EFFECT OF MEMBRANE PROPERTIES OF MICROPOROUS HOLLOW-FIBER GAS-LIQUID CONTACTOR ON CO₂ REMOVAL FROM THERMAL POWER PLANT FLUE GAS

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Introduction

In pursuit of preventive measures against the "Green House Effect" caused by CO₂ gas, many studies on CO₂ removal from the flue gas of thermal power plants have been carried out⁷⁾. As the possible CO₂ separation techniques, cryogenic, chemical absorption, adsorption and membrane methods have been considered. The quantity of CO₂ emitted from thermal power plants is enormous. It is 500 t/h in the case of a 600-MW coal-fired plant. So, it is very important to reduce energy consumption for CO₂ separation and also to make the whole system compact. The separation method considered in this paper is named hollow fiber gas-liquid contactor: separation of CO₂ has been carried out by flowing the absorbent and gas on the lumen side and outside of the hollow-fiber membrane, respectively. This method has already been applied to the artificial lung in medical science and to the gas liquid exchanger in the CELSS (Closed Ecological Life Support System in space)⁴⁾. Recently, this method was applied to CO₂ removal⁵⁾ and efforts were made to make the whole system compact by using hollow fiber membranes.

In this work, the effects of membrane properties such as the thickness and the porosity, and liquid Reynolds number of the lumen side of membrane on the mass transfer characteristics of gas-liquid contactor using hydrophobic microporous membranes are discussed for CO₂-monoethanolamine (MEA), CO₂-sodium hydroxide and CO₂-water systems.

1 Experiment

Nine different microporous hydrophobic membranes made of four types of material were used for the test as shown in **Table 1**; one polypropylene (PP) membrane, four polyethylene (PE) membranes, three polytetrafluoroethylene (PTFE) membranes and one PE membrane coated with fluoropolymer (coated membrane). A gas mixture

which consisted of CO₂ (15%), O₂ (5%) and N₂ (80%) saturated with water at 25°C was used for the experiments. As the absorbent, an aqueous solution of MEA (5 mol/l) was used. For comparison, an aqueous solution of sodium hydroxide (1 mol/l) and pure water were used. The temperature was 298 K and details of the experimental method such as the specifications of the modules and measuring methods are shown in a previous paper⁵⁾.

2 Results and Discussion

The ratio of mass transfer resistance of the membrane R_M to overall mass transfer resistance R_T in the gas-liquid contactor is defined as

$$R_M / R_T = K / k_M \quad (1)$$

where K is the experimental value of overall mass transfer coefficient [mol/(m²·Pa·s)] defined as

$$J = K \frac{P\{(y_1 - y_1^*) - (y_2 - y_2^*)\}}{\ln\{(y_1 - y_1^*) / (y_2 - y_2^*)\}} \quad (2)$$

and k_M is defined as

$$K_M = D_G \cdot \varepsilon / (t \cdot \chi \cdot H) \quad (3)$$

where the tortuosity factor χ was taken as approximately 3 from the value of PE ($\chi = 3.33$) and PTFE ($\chi = 2.38$)³⁾. Here, y_1^* and y_2^* were taken as zero. In **Table 2** the values of $(R_M/R_T) \times 100$ are shown for membranes of various thickness t . These values are at most 8%, which small enough to not make mass transfer resistance of the membrane R_M important in the CO₂ - MEA system.

Figure 1 shows the relationship between the overall mass transfer coefficient K and the porosity of the microporous membrane ε observed with CO₂ - MEA and CO₂ - NaOH systems using membranes made of PTFE and the coated membrane. These results indicate that use of microporous membranes with high porosity is effective for

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Table 1 Properties of hollow-fiber membranes

memb. No.	material	d_o [μm]	t [μm]	ε [-]	B.P. [MPa]	d_p [μm]	n [-]	A_i [m^2]
1	PP	244	22	0.45	1.23	0.036	516	0.0502
2		404	68	0.60	0.78	0.056	384	0.0493
3	PE	420	70	0.70	0.21	0.20	352	0.0480
4		400	56	0.43	0.82	0.054	384	0.0538
5		770	110	0.64	0.41	0.11	108	0.0289
6		718	133	0.65	0.49	0.93	119	0.0262
7	PTFE	1130	220	0.64	0.46	1.0	44	0.0150
8		1700	350	0.4	0.45	1.0	19	0.0092
9	PE+F	696	120	0.8	0.62	0.73	123	0.0274

PP : Polypropylene, PE : Polyethylene

PTFE : Polytetrafluoroethylene

F : PE coated with fluoropolymer

B.P. : bubble point,

Effective membrane length l is 0.155m.**Table 2** Membrane resistance

item	membrane			
	No.6(PTFE)	No.7(PTFE)	No.8(PTFE)	No.9
t [μm]	133	220	350	120
ε [-]	0.65	0.64	0.4	0.8
k_M [$\text{mol}/(\text{m}^2 \cdot \text{Pa} \cdot \text{s})$]	1.59×10^{-5}	9.46×10^{-6}	3.72×10^{-6}	2.16×10^{-5}
R_M^{*1} [$\text{m}^2 \cdot \text{Pa} \cdot \text{s}/\text{mol}$]	6.29×10^4	1.06×10^5	2.69×10^5	4.63×10^4
R_T^{*2} [$\text{m}^2 \cdot \text{Pa} \cdot \text{s}/\text{mol}$]	2.28×10^6	2.31×10^6	3.29×10^6	8.77×10^5
$(R_M/R_T) \times 100$ [%]	2.8	4.6	8.2	5.3

System : CO_2 -MEA, $\chi=3$, $C=5 \text{ mol/l}$, $T=298 \text{ K}$, $y_i=0.15$, $Re_L=50$, $D_G=1.6 \times 10^{-5} \text{ m}^2/\text{s}$, $H=1640 \text{ Pa} \cdot \text{m}^3/\text{mol}$ *1 : $R_M=k_M^{-1}$, *2 : $R_T=K^{-1}$ **Fig. 1** Relationship between overall mass transfer coefficient K and porosity of microporous membrane ε . The numbers attached to the keys indicates the membrane shown in Table 1

obtaining a large overall mass transfer coefficient K . In Fig.1 the result for the CO_2 - H_2O system is also shown for comparison. The result shows that K remains constant

Table 3 Calculated value of distance between pores l_p and liquid boundary film thickness δ_L

memb. No.	ε [-]	d_p [μm]	l_p [μm]	CO_2 -H ₂ O		CO_2 -MEA	
				δ_L [μm]	δ_L/l_p [-]	δ_L [μm]	δ_L/l_p [-]
8	0.4	0.7	0.71	38.2	54	1.3	1.8
9	0.8	0.73	0.28	47.1	168	0.40	1.4

 $T=298 \text{ K}$, $Re_L=50$

(a) Physical absorption

(b) Chemical absorption

M : hydrophobic microporous membrane

Fig.2 Conceptual diagram of CO_2 absorption mechanism in hydrophobic microporous hollow-fiber gas-liquid contactor **Fig.3** Relationship between overall mass transfer coefficient K and liquid Reynolds number of lumen side of hollow-fiber membrane Re_L

regardless of the porosity in the range from 0.4 - 0.8. It is considered that the different behavior observed in the two chemical absorption systems and the physical absorption system is caused by a different mode of diffusion of CO_2 in the absorbent after it has passed the micro pores of the membranes.

The absorption behavior after CO_2 has passed the pore of the membrane and has been absorbed in the absorbent is considered to be influenced by the distance between the adjacent pores l_p and the liquid boundary film thickness δ_L . In Table 3, the calculated value of l_p and δ_L are shown for the case of the CO_2 - H_2O system (physical absorption) and CO_2 - MEA system (chemical absorption) respectively. Here, l_p is calculated by Eq.(4) assuming that pores d_p in diameter are open with staggered arrangement.

Fig.4 Relationship between Sherwood number Sh and Peclet number Pe of lumen side of hollow-fiber membrane in CO_2 - H_2O system. The numbers attached to the keys indicates the membrane shown in Table 1

$$l_p = \frac{d_p}{2}(\sqrt{3 + 2\pi/(3\epsilon)} - 2) \quad (4)$$

δ_L is calculated as D_L/K' assuming the resistance of gas boundary film and membrane can be neglected compared with liquid boundary film resistance. Here, K' is overall mass transfer coefficient [m/s] and it was calculated as $H \cdot K$, where H is the Henry constant. The value of H for CO_2 - 5 molar aqueous MEA solution was estimated according to Hikata *et al.*¹⁾ D_L , the diffusivity of CO_2 in 5-molar aqueous MEA solution, was estimated by the Stokes - Einstein equation using the diffusivity data of CO_2 in 2 molar aqueous MEA solution¹⁾ and viscosity data of aqueous MEA solution²⁾. As can be seen in Table 3, the result that K is independent of ϵ for CO_2 - water system seems reasonable since the values of δ_L are much larger than those of l_p and CO_2 can diffuse through the whole part of the liquid boundary film as schematically shown in Fig.2(a). On the other hand, for the CO_2 - MEA system, the values of δ_L are comparable to those of l_p , suggesting that only the liquid boundary film close to the pore opening is available for the diffusion of CO_2 as shown in Fig.2(b).

As for the relationship between K and the hydrodynamic condition for the CO_2 - MEA system, several tests have been performed using PP and PE membranes. However, no clear indication could be obtained due to wetting of the membrane by MEA. Therefore, experiments were carried out using more hydrophobic PTFE membrane (No.8) with less wettability. As shown in Fig.3, K is proportional to $Re_L^{0.07}$, indicating a very small influence of Re_L on K . This is because CO_2 is absorbed in the region of irreversible pseudo first order reaction where the absorption rate is not influenced by liquid film mass transfer coefficient⁶⁾. In Fig.4 the result for the CO_2 - H_2O system is shown for comparison as the relationship between the Sherwood number Sh and the Peclet number of the lumen

side of the hollow - fiber membrane. In this case, Sh is proportional to $Pe^{0.33}$, and the influence of hydrodynamic condition is large.

These results indicate that use of microporous membranes with high porosity is effective for obtaining high values of K for chemical absorption such as in CO_2 - MEA and CO_2 - NaOH systems and that increasing Pe is effective for obtaining a high value of K in physical absorption, such as in CO_2 - H_2O systems.

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Nomenclature

A	= effective membrane area	[m ²]
C	= concentration of monoethanolamine (MEA) or NaOH in liquid phase	[mol/l]
D	= diffusivity	[m ² /s]
d	= diameter of hollow-fiber	[m]
d_p	= pore diameter	[μm]
H	= Henry constant	[Pa·m ³ /mol]
J	= flux of CO_2	[mol/(m ² ·s)]
K	= overall mass transfer coefficient based on inner surface area of hollow-fiber	[mol/(m ² ·Pa·s)]
k_L	= liquid film mass transfer coefficient	[m/s]
k_M	= membrane mass transfer coefficient based on inner surface area of hollow-fiber	[mol/(m ² ·Pa·s)]
l	= effective membrane length	[m]
l_p	= distance between pores	[μm]
n	= number of hollow-fiber membranes	[-]
P	= total pressure	[Pa]
Pe	= Peclet number	[-]
R	= mass transfer resistance	[s/m]
Re	= Reynolds number	[-]
Sh	= Sherwood number	[-]
T	= temperature	[K]
t	= membrane thickness	[μm], [m]
u	= linear velocity	[m/s]

y	= mole fraction of CO ₂ in gas phase	[-]
y^*	= mole fraction of CO ₂ in equilibrium with liquid	[-]
δ_L	= liquid boundary film thickness	[μm], [m]
ϵ	= porosity of microporous membrane	[-]
χ	= tortuosity	[-]

<Subscripts>

G	= gas
i	= inner
L	= liquid
M	= membrane
O	= outer
P	= pore
T	= total
1	= inlet of feed gas
2	= outlet of feed gas

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