H-5 HFCLM Purification of SO_2 from Flue Gas

Jun-Seok Cha
Atmospheric Chemistry Division
Air Quality Research Department
National Institute of Environmental Research

K.K.Sirkar
Membrane Separations and Biotechnology Lab.
Department of Chemical Engineering
New Jersey Institute of Technology

I. INTRODUCTION

Stack or flue gases released from coal-fired electric utility boilers contain significant amount of SO_2 pollutants. Reduction of SO_2 emissions to achieve mandated environmental standards is a national mission. In conventional flue-gas treatment, SO_2 is removed by contacting the flue gas with an aqueous solution of limestone slurry[(1)]. The spent liquor is most often discarded.

Membrane gas separation is one of the technologies under development. This is attractive due to its simplicity, modular nature and high efficiency[(2)]. The process can be a highly efficient alternative to the wet limestone scrubbing process. Liquid membranes that exhibit very high species permeability and selectivity are appealing in particular. The selectivity can be increased by orders of magnitude if facilitated transport with suitable carrier species is implemented[(3)].

A new liquid membrane structure called hollow-fiber-contained liquid membrane (HFCLM) has been investigated for gas separation[(4)]. In this configuration, an aqueous liquid functioning as a membrane is kept between two sets of microporous hydrophobic hollow fibers that are tightly packed in a permeator cell. In the HFCLM structure, any liquid can be used as a liquid membrane. However, the liquid membrane must exhibit high selectivities of SO_2 over CO_2, N_2, and other gas components of the flue gas.

The primary objectives of this work are to measure the permeability of SO_2 from the simulated flue gas mixtures through a variety of immobilized liquid membranes, select the promising liquid membranes and study the extent of flue gas purification achieved in the HFCLM permeator using selected membrane liquids.

II. EXPERIMENTAL

The first set of experiments focused on selecting membranes useful for SO_2 separation with respect to CO_2, N_2 and O_2. A standard gas mixture was used for the normal operations, however, to study the effect of gas composition on the species permeabilities, different feed gas concentrations were used. The gas stream composition in the feed line was routinely measured, under steady flow conditions, before and after each experiment. The compositions of the feed inlet, the feed outlet and the sweep outlet were measured by a HP 5890A GC using a thermal conductivity detector. The membranes selected via permeability studies that showed high selectivities were used as liquid membranes for the HFCLM permeators. The effective length of these permeators varied from 17 inches to 62 inches. The permeators contain 300 fibers in each side (feed and sweep) of 150 μm ID and 25 μm wall thickness. The required feed gas mixture was generated by mixing different gas mixtures and humidification. The pressure of the feed gas was measured. The purified feed gas stream from the permeator was dried and analyzed. Helium was used as a sweep gas. The permeator shell side was pressurized by a helium gas cylinder, which has a higher pressure than the feed and the sweep gas streams. Both the feed and the sweep gas streams were dried using membrane dryers before they entered the analyzers. The permeator was kept immersed in a water bath and the the water temperature was maintained by a constant temperature circulator. For purification studies in the vacuum mode, one end of the permeate stream was closed, and a vacuum was applied at the other end. A diaphragm vacuum pump was used to create and maintain the vacuum. Moisture from the permeate stream was eliminated by a drierite column.

III. RESULTS AND DISCUSSION

The SO_2 permeabilities and selectivities of SO_2/CO_2 and SO_2/N_2 were determined for the various liquid membranes. Excellent SO_2 permeability and extremely high selectivities for SO_2/CO_2(70-200) and SO_2/N_2(1500-3000) were obtained at 25 °C for water and the aqueous solutions of $NaHSO_3$ and Na_2SO_3. For the aqueous liquid membranes of 0.02M Fe^{2+}EDTA and 0.02M Fe^{3+}EDTA, the SO_2 permeabilities and the SO_2/CO_2 selectivities(50-200) were marginally lower. Equilibrium approximation and nonequilibrium boundary layer approximation predicted the SO_2 facilitation through the pure water membrane adequately.

Depending on the permeator length and the gas flow rates, 60-95% of SO_2 were easily removed from a feed flue gas containing 5000 ppm SO_2. The SO_2 mass transfer coefficient was found to be approximately 1.1×10^{-4} $cm^3/sec \cdot cm^2 \cdot cmHg$ at 25°C in a 17.5 inch long permeator. Some of these runs were carried our for days, showing a completely stable process.

Typical pressure drop calculated for a module with 300 100μm ID fibers ranged 0.81 to 8.09 ft water per foot of the fiber length at the flow rates of 20-200 cc/min. By using a permeator built of 240 μm ID hollow fibers, the pressure drop in feed flue gas was drastically reduced from those built with 100 μm ID fibers. A permeator with 400 μm ID hollow fibers is expected to provide even lower pressure drops at higher gas flow rates.

IV. CONCLUSIONS

An innovative hollow-fiber-contained liquid membrane permeator was investigated for removal of SO_2 from the flue gas of coal-fired boilers. Various liquid membranes were tested in this work to determine SO_2 permeability and selectivity. Using a solution of a metal chelate complex as the liquid membrane, 70-90% of SO_2 in the flue gas was eliminated by a novel liquid membrane permeation process. For SO_2 removal, water and solutions of either sodium sulfite or sodium bisulfite showed excellent results. Further research is required to optimize the design and operating conditions of this system for future applications.

V. REFERENCES

1. Drummond, C.J. and D.F.Gyorke, Research strategy for the development of flue gas treatment technology, ACS Symposium Series No. 319, 146, 1986
2. Sengupta, A. and K.K.Sirkar, Membrane gas separation, in Progress in Filtration and Separation, Vol. 4, R.J.Wakeman, Ed., 289, 1986
3. Ward III, W.J. and W.L.Robb, Carbon dioxide-oxygen separation : facilitated transport of carbon across a liquid film, Science, 156, 1481, 1967
4. Majumdar, S., A.K.Guha. and K.K.Sirkar, A new liquid membrane technique for gas separation, AIChE Journal, 34, 1135, 1988
5. Majumdar, S., A. Sengupta., J.S. Cha. and K.K. Sirkar, Simultaneous SO_2/NO separation from flue gas in a contained liquid membrane permeator, Ind. & Eng. Chem. Res. Vol. 33, No. 3, 667, 1994
6. Bhave, R.R. and K.K.Sirkar, Gas permeation and separation by aqueous membrane immobilized across the whole thickness or in a thin section of hydrophobic microporous Celgard films, Jounal of Membrane Science, 27, 41, 1986