

Zeolite synthesis from paper sludge ash at low temperature (90 °C) with addition of diatomite

Takaaki Wajima^{a,*}, Mioko Haga^a, Keiko Kuzawa^a, Hiroji Ishimoto^b, Osamu Tamada^a, Kazuhiko Ito^c, Takashi Nishiyama^a, Robert T. Downs^d, John F. Rakovan^e

^a Graduate School of Human and Environmental Studies, Kyoto University, Sakyo-ku, Kyoto 606-8501, Japan

^b Access Network Service Systems Laboratories, Nippon Telegraph and Telephone Corp., Tsukuba, Ibaraki 305-0805, Japan

^c Faculty of Management Information, Taisei Gakuin University, Sakai, Osaka 587-8555, Japan

^d Department of Geosciences, University of Arizona, Tucson, AZ, USA

^e Department of Geology, Miami University, Oxford, OH 45056, USA

Received 1 September 2004; received in revised form 26 September 2005; accepted 27 September 2005

Available online 4 November 2005

Abstract

Paper sludge ash was partially converted into zeolites by reaction with 3 M NaOH solution at 90 °C for 24 h. The paper sludge ash had a low abundance of Si and significant Ca content, due to the presence of calcite that was used as a paper filler. Diatomite was added to the NaOH solution to increase its Si content in order to synthesize zeolites with high cation exchange capacity. Diatomite residue was filtered from solution before addition of ash. The original ash without addition of diatomite yielded hydroxysodalite with a cation exchange capacity ca. 50 cmol/kg. Addition of Si to the solution yielded Na-P1 (zeolite-P) with a higher cation exchange capacity (ca. 130 cmol/kg). The observed concentrations of Si and Al in the solution during the reaction explain the crystallization of these two phases. The reaction products were tested for their capacity for PO₄³⁻ removal from solution as a function of Ca²⁺ content, suggesting the formation of an insoluble Ca-phosphate salt. The product with Na-P1 exhibits the ability to remove NH₄⁺ as well as PO₄³⁻ from solution in concentrations sufficient for application in water purification. Both NH₄⁺ and PO₄³⁻ removal showed little variation with pH between 5 and 9. Alternative processing methods of zeolite synthesis, including the addition of ash to an unfiltered Si–NaOH solution and addition of a dry ash/diatomite mixture to NaOH solution, were tested. The third process yielded materials with lower cation exchange capacity due to formation of hydroxysodalite. The second process results in a product with relatively high cation exchange capacity, and reduces the number of processing steps necessary for zeolite synthesis.

© 2005 Elsevier B.V. All rights reserved.

Keywords: Zeolite; Paper sludge ash; Diatomite; Cation exchange capacity; Hydroxysodalite; Na-P1

1. Introduction

During the manufacture of recycled paper products, paper sludge is generated as an industrial waste. Over 3 million tonnes of sludge is discharged per year in Japan, and approximately 8 and 2 million tonnes in the United States and the United Kingdom, respectively [1,2]. The amount is increasing annually. The sludge consists of organic fibers, inorganic clay-sized materials, and about 60% water, and is incinerated to paper sludge ash by burning out the organic materials, thereby reducing its waste volume. Although some part of the ash is used as cemented fills,

lightweight aggregates in the construction industry, and in other minor applications [3,4], the major part is dumped at landfill sites. The large daily output and the limited landfill capacity have caused social and environmental problems. One possible and effective alternative is to convert the ash into zeolite absorbents for environmental applications, such as water purification, and soil conditioning [5–7].

Zeolites are a group of over 40 crystalline, hydrated aluminosilicate minerals with structures based on a three-dimensional network of (Al, Si)O₄ tetrahedra that contain exchangeable alkali or alkaline earth cations [8]. Zeolites occur in natural deposits, generally associated with the alteration of glassy volcanic rocks, or are synthesized from a wide variety of high-Si and Al starting materials. Paper sludge ash contains amorphous and crystalline phases formed by incineration, and is compara-

* Corresponding author. Tel.: +81 955 20 2190; fax: +81 955 20 2191.
E-mail address: wajima@ioes.saga-u.ac.jp (T. Wajima).

ble to volcanic ash. Accordingly, the ash can be converted into zeolites [9,10].

In the past, clay minerals such as kaolinite were used for paper filler, but recently calcite has increasingly replaced kaolinite as a filler. Subsequently, incinerated ash has a higher Ca-content, in the form of anorthite ($\text{CaAl}_2\text{Si}_2\text{O}_8$) and gehlenite ($\text{Ca}_2\text{Al}_2\text{SiO}_7$). Furthermore, the decreasing use of silicate minerals as paper fillers has resulted in a lower concentration of Si in the ash. Correspondingly, the Si/Ca ratio is decreased. The low Si content of the ash makes it difficult to convert it into zeolites, or at least into more desirable zeolite phases. Zeolite formation from other ash sources, for example, coal fly ash, has also been investigated [11–14]. It is reported that amorphous SiO_2 particles added to a coal fly ash resulted in the formation of phillipsite, with high cation exchange capacity (CEC), in NaOH solution [15].

Diatomite is a fine-grained, biogenic siliceous sediment, and is available in large quantities at low cost [16]. It consists essentially of amorphous silica derived from opalescent frustules of diatoms, and has a fine porous structure with low density. Diatomite easily dissolves in basic solutions. There are examples of the synthesis of zeolites from diatomite itself [17,18], but the direct synthesis from diatomite lacks Al sources or template agents.

In this work, we synthesize zeolites at low temperature (90°C) from paper sludge ash, with addition of diatomite. To our knowledge, no previous effort has been made to use diatomite as an additive Si source in synthesizing zeolite from the paper sludge ash. The resulting zeolites exhibit cation exchange properties, and selectively sorb certain cations, such as NH_4^+ . Also, it has been reported that Ca^{2+} contained in the original paper sludge ash reacts with phosphoric acid to form apatite-like materials, which removed PO_4^{3-} from solution [6]. Therefore, we aim to obtain a material suitable for water purification, which contains zeolite phases and soluble Ca in the product. We present here the chemical reaction of paper sludge ash with diatomite, the CEC of the end product, and demonstrate the removal capacity for NH_4^+ and PO_4^{3-} from aqueous solution by sorption and precipitation with Ca, respectively.

2. Experimental methods and results

2.1. Raw materials

Paper sludge ash was obtained from a paper company in Fuji, Japan. The composition of the ash, determined by scanning electron microscopy (SEM) (Hitachi, S-2600 H) equipped with energy dispersive spectrometry (EDS) (Horiba, EX-200), is listed in Table 1. The ash is mainly composed of SiO_2 , Al_2O_3 and CaO in the form of amorphous matter and the minerals gehlenite ($\text{Ca}_2\text{Al}_2\text{SiO}_7$) and anorthite ($\text{CaAl}_2\text{Si}_2\text{O}_8$), determined by X-ray diffraction (XRD) (Rigaku, Rint-2200U/PC-LH) (Fig. 1). The ash has a low SiO_2 and a high CaO content compared to other similar materials. Such a composition is not favorable for the synthesis of zeolites [19].

Diatomite occurs in nature in two types of geological environments, marine and lacustrine. The sample used in this study has a seawater origin, and was obtained from the deposits located in

Table 1
Chemical composition of paper sludge ash and diatomite

| Oxide (wt.%) | Paper sludge ash | Diatomite |
|-------------------------|------------------|-----------|
| SiO_2 | 35.9 | 92.8 |
| Al_2O_3 | 22.8 | 3.4 |
| CaO | 33.2 | 0.3 |
| Na_2O | 0.6 | 0.5 |
| K_2O | – | 0.5 |
| MgO | 4.5 | 0.5 |
| Fe_2O_3 | 0.9 | 2.0 |
| TiO_2 | 2.2 | – |
| Total | 100.1 | 100.0 |

These data were analyzed by EMAX ENERGY package. The analytic errors are <5%.

Takanosu, Akita prefecture in Japan. The diatomite was ground to a size smaller than 30 mesh and dried at 60°C . The chemical composition of the diatomite determined by SEM-EDS is listed in Table 1. The original sample contains 50–75% water. The dried sample is composed of diatom frustules that precipitate in an amorphous silica form, but it also contains some rock fragments. The fragments are mainly made of feldspar and quartz (Fig. 1) derived from surrounding rocks. Diatomite readily dissolves in a basic solution. Fig. 2 shows Si concentrations in solution as a function of reaction time during the dissolution of diatomite in 3 M NaOH solution at 90°C . In all cases, dissolution of the amorphous silica of diatomite is nearly complete within 1 h. Hence, the dissolution time for diatomite is taken as 1 h hereafter.

2.2. Zeolite synthesis from the ash in diatomite solution

We prepared 3 M NaOH solution with Si concentrations of 0, 5, 10 and 20 g/L by addition of 0, 16, 32 and 64 g of diatomite respectively, at 90°C for 1 h. The solutions were filtered and cooled to room temperature. Paper sludge ash (100 g) was then

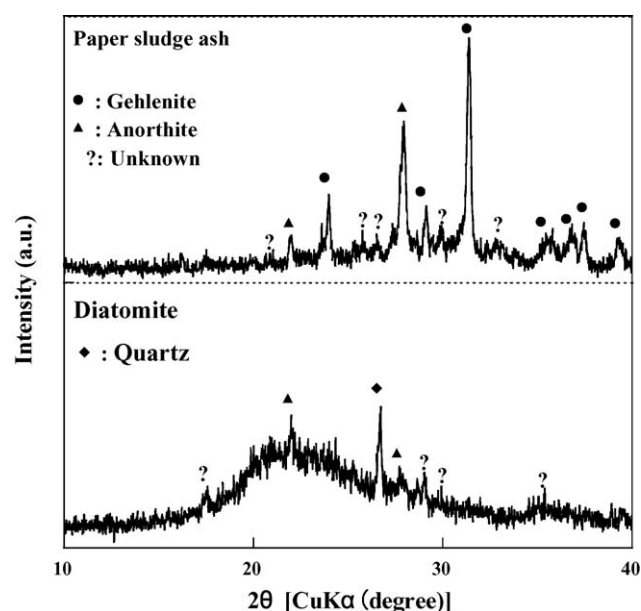


Fig. 1. Powder X-ray diffraction patterns of paper sludge ash and diatomite.

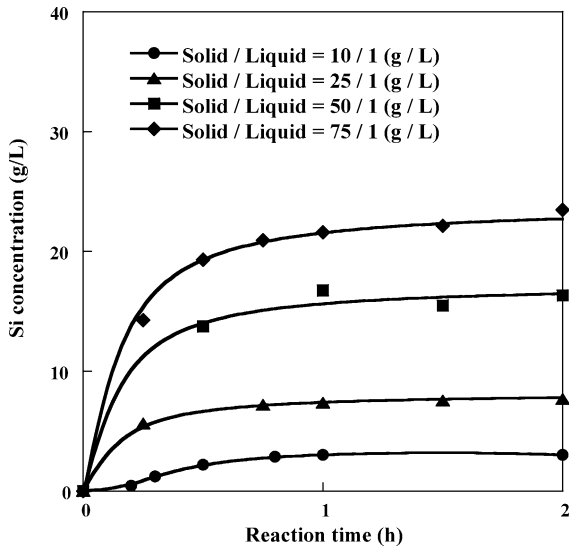


Fig. 2. The concentration of Si dissolved from diatomite in 3 M NaOH solutions at 90 °C, as a function of reaction time. The solid (diatomite)/liquid (3 M NaOH solution) ratios are inset.

added to 3 M NaOH solutions (1 L) in a 1-L Erlenmeyer flask (made of poly methyl pentene) with a dimroth condenser, and the mixture (slurry) was continuously stirred at 90 °C for 24 h and then filtered. The solid product was washed with water, that had been purified through a reverse osmosis membrane using a Millipore Mill-Q Labo system, and dried at 60 °C overnight in a drying oven. The end products were examined by XRD and SEM (Hitachi, S-2600 H).

XRD patterns of the end product from the four initial Si concentrations are shown in Fig. 3. Anorthite is absent from the products, indicating that it completely dissolves in the alkaline

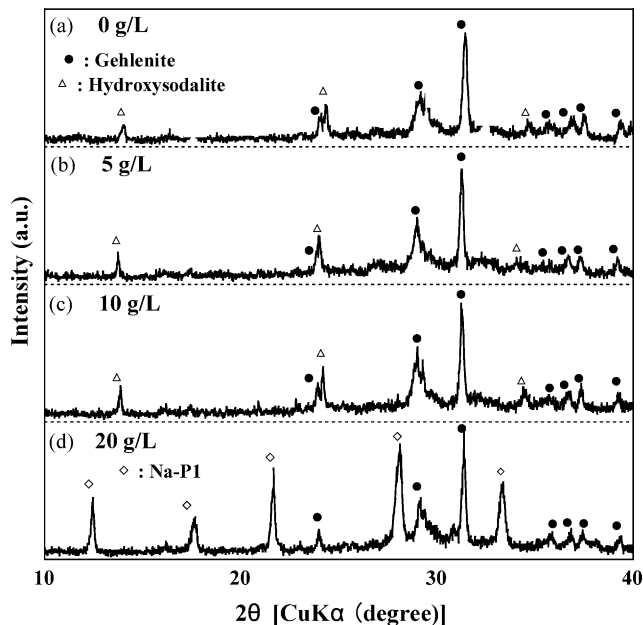


Fig. 3. Powder X-ray diffraction patterns of products synthesized in 3 M NaOH solutions with initial Si concentrations of (a) 0 g/L, (b) 5 g/L, (c) 10 g/L and (d) 20 g/L, adjusted by the addition of diatomite.

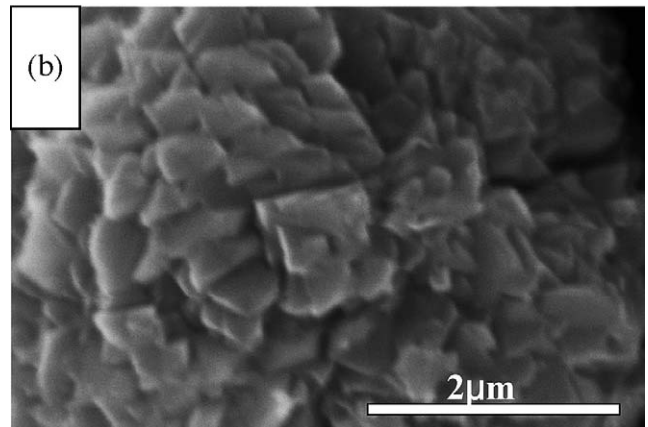
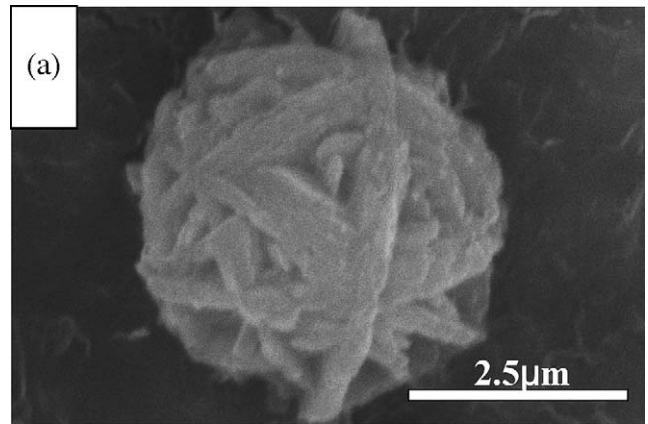


Fig. 4. Scanning electron photomicrographs of (a) hydroxysodalite and (b) Na-P1 synthesized in 3 M NaOH solution with initial Si concentrations of 0 and 20 g/L, respectively.

solution, whereas gehlenite does not seem to be affected. The zeolite phase formed is hydroxysodalite at low Si concentrations, 0, 5 and 10 g/L, and Na-P1 at high Si concentration, 20 g/L.

Fig. 4 shows SEM photomicrographs of (a) hydroxysodalite and (b) Na-P1 synthesized in 3 M NaOH with Si concentrations of 0 and 20 g/L, respectively. Hydroxysodalite ($\text{Na}_6\text{Al}_6\text{Si}_6\text{O}_{24}\cdot 8\text{H}_2\text{O}$, space group $P\bar{4}3n$, $a = 8.9 \text{ \AA}$) is a member of the sodalite group. The framework structure is composed of four- and six-membered rings of SiO_4 and AlO_4 tetrahedra. Na-P1 ($\text{Na}_6\text{Si}_{10}\text{Al}_6\text{O}_{32}\cdot 12\text{H}_2\text{O}$, space group $I\bar{4}$, $a = 10.0 \text{ \AA}$), also known as zeolite-P, is a member of the gismondine group. The framework is built of four- and eight-membered rings. It is noted that the eight-membered rings of Na-P1 are larger than the six-membered rings of hydroxysodalite, and the Si/Al ratio is greater in Na-P1 (Si/Al = 5:3) than in hydroxysodalite (Si/Al = 1:1).

Five milliliters aliquots of each slurry were removed at varying time intervals (every 1 h initially) to monitor the reaction process over a period of 24 h. The aliquots were filtered and the filtrates were analyzed by inductively coupled plasma spectrometry (ICP) (SEIKO, SPS4000) to determine the concentration of Si and Al. The concentrations of Si and Al in the solution for different initial concentrations of Si are shown as a function of the reaction time in Fig. 5. In the Si free starting solution (Fig. 5(a)),

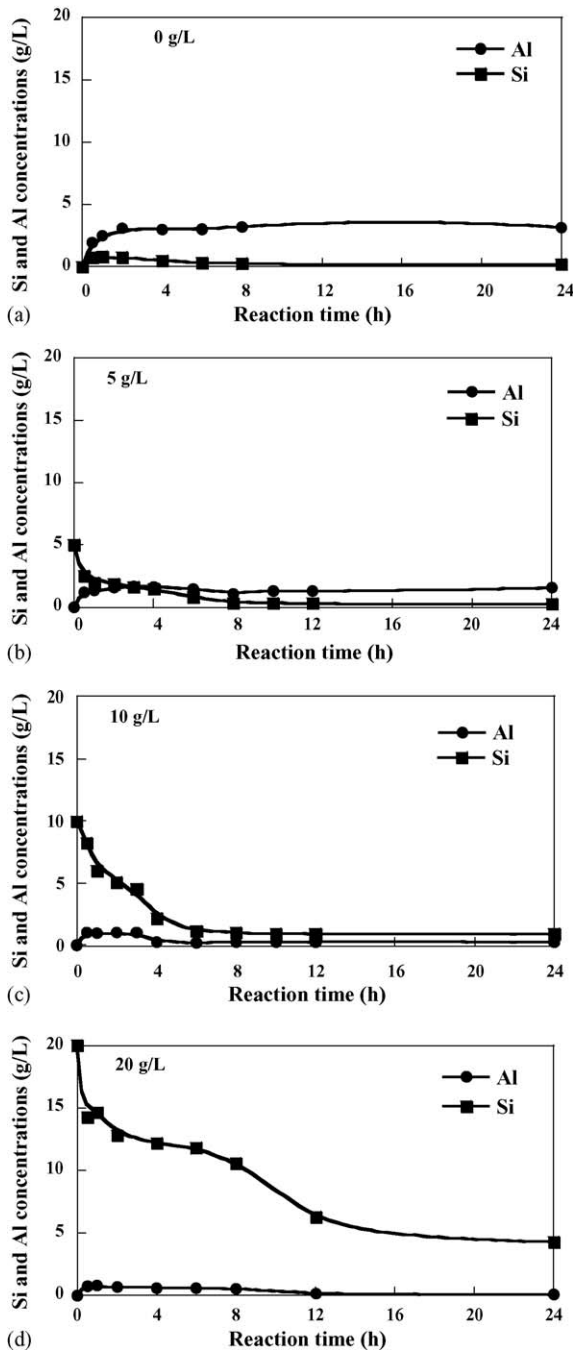


Fig. 5. Si and Al concentration curves in 3 M NaOH solution as a function of reaction time, for initial Si concentrations of (a) 0 g/L, (b) 5 g/L, (c) 10 g/L and (d) 20 g/L.

the concentration of Si increases initially after introduction of paper sludge ash, and thereafter decreases to zero leaving solely Al in the solution after 24 h. In the starting solution with 5 g/L Si (Fig. 5(b)), the concentration of Si decreases gradually to zero. Also, the concentration of Al increases initially, reaching a steady state after 2 h. The residual Al in solution is lower than in the former case, indicating that a larger amount of aluminosilicate precipitates as zeolite. In the 10 g/L Si starting solution both Si and Al precipitate out of the solution, so that an initial Si concentration of 10 g/L marks the point below which the Al/Si

ratio of the solution is greater than 1 and above which it is less than 1. Finally, for initial Si concentration of 20 g/L, Si always exceeds Al in solution throughout the entire reaction and the resulting zeolite phase changes from hydroxysodalite to Na-P1 [20,21]. Excess Si in the 20 g/L solution (Fig. 5(d)) after reaction of paper sludge ash indicates that further addition of diatomite is not required.

2.3. Cation exchange capacity (CEC) of end products

The CEC of end products was measured by the modified Schöerrenberg method [22]. The exchangeable cations in the product were replaced by NH_4^+ using 1 M ammonium acetate solution. This process was repeated three times for 20 min per exchange, yielding a total exchange time of 1 h. The sample was then washed with 80% ethanol 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 three times. Finally, NH_4^+ in the solution was analyzed by the method of Koyama et al. [23] to determine the CEC of the sample.

The cation exchange capacity of the end products versus initial concentrations of Si is shown in Fig. 6. The CEC increases with increasing initial concentration of Si in solutions reacted with paper sludge ash. Without diatomite addition, the CEC of the end product is about 50 cmol/kg, increasing to 130 cmol/kg in the end product formed from solution with a Si concentration of 20 g/L.

2.4. Interactions with NH_4^+ and PO_4^{3-}

The interactions with NH_4^+ and PO_4^{3-} were examined using three typical samples: (1) raw paper sludge ash, (2) product-0 synthesized without diatomite addition and (3) product-20 synthesized from solution with initial Si concentration of 20 g/L. NH_4^+ and PO_4^{3-} solutions with concentrations of 10 mg/L prepared with NH_4Cl and Na_2HPO_4 , respectively, were used to determine the capacity of the treated and untreated ash to

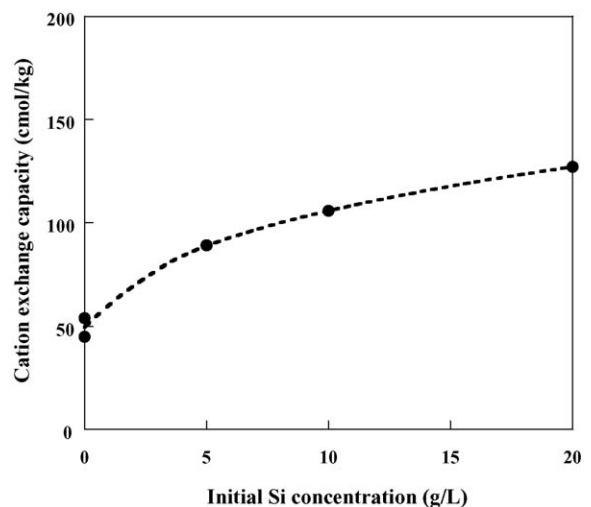


Fig. 6. Cation exchange capacity (CEC) of end products as a function of initial Si concentration in solutions reacted with paper sludge ash.

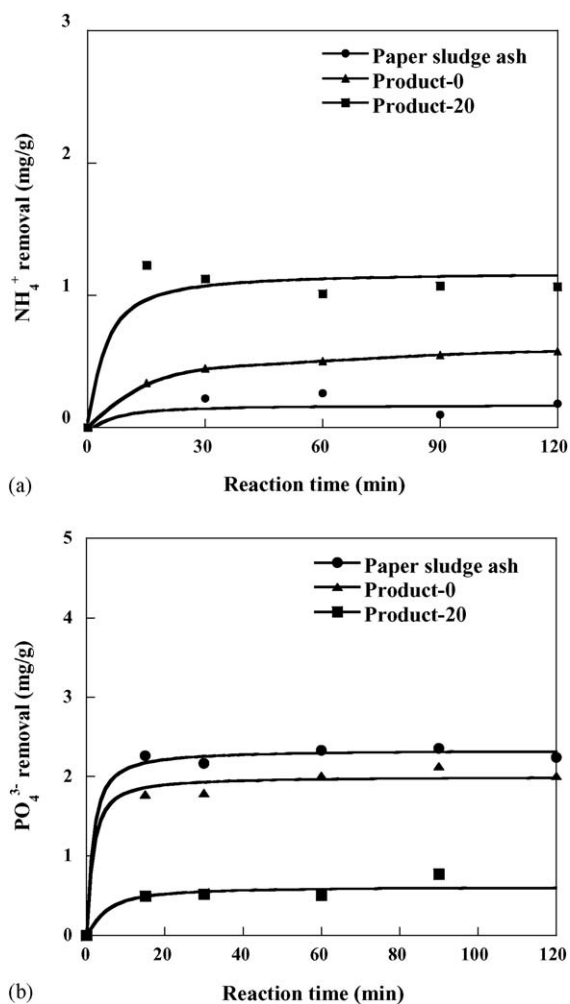


Fig. 7. Removal of (a) NH_4^+ and (b) PO_4^{3-} by paper sludge ash, product-0 and product-20 as a function of reaction time. Initial concentrations of NH_4^+ and PO_4^{3-} in the solution are 10 mg/L. One gram of sample was added to 200 mL of solution. The pH was adjusted to 7.5 by the addition of dilute HCl solution.

remove these ion complexes. One gram of sample was added to 200 mL of each solution. While stirring the pH moved naturally to 10.5 due to the basicity of the NaOH reacted ashes and was adjusted to 7.5 by the addition of dilute HCl solution (0.1–1 M). A 2 mL aliquot of suspension was removed every 30 min and filtered. The concentration of NH_4^+ in the filtrate was determined by the method of Koyama et al. [23], and the concentration of PO_4^{3-} by the method of Ishibashi and Tabushi [24].

The removal of (a) NH_4^+ and (b) PO_4^{3-} from the solution as a function of reaction time is shown in Fig. 7. The initial concentration of NH_4^+ and PO_4^{3-} in the solution, 10 mg/L, is an unusually high concentration compared to river or lake waters. The rate of removal of NH_4^+ and PO_4^{3-} was initially rapid but plateaued after roughly 30 min. The decreasing order of removal capacity for NH_4^+ is product-20 > product-0 > paper sludge ash, which reflects the variation of CEC. The removal of PO_4^{3-} follows an opposite trend compared to NH_4^+ (paper sludge ash > product-0 > product-20).

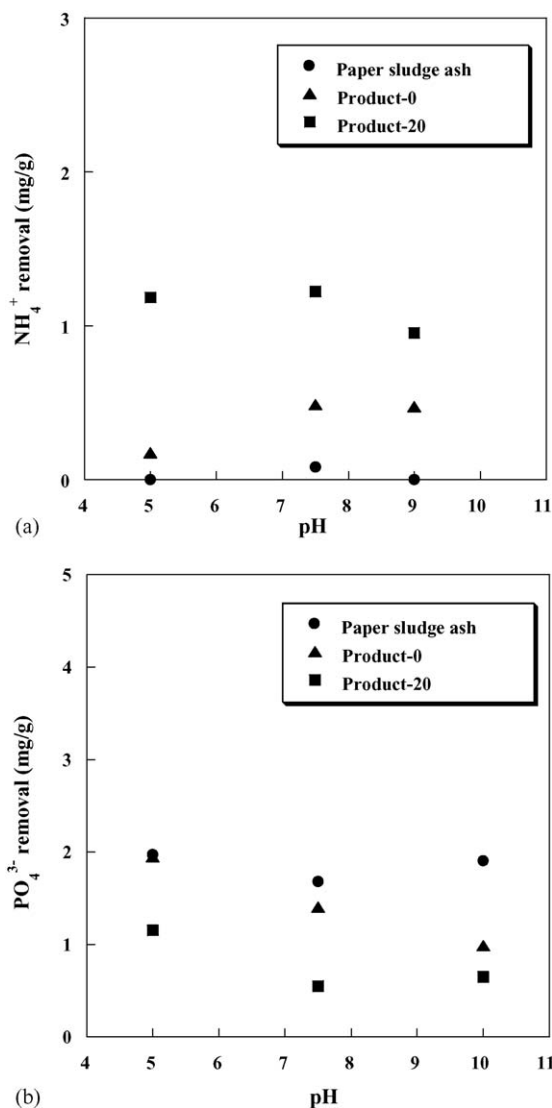


Fig. 8. Removal of (a) NH_4^+ and (b) PO_4^{3-} by paper sludge ash, product-0 and product-20 as a function of pH. The experimental conditions are the same as in Fig. 7 and the pH was adjusted to 5, 7.5 and 10 by the addition of dilute HCl.

The influence of pH on NH_4^+ and PO_4^{3-} removal is shown in Fig. 8. The NH_4^+ uptake by paper sludge ash remains low throughout the pH range 5–9. NH_4^+ uptake by product-0 increases only slightly between pH 5 and 7.5 and remains constant through pH 9. Finally, product-20 shows similar NH_4^+ uptake at pH 5 and 7.5 while slightly decreased at pH 9. PO_4^{3-} removal also shows little variation with pH between 5 and 10 (Fig. 8(b)). Both the paper sludge ash and product-20 show a minimum removal at pH 7.5. Product-0 exhibits a slight decrease between pH 5 and 10.

In order to examine the relationship between Ca^{2+} associated with end products of the zeolite synthesis reactions and the removal of PO_4^{3-} , the total Ca^{2+} released from the paper sludge ash samples was measured. A 100 mg aliquot of each sample was added to 10 mL of 1 M ammonium acetate solution at room temperature for 20 min. The concentration of Ca^{2+} in the solution was analyzed by ICP. Table 2 lists the amount of released (soluble) Ca^{2+} . The concentration of Ca^{2+} is low in product-20

Table 2
CECs and the amount of released (soluble) Ca^{2+} from three materials

| Material | CEC (cmol/kg) | The amount of released Ca^{2+} (g/kg) |
|------------------|---------------|--|
| Paper sludge ash | 15.0 | 167.6 |
| Product-0 | 54.0 | 163.6 |
| Product-20 | 127.0 | 114.2 |

compared with paper sludge ash and product-0, and the order of released Ca^{2+} correlates with PO_4^{3-} removal capacity.

2.5. Simplification of diatomite addition

In the process of diatomite addition, the residue of diatomite, which was mainly composed of rock fragments, was filtered out of the 3 M NaOH solution before the addition of paper sludge ash. Two non-filtration experiments were also carried out in an attempt to simplify the procedure. In each experiment 64 g diatomite, equivalent to 20 g/L of Si in the previous experiment, and 100 g paper sludge ash were used. In the first unfiltered experiment the diatomite was added to a 3 M NaOH solution, and was stirred at 90 °C for 1 h, then the ash was added to the solution. In the second experiment, the diatomite was dry mixed with the ash, and the powder mixture was added to the 3 M NaOH solution. For both experiments the solid reaction products, the concentrations of Si and Al in the alkaline solution, and the CECs of the products were monitored as a function of reaction time.

XRD patterns of the solid products obtained from the three experiments as a function of time are shown in Fig. 9 (a) addition of ash to a filtered Si–NaOH solution, (b) addition of ash to an unfiltered Si–NaOH solution, and (c) addition of a dry ash/diatomite mixture to a NaOH solution. In all three cases, gehlenite remains in the end product but anorthite is dissolved. Quartz, which originates from rock fragments, is detected in the latter two experiments. Na-P1 is synthesized in all three cases, however Na-P1 zeolite crystallizes earlier in experiments 2 and 3. In addition, hydroxysodalite crystallizes with Na-P1 in experiment 3.

The evolution of cation exchange capacity of the products as a function of reaction time is shown in Fig. 10 for the three experiments. The rate of cation exchange by the products of experiments 2 and 3 is faster than that of experiment 1, in the early stages of the reaction. This is consistent with a faster rate of zeolite crystallization for the two non-filtration experiments. However, in the final stage of CECs for the products of experiments 1 and 2 are comparable (120–130 cmol/kg). The formation of hydroxysodalite may be related to the lower CEC in experiment 3.

The concentrations of Si and Al in 3 M NaOH solution as a function of reaction time for the latter two experiments are shown in Fig. 11. The decrease of concentration of Si is initially fastest for experiment 2, in which ash is added to unfiltered Si–NaOH solutions. The delay in the decrease of Si during experiment 1 is clearly observed by the plateau between 2 and 8 h in the Si concentration curve (Fig. 5(d)). This corresponds to the delay

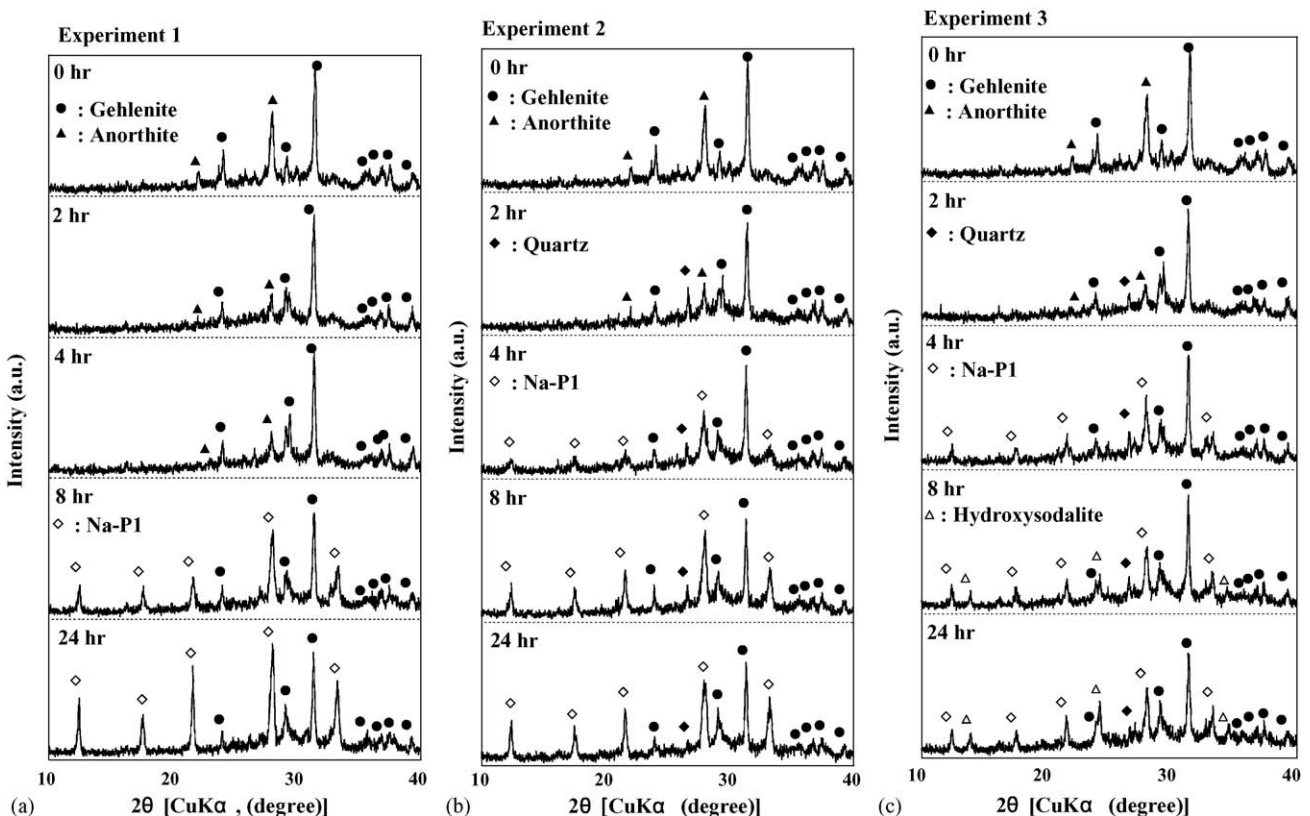


Fig. 9. Powder X-ray diffraction patterns of products as a function of reaction time for: (a) experiment 1, addition of ash to a filtered Si–NaOH solution; (b) experiment 2: addition of ash to an unfiltered Si–NaOH solution; (c) experiment 3, addition of dry ash/diatomite mixture to a NaOH solution.

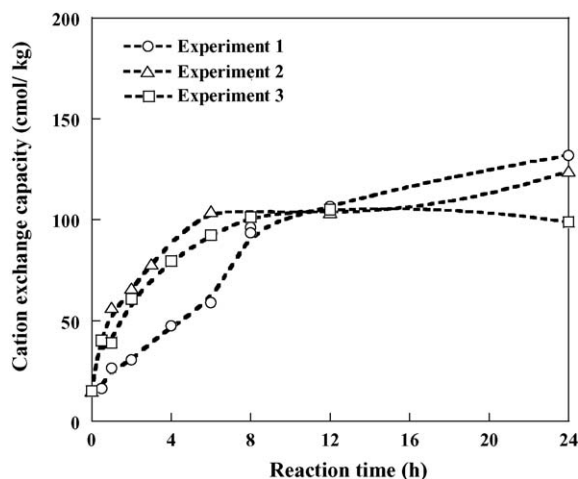


Fig. 10. Cation exchange capacity of products as a function of reaction time for: experiment 1, addition of ash to a filtered Si–NaOH solution; experiment 2, addition of ash to an unfiltered Si–NaOH solution; experiment 3, addition of dry ash/diatomite mixture to a NaOH solution.

in Na-P1 crystallization (Fig. 9) and the delay of CEC increase (Fig. 10). In contrast, in experiment 3, where a dry ash/diatomite mixture is added to NaOH solution, the dissolution of diatomite and ash and the precipitation of solutes take place simultaneously. Thus, that the concentrations of Si and Al in solution are dictated by the competition between dissolution and precipitation. In general, experiments 1 and 2 yield essentially the same end products (Figs. 9 and 10).

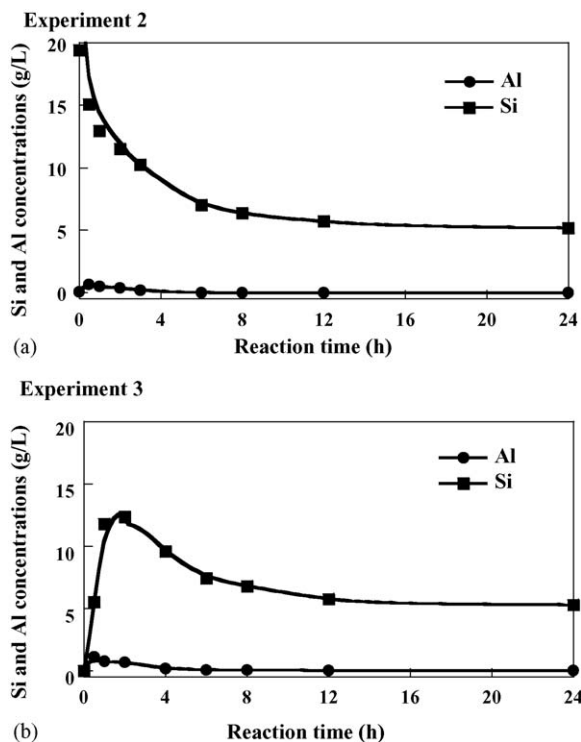


Fig. 11. Si and Al concentrations in 3 M NaOH solution as a function of reaction time for unfiltered (a) experiment 2 and (b) experiment 3.

3. Discussion

3.1. Zeolite synthesis

Henmi [9] synthesized zeolites from paper sludge ash under the conditions similar to this study and obtained an end product with a CEC of 160 cmol/kg, containing phillipsite and hydroxysodalite. This end product is quite different from that formed in our study from solution without addition of diatomite. The difference is attributed to the change of chemical composition of paper sludge ash in a decade associated with the change of paper filler from clay minerals to calcite.

Experimental formation of zeolites from natural geologic materials by methods similar to those used in this study have been reported. Burriesci et al. [25] studied zeolite formation from rhyolitic pumices at 95 °C for 5 h in 5 M NaOH solution and concluded that zeolite-P was formed from pumice with high SiO₂/Al₂O₃ ratio and low Fe content, while hydroxysodalite was formed from pumice with low SiO₂/Al₂O₃ ratio and high Fe content.

Barth-Wirshing et al. [26] synthesized zeolites from waste perlite at 100–140 °C in 0.5–6.0 M NaOH solutions with the addition of aluminum. They reported that a high percentage of hydroxysodalite formed from solutions either with high NaOH concentrations combined with addition of aluminum or with very high NaOH concentrations.

We used solutions with high NaOH concentration (3.0 M). The original paper sludge ash in this study had a low SiO₂/Al₂O₃ ratio (1.57) and the zeolite phase in the end product changed from hydroxysodalite to zeolite-P with the addition of diatomite. The result is consistent with those of Burriesci et al. [25] and Barth-Wirshing et al. [26] and the phase change from hydroxysodalite to zeolite-P in solutions with increasing SiO₂/Al₂O₃ ratios at high NaOH concentration.

Christidis et al. [27] examined the synthetic zeolites produced from perlite waste, in NaOH solutions at 100–140 °C. They found that the increase of NaOH concentration induced a change in zeolitization from zeolite-P to hydroxysodalite, and that the formation of hydroxysodalite occurred only after significant Na-uptake by the solid had taken place. This result implies that hydroxysodalite is associated with a high Na/Si ratio in solution.

In our study addition of abundant diatomite yielded zeolite-P and addition of small amounts of diatomite yielded hydroxysodalite. This can be explained by the increase in the Na/Si ratio of the solution relative to Si concentration. Hydroxysodalite in the end product, formed only after addition of a dry mixture of ash and diatomite to NaOH solution, can also be explained in terms of the Na/Si ratio, as the solution had a high Na/Si ratio just after the mixture of ash and diatomite was introduced into 3 M NaOH solution. Murayama et al. [21] studied the formation of zeolites from coal fly ash and found that Si and Al precipitated from the solutions as an amorphous aluminosilicate gel at the early stage of reaction, followed by formation of zeolites. The reaction sequence of the present study is consistent with results of Murayama et al. [21]. The concentration of Si rapidly decreased and Al exhibited low concentrations at the early stage

of reaction (Figs. 5(d) and 11(a)), but the XRD patterns exhibit no crystalline phase, implying that aluminosilicate initially precipitates as an amorphous phase. Only after 4–8 h do zeolites start to crystallize (Fig. 9). Some amorphous material remains in the end products of our reactions. This is indicated by the increased background (hump) in the powder diffraction patterns between roughly 21° and $39^\circ 2\theta$.

This study shows a method to increase the cation exchange capacity of paper sludge ash, by a factor of 2.5, via synthesis of zeolitic porous material through a reaction with 3 M NaOH solution after the addition of diatomite. Diatomite is a Si rich source and readily dissolves in the alkaline solution. The results obtained show that diatomite is an effective additive in controlling the zeolite formation, which could be applied to other ash wastes.

The CEC of the new material, however, is still lower (130 cmol/kg) than that of other synthetic zeolites (250–500 cmol/kg), determined by the same method used in this study as well as that used by Querol et al. [14], and is comparable to natural zeolites (120–180 cmol/kg), also determined by the same method used in this study. This is due to the inhibition of zeolite formation by the high Ca content of the reactants [19]. Wajima et al. [28] proposed another method to raise the CEC of zeolitic porous material formed by reaction of paper sludge ash with 2.5 M NaOH solution, by a factor of 4, through the acid leaching of Ca from the ash before zeolite synthesis in NaOH solution. The combination of our method and that of Wajima et al. [28] is expected to lead to an even higher cation exchange capacity than the products presented in this study.

3.2. Removal of NH_4^+ and PO_4^{3-}

Murayama et al. [29] prepared a zeolitic material from coal fly ash containing zeolite-P. It was kept in CaCl_2 solution to exchange Ca^{2+} for Na^+ and was successfully used for simultaneous removal of NH_4^+ and PO_4^{3-} . They claimed that the uptake of NH_4^+ from solution by zeolite was achieved through a cation exchange reaction and that the removal of PO_4^{3-} was accomplished by the formation of an “insoluble salt” by reaction with Ca^{2+} that was released from the treated fly ash.

Ishimoto et al. [6] synthesized a new material called MPM from paper sludge ash, by hydrothermal reaction, and emphasized the ability of the material to remove PO_4^{3-} from solution, suggesting the formation of apatite.

Product-20 in this study exhibits simultaneous removal of NH_4^+ and PO_4^{3-} from solution, but the original ash itself has a higher ability for PO_4^{3-} removal. The mechanism of NH_4^+ removal is by cation exchange, indicated by the correlation of NH_4^+ removal (Fig. 7) with the cation exchange capacity (Table 2). It is inferred that the removal of PO_4^{3-} takes place by the formation of an insoluble calcium-phosphate salt. The ability essentially depends on the Ca content of samples and, more specifically, depends on Ca^{2+} released from the sample to solution. The Ca^{2+} released from the treated paper sludge ash (soluble Ca^{2+}) combines with PO_4^{3-} when added to solution to form a solid calcium-phosphate phase, thereby removing these components from solution. The released (soluble) Ca^{2+} is listed

in Table 2 and the ability to remove PO_4^{3-} is correlated with the amount of released Ca (Fig. 7).

For solutions with an initial concentration of 10 mg/L at pH 7.5 the NH_4^+ uptake is ca. 0.2, 0.5 and 1.1 mg/g and the corresponding PO_4^{3-} removal is 2.2, 2.0 and 0.6 mg/g by the original ash, product-0 and product-20, respectively (Fig. 7). The NH_4^+ uptake by product-20 remains high compared with the other two samples, decreasing slightly under more basic conditions (Fig. 8). Both the paper sludge ash and product-20 show a minimum uptake at pH 7.5. Product-0 exhibits a slight decrease between pH 5 and 10. Okada et al. [30] prepared composites of γ -alumina/potassium aluminosilicate (KAS) gel to investigate simultaneous uptake of ammonium and phosphate ions, at pH 5–10 and at concentrations considerably higher than in this study. They reported an NH_4^+ uptake of 10.6 mg/g and a HPO_4^{2-} uptake of 4.6 mg/g from 1 mM $(\text{NH}_4)_2\text{HPO}_4$ solution at pH 7. This corresponds to NH_4^+ and HPO_4^{2-} concentrations of 36 and 96 mg/L, respectively. To roughly compare the results of Okada et al. [30] to those of our study the uptake at lower solution concentrations was calculated assuming a proportional relationship between the two. The result is an uptake value of 3 mg/g for NH_4^+ and 0.5 mg/g for HPO_4^{2-} at solution concentrations of 10 mg/L. These values are higher for NH_4^+ and lower or similar for PO_4^{3-} compared to the results of this study. Okada et al. [30] also reported that the NH_4^+ uptake is independent of pH but that PO_4^{3-} uptake was nonsystematically dependent on pH.

3.3. Simplification of processing

Na-P1 zeolite starts to crystallize after 8 h of reaction when ash is added to a filtered Si–NaOH solution but it crystallizes in 4 h when reacted with unfiltered solutions, experiments 2 and 3 (Fig. 9). It is unclear why the delay of zeolite crystallization occurs in the filtered experiment. The only difference from unfiltered experiments is the lack of solid residue, such as quartz, which may minimize nucleation centers for zeolite crystallization. The first two processes converge essentially to the same result (in CEC and end products), which suggests that the simpler procedure, i.e. the addition of ash to an unfiltered Si–NaOH solution (experiment 2), is preferable.

4. Conclusions

Na-P1 and hydroxysodalite were synthesized at low temperature (90°C) from paper sludge ash by adding diatomite. The zeolites exhibit higher CEC, with increasing diatomaceous Si in 3 M NaOH solution. The concentrations of Si and Al in the solution during the reaction can be used to monitor the phase change. The turning point from the formation of hydroxysodalite to Na-P1 occurs at initial Si concentration of 10 g/L in solution, resulting in a higher concentration of Si than Al. Anorthite present in the original ash dissolves and gehlenite remains in the solutions for all Si concentrations measured. The product with the Na-P1 phase synthesized at high Si concentrations exhibits a relatively high CEC and capacity for NH_4^+ uptake and sufficient ability to remove PO_4^{3-} by precipitation without the

addition of extra calcium, which is preferable for application in water purification. Neither the NH_4^+ or PO_4^{3-} removal show significant variation for pH 5–10.

Acknowledgments

We are grateful to Dr. K.J.D. Mackenzie and two anonymous reviewers for their extremely helpful reviews.

References

- [1] R.G. Barton, W.R. Seeker, H.E. Bostian, The behavior of metals in municipal sludge incinerators, *Trans. Inst. Chem. Eng.* 69 (1991) 29–36.
- [2] T.H.Y. Tebbutt, Incineration of wastewater sludges, in: *Proceedings of the Institution of Civil Engineers, Water, Maritime Energy* 112 (1995) 39–47.
- [3] M. Singh, M. Garg, Cementitious binder from fly ash and other industrial wastes, *Cement Concrete Res.* 29 (1999) 309–314.
- [4] R. Kikuchi, Recycling of municipal solid waste for cement production: pilot-scale test for transforming incineration ash of solid waste into cement clinker, *Resources Conserv. Recycl.* 31 (2001) 137–147.
- [5] H. Ishimoto, M. Yasuda, Technology for converting papermaking sludge into micro-porous crystal materials, *NTT Rev.* 9 (4) (1997) 51–56.
- [6] H. Ishimoto, T. Origuchi, M. Yasuda, Use of papermaking sludge as new material, *J. Mater. Civil Eng.* (2000) 310–313.
- [7] H. Ishimoto, M. Yasuda, O. Sasaki, Application of new materials from paper recycling for purifying domestic wastewater, *NTT Rev.* 15 (1) (2003) 43–47.
- [8] R.M. Barrer, *Zeolites and Clay Minerals as Sorbents and Molecular Sieves*, Academic Press, London, 1978.
- [9] T. Henmi, A physico-chemical study of industrial solid wastes as renewable resource – Zeolitization of coal clinker ash and paper sludge incineration ash – Memoir of the faculty of Agriculture, Ehime University 33(2) (1989) 143–149 (in Japanese with English abstract).
- [10] S.P. Mun, B.J. Ahn, Chemical conversion of paper sludge incineration ash into synthetic zeolite, *J. Ind. Eng. Chem.* 7 (5) (2001) 292–298.
- [11] W.H. Shin, H.L. Chang, Conversion of fly ash into zeolites for ion exchange applications, *Mater. Lett.* 28 (4–6) (1996) 263–268.
- [12] M. Park, J. Choi, Synthesis of phillipsite from fly ash, *Clay Sci.* 9 (4) (1995) 219–229.
- [13] V. Berkgaut, A. Shinger, High capacity cation exchanger by hydrothermal zeolitization of coal fly ash, *Appl. Clay Sci.* 10 (1996) 369–378.
- [14] X. Querol, N. Moreno, J.C. Umaña, A. Alastuey, E. Hernández, A. López-Soler, F. Plana, Synthesis of zeolites from coal fly ash: an overview, *Int. J. Coal Geol.* 50 (2000) 413–423.
- [15] K. Fukui, M. Kinugawa, T. Nishimoto, H. Yoshida, Effect of fly ash content on zeolite synthesis from coal fly ash prepared by hydrothermal treatment, *Kagaku Kogaku Ronbunshu* 28 (2) (2002) 155–160 (in Japanese with English abstract).
- [16] S. Kamigasa, H. Kato, Recent conditions and prospects of diatomite resources, *Energy Resources* 21 (2) (2000) 166–172 (in Japanese).
- [17] B. Ghosh, D.C. Agrawal, S. Bhatia, Synthesis of zeolite A from calcined diatomaceous clay: optimization studies, *Ind. Eng. Chem. Res.* 33 (1994) 2107–2110.
- [18] V. Sanhueza, U. Kelm, R. Cid, Synthesis of mordenite from diatomite: a case of zeolite synthesis from natural material, *J. Chem. Technol. Biotechnol.* 78 (2003) 485–488.
- [19] P. Catalfamo, G. Patané, 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 (2) (1994) 159–173.
- [20] R.M. Barrer, J.W. Baynham, F.W. Baltitude, W.M. Meier, Hydrothermal chemistry of silicates. Part VIII. Low temperature crystal growth of aluminosilicates and of some gallium and germanium analogue, *J. Chem. Soc.* (1959) 195–206.
- [21] N. Murayama, H. Yamamoto, J. Shibata, Mechanism of zeolite synthesis from coal fly ash by alkali hydrothermal reaction, *Int. J. Miner. Process.* 64 (2002) 1–17.
- [22] No. 111 Committee: Development of New Utilization of Materials, Natural Zeolite and its Utilization, JSPS, Tokyo, 1994, pp. 318–325.
- [23] M. Koyama, T. Hori, Y. Kitayama, IARC Reports, Kyoto University 2(2), 1976, pp. 11–14.
- [24] M. Ishibashi, M. Tabushi, Spectrophotometric determination of micro amount of phosphoric acid by solvent extraction as phosphomolybdate, *Jpn. Analyst* 8 (1959) 588–593 (in Japanese with English abstract).
- [25] N. Burriesci, M.L. Crisafulli, L.M. Saija, G. Polizzotti, Hydrothermal synthesis of zeolites from rhyolitic pumice of different geological origins, *Mater. Lett.* 2 (1) (1983) 74–78.
- [26] U. Barth-Wirshing, H. Höller, D. Klammer, B. Konrad, Synthetic zeolites formed from expanded perlite: type, formation conditions and properties, *Mineral. Petrol.* 48 (1993) 275–294.
- [27] G.E. Christidis, I. Paspaliaris, A. Kontopoulos, Zeolitisation of perlite fines: mineralogical characteristics of the end products and mobilization of chemical elements, *Appl. Clay Sci.* 15 (1999) 305–324.
- [28] T. Wajima, K. Kuzawa, H. Ishimoto, O. Tamada, T. Nishiyama, The synthesis of zeolite-P, Linde Type A, and hydroxysodalite zeolites from paper sludge ash at low temperature (80 °C): optimal ash-leaching condition for zeolite synthesis, *Am. Mineral.* 89 (2004) 1694–1700.
- [29] N. Murayama, S. Yoshida, Y. Takami, H. Yamamoto, J. Shibata, Simultaneous removal of NH_4^+ and PO_4^{3-} in aqueous solution and its mechanism by using zeolite synthesized from coal fly ash, *Sep. Sci. Technol.* 38 (1) (2003) 113–129.
- [30] K. Okada, J. Temuujin, Y. Kameshima, K.J.D. MacKenzie, Simultaneous uptake of ammonium and phosphate ions by composites of γ -alumina/potassium aluminosilicate gel, *Mater. Res. Bull.* 38 (2003) 749–756.