

# Improvement of water vapor adsorption ability of natural mesoporous material by impregnating with chloride salts for development of a new desiccant filter

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**Abstract** The aim of this study is the development of a new adsorbent for the desiccant material which can be regenerated by the domestic exhaust heat by using natural mesoporous material, Wakkanai siliceous shale. To improve this shale's performance to adsorb/desorb the water vapor, lithium chloride, calcium chloride or sodium chloride was supported into the mesopores by impregnating with each chloride solution. Especially sodium chloride was effective to increase the water vapor adsorption amount 5–7 times of that of natural shale in the relative humidity range from 50 to 70%. Moreover, the appropriate impregnating concentrations were determined as 5wt% from the relationship between the maximum water vapor adsorption amount and the mesopore volume. Based on these results, a new desiccant filter has been developed by impregnated original paper with lithium chloride and sodium chloride. This paper contained shale powder in the synthetic fibers. The dehumidification performance of this filter was evaluated under the simulated summer condition in Tokyo. From the cyclic adsorption/regeneration test, this shale and chlorides filter could adsorb and desorb 60 g/h water vapor repeatedly at the regeneration temperature of 40°C. On the other hand, a silica gel filter and a zeolite filter adsorbed and desorbed only 10 g/h and 25 g/h, respectively. These results suggested that the shale impregnated with the chlorides has the best dehumidification ability as a new desiccant material. Further, the

desiccant filter made from the shale will achieve the effective use of the low temperature exhaust heat.

**Keywords** Water adsorption · Siliceous shale · Desiccant · Impregnation · Sodium chloride

## 1 Introduction

A humidity control has attracted the attention as the energy conservation technology in the field of the air conditioning. Humidity is one of factors greatly related to comfort and health in the indoor environment. The humidity control, especially dehumidification, is important in the region that becomes hot and humid like in Japan or Southeast Asian countries, etc. in summer. Moreover, the importance of humidification in winter is recognized against the outbreak of the influenza virus.

Conventional air conditioning systems generally need to supercool the indoor air to below the dew point temperature for dehumidification. The water vapor is removed from the moist air by condensation. Since the air temperature after cooled is usually lower than the required temperature of the supply air, a reheating process is necessary to meet a comfortable condition. These supercooling and reheating processes obviously consume much energy.

In recent years the air conditioning system which separates the heat load into the sensible heat and the latent heat has received attention from the viewpoint of the energy conservation. Especially a desiccant system is focused as one of the technologies to control the latent heat load (La et al. 2010). This system removes the water vapor by adsorption or absorption without liquid condensation. Therefore only the sensible heat load of the dried air will be treated by using a condenser with much less energy than the conventional air

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conditioning systems because the supercooling and reheating processes are dispensable.

The desiccant materials can be classified to two different types. One type is a liquid desiccant based on the absorption by deliquescent material such as lithium chloride or calcium chloride. The other is a solid desiccant such as polymer sorbent (Inaba et al. 2002) or the porous materials such as silica gel, zeolite or alumina silicate (Kodama et al. 2001; Shimooka et al. 2007). Especially, the latter is being applied as a desiccant wheel in large-scale facilities in Japan, such as the supermarket or the factory, etc. However, it has not achieved a widespread diffusion to the office building or the residential house. Because the regeneration heat source at 60°C or more is necessary for current desiccant materials. Therefore it is mainly used at the facilities which can gain the exhaust heat at the temperature range from 60 to 140°C, or apply an additional heater. Obviously applying of the additional heater for the regeneration isn't effective. Then, the development of a desiccant material that can use the low temperature exhaust heat of 40°C or less is hoped for improvement of the system performance and spread as a useful air-conditioning equipment.

The water vapor adsorption by physical adsorption is desirable for the low temperature regeneration by using mesoporous material such as type-B silica gel, instead of chemical adsorption by zeolite.

Currently authors have been investigating the humidity control performance and the effective use of Wakkanai siliceous shale (WSS), which is a natural mesoporous material from Hokkaido island of Japan. WSS has a mesoporous structure similar to B-type silica gel. It is an unused resource with the huge amount. Therefore, WSS could contribute the breakthrough in the office use or domestic use of the efficient desiccant system if a new desiccant material, which is inexpensive and can be regenerated by low temperature air, is developed. Furthermore, it will become one of the effective-use ways of the unused resource.

The aim of this study is the development of a new adsorbent for the desiccant material which can be regenerated by the domestic exhaust heat by using WSS. However, the maximum amount of water vapor adsorption of WSS is around 30% of that of type-B silica gel. Therefore, it is significant to improve the WSS's water vapor adsorption ability by a simplified method without losing the possibility of low temperature regeneration. As the first step of the development of a new desiccant material, the improvement of the water vapor adsorption ability of WSS by chloride salt impregnation is examined. The chloride-supported WSS is obtained by impregnating natural WSS with various concentrations of lithium chloride and calcium chloride. In addition, sodium chloride solution is also proposed as impregnating material. The change in specific surface area, log differential pore volume distribution and the water adsorption/desorption isotherm of the chloride-supported

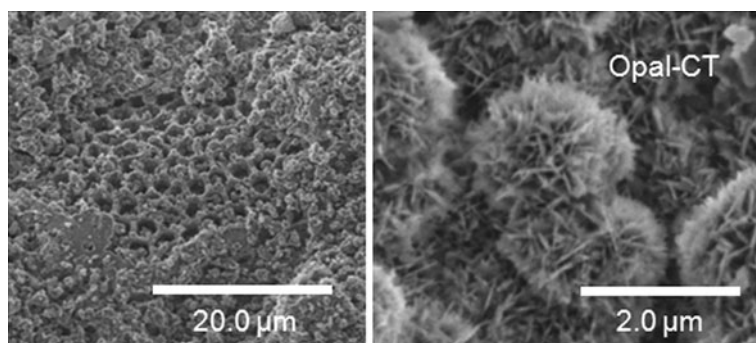
shale are investigated, and the differential of the adsorption performance among the impregnated chlorides are discussed.

Several studies have been carried out on the porous materials by the combination with deliquescent salt to improve the water vapor adsorption performance. Babkin et al. (1991), Khamid et al. (1993) have reported that Aerosil with lithium chloride and aluminum oxide with calcium chloride exhibited the better adsorption capacity than Aerosil or aluminum oxide without the chlorides. The composite materials, which is based on calcium chloride or lithium bromide as the impregnated salts, and micro- and mesoporous silica gel (the pore volumes are 0.35 and 1.0 cm<sup>3</sup>/g, respectively) as the host matrices, has been able to absorb water vapor up to 0.75 g per gram of the dry sorbent at 28°C and 61.7% of the relative humidity. It was demonstrated that these materials could be regenerated at between 70 and 120°C (Aristov et al. 2002; Tokarev et al. 2002; Dawoud and Aristov 2003). Moreover, the composite desiccant materials especially made from calcium chloride and macroporous silica gel, which mean pore diameter is 4.8 nm and porosity is 0.7, have been suggested by Zhang et al. (2005, 2006) Zhang and Qiu (2007) and Jia et al. (2006a, 2006b, 2007). They resulted in a better adsorption performance compared with normal silica gel. The impregnating concentration was varied from 10 to 40wt% to achieve the high adsorption performance. Water retention isotherm showed the adsorption amount over 10wt%. The simulated regeneration temperature was 100°C. The regeneration by using lower temperature air at 40–50°C still has not been obtained by these materials.

Additionally, one of the most important problems needing to be solved on the chloride impregnation is a carryover of deliquesced solution droplets. The carryover prohibits the widespread of the desiccant using liquid sorbents, because it leads some problems such as the salt pollution, the corrosion, or the deterioration of air quality. It is anticipated that too high content of the deliquescent material causes this problem. The adsorption amounts of reported materials were larger than the pore volumes of the porous materials. It is clear that the carryover causes under a high relative humidity condition, because the materials have adsorbed water vapor more than the amount which the pores could maintain.

In this paper, authors propose the appropriate supporting amount of chlorides which obtained from the relation between the water adsorption amount and the pore volume in order not to cause the carryover problem. The appropriate impregnating concentrations were determined from the increased water adsorption amount which can be held inside WSS's pores.

Next, a desiccant filter has been developed from the WSS paper, which contains WSS powder in the synthetic fibers and chlorides. The adsorption ability of this filter was evaluated by the cyclic adsorption/regeneration test.

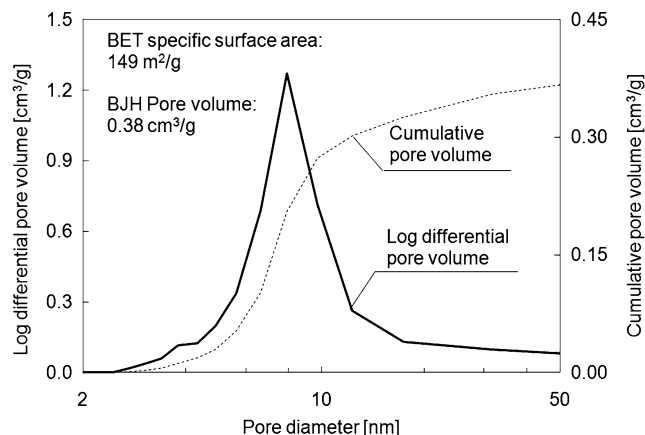
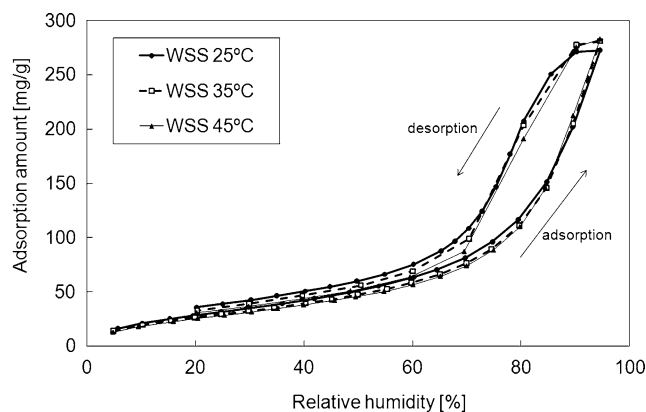
**Fig. 1** SEM pictures of WSS


## 2 Characteristics of Wakkanai siliceous shale

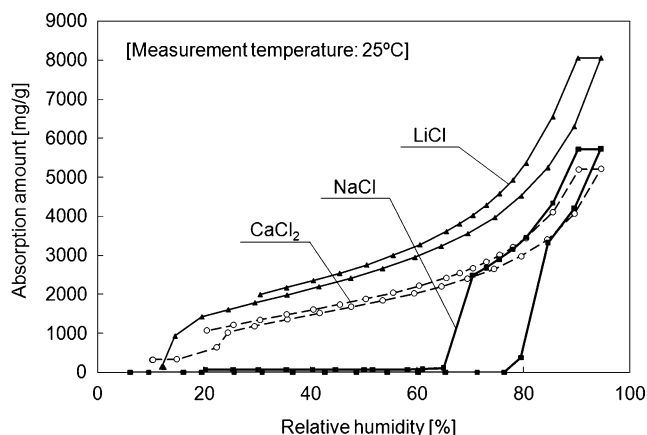
Wakkanai siliceous shale is a natural mesoporous hard mudstone which is produced in Soya area (northern area of Wakkanai city located at latitude 141.68°E and longitude 45.41°N), the northernmost part of Hokkaido in Japan. It is naturally derived from diatoms and planktonic organisms composed mostly of silicon dioxide ( $\text{SiO}_2$ ). WSS has the distributions on the belt-like foothills, which are about 50 meters high in the north-south length of more than 30 km, under the surface soil layer. Moreover, it is found that this WSS layer exists in more than 1000 meters deep in the ground. Figures 1 shows the scanning electron microscope (SEM) pictures. It is confirmed that a reliquiaie of diatom remains on the surface. Furthermore, scale-like crystals of Opal-CT can be observed, and its diameter is about 2  $\mu\text{m}$ .

Figure 2 shows the log differential pore volume and cumulative pore volume distributions and the physical properties of WSS. The mean diameter of the mesopores is 9.9 nm and the porosity is about 0.6. WSS has a characteristic pore size distribution. The pore diameter ranges mainly from 4 to 20 nm, which can contribute to the autonomous water vapor adsorption (Tomura et al. 1997a, 1997b). The measured specific surface area derived from the Brunauer, Emmett and Teller (BET) method is 149  $\text{m}^2/\text{g}$ , and the pore volume calculated by Berret, Joyner and Halenda (BJH) method is 0.38  $\text{cm}^3/\text{g}$ . These values are about 4–10 times higher than those of general diatom soil. The mesoporous which WSS has contribute to adsorption and desorption of the water vapor, and then WSS can control the humidity autonomously.

Figure 3 shows the water vapor adsorption isotherms of WSS at various measurement temperatures. These data were obtained at the steady state. The amount of water vapor adsorption increases rapidly when the relative humidity of air becomes higher than 60%. The differential adsorption amount in the relative humidity range 60 to 80% is 75 mg/g. The maximum adsorption amount reaches 270 mg of water per gram of dry material. The adsorption amount plotted against relative humidity doesn't depend on the measurement temperature, though there is a hysteresis loop which is caused by pore length and interaction energy. Furthermore,


**Fig. 2** Log differential pore volume and cumulative pore volume distributions of WSS calculated by BJH method

**Fig. 3** Adsorption isotherms of WSS measured at various temperature conditions

WSS can desorb the water vapor under low relative humidity condition. In other words, it can adsorb and desorb the water vapor according to the relative humidity change. WSS has been studied as a humidity self-control material (Tomura et al. 1997a, 1997b). Moreover, it is commercially used as a humidity self-control plaster board in Japan (Nezu and Taniguchi 2000). From this point of view, WSS is expected to be used as a desiccant material which can be regenerated by using low temperature exhaust heat, such as gained from



**Fig. 4** Absorption isotherms of chloride salts

the air-conditioning system. Additionally authors have evaluated the WSS's durability to the repetition of adsorption and desorption of the water vapor (Nakabayashi et al. 2008). It is confirmed that there is little decrease in the adsorption performance after it passed of 500 cycles.

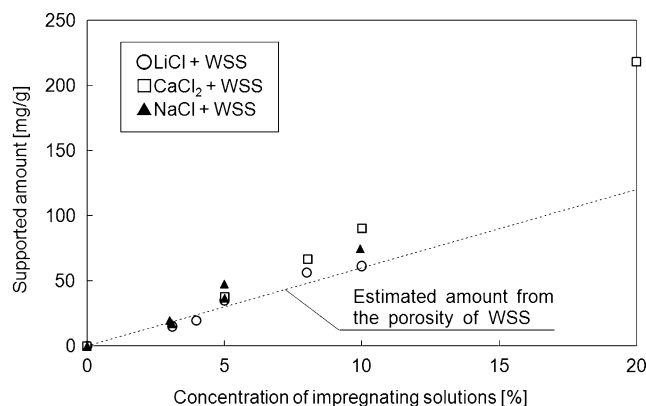
### 3 Physical properties of the chloride-supported Wakkanai siliceous shale

#### 3.1 Supporting method

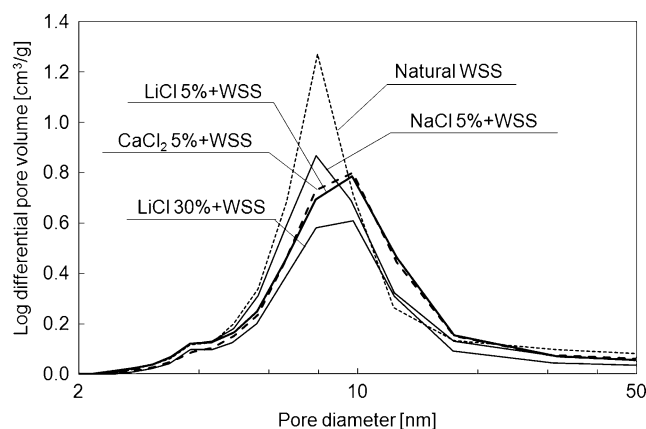
For the functional improvement of WSS, the chloride-supported Wakkanai siliceous shale was obtained by impregnating with various concentration of lithium chloride (LiCl), calcium chloride ( $\text{CaCl}_2$ ) or sodium chloride (NaCl) solution. The particle diameter of crashed WSS was 1.0–2.0 mm. WSS was impregnated with the aqueous LiCl solution in the vacuum desiccator. The inside pressure of the vacuum desiccator was above  $3.14 \times 10^3$  Pa, the saturated water vapor pressure at 25°C. Decreasing pressure for 1 hour made the chloride solution enter the pores of WSS by taking the place of the air. The chloride-supported WSS was obtained by drying the samples at 150°C for 24 hours under the atmospheric pressure after suction filtration. The weight percent concentrations of the aqueous solution were 5, 10, 20, 30, and 40wt%.  $\text{CaCl}_2$  and NaCl were also supported in the same way. The absorption isotherms of the chlorides are shown in Fig. 4. LiCl and  $\text{CaCl}_2$  start to adsorb the water vapor from dry condition, less than the relative humidity 10%. On the other side, the absorption amount of NaCl doesn't change until the relative humidity reached 75%, and shows a sharp rise with the increase of the relative humidity over 75%.

#### 3.2 Measured physical properties and discussion

The supported amounts of the chlorides are plotted as a function of the concentration of the impregnating solutions in



**Fig. 5** Supported amount of chlorides on WSS



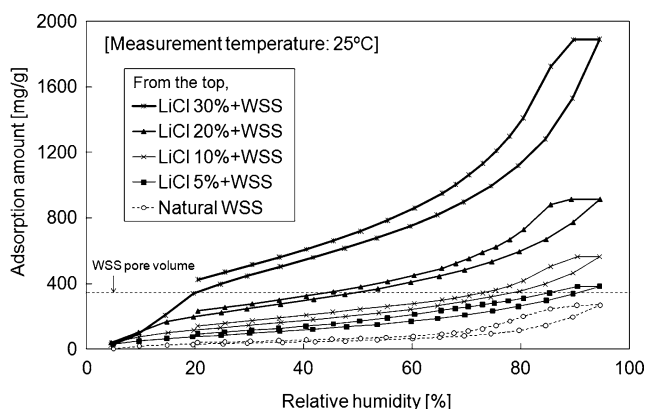
**Fig. 6** Log differential pore volume distributions of chlorides-supported WSS

Fig. 5. The supported amount increased to the concentration regardless of the kind of the chlorides. The dashed line in Fig. 5 shows the predicted supported amount calculated from the assumption that the all pores based on the porosity of WSS, 60%, were filled with the chloride solution and the almost chloride salts were remained in the pores after dried. Each plot is in agreement with or larger value than this line. The solution, which remained on the outside of the mesopores of WSS, caused these larger supported amounts.

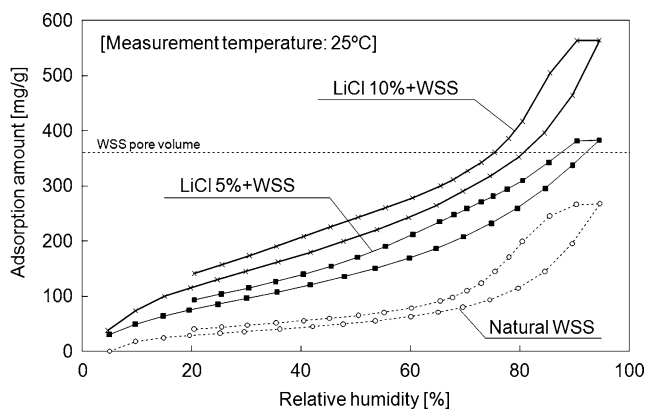
Figure 6 shows the measured log differential pore volume distributions of a LiCl-supported WSS at 5wt% (LiCl 5%+WSS), a LiCl-supported WSS at 30wt% (LiCl 30%+WSS), a  $\text{CaCl}_2$ -supported WSS at 5wt% ( $\text{CaCl}_2$  5%+WSS) and a NaCl-supported WSS at 5wt% (NaCl 5%+WSS), compared with a distribution of natural WSS. The pore volume distributions were calculated by BJH method. Table 1 summarizes the physical properties of each chloride-supported WSS. These are the specific surface area by BET method, and the pore volume and the average pore diameter by BJH method. The pore volume around the pore diameter of 8 nm decreased by impregnating with LiCl solution. From this result, LiCl was in the pores in the range

**Table 1** Specific surface area, pore volume and average pore diameter of chloride-supported WSS

	WSS	WSS + LiCl				WSS + CaCl <sub>2</sub>		WSS + NaCl	
		5%	10%	20%	30%	5%	10%	5%	10%
Supported amount [mg/g]	0	34	58	120	225	36	83	36	70
BET specific surface area [m <sup>2</sup> /g]	149	124	134	120	88	119	101	129	128
BJH Pore Volume [cm <sup>3</sup> /g]	0.37	0.33	0.35	0.32	0.24	0.33	0.32	0.33	0.34
Average pore diameter [nm]	9.9	10.7	10.6	10.7	11.1	11.1	12.6	10.3	10.5



(a)

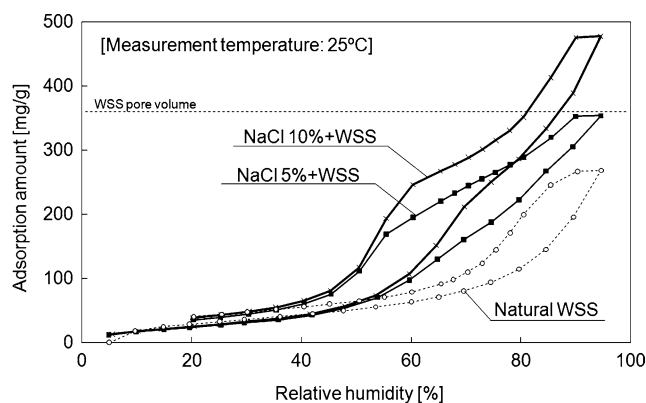
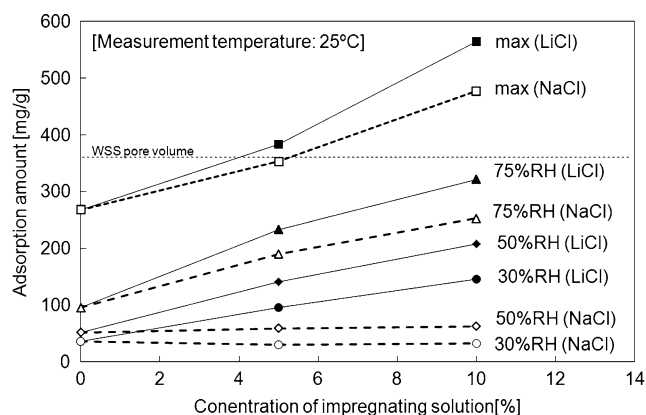


(b)

**Fig. 7** Adsorption isotherms of LiCl-supported WSS (a) and (b) is extracted from (a), isotherms which impregnating concentrations are 5 and 10wt%

from 5 to 10 nm. The specific surface area and the pore volume decreased as the impregnating concentration increased. On the other hand, the average pore diameter increased with the impregnating concentration. Furthermore, the differential between LiCl and CaCl<sub>2</sub> wasn't found. When NaCl was supported on WSS, the decreased pore volume around the pore diameter of 6 nm was smaller than LiCl or CaCl<sub>2</sub>. It indicated that each chloride salt was supported into the pores.

The water vapor adsorption isotherms of the LiCl-supported WSS were shown in Fig. 7 and these of the NaCl-


**Fig. 8** Adsorption isotherms of NaCl-supported WSS

**Fig. 9** Adsorption amount changes as a function of concentration of impregnating solution on LiCl-supported WSS and NaCl-supported WSS

supported WSS were shown in Fig. 8. Figure 7(b) shows the extracted data from Fig. 7(a). Figure 9 shows how the adsorption amount changes with the concentration of the impregnating solutions at the points of 30, 50, and 75%RH and the maximum amount.

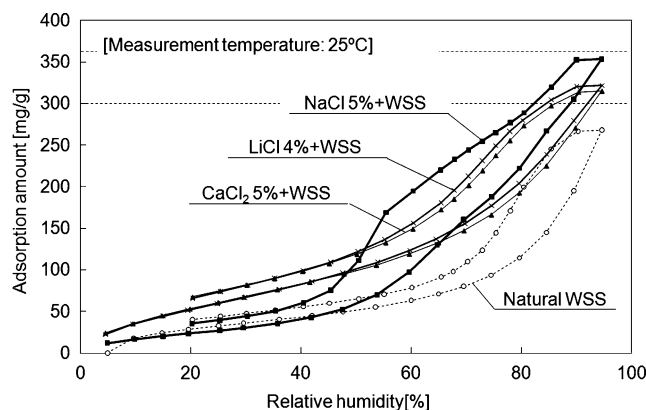
As shown in Fig. 7(a) and (b), the adsorption amount increased with increasing of the impregnating concentration. The LiCl 5%+WSS adsorbed 200 mg/g of the water vapor in the relative humidity range from 60 to 90%. This amount was same as that of natural WSS. On the other hand, in the

relative humidity range from 30 to 60%, the LiCl 5%+WSS could adsorb about 175 mg/g of the water vapor. It was confirmed that LiCl improved the adsorption performance of WSS in less than 60% range of the relative humidity. The  $\text{CaCl}_2$ -supported WSS had similar tendency.

Figures 8 and 9 show that the water vapor adsorption amount of NaCl-supported WSS increased sharply over 50%RH, while that of LiCl-supported WSS increased linearly. The adsorption amount of NaCl 5%+WSS was 120 mg/g and that of NaCl 10%+WSS was 175 mg/g, respectively, in the relative humidity range from 50 to 70%, although that of natural WSS was 25 mg/g.

These results indicate that NaCl could improve the water vapor adsorption ability of natural WSS in the relative humidity range 50 to 70%. It is concluded that a characteristic of the absorption isotherm of NaCl is an important factor. Figure 4 illustrates the absorption isotherms of the chloride salts. NaCl starts to absorb the water vapor rapidly over 75% of the relative humidity. From this characteristic, it is assumed that a mechanism of the adsorption on NaCl-supported WSS may be assumed as the followings: first, the mesopores of WSS adsorb water vapor. Second, the water vapor inside of the pores condenses by the capillary condensation. Finally NaCl which exists in pores absorb this water. On the other hand, LiCl or  $\text{CaCl}_2$  start to absorb and deliquesce in preference to the adsorption by the mesopores of WSS when the deliquescent material exists in the pores. These different mechanisms may be established from the further experiments in a later paper.

On the other hand, it was observed that the excess supporting of the chloride caused the elution of the chloride solution from the mesopores to the surface of WSS. The LiCl 30%+WSS, whose maximum water adsorption amount was 1890 mg/g, lead the elution after an exposed test at 23°C, 75%RH condition and its surface was obviously wet compared to the natural WSS. It is clear that the elution causes the carryover problem. To solve this problem, we propose to determine the appropriate concentration of the impregnating chloride solution based on the following assumptions: (1) the all of adsorbed water condenses inside the mesopores under the high humidity condition, (2) the density of the condensed water inside the mesopores is 1.0 g/cm<sup>3</sup>, (3) the maximum water adsorption amount of the porous material, which adsorbs water vapor in its mesopores by the physical adsorption, is equal to its mesopore volume. The chloride solution may be eluted from the mesopores from these assumptions when the maximum water adsorption amount of the chloride-supported material exceeds the mesopore volume. From this point of view, the appropriate impregnating concentration was determined according to the maximum water adsorption amount and its mesopore volume. As shown in Table 1, the mesopore volume of the chloride-supported WSS is between 0.30 and 0.36 cm<sup>3</sup>/g. Figure 10



**Fig. 10** Adsorption isotherms of chlorides-supported WSS with the appropriate impregnating concentration

shows the water vapor adsorption isotherms of the chloride-supported WSS with the appropriate impregnating concentration. The appropriate concentration for LiCl was determined as 4wt%, and these for  $\text{CaCl}_2$  and NaCl were determined as 5wt%, respectively. The maximum adsorption amount reached between 300 and 360 mg/g by supporting with chlorides.

From these results, a desiccant filter, which contains WSS supported with LiCl and NaCl, has been developed and evaluated.

## 4 The adsorption/regeneration test on desiccant filters

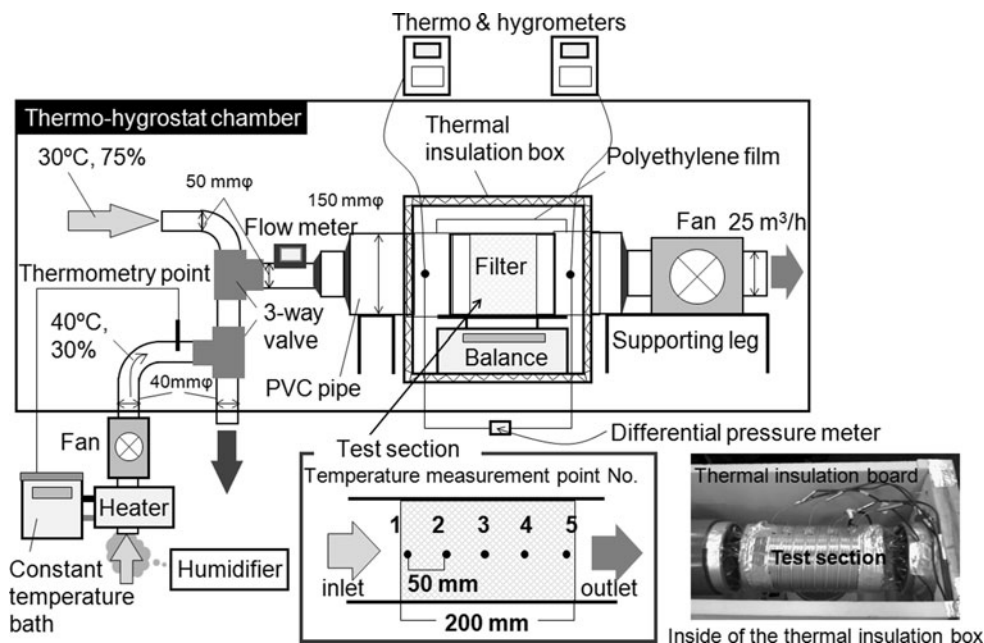
### 4.1 Experimental condition and materials

A short-term cyclic ventilating test was carried out to evaluate the adsorption/regeneration performance of two honey-combed filters including WSS and other compared filters as listed in Table 2.

Experimental apparatus of this test is illustrated in Fig. 11. A high stability controlled air temperature and relative humidity environment chamber was used to carry out this experiment. The chamber dimensions were 1670 mm in width, 3470 mm in length, and 2200 mm in height. The experimental conditions are shown in Table 3. The chamber maintained 30°C, 75%RH air as the adsorption air. This air simulated the average climate condition in the daytime of summer in Tokyo. On the other side, the regenerating air was produced at 40°C, 30%RH by heating and humidifying the air of the chamber's outside (experimental room). The regenerating condition simulated the return-air from the room (26°C, 60%RH) heated to 40°C by using the exhaust heat of the heat pump. The adsorption process was for 60 minutes and the regeneration process was for 30 minutes. Before starting the test, the filter was dried by the airflow of the regenerating condition.

**Table 2** List of tested filters

		Base material	Adsorbent	Weight
A:	WSS filter	Synthetic fiber	WSS	618 g
B:	WSS + chlorides filter	Synthetic fiber	WSS + LiCl + NaCl	666 g
C:	Silica gel filter	Synthetic fiber	Silica gel	608 g
D:	Zeolite filter		Sintered zeolite	893 g

**Fig. 11** Experimental apparatus of the adsorption/regeneration test**Table 3** Air conditions for the experiments

	Adsorption process	Regeneration process
Temperature	30°C	40°C
Relative humidity	75%	27%
Absolute humidity	20 g/kgDA	12 g/kgDA

An apparatus for air-flowing channel adopted batch-type flow and two inlet channels to switch the adsorption air and the regeneration air, respectively with two automatic three-way solenoid valves in the chamber. The main ducts connecting to the test section were composed of PVC (polyvinyl chloride) pipe and its diameter was 150 mmφ. One of the inlet channels' diameter was 50 mmφ for leading air from the chamber for the adsorption, and the other's was 40 mmφ in order to lead air from the outside of the chamber for the regenerating condition.

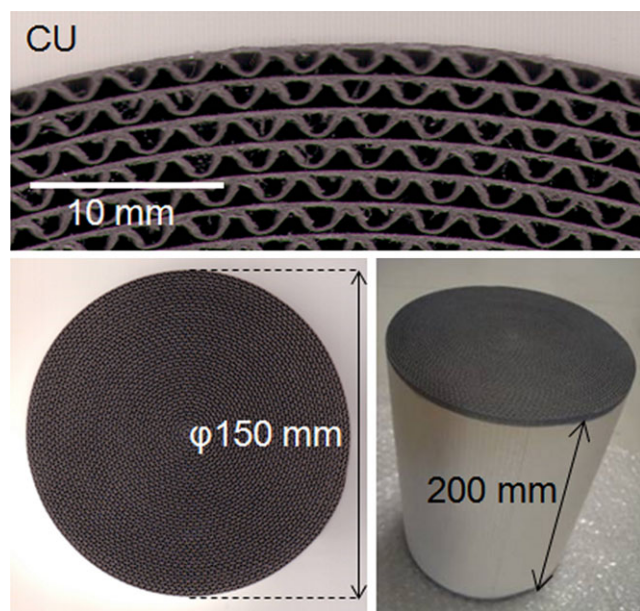
The velocity of air flow was determined with a ventilator connected at the end of the channel. Air flow was generated by a sirocco type fan and adjusted to the desired speed by an adjustable frequency inverter. A sirocco type fan extracted air. Flow rate was ensured with a digital flow meter.

Temperature, relative humidity and absolute humidity of air, at the point before and after the filter, were measured and logged with thermo and hydrometers at one minute intervals. The material temperatures of each filter were measured. These were measured at five points by using five thermocouples at intervals of 50 mm along the length of the filter. The data of the material temperature were recorded with a digital logger at five seconds intervals.

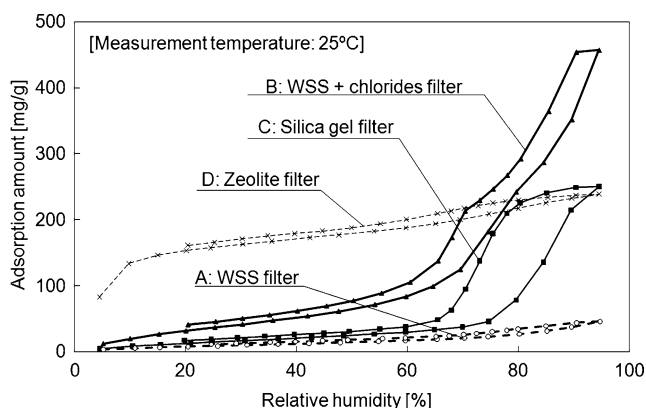
The weight changes of each filter were measured with the digital balance. The filter was put in the aluminium pipe of the same diameter as a test section. The polyethylene film was used for the joints of the test section and the PVC pipes to measure only the weight change of the filter. This test section was put on a digital balance in order to transfer the weight data to a personal computer at two seconds intervals. In addition, the test section and the digital balance were surrounded with the thermal insulation box of 25 mm in thickness to prevent the effect of the air current and temperature of the chamber.

The flow rate was set at 25 m³/h. In this time, the effective air face velocity was 0.49 m/s.

The tested filter has been made from original paper. This paper contained synthetic fibers and WSS powder which average particle diameter was 3.1 μm. The paper was impregnated with LiCl and NaCl. This paper's thickness is 200 μm,



**Fig. 12** Apparent pictures of WSS filter



**Fig. 13** Adsorption isotherms of tested filters

weight is  $50 \text{ g/m}^2$ , and WSS content is 40wt%. This paper was corrugated and formed as a honeycombed filter. This filter's diameter is  $150 \text{ mm}\phi$ , the length is 200 mm, and the cell density is  $31 \text{ cells/cm}^2$ . The appearance pictures are shown in Fig. 12. As compared with the WSS + chlorides filter, A: WSS filter without chlorides, C: a silica gel filter, which is made from a kind of type-B silica gel, and D: a zeolite filter were also tested. The characteristics of these materials are shown in Table 2. Filters were prepared by ventilating the constant air at  $40^\circ\text{C}$  and 27%RH for two hours until the weight stayed constant before the examination started.

Figure 13 shows the adsorption isotherms of the tested filters. On the WSS + chlorides filter and the silica gel filter, the amounts of adsorption increased within the range of high relative humidity, 70% or more. The maximum adsorption amounts were  $457 \text{ mg/g}$  and  $251 \text{ mg/g}$ , respectively. In the relative humidity range from 30% to 75%, the water va-

por adsorption amount of WSS + chlorides filter was about  $100 \text{ mg/g}$  and that of the silica gel filter is  $29 \text{ mg/g}$ . In contrast, the zeolite filter started adsorbing more than  $100 \text{ mg/g}$  of the water vapor at the low relative humidity under 10%. However the increase of the adsorption amount according to the relative humidity was small. The maximum adsorption amount was  $239 \text{ mg/g}$ . The adsorption amount between 30 and 75% of the relative humidity was  $45 \text{ mg/g}$ .

## 4.2 Results and discussions

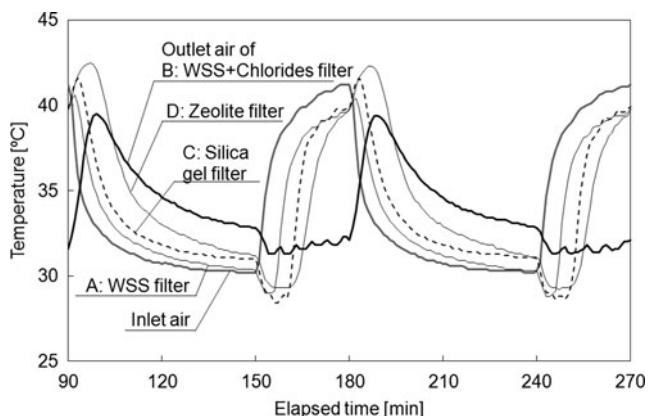
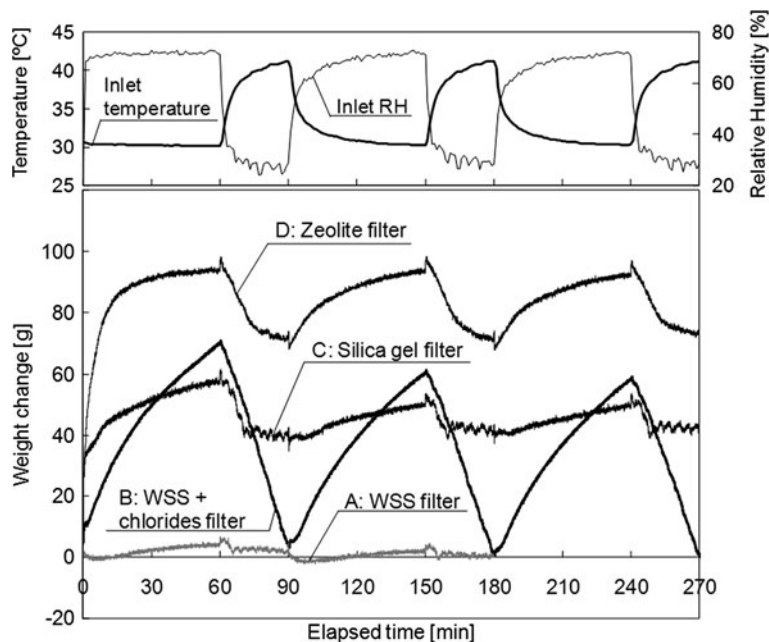
Figure 14 results the weight changes on four filters from three continuous cycles for 270 min. The weight of each filter was changed cyclically according to variation in the inlet condition.

The WSS + chlorides filter adsorbed about 59 g of water vapor per one hour in the first cycle. The adsorption amount over the flow rate was  $2.4 \text{ g/m}^3$ . Adsorption occurred for 60 minutes. Further the WSS + chlorides filter could desorb the same amount of the adsorption by  $40^\circ\text{C}$  air for 30 minutes. It was ensured that the desorption speed was twice as the adsorption speed. Moreover, it adsorbed and desorbed  $60 \text{ g/h}$  ( $2.4 \text{ g/m}^3$ ) stably in the second and third cycle. The adsorption amount over the filter's dry weight ( $666 \text{ g}$ , shown in Table 2) was  $90 \text{ mg/g}$ .

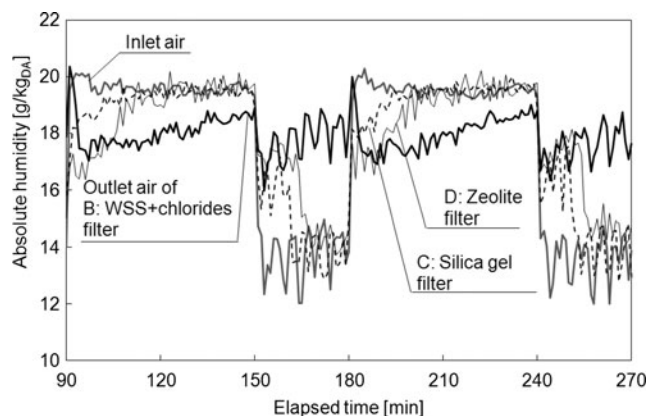
From the adsorption isotherm shown in Fig. 13, the adsorption capacity between 30 and 75% of the relative humidity was predicted as  $100 \text{ mg/g}$ . Therefore, the WSS + chlorides filter adsorbed about 90% of the adsorption capacity under these experimental conditions. The highest value can be expected to increase like the zeolite filter if the adsorption process is longer.

In contrast, the silica gel filter and zeolite filter adsorb much water vapor in the adsorption process of the first cycle. However, they couldn't desorb the water vapor under the regenerating condition at  $40^\circ\text{C}$ . In the second and third cycle, the silica gel filter adsorbed  $10 \text{ g/h}$  ( $0.4 \text{ g/m}^3$ ,  $16 \text{ mg/g}$ ) of the water vapor in the adsorption process. The regeneration finished within 10 minutes because the amount which the silica gel filter could desorb was limited to 10 g. The final weight of silica gel filter was higher than that of WSS + chlorides filter, however the adsorption amount of silica gel filter at 27% in Fig. 13 was less than that of WSS + chlorides filter. The adsorption isotherms in were obtained from the steady state, which the water vapor partial pressure was rigorously controlled for the stable adsorbed and desorbed water vapor amount with long measuring time. On the other hand, these final weights were obtained under the short-term cyclic condition. Furthermore, the adsorption heat of WSS + chlorides filter is  $2550 \text{ kJ/kg}$ , which is calculated according to Clausius-Clapeyron equation from the water vapor adsorption isotherms at the different measurement temperatures, and that of silica gel filter is  $3600 \text{ kJ/kg}$ . From

**Fig. 14** Results of weight changes on the adsorption/regeneration test under the air flow rate was 25 m<sup>3</sup>/h



**Fig. 15** Results of measured outlet temperature after air passed through each filter compared with inlet temperature



**Fig. 16** Results of measured outlet absolute humidity after air passed through each filter compared with inlet absolute humidity

these reasons, silica-gel filter needs the higher regeneration temperature and the lower humidity ratio to complete the desorption of the water vapor in 30 minutes compared to WSS + chlorides filter. The zeolite filter adsorbed 25 g/h (1.0 g/m<sup>3</sup>, 28 mg/g) in the second and third cycle. The increase ratio of the adsorption amount became smaller since 30 minutes passed. It is estimated that the amount of adsorption of the zeolite filter approaches the saturated condition. An original adsorption performance of the zeolite couldn't be demonstrated, because the regeneration temperature at 40°C was too low for the zeolite to desorb all the water vapor existed in pores.

The original WSS filter adsorbed less than 5 g/h (0.2 g/m<sup>3</sup>, 8 mg/g) of the water vapor at both first and second cycle. It was confirmed that supporting with chlorides

was effective for the performance improvement of the original WSS filter.

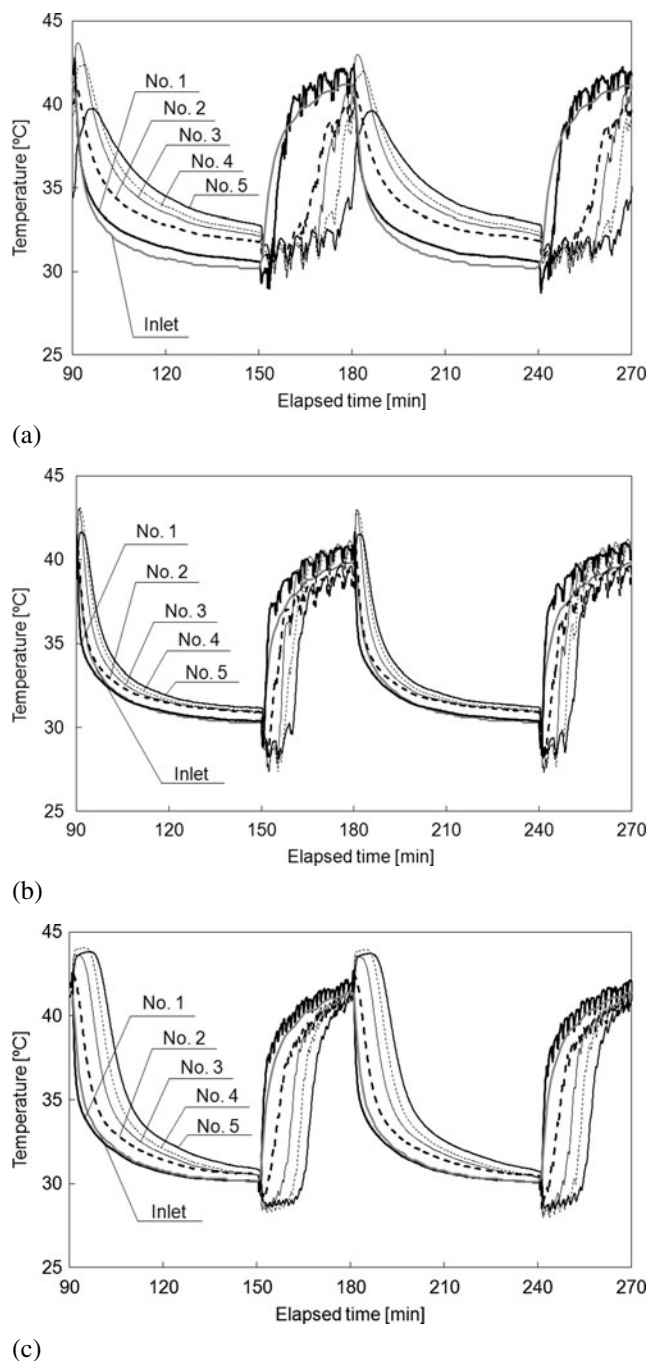
Next, the outlet temperature and absolute humidity data after the air passed through each filter in the second and third cycle are shown in Figs. 15 and 16, respectively. The outlet temperatures of each filter were also changed cyclically according to variation in the inlet condition. The outlet temperature rose up because the water vapor adsorption was the exothermic reaction at the beginning of the adsorption process (at 0 min and 90 min in the elapsed time), and then it decreased with duration. On the other side, the outlet temperature decreased with the endothermic reaction occurred by desorption when the inlet air condition was switched to that of the regeneration process (at 60 min and 120 min in the elapsed time). It followed the increase of the inlet temperature with duration.

When the air of 30°C, 75%RH passed in the adsorption process, a maximum point of the outlet temperature after the air passed through the WSS + chlorides filter was 40°C. This temperature was the lowest among the outlet temperatures of all the filters. The outlet temperature decreased gradually with following the inlet air temperature after reaching the maximum temperature. At the end of the adsorption process, the temperature difference between inlet and outlet remained 3°C. This means that the WSS + chlorides filter continued to adsorb the water vapor for 60 minutes. The outlet absolute humidity of the WSS + chlorides filter was 3 g/kg<sub>DA</sub> lower than the inlet value at the beginning, and gradually increased. The silica gel filter's outlet temperature approached the inlet temperature after it reached 42°C. Because the adsorption amount of the silica gel filter was small, then the heat generation was also small. After reaching the maximum temperature, the outlet temperature decreased immediately to the inlet temperature. The outlet temperature of the zeolite filter was the highest. It rose up to 43°C in the maximum. The temperature change following the inlet temperature was observed about 7 minutes later of the switching points at 0 min and 90 min. The reduction of temperature at 60 min and 120 min in the elapsed time continued for 12 minutes. The difference of the inlet and outlet absolute humidity was measured for 15 minutes from the beginning of the adsorption.

In the regeneration process, the outlet air temperature of the WSS + chlorides filter was kept at around 32°C, because desorption kept occurring for 30 minutes. The wavy line was caused from the on-off control of the heater and the dehumidifier in Fig. 11, so the outlet air temperature during the regeneration process reflected the influence of the inlet air temperature and humidity condition. The outlet absolute humidity of the WSS + chlorides filter was also almost as almost constant as the outlet temperature. On the other side, the outlet temperatures of the silica gel filter and the zeolite filter decreased and reached 29°C and 28°C, respectively because of the endothermic reaction. These temperatures followed the inlet air condition after desorption was finished. The outlet absolute humidity of the silica gel filter was lower than that of the inlet at the beginning of the adsorption. The difference between the inlet and the outlet was getting smaller for 20 minutes. Because the silica gel filter didn't adsorb the water vapor any more afterwards, the outlet absolute humidity was in agreement with the inlet value.

The outlet temperature of the WSS filter showed the similar tendency to the silica gel filter because the amount of the adsorption by WSS filter was also quite small. Moreover, the data of the outlet absolute humidity after throughout the WSS filter was omitted from Fig. 15 because the difference between the inlet absolute humidity was quite small.

The small adsorption heat of natural WSS causes the low outlet temperature of the WSS + chlorides filter. The adsorption heat of natural WSS is 2460 kJ/kg, at the same level



**Fig. 17** Results of measured material temperatures of (a) WSS + chlorides filter, (b) silica gel filter and (c) zeolite filter

as the condensation heat of water vapor. However, the adsorption heat resulted from the chlorides in the pores caused the temperature rise.

Figure 17(a) shows the measured material temperatures of the WSS + chlorides filter. Temperature at No. 1 decreased gradually with following the inlet air temperature after reaching 43°C at 0.6 min in elapsed time. Other points' maximum temperatures were as follows, No. 2: 41°C at 1.1 min, No. 3: 44°C at 1.7 min, No. 4: 42°C at 2.3 min,

and No. 5: 40°C at 6.7 min. This temperature rising was attributed to the adsorption heat of WSS and chlorides. The temperature difference between Nos. 1 and 5 showed that adsorption occurred with the time difference as a function of distance from the inlet side. It took longer time for adsorption and desorption at points that were further from the inlet side. On the regeneration process (at 60–90 min and 150–180 min of the elapsed time), the differences by the position appeared obviously. The temperature at No. 1, which was nearest to the inlet, followed the inlet air temperature in a few minutes. However, the temperature at other points rose up after more than 10 minutes passed. The material temperature at No. 5 started increasing when the inlet air condition was switched. On the other hand, the material temperature of the silica gel filter and the zeolite filter shown in Fig. 17(b) and (c), respectively, varied more rapidly than that of the WSS + chlorides filter, because the water vapor amounts of adsorption and desorption by these filters were small.

It is concluded that this WSS + chlorides filter's adsorption amount was the largest and could be regenerated by 40°C air under this experimental condition. This result suggested that the exhaust heat at about 40°C can be utilized.

## 5 Conclusion

In this paper, Wakkanai siliceous shale was introduced as a natural mesoporous material to develop a new desiccant filter. To improve this shale's performance to adsorb/desorb the water vapor, lithium chloride, calcium chloride or sodium chloride was supported into the pores of the shale by impregnating with each chloride solution. It was clarified that the characteristics on the water vapor adsorption were different between NaCl-supported shale and the deliquescent-material-supported shale. Especially NaCl was effective to increase the water vapor adsorption amount 5–7 times of that of natural shale in the relative humidity range from 50 to 70%. Moreover, the appropriate impregnating concentrations were determined from the relationship between the maximum water vapor adsorption amount and the mesopore volume. Therefore, we can solve the carryover problem of the chloride impregnation.

Based on these results, a new desiccant filter made from the original paper, which contains the shale powder in the synthetic fibers supported with LiCl and NaCl, has been developed. The dehumidification performance of this filter was evaluated under the simulated summer condition in Tokyo. Filters which made of silica gel and zeolite were compared. From the cyclic adsorption/regeneration test, this shale filter impregnated with chlorides could adsorb and desorb 60 g/h of the water vapor repeatedly at the regeneration temperature of 40°C. On the other hand, a silica gel filter and a zeolite filter adsorbed and desorbed only 10 g/h and 25 g/h,

respectively. These results suggested that the shale impregnated with the chlorides has the best dehumidification ability as a new desiccant material. Further, the desiccant filter made from the shale will achieve the effective use of the low temperature exhaust heat. This filter will contribute to improve the performance of the desiccant system and spread the system as effective air-conditioning equipment.

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