Conversion of fly ash into zeolites for ion-exchange applications

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Abstract

Combustion byproduct fly ash was converted into zeolites which then can be used as ion exchangers for waste treatment applications. The conversion process not only alleviates the disposal problem of large amounts of fly ash, but also turns.fly ash into a useful material. Depending on the treatment temperature and chemical composition, zeolite A and faujasite have been successfully synthesized. The ion-exchange capacity of the treated fly ash was examined. The results show that the ion exchange capacities of the treated fly ash in the forms of zeolite A and faujasite, respectively, for Cs^+ ions relative to those of the commercial zeolite A and faujasite are: 19% for zeolite A phase and 39% for faujasite phase. Our results suggest that the treated fly ash may be potentially useful in waste-water treatment and radioactive waste immobilization.

Keywords: Coal; Combustion; Fly ash; Zeolite; Faujasite; Synthetic; Waste water; Radioactive waste; Ion exchange

1. Introduction

Each year nearly 850 million tons of coal are used in the United States to generate electricity [1]. Depending on the quality of the coal, different amounts of ash, the inorganic part of the coal, will be left after combustion. Using 10% as an estimate, the ash generated annually could be as much as 85 million tons. Using the state of Pennsylvania as an example, about 36% of the fly ash produced is utilized for reclamation, asphalt shingle production, quarry-fill and sludge stabilization [2]. However, the bulk of the ash is disposed of as landfill. Due to the shortage of landfill sites and tighter environmental regulation, new ways of utilizing fly ash are needed. Recently, Yoshida and Inoue [3], LaRosa et al. [4], Shigemoto et al. [5], Lin and Hsi [6], and Shih et al. [7] showed

that various types of zeolites can be produced from volcanic and coal ash by treating them with sodium hydroxide solution. Due to their uniform pore sizes and large surface areas, zeolites are very useful materials for a wide range of applications such as molecular sieves, adsorbents, and catalysts [8]. Therefore converting fly ash into zeolites potentially eliminates the disposal problem but also turns an otherwise useless waste into a marketable commodity.

Although zeolites have been synthesized from fly ash, the properties of the converted zeolites such as zeolite A and faujasite have not been examined in detail for ion-exchange capacity. The performance of the zeolites made from fly ash will determine whether or not converting fly ash into zeolites is a viable approach to recycle fly ash. Furthermore, the formation conditions for the various types of zeolites in fly ash were complex and depended on the chemical

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composition of fly ash used. A systematic study on the conditions for forming various types of zeolites from fly ash was needed. In the present paper, we investigated the conditions, mainly the effects of curing temperature and chemical composition, for forming two types of zeolites, zeolite A and faujasite, from class F fly ash. Also the results of the ion-exchange capacity of the treated fly ash was presented. Although zeolites converted from fly ash have many potential applications, due to the difficulty in separating the zeolites from the background materials in the fly ash, the most probable application is to use the zeolites together with the fly ash. One plausible application of the treated fly ash is to use it as an ion-exchange medium for immobilizing unwanted ions. Among the various types of natural and synthesized zeolites, faujasite and zeolite A have better ion-exchange property than other types of zeolites because of their larger pores in the structures [8]. Both faujasite and zeolite A have been shown to have good ion-exchange capabilities for ions such as Cs^+ and Co^{2+} which are abundant in nuclear wastes [9,10], and NH_4^+ ions which are abundant in waste water. Therefore, the objective of this study was to examine the conditions necessary to form faujasite and zeolite A from fly ash and study the ion-exchange properties of the treated fly ash.

2. Experimental procedures

The raw materials for the experiments were class F fly ash from Eddystone power plant of PECO Energy in the state of Pennsylvania. The X-ray diffraction pattern of the untreated fly ash showed that the major component of fly ash is amorphous glass with small amounts of crystalline quartz and mullite. The chemical composition of class F fly ash had been estimated: 50 wt% SiO_2, 30 wt% Al_2O_3, 10 wt% Fe_2O_3, and others [1]. By weight, one part of fly ash was mixed with 2.5 parts of a 2.8 M sodium hydroxide solution. The mixture was stirred for 30 min in a glass beaker with rubber stopper and then aged at room temperature and ambient atmosphere

for 2 days. After aging, the mixture in the same closed beaker was cured at 38°C for several days. X-ray diffractometry was used to monitor the formation of zeolites. For the purpose of quantitative measurement of the amount of zeolites formed in each mixture, pure $BaTiO_3$ powder was added to the mixture at the start of curing step with the weight ratio of $1:30$ relative to fly ash as an internal standard in the X-ray measurement. The relative amount of zeolites formed with respect to $BaTiO_3$ can be calculated by monitoring the relative intensity of selected $BaTiO_3$ and the zeolite peaks. For the formation of zeolite A, a certain amount of aluminum hydroxide powder (Aldrich Chemical company, Inc.) were added into each mixture before aging. At different curing periods, the solid mixture in the closed beaker was taken out, washed with distilled water, centrifuged and dried in air at 80°C for 1 day. In addition, for the purpose of comparison, synthesis of pure zeolites was also carried out. In the preparation of synthetic zeolites, different amounts of aluminum hydroxide powder were dissolved in 50 ml of 6 M sodium hydroxide solution. After diluting the solution to 120 ml solution, 30 ml Du Pont Ludox HS-30 solution (density = 1.21 g/cm^3, silica = 30 wt%) was added. The amounts of aluminum hydroxide added were 14.2 g and 7.1 g, respectively, for the formation of zeolite A and faujasite. All mixtures were kept in the glass beakers with rubber stoppers and aged for 1 day at room temperature and ambient atmosphere followed by curing at 80°C and ambient pressure for 1 day. The solid part of each sample was washed by distilled water, centrifuged and dried in air at 80°C for 1 day.

The ion-exchange capacities of treated fly ash were measured for ammonium and cesium ions at two concentrations, 8 N and 0.1 N as the ion-exchange capacity of the zeolite is dependent on the concentration of the ion being exchanged. For the purpose of comparing the ion-exchange capacities, three kinds of test suspensions were studied: the treated fly ash, pure synthetic zeolite and commercial zeolite supplied by UOP Inc., Chicago, IL. The treated fly ash, denoted as treated fly ash faujasite or treated fly ash A, representing the type of zeolites that the treated fly ash contains. The pure synthetic zeolites, synthesized from Ludox and aluminum hydroxide solutions, were denoted as synthetic faujasite

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[1] The composition was provided by PECO Energy.

or synthetic zeolite A, respectively. The zeolites made by UOP Inc. were denoted according to their brand names, that is, UOP4A and UOPY54, respectively. For the 8 N NH_4^+ and Cs^+ solutions, 1.8 g of synthetic zeolites or treated fly ash was suspended in 80 ml distilled water, stirred for 20 min and allowed to equilibrate for 30 min. The pH value and the concentration of sodium ion of each solution were measured by a pH meter (Cole-Parmer Instrumental Co., Chicago, IL.) and a sodium ion probe (Orion Research Incorporated, Boston, MA.), respectively. Then 0.1 ml of 8 N NH_4 Cl or CsCl solutions were added to the mixture, stirred for 1 min and the concentration of sodium ion was measured again. The process was repeated until there was no change in the reading of the sodium ion probe. For the 0.1 N Cs^+ solutions, 0.7 g of treated fly ash, synthetic zeolite, or commercial zeolite, were suspended in 40 ml of distilled water and then followed the same test procedures as the experiments of 8 N solutions. To eliminate the presence of residual sodium hydroxide in the test samples, both the treated fly ash and synthetic zeolites were washed several times with distilled water until the pH value of each sample solution fell below 11. After washing, the samples were centrifuged and dried in air at 80°C for 1 day.

3. Results and discussion

When fly ash treated with NaOH was heated at 38°C, faujasite formed after 3 days. Furthermore, the amount of faujasite formed at 38°C as a function of the curing time showed that after 5 days, the amount of faujasite no longer changed; it fluctuated about a constant value. The particle size distribution by volume showed that the treated fly ash has an additional distribution peak relative to the untreated fly ash. The additional size distribution peak occurs at the same size as the size distribution peak for the synthetic zeolites that we made. Therefore it is concluded that the additional size distribution peak is due to the converted zeolites. From the volume percentage of the additional size distribution peak, it was estimated that the amount of converted zeolites in the fly ash is approximately 20 vol%.

It is well known that in the synthesis of zeolites the Si/Al ratio of the precursor solutions is crucial

to the formation of selected zeolites [11]. Recently, Dutta and Bronic [12] synthesized zeolite P and faujasite by changing the Si/Al molar ratio in the precursor solutions. Another factor that can affect the types of zeolites formed is the curing temperature [4]. Recently, Petrovic et al. [13] measured the enthalpy of formation of various forms of aluminosilicates and found that faujasite is a metastable phase with an enthalpy about 10 kJ/mol higher than that of quartz. Since faujasite has a larger pore size and larger molar volume than zeolite P, it can be deduced from the results of Petrovic et al. [13] that zeolite P is more stable than faujasite. Since the faujasite and zeolite A are less stable than the zeolite P [7], our approach in synthesizing faujasite and zeolite A is to slow down the reaction by curing the fly ash solutions at lower temperatures, for example, 38°C. In general, higher Si/Al molar ratios and higher temperatures tend to form zeolite P whereas lower Si/Al molar ratios and lower temperatures favor faujasite and zeolite A.

When the fly ash and NaOH mixtures were treated at 80°C rather than 38°C, zeolite P formed. The amount of zeolite P formed at 80°C as a function of the curing time showed that zeolite P formed earlier and the amount of zeolite P formed was roughly 3 times that of faujasite. The relative ease with which zeolite P was produced is consistent with the fact that zeolite P is a more stable phase than faujasite. It has previously been pointed out that faujasite can dissolve in basic solutions and transforms into zeolite P [8]. In the study of Yoshida and Inoue [3], it was found that faujasite formed first, but after 72 h of heat treatment at 90°C the faujasite began to disappear and zeolite P began to form. Therefore, faujasite may transform into zeolite P at higher treatment temperatures and for longer treatment times. However, in the present study, the synthesized faujasites after converting at 38°C did not change to zeolite P after the curing temperature increased to 80°C for up to four days of treatment. The faujasite formed from the fly ash in our procedures was very stable. The reason for this stability is not clear at the moment. It should be noted that a difference between our study and that of Yoshida and Inoue is that our faujasites were formed at 38°C while that by Yoshida and Inoue was formed at 90°C. It is possible that the faujasite formed in their study was not as stable as

ours because they used higher temperatures. The other possibility is the difference of chemical composition in the fly ash used.

By adding aluminum hydroxide to the fly ash/NaOH solution, which formed faujasite, and curing this mixture at 38°C, zeolite A formed rather than faujasite. In theory, the amount of Al added was adjusted so that the Si/Al molar ratio in the solution was close to unity. However, the SiO_2 and Al_2O_3 in the fly ash may not dissolve completely, therefore the Si/Al molar ratio in the fly ash suspension was not exactly known. To ensure that there was enough Al in the solution, the amount of aluminum hydroxide added was such that the Si/Al molar ratio was made equal to unity by assuming that no Al_2O_3 in the fly ash dissolved but all SiO_2 in the fly ash dissolved. The X-ray diffraction pattern of the fly ash treated with $Al(OH)_3$ and NaOH at 38°C showed that zeolite A did form. There were some additional bayerite peaks coexisting with the zeolite A peaks due to the extra amount of $Al(OH)_3$ added. Obviously, the Si/Al molar ratio in the solutions is less than unity. On the other hand, when the amount of $Al(OH)_3$ added was such that Si/Al = 1 assuming both SiO_2 and Al_2O_3 in the fly ash dissolve completely, no zeolite A was formed. It is very likely that in this case the Si/Al molar ratio in the solutions is larger than unity. Our results are consistent with the observation mentioned by Breck [8] that the Si/Al ratio in solutions must be less than unity in order for zeolite A to be formed.

The ion-exchange behavior was studied by measuring the Na^+ ion concentration in the test suspensions using a sodium ion probe. The 8 N of NH_4^+ or Cs^+ solutions were added in small quantities (0.1 ml) to the test suspensions and the Na^+ concentration in the suspensions was measured. The total measuring time is about 3 h when there was no concentration change of sodium ion in the mixture. As the NH_4^+ or Cs^+ ions exchange with the Na^+ ions in the zeolites, the Na^+ concentration in the test suspensions increases. As the ion-exchange capacity of the zeolites saturates, the sodium concentration in the suspensions would stabilize. The ion-exchange capacity of the treated fly ash was then compared with that of the synthetic zeolites and commercial zeolites.

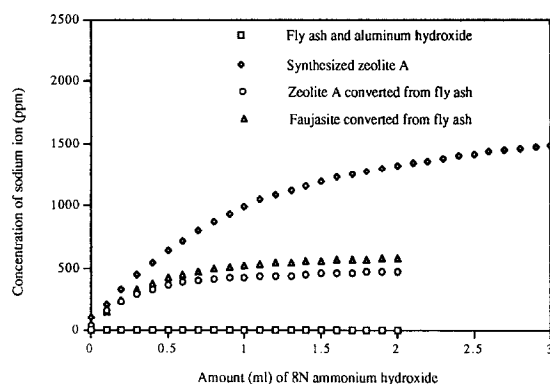The concentration of Na^+ ion in solutions of the

Fig. 1. Concentration of sodium ions in 80 ml solutions of 1.8 g zeolites or fly ash as a function of the amount of 8 N ammonium hydroxide added.

treated fly ash samples plotted as a function of the amount of 8 N NH_4OH solution added is shown in Fig. 1. Also shown in Fig. 1 are the results for the synthetic zeolites and the untreated fly ash. No ion exchange was observed in untreated fly ash while there is significant ion exchange in the treated fly ash. From the data in Fig. 1, the exchange capacity per gram of the treated fly ash A is 0.86 milliequivalents (i.e., 0.86×10^{-3} mol of sodium ion were exchanged for one gram of treated fly ash), which is about 30% of the ion-exchange capacity of synthetic zeolite A. The exchanged capacity was calculated using the difference between the Na^+ ion concentration before and after the ion exchange with NH_4^+ ions from Fig. 1. The ion-exchange capacity of the treated fly ash faujasite is higher than that of treated fly ash A, with a capacity of 1.07 milliequivalents per gram of treated fly ash. The higher ion-exchange
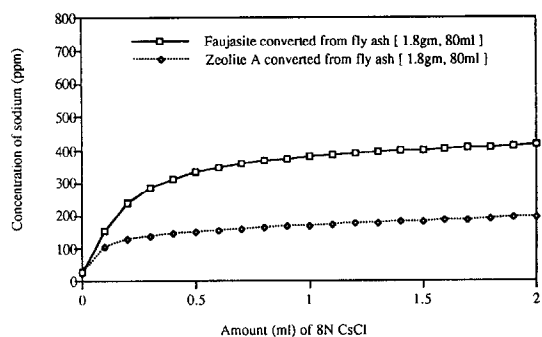

Fig. 2. Concentration of sodium ions in 80 ml solutions of 1.8 g zeolites as a function of the amount of 8 N cesium chloride added.
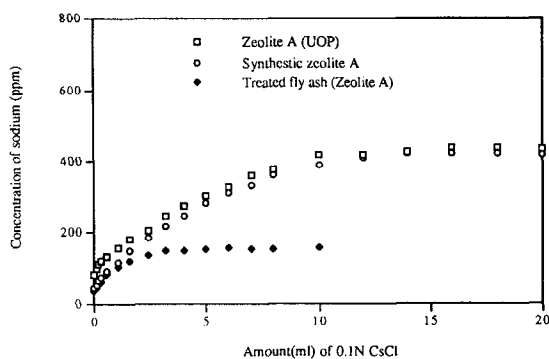
Fig. 3. Concentration of sodium ions in 40 ml solutions of 0.7 g zeolite A or fly ash as a function of the amount of 0.1 N cesium chloride added.
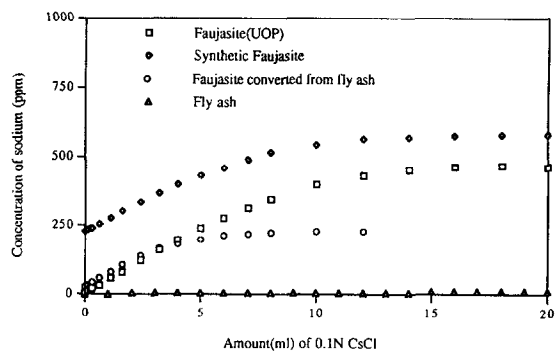

Fig. 4. Concentration of sodium ions in 40 ml solutions of 0.7 g faujasite or fly ash as a function of the amount of 0.1 N cesium chloride added.

capacity of the treated fly ash faujasite is in conformity with the higher X-ray diffraction peak intensity of treated fly ash faujasite than that of treated fly ash A.

Fig. 2 shows the ion-exchange behavior of treated fly ash with Cs^+ ion at 8 N concentration. The concentration of sodium ions in the suspension of the treated fly ash faujasite and the treated fly ash A increases with an increasing amount of cesium chloride added. Similar to the ion exchange with NH_4^+, the ion-exchange capacity of treated fly ash faujasite is higher than the ion-exchange capacity of treated fly ash A. In addition, both the treated fly ash faujasite and the treated fly ash A exchange more for ammonium ion than cesium ion at the same concentration. The number of exchanged ammonium ions is 2.5 times the number of exchanged cesium ions for the treated fly ash A and 1.37 times for the treated fly ash faujasite.

The ion-exchange capacity of treated fly ash, synthetic zeolite and commercial zeolite with solutions of cesium concentration of 0.1 N is shown in Fig. 3 for zeolite A and Fig. 4 for faujasite. The ratio of cesium exchange capacities between the treated fly ash A and commercial zeolite A (UOP4A) is 19%. The cesium exchange capacity of the treated fly ash faujasite is 0.67 milliequivalents per gram while the cesium exchange capacity of the treated fly ash A is 0.27 milliequivalents per gram. On the other hand, the cesium exchange capacity of untreated fly ash is negligible, less than 0.03 milliequivalents per gram. The ratio of cesium exchange capacity between the treated fly ash faujasite and commercial

faujasite (UOPY54) is 39%. These results indicate that the yield of faujasite converted from fly ash may be higher than the yield of zeolite A from fly ash. In addition, as the concentration of cesium chloride was increased from 0.1 N to 8 N, the cesium exchange capacities for both the treated fly ash faujasite and the treated fly ash A increase. The summary of ion-exchange capacities of treated fly ash, synthetic zeolites, and commercial zeolites are listed in Table 1. No ion exchange of zeolite P with Cs^+ ions was observed.

From the ion-exchange results presented above, it

Table 1
Ion exchange capacities of treated fly ash, synthetic zeolites, and commercial zeolites

Sample	Exchanged ion and concentration	Ion exchange capacity (milliequivalents per gram)
synthetic zeolite A, 1.8 g	8 N NH_4^+	2.79
treated fly ash A, 1.8 g	8 N NH_4^+	0.86
treated fly ash faujasite, 1.8 g	8 N NH_4^+	1.07
fly ash, 1.8 g	8 N NH_4^+	< 0.01
treated fly ash A, 1.8 g	8 N Cs^+	0.34
treated fly ash faujasite, 1.8 g	8 N Cs^+	0.78
UOP4A, 0.7 g	0.1 N Cs^+	1.42
UOPY54, 0.7 g	0.1 N Cs^+	1.7
synthetic zeolite A, 0.7 g	0.1 N Cs^+	1.02
synthetic faujasite, 0.7 g	0.1 N Cs^+	1.6
treated fly ash A, 0.7 g	0.1 N Cs^+	0.27
treated fly ash faujasite, 0.7 g	0.1 N Cs^+	0.67
fly ash, 0.7 g	0.1 N Cs^+	< 0.03

can be seen that faujasite has a higher ion-exchange capacity than that of zeolite A. This is true for all the zeolites studied in the present paper: zeolites converted from the fly ash, synthetic zeolites and the commercial zeolites. Since faujasite, $Na_2O \cdot Al_2O_3 \cdot 4.5SiO_2 \cdot 9H_2O$, has a higher molecular weight than zeolite A, $Na_2O \cdot Al_2O_3 \cdot 2SiO_2 \cdot 4.5H_2O$, it means that on a per mole basis faujasite is a more efficient ion-exchanger than zeolite A. The more efficient ion-exchange capability of faujasite may be due to its larger pore size than zeolite A. The comparison between Fig. 1 and Fig. 2 shows that for both zeolite A and faujasite, the exchange amount with NH_4^+ is more than that of Cs^+. This is probably related to the size of the two ions. Cs^+ is more difficult to exchange because of its larger ionic size than NH_4^+.

4. Conclusion

In summary, fly ash has been successfully converted into zeolites by treating it with NaOH solutions. By treating fly ash with NaOH solutions, both zeolite P and faujasite can be formed. Zeolite P was formed when the fly ash mixture was treated at 80°C, whereas faujasite can be obtained at 38°C. Zeolite P was formed with shorter treatment time and was easier to form than faujasite. By adding $Al(OH)_3$, in addition to the NaOH, to the fly ash mixtures, zeolite A can be formed. The ion-exchange property of the treated fly ash was quantitatively measured. The treated fly ash containing faujasite showed a better ion-exchange capacity than treated fly ash containing zeolite A. The ion-exchange capacity of treated fly ash faujasite is 39% of the value for commercial faujasite and that of treated fly ash A is 19% of the value for commercial zeolite A. Our results showed

that the treated fly ash has potential for the immobilization of radioactive ions in nuclear wastes (Cs^+) and harmful ions in municipal waste water (NH_4^+). Mixing treated fly ash with nuclear waste or using treated fly ash as filters to immobilize waste ions show a great promise for large-quantity uses of fly ash.

Acknowledgements

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