Study on the enrichment of Sulfur Hexafluoride in the tmosphere through polyimide hollow fiber membrane

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Abstract. Sulfur hexafluoride is per molecule the strongest greenhouse gas know, the features have brought SF6 into the climatic impact discussion aimed at reduction of emissions. The separation effects of sulfur hexafluoride in the atmosphere are studied through polyimide hollow fiber membrane with different conditions on pressure drop, gas flow and temperature. The sulfur hexafluoride concentration increased with increased pressure drop of the membrane, increased temperature and decreased non-filtrate flow flux; the recovery of sulfur hexafluoride exceeds 93%, enrichment coefficient was 18.5; sulfur hexafluoride is not detected at the flux of the filtrate flow, which means sulfur hexafluoride is riddled by membrane. The results showed that polyimide hollow fiber membrane can effectively separate sulfur hexafluoride from mixed gas

1 Introduction

The stabile trace sulfur hexafluoride in the atmospheric is produced by human activities[1]. SF_6 is mainly used in electric switch equipment as a dielectric[2] and aluminum and magnesium smelting process as a greenhouse gas[3], because which is a colorless, odorless, nontoxic and nonflammable inert gas. SF_6 is CO_2 on GWP_{100} value of 24 times, and it is one of the strongest greenhouse gases, and its volume of discharged into the atmosphere is increasing at an annual rate of 7-8%. Especially in aluminum and magnesium smelting process, in fact the vast majority SF_6 is released in the atmosphere without being consumed. Therefore enrichment and recycling are important problems to protect environment.

Gas membrane separation is a new separation technology, and compared with conventional separation methods such as cryogenic distillation and cryogenic adsorption, it has high separation efficiency, small coverage area, low energy consumption, simple operation, easy maintenance and less investment etc..

Polyimide hollow fiber membrane is glass state. polymer, and it is a kind of chain compound of which the main component of the membrane material is aromatic polyimide. It has higher wear resistance, heat resistance and excellent insulating property, but also it does not dissolve in any organic solvent, oil and dilute acids. In the middle period of the eighties it began to be used in industry such as the separation of CO_2/CH_4, H_2/N_2, H_2/CH_4, O_2/N_2, CO_2/N_2 etc.[4]. However reports on the method of SF_6 separation and enrichment are rare. Studying on the enrichment technique of SF_6 gas of air concentration with polyimide hollow fiber membrane, and this paper inspects operation parameters on the

separation performance for the enrichment of SF_6 gas of high concentration to provide a reference. The results show that, polyimide hollow fiber membrane is obvious effect about separation and enrichment of SF_6.

2 Experimental

2.1 Equipment and Installation

Polyimide hollow fiber membrane separator (Shanghai Jingteng Technology Company), diameter 55 mm, length 234 mm. Agilent6890A gas chromatograph(equipped with a micro-cell electron capture detector (μ-ECD)), the detection limit of SF6 is $2\times10-13$ L/L. CYG1102T pressure transmitter (Xi'an Sensor Control Technology Co. Ltd.), the measurement range 0~1 MPa, precision 0.25. LZB-6 Glass rotameter(Yuyao City Yinghuan flow meters Co. Ltd.), the measurement range 0.06~0.6 m3/h, accuracy 2.5. LZB-3 Glass rotameter (Yuyao City Yinghuan flow meters Co. Ltd.), the measurement range 0.1~1 L/min, accuracy 4. High purity nitrogen 99.9995%. compressed air. Concentration of SF6 gas is $6.5\times10-12$ L/L. The schematic diagram of the experimental system is shown in figure 1.

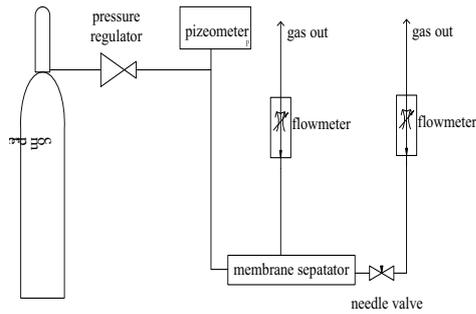
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Figure 1. Schematic diagram of the experimental system

2.2 Experimental method

In the experiment pressure reducing valve controls differential pressure, needle valve controls impermeable gas flow, permeable gas is natural emptying. The measurement of SF_6 concentration that it was separated by polyimide hollow fiber membrane was conducted using a gas chromatograph (Agilent6890A, USA).

2.3 Separation and Enrichment performance evaluation

In present work, we provide enrichment coefficients and recovery for Using to evaluate the result that SF_6 of the air was separated and enriched by Polyimide hollow fiber membrane.

The definition of enrichment coefficient is the ratio of SF_6 concentration in the air and in the impermeable gas such that:

$$Y = \frac{V_1}{V_2}$$

Where Y is enrichment coefficient, V_1 (L/L) is SF_6 concentration in the air and V_2 (L/L) is SF_6 concentration in the impermeable gas.

Recovery calculation formula such that:

$$P = \frac{F_1 \times C_1}{F_1 \times C_1 + F_2 \times C_2}$$

Where P is recovery of SF_6, C_1 (L/L) is SF_6 concentration in the impermeable gas, C_2 (L/L) is SF_6 concentration in the permeable gas, F_1 (L/min) is the flow of the impermeable gas and F_2 (L/min) is the flow of the permeable gas.

In the recovery formula we require the SF_6 concentration in the permeable gas, but the SF_6 concentration of the permeable gas was lower than the gas chromatograph detection limit in the experiment. Therefore for calculating recovery, we think that SF_6 concentration in permeability gas is the detection limit about that SF_6 is analysed by gas chromatograph.

3 Result and Discussion

3.1 Infiltration time has influence on enrichment of SF_6

At this test temperature of 25℃, through pressure reducing valve controls, that the membrane differential pressures is 0.1 MPa, 0.15 MPa, 0.2 MPa and 0.25 MPa, respectively. Through needle valve controls, that the flow of impermeable gas is 0.4 L/min. In the above conditions, respectively in 0.5 min, 1.5 min, 3 min sampling, then every 3 min sampling.

The schematic diagram of that the SF_6 concentration in the impermeable gas changes with time is shown in figure 2.
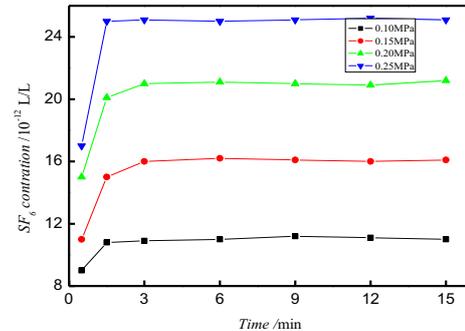

Figure 2. Relationship of SF_6 concentration and infiltration time

At different pressure differentials, SF_6 gas concentration is basic balance after three minutes. The SF_6 concentration in the impermeable gas is to stabilize in a relatively short period, which show that the ability of adsorbing and dissolving in polyimide hollow fiber membrane separator is weak, and SF_6 is separated fast from the mixed gases.

3.2 The result of differential pressure at membrane separator influencing on SF_6 enrichment

Fig. 3 shows the result that differential pressure at membrane separator influences on SF_6 enrichment when the temperature is 25℃ and the flow is 0.1 L/min, 0.2 L/min, 0.4 L/min, 0.6 L/min, 0.8 L/min and 1.0 L/min, respectively. With increasing the pressure difference, the concentration of the gas is increase in membrane separator, therefore the concentration of SF_6 in impermeable gas shows a trend of increase. When membrane separator differential pressure is certain, the concentration of SF_6 shows a trend of increase with the flow of impermeable gas increasing. The above phenomenon indicates that when the flow of impermeable gas increasing, the gas flow velocity is increase and the residence time is reducing in membrane separator[5], so that the percolation of O_2 and N_2, etc. decreases, and the content in the permeability gas increases.
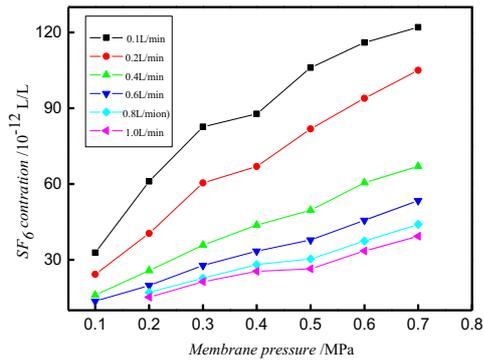
Figure 3. The effect of different pressure influence on SF_6 separation

3.3 The effect of temperature influence on SF_6 separation

When the impermeable gas flow is 0.4 L/min, and the temperature is 18 ℃, 25 ℃ and 29 ℃, respectively, SF_6 concentration in impermeable gas is measured with the condition of differential pressure. The result shows that SF_6 concentration in impermeable gas increases with increasing temperature.

Polyimide belongs to rigid polymer chain, the diffusion of gas molecules occurs mainly in the molecular chain with high packing density. Because polymer chain motion increases with higher temperature, the gaps increase in the polymer chain, accordingly N_2, O_2 and other gases diffusion coefficient increase, this phenomenon is beneficial to their penetration. So that the above cause makes SF_6 gas concentration increase.
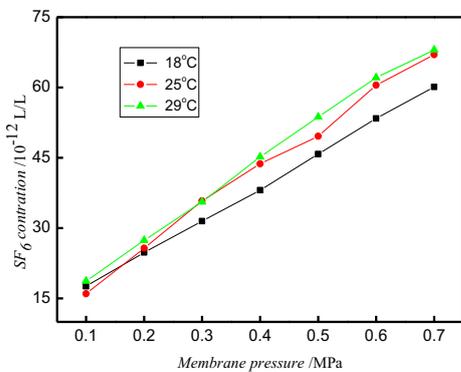

Figure 4. The effect of temperature influence on SF_6 separation

3.4 The enrichment of SF_6 in the atmosphere through polyimide hollow fiber membrane

3.4.1 Enrichment coefficient

According to the experimental results, SF_6 gas concentration in the atmosphere is 6.5×10^{-12} L/L and the largest concentration of the SF_6 enrichment is 1.2×10^{-10} L/L. Through calculating SF_6 enrichment coefficient is 18.5.

According to the penetration amount formula :

$$Q = S \times A - \triangle P / L$$

Where Q is the gas penetration amount, A is membrane area, L is membrane thickness, $\triangle P$ is the differential pressure about tow ends and S is the gas penetration coefficient.

According to the formula analysis, increasing the membrane area can increase the gas penetration amount. Therefore increasing the SF_6 concentration of the impermeable gas or by multiple membrane separation, all which can make SF_6 enrichment coefficient increase.

3.4.2 Recovery rate

Fig.5 shows the result that the different recovery rate of SF_6 at different condition. The recovery rate of SF_6 is up to 93% with polyimide hollow fiber membrane separator enrichment, which mainly reason is polyimide belongs to rigid polymer chain, that the rigid molecular network more like "molecular sieve", so that the different of gas molecule size decides its permeability difference with the same kind of polyimide membrane. Because SF_6 molecule size is bigger, it is not easy through the aperture of smaller "molecular sieve". Based on the above reason, the SF_6 concentration of the permeable gas is lower than the gas chromatograph detection limit in the experiment that is explained.
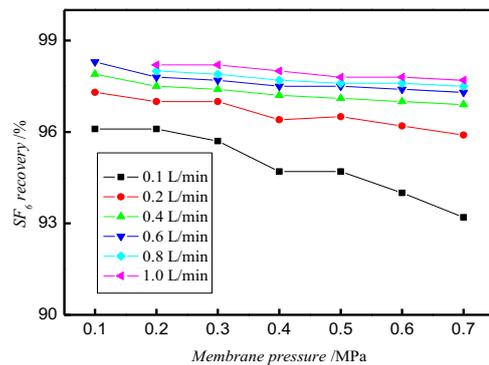

Figure 5. The recovery rate of SF_6 at different condition

Under the certain flux, the membrane differential pressure increase loads to the recovery rate of SF_6 reduce. Because membrane differential pressure increases, to largen the driving force, that the result leads to the flux of the penetration gas also increase. The reason changes the components of the permeable gas and causes the recovery rate of SF_6 reducing.

The enrichment effect shows when the certain flux, differential pressure increases, enrichment coefficient increases and recovery rate decreases. Enrichment ratio will be considered in real application, therefore, it is main to select bigger operating pressure. Thought bigger operating pressure and lower flux, the methods all can increase the enrichment coefficient.

4 Conclusion

Polyimide hollow fiber membrane for separation and enrichment SF_6 of in the mixed gases has good effect.

(1) The SF_6 enrichment coefficient increases with higher differential pressure and temperature and lower flux in the impermeable gas.

(2) SF_6 gas recovery rate is higher to be up to 93% in the experiment

(3) The enrichment coefficient is increase with increasing differential pressure and decreasing flow, but meanwhile SF_6 gas recovery rate become lower.

References

1. J. Harnisch, R. Borchers, P. Fabian, H.W. Gaeggeler, U. Schotterer, Nature[J]. 1996, 384, 32.
2. M. K. W. Ko, N. D. Sze, W. Wang, G. Shia, A. Goldman, F. Murcray, D.Murc-ray, C. Rinsland, J. Geophy[J]. Res. 1993, 98 (D6), 10499-10507.
3. Maiss, M., Brenninkmeijer, A.M. Atomspheric SF_6: Trend, source, and prospects[J]. Environ.Sci. Technol. 1998, 32, 3077-3086.
4. Ik-Jae Chung, Kwang-Rae Lee, Sun-Tak Hwang. Separation of CFC-12 from air by polyimide hollow-fiber membrane module[J]. Journal of Membrane Science. 1995, 105, 177-185.
5. Muslikhin Hidayat, Anders Rasmuson. Some aspects on gas-solid flow in a U-bend: Numerical investigation. Powder Technology. 2005, 153, 1-12.