研 究 報 文

CaCl₂, LiCl 及びコロイダルシリカを用いて処理した多孔及び緻密全熱交換紙の水蒸気透過挙動

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Water Vapor Transmission Behavior through Porous and Dense Enthalpy Exchange Sheets Treated with CaCl₂, LiCl and Colloidal Silica

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This report is concerning the sheet to be utilized to the air-to-air heat exchanger. Observation on the characters of the moisture permeation for two types of the enthalpy sheet (porous and dense enthalpy sheets) has been conducted. To improve the efficiency of the moisture permeation through the enthalpy sheet, the moisture absorbents CaCl₂, LiCl and colloidal silica have been used. Throughout the wet cup test according to the ASTM standards, the tests of the moisture permeation according to the changes of the air gap have been conducted. For both of the porous and dense enthalpy sheets, it showed 2 to 2.5 times of increase for the permeability of water vapor when the air gap reduced from 13 mm to 6 mm. Also, according to the treatment of the moisture absorbent, the permeability of water vapor increased, but after the certain amount of the processing no further increase of the permeability was shown. For the dense enthalpy sheet compared with the porous enthalpy sheet, it showed more increase of permeability of water vapor due to the moisture absorbent and also it was seen that the dense enthalpy sheet has the similar permeability of water vapor to the porous enthalpy sheet's when processing the moisture absorbent.

Keywords : air-to-air heat exchanger, enthalpy sheet, wet cup test, air gap, permeability, moisture absorbent

分類 : Y₁ 基礎化学一般, Y₆ 物理化学

1. Introduction

Throughout the oil shock in 1970, the demands for the energy efficiency have been dramatically in-

creased. Due to these demands, the studies to increase the heat efficiency were continuously conducted and sealing and insulation of the buildings have been enforced. Although the rate of the natural

ventilation depending on the places are two to 5 times, which is required to maintain the healthy indoor air quality, these efforts are not good enough because of the increasing interest in improving the energy efficiency¹⁾.

The air-to-air heat exchanger is the ventilation device to satisfy the energy saving and IAQ improvement and this is being equipped with most of the air conditioning equipments. The air-to-air heat exchanger can be categorized into two types depending on the heat exchange element. One is the sensible heat exchanger made of metal or plastic exchanging only sensible heat and the other is the enthalpy exchanger made of paper or material for the accumulated heat which exchange the sensible and latent heat at the same time. The enthalpy exchanger can also be categorized into permeable plate, energy wheel and rotary dehumidifier²⁻⁴⁾. Among the enthalpy exchanger types, the enthalpy exchangers, the simply permeable plate type, which consist of the supply air, exhaust air FAN but do not require the moving parts and can be installed on the ceiling, are mostly used.

Contrary to these increasing use of them, a valuation basis for developing the enthalpy exchange element, which is the main part of the enthalpy exchanger, is not well prepared since the studies and standards of the valuation of the enthalpy exchanger's performance is formed with the element types⁵⁻⁷⁾. A good characteristic of an enthalpy exchanger sheet is to maximize the water vapor transmission and to minimize the permeation of harmful gases, and therefore to improve the performance of enthalpy exchange. Therefore, the performance valuation of the enthalpy exchange element should be conducted before making it to develop the enthalpy exchanger with high quality. In both these parameters, the water vapor transmission (WVTR) is the most important factor in respect of energy saving. The ways of having the water vapor transmission test to measure the accumulated heat are ASTM 96-00 and JIS, and these methods consist of the wet cup method measuring the permeation amount of the water from the internal to the external cell filled with water and the dry cup method measuring the absorption amount of the water from the external to the internal

cell filled with CaO ^{5,6)}. Both of these methods can only determine the relative water vapor transmission since there is a lack of the approach to the test methods of the resistance caused by water penetration, the resistance of the specimen itself, and the boundary layer resistances to the air layers between both sides of the specimen⁸⁾.

Therefore, in this study, the previous standards have been reviewed to examine the performance of the water vapor transmission, affecting the enthalpy's exchange efficiency and with these improved methods the performance of the enthalpy sheet has been measured. The water vapor transmission of the enthalpy exchange sheet before it is made in was examined.

By evaluating the porous and dense enthalpy exchange sheets, the pore structure of the water vapor transmission according to the pore structure and the influence of the moisture absorbent such as CaCl_2 , LiCl and colloidal silica that have been mainly used in liquid desiccant were examined⁹⁾.

2. Experimental

2.1 Enthalpy sheet preparation

Anhydrous calcium chloride (chemical pure grade) and anhydrous lithium chloride (extra pure grade) used as the moisture absorbent were purchased from Junsei Chemical Co., Ltd (Tokyo, Japan) special purification was used as well. The Colloidal silica stabilized by Na, whose diameter is 10 nm–20 nm, pH 9.5–pH 10, and viscosity 1.0 mPs–3.0 mPs, is the suspension solution with 20% of SiO_2 , and purchased from Nissan Chemical Industries, Ltd. (snowtechs 20, Tokyo, Japan).

The dense and the porous enthalpy exchange sheet have been provided from Mitsubishi Paper Mills Co., Ltd without being proceed in the moisture absorbent and the ultra-pure de-ionized water was used in soak.

The process of the moisture absorbent soak is as below. First of all, after making the moisture absorbent solution at the desired density, the enthalpy exchange sheets were prepared with the standard size (6 cm × 6 cm) and measured before soak. The surrounding condition was 20°C, 20% RH. After putting the moisture absorbent solution (300 ml) into the Petri dish, the enthalpy exchange sheet was soak into it for

3 minutes in order to the moisture absorbent was fully absorbed into the enthalpy exchange sheet. Meanwhile the moisture absorbent solution was covered with the lid to prevent the moisture in the air from flowing into it since the moisture absorbent solution tends to stay equal to the moisture in the air. After handling the moisture absorbent, the sheet was taken out, laid on the glass plate and the moisture absorbent on the enthalpy exchange sheet was removed with the rubber roller. The weight of the enthalpy exchange sheet was measured quickly due to the concerns about the moisture evaporation. The enthalpy exchange sheet was dried with the heat plate and was proceed in heat treatment (120°C–130°C) to keep it level. Thickness measurements were obtained with a thickness gauge (Mitutoyo, Japan) at a minimum of five positions on an enthalpy sheet. The standard deviation of thickness for each specimen was typically less than 10%. The uptake of the moisture absorbent was determined by the formula as below.

$$\text{Absorbent uptake} = (W_{\text{wet}} - W_{\text{dry}}) \times C_{\text{absorbent}}$$

where W_{wet} is the weight of wet enthalpy sheet that was removed excess water and W_{dry} is the weight of dry enthalpy sheet, and $C_{\text{absorbent}}$ is the weight concentration of absorbent solution.

2.2 Water vapor transmission measurement

The schematic diagram of the experimental apparatus of water vapor transmission rate (WVTR) is illustrated in Fig.1. The technique used to measure WVTR was a modification of the wet cup method described by ASTM E 96-00⁹⁾. In this method the test film covered a Petri dish filled with ultra-pure de-ionized water. The mass of water lost from the dish was

observed as a function of time, and the WVTR was calculated from the steady-state region. A window of known area was cut into an acryl resin, and the specimen was attached to the acryl resin with 5-Minute[®] epoxy. The acryl resin with a enthalpy exchange sheet was attached with aluminum tape to the top of a plastic Petri dish that was 38.5 cm² in area. Using a syringe, 48.2 ml of ultra-pure de-ionized water was added to the Petri dish, and the hole was sealed with aluminum tape. With 48.2 ml of water in the dish, the air gap between water surface and enthalpy sheet was 6 mm. The WVTR at 13 mm air gap was also measured to examine the effect caused by the air gap. After allowing the epoxy to cure for 1 hr, the sample dish was weighed and placed in a constant temperature and humidity air conditioner at 25°C ± 0.5°C and 50% RH ± 1.5% RH with air circulation rate of about 0.5 m s⁻¹. The sample dish was periodically removed and weighed. The weight loss as a function of time was recorded. The sample dish was typically removed from the constant temperature and humidity air conditioner for weighing once every hour.

3. Results and discussion

3.1 Water vapor transmission rate

Representative tests of porous and dense enthalpy sheets treated with CaCl₂ are shown in Fig.2. The water loss as the time passed showed the linear trend and from this trend, the moisture permeation showed the steady-state. All of the tests were checked to be normal after leaving as they were inside the chamber with constant temperature and constant moisture for more than 8 hrs and the water vapor transmission

Constant temperature and humidity conditions: 25 °C, 50% RH

Fig.1 Schematic diagram of water vapor transmission rate test.

Fig. 2 Weight loss as a function of time in the wet cup test.

rate was resulted from the reduction of the moisture in general condition. Reaching the balance of the moisture inside of the test dish to the test temperature inside of the chamber with the constant temperature and moisture took the first 1 hr and after that all of the tests showed the linear trends.

WVTR as a function of time normalized to the testing area (A) can be calculated as below.

$$WVTR = \frac{\text{mass } H_2O \text{ lost}}{\text{time} \times \text{area}} = \frac{\text{flux}}{\text{area}}$$

with units of $\text{g day}^{-1}\text{m}^{-2}$. The WVTR is related to a material characteristic, the water vapor permeability, ζ , with units of $\text{cm}^3 \text{cm cm}^{-2} \text{s}^{-1} \text{cmHg}^{-1}$ as

$$\zeta = WVTR \left(\frac{l}{\Delta p} \right)$$

where l is the enthalpy sheets thickness (cm) and Δp is the pressure difference across the enthalpy sheets (cmHg)⁴⁾.

Photo. 1 shows WVTR according to the air gap of the porous enthalpy exchange sheet. In the wet cup method of ASTM 96-00 standard, the distance between the specimen and the surface of the water is prescribed as $19 \text{ mm} \pm 6 \text{ mm}$ ⁴⁾. This prescription as-

sumes the interior of test cell, the distance between the surface of the water and the surface of the specimen is 100% RH. However, as shown in Fig. 3, at 6 mm air gap, WVTR showed Figures almost 2 times bigger compared at 13 mm, minimum distance prescribed. Showing the different WVTR according to the air gap means that the resistance taken to move up to the surface of the enthalpy exchange sheet from the surface of the water increases since there is the concentration gradient inside of the water permeation cell.

Hu et al. calculated the water permeation at a stationary air layer with Schirmer's equation⁸⁾.

$$\zeta_{air} = \left[\frac{(2.306 \times 10^{-5}) P_0}{R_v T P} \right] \left[\frac{T}{273.15} \right]^{1.81}$$

where T is the temperature (K), P is the ambient pressure (Pa), P_0 is the standard atmospheric pressure (101,325 Pa), and Δp is the ideal gas constant ($461.5 \text{ J K}^{-1} \text{ kg}^{-1}$ for water). The water vapor transmission rate is obtained from the permeability as

$$WVTR = \frac{\zeta_{air} \Delta P}{W}$$

where W is the thickness of the air layer and Δp is the

Photo. 1 Scanning electron micrographs of enthalpy sheets : (a) porous enthalpy sheet and (b) dense enthalpy sheet (cutting plane photographed by Mitsubishi Paper Mills Ltd.).

pressure difference between the two surfaces. With this formula 6 mm of the air gap turned to be the optimum by calculating the water vapor permeability to the stagnant layer inside of the test cell. Methods prescribed in ASTM standard can measure the relative WVTR but can't measure the absolute value. The test should be conducted with the air gap within 6 mm in order to get the absolute value of WVTR for the enthalpy sheet by meeting the requirement prescribed.

3.2 WVTR through porous enthalpy sheet

Table 1 and Fig. 3 show the WVTR and the water vapor permeability according to the air gap of each type's moisture absorbent. The permeability is the characteristic considered in the water vapor partial pressure on both side of the sheets when having the test for moisture permeation and the thickness of the sheet.

The WVTR decreased as the treatment of moisture absorbent in some case, while the permeabilities of

water vapor increased 5%–20% for the enthalpy sheets treated with moisture absorbents. The enthalpy sheet processed with CaCl₂ and LiCl showed relatively high permeability of water vapor compared with the enthalpy sheet processed with silica. This is because moisture absorbent ability of CaCl₂ and LiCl is relatively higher than that of silica so that the amount of the condensed water vapor permeated into the fiber increases. However, for porous enthalpy sheet, the water vapor mostly permeates throughout the pores. Therefore, the permeability of the water vapor under the water vapor partial pressure, in which there is little resistance when the water vapor permeates throughout the enthalpy sheet, is not influenced by the processing of the moisture absorbent.

Water vapor permeation throughout the porous enthalpy sheet consists of the movement throughout the pore existed inside and the movement by the condensation of fiber¹⁰⁾. The moisture absorbent can give the

Table 1 WVTR through porous enthalpy sheets with different air gap

	WVTR ($\text{g day}^{-1}\text{m}^{-2}$)		
	6 mm air gap	13 mm air gap	$\text{WVTR}_{6\text{mm}}$
			$\text{WVTR}_{13\text{mm}}$
Original	2,053.29	883.58	2.32
5 wt% CaCl_2	1,948.83	949.88	2.05
5 wt% LiCl	2,182.04	832.82	2.62
5 wt% colloidal silica	1,754.73	651.20	2.69

Fig.3 Permeability of water vapor through porous enthalpy sheet.

positive effect to the movement by the condensation by increasing the moisture absorption while it can also give the negative effect obstructing the movement of the water vapor by blocking some of the pores on the surface of the enthalpy sheet, decreasing the pore size at the same time. **Photo.2** shows the SEM pictures of the surface of the porous enthalpy sheet before and after processing the moisture absorbent.

As shown in Figure, as the uptake of the moisture

absorbent increases, the cellulose fiber on the surface of the enthalpy sheet is covered with the moisture absorbent, which turns out to operate as the additional resistance to the permeation of water vapor.

According to the processing of more than 1 g m^{-2} moisture absorbent, LiCl and CaCl_2 showed the regular value of the permeability of water vapor (**Fig.4**). It showed the permeability increase caused by the main effect throughout the pore and additional effect throughout the moisture absorbent and also showed

Photo. 2 Scanning electron micrographs of porous enthalpy sheets : (a) untreated sheet, (b) 5 wt%CaCl₂, (c) 5 wt%LiCl, and (d) 5 wt%colloidal silica.

the increase of the amount of water vapor condensed by fiber as the increase of processing the moisture absorbent. However, the overall permeation showed the regular value since the moisture diffusion throughout the fiber is lower than that throughout the pore. For silica, it showed no increase of amount of permeation of water vapor as the amount of processing moisture absorbent increased. It is assumed that the hygroscopic property of silica is lower than that of LiCl and CaCl₂.

3.3 WVTR through dense enthalpy sheet

Table 2 and Fig. 5 show the results of WVTR and water vapor permeability according to the changes of air gap on the dense enthalpy sheet. The distance between the enthalpy sheet and water surface is 13 mm and 6 mm, just same as for the porous sheet. Different from the porous enthalpy sheet, the dense enthalpy sheet removed most of pores between fibers in order

to exclude the mixture of the noxious gas from the indoor air when it is applied to the ventilation system. Therefore, it seems that the major factor causing the water vapor permeation is the condensation by fibers rather than diffusion by pores. As shown in figure, the permeability of water vapor showed more than 2 times of increase for all circumstances as the air gap decreased. As mentioned before, the distribution of water vapor pressure inside of the air gap became even as the air gap decreased so that it caused the increase of permeability. Furthermore, the water vapor permeability of the dense enthalpy sheet without processing moisture absorbent showed 1.3 to 1.7 times of increase according to the processing of the moisture absorbent. Different from the porous enthalpy sheet, the dense enthalpy sheet depends more on the movement by the dissolution than the moisture movement throughout the pores so the increase of

Fig. 4 Effect of moisture absorbent to permeability of water vapor through porous enthalpy sheet.

Table 2 WVTR vapor through dense enthalpy sheets with different air gap

	WVTR ($\text{g day}^{-1}\text{m}^{-2}$)		
	6 mm air gap	13 mm air gap	$\frac{WVTR_{6\text{mm}}}{WVTR_{13\text{mm}}}$
Original	1,500.60	658.42	2.27
5 wt% CaCl_2	1,947.28	827.87	2.35
5 wt% LiCl	1,930.62	899.33	2.15
5 wt% colloidal silica	1,520.87	623.63	2.48

moisture amount of the enthalpy sheet by moisture absorbent caused the overall increase of the permeability of water vapor. Comparing with the porous enthalpy sheet, it has about 70% of the permeability out of the porous enthalpy sheet's when not processing the moisture absorbent but it increased the same as the porous enthalpy sheet's when processing. Considering the possibility of mixing the noxious gas from the indoor air, the dense enthalpy sheet capable of excluding permeation of the noxious gas effectively is the enthalpy sheet with a high quality. Fig. 6 shows the permeation behavior of the dense enthalpy sheet

for the permeability of water vapor according to the amount of processing moisture absorbent. All the circumstances processed with moisture absorbent, compared with ones without moisture absorbent process, showed the increase of the permeability of water vapor. As mentioned above, it seems to be caused by the increase of solubility of the water vapor by the moisture absorbent. Same as for the porous enthalpy sheet, it showed no more increase compared with the uptake of the moisture absorbent after certain amount of processing moisture absorbent. While the amount of the moisture of which the enthalpy sheet contains

Fig.5 Permeability of water vapor through dense enthalpy sheet.

Fig.6 Effect of moisture absorbent to permeability of water vapor through dense enthalpy sheet.

increased according to the processing of the moisture absorbent, the diffusivity speed, one that the moisture of the enthalpy sheet takes to permeate to the oppo-

site side, became the rate determining step, showing the regular permeability.

Additionally, the surface of the enthalpy sheet got

Photo. 3 Scanning electron micrographs of dense enthalpy sheets : (a) untreated sheet, (b) 5 wt%CaCl₂, (c) 10 wt%CaCl₂, and (d) 15 wt%CaCl₂.

covered with the moisture absorbent according to the processing moisture absorbent (Photo. 3). It could be said that this affect the permeability to become regular. However, different from the porous enthalpy sheet, it showed similar permeation efficiency to the porous enthalpy sheet when given little influence of pore block of the moisture absorbent since most of them are condensed in fiber and permeate.

4. Conclusion

The most important efficiency factor required for the enthalpy sheet is the high efficiency of moisture permeation and the ability to exclude noxious gas. Among the methods used to measure the efficiency of moisture permeation, ASTM 96-00 prescribes the wet cup method and the air gap is prescribed to be 19 mm ± 6 mm on the tests but the quantitative evaluation for the efficiency of moisture permeation as the

important factor of the enthalpy sheet is difficult because the permeability of water vapor increases according to the decrease of the air gap. Therefore, by reducing the air gap to 6 mm and examining the permeation efficiency of the enthalpy sheet, considering the permeation speed of the moisture in the air, the very close value to the real value of the water vapor transmission rate that enthalpy sheet has could be measured. Also the permeation characters of the water vapor for each of the two types of the enthalpy sheet used now, the porous and dense enthalpy sheet, were observed. On the porous enthalpy sheet, the water vapor permeation throughout the pores mainly happens so that there is not much influence caused by the processing of the moisture absorbent. On the other hand, there is relatively more influence caused by the moisture absorbent compared with the porous enthalpy sheet since the permeability of water vapor

is determined by the behavior of solution-diffusion by the condensation of the cellulose fibers on the dense enthalpy sheet. With the improvement of the permeability of water vapor by processing the moisture absorbent, the efficiency of the dense enthalpy sheet for the latent heat exchange could be elevated up to that of the porous enthalpy sheet.

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1. 緒 言

1970年代のオイルショックを経て、エネルギー効率化の必要性は急速に増加してきた。このため熱利用の効率化の研究は継続的に進められ、建造物の高気密、高断熱化が進んでいる。屋内空気品質を健康的に保つために必要とされる自然換気の割合は、場所に依存して2ないし5回であるが、省エネルギー化への関心の高まりからすればこれでは不十分である¹⁾。

空調用熱交換器は省エネルギーと室内空気品質向上の両方を満足させる換気装置であり、ほとんどの空調設備に装着されている。熱交換器は、その熱交換素子によって2種に分類できる。ひとつは金属やプラスチックで作られた顕熱のみを交換するもので、もうひとつは紙や蓄積された熱に対応する素材による、顕熱と潜熱を同時に交換できる全熱交換器である。また全熱

交換器は浸透板、energy wheelと回転式除湿機に分類できる²⁻⁴⁾。これらの全熱交換器の中でも、吸気と排気ファンで構成され可動部を必要とせず、天井内にも設置できる単純な浸透板タイプのものが利用の大半を占める。

このような使用の増加とは逆に、全熱交換機の中核である全熱交換素子の開発のための評価基準は、それらの性能に関する研究や規格が熱交換素子の種類によって区別されるため、充実していると言え難い⁵⁻⁷⁾。熱交換紙の優れた特性とは、水蒸気の透過量を最大化し、有害ガスの透過を最小化することにより、熱交換性能を向上させる所にある。従って、高品質の熱交換器を作成するには、事前に熱交換素子の性能評価を行うべきである。これらの両パラメータにおいて、水蒸気透過速度(WVTR)が最も重要な要素である。蓄積された熱を測定する水蒸気透過度試験を規定する試

試験は ASTM 96-00 および JIS である。またこれらの試験は、水で満たされたセルの内から外への透過量を測定するウェットカップ法と、CaO で満たされたセルの内への吸収量を測定するドライカップ法で構成される^{5,6)}。ただし水の浸透によって起きる抵抗、試料そのものの抵抗および試料両面から空気層への境界面抵抗の測定法についての研究が不足しているため、これら両試験法で決定できるのは相対的な水蒸気透過速度のみである⁸⁾。

従って本研究では、熱交換効率に影響する水蒸気透過度を調べるため従来の規格を見直し、改良した方法で熱交換紙の性能を測定した。熱交換紙の水蒸気透過速度は、機器への取付け以前に調べている。

多孔性および緻密熱交換紙を評価することにより、多孔構造に依存した水蒸気透過速度と、主に液状乾燥剤に利用される CaCl_2 、 LiCl 、コロイダルシリカ等の吸湿剤の影響が調べられた⁹⁾。

2. 実 験

2.1 熱交換紙の調製

吸湿剤として、市販の無水 CaCl_2 (chemical pure grade) 及び無水 LiCl (extra pure grade) (共に Junsei Chemical Co., Ltd) をさらに精製して使用した。またコロイダルシリカも市販品 (snowtechs 20, Nissan Chemical Industries Co., Ltd) (安定剤 Na, 粒子径 10-20 nm, pH 9.5-10, 粘度 1.0-3.0 mPs, 固形分 20%) を用いた。

多孔性及び緻密性熱交換紙は、三菱製紙株式会社から提供された吸湿剤未処理のものを使用し、超純水を浸漬に使用した。

吸湿剤の浸漬工程は下記の通り。まず吸湿剤溶液を目的の濃度で調整し、標準サイズ (6 cm×6 cm) の熱交換紙を秤量し、ペトリ皿中で 300 ml の溶液に 3 分間浸漬した。環境は 20℃, 20% RH であった。この間吸湿剤溶液が空気中の水分を吸収しないよう蓋で覆った。その後シートを取り出しガラス板上に置き、ゴムローラーでシート上の吸湿剤を除いた。水分の蒸発に考慮してシート重量を速やかに測定した。シートをホットプレート上で乾燥し、平滑に保つため 120-130℃ で熱処理を行った。厚さの測定値は厚さ計 (Mitutoyo, Japan) によりシート上の最低 5 箇所から得た。各試料の厚さの標準偏差は通常 10% 以下であった。吸湿剤の定着量は以下の式により決定した。

$Absorbent\ uptake = (W_{wet} - W_{dry}) \times C_{absorbent}$
 W_{wet} は余剰水分を除いた未乾燥シートの重量, W_{dry} は乾燥シート重量, $C_{absorbent}$ は吸湿剤の重量濃度である。

2.2 水蒸気透過度測定

水蒸気透過度 (WVTR) 測定の実験装置の模式図を図 1 に示す。WVTR の測定法は、ASTM E 96-00 によるウェットカップ法の改良版である⁴⁾。この測定法では、試験フィルムは超純水を満たしたペトリ皿上を覆う。皿から失われた水分量は時間の関数として得られ、WVTR が算出された。面積既知の窓をアクリル樹脂から切り抜いて作り、試験紙を 5-Minute[®] エポキシにより接着した。試験紙のついたアクリル樹脂はアルミテープで 38.5 cm² のペトリ皿上部に接着した。シリンジを用いて 48.2 ml の超純水を注入し、アルミテープで穴をふさいだ。このときの水面と試験紙の距離は 6 mm であった。空隙幅の影響を調べるため、距離が 13 mm の場合も WVTR の測定を行った。エポキシのキュアのため 1 時間放置した後試験体を秤量し、25±0.5℃, 50±1.5% RH の恒温恒湿条件に置いた。換気率は約 0.5 m s⁻¹ であった。試験体は 1 時間おきに恒温恒湿器から取り出して秤量し、重量の減少を時間の関数として測定した。

3. 結果と考察

3.1 水蒸気透過度

多孔紙、緻密紙および CaCl_2 処理の緻密紙についてのテスト結果を図 2 に示す。時間経過と水分の減少量の関係は直線状であり、水蒸気透過が一樣であることを示している。すべての試験は、恒温恒湿条件に 8 時間以上置かれたためと、水蒸気透過度が一般条件での水分減少から得られたことから、正常であると確認された。試験体内の湿度が試験温度での定常状態に達するまで 1 時間を要し、その後はすべての試験で一定となった。

試験面積について正規化された時間関数としての WVTR は次のように計算できる。単位は g day⁻¹m⁻² である。

$$WVTR = \frac{\text{mass } H_2O \text{ lost}}{\text{time} \times \text{area}} = \frac{\text{flux}}{\text{area}}$$

WVTR は材料特性、即ち水蒸気透過度 ϕ と次のように関係している。また単位は cm³ cm cm⁻² s⁻¹ cmHg⁻¹ である。

$$\phi = WVTR \left(\frac{l}{\Delta p} \right)$$

l はシート厚さ (cm), Δp はシート内外の圧力差 (cmHg) である⁴⁾。

写真 1 に多孔紙における、空隙幅に依存する WVTR 変化を示した。ASTM 96-00 規格のウェットカップテストでは、試料と水面間の距離は 19±6 mm と規定

されている⁴⁾。この規定では、テストセル内部の試料と水面間では湿度が100%と見なされている。しかしながら図3のとおり、空隙幅が6 mmの場合には規定の最小値である13 mmに比べて2倍以上のWVTR値を示している。空隙幅に伴いWVTRが異なる値を示すということは、水面から試料表面へ水蒸気が上昇する際、濃度勾配が存在することによる抵抗を受けることを示している。

HuらはSchirmerの式により静止した空気層での水分浸透を計算している⁸⁾。

$$\xi_{air} = \left[\frac{(2.306 \times 10^{-5}) P_0}{R_s TP} \right] \left[\frac{T}{273.15} \right]^{1.81}$$

T は温度(K)、 P は周囲の気圧(Pa)、 P_0 は標準気圧(101,325 Pa)、 R_s は理想気体定数(461.5 J K⁻¹ kg⁻¹ for water)である。水蒸気透過速度は透過度から次のようにして得られる。

$$WVTR = \frac{\xi_{air} \Delta P}{W}$$

W は空隙幅、 ΔP は2面間の圧力差である。この式より、空隙幅6 mmという条件がテストセル内部の静止空気層への水蒸気透過度を計算する上で最適値であると判明した。ASTM規格に規定される試験法では相対的なWVTRは測定できるが、絶対値については不可能である。WVTRの規定を満足する絶対値を得るために空隙幅は6 mm以内で試験を行うべきである。

3.2 多孔紙のWVTR

表1と図3に、多孔紙の空隙幅によるWVTRおよび水蒸気透過度変化を各吸湿剤処理及び未処理紙について示した。水蒸気浸透性は、水分浸透とシート厚が既知である場合にシート両面の水蒸気分圧に関連して得られる特性である。

吸湿剤処理によってWVTRは減少したものもあったが、水蒸気透過度は5-20%の増加が見られた。CaCl₂およびLiCl処理のシートはシリカ処理に比べて高い水蒸気浸透性を示した。これはCaCl₂およびLiClの吸湿特性がシリカより比較的高いために、繊維に凝結して浸透した水蒸気が増加したためと考えられる。しかし多孔紙においては、水蒸気はほぼ全量が細孔中を透過する。従ってシート中を透過する際にほとんど抵抗を持たないような水蒸気分圧下では、吸湿剤処理による浸透性への影響は無い。

多孔紙中の水蒸気透過は、内部細孔中の透過と繊維への凝結による移動から成る¹⁰⁾。吸湿剤は凝結の増加により水蒸気透過に対して促進効果を持つが、シート表面の細孔の被覆、及び細孔のサイズ減少という形で阻害効果も併せ持つ。写真2に吸湿剤処理後の多孔紙

のSEM写真を示した。

図のとおりシート表面のセルローズ繊維は吸湿剤に覆われ、吸収される水分は増加するが、このことが同時に水蒸気浸透にとって新たな抵抗として作用する。

LiClおよびCaCl₂処理においては、処理量が1 g m⁻¹を超えた場合、水蒸気浸透性は一定の値を示した(図4)。これは多孔紙への水蒸気浸透の増加は主として細孔中への影響に依存して起こり、吸湿剤は副次的な効果であること、また処理量の増加に伴い繊維に凝結する水分量が増加したことを示している。しかし、繊維中への水分拡散は細孔中の透過より少ないために透過度全体としては一定となる。シリカについては、処理量の増加による透過度の増加は見られなかった。シリカの吸湿性はLiClおよびCaCl₂よりも低いと考えられる。

3.3 緻密紙のWVTR

表2と図5に緻密紙における空隙幅とWVTRの関係を示した。空隙幅は多孔紙と同じく13 mmおよび6 mmである。多孔紙と違い、緻密紙は換気系に使用する際室内気からの有害ガス混合物の混入を防ぐため、繊維間の細孔は排除されている。従って、水蒸気透過は繊維への凝結が主たる要素になると考えられる。図のとおり、WVTRは空隙幅の減少に伴い全てのサンプルで2倍以上の増加を示した。前述のとおり空隙幅の減少に伴い空隙内で水蒸気分圧が一定となり、透過度の増加が起きた。さらに、吸湿剤処理によって1.3から1.7倍の水蒸気透過度の増加を示している。多孔紙とは異なり、緻密紙の水分浸透の要因は溶解による移動によるところが大きい。よって吸湿剤によるシート中の水分量の増加は、全水蒸気透過度の増加の原因となる。吸湿剤未処理の緻密紙は、未処理の多孔紙に比して70%程度の浸透性を持つが、処理後は多孔紙と同程度まで増加している。室内気からの有害ガスの混入の可能性を考えれば、効率的に有害ガスの浸透を防除できる緻密紙は高品質である。図6は吸湿剤処理量による緻密紙の水蒸気浸透性変化を示している。全てのサンプルで未処理時に比較して透過度の増加が見られた。上記のとおり、これは吸湿剤により水蒸気の溶解性が増加したためと考えられる。また多孔紙と同じく、ある量以上の処理においてはそれ以上の浸透性増加は見られなかった。吸湿剤処理量に伴いシート中の水分量は増加しているが、紙中の水分が反対側に達するまでの時間といった拡散速度が律速段階となり、一定の値を示している。

さらに、吸湿剤処理によりシート表面は覆われる(写真3)。このことが浸透性を一定にするよう影響して

いると言える。しかし多孔紙と違い、大部分の水蒸気は繊維に凝結して透過するため細孔被覆の影響がほとんど無く、多孔紙に近い透過効率を示している。

4. 結 論

全熱交換紙に求められる最も重要な性能は、高い水蒸気の透過率と有害ガスの防除能である。水蒸気透過率を測定する試験法の中では、ASTM 96-00 がウェットカップ法を規定し、空隙幅を 19 ± 6 mm としているが、熱交換紙の重要な性能である水蒸気浸透率は、空隙幅の減少に伴って増加するため定量的な測定は困難である。従って空隙幅を 6 mm まで減少させ、透過

効率を計測し、空気中の水蒸気透過速度を考慮することで熱交換紙の持つ真の水蒸気透過速度に近い値を測定することができた。また現在使用されている多孔及び緻密 2 種の熱交換紙について透過特性が得られた。多孔紙においては、シート内の細孔中への水蒸気浸透が主として発生し、吸湿剤処理の影響は小さい。一方緻密紙においては繊維への凝結と溶解、拡散挙動により水蒸気浸透性が決定されるため、吸湿剤処理により比較的大きな影響を受ける。吸湿剤処理により、潜熱交換器に使用する緻密紙の水蒸気透過率を多孔紙と同等な水準まで向上させることができた。