Environ. Sci. Technol. **1999**, *33,* 1464−1469

The Adsorption of SO_2 by Zeolites Synthesized from Fly Ash

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Zeolites X, Y, and Na-P1 (90 °C) and analcime and sodalite (150 °C) were synthesized from Class F fly ash using 3 M sodium hydroxide solutions and autogenous pressures. The partially zeolitized fly ashes were dried overnight in air at room temperature and then characterized using X-ray diffraction and SEM. On occasion, a few samples were dried to constant weight for an additional 8−10 min in a microwave oven to remove bound water as well. The dried samples were evaluated for their ability to adsorb sulfur dioxide (SO_2) from a simulated stack gas containing ∼2000 ppm SO_2. Determinations were made in real time using a UV/vis spectrophotometer followed by a total sulfur analysis of the "loaded" samples once testing was complete. Breakthrough curves indicate that the zeolites in the samples are able to remove all of the SO_2 in the simulated flue gas (zero SO_2 emission) for varying periods of time, and that the actual amount of SO_2 removed by the zeolite depended on the type and degree of "dryness" of the zeolite or zeolite-like material present. For example, a 7 day 150 °C cured sample containing analcime and sodalite was able to adsorb 6−7 mg of SO_2 per gram of sample regardless of the source of the fly ash, whereas a 90 °C cured sample containing X, Y, and Na-P1 was significantly less efficient.

Introduction

Much of the coal in United States is burned by utilities to generate electricity. Unfortunately, not all coals were created equal. Some contain relatively large amounts of secondary sulfide minerals which oxidize and form sulfur dioxide (SO_2) during the combustion process. In the not so distant past, SO_2 emissions were unregulated. As a result of the build up of SO_2 in the atmosphere and the ensuing damage caused by acid rain, the concentration of SO_2 in flue gases discharged to the atmosphere is now regulated by Federal and State agencies.

Installation of scrubbers and/or the use of low sulfur-containing coal are two options currently used by utilities to reduce their SO_2 emissions. At this point in time, the majority of utilities control their SO_2 emissions using lime-based scrubbing. Although the desulfurization process has a number of advantages, it also has two serious disadvantages. In the short term, the purchase, processing, and landfill disposal costs associated with lime-based scrubbing add approximately 4% to the price of the electricity generated by the plant (*1*). As regulations become more stringent, this cost will increase. Perhaps less obvious but far more significant is the fact that the use of larger amounts of lime-based materials to remove even more SO_2 from flue gases will add increasingly larger amounts of CO_2 to the atmosphere. Clearly, the utilities are in a very difficult position. Alternates will have to be found. It is known that SO_2 is adsorbed on a molecular sieve quite efficiently (*2, 3*). It is also recognized that the use of a commercial zeolite such as Silicalite is not cost-effective. The research described below suggests that an alternative adsorption medium (zeolites) may in fact be synthesized on site by a utility from its own fly ash. Zeolite formation from fly ash has been successfully carried out by LaRosa et al. (*4, 5*), Grutzeck and Siemer (*6*), Grutzeck (*7*), and a host of other researchers (*8*−*21*). If this process proves to be economically as well as technically feasible, the use of utility-synthesized zeolites to regulate gases from emissions may result in the installation of adsorption control equipment with lower capital and operating costs.

Zeolites form in nature, but the process is relatively slow, taking hundreds to thousands of years. During this time, volcanic ashes are converted to zeolites by the action of alkaline/saline surface and/or groundwater on deposits of the glassy ashes (*22*−*24*). With the use of hydrothermal processing techniques, synthesis times can be shortened to a matter of hours (*25*). It is estimated that a utility can convert its own fly ash into zeolite-containing materials using conventional low-cost processing (e.g., mixing the fly ash with sodium hydroxide and curing the resulting slurry in heated ponds) for approximately $50−100 per ton. Existing data suggest that these zeolites can be used to adsorb ammonium ions from solution (*19, 20*); the current work suggests that fly ash-derived zeolites can also act as chemical adsorbents for SO_2.

It is proposed that such zeolite-containing materials can be injected into the exhaust gases much like lime-based materials are in dry FGD processing. Alternately, the zeolites could be used in a fixed bed configuration. The zeolites selectively adsorb molecules that are smaller than the pore size of the zeolites in question which is ∼7 Å. Sulfur dioxide with a diameter of about 3.7 Å (*22*−*24, 26*) is likely to be adsorbed on all surfaces of the zeolites. Substituting zeolites for lime-based scrubbing would reduce transportation and disposal costs of lime and also reduce fly ash disposal to a certain extent because the loaded zeolites could be processed to recover the SO_2 gas and then used as soil conditioners.

Materials, Sample Preparation, and Methods

Materials and Sample Preparation. Samples of Class F fly ash from three power stations in the Eastern United States (Hatfield, Rivesville, and Armstrong) were obtained from Allegheny Power Company. These were chemically analyzed and used to prepare the zeolitic materials described below. Analyses of the fly ash are given in Table 1. All are typical Class F ashes, consisting of finely divided micrometer-sized fly ash spheres (quenched glasses), minor amounts of quartz, mullite, and varying amounts of scoriaceous carbon. Two of the ashes have rather high carbon contents (Rivesville and Armstrong) which make them unsuitable for use in portland cement concrete. Previous work with a fly ash from Pennsylvania Power & Light's Montour power station has shown that a "low carbon" fly ash was readily transformed into a zeolitic material (*4*−*7*) that was capable of adsorbing ammonium ions from solution (unpublished data). For this reason, it was expected that the current set of experiments would provide insight into the effect of carbon content on the zeolitization process as well as on the zeolites' ability to adsorb SO_2.

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10.1021/es9802091 CCC: $18.00
Published on Web 03/31/1999

TABLE 1. Chemical Analyses (wt %) of the Fly Ash Samples Used in This Study

fly ash	Hatfield	Rivesville	Armstrong
SiO_2	48.41	53.08	43.05
Al_2O_3	24.13	22.49	22.26
Fe_2O_3	14.84	10.16	20.21
CaO	4.26	1.56	1.59
SO_3	0.64	0.08	0.05
MgO	0.94	0.54	0.54
Na_2O	0.68	0.37	0.24
K_2O	1.56	1.75	1.88
P_2O_5		0.33	0.31
moisture content	0.22	0.22	0.67
loss on ignition	2.60	8.35	8.53
totals	98.28	98.93	99.33

TABLE 2. Phases Typically Present in Zeolitized Class F Fly Ash Samples[a]

temp (°C)	concn NaOH molarity	curing time of samples 1 day	3 days	7 days
60	0.1	nr	nr	nr
60	3	nr	nr	tr zeolite X (Na)
90	0.1	nr	nr	nr
90	3	zeolite X (Na)	zeolite X (Na)	zeolite Na-P1, Y (Na)
150	0.1	nr	nr	nr
150	3	analcime	analcime, sodalite	analcime, sodalite

[a] Phases present in the fly ash (i.e., mullite, quartz, and glass) were unchanged: nr, no reaction; tr, trace. When zeolites did form, they formed in varying amounts depending on reaction conditions. At best conversions were ~50%. Mullite, quartz, and glass tended to continue to coexist with the zeolites.

Typically, 5 g of fly ash, 12.5 g of sodium hydroxide solution (0.l or 3 M), and 1 g of salt (NaCl) were mixed and heated at 60, 90, and 150 °C in Teflon-lined hydrothermal pressure vessels (Parr bombs) for varying lengths of time (l, 3, and 7 days). The samples made with 3 M NaOH solution showed a greater degree of fly ash conversion and also produced a wider range of zeolites compared to those containing 0.l M NaOH. Experience has shown that 90 and 150 °C are optimum conditions for forming potential adsorbents (zeolites). The results in Table 2 are intended to show that the different zeolites that formed depended more on temperature and time of reaction than the composition of the fly ash; that is, carbon content did not effect phase formation. In addition to air-drying, a few of the zeolites were also dried to constant weight in a microwave oven for about 8−10 min prior to testing for SO_2 adsorption.

Methods. A simulated stack gas containing ~2000 ppm SO_2, 10% O_2, 10% CO_2, and 80% N_2 was used throughout the experimental program. The apparatus (Figure 1) consists of an adsorber cell made to contain the zeolite samples and a spectrophotometer to record concentrations of SO_2 in the effluent gas stream. The adsorber cell is 10 cm in length and 1 cm in diameter and contains a glass frit which supports the zeolite as the simulated stack gas passes through the sample. Typically 2 g of sample was placed in the adsorber cell and the simulated stack gas was passed through the sample at a constant l0 cm^3/s flow rate. Breakthrough curves for SO_2 in the effluent gas were determined by passing the "zeolite-treated" gas through a glass adsorption cell made to fit in a 2300 UV/vis Varian spectrophotometer tuned to measure SO_2's adsorption band at 284 nm. The adsorption cell pictured in Figure 1 was fitted with quartz end plates to make it transparent to this wavelength. The cell measures 10 cm in length and is ~2.5 cm wide. To date, all adsorption experiments were conducted using room temperature gas.

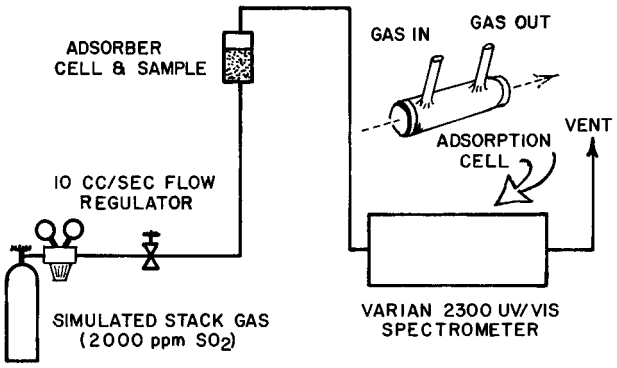

FIGURE 1. Schematic representation of experimental set up used to test SO_2 adsorption.

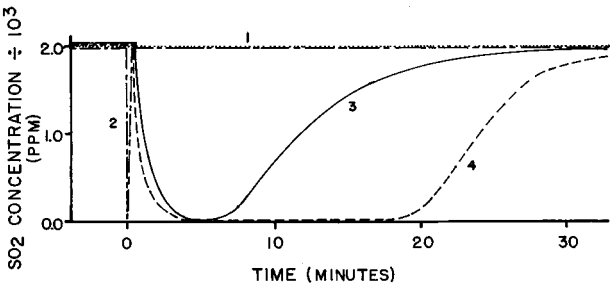

FIGURE 2. Breakthrough curves for various conditions: (1) baseline, (2) sand, (3) 110 °C air-dried zeolite, and (4) microwaved-dried zeolite.

To calibrate the apparatus, we carried out two experiments. The simulated flue gas was passed first through an empty adsorption column and then through the same column filled with quartz sand. The concentration of effluent SO_2 was monitored (without adsorption by zeolites) using SO_2's adsorption band at 284 nm as a function of time (Figure 2, traces 1 and 2). As expected, there was little or no perturbation to the SO_2 content of the gas. The baseline (Trace 1) is essentially flat because the SO_2 in the gas is adsorbing some of the 284 nm wavelength beam of light. The quartz sample (Trace 2) suggests that some adsorption occurs, but it is very short-lived. Once the apparatus was calibrated, the relative SO_2 adsorption efficiencies of the various zeolites were estimated from their breakthrough curves and total sulfur analyses.

Results and Discussions

Characterization. X-ray diffraction patterns of the three fly ashes revealed that they were composed mainly of a silica-rich glassy phase (2θ ~24−26°) with minor amounts of mullite ($Al_6Si_2O_{13}$) and quartz (SiO_2) See Figure 3 for a representative X-ray diffraction pattern of the Rivesville fly ash. Treating the fly ash with 3 M NaOH at 90 °C resulted in the formation of crystalline zeolite X ($Na_2Al_2Si_{2.5}O_{9.6}\cdot 2H_2O$) at 1 day (see Figure 4), and a combination of zeolite Y ($Na_2Al_2Si_{4.5}O_{13}\cdot XH_2O$) and zeolite Na-P1 ($Na_6Al_6Si_{10}O_{32}\cdot 12H_2O$) at 7 days (see Figure 5). At 150 °C, zeolite-like analcime C ($Na(Si_2Al)O_6\cdot H_2O$) and sodalite ($Na_4Al_3Si_3O_{12}Cl$) (see Figure 6) formed instead. These results are similar to those found in the literature, suggesting that the synthesis process is relatively insensitive to starting material composition, more so a function of temperature and time. It was also shown that the original fly ash reacted to different degrees as evidenced by the shift in the amorphous hump attributed to the fly ash from ~24−26° 2θ to 31−32° 2θ. This latter peak position is characteristic of hydrated calcium silicate cement-based

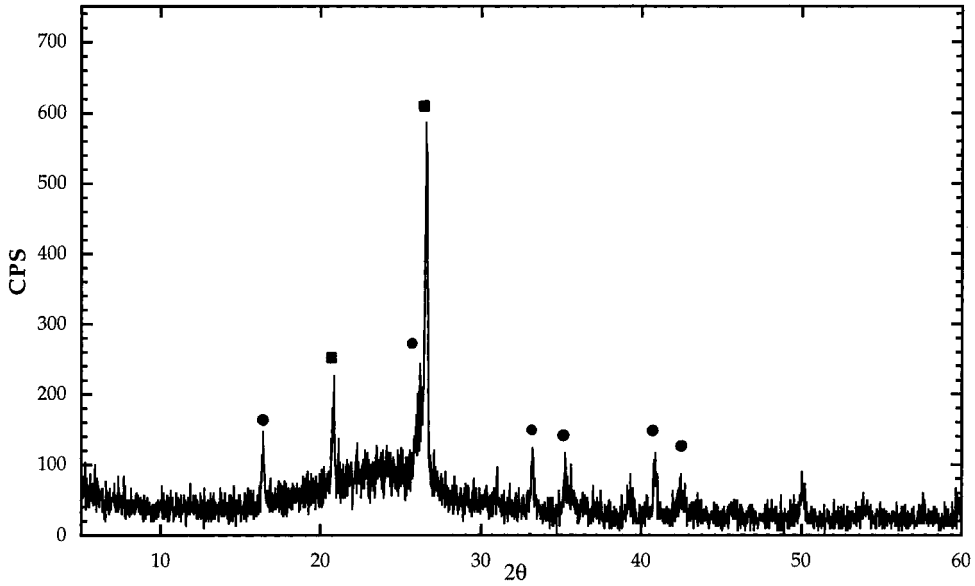

FIGURE 3. Representative sample of fly ash typical of Class F fly ash produced by Allegheny Power: (●) = mullite, (■) = quartz.

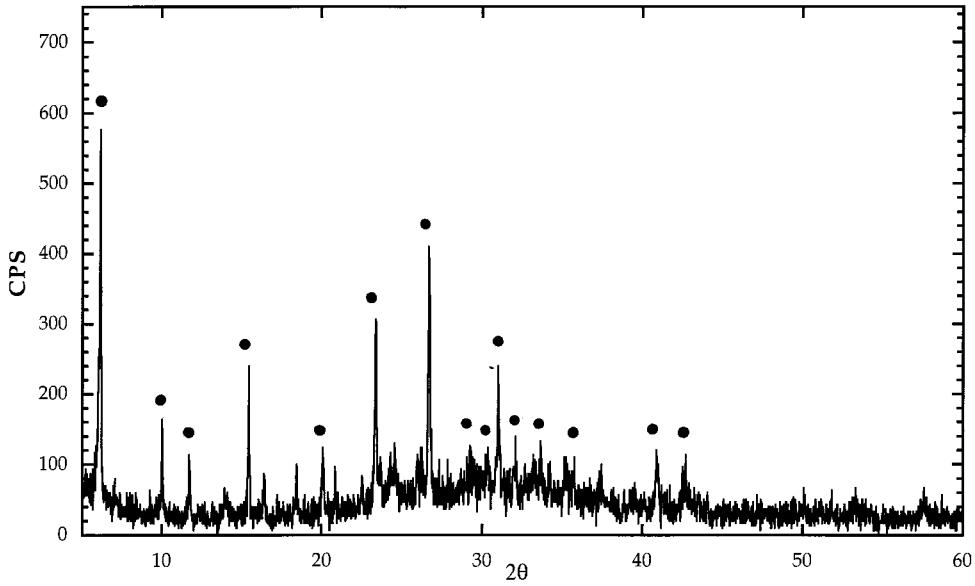

FIGURE 4. Fly ash cured with 3 M NaOH at 90 °C for 1 day: (●) = zeolite X (Na).

materials. Samples at 150 °C normally contained less residual glass than their lower-temperature counterparts. Results of the systematic study are given in Table 2. Each of these samples exhibited different adsorption capacities when exposed to SO_2-containing flue gas.

Comparison of Zeolite SO_2 Adsorption Characteristics. As noted earlier, the breakthrough curves for the test runs made without any zeolites are given in Figure 2. Flow rates were held constant at l0 cm^3/s. Trace 1 runs parallel to the abscissa (time in minutes), indicating that the concentration of SO_2 in the gas remained constant with time. The sample column was then filled with coarse sand and the gas passed through at the same flow rate. The resulting breakthrough curve (Trace 2) showed little/no adsorption of the gas by the sand; the graph returned to its initial concentration with little, if any, time lag. The next step involved the evaluation of the synthesized zeolites. It was reasonably assumed that sample densities were approximately the same, so the gas was passed through equal weights (2 g) of finely ground portions of the various samples until the SO_2 in the treated gas returned to its initial concentration. Trace 3 represents the behavior typical of a zeolite-containing sample, in this instance an air-dried analcime/sodalite-containing sample cured at 150 °C for 7 days. The breakthrough curve shows that, once the cell was loaded with the zeolite, the concentration of SO_2 in the effluent dropped and remained at zero for nearly 7 min (treating approximately 4 L of gas) and then gradually recovered as the zeolite became saturated with SO_2. Note that the equivalent microwave-dried zeolite sample (Trace 4) remained at zero for a considerably longer period of time (20 min) and therefore was able to adsorb about three times as much SO_2 than its air-dried counterpart.

Additional breakthrough curves for SO_2 adsorption for microwave-dried zeolite samples are given in Table 3 and in Figure 7. Those pictured are typical of the samples that were studied. It is evident from the plot that the analcime−sodalite mixture (Trace 1) was a more effective adsorbent than either zeolite X (Trace 2) or a zeolite Y−Na-P1 combination (Trace 3) synthesized at 90 °C for 3 and 7 days, respectively. Interestingly enough, fly ash source played little role in the adsorption process. Temperatures governed the nature of the zeolites that formed, and these were always the same at a given temperature regardless of the carbon content of the fly ash. As a check, the zeolite samples pictured in Figure 7

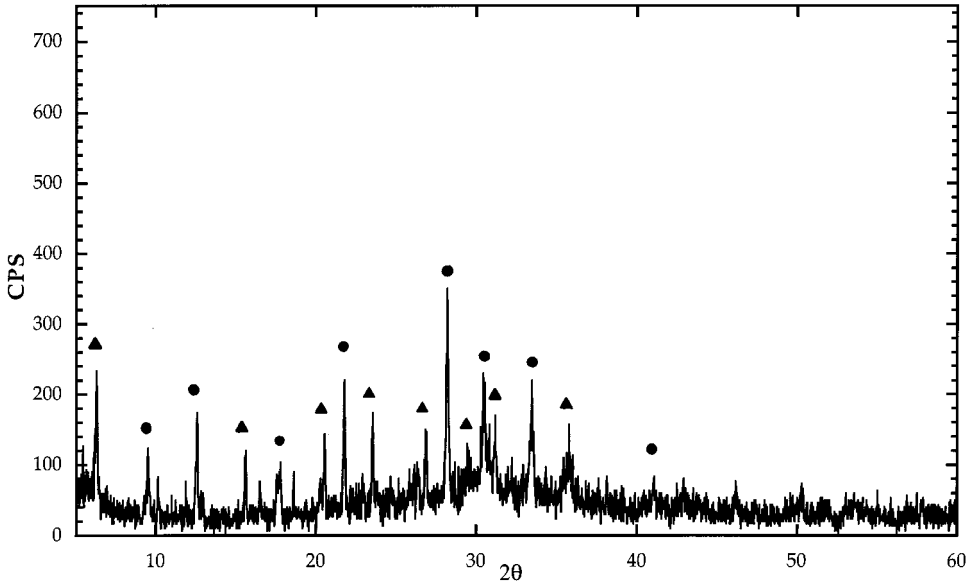

FIGURE 5. Fly ash cured with 3M NaOH at 90 °C for 7 days: (●) = zeolite Na-P1, (▲) = zeolite Y (Na).

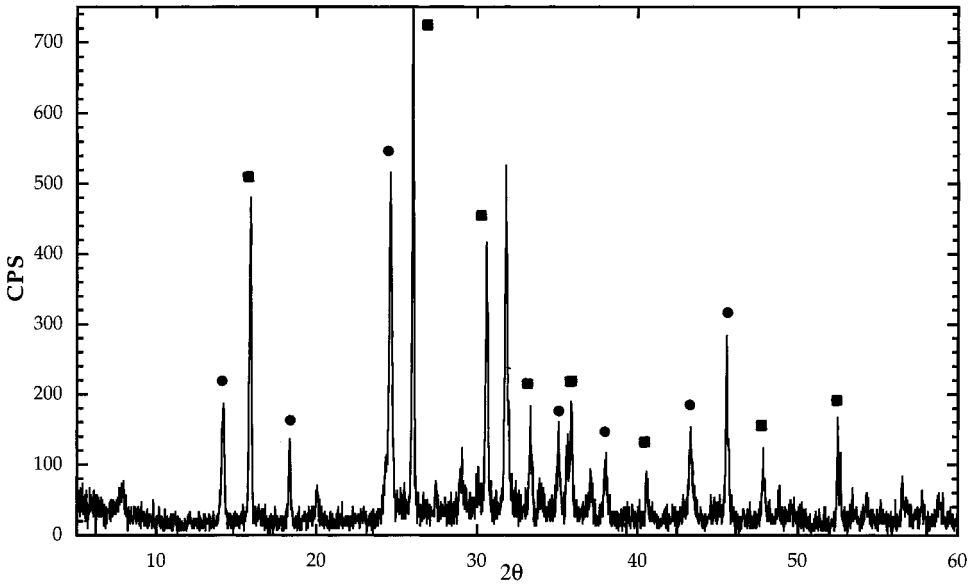

FIGURE 6. Fly ash cured with 3 M NaOH at 150 °C for 7 days: (●) = sodalite, (■) = analcime.

TABLE 3. Time to Breakthrough of the Class F Fly Ash Samples (Minutes)

temp (°C)	concn NaOH molarity	curing time of samples 1 day	3 days	7 days
60	0.1	nil	nil	nil
60	3	nil	nil	nil
90	0.1	nil	nil	nil
90	3	trace	trace	trace
150	0.1	nil	nil	nil
150	3	trace	7	22

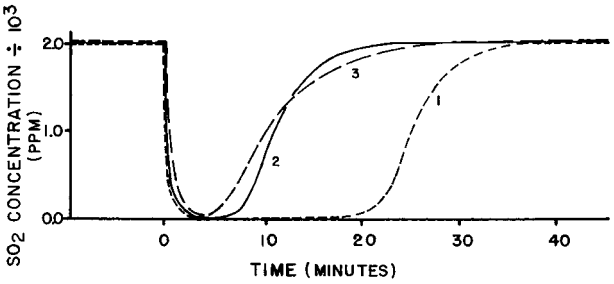

FIGURE 7. Breakthrough curves for treated fly ash samples containing the following zeolites: (1) sodalite plus analcime, (2) zeolite X (Na), (3) zeolite Y (Na), and (4) zeolite Na-P1.

were independently analyzed for their total sulfur content using a Leco total sulfur analyzer (Table 4). It was calculated that the analcime−sodalite sample adsorbed about 6−7 mg of SO_2/g of sample which is in keeping with sulfur uptake using breakthrough curve calculations.

SEM Analyses. As a final step, the microstructure of the 90 and 150 °C samples was compared and contrasted. Figure 8 represents a sample prepared from the Hatfield Class F fly ash at 90 °C for 7 days. Figure 8a depicts a remnant fly ash sphere covered with Na-P1 crystals while Figure 8b from the same sample contains a cluster of Na-P1 crystals. Figure 9 represents a sample of Rivesville Class F fly ash treated at 150 °C for 7 days. At the higher temperatures large spherical analcime crystals are seen to coexist with smaller sodalite crystals in both views (a and b). Clearly both fly ashes undergo zeolitization. Note that, in each case, there is a measurable

TABLE 4. Total Sulfur Analyses of Zeolitized (7 days, 150 °C, 3 M NaOH) Fly Ash Samples

sample	fly ash before adsorption testing S content (wt %)	sample after testing S content (wt %)	SO_2 capacity (Mg SO_2/g of solid)
Rivesville	0.21	0.51	6.0
Hatfield	0.36	0.69	6.6

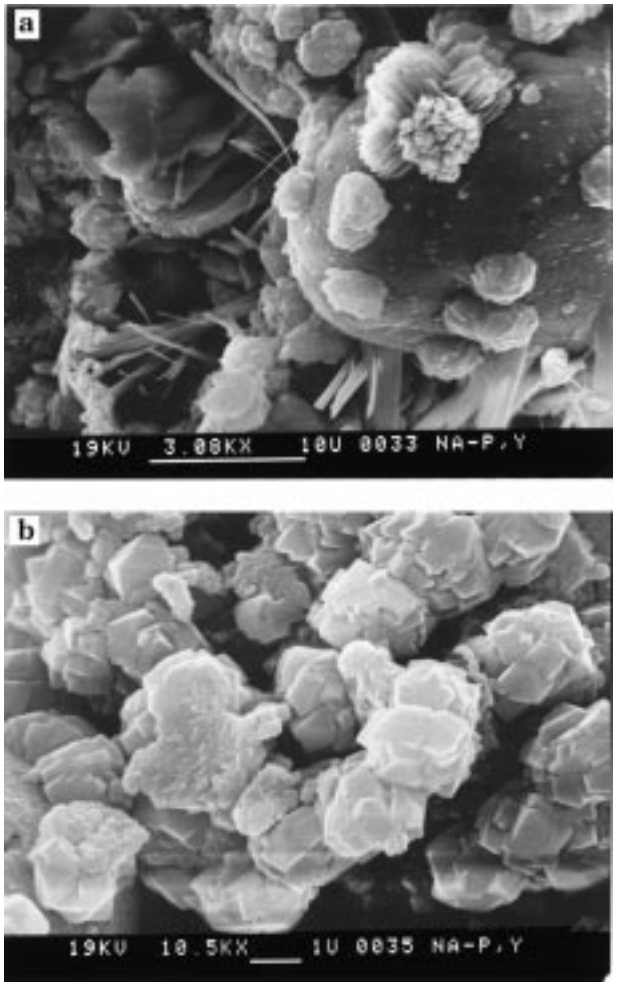

FIGURE 8. Zeolite formation in a sample of Hatfield Class F fly ash that was mixed with 3 M NaOH and reacted at 90 °C for 7 days: view a, fly ash grain (upper right) with overgrowths of zeolite Na-P1; view b, zeolite Y. Bars at bottoms of photos are 10 and 1 μm long, respectively.

amount of agglomeration which increases the particle size of the reacted grains, e.g., Figure 8b. Also of note is the fact that analcime crystals tend to nucleate and grow on the scoriaceous carbon particles present in the sample. The fact that agglomeration occurs can be used to one's advantage if the material is to be used in a fixed bed adsorber. Chemical adjustments can be made to encourage or discourage the process.

Adsorption of SO_2 on utility-synthesized zeolites has the potential of becoming an effective and perhaps even a cost-effective way of removing SO_2 from flue gases. Note that the reported data represent minimum values inasmuch as some of the glassy material attributed to the fly ash was still present in these samples. With further reaction and microwave treatment, this value could very well approach that reported in the literature (*2*, *3*) for Silicalite (−20 mg of SO_2/g). Continuing studies to maximize reactivity and evaluate the adsorption capacity of fly ash-based zeolites at different temperature and pressure conditions are in progress.

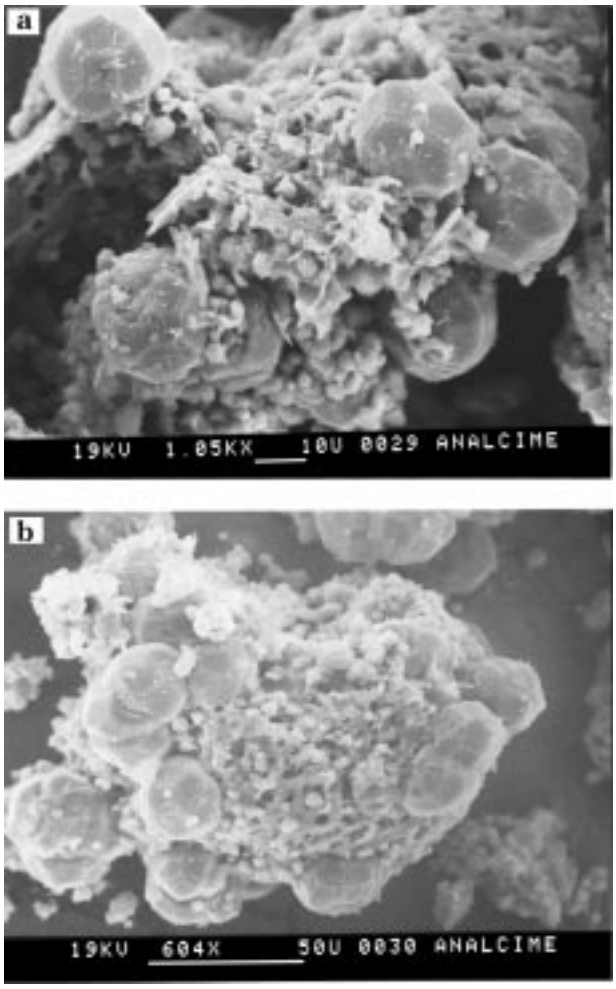

FIGURE 9. Zeolite formation in a sample of Rivesville Class F fly ash that was mixed with 3 M NaOH and reacted at 150 °C for 7 days. Both micrographs depict prominent analcime formation. Bars at bottoms of photos are 10 and 50 μm long, respectively.

Acknowledgments

This work was supported by a grant from the U.S. Department of Energy FETC (DE-FG22-96PC9621). Thanks also to Allegheny Power and PP&L for supplying fly ash samples.

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Received for review March 3, 1998. Revised manuscript received February 8, 1999. Accepted February 24, 1999.

ES9802091