from the extracted Si by addition of an aluminum solution at 80 °C in the second step.

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2. Experimental

2.1. Materials

The waste porcelain was ground by a mill. Particles less than 1 mm were sorted and washed with distilled water. Table 1 shows the chemical composition of powdered waste porcelain, determined by X-ray fluorescence spectrometry (XRF) (RIGAKU, ZSX101e). The porcelain mainly composed of SiO_2 and Al_2O_3, corresponding to 69.8 and 18.5 wt.%, respectively. Other oxides, such as Na_2O, K_2O, MgO, CaO, Fe_2O_3, and ZnO occurred in lesser amounts.

2.2. Si extraction from powdered waste porcelain and CEC of zeolitic residual

Raw materials were added to 0.5, 1, 2, 3, 4, 5, and 10 M NaOH solutions in a TPX tube, and the *S*/*L* were 1/10, 1/4, and 1/2. The tubes were heated at 80 °C for 0–24 h in a water bath. The solid residue (zeolitic residue) was filtered, washed with distilled water, and dried in the drying oven at 60 °C overnight. The characterization of the residues was assessed by X-ray powder diffractometer (XRD) (RIGAKU, XRD-DSC-XII) and scanning electron microscope (SEM) (TOPCOM, SM-200). The Si and Al concentrations in the filtrate were analyzed by ICP-AES (SHIMADZU, ICPS-7500).

The CEC of the zeolitic residue was measured by the modified Schöerrenberg's method [11] as follows. The exchangeable cations in the product were replaced by NH_4^+ using a 1 M ammonium acetate solution. This process was repeated three times. The sample was subsequently washed with 80% EtOH to remove excess salt. The NH_4^+ included in the samples was then replaced with 10% KCl solution three times. Finally, NH_4^+ extracted into the solution was analyzed by spectrophotometery (SHIMADZU, UV-mini-1240) using Koyama's method [12] to determine the CEC of the sample.

2.3. Synthesis of pure zeolite from extracted Si solution

Raw material (12.5 g) was added to a 4 M NaOH solution (50 mL), and heated at 80 °C for 12 h. At the end of the heating period, the reaction mixture was filtered, and the filtrate was diluted 50% with distilled water. This diluted solution (2 mL) and aluminate solution (1 mL) were mixed to adjust the Si/Al molar ratio between 0.5 and 4.0 in the TPX tube. The mixed solution was heated at 80 °C for 24 h. The resulting reaction mixture was filtered, and the solid product was washed with distilled water, and dried in a drying oven at 60 °C overnight. The characterization of the product was carried by XRD and SEM. The Si and Al concentrations in the filtrate were analyzed by ICP-AES.

Table 1
Chemical composition of powdered waste porcelain

	wt.%
SiO_2	69.8
Al_2O_3	18.5
Na_2O	0.6
K_2O	6.2
MgO	0.3
CaO	3.0
Fe_2O_3	0.7
ZnO	0.7
Total	99.8

3. Results and discussion

3.1. Si extraction and zeolitic residual in the first step

The optimum conditions for Si extraction from waste porcelain and the CEC of zeolitic residue, as well as the effects of the NaOH concentration and *S*/*L* ratio on Si extraction and the CEC of the residue were investigated. Fig. 1 shows Si and Al concentrations extracted from waste porcelain into alkali solutions after 24 h reaction at 80 °C. In all cases, the Si concentration is higher than the Al concentration. The Si concentration increases with increasing NaOH concentration, and becomes almost constant in NaOH solutions over 3–4 M. The extracted concentration of Si at *S*/*L* = 1/10 is lower than those at *S*/*L* = 1/4 and 1/2, and the curve for *S*/*L* = 1/2 is almost same with that for *S*/*L* = 1/4. It is considered that the extraction of Si from porcelain is saturated at *S*/*L* = 1/4 in 3–4 M NaOH solutions. The condition for the highest extraction of Si from the waste is to treat with NaOH solution over 3–4 M at *S*/*L* = 1/4 or 1/2.

Fig. 2 shows the CEC of the zeolitic residue obtained from waste porcelain after 24 h reaction at 80 °C. The CEC of the residues increases to 4 M NaOH solutions, and had a maximum of ca. 160 cmol/kg in 4–5 M NaOH at *S*/*L* = 1/10 or 1/4. The extraction of Si increases with increasing NaOH concentration, and is saturated at *S*/*L* = 1/4. It is considered that the large amount of remained phases (not zeolitic phases) in waste

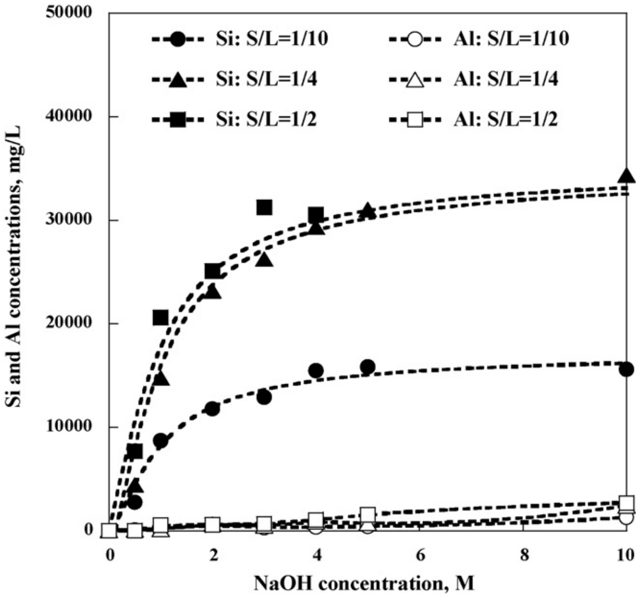

Fig. 1. Si and Al concentrations extracted from waste porcelain into alkali solutions after 24 h reaction at 80 °C.

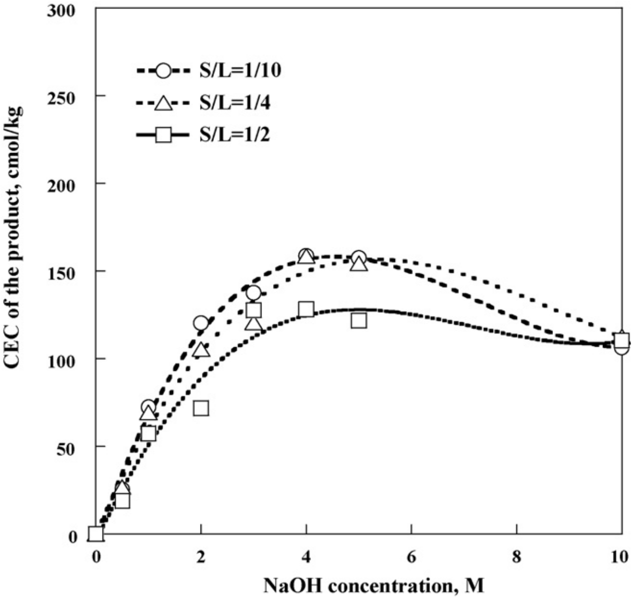

Fig. 2. CEC of the zeolitic residue obtained from waste porcelain after 24 h reaction at 80 °C.

porcelain at low NaOH concentration or at $S/L = 1/2$ causes the low CEC of the residue. The condition for the residue with highest CEC is to treat with 4–5 M NaOH solution at $S/L = 1/10$ or 1/4.

It is preferable for industrial application to treat the waste with low NaOH concentration solution. The best NaOH concentrations and S/L ratios for both high extraction of Si from the waste, and a zeolitic residue with a high CEC, is to treat the waste porcelain with 4 M NaOH solution at $S/L = 1/4$.

We investigated the time dependency for Si extraction and CEC of the zeolitic residues. Fig. 3 shows Si and Al concentrations extracted into the 4 M NaOH solution at $S/L = 1/4$, and the CECs of the obtained residue during the alkali reaction at 80 °C. Throughout the alkali reaction, the Si concentration is always higher than Al concentration, and becomes constant after 12 h. The CEC of the residual becomes constant after 8 h.

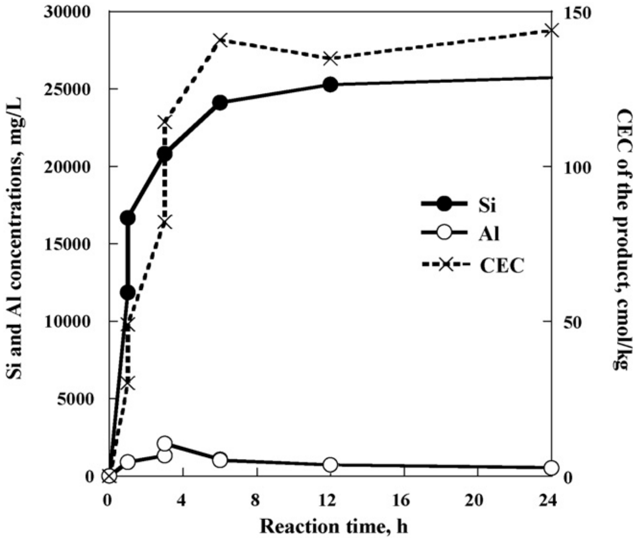

Fig. 3. Si and Al concentrations extracted into 4 M NaOH solution at $S/L = 1/4$, and the CECs of the obtained residue during the alkali reaction at 80 °C.

The best reaction period for both high Si extraction and zeolitic residue with high CEC is to treat the waste porcelain for 12 h.

From these results, optimum conditions inferred for the first step are that waste porcelain is to be treated with a 4 M NaOH solution and $S/L = 1/4$ for 12 h.

We subsequently determined the properties of the residue obtained under these optimum conditions. Fig. 4 shows X-ray diffraction patterns of raw material and the zeolitic residue obtained at the optimum conditions. The mineral phases of the raw material are mainly quartz and mullite as crystalline substances, and an amorphous glass phase. On the other hand, the mineral phases in the product are Na–P1 and hydroxysodalite as new product phases, and quartz and mullite as remained phases, but the amorphous glass phase is diminished.

Fig. 5 shows SEM photographs of raw material and the product obtained at the optimum conditions. Although raw materials are fragments of porcelain as shown in Fig. 5(a), the products are an agglomerate of synthetic zeolite crystal and residues of porcelain such as needle-like mullite crystals, as shown in Fig. 5(b).

It is considered that the amorphous glass phase dissolves into the alkali solution in order to crystallize the zeolite phases. Also, a high Si content (ca. 26,000 mg/L) remained in the solution, as shown in Fig. 3.

3.2. Synthesis of pure zeolite during the second step

A high concentration of Si (ca. 26,000 mg/L) could be extracted under optimum conditions during first step. During

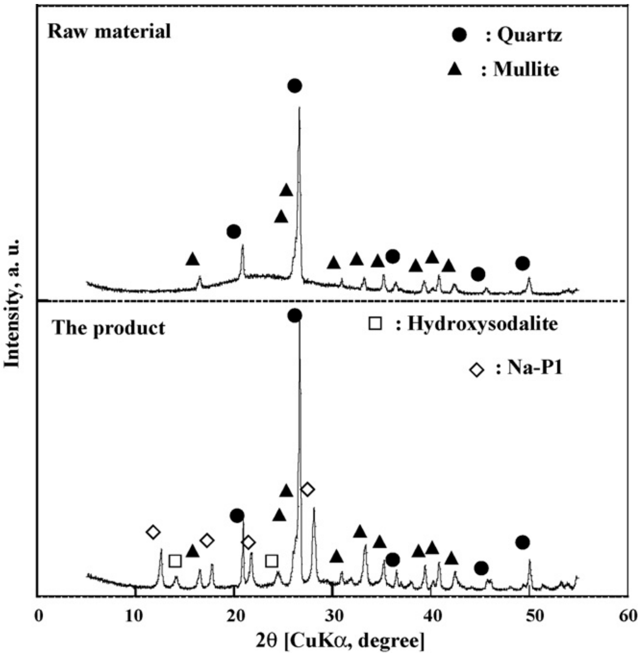

Fig. 4. X-ray diffraction patterns of raw material and the products obtained at the optimum condition.

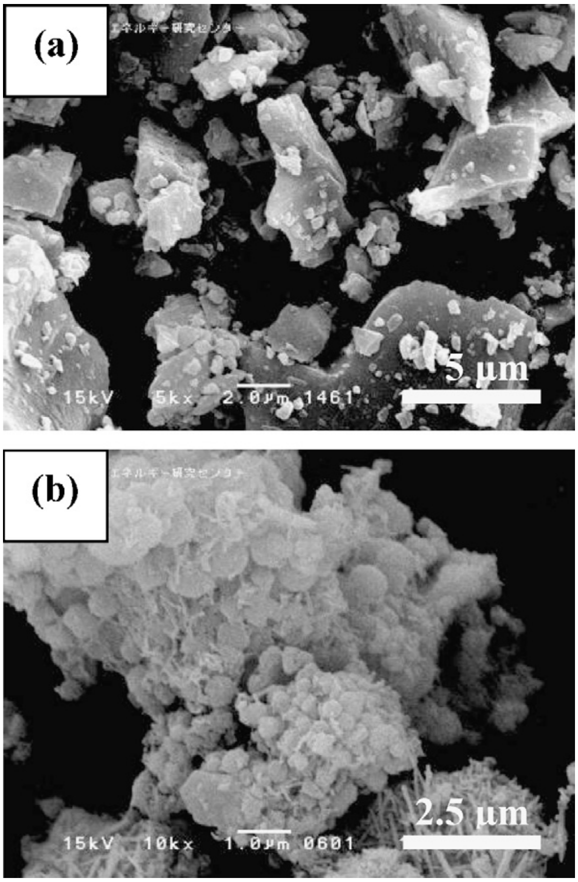

Fig. 5. SEM photographs of (a) raw material, and (b) the product obtained at the optimum condition.

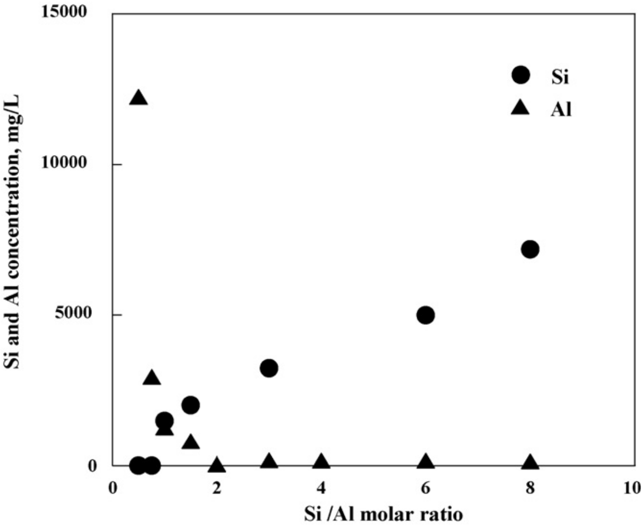

Fig. 6. Si and Al concentrations remaining in the solution after 24 h reaction at 80 °C.

the second step, we tried to synthesize pure zeolite from the extracted Si solution from the first step. The extracted solution of Si was diluted with distilled water to ca. 13,000 mg/L to decrease the Na concentration. An aluminate solution was added to this solution, and aluminum silicates precipitated in the mixed solution. Incubation at 80 °C of this aluminum silicate precipitate with the left-over solution resulted in the synthesis of zeolite.

The amounts of Si and Al in the solution after 24 h reaction depend on added amount of Al. Fig. 6 shows the Si and Al concentrations which remained in the solution after 24 h reaction at 80 °C. In the case of $Si/Al < 1$, a high Al content remains in the solution, while little Si remains. In the range of $1 < Si/Al < 2$, Al decreases and Si starts to increase in the solution. This region is the range whereby a high Al content changes to a high Si content remaining in solution. In the case where $Si/Al > 2$, a high Si content remained in the solution, and hardly any Al remained.

The different product phases are synthesized on each condition. Fig. 7 shows the X-ray diffraction patterns of products synthesized from a mixture of extracted Si and aluminate solution with various Si/Al molar ratios. Na–A, Na–X, and Na–P1 zeolites were synthesized at Si/Al ratios ranging from 0.5 to 8. Na–A was synthesized from a solution with Si/Al ratio < 1.0, and a mixture of Na–A, Na–X, and Na–P1 was synthesized from solutions with Si/Al ratio = 1.0–2.0. Finally, Na–P1 was synthesized from the solution with Si/Al ratio > 2.0.

Each zeolite phase crystallizes with a different morphology. Fig. 8 shows SEM photographs of products synthesized from a mixture of extracted Si and aluminate solution with (a) Si/Al = 0.5, (b) Si/Al = 1.0, and (c) Si/Al = 2.0. In the case of (a), only Na–A ($Na_{12}Al_{12}Si_{12}O_{48}\cdot 27H_2O$) was synthesized. Na–A crystallizes in a typical cubic form, and is a member of the LTA group. Its structural framework comprises 4- and 8-membered rings. In the cases of (b) and (c), a mixture of Na–A, Na–X ($Na_{22}Si_{26}Al_{22}O_{96}\cdot 55H_2O$), and Na–P1 ($Na_6Si_{10}Al_6O_{32}\cdot 12H_2O$), only the latter was synthesized. Na–X crystallizes in a typical

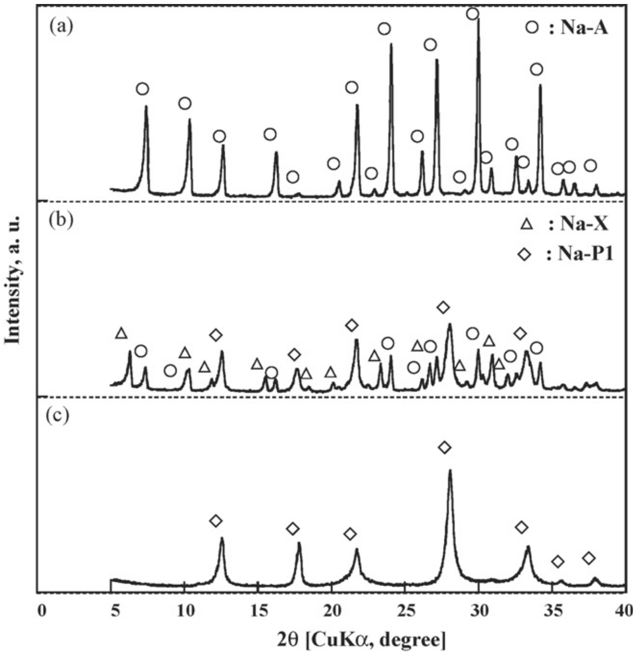

Fig. 7. X-ray diffraction patterns of the product synthesized from extracted Si and aluminate solution with various Si/Al molar ratios. (a) Si/Al = 0.5, (b) Si/Al = 1.0, (c) Si/Al = 2.0.

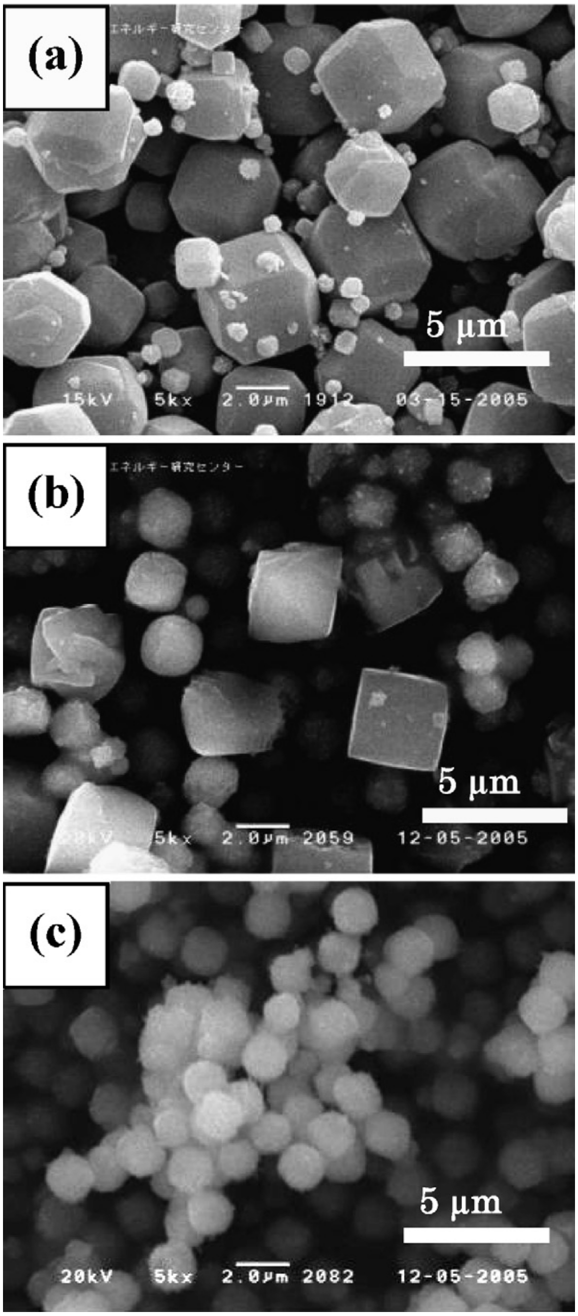

Fig. 8. SEM photographs of the product synthesized from extracted Si and aluminate solutions with (a) Si/Al = 0.5, (b) Si/Al = 1.0, and (c) Si/Al = 2.0.

octahedral form, and is a member of the faujasite group. Its structural framework consists of 4- and 8-membered rings. Na–P1 is a member of the gismondine group. Its structural framework comprises 4- and 8-membered rings. Note that the order of Si/Al ratios in zeolite structure is Na–A (1:1) < Na–X (13:11) < Na–P1 (5:3). Hollman et al. [13] reported that zeolite was synthesized from a silica extract from coal fly ash and aluminate, and the obtained phases are Na–A at Si/Al = 0.8, Na–X at Si/Al = 1.8, and Na–P1 at Si/Al = 2.0. The order of Si/Al molar ratio for zeolite is Na–A < Na–X < Na–P1. It is assumed that the product phase changes from Na–A to Na–X, and finally to Na–P1 with increasing Si/Al ratios of the alumino silicate gel, due to increase of the Si/Al ratio in the mixed solution.

4. Conclusions

This study attempted to convert waste porcelain into useful materials at 80 °C using a two-step alkali conversion.

In the first step, the optimum condition for both high Si extraction from the waste, and the residue with a high CEC was with 4 M NaOH, *S*/*L* = 1/4 after 12 h incubation. At this optimum condition, the concentration of Si extracted from the waste was ca. 26,000 mg/L, and the residue contained zeolitic (Na–P1 and hydroxysodalite) materials and residual phases (quartz and mullite), which had a high cation exchange capacity (160 cmol/kg).

During the second step, Na–A, Na–X, and Na–P1 zeolite were synthesized from the extracted solution of the first step, with addition of an aluminate solution. Na–A was synthesized from the solution with Si/Al molar ratio < 1, and Al remained in the solution. A mixture of Na–A, Na–X, and Na–P1 was synthesized from the solution with 1 < Si/Al molar ratio < 2, which was the range whereby a high Al content changed to a high Si content remaining in solution. Na–P1 was synthesized from the solution with a Si/Al molar ratio > 2, and a high Si remained in the solution. With increasing Si/Al molar ratios of the solution, the product phase changed from Na–A → Na–X → Na–P1, and the remaining Si content increased in the solution.

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