SO₂ Removal from Flue Gases using
Utility Synthesized Zeolites

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by

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Abstract

Historically, sulfur dioxide (SO_2) emissions were unregulated. As the environmental consequences of such emissions began to surface, increasingly stringent, federal and state government mandated pollution control requirements were imposed on the electric power generating industry. Coal-burning utilities were forced to make one of two choices. They could install flue gas scrubbing equipment or start to burn lower sulfur-containing coal. The proposed research is directed at those utilities that have made the second choice, or utilities desiring to undertake new plant construction.

First, it is well known that natural and synthetic zeolites (molecular sieves) can adsorb large quantities of SO_2 from flue gas and do it more efficiently than lime based scrubbing materials. The seminal work by Chriswell and Gollakota (1987) using Silicalite (a very silica rich synthetic zeolite) has demonstrated this fact beyond a doubt. In addition, older published studies have repeatedly demonstrated that natural zeolites such as mordenite ($\text{Na}_{86}[\text{Al}_{86}\text{Si}_{106}\text{O}_{384}]\cdot 264\text{H}_2\text{O}$), chabazite ($(\text{Ca}_2[\text{Al}_4\text{Si}_8\text{O}_{24}]\cdot 13\text{H}_2\text{O})$ and erionite ($(\text{Ca},\text{Mg},\text{Na}_2, \text{K}_2)_{4.5}[\text{Al}_9\text{Si}_{27}\text{O}_{72}]\cdot 27\text{H}_2\text{O}$) have a high capacity for SO_2 adsorption [e.g. 200 mg/g (static) and 40mg/g (dynamic)], even in the presence of large amounts of carbon dioxide and water vapor. Similar studies using synthetic zeolites X ($\text{Na}_{86}[\text{Al}_{86}\text{Si}_{106}\text{O}_{384}]\cdot 264\text{H}_2\text{O}$), Y ($\text{Na}_{56}[\text{Al}_{56}\text{Si}_{136}\text{O}_{384}]\cdot 250\text{H}_2\text{O}$) and ferrierite ($(\text{Na}_{1.5}\text{Mg}_2[\text{Al}_{5.5}\text{Si}_{30.5}\text{O}_{72}]\cdot 18\text{H}_2\text{O})$) have found that these zeolites work as well as their natural counterparts. Since these zeolites are generally resistant to acid attack and are stable at high temperatures, they have been promoted as a way of treating emissions from sulfuric acid plants. However, we are unaware of any utility using this technology. Zeolites are too expensive for this large scale use.

Second, it is also well known that zeolites are easy to synthesize from natural and synthetic glasses, an entire industry is based on this technology. What is new, however, is the fact that the named principal investigator and his students recently demonstrated that it was possible to synthesize zeolites from Class F fly ashes using relatively simple low temperature processing. For example, by adding sodium hydroxide solutions to fly ash and treating the resultant slurry at 80°C for 6 days, it was possible to produce zeolites Na-P1 ($\text{Na}_{86}[\text{Al}_{86}\text{Si}_{106}\text{O}_{384}]\cdot 264\text{H}_2\text{O}$) and Y. By adding more lime to the system it was also possible to produce chabazite and a calcium silicate hydrate binder.

Therefore, our objective is to use laboratory scale studies of zeolite synthesis, characterization and adsorption to study the potential of using utility synthesized zeolites to adsorb SO_2 from utility flue gases. As zeolites are synthesized, they will be dried and screened to identical sizes (surface area). Then they will be tested for their ability to adsorb SO_2 from a simulated stack gas containing 2000 ppm SO_2 . Work to date has focused upon the building of the apparatus necessary for the study, adapting a furnace and controller to control the temperature of the gas and sample, acquiring fly ash samples from Allegheny Power and PP&L companies, and synthesizing a variety of zeolite test specimens.

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1.0 Introduction

Much of the United States' coal is now considered too high in sulfur to burn without SO₂ emission control. Historically, SO₂ emissions were unregulated. However, as the consequences of such emissions began to become known, increasingly stringent federal and state government mandated pollution control requirements were imposed on the electric power generating industry. As a result, the Nation's coal-burning utilities made one of two choices. They either installed flue gas scrubbing equipment or started to burn lower sulfur-containing coal.

The research described below is directed at those utilities that have made the second choice. By burning lower sulfur-containing coal, a utility's management has delayed the inevitable investments necessary to retrofit the utility's boilers with currently available wet or dry scrubbing equipment. By making this choice, management has bought itself some time, with the hope that a new technology will emerge which is easier to use than treating stack gases with lime/limestone, a technology which will be more efficient and at the same time less damaging to ducting and flues and generate little or no additional waste. For the two reasons given below, we believe that such a new technology may now be within reaching distance.

First, it is well known that natural and synthetic zeolites (molecular sieves) can adsorb large quantities of SO₂ from flue gas and do it more efficiently than lime based scrubbing materials. The seminal work by Chriswell and Gollakota¹ and Gollakota and Chriswell² using Silicalite (a very silica rich synthetic zeolite) has demonstrated this fact beyond a doubt. In addition, previously published reviews such as that by Mumpton³ have repeatedly documented the fact that natural zeolites such as mordenite (Na₈[Al₈Si₄₀O₉₆].24H₂O), chabazite (Ca₂[Al₄Si₈O₂₄].13H₂O) and erionite (Ca,Mg,Na₂,K₂)_{4.5}[Al₉Si₂₇O₇₂].27H₂O have a high capacity for SO₂ adsorption [e.g. 200 mg/g (static) and 40mg/g (dynamic)^{*}], even in the presence of large amounts of carbon dioxide (CO₂) and water vapor. Similar 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 found that these zeolites work as well as their natural counterparts^{1,2,4}. Vaughan⁵ suggests that, because these zeolites are generally resistant to acid attack and are stable at high temperatures, they have been promoted as a way of treating emissions from sulfuric acid plants. For instance, in the 1970s Linde and Monsanto began to sell a system which used a proprietary zeolite (PuraSiv S) for this purpose. Their zeolites were reusable, they could be regenerated by heating them to high enough temperatures (~400°C) to drive off the SO₂ which is then recycled⁶. However, we are unaware of any utility using this technology. Zeolites are apparently too expensive for this large scale application. For example, synthetic zeolite A used in detergents costs ~\$700 a ton, and natural zeolites such as clinoptolite (one of the most common zeolites used for ammonia removal from waste water) costs ~\$500 a ton^{**}.

Second, the named principal investigator and his students demonstrated that it was possible to synthesize zeolites from Class F fly ashes using relatively simple processing, processing that can be easily scaled-up by the utilities for their own on-site use. For example, by adding sodium hydroxide solutions to the fly ash and treating the resultant slurry at 80°C for 6 days, it was possible to synthesize zeolites Na-P1 (Na₈[Al₈Si₈O₃₂].16H₂O) and Y⁷. By adding more lime to the system it was also possible to produce chabazite and calcium silicate hydrate (C-S-H)⁸. When temperatures were reduced to 25°C and reaction times were extended to a month, crystalline materials were also obtained⁹. More recently, McCarthy¹⁰ 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.

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

^{**} These are prices quoted by PQ Corporation and the Lake Tahoe Sanitary District, respectively.

Interestingly enough, the sample contained crystalline C-S-H (tobermorite), nosean ($\text{Na}_{10}\text{Al}_6\text{Si}_6\text{O}_{24}\text{SO}_4$) and the zeolite Na-P1.

2.0 Objectives

Clearly, zeolites can adsorb large quantities of SO_2 from flue gases and probably can do it more efficiently than lime-based materials. Given the above facts, it is our objective to synthesize highly SO_2 adsorbent zeolites such as chabazite, erionite, zeolite X, zeolite Y, zeolite Na-P1 and possibly mordenite from fly ash, on site or adjacent to a utility, using the utility's own fly ash and waste heat. By mixing the fly ash with ~\$30 worth of 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. The zeolites are strong but yet soft enough that they can be ground, sieved to size, and placed on screens to make fixed bed adsorbents. The flue gases can then be directed through a number of these zeolite beds to remove SO_2 . If the technology works as expected, a utility could use its own zeolites to reduce its SO_2 emissions to near zero, begin to accumulate SO_2 credits, and not generate any significant amount of additional waste.

3.0 Results and Discussion

3.1 Research Progress

Work to date has focused upon the building of the glass ware needed to study the uptake of SO_2 from a simulated stack gas as a function of composition and temperature. The sample cell needed to fit our Varian Model 2300 spectrophotometer has been fabricated (Pyrex tube with quartz end windows) and a light-tight lid for the sample compartment of the spectrometer is currently being made in the shop. When complete, the lid will be permanently fitted the sample cell. A Kanthal resistance furnace has been adapted to take a vertical Pyrex tube filled with equal amounts by weight of the zeolite samples. Prior to testing the zeolite samples will be screened and dried at 300°C. Because the densities of the zeolites are nearly the same, the screening process will assure that the zeolites have approximately the same surface area. Flow rates and time to breakthrough for the SO_2 will be monitored for each sample. Samples will be ranked as per their performance. The furnace will allow us to maintain temperature at various flue-gas temperatures (200°-500°C). A synthetic stack gas has been purchased which contains 2000 ppm SO_2 mixed with O_2 and N_2 . Zeolite samples have been fabricated using 3-5N sodium hydroxide (NaOH) solutions and both Class F and dried FGD Class F fly ash. Typically, the zeolites: Na-P1, Y and cancrinite are produced at 80°-130°C.

3.2 Personnel

Mr. Anand Srinivasan has joined the project. He is a MS candidate in Penn State's Environmental Pollution Control interdisciplinary Masters Degree Program. He has a BS in Chemical Engineering from R.V. College of Engineering, India-July 1996.

3.3 Future Work

In the next six months it is expected that the test apparatus will be built and debugged and that preliminary results will be available for the back-log of samples now in our possession. It is also expected that the fly ash samples requested from Allegheny Power and PP&L will have arrived, will have been analyzed and characterized, and be incorporated into the experimental program.

4.0 Conclusion

Work is on schedule and looks promising.

5.0 References

1. Chriswell, C. and S. Gollakota, "Adsorption of Sulfur Dioxide from Combustion Gases on a Regenerable Molecular Sieve", Preprints of Papers, Amer. Chem. Soc., Div. Fuel Sci. 32, (1) 505-12 (1987).
2. Gollakota, S.V. and C.D. Chriswell, "Study of an Adsorption Process Using Silicalite for Sulfur Dioxide Removal from Combustion Gases", Industrial Eng. Chem. Res. 27, 139-43 (1988).
3. Mumpton, F. A. , "Natural Zeolites: A New Industrial Mineral Commodity", pp. 3-27 in Natural Zeolites-Occurrence, Properties, Use, L. B. Sand and F. A. Mumpton, Eds., Pergamon Press, Oxford (1978).
4. Barrer, R.M., Zeolites and Clay Minerals as Sorbents and Molecular Sieves, 497 pp., Academic Press, London (1978).
5. D. E. W. Vaughan, "Properties of Natural Zeolites", pp. 353-371 in Natural Zeolites - Occurrence, Properties, Use, L. B. Sand and F. A. Mumpton, Eds., Pergamon Press, Oxford (1978).
6. Miller, W.C., "Adsorption Cuts SO₂, NO_x, Hg", Chemical Engineering August 6, 1973 (1973).
7. LaRosa, J., S. Kwan and M.W. Grutzeck, "Zeolite Formation in Class F Fly Ash Blended Cement Pastes," J. Amer. Ceram. Soc. 75, 1574-80 (1992).
8. LaRosa, J., S. Kwan and M.W. Grutzeck, "Self-Generating Zeolite Cement Composites", Mat. Res. Soc. Symp. Proc. Vol. 245, 211-216, Mat. Res. Soc, Pittsburgh (1991).
9. Grutzeck, M.W., "Zeolite-Cement Composites", in Mineral Admixtures in Cement and Concrete, Vol. 4, S. Sarkar Ed., ABI Books (P) Ltd., New Delhi (1993).
10. McCarthy, G.J., Personal communication, letter 29 August 1995.

6.0 Appendices

None