

Synthesis of zeolites from municipal incinerator fly ash

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Abstract

In this work, synthesis of zeolite-like materials from a municipal incinerator fly ash (MIFA) was carried out by means of hydrothermal processing. MIFA is generally hazardous in nature. Therefore, many technologies have been developed for the treatment, disposal, and utilization of this special waste. In this investigation, conversion of MIFA to zeolite-like materials was conducted in reaction bombs that were subjected to heating in a rocking chamber. Aqueous NaOH was used as a mineralizer to assist the conversion reaction. Experimental parameters studied include the mineralizer concentration, solid/liquid (i.e., MIFA/mineralizer) ratio, reaction time, and operating temperature. Powder patterns of X-ray diffraction analysis have shown that several types of zeolite such as gismondine and gmelinite were successfully synthesized under certain experimental conditions. Therefore, it is technically feasible to synthesize zeolites from MIFA. Based on the promising results obtained, further studies are under way to upgrade the quality of synthesized products so that their applications could be expanded. © 1998 Elsevier Science B.V. All rights reserved.

Keywords: Municipal incinerator fly ash; Synthesis; Zeolite

1. Introduction

Due to the shortage of landfill space for municipal solid waste (MSW), R.O.C. EPA has decided to adopt incineration to a much greater extent to ease the disposal problems of MSW. In Taiwan, a majority of the existing landfills will come to their ends of life within two years. In addition, it is very difficult to obtain new landfill sites in Taiwan at the present time. Since incineration can greatly reduce the volume and weight of MSW,

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21 large-scale municipal incineration plants will be constructed in Taiwan by the year of 2001 [1]. It was estimated that more than 1100 MT/day of municipal incinerator ashes (including fly ash and bottom ash fractions) will be generated at that time [2]. About 15% of such ashes is municipal incinerator fly ash (MIFA), which is generally hazardous in nature [3–5]. This ash must be managed on a daily basis. Therefore, a proper treatment and/or disposal of this special waste is needed. Several treatment, disposal, and utilization options for MIFA have been reported by Wiles [5].

In this investigation, hydrothermal processing was employed to recycle MIFA by converting it to zeolite-like materials through synthesis. More than 100 types of zeolite have been synthesized from various raw materials in the past. For example, coal-fired power plant fly ash has been successfully converted to many types of zeolite such as phillipsite, analcime, and zeolite P [6–16]. To the best knowledge of the authors, however, conversion of MIFA to zeolite-like materials has not been reported in the literature by researchers other than the present authors. Therefore, the objective of this paper was to present in more detail the research findings of synthesizing zeolites from MIFA reported elsewhere by the present authors [17–20].

2. Experimental

2.1. Materials

In this study the municipal incinerator fly ash specimen (designated MIFA S) was obtained from a large-scale modern waste-to-energy plant (i.e. municipal incineration plant) in northern Taiwan. This municipal incineration plant employs cyclones, spray dry scrubber, and fabric filters as air pollution control devices. The MIFA specimen studied is the larger size fraction of particulates collected by cyclones before the spray dry scrubber. The MIFA specimen was subjected to sieving to obtain the minus 200 mesh ($< 75 \mu\text{m}$) fraction and wet magnetic separation to remove ferro-magnetic materials, then oven-dried at 105°C for 24 h before testing. The mineralizer used is an aqueous NaOH. All chemicals used are reagent grade. Water used meets the standards of ASTM Type I deionized water.

2.2. Equipment

In this investigation, the equipment employed for synthesis was custom-made by a local factory. It consists of six reaction bombs, which are placed in a rocking chamber connecting with a PID temperature controller. Each reaction bomb was made of SUS No. 304 stainless steel exterior and Teflon liner for containing the raw materials and mineralizer for reaction.

2.3. Methods

2.3.1. Characterization of municipal incinerator fly ash

Before the synthesis MIFA S was characterized by its particle size distribution, chemical composition, total content of heavy metals, TCLP leaching toxicity, and loss

on ignition The particle size distribution was analyzed by various standard sieves and Coulter LS 100 Particle Size Analyzer. The chemical composition was analyzed according to ASTM E886-88. The total content of heavy metals and leaching toxicity were determined by U.S. EPA SW-846 Methods 3050 and 1311, respectively. The loss on ignition was determined according to ASTM C311-90. Other properties such as cation exchange capacity, BET surface area, and average pore radius were also determined by various methods described in Section 2.3.3. For the purpose of comparison, X-ray diffraction analysis was carried out as well. Its operating conditions were given in Section 2.3.3.

2.3.2. Synthesis of zeolite-like materials

The pretreated MIFA specimen and mineralizer were placed in the reaction bombs, then subjected to heating for the synthesis of zeolite-like materials. The experimental variables are the mineralizer concentration, solid-to-liquid (i.e. MIFA/mineralizer) ratio, reaction time, and operating temperature. After the reaction, the solid–liquid separation followed. The liquid fraction (i.e. residual liquid) was characterized for its heavy metal concentrations as described in Section 2.3.3. The solid fraction was thoroughly rinsed with deionized water, then oven-dried at 105°C for 24 h. The dry synthesized products were ground and stored for later analyses.

2.3.3. Characterization of synthesized products and residual liquids

The synthesized products obtained from each batch reaction were characterized by the properties listed as follows: (1) cation exchange capacity (CEC), by U.S. EPA SW-846 Method 9081; (2) BET surface area and average pore radius, by Micromeritics Surface Area Analyzer, Model ASAP 2010; and (3) mineral species, by X-ray diffraction (XRD) analysis using Cu K α radiation, 40 kV, 30 mA, and a scanning rate of one degree per minute from 10° to 70° or 80° for 2 θ . The results of determined d-spacing and relative intensities for corresponding 2 θ values were analyzed according to a data base provided by the Joint Committee on Powder Diffraction Standards (JCPDS). In so doing, each of the mineral species including zeolite-like materials was identified according to the major and minor peaks designated by JCPDS. Due to the complexity of crystalline phases, the overlapping of peaks for different mineral species is a commonplace. The residual liquid after reaction was digested by 30% H₂O₂ before the determination of various heavy metal concentrations by flame atomic absorption spectroscopy.

3. Results and discussion

3.1. Characteristics of municipal incinerator fly ash

Characterization results of MIFA S studied in this work are shown as follows [21]: (1) pH in 0.01 M CaCl₂: 10.69; pH in H₂O: 10.11; (2) total contents of heavy metals (mg/kg): lead, 4450 ± 26; cadmium, 189.0 ± 0.2; chromium, 195.8 ± 4.3; zinc, 11 558 ± 117; and copper, 1532 ± 9; (3) TCLP leaching toxicity (mg/l): lead, 2.45 ± 0.25;

cadmium, 7.50 ± 0.55 ; chromium, 0.23 ± 0.04 ; zinc, 256.6 ± 59.7 ; and copper, 0.23 ± 0.02 ; (4) particle size (μm): mean, 22.86; and median, 25.73; (5) loss on ignition (%): 5.53. The TCLP test result has indicated that the leached cadmium concentration of MIFA S is greater than the current R.O.C. EPA regulatory threshold (i.e. 1 mg/l). Therefore, MIFA S studied in this work was identified as a hazardous waste. In addition, the chemical composition of MIFA S was also presented as follows: (1) SiO_2 , 21.99%; (2) Al_2O_3 , 10.16%; (3) Fe_2O_3 , 3.29%; (4) CaO , 18.12%; (5) MgO , 2.80%; (6) Na_2O , 5.93%; and (7) residual, 37.72%. The weight percentages of SiO_2 and Al_2O_3 in this MIFA specimen are much less than those in coal-fired power plant fly ashes reported in the literature [9,22]. For coal-fired power plant fly ash, the weight percentages are in the neighborhood of 50% and 25% for SiO_2 and Al_2O_3 , respectively. These two mineral species are considered to be important to the formation of zeolite-like materials. Furthermore, it is worth pointing out that the unknown 'residual' contains the largest fraction of MIFA S. This might be detrimental to the formation of zeolite-like materials. For MIFA S, the values of CEC, BET surface area, and average pore radius were determined to be 7.80 meq/100 g, $2.54 \text{ m}^2/\text{g}$, and 45.85 \AA , respectively. No zeolite species is identified in the powder pattern of XRD analysis for MIFA S.

3.2. Characteristics of synthesized products

3.2.1. Effects of mineralizer concentration

Effects of the mineralizer concentration on BET surface area and average pore radius are indicated in Fig. 1. Normally, when the alkalinity of a mineralizer is not high enough for synthesis, the zeolite structure will not be developed well. In the case of 1 N NaOH,

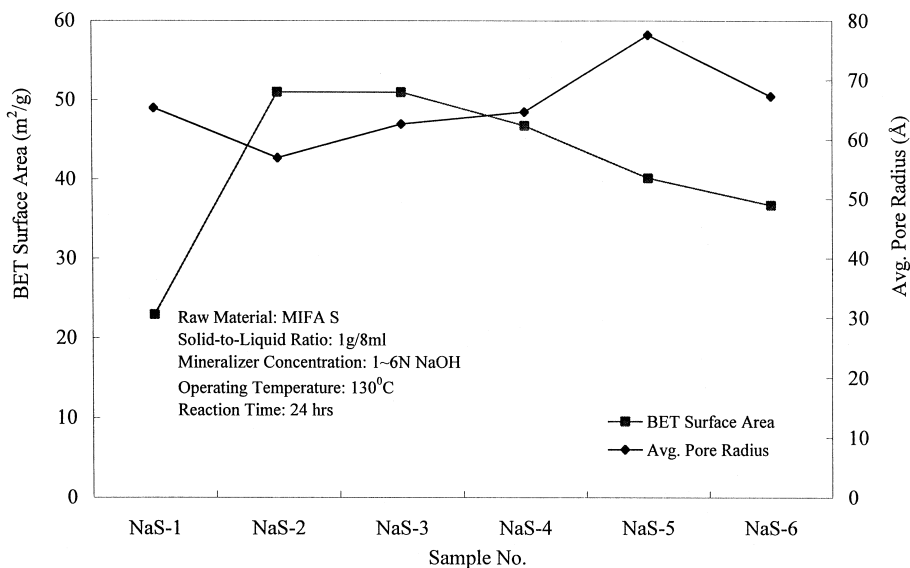


Fig. 1. Effects of the mineralizer concentration on BET surface area and average pore radius of synthesized products originated from MIFA S.

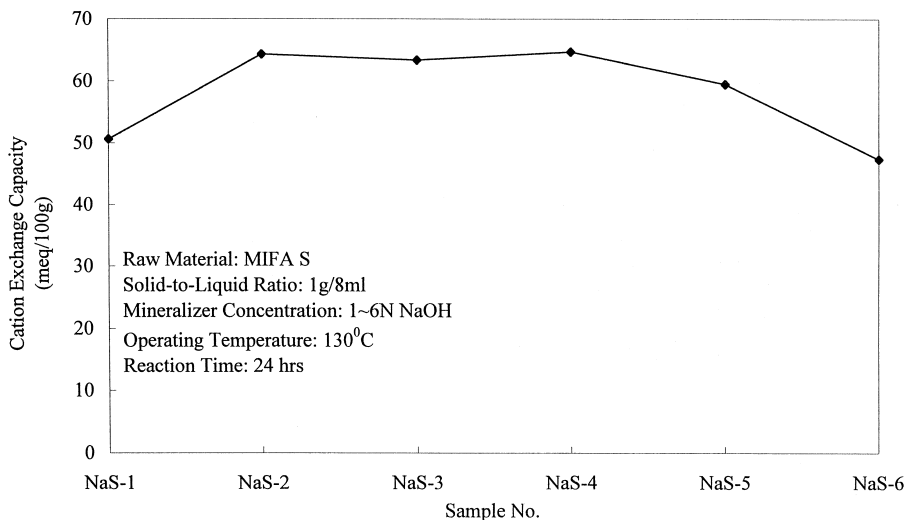


Fig. 2. Effects of the mineralizer concentration on cation exchange capacity of synthesized products originated from MIFA S.

the synthesized product of poor crystallinity thus resulted in a much smaller BET surface area. When the concentration of mineralizer was increased to 2 N or higher, zeolite-like materials were formed. Thus, greater values of BET surface area were obtained for these synthesized products. A decrease of specific surface area was noticed when a concentration of greater than 4 N was used. It is postulated that the zeolite type has changed from one to another in the neighborhood of this mineralizer concentration. In fact, XRD results to be presented later have shown that gismondine has been transformed to other types of zeolite (i.e. gmelinite and sodium aluminum silicate hydrate) around this mineralizer concentration. However, the increase of average pore radius due to this transformation of zeolite type was not very significant.

Likewise, the mineralizer concentration affected the CEC values of synthesized products (see Fig. 2). When 1 N NaOH was used, 50.61 meq/100 g of CEC was obtained. When the mineralizer concentration was maintained in the range of 2–4 N, a CEC value about 64 meq/100 g would be obtained. When the change of zeolite type occurred, the CEC value dropped. A CEC value of this magnitude for synthesized products obtained in this study is much smaller than that of commercial zeolites. In general, the CEC values of commercial zeolites are in the range of 200–300 meq/100 g, but some are as high as 920 meq/100 g [23].

3.2.2. Effects of solid-to-liquid ratio

Fig. 3 shows effects of the solid-to-liquid (i.e., MIFA/mineralizer) ratio on BET surface area and average pore radius for MIFA S after synthesis. In general, the variation of BET surface area is trivial, in the range of 38–43 m²/g. Similarly, average pore radii for synthesized products ranged from 66 to 70 Å. However, all synthesized products have greater values of BET surface area and average pore radius than those for

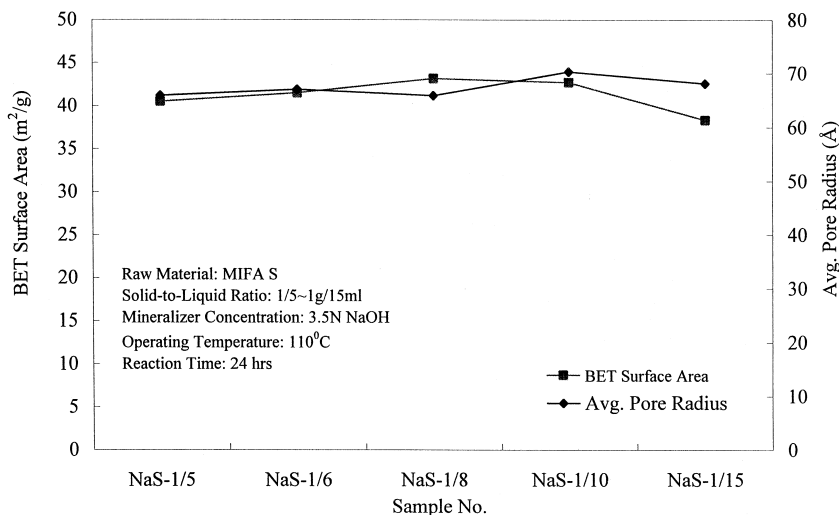


Fig. 3. Effects of the solid-to-liquid on BET surface area and average pore radius of synthesized products originated from MIFA S.

MIFA S before synthesis, namely 2.54 m²/g and 45.85 Å, respectively. It is worth pointing out that a mineralizer concentration of 3.5 N was used for the study of MIFA/mineralizer effects. From Fig. 1 it is clear that a mineralizer concentration of 3.5 N is high enough for MIFA S to convert to zeolite-like materials. As long as a mineralizer's concentration is greater than the threshold value for the development of a zeolite structure, effects of the MIFA-to-mineralizer ratio on specific surface area and average pore radius are found to be insignificant.

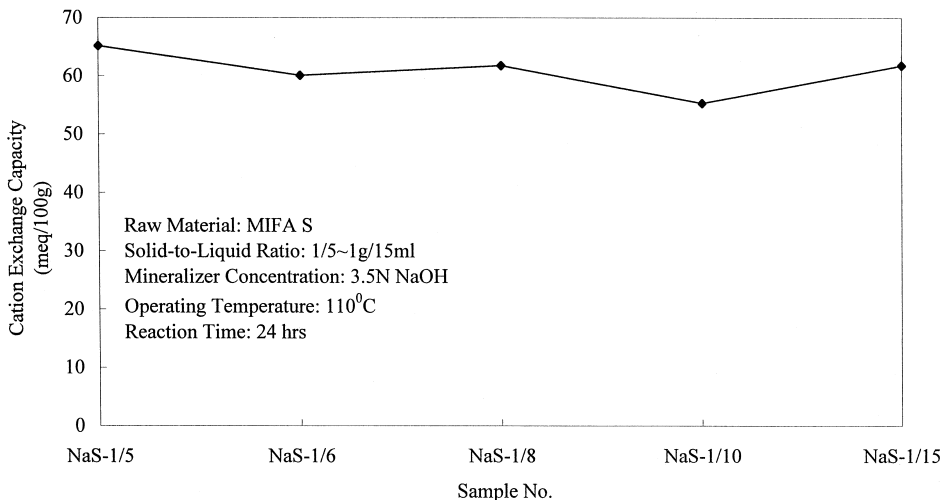


Fig. 4. Effects of the solid-to-liquid ratio on cation exchange capacity of synthesized products originated from MIFA S.

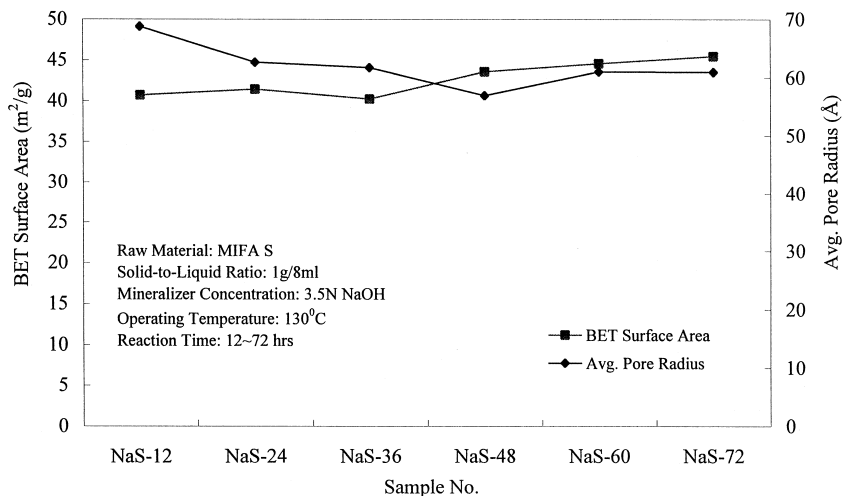


Fig. 5. Effects of the reaction time on BET surface area and average pore radius of synthesized products originated from MIFA S.

A similar effect of the solid-to-liquid ratio on CEC value was also found in Fig. 4. The same reason for this phenomenon has been given above.

3.2.3. Effects of reaction time

Similar to that of the solid-to-liquid ratio, effects of the reaction time on BET surface area and average pore radius were found to be insignificant in this work (see Fig. 5). For

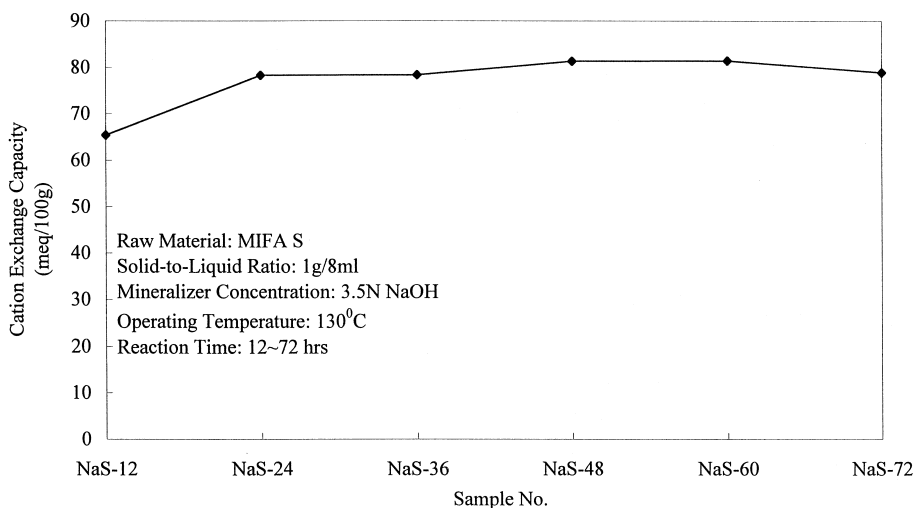


Fig. 6. Effects of the reaction time on cation exchange capacity of synthesized products originated from MIFA S.

all the reaction time tested, namely 12–72 h, BET surface areas ranged from 40.2 to 45.5 m²/g and average pore radii ranged from 56.9 to 68.7 Å. It is postulated that a profound effect of the reaction time in this regard would be observed if the reaction time varies from hours to week(s). In this study the synthesized products have much smaller values of specific surface area and much greater values of average pore radius in comparison with commercial adsorbents. For example, the values of specific surface area and pore size for activated carbons are 600–1600 m²/g and 3–500 Å, respectively [24]. The present quality of synthesized products would limit their applications to a great extent. Therefore, further studies to improve the quality of synthesized products are needed.

Regarding CEC, a reaction time of 12 h seemed to be not long enough for the structure development of zeolite-like materials. Therefore, it yielded the lowest CEC value (i.e. 65.4 meq/100 g) in this study. From Fig. 6, it is clear that a reaction time of 24 h would be an appropriate one for synthesizing zeolites from MIFA S.

3.2.4. Effects of operating temperature

Fig. 7 shows that the operating temperature would greatly affect BET surface areas and average pore radii of synthesized products. Though operating temperatures ranging from 110°C to 190°C yielded specific surface areas in the neighborhood of 45 m²/g, an operating temperature of 130°C yielded the greatest BET surface area. For an operating temperature lower than 110°C, perhaps it was too low in temperature for an ideal conversion to occur. Thus, a rather small BET surface area was obtained. On the other hand, for an operating temperature higher than 190°C, the BET surface area began to drop substantially. This might be ascribed to the formation of different mineral species in the synthesized product at this critical temperature of 190°C. Detailed discussion will

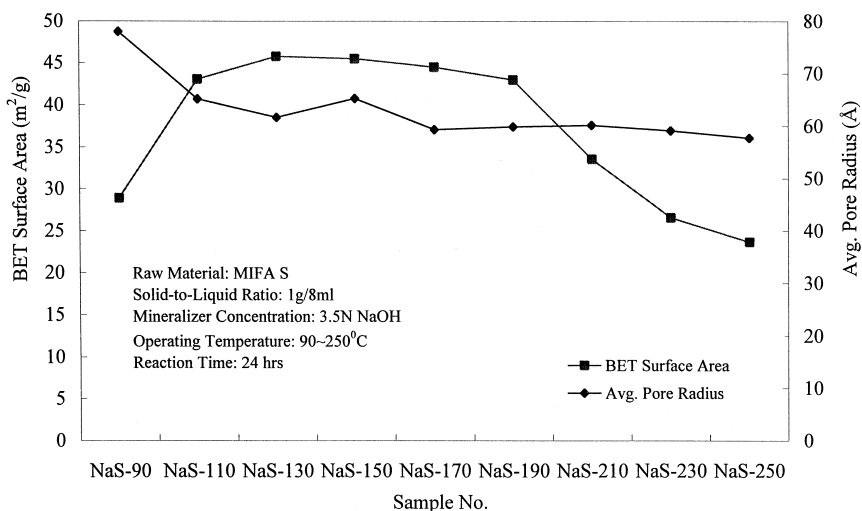


Fig. 7. Effects of the operating temperature on BET surface area and average pore radius of synthesized products originated from MIFA S.

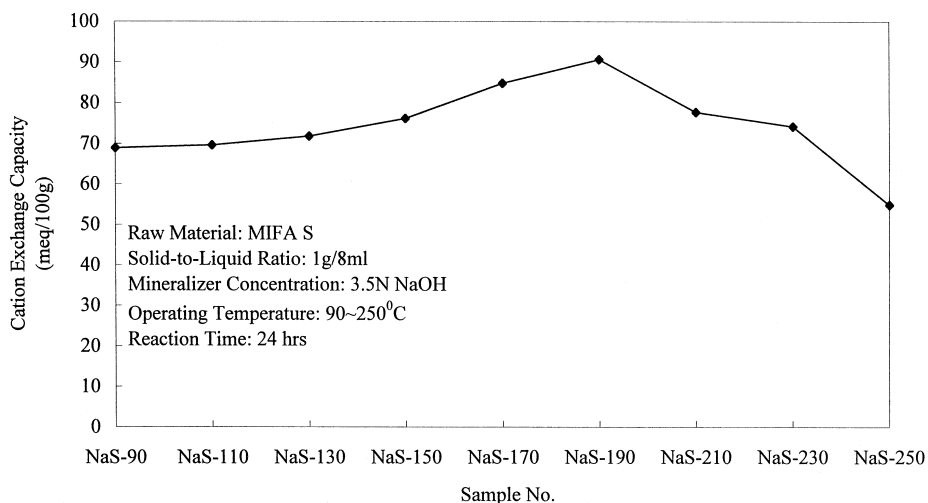


Fig. 8. Effects of the operating temperature on cation exchange capacity of synthesized products originated from MIFA S.

be given in Section 3.2.5. As for average pore radii, except the one for 90°C they are in the range of 57–65 Å for all temperatures tested.

As shown in Fig. 8, the CEC value of synthesized products increased as the operating temperature increased up to 190°C. Then the CEC value decreased with the increasing temperature. For the cases of 190°C and 250°C, results of XRD analysis show that they have the same major mineral species. Perhaps the difference in CEC values for these two cases are due to the difference in percentages of various zeolite-like materials.

3.2.5. X-ray diffraction analysis

Results of X-ray diffraction analysis have proved that hydrothermal processing is capable of converting MIFA S to zeolite-like materials. As indicated above, no zeolite species is identified in the MIFA specimen. After synthesis, however, several types of zeolite have been identified. XRD powder patterns for the synthesized products resulted from various MIFA/mineralizer ratios are similar, but different in relative intensities for various mineral species. On the other hand, different types of zeolite were formed under different mineralizer concentrations. For example, gismondine (a zeolite of the phillipsite group) was identified when 3.5 N NaOH was used; whereas gmelinite and sodium aluminum silicate hydrate (other types of zeolite) were identified when 6 N NaOH was used.

Figs. 9–11 and Figs. 12–14 show the effects of reaction time and operating temperature, respectively on the formation of zeolite-like materials. As shown in Fig. 9, a reaction time of 12 h are long enough for the formation of gismondine and sodium aluminum silicate hydrate. However, a substantial amount of residual quartz existed. From the variation of relative intensities for d spacing at 3.34 Å, it was found that most of quartz has involved in the formation of various zeolites as the reaction time increased.

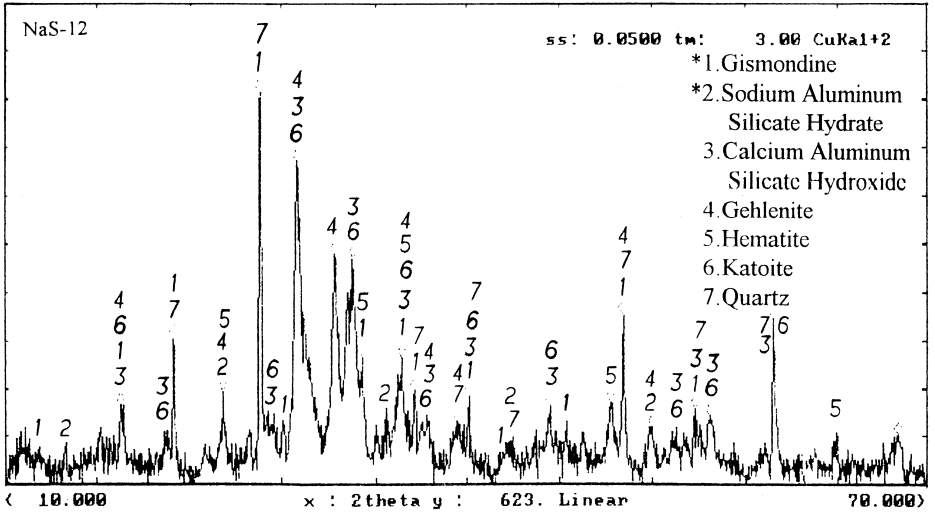


Fig. 9. Powder pattern of X-ray diffraction analysis for Sample No. NaS-12.

For a reaction time of 36 h, two additional zeolites (i.e. cancrinite and zeolite X) were identified (see Fig. 10). The amount of residual quartz greatly diminished after 72 h reaction (see Fig. 11). For an operating temperature of 90°C, Fig. 12 clearly shows that no zeolite species exists. It also shows that the relative intensity for quartz is the strongest. This is an indication that most of quartz is not fully involved in the conversion process at this operating temperature. When the operating temperature was increased to

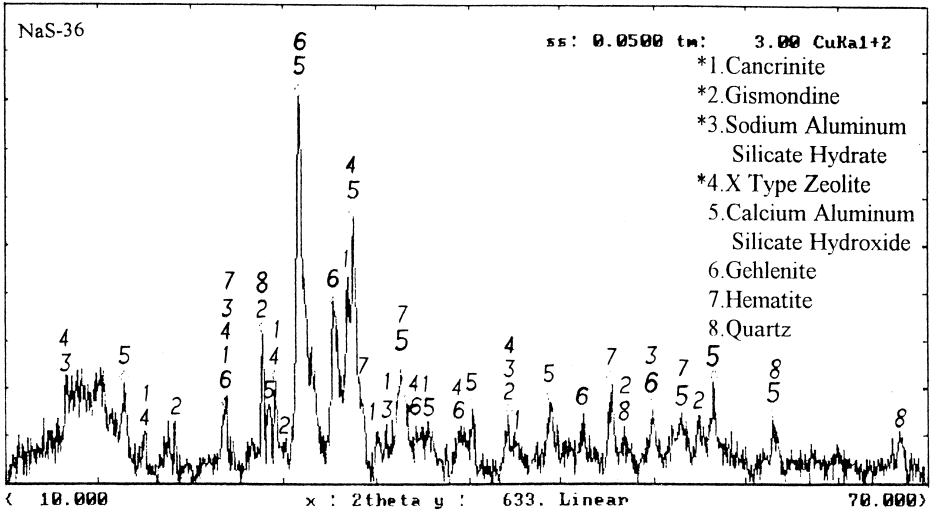


Fig. 10. Powder pattern of X-ray diffraction analysis for Sample No. NaS-36.

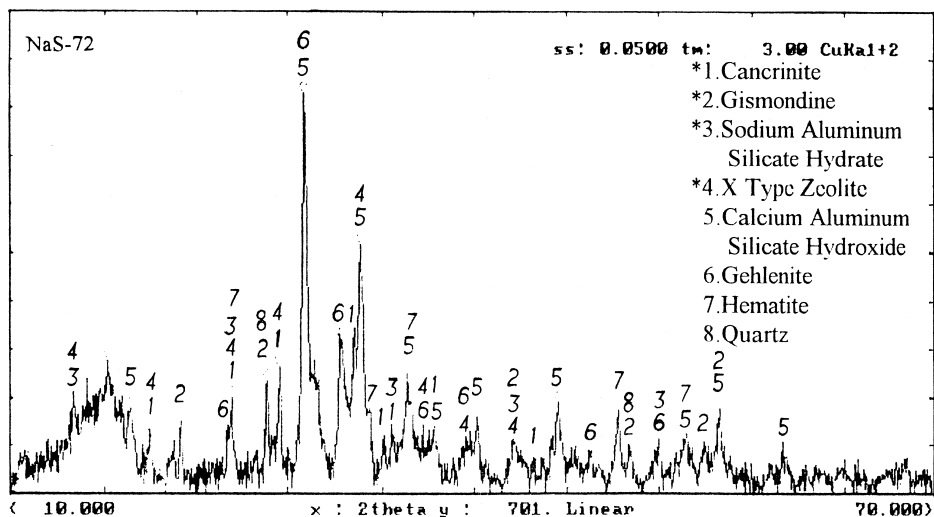


Fig. 11. Powder pattern of X-ray diffraction analysis for Sample No. NaS-72.

150°C, zeolites such as cancrinite, zeolite X, sodium aluminum silicate hydrate, and sodium aluminum sulfide silicate were identified (see Fig. 13). The powder patterns of XRD analysis for operating temperatures beyond 170°C are similar in mineral species, but different in relative intensities for some peaks. Quartz was found to disappear when the synthesis was conducted at 170°C or greater. It was also noticed that the crystalline

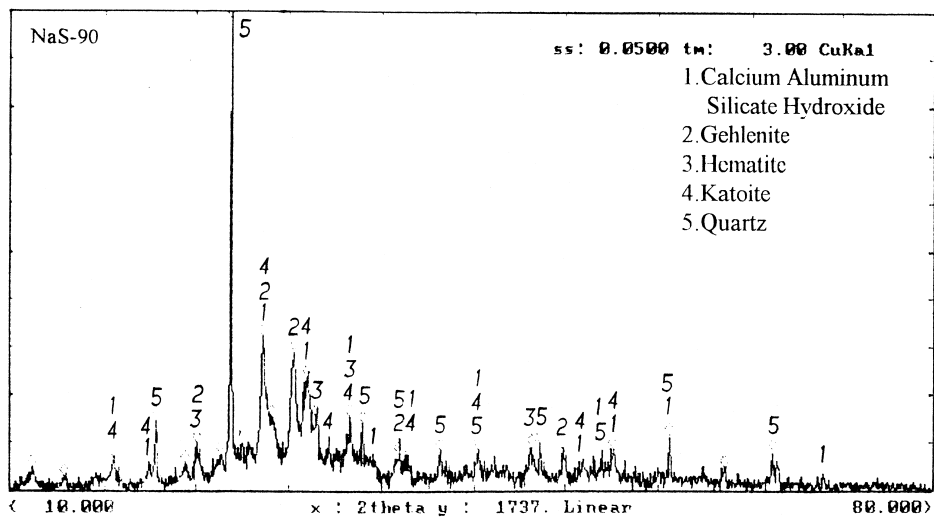


Fig. 12. Powder pattern of X-ray diffraction analysis for Sample No. NaS-90.

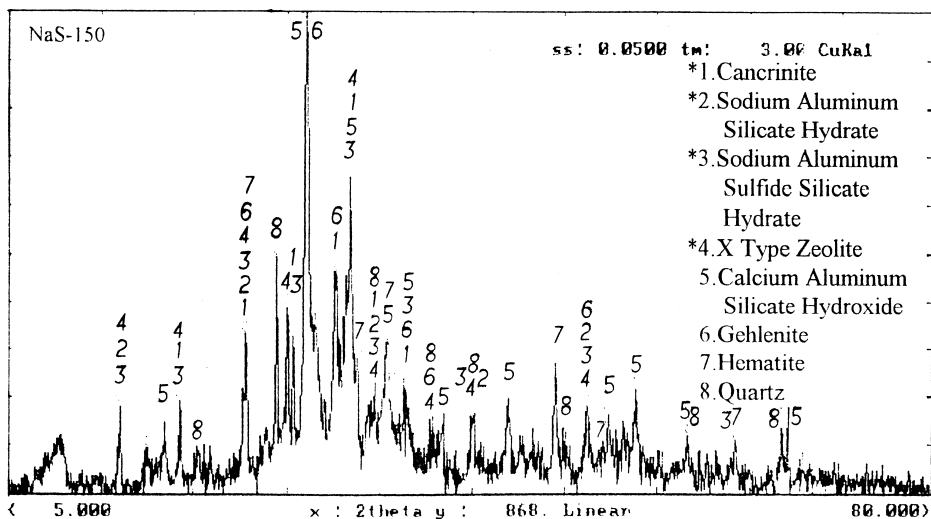


Fig. 13. Powder pattern of X-ray diffraction analysis for Sample No. NaS-150.

structure of an unidentified mineral species began to establish at $2\theta = 7.4^\circ$ for the operating temperature of 190°C (see Fig. 14). The relative intensity of this unidentified peak increased with increasing temperature up to 210°C , then levelled off. As shown in Fig. 7, the formation of this unidentified mineral species would account for the decrease of BET surface area for the operating temperatures equal and beyond 190°C .

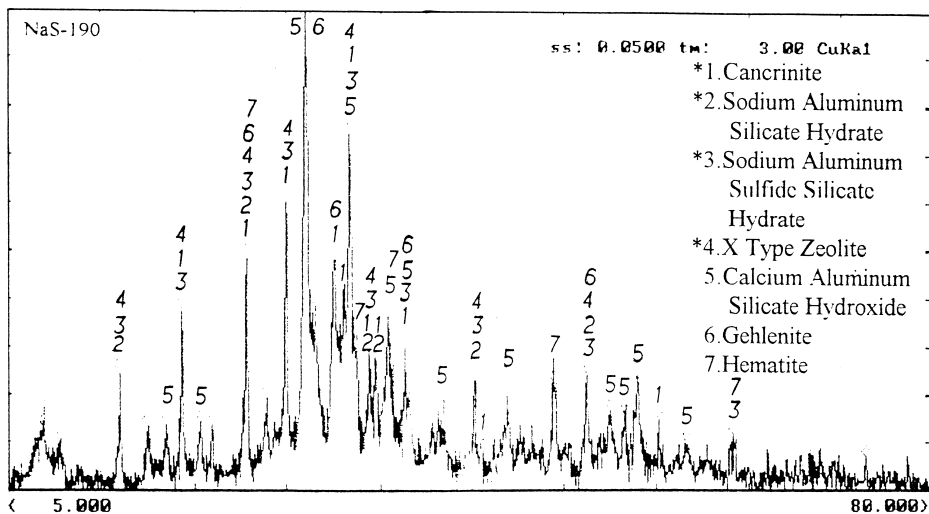


Fig. 14. Powder pattern of X-ray diffraction analysis for Sample No. NaS-190.

Table 1

Heavy metal concentrations of the residual liquids after synthesis under various mineralizer concentrations

Sample No.	Heavy metal concentration in the residual liquid (mg/l)				
	Cd	Pb	Cr	Cu	Zn
NaS-1	0.17	102.2	< 0.06	0.20	156.6
NaS-2	0.24	196.0	< 0.06	2.20	516.4
NaS-3	0.38	318.4	0.09	4.71	702.4
NaS-4	0.54	389.4	0.13	6.22	745.4
NaS-5	0.90	493.6	0.28	4.99	850.2
NaS-6	0.98	482.2	0.24	4.14	864.8

(1) Sample Nos. NaS-1 ~ NaS-6 denote various synthesized products.

(2) Synthesis conditions are as follows: (a) reaction temperature, 130°C; (b) reaction time, 24 h; and (c) MIFA-to-mineralizer ratio, 1 g/8 ml.

(3) Mineralizer concentrations are 1 N, 2 N, 3 N, 4 N, 5 N and 6 N for Sample Nos. NaS-1 ~ NaS-6, respectively.

3.2.6. TCLP leaching toxicity

Experimental results have indicated that all synthesized products are nonhazardous based on their TCLP leaching toxicity. Concentrations of leached metals (e.g. Cd and Pb) for all synthesized products are far below the current R.O.C. EPA regulatory limits. Therefore, the synthesized products obtained in this study are environmentally safe to use.

3.3. Heavy metal concentrations of the residual liquids after synthesis

Tables 1 and 2 show the concentrations of various heavy metals of the residual liquids after synthesis. It is clear that Pb and Zn are easily leached out in this synthesis system even with a mineralizer concentration of 1 N NaOH or a solid-to-liquid ratio of 1 g/5 ml. It was found that the leached concentration of Pb in the residual liquid

Table 2

Heavy metal concentrations of the residual liquids after synthesis under various MIFA-to-mineralizer ratios

Sample No.	Heavy metal concentration in the residual liquid (mg/l)				
	Cd	Pb	Cr	Cu	Zn
NaS-1/5	0.37	227.6	0.46	4.84	720.0
NaS-1/6	0.38	194.4	0.26	3.39	711.0
NaS-1/8	0.41	181.0	0.40	4.61	639.8
NaS-1/10	0.36	113.6	0.26	0.45	595.2
NaS-1/15	0.46	119.0	0.47	3.94	482.2

(1) Sample Nos. NaS-1/5 ~ NaS-1/15 denote various synthesized products.

(2) Synthesis conditions are as follows: (a) reaction temperature, 110°C; (b) reaction time, 24 h; and (c) mineralizer concentration, 3.5 N.

(3) MIFA-to-mineralizer ratios are 1 g/5 ml, 1 g/6 ml, 1 g/8 ml, 1 g/10 ml and 1 g/15 ml for Sample Nos. NaS-1/5 ~ NaS-1/15, respectively.

increased with an increasing mineralizer concentration regardless of the variation of other synthesis parameters. This finding is in good agreement with the fact that Pb is easily leached out in the municipal incinerator 'reaction products', which has a pH around 12.5 [25–27].

4. Conclusions

In this investigation, a specimen of municipal incinerator fly ash was mixed with aqueous NaOH as a mineralizer, then subjected to hydrothermal processing. It is aimed to convert this hazardous waste to an useful product in order to ease the disposal problem of MIFA. Based on the experimental results obtained, the following conclusions can be drawn:

1. It is technically feasible to recycle MIFA by converting it to zeolite-like materials.
2. To successfully convert MIFA to zeolite-like materials, a critical alkalinity of mineralizer is required.
3. Different species of zeolites will be formed at different alkalinity of mineralizer if other conditions of synthesis remain the same.
4. The residual liquid after the synthesis contains high concentrations of heavy metals such as Pb and Zn. It needs to be properly treated before discharge.
5. Though poor in quality, the zeolite-like materials obtained in this study are environmentally safe to use.
6. An improvement of the quality of synthesized products is needed to expand their applications.

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