

Synthesis of Zeolitic Material from Paper Sludge Ash Using Diatomite

Takaaki Wajima* and Kenzo Munakata

Department of Materials-process Engineering and Applied Chemistry for Environments, Akita University, Akita 018-8502, Japan

Paper sludge ash (PSA) was partially converted into zeolites by reaction with 3 M NaOH solution at 90°C for 24 h. The PSA had a low abundance of Si and significant Ca content, due to the presence of calcite that was used as paper filler. Diatomite, which contains amorphous silica and dissolves easily in alkali solution, was mixed with the ash, and then added to the NaOH solution to increase its Si content during alkali reaction and thus synthesize zeolites with high cation exchange capacity (CEC). The original ash without addition of diatomite yielded hydroxysodalite with CEC ca. 0.5 mmol/g. Addition of diatomite to the ash yielded zeolite-P with a higher CEC (ca. 1 mmol/g). 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 adsorption capacity for nutrients from liquid fertilizer, such as K^+ , NH_4^+ and PO_4^{3-} . The product with zeolite-P exhibits high ability to adsorb these nutrients from liquid fertilizer, which is desirable for application in soil improvement. [doi:10.2320/matertrans.ME201104]

(Received July 22, 2011; Accepted December 8, 2011; Published February 1, 2012)

Keywords: paper sludge ash, diatomite, zeolite-phosphorus, hydroxysodalite, nutrients, soil improvement

1. Introduction

The vast amount of paper used in everyday life generates a large amount of waste, 50–60% of which is recycled. During the manufacture of recycled paper products, paper sludge is generated as an industrial waste. More than 3 million tons of sludge is discharged per year in Japan, and approximately 8 million tons and 2 million tons in the United States and the United Kingdom, respectively.^{1,2)} The amount is increasing annually. The sludge is typically composed of 50% water, 25% organic matter and 25% minerals (calcite and kaolin), and is incinerated to paper sludge ash (PSA) by burning the organic materials to recover energy and reduce volume. Approximately 800,000 tons per year of PSA is produced in Japan. Although a small proportion of ash has been used as cement fillers, lightweight aggregates in the construction industry and other minor applications,^{3,4)} most is dumped in landfills. The large daily output of PSA and the limited landfill capacity causes social and environmental problems. It is, therefore, essential to develop new techniques to further recycle the ash.

Recently, the conversion of PSA into zeolites has been investigated.^{5–7)} Zeolites are a group of more than 40 crystalline hydrated aluminosilicate minerals with structures based on a three-dimensional network of aluminium and silicon tetrahedra linked by sharing of oxygen atoms.⁸⁾ Due to their unique pore structures and ion-exchange properties, zeolites (including those synthesized from PSA) are applied to such tasks as water purification and soil improvement.^{9,10)}

Conversion of the ash into useful mineral products depends largely on the chemistry of the raw ash. In the past, kaolinite, which can be converted into a zeolite phase, was used as a paper filler, but recently calcite has increasingly replaced kaolinite as the filler to achieve whiteness and opacity.¹¹⁾ As a result, production of incinerated ash with a higher Ca content, in the form of anorthite ($CaAl_2Si_2O_8$) and gehlenite ($Ca_2Al_2SiO_7$), is increasing. The ash with a high Ca content either cannot be fully converted into zeolites, or is converted into hydroxysodalite, with a low cation exchange

capacity (CEC).^{12–14)} For stable production, it is important to develop a process for the manufacture of zeolites with a high CEC from Ca-rich ash.

Zeolite formation from other ashes, for example coal fly ash, has also been investigated.^{15–18)} Many synthetic processes, such as the fusion method, the dry or molten method, addition of mineralizer, and acid-leaching, have been developed to achieve synthesis of products with high CEC.^{19–22)} It was reported that amorphous SiO_2 particles added to a coal fly ash resulted in the formation of phillipsite, with a high CEC, in NaOH solution.²³⁾ It has been suggested that water glass can be added to a solution with Ca-rich ash to synthesize zeolites with high CEC.^{24,25)}

Diatomite is a fine-grained, biogenic, siliceous sediment, and is available in large quantities at low cost.²⁶⁾ It comprises essentially amorphous silica derived from opalescent frustules of diatoms, and has a fine porous structure with low density. Due to its properties, diatomite dissolves easily in basic solutions. In our previous study, PSA was added to NaOH solution with high Si content extracted from diatomite, and converted into products with high CEC, including zeolite-P.²⁷⁾ In addition, Ca^{2+} contained in the original ash was shown to react with phosphoric acid to form apatite-like materials, removing PO_4^{3-} from the solution.²⁸⁾ We thus obtained a material suitable for water purification, which contained zeolite phases and soluble Ca in the product.²⁹⁾

In the present study, we synthesized zeolitic material from PSA by simply mixing the ash and diatomite before the synthesis, and aimed to obtain a material suitable for soil improvement, containing zeolite phases for NH_4^+ and K^+ uptake, and soluble Ca for PO_4^{3-} uptake in the product. We present here the chemical reaction of PSA with diatomite and the CEC values of the end products, and demonstrate the adsorption capacity of the product for nutrients from liquid fertilizer.

2. Materials and Methods

2.1 PSA and diatomite

PSA was obtained from a paper company in Fuji, Japan.

*Corresponding author, E-mail: wajima@gipc.akita-u.ac.jp

Table 1 Chemical compositions of PSA and diatomite.

Oxide (mass%)	SiO ₂	Al ₂ O ₃	CaO	Fe ₂ O ₃	MgO	Na ₂ O	K ₂ O	TiO ₂	Total
PSA	24.2	17.8	44.7	2.5	5.0	—	0.2	3.5	97.9
Diatomite	85.1	3.7	0.8	4.8	0.6	—	1.3	0.6	96.9

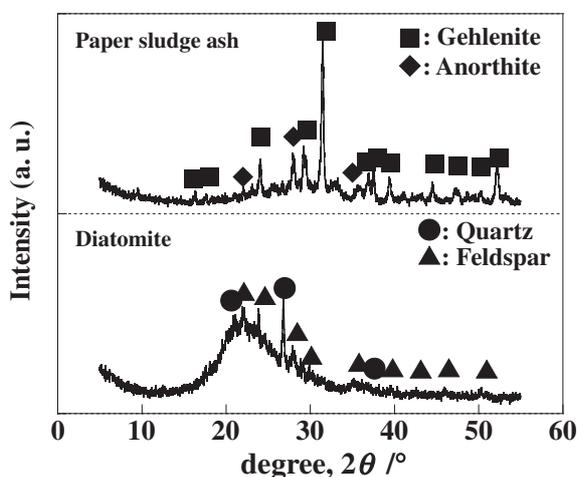


Fig. 1 Powder X-ray diffraction patterns of PSA and diatomite.

The composition of the ash, determined by X-ray fluorescence spectrometry (XRF) (XRF-1700, SHIMADZU), is given in Table 1. The ash was composed mainly of SiO₂, Al₂O₃ and CaO in the form of amorphous matter, and the minerals gehlenite and anorthite, as determined by X-ray diffraction (XRD) (XRD-DSC-XII, SHIMADZU) (Fig. 1). The ash had low SiO₂ and high CaO content compared with other similar materials. Such a composition has phosphate adsorption ability, but is not favorable for the synthesis of zeolites.^{12–14,25)}

Diatomite occurs in nature in two types of geological environments, marine and lacustrine.²⁹⁾ The sample used in this study had a seawater origin, and was obtained from the deposits located in Takanosu, Akita prefecture, 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 XRF is given in Table 1. The original sample contained 50–75% water. The dried sample was composed of diatom frustules that had precipitated in an amorphous silica form, but also contained some rock fragments. The fragments were mainly feldspar and quartz (Fig. 1) derived from surrounding rocks.

2.2 Zeolite synthesis

PSA (100 g) was dry mixed with 0, 16, 32, 64, 96 or 128 g of diatomite, then added to 3 M NaOH solution (1 L) in a 1 L Erlenmeyer flask (made of poly(methyl pentene)) with a Dimroth condenser. The mixture (slurry) was continuously stirred at 90°C for 24 h. 5 mL aliquots of each slurry were removed at varying time intervals (every 1 h initially) to monitor reaction progress over a period of 24 h. The aliquots were filtered, and the concentrations of Si and Al in the filtrates determined by the inductively coupled plasma atomic

emission spectroscopy method (ICP-AES) (ICPS-7500, SHIMADZU). The solid residues (products) were washed with distilled water, and oven dried at 60°C overnight. The end products were examined by XRD and field emission scanning electron microscopy (FE-SEM) (SU-70, HITACHI). The CEC of the products was measured by the method reported by Wajima *et al.*²⁷⁾ The relative crystallinities of the zeolites in the products were calculated by the method reported by Machado and Miotto.³⁰⁾ Hydroxysodalite and zeolite-P prepared by the procedure reported by Kato *et al.*³¹⁾ were used as standards.

2.3 Nutrient adsorption ability

The nutrient adsorption ability was examined for two samples: raw PSA and the product synthesized from a mixture of the ash (100 g) and diatomite (64 g). Commercial liquid fertilizer (Hanakojo, Sumitomo Chemical Garden Products inc.) was used to determine the capacity of the samples to adsorb nutrients, especially K⁺, NH₄⁺ and PO₄³⁻. This liquid fertilizer contained 41.7 mg/L of NH₄⁺, 60.9 mg/L of K⁺ and 185.3 mg/L of PO₄³⁻. 0.1 g of each sample and 10 mL of liquid fertilizer were mixed and shaken with a reciprocal shaker. After shaking for 2 h at room temperature, the suspension was centrifuged to collect the supernatant. The nutrient concentrations of liquid fertilizer and the supernatant were determined by ion chromatography (DX-120, Dionex).

The amounts of nutrients adsorbed, q (mmol/g), were calculated using the following equation:

$$q = (C_0 - C)/(M \times S)$$

where C_0 and C are the concentrations of nutrients in initial solution and the treated solution (mg/L), respectively, and M is the molecular weight of each ion (g/mol). The slurry concentration, S (g/L), is expressed by:

$$S = w/L$$

where L is the volume of the solution (L), and w is the weight of the sample (g).

The recovery percentage of nutrients, R (%), was calculated using the following equation:

$$R = (C_0 - C)/C_0 \times 100$$

3. Results and Discussion

XRD patterns of the products synthesized from mixtures of PSA and diatomite are shown in Fig. 2. Without addition of diatomite, only hydroxysodalite formed. On addition of diatomite, a mixture of hydroxysodalite and tobermorite formed first at 16 g diatomite per 100 g; zeolite-P started to form at 32 g diatomite per 100 g; and finally only zeolite-P formed at a high content of diatomite (more than 64 g per 100 g).

The CEC of the products as a function of diatomite content is shown in Fig. 3. CEC increased with increasing addition of diatomite. Without diatomite addition, CEC was about 0.5 mmol/g, and increased to 1.0 mmol/g for more than 64 g diatomite per 100 g (64 mass%). It was previously reported that CEC of zeolite-P was higher than that of hydroxysoda-

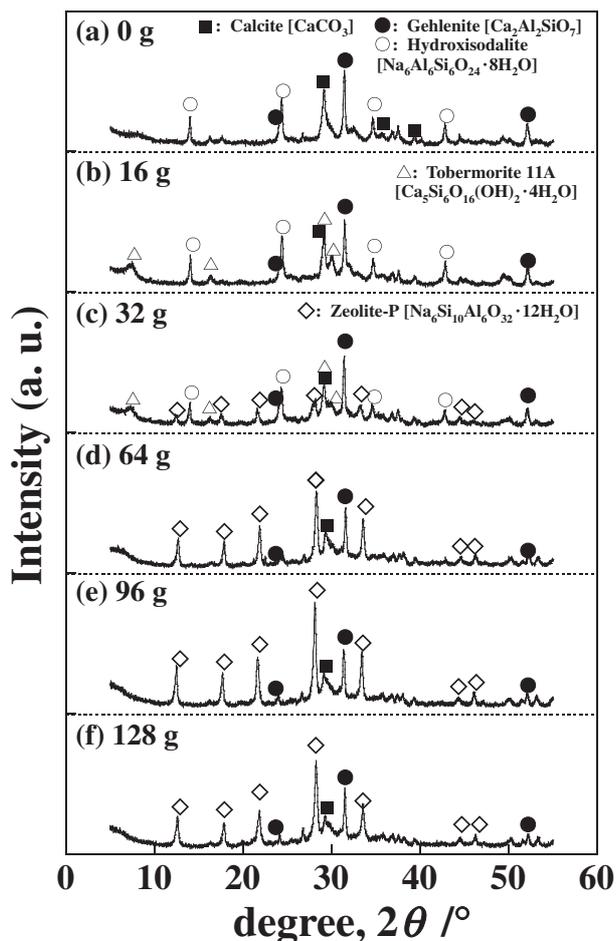


Fig. 2 Powder X-ray diffraction patterns of products synthesized in 3 M NaOH solution from mixtures of PSA and diatomite.

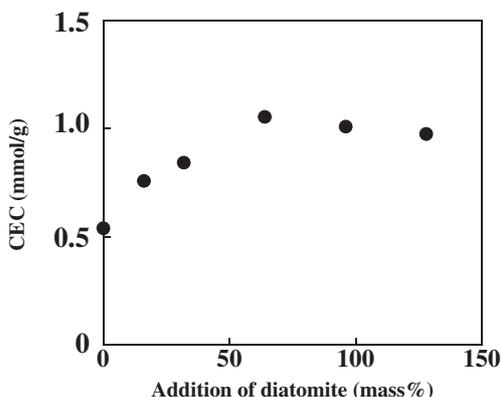


Fig. 3 CEC of products as a function of diatomite content in mixture with PSA.

lite.¹⁸⁾ It is considered that the increase in CEC was caused by a change in the zeolite phase.

Figure 4 shows the SEM image of the product synthesized from the mixture of the ash and 96 g of diatomite. The zeolite-P crystals cover the surface of the material. Zeolite-P ($\text{Na}_6\text{Si}_{10}\text{Al}_6\text{O}_{32}\cdot 12\text{H}_2\text{O}$) is a member of the gismondine group. The framework is built of 4- and 8-membered rings. It is noted that the Si/Al ratio is greater in zeolite-P (Si/Al = 5 : 3) than in hydroxysodalite ($\text{Na}_6\text{Al}_6\text{Si}_6\text{O}_{24}\cdot 8\text{H}_2\text{O}$) (Si/Al = 1 : 1).

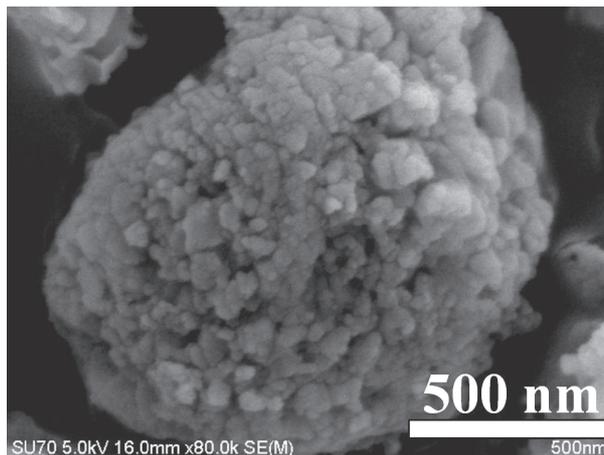


Fig. 4 SEM photograph of the product synthesized from the mixture of the ash and 96 g of diatomite.

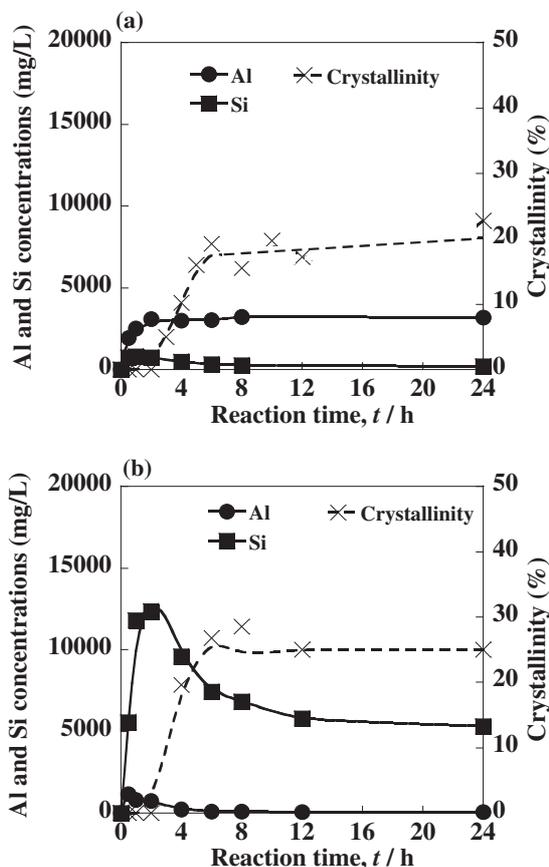


Fig. 5 Al and Si concentrations in 3 M NaOH solution, and the relative crystallinities of the product phases in the solid during the alkali reactions in (a) the ash without diatomite, and (b) the mixture of ash with 64 g of diatomite.

The reaction process was monitored by analyzing the Si and Al contents in the solution, and the relative crystallinities of the product phases in the solid, during the alkali reaction in (a) raw PSA, and (b) the mixture of the ash and 64 g of diatomite (Fig. 5). In case (a), the Al concentration always exceeded that of Si regardless of the reaction time with alkali. The initial concentrations of Si and Al increased after introduction of the ash, and then the Si concentration

decreased to zero, leaving Al in the solution after 24 h of reaction. Due to the Al-rich solution, hydroxysodalite, which has the lowest Si/Al ratio of the zeolites, was formed. The relative crystallinity of hydroxysodalite gradually increased after introduction of the ash, then sharply increased after starting the reduction of Si content in the solution, and finally became almost constant (at about 20%) after 6–8 h of alkali reaction. For (b), in contrast to case (a), the amount of Si exceeded that of Al throughout the entire reaction. The initial concentrations of Si and Al increased, and then the Al concentration decreased to zero, leaving Si in solution after 24 h of reaction. Due to the Si-rich solution, zeolite-P, which has a higher Si/Al ratio than hydroxysodalite, appeared. The relative crystallinity of zeolite-P gradually increased in the early stage, sharply increased after starting the reduction of Al content in the solution, and finally became almost constant (ca. 25%) after 6–8 h of alkali reaction. Therefore, zeolite formation occurs similarly at same reaction time, but the different chemical composition of the solution causes formation of a different type of zeolite crystal.

The formation of zeolites from coal fly ash was studied and found that zeolite synthesis from coal fly ash consists of three reactions: dissolution, gelation and crystallization.^{23,32} The reaction sequence in the present study, as shown in Fig. 5, is consistent with these results. The reactions of dissolution, gelation, and crystallization start simultaneously after introduction of the ash or the mixture of the ash and diatomite. In the early stage of reaction, the increase in the amount of Si and Al in the solution due to dissolution from the ashes or the mixture is greater than the decrease due to gelation, and the amounts of Si and Al in the solution increase for 1–2 h. Then, the gelation reaction overtakes the dissolution, and the concentrations of Si and Al rapidly decrease up to 6 h. The gel is transformed into a zeolite phase and covers the surface of the raw materials, stopping the dissolution. The crystallization of zeolite continues up to 6 h of reaction, due to the occurrence of gelation, and is saturated after 6 h of reaction due to saturation of the gelation (Fig. 5). The resulting product with zeolite phases has a higher CEC than the starting materials (Fig. 3). During the gelation reaction, the Si/Al ratio in the solution with the mixture of the ash and diatomite is higher than that in the solution with raw ash. Therefore, the product from raw ash is hydroxysodalite, which has a low Si/Al ratio, and that from the mixture is zeolite-P, which has a high Si/Al ratio. These results are in good agreement with the Barrer prediction.³³

On the basis of these results we concluded that zeolitic material with high CEC, including zeolite-P, could be synthesized by simply mixing the ash with diatomite before the synthesis, to increase the supply of Si in the alkali solution.

Adsorption amounts and recovery ratios for nutrients using raw ash and the product are shown in Table 2. Raw ash has high adsorption ability for PO_4^{3-} (0.14 mmol/g) due to the soluble Ca in the ash, but far lower ability for cations (NH_4^+ : 0.01 mmol/g and K^+ : 0.01 mmol/g). On the other hand, the product has high adsorption ability for all nutrients, NH_4^+ (0.14 mmol/g), K^+ (0.12 mmol/g) and PO_4^{3-} (0.10 mmol/g), due to the zeolite phase for cations and soluble Ca for PO_4^{3-} . In the case of 10 g/L addition, recovery percentages of all

Table 2 Adsorption amounts and recovery ratios for nutrients using raw ash and the product.

Sample		NH_4^+	K^+	PO_4^{3-}
Raw ash	q (mmol/g)	0.01	0.01	0.14
	R (%)	3.4	6.6	70.8
The product	q (mmol/g)	0.14	0.12	0.10
	R (%)	61.4	74.5	53.7

nutrients from liquid fertilizer are higher than 50% using the product (NH_4^+ : 61.4%, K^+ : 74.5%, PO_4^{3-} : 53.7%), while only PO_4^{3-} can be recovered from liquid fertilizer using raw ash. The product exhibited an excellent capacity for NH_4^+ , K^+ and PO_4^{3-} uptake, which is desirable for application in soil improvement.

4. Conclusions

Zeolite-P, tobermorite and hydroxysodalite were synthesized at low temperature (90°C) from paper sludge ash (PSA) mixed with diatomite. The zeolites exhibit higher CEC with increasing proportion of diatomite in the ash/diatomite mixture. The concentrations of Si and Al in the solution during the reaction can be used to monitor the phase change. Crystallization of only zeolite-P occurs when 64 g of diatomite is added to 100 g of ash, resulting in a much higher concentration of Si than Al. In the original ash without diatomite addition, the concentration of Al in the alkali solution always exceeded that of Si during the synthesis, and hydroxysodalite with a low Si : Al ratio (1 : 1) was formed. In the mixture of ash and diatomite, the concentration of Si always exceeded that of Al during the synthesis, and zeolite-P with a higher Si : Al ratio (5 : 3) was formed. The zeolite-P phase synthesized at a high proportion of diatomite exhibits a relatively high CEC and capacity for NH_4^+ , K^+ and PO_4^{3-} uptake, which is desirable for application in soil improvement.

REFERENCES

- 1) R. G. Barton, W. R. Seeker and H. E. Bostian: *Trans. Inst. Chem. Eng.* **69** (1991) 29–36.
- 2) T. H. Y. Tebbutt: *Proc. Inst. Civil Eng. Water Marit. Energy* **112** (1995) 39–47.
- 3) M. Singh and M. Garg: *Cem. Concr. Res.* **29** (1999) 309–314.
- 4) R. Kikuchi: *Resour. Conserv. Recycl.* **31** (2001) 137–147.
- 5) T. Henmi: *Mem. Facul. Agric. Ehime Univ.* **33** (1989) 143–149.
- 6) H. Ishimoto and M. Yasuda: *NTT REV.* **9** (1997) 51–56.
- 7) S. P. Mun and B. J. Ahn: *J. Ind. Eng. Chem.* **7** (2001) 292–298.
- 8) R. M. Barrer: *Zeolites and Clay Minerals as Sorbents and Molecular Sieves*, (Academic Press, London, 1978).
- 9) H. Ishimoto, T. Origuchi and M. Yasuda: *J. Mater. Civ. Eng.* **12** (2000) 310–313.
- 10) H. Ishimoto, M. Yasuda and O. Sasaki: *NTT REV.* **15** (2003) 43–47.
- 11) Editing Committee on All about Paper (ECAP): *All about Paper: I.*, (Gihodo, Japan, 1995).
- 12) P. Catalfamo, G. Patané, P. Primerano, S. D. Pasquale and F. Corigliano: *Mater. Eng.* **5** (1994) 159–173.
- 13) T. Ando, M. Saito, S. Muramatsu, K. Hiyoshi, J. Haruna, N. Matsue and T. Henmi: *J. Clay Sci. Soc. Jpn.* **42** (2003) 158–166.
- 14) T. Ando, M. Saito, S. Muramatsu, K. Hiyoshi, J. Haruna, N. Matsue and T. Henmi: *J. Clay Sci. Soc. Jpn.* **42** (2003) 208–217.

- 15) W. H. Shin and H. L. Chang: *Mater. Lett.* **28** (1996) 263–268.
- 16) M. Park and J. Choi: *Clay Sci.* **9** (1995) 219–229.
- 17) V. Berkgaut and A. Shinger: *Appl. Clay Sci.* **10** (1996) 369–378.
- 18) X. Querol, N. Moreno, J. C. Umaña, A. Alastuey, E. Hernández, A. López-Soler and F. Plana: *Int. J. Coal Geol.* **50** (2000) 413–423.
- 19) N. Shigemoto, H. Hayashi and K. Muyauro: *J. Mater. Sci.* **28** (1993) 4781–4786.
- 20) M. Park, C. L. Choi, W. T. Lim, M. C. Kim, J. Choi and N. H. Heo: *Microporous Mesoporous Mater.* **37** (2000) 81–89.
- 21) D. Wu, B. Zhang, L. Yan, H. Kong and X. Wang: *Int. J. Miner. Process.* **80** (2006) 266–272.
- 22) T. Wajima, K. Kuzawa, H. Ishimoto, O. Tamada and T. Nishiyama: *Am. Mineral.* **89** (2004) 1694–1700.
- 23) K. Fukui, M. Kinugawa, T. Nishimoto and H. Yoshida: *Kagaku Kogaku Ronbunshu* **28** (2002) 155–160.
- 24) T. Ando, T. Sakamoto, O. Sugiyama, K. Hiyoshi, N. Matsue and T. Henmi: *Clay Sci.* **12** (2004) 243–248.
- 25) T. Wajima, T. Shimizu and Y. Ikegami: *J. Environ. Sci. Health-A* **42** (2007) 345–350.
- 26) S. Kamigasa and H. Kato: *Energy Resour.* **21** (2000) 155–160.
- 27) T. Wajima, M. Haga, K. Kuzawa, H. Ishimoto, O. Tamada, K. Ito, T. Nishiyama, R. T. Downs and J. F. Rakovan: *J. Hazard. Mater. B* **132** (2006) 244–252.
- 28) T. Wajima and K. Munakata: *J. Environ. Sci.* **23** (2011) 718–724.
- 29) T. Wajima, T. Shimizu and Y. Ikegami: *J. Chem. Technol. Biotechnol.* **83** (2008) 921–927.
- 30) N. R. C. F. Machado and D. M. M. Miotto: *Fuel* **84** (2005) 2289–2294.
- 31) Y. Kato, K. Kakimoto, H. Ogawa, M. Tomai and E. Sakamoto: *Kogyo-Yousui* **331** (1986) 27–33.
- 32) N. Murayama, H. Yamamoto and J. Shibata: *Int. J. Miner. Process.* **64** (2002) 1–17.
- 33) R. M. Barrer: *Hydrothermal Chemistry of Zeolites*, (Academic Press, New York, 1992).