

A General Method for the Conversion of Fly Ash into Zeolites as Ion Exchangers for Cesium

Hsiao-Lan Chang and Wei-Heng Shih*

Department of Materials Engineering, Drexel University, 32nd and Chestnut Streets, Philadelphia, Pennsylvania 19104

A general method of converting various coal ashes into zeolites was investigated. Fly ashes from several utility power plants were fused with sodium hydroxide at 550 °C followed by dissolution in water and hydrothermal treatment. It was found that the solutions of fused powders can be cured at 60 °C under ambient pressure to precipitate faujasites. Atomic absorption spectroscopy of supernatant of solutions cured for various amounts of time showed that the concentration of Al species in the solutions has a dominant effect on the precipitation of faujasites. The fused ash solution that contained a higher amount of Al in the supernatant produced a larger amount of faujasite. The ion-exchange capabilities of the converted faujasites with respect to Cs⁺ ions were measured. It was found that a higher yield of faujasites gives rise to a higher ion-exchange capability. SEM-EDXS indicated that, in addition to ion exchange, precipitation of a cesium compound in solution also occurred. Moreover, the supernatant of the fused powder solution can produce purer zeolites, and the sediments can be reused to generate solution for further precipitation of zeolites.

I. Introduction

Large quantities of coal are used in electric power plants throughout the world every year. The disposal of the huge amount of ash generated from the combustion of coal poses a serious environmental problem. Using the state of Pennsylvania as an example, about 36% of the fly ash was utilized for reclamation, asphalt shingle production, quarry-fill, and sludge stabilization.¹ The bulk of the ash was disposed of as landfill. Due to the shortage of landfill sites and tighter environmental regulation, new ways of utilizing fly ash are needed. Recently, several authors have shown that zeolites can be converted from various combustion fly ashes.^{2–11} Due to their uniform pore sizes and large surface areas, zeolites are very useful materials for a wide range of applications such as ion exchange, molecular sieves, adsorbents, and catalysts.¹² Moreover, LaRosa et al.^{4,5} showed that the converted zeolites can increase the rate of strength development in concrete. Therefore, converting fly ash into zeolites not only alleviates the disposal problem but also turns an otherwise waste material into a useful one.

Previously, we have shown that one batch of Eddystone ash from PECO Energy Inc. can be converted to faujasite at 38 °C (this approach is called the low-temperature process).^{8,9} However, when the same procedure was applied to another batch of Eddystone ash, the faujasite was not obtained. Furthermore, treatments of fly ashes from other power plants did not yield the same results. These studies indicate that, due to the varying compositions of different ashes, the conversion process of ash has to be changed accordingly. This also raised the question of whether a general method to convert any fly ash into zeolites, such as faujasites and zeolite A, can be found. Recently, Shigemoto et al.⁶ converted fly ash to faujasites by fusing sodium hydroxide with fly ash prior to hydrothermal reaction. It was found that the fusion process increased the yield of faujasites significantly. It was indicated by

Shigemoto et al.⁶ that fusion can dissolve more silicates and aluminosilicates from fly ash, thereby increasing the yield of zeolites. In fact, alkali fusion has been a general method for decomposing materials containing Si and Al in chemical analysis.¹³ In this paper, we will present our study on the conversion of three different fly ashes into zeolite P, zeolite A, and faujasite using a fusion approach. It will be shown that this general fusion approach can be applied to all fly ashes and the yield of zeolites can be higher than that obtained from our previous low-temperature process^{8,9} and from other researchers.¹⁰ Furthermore, it will be shown that the concentration of Al species dissolved in the curing solutions plays the determining role of controlling the yield of faujasite. The role of Al in the nucleation of faujasite has previously been shown by Ginter et al.¹⁴

Due to the high pH condition of the ion-exchange tests, it is also possible that precipitation of metallic compounds, in addition to being ion exchanged, may occur. Singer and Berkgaut¹¹ showed that there was indication of Pb precipitation in their study of the conversion of fly ash into zeolite P. In this paper, we used EDXS (energy-dispersive X-ray spectroscopy) in SEM (scanning electron microscopy) to measure the concentration of the Cs ions, both within and outside of the converted faujasites, to investigate whether precipitation of a cesium compound occurs or not.

II. Experimental Procedure

The raw materials for the experiments were class F fly ash from three power plants: Eddystone, Goudey, and Conemiaugh. The composition of ash was studied by scanning electron microscopy (Amray 1830D4) using the EDXS mode. Each averaged datum was obtained from five different spherical particles. The spot size of the electron beam was 0.5 μm. The zeolite phase and the relative amount of zeolites were studied by X-ray diffraction (Siemens D500) using the internal standard method with BaTiO₃ as the standard. The intensity

ratio between the (533) peak of faujasite and the (110) peak of BaTiO₃ is used as a measure for the amount of faujasite generated. Particle size distribution was measured with a Horiba laser scattering particle size distribution analyzer. The specific surface area of the powders was measured using a BET surface area analyzer (Quantachrome NOVA 2200).

The fusion process began with mixing fly ash with NaOH powder (fly ash/NaOH = 1/1.2 in weight) and treating the resulting mixture in air at 550 °C for 1 h at a heating rate of 1 °C/min. After fusion, the powder was ground and 8.8 g of fused fly ash powder was dissolved in 43 mL of distilled water, followed by aging with stirring for 1 day at room temperature and ambient pressure. Heat treatment of the fused fly ash solutions results in the precipitation of zeolites. The heat treatment temperature used in the current study was higher than the 38 °C used in our previous studies.^{8,9} Previously, when curing the fly ash solution, only 38 °C curing could result in faujasite formation. Higher curing temperatures would precipitate zeolite P. On the other hand, the fusion process allowed a higher curing temperature, 60 °C, for the precipitation of faujasites. This is probably due to the higher amounts of dissolved aluminosilicates and silicates in the fused fly ash solutions.

At various curing times, the fused fly ash solution was separated into a supernatant and a sediment by centrifugation. The supernatant was diluted 50 times and characterized by atomic absorption spectroscopy (Varian AA-1275 Series) for the ionic concentrations of Si, Al, and Fe. The concentration of Na ion was measured with a sodium ion probe (Orion Inc.). The sediment was washed two times with distilled water, centrifuged, and dried at 80 °C for 12 h. Also, to obtain quantitative information about the amount of zeolites formed, BaTiO₃ was added to the mixture before curing and used as a standard in the X-ray measurement of the relative amount of zeolites obtained. The relative amount of zeolites formed can be monitored by studying the relative height of intensity of BaTiO₃ and the zeolites.

The ion-exchange behavior was studied with 0.1 N Cs⁺ solutions at room temperature. The ion-exchange experiment involved preparing 38 mL of water containing 0.9 g of treated fly ash. Then 2 mL of a 2 N CsCl solution was added to the treated fly ash solution. The pH values of the treated fly ash solutions were typically 11. The Na⁺ concentration in the treated fly ash solution was measured using a sodium ion probe. As the Cs ions exchanged with the Na⁺ ions in the zeolites, the Na⁺ concentration in the solution would increase. We measured the Na⁺ concentration as a function of time to verify that the Cs ions had exchanged with sodium ions and reached an equilibrium. The ion-exchange property of the treated fly ash is characterized by the ion-exchange capability, which was defined as the increased amount of Na⁺ in the treated fly ash solution before and after the addition of test ions.

III. Results and Discussion

The composition of the fly ashes was studied by EDXS in SEM, and the results are shown in Table 1. It is shown that ashes from different power plants have different compositions. The mean particle sizes of the three ashes are quite similar, although the size distributions are slightly different. The mean particle sizes

Table 1. Chemical Compositions and Mean Particle Size of Untreated Fly Ashes

	Eddystone	Goudey	Conemiaugh
compositions (wt %)			
SiO ₂	65.42	67.17	59.43
Al ₂ O ₃	28.23	20.41	26.30
Fe ₂ O ₃	2.14	4.07	8.12
Na ₂ O	0.64	0.40	0.44
K ₂ O	0.26	2.92	2.92
CaO	1.72	2.02	1.45
others ^a	1.59	3.01	5.84
mean particle size (μm)	0.69	0.76	0.73

^a Others include Ti, Mg, P, and S oxides.

of the three ashes are also shown in Table 1. As a representative, the X-ray diffraction (XRD) pattern of Goudey fly ash is shown in Figure 1. The crystalline phase of Goudey ash consists of quartz and mullite. The XRD pattern of fused Goudey fly ash is also shown in Figure 1. It is shown that a large amount of sodium silicate exists in the fused ash, indicating that fusion is very effective in extracting the silicon species in the fly ash. From the disappearance of quartz and mullite peaks, it is deduced that both quartz and mullite in the fly ash have reacted with NaOH. It was shown by Weldes and Lange¹⁵ that the higher the sodium content in sodium silicates, the higher the solubility of sodium silicates. Therefore, the formation of sodium silicates increases the solubility of silicates.

The fused fly ash was mixed with water and aged for 1 day at room temperature. From the XRD pattern in Figure 1, it is shown that, after 1 day of aging, no crystalline phase was formed. On the other hand, when the fused fly ash solutions were cured at 60 °C for 4 days, faujasite was formed. The XRD pattern of faujasites is shown in Figure 2. On the other hand, if the curing temperature was 90 °C, a clear XRD pattern of zeolite P can be seen without the formation of faujasite. Clearly there are significant differences between different curing temperatures. Stirring the solution during curing makes the formation of zeolite P occur at an earlier time.

The faujasite can be formed as early as after 2 days of curing. Previously we have shown⁹ that the converted faujasites have good ion-exchange capability due to their larger pore size than that of zeolite P and zeolite A.¹² Therefore, in this study, we focused our attention on the synthesis of faujasites. The XRD intensity of faujasites precipitated from the three ashes relative to that of BaTiO₃ is shown in Figure 3 as a function of curing time. Figure 3 shows that the fusion method can generate faujasites from the three ashes. In sharp contrast, the low-temperature process at 38 °C cannot form faujasite from the three ashes. Thus, fusion is shown to be a general method for treating fly ash, regardless of the compositional variations of the ashes. The improved results from the fused fly ash are probably related to the fact that more aluminosilicates have dissolved in the solutions due to the formation of sodium silicates and possibly amorphous aluminosilicates. The higher concentration of silicates and aluminosilicates in the fused fly ash solution can precipitate zeolites much easier than the low-temperature process.

Although all three ashes can be converted to faujasites, the yield of each ash was different. The Conemiaugh ash was found to yield the highest amount of faujasites among the three ashes. To learn more about the differences between the three ashes, the chemical

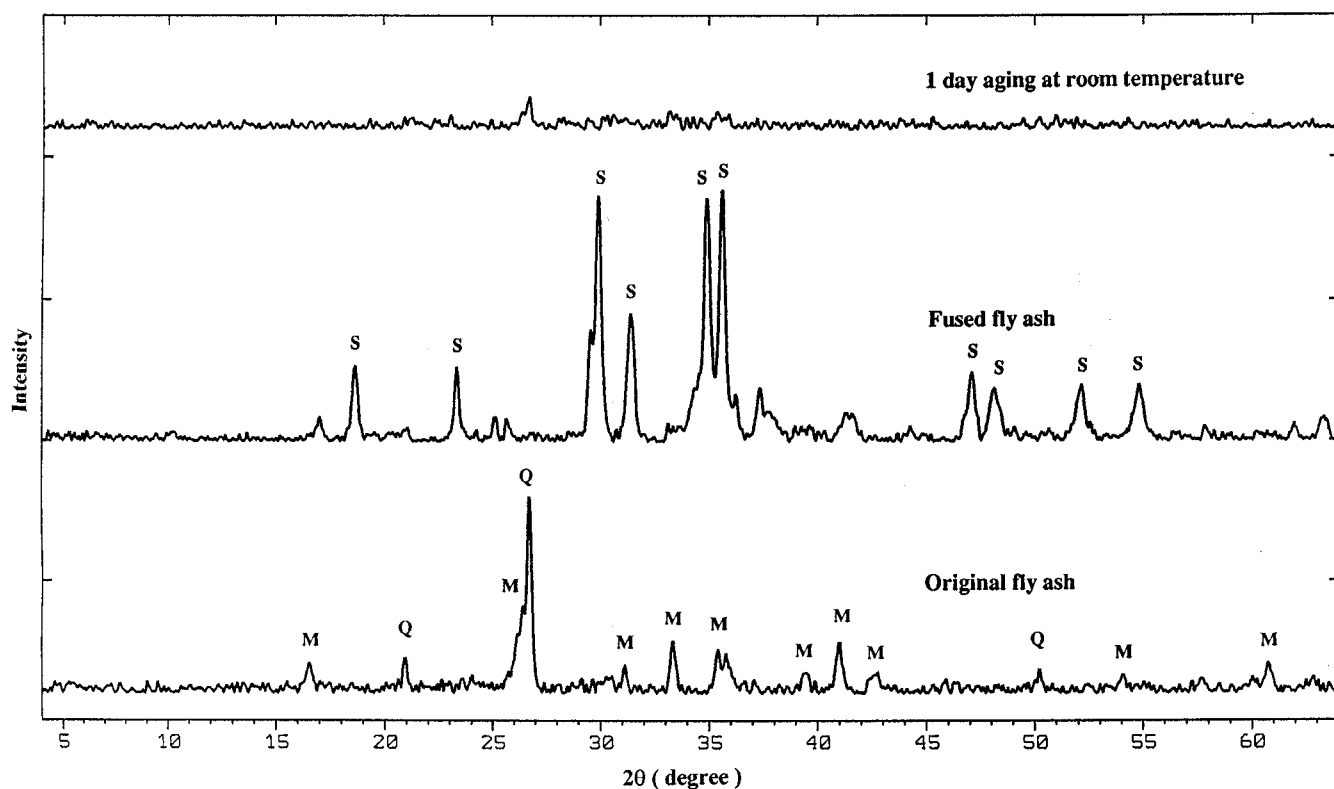


Figure 1. X-ray diffraction pattern of fly ash, fused fly ash, and the sediment of fused fly ash solution after 1 day of aging. M = mullite, Q = quartz, and S = sodium silicate.

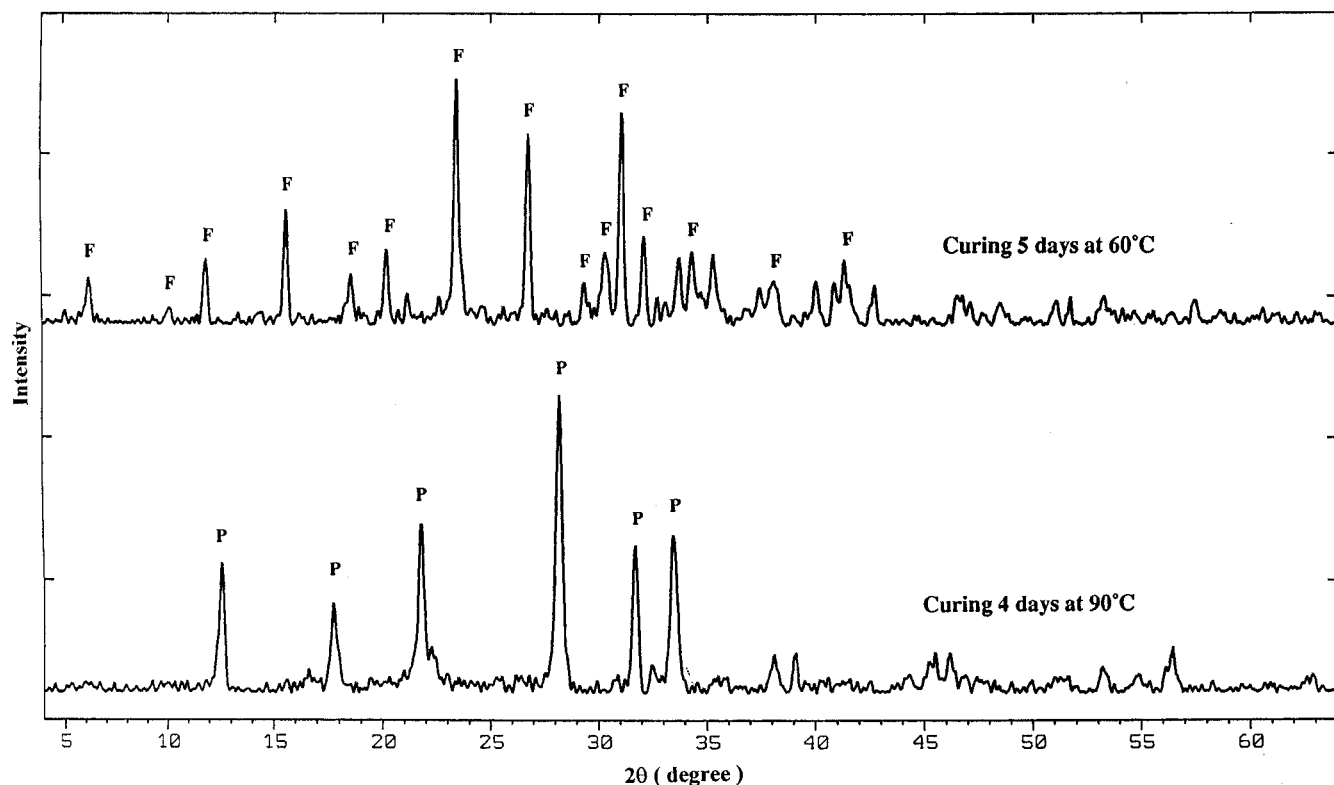


Figure 2. X-ray diffraction pattern of faujasites and zeolite P obtained at 60 and 90 °C curing, respectively. F = faujasite and P = zeolite P.

compositions of the supernatant of the curing solutions were characterized with atomic absorption spectroscopy (AAS). The concentrations of Si, Al, and Na in the supernatant of the curing solutions of the three ashes were plotted as a function of curing time in Figure 4a–c. It was found that, after 2 days, the concentration of

Al became negligibly small. However, the concentration of Si and Na continued to vary after 2 days and began to saturate after 6 days of curing. The results of Figure 4 are similar to the results of Ginter et al.¹⁶ in their study of the aging effect on the formation of faujasites. It was proposed by Ginter et al.¹⁶ that the formation of

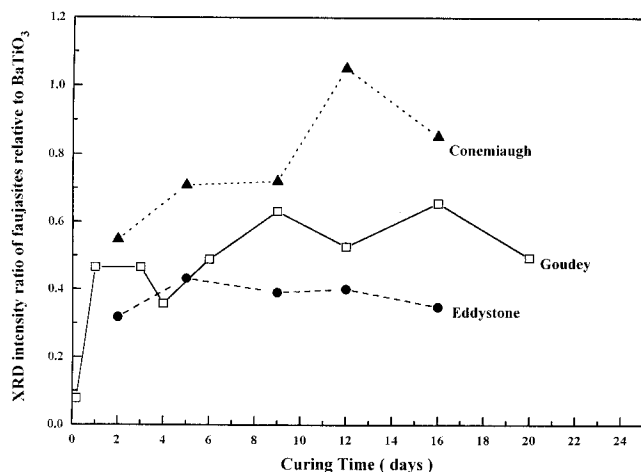


Figure 3. XRD intensity ratio of treated fly ash relative to BaTiO₃.

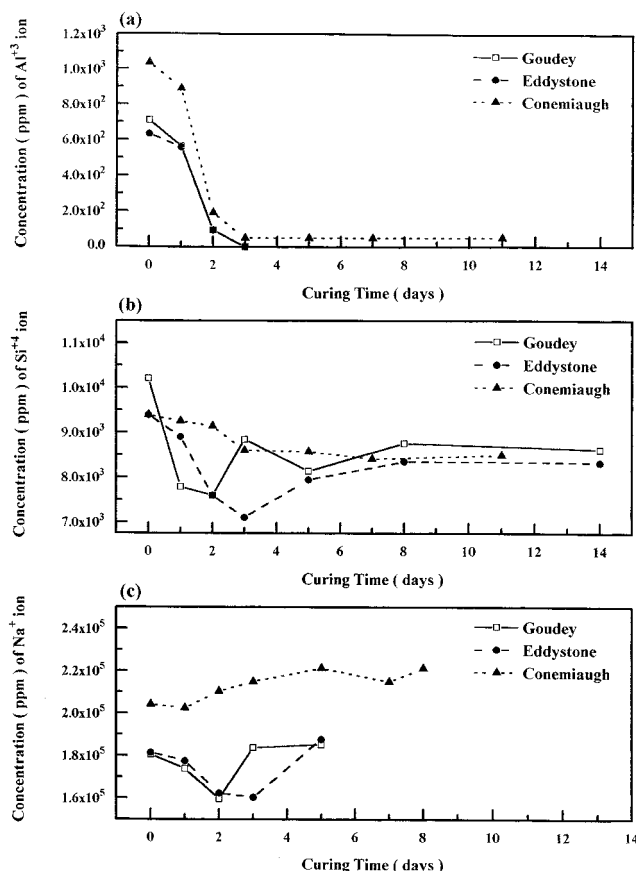


Figure 4. Concentration of Al, Si, and Na ions in the supernatant of the curing solutions as a function of curing time for the three ashes.

amorphous Al-rich nuclei during aging is critical to the precipitation of faujasites. They argued that the Al-rich nuclei transformed to faujasite during heat treatment followed by the addition of Si and Al species to the nuclei, resulting in the growth of faujasites. The formation of Al-rich nuclei can explain why Al species is consumed. In spite of what is the true mechanism in the precipitation of faujasite in the solutions, it is clear that Al is the controlling species in the formation of faujasites. The fact that the Al concentration of Conemiaugh ash was higher than the other two ashes at all times and the Conemiaugh ash produced higher amounts of faujasite lends supports to this idea.

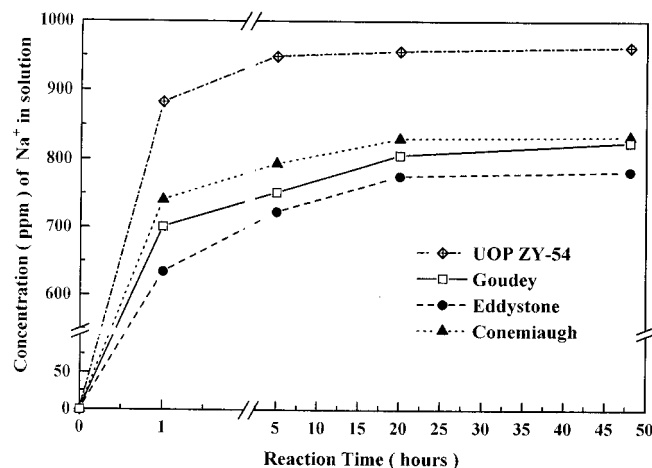


Figure 5. Concentration of Na in the solutions with 0.1 N Cs as a function of reaction time for the treated fly ash and the commercial zeolite.

It is speculated that the aluminosilicates dissolved faster than silicates in the fused fly ash solutions. Therefore, after 2 days of curing, the dissolved Al and Si species were consumed for the formation of faujasites. In the meantime there might still be more silicon species dissolving in the solutions, resulting in the continuing variation of the Si concentration. Also, as postulated by Ginter et al.,¹⁴ the formation of an aluminosilicate network may release Na⁺ from sodium silicates to the solution, thereby increasing its concentration. It is also possible that the continuing variation of the Na⁺ concentration after 2 days is related to the ion exchange of impurities in the fly ash with Na⁺ ions in the faujasite. The ion exchange of the impurities in the fly ash with Na⁺ in the faujasite releases Na⁺ into the solutions, thereby increasing the Na⁺ concentration. As a result, the concentration of Si and Na might continue to vary before reaching equilibrium. The concentration of Fe was also measured by AAS. It was found that the amount of Fe in the curing solutions was negligibly small, indicating that Fe did not dissolve and did not participate in the synthesis.

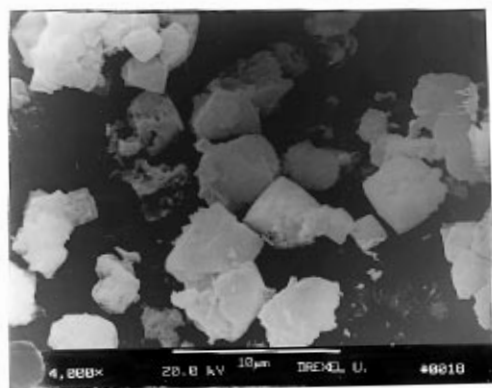
The treated fly ashes were tested for their ion-exchange performance. The ion-exchange behavior with Cs⁺ ions of the treated fly ash cured at 60 °C for 20 days is shown in Figure 5. Figure 5 shows the sodium concentration in the treated fly ash solution as a function of the reaction time between the treated fly ash and the Cs⁺ ions. The ion-exchange reaction between the treated fly ash and Cs⁺ ions saturated after about 5 h. The ion-exchange behavior is characterized by the difference between the initial sodium concentration and the equilibrium sodium concentration after the addition of Cs ions. As seen in Figure 5, the Conemiaugh ash shows a higher ion-exchange capability than the other ashes, indicating that a higher amount of faujasites were generated from Conemiaugh ash. The higher yield of faujasites from Conemiaugh ash is consistent with the XRD results presented in Figure 3. The ion-exchange capabilities of the treated fly ashes with Cs⁺ ions are collected in Table 2. Also included in Figure 5 are the results of ion exchange of a commercial faujasite from UOP Inc. The ion-exchange capability of treated Conemiaugh ash is more than 80% that of the UOP ZY-54 faujasite. On the other hand, the ion-exchange capability of zeolite P is very small. The better perfor-

Table 2. Ion-Exchange Capability (mequiv/g^a) of Treated Fly Ashes and Commercial Zeolite, UOP ZY-54, with Respect to Cs Ions

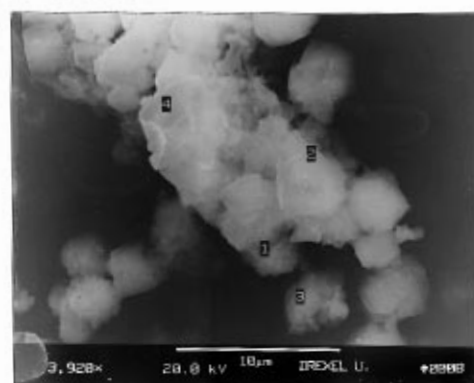
	UOP ZY-54	faujasite			zeolite P Eddystone
		Eddystone	Goudey	Conemiaugh	
0.1 N CsCl _(aq)	1.86	1.51	1.60	1.61	0.15

^a mequiv/g = exchanged amount of 10⁻³ mol of sodium ions/g of treated fly ashes or commercial zeolite.

(a)



(b)



SEM-EDXS Measurement of Faujasite Converted From Conemiaugh Ash

	# 1	# 2	# 3	# 4
Ion Exchange Capability (mequiv/g)	3.70	1.52	3.62	1.62
Si/Al molar ratio	1.28	1.27	1.33	1.17

Figure 6. (a) SEM micrographs of treated fly ash. (b) SEM micrograph of treated fly ash and the Si/Al ratio and Cs ion-exchange capacity at different locations in the micrograph measured by EDXS.

mance of faujasites than zeolite P probably originates from faujasites having larger pore sizes associated with the D6R and β -cage units in their structures.¹² There is a possibility that the addition of CsCl may cause some amount of dissolution of zeolites, thereby increasing the concentration of Na. However, this is not expected since the ion-exchange process is at room temperature. Furthermore, as shown in the following section, the ion-exchange capability obtained from the sodium probe method is consistent with the results obtained from SEM characterization of the Cs content in faujasites after ion-exchange. Therefore, the possibility of zeolite dissolution during the ion exchange measurement is very small.

We have investigated the Cs content in the treated fly ash that have been ion exchanged with Cs using EDXS in SEM. The distribution of Cs content in different parts of the sample is shown in Figure 6b. It was found that there were regions where the Cs content

Table 3. Si/Al and Na/Al Molar Ratios of Treated Fly Ashes and Commercial Zeolite UOP ZY-54

	a. Before Ion Exchange			
	UOP ZY-54	faujasite		
		Goudey	Eddystone	Conemiaugh
Si/Al	2.64 ± 0.02	1.19 ± 0.07	1.23 ± 0.09	1.21 ± 0.07
Na/Al	1.14 ± 0.07	1.00 ± 0.10	0.99 ± 0.30	0.92 ± 0.12
	b. After Ion Exchange with Cs Ion			
	UOP ZY-54	faujasite (Conemiaugh)		
		Si/Al		
		2.89 ± 0.21	1.32 ± 0.10	

is much higher than that in the faujasites. Using the Cs content that was measured in the SEM, we estimated the Cs-exchange capability in different regions of the sample. It was found that, for UOP ZY-54, most areas have a Cs-exchange capability in the neighborhood of 1.8 mequiv/g, similar to the ion-exchange capability measured by the sodium probe. However, there were regions of high Cs content, which corresponds to an ion-exchange capability of 4 mequiv/g. On the other hand, for faujasite converted from Conemiaugh, most areas have a Cs-exchange capability in the neighborhood of 1.6 mequiv/g, similar to the ion-exchange capability measured by the sodium probe. The ion-exchange capability of the treated fly ash is about twice that of the ion-exchange capability obtained by Amrhein et al. using their treated fly ash.¹⁰ There are also regions of high Cs content in the treated Conemiaugh fly ash, and the ion-exchange capability of those high Cs regions is in the range of 3.6–3.7 mequiv/g. It is speculated that these regions with high Cs content are areas where Cs ions reacted with aluminosilicates and precipitated as certain cesium compounds due to the high pH condition of the treated fly ash solutions. This observation is consistent with the fact that metal compounds tend to precipitate at alkaline conditions. Therefore, besides the ion-exchange property of the zeolites, additional Cs may be removed from the solutions due to precipitation of Cs compounds. The possibility of metal compound precipitation in treated fly ash solutions has been indicated by Singer and Berkgaug.¹¹

The Si/Al ratio of faujasites can be measured by the EDXS in SEM, provided faujasites can be identified in the SEM micrographs. Figure 6a shows a typical morphology of treated Conemiaugh ash. There are many crystallites with facets, and their morphologies are very similar to that of the UOP ZY-54 sample. In addition, the morphologies of particles in Figure 6a are very different from those of typical fly ash particles that are spherical with a wide distribution of sizes. Therefore, we can identify the faujasites from the SEM micrographs. The Si/Al ratios of different particles were then measured by EDXS in SEM. The results are shown in Figure 6b, with the Si/Al ratios of different faujasite particles listed. The Si/Al ratio varies somewhat from particle to particle. The average Si/Al ratios for all the treated ashes and the UOP zeolite were measured, and the results are summarized in Table 3a. Clearly, the UOP faujasite has a higher Si/Al ratio than that converted from fly ash. Faujasites with different Si/Al ratios are expected to have different ion-exchange behavior since their structures are slightly different.¹² For example, it is known that faujasite Na-X has a

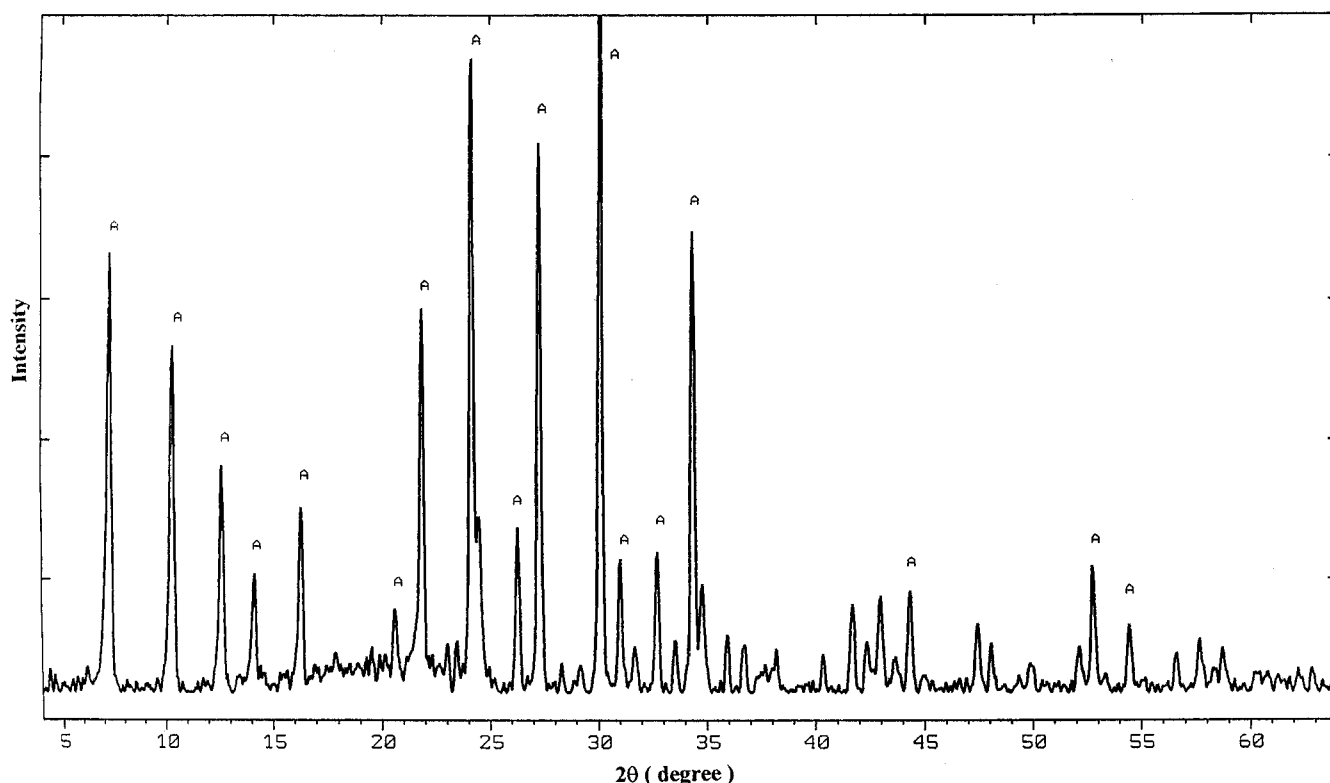


Figure 7. X-ray diffraction pattern of zeolite A converted from the supernatant of the Conemiaugh ash and $\text{Al}(\text{OH})_3$ solution.

higher ion-exchange capacity than faujasite Na-Y due to a lower Si/Al molar ratio in faujasite Na-X.¹²

The different compositions in the faujasites can also explain why the ratio of the ion-exchange capabilities between converted faujasites is not equal to the yield ratio obtained from XRD results. The Si/Al ratios of the three treated fly ashes are similar. It should be noted that the Si/Al ratio of the treated fly ash is not equal to the Si/Al ratio of the converted faujasites since the treated fly ash includes the unreacted fly ash. Using the Si/Al ratio in the unreacted fly ash, which is shown in Table 1, and the percentage of faujasite in the treated fly ash, which is estimated based on the specific surface area shown later, we calculated the Si/Al ratio of the converted faujasite to be less than 1.7. Therefore, it can be concluded that the Si/Al ratio of UOP ZY-54 has a higher value than that of the converted faujasites. Also included in Table 3a is the Na/Al molar ratios for all the treated fly ashes and UOP zeolites. The overall ratio of Na/Al = 1 in the treated fly ash is consistent with the fact that Na is loosely bonded to the zeolite structure to balance the charge due to the substitution of Al for Si. The results presented in Table 3a are for zeolites before ion exchange. The Si/Al molar ratios for UOP ZY-54 and treated Conemiaugh ash after ion exchange are shown in Table 3b for comparison. It can be seen that the Si/Al ratio of zeolites increases slightly after ion exchange. The reason for the slight difference in Si/Al ratios before and after ion exchange is not understood at the moment.

The conversion of fly ash to zeolites by the supernatant of the dissolved fused powder solutions was also studied. When $\text{Al}(\text{OH})_3$ was added to the supernatant of fused Conemiaugh ash, zeolite A can be formed at a curing temperature of 60 °C. The XRD pattern of zeolite A is shown in Figure 7. The high intensity of zeolite A shown in Figure 7 indicates that the purity of zeolite A obtained from the supernatant is much higher than that

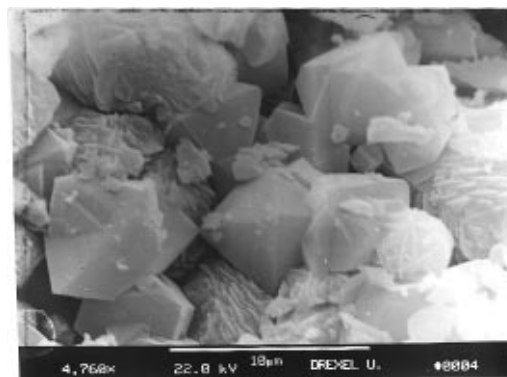


Figure 8. SEM micrograph of converted zeolites from the supernatant of the Conemiaugh ash solution. The dominant octahedral-shaped crystallites are faujasites. The spheres (balls of wool) are not identified.

obtained from the fused fly ash solutions. Similarly, by treating the supernatant, faujasites can be formed and the XRD pattern was much clearer with higher intensity than that obtained from the fused fly ash solution.

The formation of zeolites from the supernatant demonstrated that it is possible to obtain pure zeolites from fly ash. Previously, in the low-temperature process, we could only obtain zeolites from the fly ash solution but not from the supernatant of the fly ash solution. With the fusion method, higher amounts of silicates and aluminosilicates are in the supernatant and the formation of zeolites is easier. Also, previously, zeolites were precipitated within the fly ash solutions and mixed with the fly ash. It was very difficult to separate the precipitated zeolites from the unreacted fly ash. The formation of zeolites from the supernatant of the fused fly ash solution demonstrated that zeolites can be separated from unreacted fly ash. Figure 8 shows the SEM micrograph of faujasites precipitated from the supernatant of the Conemiaugh ash solution. The

Table 4. Specific Surface Area (m²/g) of Treated Fly Ashes and Commercial Zeolite UOP ZY-54

UOP ZY-54	faujasite					zeolite P (Eddystone) solution
	Goudey		Eddystone solution	Conemiaugh		
	super- natant	solu- tion		super- natant	solu- tion	
950	654.6	511	272.9	640.2	445	54.4

octahedral structure of faujasites can be clearly seen. Furthermore, the formation of zeolites from the supernatant of the fused fly ash solution indicates the possibility of using the sediment of the fused fly ash solution to generate more zeolites. We can mix the sediment of fused fly ash solutions with water to form a new solution and then separate out the supernatant for the production of more zeolites. In other words, the sediments of the fly ash solution can be used to obtain zeolites as well. This approach will increase the yield of zeolites from fly ash.

Zeolite P was also converted from Goudey ash when the fused fly ash solution was treated at 90 °C. The trend found for the fused fly ash solution that higher curing temperatures produce zeolite P and lower curing temperatures produce faujasite is similar to the trend found for the fly ash solution without fusion.⁹ However, for the fly ash solution without fusion, the curing temperature must be below 38 °C for the formation of faujasite, whereas for the fused fly ash solution, faujasite can be formed by curing the solution at 60 °C. Apparently, the higher amounts of silicates and aluminosilicates in the fused fly ash solution increase the stability of faujasites and the curing temperatures can be higher. The reason why higher curing temperatures result in zeolite P whereas lower temperatures produce faujasite may be related to the kinetics of the process. Zeolite P is thermodynamically more stable than faujasite.¹⁷ Higher curing temperatures allow the more stable state of zeolite P to be reached. Lower curing temperatures may provide a kinetic path that stabilizes the faujasite phase. Also, it is possible that the formation of zeolite P and faujasite is related to the structural units of the zeolites. It has been shown that high temperature and low Si concentration favor the formation of monomer and small oligomer silicate species such as S4R units whereas low temperature and high Si concentration favor larger silicate species such as D6R and β -cage.¹⁸ It is known that zeolite P is based on S4R units and faujasite is built from D6R units and β -cages. Therefore, it is possible that, due to the different curing temperatures and different silicate concentrations, different silicate species exist in the solutions, resulting in different zeolites. The ion-exchange capability of P was also studied, and it is relatively low compared to faujasites. The ion-exchange behavior of zeolite P with respect to Cs⁺ is included in Table 2.

The surface area of the treated fly ash was also characterized. It was found that fly ash has a very small surface area, on the order of 2–3 m²/g. On the other hand, treated fly ash containing faujasites has a large surface area ranging from 250 to 650 m²/g, depending on whether the fused fly ash solution or the supernatant is used for curing. The results are summarized in Table 4. When the supernatant of the fused fly ash solution is used, the faujasites were pure and the specific surface area is large. On the other hand, when the whole solution is used, the faujasites obtained were mixed with unreacted fly ash and the specific

surface area was smaller. The specific surface area that we obtained here is much higher than the 42 m²/g of the treated fly ash studied by Amrhein et al.¹⁰ This is consistent with the fact that the ion-exchange capability of our faujasites is twice that of Amrhein et al.¹⁰ Because the treated fly ash obtained from solution is a mixture of faujasites and fly ash, its surface area is in between that of pure faujasites and fly ash. The ratio of surface area between treated fly ash from solution and from supernatant is between 70 and 80%, indicating that the amount of faujasites in the treated fly ash from solution is on the order of 70 and 80%. The commercial zeolite, UOP ZY-54, has a large surface area of 950 m²/g. On the other hand, the surface area of treated fly ash containing zeolite P is 54 m²/g, much smaller than the treated fly ash containing faujasites. Our surface area of treated fly ash containing zeolite P is consistent with the results of Lin and Hsi,⁷ who found a maximum value of 94 m²/g for their treated fly ash.

IV. Conclusions

It is shown that a general fusion method can convert various ashes with wide variations in composition into faujasite. Fusion of NaOH with fly ash produced sodium silicate and amorphous aluminosilicate, which can be easily dissolved in aqueous solution. The higher amount of Si and Al species in the solution gives rise to a higher yield of zeolites from the fusion method. Furthermore, the atomic absorption study on the ionic concentration in the supernatant of the curing solutions showed that Al species may be the controlling parameter in the synthesis. Once the Al species is consumed, the yield of zeolite saturates. The ion-exchange behavior of the faujasites converted from various fly ashes by the fusion method is presented. In general, the trend in the ion-exchange behavior of the converted faujasites is consistent with the XRD results on the yield of faujasites converted. The different ion-exchange capabilities in the faujasites converted from different ashes come from the different Si/Al molar ratios of the faujasites produced from the different ashes.

Acknowledgment

This work is supported by DOE Grant DE-FG22-94PC94215.

Literature Cited

- (1) Seebacher, J. A. Presented at the Workshop on Utilization of Fly Ashes and Other Coal Combustion By-Products, The Pennsylvania State University, University Park, PA, April 24, 1993.
- (2) Yoshida, A.; Inoue, K. *Zeolites* **1986**, *6*, 467–473.
- (3) Henmi, T. *Clay Sci.* **1987**, *6*, 277–282.
- (4) LaRosa, J. L.; Kwan, S.; Grutzeck, M. W. *J. Am. Ceram. Soc.* **1992**, *75* (6), 1574–80.
- (5) LaRosa, J. L.; Kwan, S.; Grutzeck, M. W. Presented at the Workshop on Utilization of Fly Ashes and Other Coal Combustion By-Products, The Pennsylvania State University, University Park, PA, April 24, 1993.
- (6) Shigemoto, M.; Hayashi, H.; Miyaura, K. *J. Mater. Sci.* **1993**, *28*, 4781–86.
- (7) Lin, C.-F.; Hsi, H.-C. *Environ. Sci. Technol.* **1995**, *29*, 1109–1117.
- (8) Shih, W.-H.; Chang, H.-L.; Shen, Z. *Mater. Res. Soc. Symp. Proc.* **1995**, *371*, 39–44.
- (9) Shih, W.-H.; Chang, H.-L. *Mater. Lett.* **1996**, *28*, 263–68.

- (10) Amrhein, C.; Haghnia, G. H.; Kim, T. S.; Mosher, P. A.; Gagajena, R. C.; Amanios, T.; De La Torre, L. *Environ. Sci., Technol.* **1996**, 30, 735–742.
- (11) Singer, A.; Berkgaut, V. *Environ. Sci., Technol.* **1995**, 29, 1748–1753.
- (12) Breck, D. W. *Zeolite Molecular Sieves*; John Wiley & Sons: New York, 1974.
- (13) Hillebrand, W. F.; Lundell, G. E. F.; Bright, H. A.; Hoffman, J. I. *Applied Inorganic Analysis*, 2nd ed.; Wiley: New York, 1962.
- (14) Ginter, D. M.; Bell, A. T.; Radke, C. J. *Zeolites* **1992**, 12, 742–749.
- (15) Weldes, H. H.; Lange, K. R. *Ind. Eng. Chem.* **1969**, 61 (4), 29–44.
- (16) Ginter, D. M.; Went, G. T.; Bell, A. T.; Radke, C. J. *Zeolites* **1992**, 12, 733–741.

(17) Petrovic, I.; Navrotsky, A.; Davis, M. E.; Zones, S. I. *Chem. Mater.* **1993**, 5, 1805–1813.

(18) Kinrade, S. D.; Swaddle, T. W. *Inorg. Chem.* **1988**, 27, 4253–59.

Received for review May 21, 1997

Revised manuscript received September 29, 1997

Accepted September 30, 1997[®]

IE970362O

[®] Abstract published in *Advance ACS Abstracts*, December 1, 1997.