**Abstract:** Incinerated ash with a relatively high Ca content, paper sludge ash, was converted to zeolitic materials with high cation-exchange capacities (CECs) by aging at 80 °C in NaOH solution via step-wise acid leaching with HCl to reduce the ash Ca content. The extraction of Ca, Mg, Si, and Al from the ash into the acid solutions during leaching and the products obtained from the leached ash by reaction with an alkali were examined. The contents of Ca and Mg in the ash were more easily extracted from the ash than those of Si and Al in the initial leaching. The leachant pH decreased with increasing numbers of leaching steps, and the amounts of Si, Al, and Ca extracted from the ash increased as a result of the dissolution of gehlenite (Ca$_2$Al$_2$SiO$_7$), one of the main minerals in the ash. Zeolites A and P were synthesized from the leached ashes, and hydroxysodalite was synthesized from the raw ash. With increasing numbers of leaching steps of the ash, the obtained product contained lower released Ca, whereas the product contained higher released Na and has higher CEC, depending on the zeolite phases in the product. The product with the highest CEC was synthesized from third-leached ash, and its CEC was 1.5 mmol/g, which is about four times higher than that of the raw ash (0.4 mmol/g).

**Keywords:** paper sludge ash; acid leaching; cation exchange capacity; zeolite synthesis; leachant pH

---

1. Introduction

In the manufacture of recycled paper, industrial wastes (paper sludge) are discharged, and the amounts are increasing annually around the world, e.g., 11 million tons in Europe [1], 5.1 million tons in Japan [2] and 26 million tons in Korea [3]. Combustion is primarily used to reduce the volume of waste sludge for landfilling (80–90% reduction) and partly to recover energy, which produces paper sludge ash. Although paper sludge ash is used as a cement additive, soil amendment, water purification and so on [4–11], a large amount of ash is currently disposed of by dumping. This has caused environmental concerns and high costs to industry due to the shortage of landfill sites for waste disposal. There is thus a lot of interest in finding alternative routes to landfilling and the valorization of paper sludge ash, currently classified as waste.

In the last few decades, fly ash has been used as a raw material for the synthesis of microporous aluminosiliceous minerals known as zeolites, and chemical conversion from fly ash into zeolites has been investigated [12–15]. The conversion involves the transformation of aluminosilicate, which is a major component of ash, into zeolites by reaction with alkalis. Because of their unique porous structures and ion-exchange properties, zeolites, including those synthesized from paper sludge ash, are used in applications such as water purification, gas removal, catalysts and so on [15–18].

Paper fillers contain calcite, therefore paper sludge ash has a high Ca content in the main forms of anorthite and gehlenite. It has been reported that ash with a high percentage of Ca was converted to
zeolites with low cation-exchange capacity (CEC) [19]. It has also been reported that Ca compounds in the ash prevent separation of the product slurry into solid and liquid phases during filtration and sedimentation [20]. Therefore, reduction of the Ca content is an important issue in the production of desirable zeolite materials.

In our previous studies, we applied acid leaching to the ash to reduce its Ca content, and converted the leached ash into a zeolitic material with high CEC, including zeolite-P, which was examined for the effect of acid species, concentration, and leaching time on the synthesis of zeolitic material. It was confirmed that two mineral phases in the paper sludge ash, gehlenite and anorthite, were present, and anorthite could be converted into zeolitic phases by dissolution into alkali solution, while gehlenite could not without dissolving into alkali solution, during the zeolite synthesis [21–23]. Acid leaching is an easy process with a low energy consumption, and the two waste solutions produced from acid leaching (acid) and zeolitization (alkali) can be simultaneously neutralized by mixing them. Additionally, the Ca-P zeolitic product with the simultaneous removal of NH$_4^+$ and PO$_4^{3−}$ can be prepared from the Ca obtained from paper sludge ash via acid leaching process and the zeolite-P from leached ash with high Si and Al contents after alkali reaction [24]. It is important to prepare the acid leached ash with low contents of Ca and Mg, which disturb the zeolite synthesis, and high contents of Si and Al, which are used to construct the zeolite structure, by removing gehlenite and the remaining anorthite to synthesize the zeolitic material with a high CEC. However, little information is available on the effective condition control of the acid leaching process for the synthesis of zeolitic material with high CECs from paper sludge ash.

In this study, step-wise acid leaching with dilute HCl was applied for the synthesis of zeolitic materials with high CECs from paper sludge ash. We extracted Ca and Mg, which disturb the zeolite synthesis, from the paper sludge ash using dilute HCl solution, while Si and Al remained, which were used to construct the zeolite structure and to obtain zeolitic products with high CEC. The effects of step-wise acid leaching with dilute HCl on the properties of leached ash to enable zeolitic materials with high CECs were investigated to clarify the effective control condition of acid leaching.

2. Materials and Methods

2.1. Paper Sludge Ash

Paper sludge ash was obtained from a paper company in Japan. The composition of the ash, determined using X-ray fluorescence spectrometer (Epsilon 1, Malvern Panalytical, Malvern, UK), is shown in Table 1. The ash consisted mainly of SiO$_2$, Al$_2$O$_3$, and CaO, and some low-concentration impurities such as MgO, Fe$_2$O$_3$, TiO$_2$, Na$_2$O, and K$_2$O. The chemical composition of this ash was similar to those found in the literature [4].

| Sample                  | Chemical Composition (wt.%) |
|-------------------------|-----------------------------|
|                         | SiO$_2$ | Al$_2$O$_3$ | CaO | MgO | Fe$_2$O$_3$ | TiO$_2$ | Na$_2$O | K$_2$O |
| Paper sludge ash        | 28.2    | 19.0        | 42.2 | 4.0 | 1.5         | 2.6     | 0.2     | 0.2    |
| 1st-leached ash         | 34.5    | 23.0        | 31.6 | 3.9 | 1.8         | 3.1     | N.D.    | N.D.   |
| 2nd-leached ash         | 35.5    | 24.0        | 25.1 | 3.8 | 2.2         | 3.8     | N.D.    | N.D.   |
| 3rd-leached ash         | 45.7    | 21.7        | 18.8 | 3.7 | 2.6         | 4.8     | N.D.    | N.D.   |
| 4th-leached ash         | 52.5    | 20.6        | 12.0 | 4.1 | 2.6         | 5.1     | N.D.    | N.D.   |
| 5th-leached ash         | 62.6    | 14.0        | 8.5  | 4.6 | 2.2         | 5.5     | N.D.    | N.D.   |
| 6th-leached ash         | 68.5    | 11.3        | 6.6  | 4.5 | 1.8         | 5.5     | N.D.    | N.D.   |
| 7th-leached ash         | 70.4    | 10.5        | 5.7  | 4.6 | 1.7         | 5.3     | N.D.    | N.D.   |
| 8th-leached ash         | 72.3    | 9.6         | 5.4  | 4.2 | 1.6         | 5.2     | N.D.    | N.D.   |
| 9th-leached ash         | 73.2    | 9.3         | 5.2  | 4.1 | 1.5         | 5.1     | N.D.    | N.D.   |

N.D.: Not detected.
2.2. Step-Wise Acid Leaching

The ash was leached using 1 M HCl solution. Ash (25 g) was added to the acid solution (100 mL; solid/liquid ratio 1/4). This mixture was stirred for 2 h with a magnetic stirrer. The solid was then separated from the solution by centrifugation, added to fresh acid solution, and stirred for 2 h. This procedure was repeated nine times. The solid obtained at each step was washed with pure water, which was purified using reverse osmosis membranes (Millipore Mill-Q Labo system, Merck, Tokyo, Japan), to neutralize the washing solution and dried at 60 °C overnight in a drying oven. The solid samples were examined using X-ray diffraction (XRD; Rint-2200U/PC-LH, Rigaku, Kyoto, Japan). The pH of each leachant was determined using a pH meter (PH/ION METER F-23, Horiba, Kyoto, Japan). The concentrations of Si, Al, Ca, and Mg (the four main elements in the ash) leached in the solution at each step were determined using inductively coupled plasma atomic emission spectroscopy (ICP-AES; SPS4000, Seiko, Tokyo, Japan), and the extraction ratios of each element from the ash was calculated as follows:

\[
\text{Extraction ratio} = \frac{(C_M \times V)}{(P_{M,0} \times W)} \times 100 \quad [\text{M: Si, Al, Ca and Mg}] \tag{1}
\]

where \(C_M\) is the measured concentration of elements in solution (g/L), \(V\) is the volume of the solution (L), \(P_{M,0}\) is the percentage of elements in the ash (%), and \(W\) is the mass of the ash.

2.3. Zeolite Synthesis

The leached ashes were zeolitized. An ash sample (5 g) was added to 2.5 M NaOH solution (50 mL) in a 100 mL polymethylpentene Erlenmeyer flask with a Dimroth condenser. Zeolitization was performed at atmospheric pressure at 80 °C for 24 h. The solid product was separated from the solution by filtration, washed with pure water, and dried at 60 °C overnight in a drying oven. The product was examined using XRD, and the concentrations of Si and Al in the solution after synthesis were determined using ICP-AES. The morphologies of the product were observed using scanning electron microscopy (SEM; S-2600H, Hitachi, Tokyo, Japan).

2.4. Determination of Amount of Released Ca and Na, and Product CECs

The product CEC was determined using a modified Schöerrenberg’s method [25]. The exchangeable cations in the product were replaced by \(\text{NH}_4^+\) using 1 M ammonium acetate solution. This process was repeated three times, for 20 min per exchange. The concentrations of Ca and Na in the ammonium acetate solution were determined using ICP-AES. The sample was then washed with 80% ethanol solution to remove excess salt. \(\text{NH}_4^+\) was then replaced by \(\text{K}^+\) using 10% KCl solution for 20 min. This process was repeated three times. Finally, the CEC of the sample was determined based on the amount of \(\text{NH}_4^+\) in the KCl solution, using the thymor blue method.

It is noted that all analytical errors for the data in this paper are less than 10%.

3. Results and Discussion

3.1. Acid Leaching of Paper Sludge Ash

Figure 1 shows the XRD patterns of the ashes leached with 1 M HCl solutions at each leaching step. It is noted that mineralogical compositions indicated in this figure are theoretical values. Gehlenite and anorthite were the main crystalline components of the raw ash. The concentration of gehlenite decreased with increasing numbers of leaching steps up to three, shown by a weakening of its XRD peaks, and only anorthite remained in the ash. The amount of anorthite also decreased up to the sixth step. These results confirm that gehlenite is more soluble than anorthite, and that only gehlenite crystalline phases in the raw ash can be removed by three steps of acid leaching. It is noted that peaks from talc, quartz, mullite, hematite, calcite and other phases appeared after six steps, due to the disappearance of other strong mineral peaks.
With increasing numbers of leaching treatment, pH of the leachant decreases to zero up to the leaching stages of 5–6 steps (Figure 2a), extraction ratios of Ca and Mg gradually decrease (Figure 2b), while those of Si and Al increase at the initial leaching stage of 1–3, and the leachant pH slightly decreased from 3.5 to 2.5, due to the dissolution of amorphous and gehlenite phases. In the leaching stage of 4–6, high contents of Si and Al were extracted from the ash than those of Ca and Mg, and the leachant pH drastically decreased to almost zero, due to the main dissolution of anorthite.

Considering the result of Figure 1, high contents of Ca and Mg were firstly extracted from the ash than those of Si and Al in the initial leaching stage of 1–3, and the leachant pH slightly decreased from 3.5 to 2.5, due to the dissolution of amorphous and gehlenite phases. In the leaching stage of 4–6, high contents of Si and Al were extracted from the ash than those of Ca and Mg, and the leachant pH drastically decreased to almost zero, due to the main dissolution of anorthite.

Table 1 shows the chemical compositions of raw ash and leached ashes. With increasing the number of acid leaching, Ca content in the ash gradually decreases, while Si content increases. The Si content in raw ash is 1.5 times as high as Al content, while Al extraction is higher than Si extraction, to obtain the ash with poor Al content.
Zeolite Synthesis from Leached Ash and Procut Properties

Figure 3 shows the XRD patterns of the products synthesized from ash leached with 1 M HCl solution as a function of the number of leaching treatments. It is also noted that mineralogical compositions indicated in this figure are theoretical values. Zeolites A and P were synthesized from the ash leached once and more than twice, respectively; hydroxysodalite was synthesized from the raw ash. The anorthite peaks in the product patterns were less intense than that in the raw ash pattern, indicating that most of the anorthite dissolved in the alkali solution during synthesis; gehlenite, tacle, quartz, mullite and other phases in leached ashes were mostly unaffected. These results suggest that anorthite is involved in zeolite synthesis, but most of gehelenite, tacle, quartz, mullite and phases are not dependent, which is in good accordance with the results of previous papers [21–23]. It is noted that zeolite synthesis from the ash leached at 6–9 steps of leaching would occur by partially dissolving some silicate minerals, such as quartz, mullite and other phases.

**Figure 2.** (a) Leachant pH and the step-wise extraction ratio of (b) Ca, Mg, (c) Si and Al into 1 M HCl solutions as a function of the number of leaching treatments.

**Figure 3.** XRD patterns of products synthesized from ashes leached with 1 M HCl solution, as a function of the number of leaching treatments.
Figure 4 shows SEM images of (a) the product from raw ash, (b) the product from the first leached ash, and (c) the product from fourth leached ash. The products have different morphologies. The product from raw ash consists of aggregates of ball-like particles (Figure 4a), and that from the first leached ash is a mixture of ball-like and cubic particles (Figure 4b). The product from the fourth leached ash consists of prismatic particles (Figure 4c).

Figure 4. SEM images of products from (a) raw ash, (b) ash leached once, and (c) ash leached four times.

Figure 5 shows the amounts of Ca and Na released from the products, synthesized from leached ashes, into ammonium acetate solution, as a function of the number of leaching treatments for the ash. With increasing numbers of leaching treatments for the ash (raw materials of the product), the amount of Ca released from the product gradually decreased, as a result of removal of Ca by acid leaching before zeolite synthesis. With increasing numbers of leaching treatments up to three, the amount of Na released from the product increased, and then gradually decreased.

Figure 5. Amounts of Ca and Na released from products, synthesized from leached ashes, into ammonium acetate solution, as a function of the number of leaching treatments for the ash.

Figure 6 shows the CECs of the leached ashes and the products synthesized from them, as a function of the number of leaching steps for the ash. For the leached ash, the CEC increased from 0 to 0.4 mmol/g with increasing numbers of leaching treatments up to three, and then decreased to zero. As shown in Figures 1 and 2, at fewer than three leaching treatments, gehlenite dissolved and the solution pH was around 3. Under these conditions, Si and Al dissolved from gehlenite and other phases to form an aluminosilicate gel with a CEC. However, for more than three leaching steps, the solution pH was less than 1, and high amounts of Si and Al were removed from the ash without formation of an aluminosilicate gel [21]. The CEC of the product is similar to the amount of Na released from the product, because of ion exchange of Na-type zeolitic phases in the product. When the number of leaching treatments was increased to three, the CEC of the product from the leached ash increased to 1.5 mmol/g, which is about four times higher than that of the product from raw ash, and then gradually decreased.
With increasing numbers of acid-leaching steps, Ca extraction increased, and the Si concentration in the alkali solution was lower than that of Al, because of poor Ca extraction. However, when leaching was performed more than five times, the amount of Al in the ash was low, and much Si remained in solution after the synthesis, because of the shortage of Al. The yields of zeolite P in the products from the ashes after leaching treatments for the ash increased to 1.5 mmol/g, which is about four times higher than that of the product from raw ash, and then gradually decreased.

Figure 7 shows the concentrations of Si and Al in NaOH solutions after zeolite synthesis. The concentration of Si in the solution after synthesis increased, and that of Al decreased, with increasing numbers of leaching treatments for the ash. The product from the first leached ash was zeolite A, and the Si concentration in the alkali solution was lower than that of Al, because of poor Ca extraction. With increasing numbers of acid-leaching steps, Ca extraction increased, and the Si concentration in the alkali solution increased; zeolite phase production was promoted, and the zeolite phase changed to zeolite P, which has a high Si:Al ratio. However, when leaching was performed more than five times, the amount of Al in the ash was low, and much Si remained in solution after the synthesis, because of the shortage of Al. The yields of zeolite P in the products from the ashes after leaching more than five times therefore decreased, and the product CEC decreased.

From these results, ash was treated with HCl before a drastic decrease in pH occurred, due to the disappearance of gehlenite buffering, to obtain the leached ash with low contents of Ca and Mg and high contents of Si and Al for the synthesis of the product with the highest CEC (about 1.5 mmol/g), including zeolite P.
4. Conclusions

We converted paper sludge ash to zeolitic products with high CECs through step-wise acid leaching with dilute HCl. Ca and Mg were firstly extracted from the ash and then Si and Al, via acid leaching. High amounts of Ca and Mg and low amounts of Si and Al were initially extracted, and then the Ca and Mg extractions drastically decreased and high contents of Si and Al were extracted. This changing point corresponds to the disappearance of gehlenite phase in the ash, and we can observe the drastic change in leachant pH. Zeolitic products were synthesized from the leached ashes with 2.5 M NaOH solution at 80 °C for 24 h, and zeolites A and P were synthesized from the leached ashes. The product with the highest CEC can be synthesized from the ash leached on the start of drastic change in leachant pH, and the highest CEC of the product was 1.5 mmol/g, which is about four times higher than that of the product from raw ash (0.4 mmol/g).

Funding: This research received no external funding.

Conflicts of Interest: The author declares no conflict of interest.

References

1. Monte, M.C.; Fuente, E.; Blanco, A.; Negro, C. Waste management from pulp and paper production in the European Union. Waste Manag. 2009, 29, 293–308. [CrossRef] [PubMed]
2. Kinoshita, N.; Ujike, I.; Kawaai, K.; Kawaguchi, T.; Yasuhara, H.; Nagae, T. Performance evaluation of low carbon concrete using paper sludge ash. J. MMIJ 2017, 133, 132–139. [CrossRef]
3. Jang, H.; Lim, Y.T.; Kang, J.H.; So, S.; So, H. Influence of calcination and cooling conditions on pozzolanic reactivity of paper mill sludge. Constr. Build. Mater. 2018, 166, 257–270. [CrossRef]
4. Segui, P.; Aubert, J.E.; Husson, B.; Measson, M. Characterization of wastepaper sludge ash for its valorization as a component of hydraulic binders. Appl. Clay Sci. 2012, 57, 79–85. [CrossRef]
5. Mavroulidou, M.; Avoliiy, S. A study on the potential use of paper sludge ash in concrete with glass aggregate. Waste Manag. Res. 2018, 36, 1061–1065. [CrossRef]
6. Bui, N.K.; Satomi, T.; Takahashi, H. Influence of industrial by-product and waste paper sludge ash on properties of recycled aggregate concrete. J. Clean. Prod. 2019, 214, 403–418. [CrossRef]
7. Monower, S.; Hassan, A.-N.; William, A.; Linda, S.; Nicola, D. Analytical investigation of hydration mechanism of non-Portland binder with waste paper sludge ash. Constr. Build. Mater. 2019, 211, 80–87.
8. Wajima, T.; Shimizu, T.; Ikegami, Y. Stabilization of mine waste using paper sludge ash under laboratory condition. Mater. Trans. 2007, 48, 3070–3078. [CrossRef]
9. Mavroulidou, M. Use of waste paper sludge ash as a calcium-based stabilizer for clay soils. Waste Manag. Res. 2018, 36, 1066–1072. [CrossRef]
10. Wajima, T.; Rakovan, J.F. Removal of fluoride ions using calcined paper sludge. J. Therm. Anal. Calorim. 2013, 113, 1027–1035. [CrossRef]
11. Wajima, T.; Rakovan, J.F. Removal behavior of phosphate from aqueous solution by calcined paper sludge. Colloid. Surf. A 2013, 435, 132–138. [CrossRef]
12. Querol, X.; Moreno, N.; Umana, J.C.; Alastuey, A.; Hernandez, E.; Lopez-Soler, A.; Plana, F. Synthesis of zeolites from coal fly ash: An overview. Int. J. Coal Geol. 2002, 50, 413–423. [CrossRef]
13. Musyoka, N.M.; Petrik, L.F.; Balfour, G.; Ndungu, P.; Gitari, W.M.; Hums, E. Synthesis of zeolites from coal fly ash: Application of a statistical experimental design. Res. Chem. Intermed. 2012, 38, 471–486. [CrossRef]
14. Li, Y.; Liang, G.; Chang, L.; Zi, C.; Zhang, Y.; Peng, Z.; Zhao, W. Conversion of biomass ash to different types of zeolites: A review. Energy Sour. A 2019, 7, 1–14. [CrossRef]
15. Belviso, C. State-of-art applications of fly ash from coal and biomass: A focus on zeolite synthesis processes and issues. Prog. Energy Combust. Sci. 2018, 65, 109–135. [CrossRef]
16. Koshy, N.; Singh, D.N. Fly ash zeolites for water treatment applications. J. Environ. Chem. Eng. 2016, 4, 1460–1472. [CrossRef]
17. Jiang, Z.; Yang, J.; Ma, H.; Ma, X.; Yuan, J. Synthesis of pure NaA zeolites from coal fly ashes for ammonium removal from aqueous solutions. Clean. Technol. Environ. Policy 2016, 18, 629–637. [CrossRef]
18. Lee, C.-H.; Park, S.-W.; Kim, S.-S. Breakthrough analysis of carbon dioxide adsorption on zeolite synthesized from coal fly ash. *Korean J. Chem. Eng.* **2014**, *31*, 179–187. [CrossRef]

19. Catalfamo, P.; Patane, G.; Primerano, P.; Pasquale, S.D.; Corigliano, F. The presence of calcium in the hydrothermal conversion of amorphous aluminosilicates into zeolite: Interference and removal. *Mater. Eng.* **1994**, *5*, 159–173.

20. Murayama, N.; Ishimoto, H.; Shibata, J. Hydrothermal synthesis and physical property evaluation of zeolite from paper sludge ash. *J. Min. Mater. Process. Inst. Jpn.* **2000**, *116*, 31–36.

21. Wajima, T.; Kuzawa, K.; Ishimoto, H.; Tamada, O.; Nishiyama, T. 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. Miner.* **2004**, *89*, 1694–1700. [CrossRef]

22. Wajima, T.; Ikegami, Y. Zeolite synthesis from paper sludge ash via acid leaching. *Chem. Eng. Commun.* **2008**, *195*, 305–315. [CrossRef]

23. Wajima, T.; Munakata, K. Removal of Ca from paper sludge ash by acid leaching and synthesis of high cation exchange capacity zeolite material. *Int. J. Soc. Mater. Eng. Resour.* **2011**, *18*, 7–10. [CrossRef]

24. Wajima, T.; Munakata, K. Preparation of zeolitic material with simultaneous removal of NH$_4^+$ and PO$_4^{3-}$ from paper sludge ash via acid leaching. *J. Mater. Cycles Waste Manag.* **2014**, *16*, 367–372. [CrossRef]

25. No. 111 Committee: Development of New Utilization of Materials (DNUM). In *Natural Zeolite and Its Utilization*; JSPS: Tokyo, Japan, 1994; pp. 318–325.