

Absorption of SO₂ from flue gas using PVDF hollow fiber membrane contactors

Bal Raj Deshwal, 박현희, 박보령, 문승현, 김인원¹, 이형근*
한국에너지기술연구원, ¹ 건국대학교 화학공학과
(hklee@kier.re.kr*)

1. Introduction

SO₂ is the most pervasive air pollutant. The emission of SO_x is a major environmental concern because of its hazardous effects on human health and the ecosystems. Wet scrubbing is still the dominant process for the removal of acidic gases but they suffer from several disadvantages such as large space, high capital cost, corrosion and a variety of operational problems e.g. liquid channeling, flooding, entrainment and foaming [1].

The membrane gas absorption (MGA) system has proved as an emerging technology for absorption of toxic gases and has been tested for the capture of CO, CO₂, SO₂, H₂S, NH₃, VOC and Hg vapors [2-9]. This technology has also been demonstrated in numerous liquid/liquid and gas/liquid applications. In general, a MGA system contains a micro-porous membrane that separates the gas and the liquid phases. Mass transfer occurs as the gas diffuses through the membrane and absorbs into the absorbent. This process has several advantages over the conventional methods. It has operational flexibility, independent gas and liquid flow, large surface area to volume ratio, compact size and linear scale up. MGA system may lead to about ten-fold reduction in the absorber size.

PTFE, polypropylene and PVDF have been extensively used for the preparation of hydrophobic membranes. Among these polymers, only PVDF has a good solubility in many organic solvents. Besides, it is thermally stable, possess high chemical resistance. Therefore this material is ideal for preparation of hollow fiber membranes by the wet phase inversion process, a versatile and simple technique used for the preparation of polymeric membranes [2].

The present study deals with preparation of PVDF asymmetric HF membrane using N-methylpyrrolidone (NMP) as the solvent and its utilization in the removal of SO₂ from the flue gas. The effect of various operating variables on the SO₂ removal efficiencies has been investigated. The absorption efficiency of various absorbents viz. NaOH, Na₂SO₃, Na₂CO₃ and NaHCO₃ has been compared in multi-stage G-L contactors.

2. Experimental Section

2.1. Preparation of PVDF asymmetric hollow fiber membranes

The asymmetric HF membranes were prepared by dry-jet wet phase inversion method. The polymer solution consisted of 20% PVDF (Kynar® k-761, USA) and 80% N-methyl-2-pyrrolidone (NMP) by mass. The required quantity of NMP was taken in 3L wide-neck reaction flask and PVDF powder was added. The resulting mixture was stirred thoroughly at 60°C for about 24hr to ensure the complete dissolution and then filtered using glass filter. The degassed dope was then transferred to a stainless steel reservoir and pressurized to 3~5 atm using nitrogen. The tube-in-orifice spinneret with an orifice diameter/inner diameter of the tube of 0.35/0.6 mm was used to obtain the HF membranes. Water was used as an internal as well as external coagulant. The fibers were spun by the dry-jet wet process (air gap = 20cm) at the room temperature. The prepared hollow fiber membranes were immersed in water bath to ensure complete solidification and thoroughly washed in water.

2.2. Characterization PVDF asymmetric HF Membrane

The cross-sectional structure of HF Membrane was examined by the scanning electron microscope (Hitachi, Model: S-4700, Japan). The inner and outer diameter of HF were found to be 765 and 986µm respectively. The average pore radius (r) and the effective surface porosity (ϵ/L_p) of the HF membranes were obtained using gas permeation method [10-11] using the following equations [10-11]:

$$r = \frac{16}{3} \left(\frac{S_o}{I_o} \right) \left(\frac{8RT}{\pi M} \right)^{\frac{1}{2}} \mu \quad \text{and} \quad \frac{\varepsilon}{L_p} = \frac{8\mu R T S_o}{r^2}$$

2.3. SO₂ absorption in multi stage gas-liquid HF membrane contactors

The membrane module consisted of acryl tube and hollow fibers. Each HF module is equipped with the gas and liquid sampling ports. Three hollow fiber modules (diameter = 10mm, length = 150mm, number of fibers = 20) were connected in series. The effective fiber length was 0.125m, packing fraction was 0.24, volume of HF module was $9.543 \times 10^{-6} \text{m}^3$ and contact area was $6.02 \times 10^{-3} \text{m}^2$. The experimental set up for the absorption of SO₂ is shown in Fig. 1. Feed gas mixture of varying concentrations was prepared by mixing gas streams containing 5% of SO₂ and N₂ gas adjusted with mass flow controllers. The feed gas mixture (P = 0.45atm) was passed through the lumen side of the hollow fiber, while absorbent solution was fed into the shell side of the membrane module in the counter-current direction. The inlet and outlet SO₂ concentrations were analyzed using IR SO₂ gas analyzer (SIEMENS, Model: Ultramat-23, Germany).

3. Results and Discussion

3.1 Morphology of prepared PVDF hollow fiber membranes

SEM micrographs of the hollow fiber membrane are shown in the Fig. 2. The inner and outer diameter of hollow fiber membrane were found to be 765 and 986 μm , respectively. Fig. 2 manifests the occurrence of finger-like structures near the outer and inner walls of hollow fibers due to the rapid precipitation, and sponge-like structures in the middle of the HF's due to slow precipitation [12,13]. Using gas permeation method, the hollow fiber membrane was found to have an average pore radius (r) of 0.0854 μm and the effective surface porosity (ε/L_p) of $1.67 \times 10^2 \text{m}^{-1}$ respectively.

3.2. Absorption of SO₂ gas using PVDF asymmetric HF membranes

A series of experiments were performed to examine the effect of various operating variables on the SO₂ removal efficiency using PVDF asymmetric HF membranes. The overall mass transfer coefficient (K_G) and SO₂ removal efficiency (R) can be calculated using following equation [14].

$$K_G = \frac{Q_G}{A} \ln \left(\frac{C_{SO_2(in)}}{C_{SO_2(out)}} \right) \quad \text{and} \quad R = \frac{C_{SO_2(in)} - C_{SO_2(out)}}{C_{SO_2(in)}}$$

where Q_G is flow rate of feed gas (m^3/s), A is total outer surface area of the hollow fibers (m^2), $C_{SO_2(in)}$ and $C_{SO_2(out)}$ are inlet and outlet concentration of SO₂ (ppm).

3.2.1. Effect of liquid flow rate on the SO₂ removal at different module stages

Fig. 3 shows that the SO₂ removal efficiency increased sharply in the beginning as the liquid flow rate was increased from 1 mL/min to 3 mL/min. Thereafter, almost a steady state is obtained. At low liquid low rate, NaOH available at the membrane surface is insufficient, thus SO₂ transfer is suppressed by liquid film resistance. As the liquid flow rate increases, SO₂ transfer dominates and is controlled by gas film and membrane resistance. SO₂ removal efficiency increased from 32 to 52.8% to 68.5% on moving from one to three module stage.

3.2.2. Effect of inlet SO₂ concentration on the SO₂ removal

SO₂ removal efficiency decreased as the feed SO₂ concentration was varied from 200 ppm to 2000 ppm. As the increasing SO₂ concentration will require larger amount of NaOH for absorption, however liquid flow rate is constant, thus SO₂ removal efficiency is expected to decrease and it is indeed true as can be seen in Fig. 4.

3.2.3. Effect of gas flow rate on the SO₂ removal at different module stages

The feed SO₂ gas flow rates were varied from 2 L/min to 15 L/min by maintaining the other variables constant. Fig. 5 shows that the SO₂ removal efficiency decreased with increasing gas flow rate. This probably is due to smaller residence time (0.027 to 0.11 seconds) of gas at higher gas flow rates, which reduces the rate of diffusion of SO₂ gas through the HF membrane.

The effect of the gas velocity on the overall mass transfer coefficients was also studied theoretically. Fig. 6 shows the effect of the Graetz number, Gz (gas velocity) on Sherwood number, Sh (the overall mass transfer coefficient, K_{AG}). In these experiments, the number of fibers (N_f) was 20 and total fiber length (L_f) was 0.375m. As can be seen, the overall mass transfer coefficient varied with gas velocity. It may be due to high gas phase resistance.

For a non-wetted micro-porous membrane, assuming that the pores are gas filled, the membrane's coefficient (k_{AM}) can be calculated independently using their pore structures property using equation $k_{AM} = D_{A,e} \varepsilon / L_p$ and was found to be 1.266×10^{-3} m/s. The value of membrane coefficient determined by gas absorption method is higher than that obtained from gas permeation data. It indicates partially wetting of hollow fiber membrane.

3.2.4. Effect of concentration/Nature of absorbent on the SO₂ removal

Experiments were carried out by varying the concentration of NaOH solution from 0.01M to 2M. SO₂ removal efficiency increased with increasing concentrations of the absorbent as can be seen in Fig. 7. The effect of different absorbents namely NaOH, Na₂SO₃, Na₂CO₃ and NaHCO₃ was studied at the liquid flow rate of 14 mL/min, feed SO₂ concentration of 400 ppm, and gas pressure of 0.46 atm at constant concentration of 0.02 mol/L. Na₂CO₃ solution proved to be the most promising absorbent among them as can be seen in Fig. 8.

4. Conclusion

In brief, the PVDF HF membranes were prepared from polyvinylidene fluoride and N-methyl-2-pyrrolidone by the dry-jet wet phase inversion process. Mean pores size and effective porosity were evaluated by the gas permeation method. The membrane morphology was examined with help of SEM. PVDF hydrophobic membranes were tested for the absorption of SO₂ from the flue gas. The effect of various operating variables on the SO₂ removal has been investigated.

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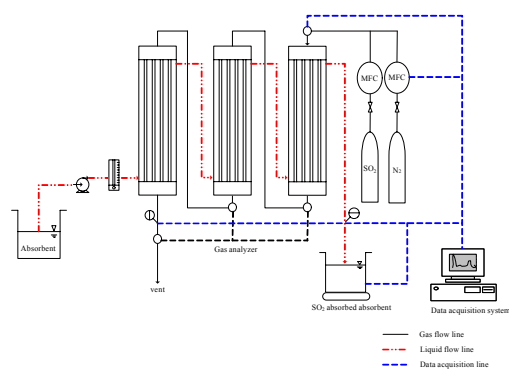


Fig. 1. A Schematic diagram of the multi-stages G-L contactor system.

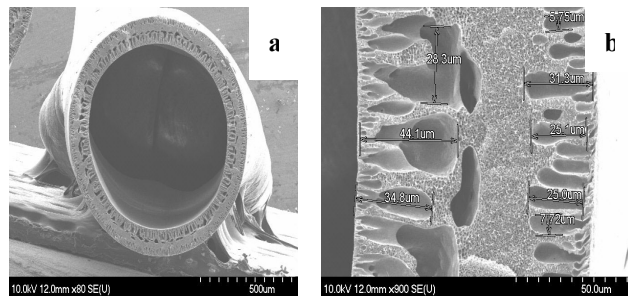


Fig. 2. SEM micrographs of PVDF HF membrane (a - overall cross section, b - partial cross section)

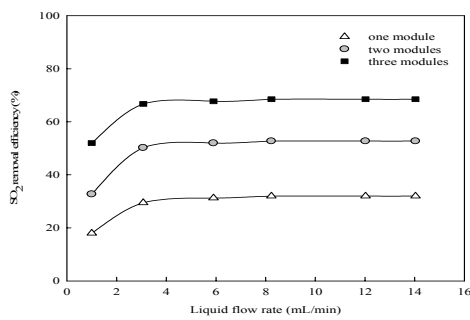


Fig. 3. SO₂ removal vs Liquid flow rate (NaOH=2M, Inlet SO₂=400ppm, Q_G =2L/min).

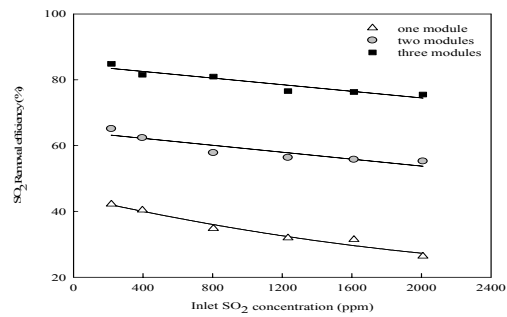


Fig. 4. Effect of inlet SO₂ conc. on SO₂ removal (NaOH=2M Q_G = 2 L/min, Q_L = 14.0 mL/min).

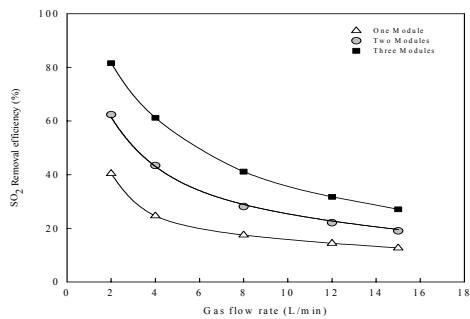


Fig. 5. Gas flow rate vs SO₂ removal (NaOH =2M, Inlet SO₂ = 400ppm, Q_L=14.0mL/min).

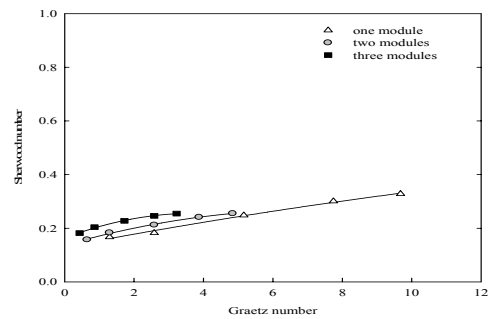


Fig. 6. Sherwood number vs Graetz number

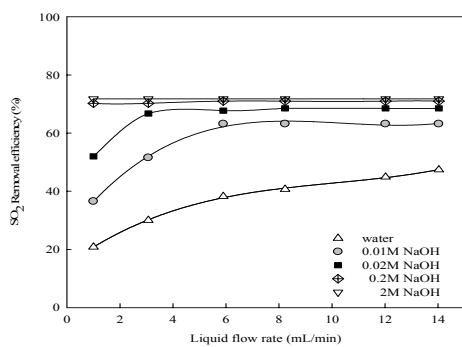


Fig. 7. Absorbent conc. vs SO₂ removal (Inlet SO₂ = 400 ppm, Q_G =2 L/min).

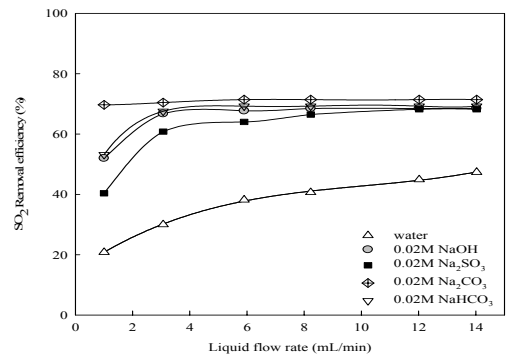


Fig. 8. SO₂ removal with different absorbents (Inlet SO₂ =400 ppm, Q_G =2 L/min).