36867 PDF

BIOTRANSFORMATION OF SULFUR AND NITROGEN OXIDES IN STACK GASES

Rakesh Govind, Rama Puligadda
Department of Chemical Engineering
University of Cincinnati
Cincinnati, OH 45221

and

Dolloff F. Bishop
Risk Reduction Engineering Laboratory
U.S. Environmental Protection Agency
26W. Martin Luther King Drive
Cincinnati, OH 45268

INTRODUCTION

The Nation's large supply of high sulfur coal and increasingly stringent emission regulation led to priority development of advanced innovative processes for treating pollutants in flue gases from coal combustion. The principal pollutants in flue gases, sulfur oxides (SO_2,SO_3) and nitrogen oxides (NO_x) cause acid rain. Thus, the Department of Energy's Clean Coal Program is funding projects to commercialize technologies that minimize emission of sulfur and nitrogen oxides at power plants. The emerging technologies should be applicable to coal-fired combustors in the electric utility, industrial and commercial sectors. The technologies should also achieve high degrees of reliability and have low operating and capital costs. The status of flue gas cleanup technology is summarized in the folowing sections.

Flue gas cleanup technology provides emission control of sulfur dioxide, nitrogen oxides, and particulate matter (PM) in combustion of coal using two generic categories of processes: One category, dry sorbent injection, uses dry sorbents such as limestone injected directly into the combustion zone or downstream of a coal- fired boiler, to capture sulfur dioxide insitu. In this strategy, a low-NO_x combustion environment is usually maintained to aid capture. The second category, post combustion gas cleanup, uses sorbents in a slurry, aqueous liquor, or dry powder injected into the combustion gas leaving coal-fired boilers to effect post combustion capture of SO_2. Processes in both categories employ various approaches to control emission of particulate matter (PM).

In the last 10 to 20 years, a wide variety of dry sorbent injection and post combustion gas cleanup systems (1-12) have evolved. A representative system for dry sorbent injection is the Limestone Injection Multistage Burner (LIMB) used at utility power- generating stations in existing pulverized coal-fired (PC) boilers firing run-of-mine (ROM) coal. The boilers are equipped with conventional particulate matter (PM) controls (typically an electrostatic precipitator). The LIMB system injects dry alkali metal limestone or hydrated lime into the furnace operating with low-NO_x combustion environment achieved through modifications of the burner assembly or combustion operating conditions. LIMB is an emerging technology undergoing research and development at the bench, pilot, prototype, and demonstration plant levels. The thrust of ongoing research is to identify factors that govern performance to optimize removal efficiency.

Numerous activities by both private and public sectors to improve emission control systems are summarized as follows:

1. Research for control of particulate matter (PM) is focussed on performance improvement and optimization. Due to concern for health risks from trace element and inhalable particulate matter, emphasis is placed on the removal of submicron-sized particles.

2. Research in existing flue gas desulfurization (FGD) systems is focused on the use of organic acids or magnesium salts to enhance SO_2 removal efficiency and reagent utilization. Results indicate that a removal efficiency of 95 % can be achieved at reduced operating costs.
3. Research in existing and new FGD systems is to reduce fresh water consumption and clean-up of waste water discharges since these requirements may improve siting and operational problems at coal power plants.
4. A promising low-cost FGD option for SO_2 control is dry injection of sorbent in flue gas before the fabric filter. This process has been demonstrated by the Electric Power Research Institute (EPRI) at full-scale and is applicable to both new and existing low-sulfur coal power plants. Additional research is proceeding on high-sulfur coal applications for use with electrostatic precipitators, for improved waste fixation and disposal, for system optimization and for use of lower-cost alternate reagents.
5. Advanced limestone/gypsum FGD processes are being developed for application which produce marketable gypsum by forced oxidation of the spent slurry.
6. For post-combustion control of NO_x, selective catalytic and selective non-catalytic reduction systems are the most advanced. Pilot- scale systems of these two technologies have been successfully tested on coal-fired power plants. However, these processes are more expensive than modification of burners for low NO_x emission. Major improvements are needed in the process control subsystems, extension of catalyst life, elimination of ammonia leakage, and reduction in overall cost.

Long term research efforts are focused on advanced SO_2 control, combined SO_2/ NO_x control and PM removal. The primary emphasis in advanced SO_2 control technologies is placed on reagent regeneration and saleable product processes to eliminate or minimize solid waste disposal problems.

Biological desulfurization of coal is a pretreatment method that attempts to remove both pyritic and organic sulfur in coal before combustion. In the past, several laboratory studies have been reported to remove sulfur from coal using microorganisms (13-18). Two main microorganisms that have been studied are *Thiobacillus ferroxidans*, a mesophilic (10°C-37°C) bacterium isolated from acid mine drainage, and *Sulfolobus acidocaldarius*, a thermophillic (55°C-80°C) bacterium. Both organisms aerobically oxidize pyritic sulfur, primarily FeS_2, and organic sulfur to soluble sulfates. Atlantic Research Corporation, Virginia (19) developed a unique microorganism (CBI) capable of removing a portion of the organic sulfur from coal. CBI primarily attacked thiophenic sulfur in coal, removing the sulfur as a water soluble sulfate. In laboratory batch and bench-scale continuous systems, CBI removed up to 47% of the organic sulfur. The sulfur removal depended on coal type, particle size and surface properties. Attia and Elzeky (20) used *thiobacillus ferrooxidans* bacteria to selectively modify the pyrite surface chemical behavior to improve pyrite sedimentation in the flotation of coal. They studied the effects of variables (bacterial conditioning time, concentration of bacterial cells, pH, temperature and nutrient solution) on the flotation behavior of pyrite and coal suspensions. Their results indicated that about 40% reduction in the pyrite content of coal was achieved with bacterial pre-conditioning of less than 15 minutes, while coal flotation was unaffected.

METHODOLOGY

Current sulfur and nitrogen oxide control approaches for contaminated gas streams such as stack gases have limitations and are relatively expensive. Practical methods for removal of carbon dioxide are not available. In this paper, the controlled use of biotransformation to remove these oxide pollutants from contaminated gases involves complex biooxidation and bioreduction of the oxides in appropriate bioreactors, ultimately to elemental sulfur, nitrogen gas and biomass. Two separate bioreactor experiments were conducted to investigate the application of biological reactors for removal of sulfur dioxide, nitrogen oxides and carbon dioxide from stack gases.

Biofilter Studies

An experimental biofilter was operated for 5 months to study biological removal of sulfur dioxide, nitrogen oxides and carbon dioxide from stack gases. A 2-inch diameter stainless-steel tube was used to construct the biofilter and ceramic straight-passage monolith with 100 cells/square inch, obtained from Corning Glass, Inc., NY, was used as the support media. The height of the biofilter was 3 feet. Stack gas, with flowrate that was varied in the range 1-2 liters/minute, was introduced at the top of the biofilter. The recycled OECD nutrients (21) were also trickled down the biofilter cocurrent with the flow of the stack gas. 30 mg of *Thiobacillus* (obtained from ATCC culture bank and grown in specialized culture reactors) was suspended in 0.5 liters of OECD nutrients and recirculated through the biofilter to seed the ceramic media with the desired organisms. About 16 gms of the culture was attached after 2 hours of recirculation of the suspended culture through the biofilter.

Stack gas, with the following composition: Carbon dioxide (41.56%), Nitrogen (50%), Oxygen (8%), Sulfur dioxide (0.4%), nitrogen oxides (0.04%), was introduced at the top of the biofilter at an initial flowrate of 1 liter/minute, which resulted in a 2-minute gas phase empty-bed residence time. OECD nutrients with the following composition: (21): KH_2PO_4 (85 mg/L)), K_2HPO_4 (217.5 mg/L)), $Na_2HPO_4.2H_2O$ (334 mg/L), NH_4Cl (25 mg/L), $MgSO_4.7H_2O$ (22.5 mg/L), $CaCl_2$ (27.5 mg/L) and $FeCl_3.6H_2O$ (0.25 mg/L), $MnSO_4.H_2O$ (0.0399 mg/L), H_3BO_3 (0.0572 mg/L), $ZnSO_4.7H_2O$ (0.0428 mg/L), $(NH_4)_6Mo_7O_{24}$ (0.0347 mg/L), $FeCl_3$.EDTA (0.1 mg/L), and yeast extract (0.15 mg/L) were also introduced at the top of the biofilter at a flowrate of 4 liters/day. The biofilter was operated at ambient temperature of 25°C.

Suspended Culture Bioreactor

A bioreactor experiment was conducted to evaluate SO_2/NO_x removal from stack gases by suspended culture bacteria. The design and operating conditions for the bioreactor have been summarized in Table 1. Stack gas, consisting of carbon dioxide, nitrogen, sulfur dioxide, nitrogen oxides and oxygen was bubbled at a rate of 1.5 liters per minute through the bioreactor. The bioreactor, a 4-inch diameter glass column, 3 feet tall, was filled with 2 feet of deionized distilled water and 20 gms of activated sludge as seed. There was no further addition of activated sludge to the reactor. The reactor was mixed by the incoming stack gas flow. The reactor detention time was 4 minutes for the gas stream. The reactor detention time has not been optimized.

The incoming gas stream and the exiting gas stream compositions (refer to Table 1) were analyzed by a sulfur dioxide and nitrogen oxides Beckman Analyzer. OECD nutrient media was batch fed daily to the reactor (0.2 liters) and an equivalent amount of liquid was withdrawn (Table 1) from the reactor. The exit gas was also analyzed using a gas chromatograph.

RESULTS

Biofilter Studies

Complete removal of sulfur and nitrogen oxides was observed in this experiment. No oxygen or hydrogen sulfide was present in the exit gas stream. The carbon dioxide composition was reduced to 32.4%, from an initial feed gas composition of 41.56%. The composition of nitrate in the exit liquid stream was 12 ppm and sulfate composition was 10 ppm. Free sulfur was obtained from the liquid stream. The amount of free sulfur, quantitated by filtering and weighing, closely agreed with the complete conversion of sulfur dioxide to sulfur.

The biofilter consisted of two distinct zones: (1) oxidation zone, in which the sulfur dioxide and nitrogen oxides were converted abiotically and biologically to sulfate and nitrate in the liquid phase; and (2) reduction zone, in which the sulfate and nitrate were converted to hydrogen sulfide, sulfur and nitrogen gas. The hydrogen sulfide formed also reacted with sulfur dioxide in the gas phase to form sulfur, which exited with the nutrient liquid flow.

The following are the possible reactions occuring in the oxidation and reduction zones:

Oxidation zone: Biological reactions

$$1/2\ O_2 + H_2O + SO_2 \xrightarrow{\text{Bacteria}} SO_4^{=} + 2H^+$$

$$1/2\ O_2 + H_2O + NO \xrightarrow{\text{Bacteria}} NO_3^- + 2H^+$$

$$1/2\ O_2 + H_2O + 2NO_2 \xrightarrow{\text{Bacteria}} 2NO_3^- + 2H^+$$

Sulfur dioxide is also oxidized to sulfate abiotically.

Reduction zone: Biological reactions

$$SO_4^{2-} + \text{organic source} \xrightarrow{\text{Bacteria}} H_2S + \text{alkalinity}$$

$$NO_3^- + \text{organic source} \xrightarrow{\text{Bacteria}} 1/2\ N_2 + \text{alkalinity}$$

$$SO_4^{=} + \text{organic source} \xrightarrow{\text{Bacteria}} S^0 + \text{alkalinity}$$

With nutrient recycle, the alkalinity (HCO_3^-) produced in the bioreduction zone neutralizes the acidity produced due to the formation of sulfate and nitrate in the oxidation zone. Waste activated sludge was continuously added to the biofilter and primarily served as the organic source for the bioconversion of sulfate to hydrogen sulfide. The steady-state pH of the exit nutrient stream was 9.2. The majority of the carbon dioxide in the gas stream was absorbed by the bicarbonate to form carbonate. The H_2S produced in the reduction zone combined with sulfur dioxide (SO_2) in the gas phase to form free elemental sulfur.

$$2H_2S + SO_2 \longrightarrow 3S^0 + 2H_2O$$

The major problem encountered in this experiment was the senstivity of the exit gas composition to inlet stack gas flowrate. If the stack gas flowrate was abruptly changed even by a small amount, the conversion of sulfur dioxide would immediately drop and then again achieve 100% conversion after a period of 2-3 hours. For example, at a stack gas flowrate of 1.2 liters/minute, immediately after being changed from a steady-state flow of 1 liter/minute, the conversion of sulfur dioxide immediately dropped from a steady-state value of 100% to 85%; i.e., 15% of the incoming sulfur dioxide was observed in the exit gas stream. Nitrogen oxides were also observed in the exit gas stream, although their composition was very low due to low inlet composition. However, if the biofilter was operated for about 3 hours at a steady-state stack gas flowrate of 1.2 liters/minute, then the sulfur dioxide and nitrogen oxide conversion again reached a steady-state value of 100%.

The instability of the biofilter process to changes in stack gas flowrate was mainly due to disruption of the oxidation-reduction zones, due to penetration of oxygen, present in stack gas, into the reduction zone. However, after the reactor had been operated for some time, usually a few hours, bacterial growth responded to restore the balance of the oxidation-reduction zones, thereby again attaining complete conversion of the sulfur and nitrogen oxides to sulfur and nitrogen gas.

Suspended Culture Bioreactor

After acclimation, complete removal of sulfur dioxide, nitrogen oxides and oxygen was observed in the bioreactor for a period of two months. 30% of incoming carbon dioxide was removed in the bioreactor. The reactor pH remained at near neutral values. The chemoautotrophic sulfate reducing bacteria also use carbon dioxide from the stack gas to support biomass development. Thus CO_2 conversion to biomass and alkalinity (HCO_3^-) also occurs in the process. Chemoautotrophic bacteria function over a wide range of temperature from normal ambient to high temperatures nearing the boiling point of water. Temperature optimization of the processes have not been attempted. About 25% of the sulfur (SO_2) entering the reactor was released as H_2S in the exit gas. The carbon dioxide in the exit liquid was determined by acidification and measurement of CO_2 evolution. The bulk of the carbon dioxide removed from the stack gas was converted to carbonate in the liquid phase. The biomass produced by chemoautotrophic sulfate reducing bacteria supplied some of the organic material needed for sulfate reduction. Waste activated sludge was added to the reactor and primarily served as the organic source for sulfate reduction.

Analysis of the 0.2 liter aqueous stream from the bioreactor revealed that the nitrate/nitrite composition during the two month study varied between 50-120 ppm, the sulfate concentration was steady at 180 ppm. Qualitatively, particulate sulfur was present in the biomass.

The naturally adapted organisms and the water in the bioreactor support the following complex reactions:

Dissolution and Oxidation in Water:

$SO_2 + H_2O \Longrightarrow H_2SO_3$
$2SO_2 + 2H_2O + 1/2O_2 \longrightarrow H_2SO_4 + H_2SO_3$
$H_2SO_3 + 1/2O_2 \longrightarrow H_2SO_4$
$2NO + O_2 \longrightarrow 2NO_2$
$2NO_2 + H_2O \longrightarrow HNO_2 + HNO_3$
$CO_2 + H_2O \Longrightarrow H_2CO_3$

Bioreduction:

$$CH_3COO^- + SO_4^{2-} \xRightarrow{\text{Bacteria}} H_2O + CO_2 + HCO_3^- + S^{2-}$$

$$3CH_3COO^- + 4SO_3^{2-} \xRightarrow{\text{Bacteria}} 3H_2O + 3CO_2 + 3HCO_3^- + 4S^{2-}$$

$$2H^+ + S^{2-} \longrightarrow H_2S$$

$$SO_4^{2-} + 2H^+ + 3H_2S \longrightarrow 4S + 4H_2O$$

Nitrite and nitrate ions are also biologically reduced to nitrogen gas. The alkalinity (HCO_3^-) produced by the reduction neutralizes the acids produced in the oxidation reactions and by the dissolution of the gases in the water of the bioreactor. The steady-state pH in the bioreactor was 9.0.

Sulfur, biomass, sulfate and nitrate ions are removed from the reactor in the effluent aqueous stream. The small residuals of soluble sulfate and nitrate ions may be separated from the particulate sulfur and biomass in the stream. With or without separation, the soluble sulfate and nitrate ions may be reduced in a second reactor using waste organic sources, such as sewage sludge.

CONCLUSIONS

Biological conversion of sulfur dioxide and nitrogen oxides in stack gases is possible using either immobilized biofilms or suspended culture reactors. Complete conversion of sulfur and nitrogen oxides are achieved in the reactors with the final products being sulfur and nitrogen gas, respectively. Detailed reactions explaining the experimental data have been presented in this paper. Biotransformation of stack gas contaminants offers an alternative approach to manage combustion of high sulfur coal, without requiring landfilling or disposal of sludge.

REFERENCES

1. McCrea, D.H., Forney, A.H., and Myers, J.G., Recovery of Sulfur from Flue gas Using a Copper Oxide Absorbent. J.Of Air Pollution Control Association, Vol. 20. No. 12. 819, Dec. 1970.

2. Strakey, J.P., Bauer, E.R., and Haynes, W.P., Removal of SO_2 and NO_x from flue gad in Fluidized bed copper oxide process. Presented at the Sixth National Conference on Energy and Environment, Pittsburgh, Pa., May 21- 24, 1979.

3. Demski, R.J., Gasoir, S.J., Bauer, E.R., Jr., Yeh, J.T., Strakey, J.P., and Joubert, J.I., Simultaneous removal of SO_2 and NO_x from flue gas employing a fluidized bed copper oxide process. Presented at the 1092 Summer National Meeting of the AIChE, Cleveland, Ohio, August 29- September 1, 1982.

4. Yeh, J.T., Demski, R.J., Strakey, J.P., and Joubert, J.I., PETC Fluidized bed copper oxide process for combined SO_2 /NO_x removal from flue gas. Presented at the 1984 Winter National meeting of the AIChE, Atlanta, Ga., March 11- 14, 1984.

5. Drummond, C.J., Yeh, J.T.,Joubert, J.I., and Ratafia- Brown, J.A., The design of a dry, regenerative fluidized bed copper oxide process for the removal of sulfur dioxide and nitrogen oxides from coal fired boilers. Presented at the 78th Annual Meeting and Exhibition of the Air Pollution Association, Detroit, Michigan, June 16 -21, 1985,

6. McArdle, J.C., Leshick, D.G., and Williamson, R.R., Sorbent Life Cycle Testing of the Fluidized bed copper oxide process, Presented at the 1987 Spring National Meeting of the AIChE, Houston, Texas, March 29- April 2, 1987.

7. Tseng, H.P., Haslbeck, J.L., and Neal, L.G., Evaluation of the NOXSO combined NO_x/SO_2 flue gas treatment process. Report to the U.S. Department of Energy , Contract No. DE-AC22-FE6-0148, September 30, 1983.

8. Haslbeck, J.L., and Neal, L.G., Technical evaluation of the NOXSO combined NO_x/SO_2 flue gas treatment process. Presented at the 1985 Spring National Meeting of the AIChE, Houston, Texas, March 24-28, 1985.

9. Yeh, J.T., Drummond, C.J., Haslbeck, J.L., and Neal, L.G., The NOXSO process : Simultaneous removal of SO_2 and NO_x from flue gas. Presented at the 1987 Spring National Meeting of the AIChE , Houston, Texas, March 29- April 2, 1987.

10. Markussen, J.M., Yeh, J.T., and Drummond, C.J., Enhanced removal of nitrogen oxides in a spray dryer using a lime slurry containing sodium hydroxide. Presented at the 1986 Spring National Meeting of the AIChE, New Orleans, April 6-10, 1986.

11. Walker, R.J., Drummond, C.J., and Ekmann, J.M., Evaluation of Advanced separation techniques for application to flue gas cleanup process for the simultaneous removal of sulfur dioxide and nitrogen oxides, DE/PETC/TR-85/7 (DE85013006), June 1985.

12. Joubert, J.I., Drummond, C.J., Development of advanced flue gas emissions control technologies at the Pittsburgh Energy Technology Center, in "Coal Combustion", ed by J. Feng, Hemisphere Pub. Corp. N.Y. P. 853, 1988.

13. Kargi, F., and Robinson, J.M., Microbial Desulfurization of coal by Thermophilic Microorganism Sulfolobus Acidocaldarius, Biotechnology and Bioengineering, 24, p. 2115. (1982).

14. Kargi, F., Microbiological coal desulfurization, Enzyme Microb. Technol. 4. Jan. p. 13. (1982).

15. Kos, C.A., Poorter, R.P.E., Bos, P., and Kuenen, J.G., Geochemistry of sulfides in coal and microbial leaching experiments, Int. Conf. on coal science , Dusseldorf, p.842. (1981).

16. Dugan, P.R., Apel, W.A., Microbial desulfurization of coal, in : Metallurgical Application of Bacterial Leaching and Related Phenomena, L.E. Muer, A.E. Torma, and J.A. Brierly (BOS). Academic Press. N.Y., p. 223. (1978).

17. Detz, C.M., and Barvinchak, G., Microbial desulfurization of coal, Min. Congr. J. 65. p.75. (1979).

18. Isbister, J.D., and Kbylinski, E.A., microbial desulfurization of coal, in : Processing and Utilization of High Sulfur Coal, ed. by Y. A. Attia, Elsevier, N.Y., p. 627, (1985).

19. Murphy, J., Riestenbery, E, Mohler, R, Marek, D., Beck, B., and Skidmore, D., Coal desulfurization by microbial processing. in : Processing and Utilization of High Sulfur Coal, ed. by Y.A. Attia Elsevier, N.Y., p. 643. (1985).

20. Attia, Y.A., Elzeky, M.A., Biosurface modification in the separation of pyrite from coal by froth flotation. in : Processing and Utilization of High Sulfur Coals, ed. by Yosry. A. Attia, Elsevier, N.Y. p. 673. (1985).

21. OECD Guidelines for Testing of Chemicals, EEC Directive 79/831, Annex V, Part C: Methods for Determination of Ecotoxicity, 5.2 Degradation. Biotic Degradation. Manometric Respirometry. Method DGXI, Revision 5, 1983.

FOR MORE INFORMATION:

Rakesh Govind
Department of Chemical Engineering
University of Cincinnati
Cincinnati, OH 45221
Phone: 513/556-2666

Table 1. Design and Operating Conditions of the Suspended Culture Bioreactor

Diameter of reactor	4 inches	
Height of liquid in reactor	24 inches	
Amount of activated sludge added at start of experiment	20 gms	
Gas phase retention time	4 minutes	
Inlet Gas flowrate	1.5 liters per minute	
Outlet Gas flowrate	1.2 liter per day	
Inlet Gas Composition:	Carbon dioxide	41.56%
	Nitrogen	50.00%
	Oxygen	8.00%
	Sulfur dioxide	0.40%
	Nitrogen oxides	0.04%
Exit gas composition:	Carbon dioxide	36.4%
	Nitrogen	62.6%
	Moisture	0.88%
	Hydrogen sulfide	0.12%
	Sulfur oxides	0.00%
	Nitrogen oxides	0.00%
Reactor temperature and pH	27^{o}C; 9.0	
Amount of nutrient media fed daily to reactor	0.2 liters (OECD composition)	
Amount of reactor liquid withdrawn daily	0.2 liters	
Exit liquid composition (average) nitrate/nitrite	100 ppm	
sulfate	180 ppm	
free sulfur	present	