SEMI-ANNUAL PROGRESS REPORT

SO₂ Removal from Flue Gases Using
Utility Synthesized Zeolites

Grant No. DE-FG22-96PC96210

5th Semi-Annual Report (96210R05)

by

Michael Grutzeck
Materials Research Laboratory
The Pennsylvania State University
University Park, PA 16802

Submitted to

AAD Document Control
The United States Department of Energy
Federal Energy Technology Center
626 Cochran's Mill Road
P.O. Box 10940
Pittsburgh, PA 15236-0940

April 30, 1999

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Abstract

It is well known that natural and synthetic zeolites (molecular sieves) can adsorb gaseous SO₂ from flue gas and do it more efficiently than lime based scrubbing materials. Unfortunately their cost (\$500-\$800 per ton) has deterred their use in this capacity. It is also known that zeolites are easy to synthesize from a variety of natural and man-made materials. The overall objective of the current work has been to evaluate the feasibility of having a utility synthesize its own zeolites, on-site, from fly ash and other recycled materials and then use these zeolites to adsorb SO₂ from their flue gases.

Work to date has shown that the efficiency of the capture process is related to the degree of crystallinity and the type of zeolite that forms in the samples. Normally, those samples cured at 150°C contained a greater proportion of zeolite and as such were more SO₂ adsorptive than their low-temperature counterparts. However, in order for the project to be successful, on site synthesis must remain an option, i.e. ~100°C synthesis. In light of this, the experimental focus now has two aspects. First, compositions of the starting materials are being altered by blending the current suite of fly ashes with ground glass cullet and silica fume to promote the formation and growth of well crystallized and highly adsorptive zeolites. Second, greater degrees of reaction at significantly lower temperatures are being promoted by ball milling the fly ash prior to use, by the use of more concentrated caustic solutions, and by the addition of zeolite seeds to the reactants. In all cases studies will focus on the effect of structure type and degree of conversion on SO₂ adsorption.

Future work will concentrate on the study of the effect of weathering on the suitability of converting fly ash into zeolites. This is an especially important study, considering the acres of fly ash now in storage throughout the United States.

SO₂ Removal from Flue Gases using Utility Synthesized Zeolites

Grant No. DE-FG22-96PC96201

1.0 Introduction

The removal of sulfur dioxide (SO₂) from flue gases became mandated by NSPS legislation more than 25 years ago. To comply, utilities have made a choice, either scrub using a lime-based scrubbing system or burn low-sulfur containing coal. The majority of the coal burning utilities in Pennsylvania have chosen lime-based scrubbing. Although lime based scrubbing is a proven technology it does have a number of disadvantages. In addition to the cost associated with the purchase of lime-based scrubbing materials and the cost of disposing of the calcium sulfate/sulfite that is generated by the process, there is another more serious consequence of scrubbing with lime, the use of lime based materials based on calcite (CaCO₃) always add additional CO₂ to the atmosphere. Once CO₂ becomes a monitored greenhouse gas, using lime-based scrubbing could become even more expensive.

The work accomplished during the past 30 months of funding suggests that an alternate technology, which uses utility synthesized zeolites to remove SO₂ emissions from flue gases, could be used instead of lime to scrub exhaust gases. Synthesizing zeolites from fly ash, on-site by the utility could very well cost more than an outright purchase of lime, but, by using fly ash to make the zeolites, little additional waste is generated and no CO₂ is directly or indirectly emitted to the atmosphere during the scrubbing process. When these facts are taken into account, they could very well offset the higher cost associated with using fly ash derived zeolites.

2.0 Background

The concept of using zeolites to clean-up off gas emissions is not new. Sulfuric acid manufacturing plants have been the most common industrial users of zeolites to clean-up their SO₂ emissions. For instance, in the 1970s Linde and Monsanto began to sell a system which used a proprietary zeolite (PuraSiv S) for this purpose (Miller, 1973). Their zeolites were reusable, they could be regenerated by heating them to ~400°C to drive off the SO₂ which is then recycled. More recently, Chriswell and Gollakota (1987), and Gollakota and Chriswell (1988) published papers that showed that the use of acid resistant Silicalite (a synthetic zeolite molecular sieve manufactured by Union Carbide Corporation) would give zero release and adsorb ~38 mg SO₂ per gram of zeolite at 25°C from a simulated coal burning flue gas. Related studies using synthetic zeolites X (Na₈₆[Al₈₆Si₁₀₆O₃₈₄]. 264H₂O), Y (Na₅₆[Al₅₆Si₁₃₆O₃₈₄]

.250H₂O) and ferrierite (Na_{1.5}Mg₂[Al_{5.5}Si_{30.5}O₇₂] .18H₂O) have suggested that these zeolites could be used instead of Silicalite (Barrer, 1978).

Previously published reviews such as that by Mumpton (1978) have repeatedly documented the fact that natural zeolites such as mordenite (Na₈[Al₈Si₄₀O₉₆].24H₂O), chabazite (Ca₂[Al₄Si₈O₂₄].13H₂O) and erionite (Ca,Mg,Na₂,K₂)_{34.5}[Al₉Si₂₇O₇₂].27H₂O have a high capacity for SO₂ adsorption [e.g. 200 mg/g (static) and 40 mg/g (dynamic)*], even in the presence of large amounts of carbon dioxide (CO₂) and water vapor.

Vaughan (1978) suggests that, because these zeolites are generally resistant to acid attack and are stable at high temperatures, all of these zeolites could be used to control SO₂ emissions. The technology works very well, but normally natural and synthetic zeolites at \$600-800 a ton are too costly to compete with lime-based scrubbing.

However, if a utility was able to synthesize zeolites from fly ash on-site and then use them to control its SO₂ emissions, the cost of producing the zeolites becomes less of an issue. Based upon the finding of the author and his colleagues it now seems possible to synthesize large quantities of zeolites from fly ash and alkali solutions at a cost of \$50. For example, treating a slurry of fly ash and 2.8M NaOH solution at 80°C for 6 days, caused it to form zeolites Na-P1 (Na₈[Al₈Si₈O₃₂].16H₂O) and Y (LaRosa et al., 1992). By adding additional lime to the system it was also possible to produce chabazite and calcium silicate hydrate (C-S-H) (LaRosa et al., 1991). When the temperature was reduced to 25°C and reaction times were extended to a month, similar crystalline materials were obtained (Grutzeck, 1993).

More recently, Grutzeck and Siemer (1997) were able to synthesize Zeolite A (Na₁₂[Al₁₂Si₁₂O₄₈].4.5H₂O) at 80°C and Na-P1 and hydroxysodalite (Na₆[Al₆Si₆O₂₄].7.5H₂O) at 130° and 180°C from Class F ash and a caustic sodium aluminate slurry. Grutzeck(1997) also used potassium sulfate-rich cement kiln dust combined with fly ash and alkali hydroxides to make Na-P1, analcime (Na₁₆[Al₁₆Si₃₂O₉₆].16H₂O), and a cancrinite-like phase (Na₁₄[Al₁₂Si₁₃O₅₁].6H₂O). More recently, McCarthy (1995) characterized a high-sodium lignite by-product (scrubber ash mixed with fly ash) that had been disposed of in a land fill for 10 years. Interestingly enough, the sample contained crystalline C-S-H (tobermorite), nosean (Na₈[Al₆Si₆O₂₄SO₄ or more likely a hydroxysodalite) and the zeolite Na-P1. These are suggestive that the process is rather insensitive to synthesis conditions, but as it is shown later in the report, this is not entirely true.

3.0 Objectives

* Under dynamic conditions this is equivalent to 80 pounds of SO₂ per ton of zeolite.

It is clear that zeolites can adsorb large quantities of SO₂ from flue gases and probably can do it more efficiently than lime-based materials. Given the above facts, it has been our objective to evaluate the possibility of synthesizing highly SO₂ adsorbent zeolites on site (or adjacent to a utility), using the utility's own fly ash, and then use the zeolites to scrub SO₂ from their own flue gas. By mixing the fly ash with sodium hydroxide solution, allowing it to react in insulated and lined ponds for a sufficient amount of time, and then washing, drying and sieving the zeolitic material, it should be possible to produce a ton of zeolite for less than \$50. Alternately, a portable autoclave could be brought on site and zeolites could be synthesized hydrothermally in a matter of days. The hydrothermally synthesized zeolites would be somewhat more expensive to produce (~\$100 per ton), but at the same time, they would be more robust and more SO₂ adsorbent because higher temperatures seem to promote a greater degree of reactivity in a shorter period of time.

If the technology works as expected, a utility could use its own zeolites to reduce its SO₂ emissions to near zero, begin to accumulate SO₂ credits, and not generate any significant amount of additional waste and also reduce the direct/indirect release of CO₂ to the atmosphere.

4.0 Results and Discussion

4.1 Research Progress

The work accomplished during the past 30 months of the grant established the fact that fly ash based zeolites could in fact be used to remove SO₂ from a simulated flue gas. Although the project has been successful, removal efficiencies are about 40% that of Silicalite (34 lbs. versus 80 lbs. SO₂ per ton of zeolitic material). However the fly ash samples are only partially converted to zeolite and still contain a significant amount of the unreacted glassy phase. Work during the last 6 months has concentrated on ways of increasing reactivities. Processing conditions have been modified to include more alkaline solutions and the use of higher temperatures (up to 90°C) and longer reaction times (up to 56 days). Work is also concentrating on new ways of optimizing SO₂ uptake by altering the bulk compositions of the starting materials. Ground glass cullet have been added as a means of promoting the formation of a wider variety of zeolites with the hope that ones with greater adsorptive capacity can be found.

Work has also concentrated on the redesign of our adsorption test cell. A larger capacity cell was designed to increase accuracy of measurements using flow rates more representative of conditions seen in a bag house setting. The cell is fabricated from stainless steel tubing and is gas tight up to 5 psi needed to pass the simulated gas through the fixed bed adsorber. Two grams of powdered zeolite are contained between two plugs of glass wool. The spectrophotometer is

set on 284 nm wavelength and is able to monitor the amount of SO₂ in the gas as a function of time. The gas flow rate is monitored using a flow meter. Normally rates are kept at 6 cc/sec. In as much as SO₂ content is known and total gas passed prior to breakthrough, the amount of SO₂ adsorbed can be calculated. A graphic representation of adsorption results per gram of tested zeolitic material is given in Figure 1.

Figure 1. SO₂ and NO_x Capture Efficiencies of Various Zeolitic Products.

The results are typical of those obtained for zeolites synthesized at 100°C. It is notable that our best zeolite is about 1/2 as good as microwave dried clinoptilolite. This was a Na-P1 containing sample. It was regeneratable, but less effective at adsorbing SO₂ the second time. The effect of microwave drying is being investigated as a means of drying zeolites and increasing their capacity for SO₂.

One interesting observation was the fact that these same zeolites were able to adsorb NO₂ from a gas mixture containing 2000 ppm NO₂ (balance N₂). The sample tested was reacted at 90°C for 56 days. It was non-crystalline (X-ray amorphous) which is notable in as much as adsorption is usually correlated with crystallinity. Perhaps, short range order is enough to capture certain gases. This work will be followed up if a request for new funding is granted.

It is proposed that zeolites can be synthesized, dried, granulated and stored in a silo until they are needed. The silo could feed a metal mesh conveyer belt that would, at some predetermined exiting SO₂ level, indicating breakthrough conditions, refresh itself with a new load of zeolites. The intermittently movable bed of zeolite adsorber could be placed at the back end of the bag house where temperatures are lower and the chances of the bed clogging with fly ash are less of a problem. Flow rates should be slow at this point, requiring a large area but rather thin bed. Zeolites tend to provide zero release for the entire period that they are adsorbing SO₂. Breakthrough occurs

rather rapidly and dramatically. Thus they are ideally suited for an intermittently refreshed filter bed operation. The fully charged material can be heated to extract the SO₂ and then reused, or sold as an agricultural acidifying soil conditioner.

4.2 Personnel

Mr. Anand Srinivasan obtained a Master of Engineering Degree in Chemical & Environmental Engineering in May 1998. He has taken a job with Bayer Company in Pittsburgh. In the interim we have been able to obtain another rather able graduate student to continue the above work. Her name is Suman Bopaiah. She has a Bachelor of Environmental Engineering from Sri Jayachamarajendra College of Engineering in Mysore. She started her studies in the fall 1998. She has been working on zeolite synthesis from fly ash and fly ash+glass cullet mixtures. She has reacted her samples for up to 56 days at 40°, 60° and 90°C. She has tested these samples and compared them to various natural zeolites. These data are the bases of the data given in Figure 1. She gave a paper at the American Ceramic Society Meeting in Indianapolis (April 25-28, 1999). ¹ The session dealt with environmental issues in the ceramic industry and was well accepted. Ms. Bopaiah is currently trying to graduate in the fall of 1999.

4.3 Papers Published this 6 Month Period

- Srinivasan, A. and M.W. Grutzeck, "The Adsorption of SO₂ by Zeolites Synthesized from Fly Ash," Environ. Sci. & Tech. 33,(9), 1464-1469 (1999).

4.4 Future Work

In the next six months it is expected that:

- Studies will focus on the effect temperature and composition on the zeolite structure type, degree of reaction, degree of crystallinity and adsorption efficiency of the zeolite-containing samples.
- Experimental evaluation of the relative merit of various processing techniques that can be used to accelerate reaction rates, i.e. ball milling (reduce particle size) and seeding.

¹Bopaiah, S. and M.W. Grutzeck, "Evaluation of Utility Synthesized Zeolites for SO₂ Capture," Abstract of a Talk Presented at the Amer. Ceramic Society Annual Meeting, Amer. Ceram. Soc. Bull. 78 (4), p 203 (1999).

- If time allows, experiments will be initiated to explore the effect of weathering on fly ash reactivities. These are of importance as hundreds of acres of weathered fly ash are stockpiled throughout the United States.

5.0 Conclusion

Work is on schedule and we now anticipate continuing the study by focusing on means of optimizing the efficiency of using on-site utility synthesized zeolites to adsorb SO₂ and other gases from flue gas. If the technology works as expected, a utility could use its own “produced-on-site” zeolites to reduce the concentration of SO₂ in their flue gases to near zero without generating any significant amount of additional waste. Because the process is more efficient than lime-based scrubbing, a utility could realistically meet more stringent EPA Clean Air standards (CAAA 1990) and/or begin to accumulate SO₂ credits.

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