#### **ORIGINAL RESEARCH ARTICLE**

# Study on the hydrothermal recovery characteristics of nano-ceramic membranes on regenerative gas

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#### **ABSTRACT**

In view of the large energy consumption of the regeneration process in the chemical absorption decarburization process, on the basis of the enrichment classification flow process, the nanoscale ceramic film is used as a new heat exchanger between the enriched liquid and the regeneration gas. The porous ceramic film is capable of coupling thermal-mass transfer to effectively recover part of the water vapor and the heat carried in the regeneration gas, so as to reduce the regenerative energy consumption of the system. The effects of parameters such as regeneration temperature, flow rate, molar fraction of water vapor, and MEA enrichment temperature, flow rate, and MEA concentration of shunt on the hydrothermal recovery effect of ceramic membranes of different pore sizes and lengths were studied by using the heat recovery flux and water recovery rate as the indicators. The results show that the hydrothermal recovery performance of the ceramic membrane increases with the increase of MEA enrichment flow, but decreases significantly with the increase of the enrichment temperature. At the same time, with the increase of regenerative gas velocity and the molar fraction of water vapor in the regenerative gas, the heat recovery flux will increase. The heat recovery performance of the 10 nm ceramic membrane is better than that of the 20 nm ceramic membrane.

Keywords: Ceramic Membrane; Chemical Absorption Method; Regeneration Gas; Heat Transfer; Mass Transfer

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#### 1. Introduction

As a relatively mature carbon capture technology in recent stages, chemical absorption method is widely used in the process of carbon dioxide decarburization, and the most commonly used absorbent is amine and its derivatives and inorganic solution absorber. Among them, ethanolamine (MEA) absorbers are widely used and studied<sup>[1,2]</sup>. The chemical absorption method has a high CO2 absorption rate and high recovery purity, but the main factor currently limiting its large-scale commercial application is its high regeneration energy consumption<sup>[3]</sup>, resulting in a reduction in power generation efficiency of about 10% after the decarbonization system is installed in the power plant<sup>[4]</sup>. Since the heat required for CO<sub>2</sub> regeneration usually comes from the large amount of water evaporated from the lean CO<sub>2</sub> absorber solution at the bottom of the regeneration tower, the regenerative CO<sub>2</sub> discharged from the top of the regeneration tower will carry a large amount of water vapor with higher temperatures. In the traditional process, most of the heat carried by this part of the water vapor is taken away by the cooling water in the regenerative gas cooler at the top of the tower, resulting in waste of heat, and recovering the waste heat of this part is an

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effective way to reduce the regeneration energy consumption of the CO<sub>2</sub> chemical absorption system.

The rich amine split flow process can effectively recover the regenerative waste heat<sup>[5-7]</sup>. In this process, the enriched liquid with a lower outlet temperature of the absorption tower is divided into two streams before entering the lean-rich amine heat exchanger, one of which is a rich liquid with a small flow rate is directly injected into the top of the regeneration tower without passing through the heat exchanger of the rich and poor liquid, and the other rich liquid with a large flow is injected from the lower position of the regeneration tower after being heated by the heat exchanger of the rich and poor liquid. This process lowers the temperature at the top of the regeneration tower, thereby recovering a large amount of water vapor latent heat. Simulation results in the literature show that the fractional flow process of rich liquid can reduce the total system energy consumption 2.3%~9.9%<sup>[5]</sup>, but the shorter gas-liquid contact time during this process limits the system's consumption reduction effect. Therefore, the heat exchanger can be increased as a medium for heat exchange between gas and liquid to ensure the contact time between gas and liquid, and the regenerative heat is recovered into the rich liquid through the form of heat conduction[8-10]. Since conventional metal heat exchangers, with large area coverage and high investment, cannot operate at low heat transfer temperatures, limiting heat transfer efficiency, the use of nano-ceramic membrane heat exchangers instead of traditional metal heat exchangers is conducive to solving these problems<sup>[11]</sup>. Compared with conventional heat exchangers, nano-ceramic membrane heat exchangers have the following advantages: (1) the thermal conductivity of the ceramic film is higher, and the heat transfer and mass transfer process can be carried out at the same time, so that the membrane heat exchanger has better performance in thermal mass recovery; (2) traditional heat exchangers are generally used for high-quality heat recovery, with specific temperature requirements and material limitations, it is difficult to work at a low heat transfer temperature difference, and membrane heat exchangers can

overcome these shortcomings; (3) the unique pores of the nano-ceramic membrane make it higher than the surface area, which helps to reduce the volume of the heat exchanger; (4) the excellent thermal stability, chemical stability and mechanical stability of ceramic film make it have a higher service life<sup>[12]</sup>. Bao et al.[13] experimentally compared the heat exchange effect of the ceramic membrane heat exchanger with that of conventioanl stainless steel heat exchanger, it was found that the convection Nu number of the membrane tube bundle was 50% to 80% higher than that of the stainless steel tube bundle, which further verified the feasibility of the ceramic membrane heat exchanger to replace the traditional heat exchanger. At present, hydrophilic ceramic membrane heat exchangers have been widely used in the study of hydrothermal recovery of flue gases<sup>[13-18]</sup>, but there are few reports of their use in recovering hydrothermal heat in regenerative gas, and in the process of hydrothermal recovery, many key heat and mass transfer problems have not been explored.

Therefore, on the basis of the fractional flow process of the enrichment, the nano-ceramic membrane was selected as the heat transfer medium between the regeneration gas and the MEA enrichment liquid, and the effects of the parameters of the regenerative gas temperature, flow rate, H<sub>2</sub>O/CO<sub>2</sub> molar ratio and the MEA enrichment temperature, flow rate and MEA concentration of the shunt on the hydrothermal recovery effect of the ceramic film were studied by using the heat recovery flux and water recovery rate as indicators, and the hydrothermal recovery performance of different pore size ceramic films was compared.

### 2. Experimental system

#### 2.1 Experimental material

In this experiment, MEA solution was used as the research object in liquid phase, and the MEA enrichment liquid was prepared by using analytical pure MEA (purity ≥99.95%), which was purchased from Shanghai Hushi Chemical Reagent Co., Ltd. in Shanghai, China. Pure MEA is thoroughly mixed with a certain mass of deionized water to obtain a MEA solution of different mass fractions. MEA en-

riched with a  $CO_2$  load of 0.45 mol/mol, formulated by the classical bubbling absorption method. High purity  $CO_2$  cylinder gas was purchased from Hangzhou Jingong Materials Co., Ltd. (purity  $\geq 99.99\%$ ).

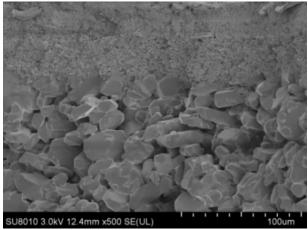


Figure 1. Cross-section SEM image of ceramic membrane tube.

The ceramic membrane tube selected in the experiment was purchased from Nanjing Aiyuqi Membrane Technology Co., Ltd., and packaged with the 304 stainless steel shell to form a single-channel ceramic membrane heat exchanger. Figure 1 shows a cross-sectional image of a ceramic membrane tube obtained by field emission scanning electron microscopy (SU-8010). It can be clearly seen from the figure that it is composed of three layers with different pore sizes, namely the support layer, the middle layer and the separation layer, which is consistent with the description of Chen et al. [19], the pore size of the separation layer is the smallest, which is nanoscale, and the pore size of the support layer is the largest, which is micron level. Generally, the ceramic membrane is divided into two structures according to the position of the separation layer, one is on the inside of the membrane tube, and the other is on the outside of the membrane tube. In this experiment, the ceramic membrane with the separation layer on the inside of the membrane tube was selected, and the average pore size was 10 nm and 20 nm, respectively. At the same time, in order to consider the influence of length, two lengths of 200 mm and 300 mm are selected to form four different specifications of ceramic membrane heat exchangers. Ceramic membrane tube and housing properties are shown in Table 1. The pore size distribution and specific

surface area of the separation layer were tested using a specific surface area and porosity analyzer (ASAP 2460, Micromeritics Instrument Corporation, USA) and the total porosity was tested with a mercury pressure meter (AutoPore IV 9510, Micromeritics Instrument Corporation, USA).

**Table 1.** Properties of ceramic membrane tubes and membrane heat exchanger housings

Performance metrics	Numeric value
Ceramic film	
Inner diameter/mm	8
Outer diameter/mm	12
The average pore size of the separa-	10/20
tion layer/nm	
BET specific surface area/m <sup>2</sup> ·g <sup>-1</sup>	0.509 (10 nm)/0.399
	(20 nm)
Total porosity/%	12.02 (10 nm)/14.89
	(20 nm)
Effective length/mm	200/300
Shell	
Material	304 stainless steel
Inner diameter/mm	16
Outer diameter/mm	20

#### 2.2 Experimental apparatus

regenerative water heat recovery tem based on ceramic membrane heat exchanger mainly includes ceramic membrane heat exchange chamber, steam generator system, gas preheating system and liquid phase conveying system, and its flow chart is shown in Figure 2. In the experiment, the simulated regeneration gas is a mixture of H<sub>2</sub>O (g) and CO<sub>2</sub>, and the inlet flow of pure water and CO<sub>2</sub> is controlled according to the molar ratio of H<sub>2</sub>O/CO<sub>2</sub>. The flow rate of the inlet pure water is precisely controlled by the peristaltic pump, entering the steam generator to generate water vapor, cylinder CO<sub>2</sub> is controlled by the mass flow meter, entering the system and the generated water vapor is fully mixed and uniform, after heating to form a certain temperature of simulated regeneration gas, and then from top to bottom into the vertical fixed ceramic membrane heat exchanger tube. At the same time, the MEA enriched liquid is heated to the desired temperature in the water bath pot and then fed from the bottom up by the peristaltic pump (BT600M/YZ1515x) to the heat exchanger shell, forming a reverse flow with the regeneration gas, and the gas-liquid phase transfers heat matter in the membrane heat exchanger, simulating the process of recovering hydrothermal heat in the regeneration gas.

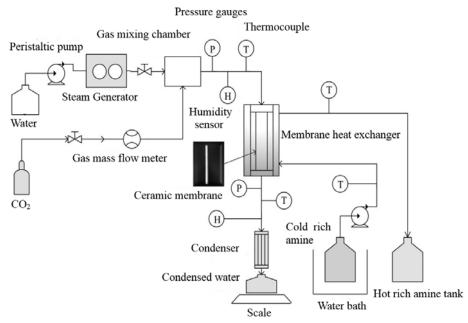


Figure 2. Flowchart of the membrane heat exchanger water heat recovery system.

The partial pressure of vapor in the vapor phase is greater than that in the liquid phase, and the water vapor and condensate water in the regenerative gas under the action of the partial pressure difference will be transmitted through the membrane pores to the rich side. The ceramic membrane pore sizes selected for the experiment are 10 nm and 20 nm. During the process, water vapor rapidly condenses capillary condensation in the membrane pores<sup>[20]</sup>, and the condensate on the gas side is continuously sucked into the membrane pores into the rich side under the action of capillary force. The heat exchanged rich amine leaves the membrane heat exchanger and is collected into the solution tank, and the reinventive gas is discharged from the end of the ceramic membrane heat exchanger. In the experiment, the liquid-side pressure was kept at atmospheric pressure, and the gas pressure during the pipe range was controlled by a pressure regulating valve at a gauge pressure of 50 kPa. The inlet and outlet temperature of gas and liquid is measured by the K type thermocouple, and the total mass flux of water is calculated by weighing and increasing the weight of the outlet gas after condensation. At the same time, the gas inlet and outlet humidity is measured by a humidity sensor to verify the mass flux of the water.

#### 2.3 Analytical calculation methods

In the process of recovering the regenerative hydrothermal heat of the membrane heat exchanger, a part of the heat is recovered through the thermal conductivity of the ceramic film, which can be regarded as the recovery of apparent heat; part of the heat is transformed from the vapor phase water vapor into the enriched liquid recovery, which is the recovery of latent heat. It is worth noting that the pore structure of the nano-ceramic membrane causes water vapor to condense capillary condensation within the pores. In the process of capillary condensation, a "crescent-shaped" interface is formed in the membrane pores, where water vapor condenses, and the condensate continuously penetrates into the enriched liquid, which just blocks the flow of CO<sub>2</sub> in the enriched liquid to the membrane tube, so in the process of heat transfer and mass transfer of ceramic membranes, the mass transfer flux of CO<sub>2</sub> is ignored, and only the mass transfer flux of water vapor is calculated.

Heat recovery flux  $q_{rec}$  [kJ/kg (CO<sub>2</sub>)] is an important indicator for evaluating the heat recovery effect of ceramic membrane heat exchangers, which can be divided into two parts: explicit heat recovery and latent heat recovery, which can be calculated using the following formula:

$$q = \frac{C_{\text{MEA}}\rho_{\text{MEA}}m_1\Delta T_1 m_{\text{w}} h_{\text{w}}(T)}{m_{\text{co}_2,\text{in}}}$$
(1)

In the formula:  $C_{\text{MEA}}$  is the average specific heat capacity of MEA rich liquid, kJ/(kg·K);  $\rho_{\text{MEA}}$  is the average density of MEA enriched liquids, kg/L;  $m_1$  is MEA enrichment flow, L/h;  $\triangle T_1$  is the temperature difference between the inlet and outlet of the rich liquid in the shell of the ceramic membrane heat exchanger, °C;  $m_{\text{w}}$  is the mass flux of transmembrane water, kg/h;  $h_{\text{w}}$  (T) is the specific enthalpy of water at T temperature, kJ/kg;  $m_{\text{co}_2,\text{in}}$  is the mass of the vapor phase inlet CO<sub>2</sub>, kg.

The water recovery flux, i.e. the transmembrane mass transfer flux of water vapor  $J_{\rm w}$  [kg/(m<sup>2</sup>·h)] can be calculated using the following formula:

$$J = \frac{(\omega_{\rm in} - \omega_{\rm out})m_{\rm g}}{A} = \frac{m_{\rm w}}{A}$$
 (2)

In the formula:  $\omega_{in}$  and  $\omega_{out}$  are the humidity of the inlet and outlet purge gas, g/kg, respectively;  $m_g$ 

is the purge flow of the purge air, kg/h; A is the area of gas-liquid contact,  $m^2$ .

The water recovery rate  $\eta$  can be used as a reference for evaluating the mass transfer performance of membrane heat exchangers and can be calculated using the following formula:

$$\eta = \frac{m_{\rm w}}{m_{\rm h_2 o, in}} \tag{3}$$

In the formula:  $m_{\rm h_2 o, in}$  is the total content of H<sub>2</sub>O in the gas phase inlet, kg/h.

## 3. Experimental results and analysis

#### 3.1 Effect of fluid-rich flow rate

The influence of the flow rate of the rich liquid on the heat transfer and mass transfer performance of the membrane heat exchanger is shown in **Figure 3**.

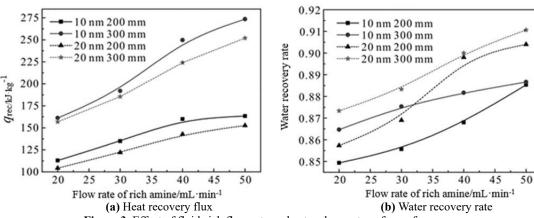


Figure 3. Effect of fluid-rich flow rate on heat and mass transfer performance.

It can be seen that the heat recovery flux  $q_{\rm rec}$  of the four specifications of membrane heat exchangers has increased significantly with the increase of the flow rate of the rich liquid. The increase of the flow rate of the rich liquid makes the mal boundary layer at the wall of the membrane heat exchanger thinner, the heat transfer heat resistance becomes smaller, and the heat exchange effect of the gas-liquid two phases is strengthened<sup>[21]</sup>. At the same time, with the increase of the flow rate of the rich liquid, the water recovery rate also increases, which means that at a relatively large flow rate, more water vapor is recovered and more latent heat is recovered. Therefore, when the flow rate of the rich liquid increases, there is more sensi-

ble heat and latent heat recovery, resulting in a significant increase in the total heat recovery flux. In addition, after the flow rate is greater than 40 mL/min, the increase in the heat recovery flux with the continuous increase of the flow rate has a tendency to decrease, because the heat transfer effect between the gas and liquid is limited by thinning the thermal boundary layer at the ceramic membrane wall. Therefore, at a lower enriched fluid flow rate, increasing the flow rate of the rich liquid can greatly increase the heat recovery flux, but continuously increasing the flow rate of the rich liquid does not bring about an unlimited increase in the heat recovery flux. Therefore, in practical engineering applications, the flow rate of the rich liquid

is not as large as possible, and it is necessary to comprehensively determine the flow rate that minimizes the total energy consumption.

With the same pore diameter and different lengths, the heat recovery of the 300 mm membrane heat exchanger is greater than that of the 200 mm membrane heat exchanger. The increase in length increases the effective contact area of the heat exchange process, and the gas-liquid contact is more complete, resulting in better heat recovery results. Considering that the length of the heat exchanger should not be too long, the contact area can be increased in other ways, and theoretically the gas-liquid contact area can be increased by multi-channel or single-channel multi-tube bundle ceramic membranes to improve the heat exchange effect, but further experimental verification is required.

For the same length and different pore sizes, the heat recovery effect of the 10 nm ceramic film is better than that of the 20 nm ceramic film, and the effect is more obvious with the increase of the flow rate of the rich liquid. Although the pore size and porosity of the 20 nm ceramic membrane separation layer are greater than those of the 10 nm ceramic membrane, and the water-transmitted mass through the ceramic membrane is greater, it can be seen from Table 1 that the specific surface area of the 10 nm ceramic membrane is greater than that of the 20 nm ceramic membrane, which affects the heat transfer process of the gas-liquid phase<sup>[22]</sup>. The 20 nm ceramic membrane heat exchanger has a higher regenerative outlet temperature and the heat transfer process is limited. In general, the difference between the heat recovery effects of the two pore sizes is not large, and the difference is 3% to 8%. Therefore, the pore size is not directly related to the heat recovery effect of the membrane, and the selection of ceramic membranes with large pore size may even have a counter-effect, which needs to be comprehensively evaluated in combination with physical characteristics such as specific surface area and porosity.

#### 3.2 Effect of the rich liquid temperature

The influence of the enriched liquid temperature on the hydrothermal recovery effect of the membrane heat exchanger is shown in Figure 4. It can be seen that with the increase of the inlet temperature of the enriched liquid, the heat recovery amount decreases. When the regeneration temperature is fixed, the inlet temperature of the rich liquid increases, and the temperature difference between the gas-liquid phase decreases, and the temperature difference is an important driving force for the transmission of gas phase water vapor across the membrane to the liquid phase, the larger the temperature difference, the greater the mass transfer driving force between the two phases, and the more heat is recovered. The reduction of the temperature difference greatly limits the mass transfer process between the gas-liquid phases, resulting in a decrease in the heat recovery flux.

Similarly, the heat recovery effect of 10 nm and 300 mm ceramic membrane is better, which is also determined by the effective contact area of gas and liquid, the specific surface area of the ceramic membrane, the porosity and other factors.

#### 3.3 Effects of rich liquid concentration

The effect of 10% to 40% concentration of MEA solution on membrane hydrothermal recovery is shown in Figure 5. It can be seen from the figure that the concentration change has little effect on the heat recovery amount, and with the increase of the concentration of the rich liquid, the heat recovery amount decreases by 2% to 10%. The greater the concentration, the greater the viscosity of the solution, and when the flow rate of the rich liquid is constant, the viscosity increases, causing an increase in mass transfer resistance, resulting in a decrease in the water recovery flux<sup>[23]</sup>, which can be supported by the decrease in the water recovery rate in the figure. The decrease in mass transfer flux reduces the latent heat recovered, resulting in a decrease in the total heat recovery flux, but the magnitude of the decrease is limited, and the effect of solution concentration can even be negligible compared with the effects of liquid phase flow rate and temperature.

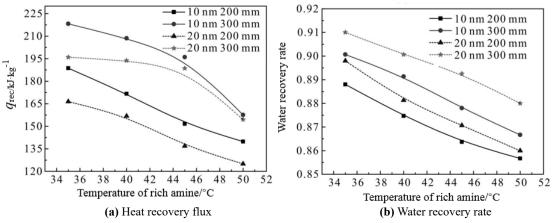


Figure 4. Effect of rich liquid temperature on heat and mass transfer properties.

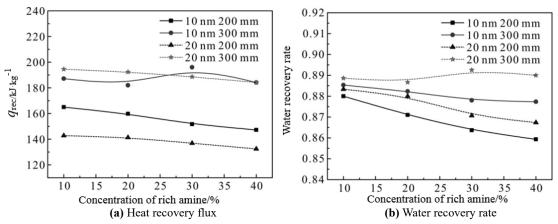


Figure 5. Effect of enriched liquid concentration on heat and mass transfer properties.

#### 3.4 Effects of regenerative gas velocity

**Figure 6** shows the effect of regenerative gas velocity on the hydrothermal recovery performance of a membrane heat exchanger. It can be seen that with the increase of the regenerative gas flow rate, the heat recovery flux shows a downward trend. An increase in regenerative gas velocity means that

there is more water vapor content in the regenerative gas under the same circumstances, which may lead to more latent heat of water vapor recovered across membranes, and the increase in flow rate can thin the thermal boundary layer on the gas phase side, which is conducive to heat exchange<sup>[19]</sup>.

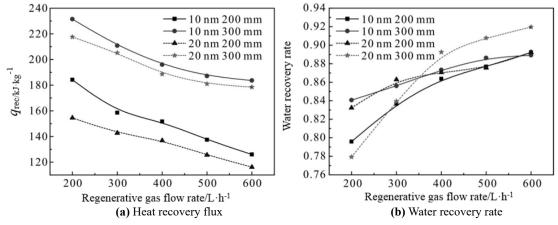


Figure 6. Effect of regenerative gas velocity on heat and mass transfer performance.

However, it should be noted that the increase in the flow rate shortens the residence time of the regenerative gas in the membrane tube, and the heat exchange of the enriched liquid in the shell is not sufficient, and part of the water vapor and the heat it carries are not transported to the enriched liquid across the membrane before it is flown out of the membrane tube together with the regenerative gas, and the waste of this part of the heat leads to a decrease in the heat recovery flux of the membrane heat exchanger. Therefore, in order to obtain a better heat recovery effect, the regeneration gas flow rate should not be too large.

Among the four sizes of membrane heat exchangers, the heat recovery effect of 10 nm, 300 mm ceramic membrane is still optimal. In this ceramic membrane, when the regenerative gas velocity increases from 200 L/h to 600 L/h (an increase of 200%), the heat recovery flux drops from 231.45 kJ/kg CO<sub>2</sub> to 183.68 kJ/kg CO<sub>2</sub>, a decrease of 21%. The reduction is much smaller than the increase in the flow rate of the enrichment, indicating that the effect of the change of the flow rate of the rich liquid on the heat recovery effect of the system is

more significant than the change of the regenerative gas velocity.

#### 3.5 Effects of regenerative gas temperature

The effect of the regenerative temperature on the heat and mass transfer performance of the system is shown in Figure 7. It can be seen that with the increase of the regenerative gas temperature, the heat recovery flux continues to rise. This result is related to the result of the change in the temperature of the liquid enrichment, the higher the regenerative gas temperature, the lower the temperature of the rich liquid, the greater the temperature difference between the two phases of gas and liquid. The greater temperature difference makes the driving force of water vapor in the gas phase transfer to the liquid phase larger, and more water vapor undergoes phase change into the rich liquid to obtain the recovery of latent heat. It is also clear from Figure 7(b) that water recovery continues to rise as the regeneration temperature rises, which is consistent with the explanation in this article.

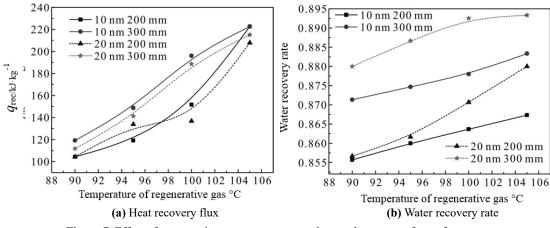


Figure 7. Effect of regenerative gas temperature on heat and mass transfer performance.

When the regenerative gas temperature rises from 90 °C to 105 °C, the heat recovery flux of the 10 nm, 300 mm ceramic membrane heat exchanger increases from 119.12 kJ/kg (CO<sub>2</sub>) to 222.64 kJ/kg (CO<sub>2</sub>), increased by 87%; while under the same conditions, the temperature of the enriched liquid changed by the same amplitude, and the corresponding heat recovery flux changed by only 27%. It can be seen that the heat recovery flux is more sensitive to the change of regeneration temperature.

### 3.6 Effects of H<sub>2</sub>O molar fraction in regenerative gas

In previous experiments, the  $H_2O$  molar fraction in maintaining regenerative gas was 0.5. This subsection examines the hydrothermal recovery performance of the system when the molar fraction of  $H_2O$  in regenerative gas changes, and the results are shown in **Figure 8**.

As can be seen from the figure, the heat recovery flux is very sensitive to the H<sub>2</sub>O molar fraction in the regenerative gas, and the higher the H<sub>2</sub>O molar fraction, the heat recovery flux rises almost in a straight line. It is not difficult to understand that the increase in the content of water vapor in the regen-

eration gas brings about an increase in the latent heat of recovery, leading to an increase in the heat recovery flux. In the actual industrial application process, due to the different types of absorbing liquids and different operating conditions, the molar fraction of water vapor in the regeneration gas is generally  $0.5 \sim 1$ , the application of ceramic membrane heat exchangers in the water heat recovery process with high water vapor content can give full play to its advantages.

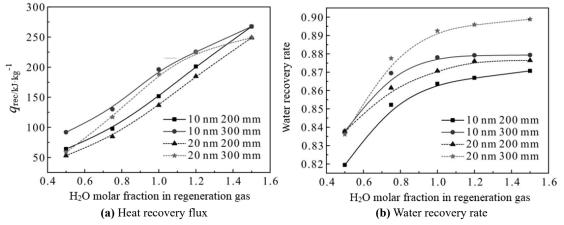


Figure 8. Effect of molar fraction of water vapor on heat and mass transfer performance.

It can also be seen from the figure that the water recovery rate increases with the increase of the molar fraction of water vapor, but the upward trend is gradually slowing down, indicating that the system itself has a certain limit to the water recovery of a certain specification ceramic membrane heat exchanger, and there may be a different water recovery limit value for different specifications of the ceramic membrane heat exchanger.

## 4. Heat and mass transfer analysis for hydrothermal recovery

#### 4.1 Mechanism of heat and mass transfer

Compared with traditional heat exchangers, an important property of porous ceramic membranes is the pores in the ceramic membrane allow the water vapor in the gas phase to be transmitted through the membrane pores to the liquid side. Depending on the difference in the adsorption force of different pore sizes, the holes can be divided into large pores (d > 50 nm), mesopores ( $2 \text{ nm} < d \leq 50$  nm), and micropores ( $d \leq 2 \text{ nm}$ ). In micropores, the superposition of surface forces relative to the pore wall plays a leading role in adsorption; in the range of mesopores, the capillary force is more pronounced; while in large pores, the pore wall action has little impact on adsorption<sup>[24]</sup>. During the passage of gas through the porous membrane, different transport

mechanisms occur, mainly determined by temperature, pressure and membrane pore size<sup>[25]</sup>. The separation layer pore size of the porous ceramic membrane used in this study is 10 nm and 20 nm, which is in the mesopore range, so the capillary force is significant, that is, the capillary condensation process occurs in the membrane pores. Capillary condensation refers to the liquefaction condensation phenomenon that occurs when the gas encounters structures such as pores and porous media, that is, the substance condenses from the gas phase into a liquid phase and exists in the pores of the capillary structure or porous medium. This is because in capillary structures or porous media, the average free path of gas phase molecules decreases, so that the interaction between molecules with van der Waals forces is enhanced, and gas molecules are more likely to condense into liquid phase<sup>[26,27]</sup>.

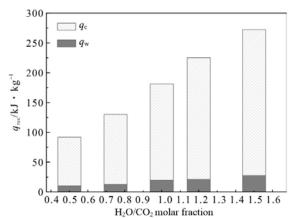
In the experiment, there is a certain pressure difference and temperature difference between the two sides of the ceramic membrane, and under the action of the two, the gas is transmitted from the higher pressure and temperature side to the lower side. Carman *et al.*<sup>[28]</sup> pointed out that under the mechanism of capillary condensation, the mass transfer thrust is no longer the partial pressure difference of the gas, but the capillary pressure is much larger, and at the same time, most of the holes are filled with condensate of the condensable com-

ponents, blocking the mass transfer channels of the refractory or non-condensing components, making the membrane separation factor significantly improved. In this experiment, the gas is a mixture of CO<sub>2</sub> and water vapor, and the water vapor is transmitted to the liquid phase side as a condensable component under the action of pressure difference, temperature difference and capillary force. According to the characteristics of capillary condensation, water vapor can be condensed under the pressure below saturated vapor pressure  $P_{\text{sat}}$ , and once the condensation phenomenon occurs, a crescent-shaped gas-liquid interface be formed between the gas-liquid phases, so that even under conditions below saturated vapor pressure, the gas-liquid phase balance can be maintained. After this crescent-shaped interface is formed, under the action of capillary force, the water vapor condensate in the gas phase will continue to flow into the liquid phase through the membrane pores, recovering the large amount of latent heat it carries<sup>[29]</sup>. At the same time, the membrane pores are continuously filled with water vapor condensate, which blocks the cross-membrane transmission of CO<sub>2</sub> in the gas phase and the CO<sub>2</sub> loaded in the liquid phase, and realizes the mass transfer process of the single component of water vapor from the gas phase to the liquid phase, which is very conducive to the recovery of water vapor in the regeneration gas.

Water vapor condenses at the gas-membrane interface and flows into the liquid phase under capillary action, on the one hand, by recovering the water vapor in the regenerative gas, the latent heat in the water vapor is also recovered; on the other hand, the gas temperature is reduced and the liquid temperature is increased by means of membrane heat conduction and convective heat exchange between the two phases, and the temperature change makes some of the sensible heat in the regeneration gas also recovered. Therefore, the heat recovered from the regenerative gas includes two parts: sensible heat and latent heat.

#### 4.2 Heat and mass transfer process analysis

In the membrane heat transfer process, heat transfer and mass transfer process are carried out at the same time, and the heat recovery flux and water recovery rate can be used to express the heat transfer and mass transfer effects of the system respectively. In this process, the heat is exchanged through heat conduction and convective heat transfer, and the latent heat released by the water vapor condensed in the ceramic membrane tube process in the regeneration gas and the condensed water that does not pass through the membrane, the sensible heat released by the regenerative gas cooling is transferred to the rich liquid for recovery through the thermal conductivity of the ceramic membrane. The heat transferred through the condensate of the membrane is recovered to the rich side in the form of convective heat transfer. Therefore, in order to determine the main forms of heat recovery in the heat recovery process of the system, a correlation analysis is required. Taking the 10 nm, 300 mm ceramic membrane as an example, the specific source of heat recovery during the heat recovery process of the system is analyzed, and the results are shown in Figure 9.



**Figure 9.** Variation in thermal conductivity and convective heat exchange in the heat recovery flux.

In the figure,  $q_c$  represents the heat transferred through the thermal conduction and  $q_w$  represents the heat transferred by convective heat transfer. It is clear that in the heat recovery process, most of the heat is transferred through the thermal conduction process with the ceramic film, and this part of the heat transferred by convection accounts for about 10% of the total heat recovery flux. Therefore, the thermal conduction process dominates the heat transfer of the whole process, and the heat transfer caused by mass transfer accounts for only a small part, but in general, this small part of

the energy also plays a role in promoting the heat transfer of the entire system. This shows that in practical applications, the selection of ceramic films with large thermal conductivity can greatly improve the heat recovery effect of the system.

#### 5. Conclusions

- (1) The heat recovery flux of the system increases with the increase of the enriched liquid flow rate and the decrease of the enriched liquid temperature, increases with the decrease of the regenerative gas flow rate and the increase of the regenerative gas temperature, and increases with the increase of the molar fraction of water vapor in the regenerative gas, and in comparison, the effect of the concentration of the enriched liquid is smaller.
- (2) Compared with the change of regenerative gas flow rate, the impact of the change of rich fluid flow rate on the heat recovery effect of the system is more significant. The heat recovery flux is more sensitive to changes in the regenerative temperature than the enriched liquid temperature.
- (3) When the pore diameter is the same, the longer the length of the membrane tube, the better the heat recovery effect of the system, which is related to the effective contact area of its heat exchange and the residence time of the heat exchange.
- (4) When the length of the membrane tube is the same, the heat recovery effect of the 10 nm pore size membrane is better than that of the 20 nm pore size membrane, which is related to the pore distribution and specific surface area of the membrane itself. Therefore, when selecting ceramic film, it is not the larger the pore size, the better, it is necessary to select a membrane with a large porosity and specific surface area on the basis of ensuring that the heat exchange contact area and heat transfer time are sufficient.

Ceramic membrane heat exchanger is effective for the regenerative hydrothermal recovery, but there is still more to be studied in depth. In this paper, only the ceramic membranes of two pore sizes and two lengths are experimentally studied, and other pore sizes, other lengths, and other thicknesses of ceramic films are also needed to be studied. In addition, a single-tube ceramic film is used in this paper, and the heat transfer and mass transfer pro-

cess in the multi-channel ceramic film is more complex and requires more in-depth research.

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#### **Conflict of interest**

The authors declare that they have no conflict of interest.

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