12th IEA Heat Pump Conference 2017

Study on Adsorption Heat Pump using Natural Mesoporous Material impregnated with chloride component

Junya Togawa[a]*, Makoto Nakamura[b], Katsunori Nagano[b], Takuya Matsumoto[a], Seiya Omae, Hiroaki Kuroishi[a], Katsuhiko Harada[a]

[a]*Nihon Netsugen System Co. Ltd., 2-10 Ichigayahonmura-cho Shinjuku-ku Tokyo, 162-0845 Japan*
[b]*Hokkaido University, Kita 13 Nishi 8, Kita-ku, Sapporo, 060-8628, Japan*

Abstract

This study is a development of adsorption heat pump using a natural meso-porous material, which called Wakkanai siliceous shale (WSS). At first, to increase the water sorption property, the WSS powder impregnated with various chloride components were prepared. Water sorption property against the water vapor pressure was evaluated at the sorption and regeneration temperature conditions. From these results, the lithium chloride was chosen for the WSS composite material. To evaluate the cooling performance, the adsorbent powder of the composite materials with WSS and LiCl was filled in the aluminum fin gap on the small heat exchanger. From the experimental results, the cooling water of 15 °C was obtained at the 80 °C of the regeneration temperature, and the specific cooing power against the adsorbent weight and COP cooling was 360 W/g and 0.31, respectively.

© 2017 Stichting HPC 2017.
Selection and/or peer-review under responsibility of the organizers of the 12th IEA Heat Pump Conference 2017.

Keywords: Type your keywords here, separated by semicolons ;

1. Introduction

From the view point of the effective utilization of renewable energy, the adsorption heat pump cooling systems (AHP) have been attracted. This system can be produced the cooling energy for space cooling by using heat sources less than 100 °C, which was obtained by the waste heat or the solar thermal energy. However, the diffusion of AHP system in the market is slight compared with the absorption heat pump system. To expand the marketability, the enhancement of the cooling performance, cost reduction and compact design are required.

Nowadays, to improve the adsorbent performance, a novel zeolite type adsorbent such as AQSOA has been studied [1,2]. However, the adsorbent is extremely expensive for the reason of the higher synthesis cost and slight demand for the industrial process [3]. Therefore, some commercial product of AHP system with AQSOA adsorbent has been developed, but the price of AHP is about 3 times higher than the conventional air conditioning system. The price of AHP unit is strongly depended on the adsorbent cost. For selling expansion, the adsorbent cost reduction was required.

As one possible solution for the reduction of the adsorbent cost, the composite materials, which were made by the combination with the porous materials such as mesoporous silica gel and salts ($CaCl_2$, $LiNO_3$ and $Ca(NO_3)_2$ have been proposed [4-7]. It was concerned that these composite materials has the risk of the long term stability and corrosion by the salt. From our previous work [8], it was observed that the pores size of silica gel was expanded by the impregnation of 5 wt % NaCl solution. This result indicates that the stability of the silica gel

* Corresponding author. Tel.:+81-11-706-6287; fax: +81-11-706-6286.
E-mail address: togawa@netsugen.com.

with chloride component may not be expected against the long term utilization accompanied with the hydro-thermal cycling, because the silica gel pore formed by the gap of amorphous SiO2 particles was broken by the chloride solution.

From our related study of desiccant rotor development, it was demonstrated that the natural mesoporous material, which has the stable pore structure formed by the hard crystalline gap, is suitable as the porous media for the impregnation of the chloride component [9]. In this paper, to develop the composite material for achieving the high water sorption ability, high stability and low cost, it was prepared by impregnating LiCl into the natural mesoporous material of Wakkanai siliceous shale.

2. Material and method

2.1. Wakkanai siliceous shale (WSS)

Wakkanai siliceous shale (WSS) is a natural mesoporous rock, which is produced in Soya area, the northernmost part area of Hokkaido in Japan, as shown in Fig. 1(a). It is naturally derived from diatoms and planktonic organisms. The chemical components are mostly SiO_2. From the scanning electron microscope (SEM) pictures of Fig. 1(b), a scale-like crystalline Opal-CT can be observed.

Fig. 2 shows the log differential pore volume distributions obtained by the nitrogen adsorption at the liquid nitrogen temperature of 77 K. The distribution of the pore diameter is the mesoporous size from 4 to 20 nm, the measured specific surface area derived from the Brunauer, Emmett and Teller (BET) method is 149 m^2/g, and the pore volume calculated by Berret, Joyner and Halenda (BJH) method is 0.30 cm^3/g. This mesoporous structure has been formed by the gap between the Opal-CT crystals as shown in Fig. 1(b). The total pore volume including the mesopore and macropore obtained by the mercury intrusion porosimeter is 0.64 cm^3/g.

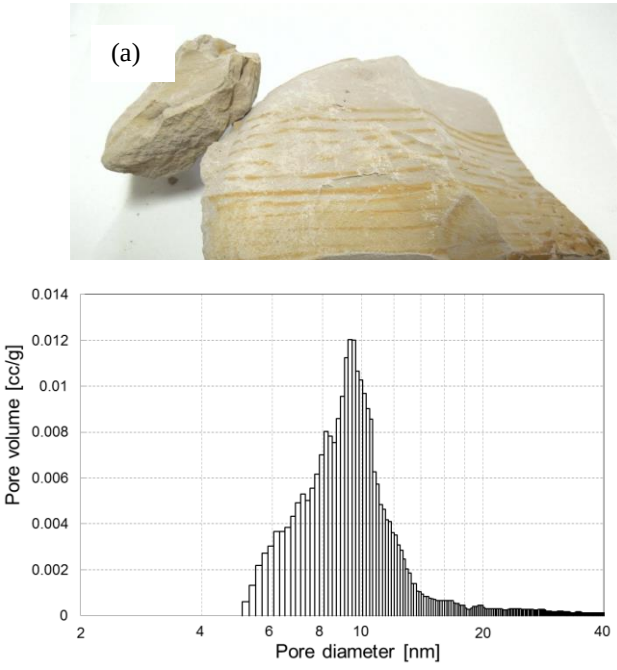


Fig. 2 Pore size distribution of WSS

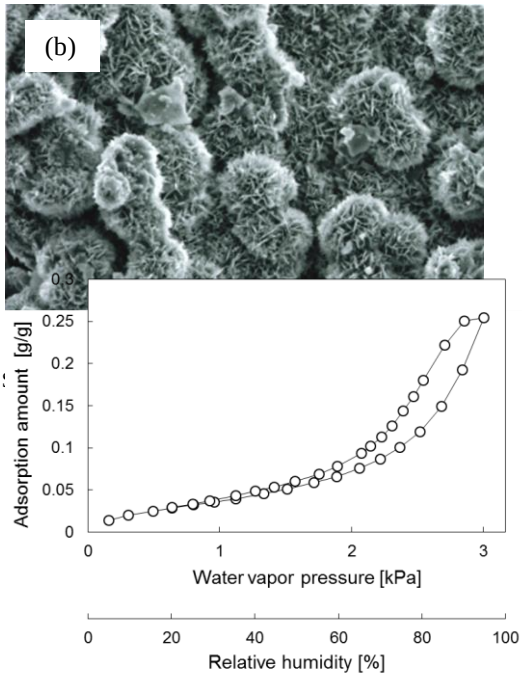


Fig. 3 water adsorption isotherm of WSS micro powder

In this study, to make the composite adsorbent with chloride for the AHP, the WSS micro powders obtained by dry type ultra-fine mill machine were prepared. The particle size distribution of WSS micro powders was 0.5 – 20 μm and the average diameter was 5 μm. Fig. 3 shows the water vapor adsorption isotherms of WSS micro powder against the water vapor pressure and the relative humidity at 25 °C. The amount of water vapor adsorption increases rapidly when the relative humidity of air becomes higher than 60%. The maximum adsorption amount reaches 0.27 g of water amount over the dry weight of WSS powder. However, in the AHP system, the water adsorption amount under 2.3 kPa is important by the reason of the evaporation temperature. The adsorption amount of water under the low vapor pressure of 2.3 kPa is about 0.10 g/g.

2.2. Preparation of the composite materials

LiCl and LiBr were used as absorbent for the composite materials. It was prepared by following procedures.

1) The WSS micro powders were dried at 150 °C in an oven for 24hr, and then dry WSS powder was obtained.

2) The designated amount of LiCl and LiBr are taken, respectively. The aqueous solutions are prepared by the dissolve in appropriate amount of water.

3) The dry WSS powders were soaked into the aqueous solution of LiCl and LiBr, respectively.

4) The slurry was vacuumed in a vacuum container to 3.14 kPa and keep for 1 hour.

5) The slurry was dried in the oven at 150 °C for approximately 24 hours until the dry composite materials were obtained. The 20 wt % and 40 wt % of composite materials is obtained for this work.

2.3. Preparation of the heat exchanger with adsorbent

Figure 4 (a) showed the corrugated fin type aluminum heat exchanger for the AHP test. The dimension of heat exchanger is 150mm× 120mm×15mm (0.36 L). The slurry of the WSS + 20 wt% LiCl directly filled into the corrugated fin as shown Figure 4. The amount of adsorbent filled in the heat exchanger (m_{dry}) is about 110g and the density of adsorbent is 305 g/L. Before the experiment test of AHP, the heat exchanger with adsorbent put in the oven, and keeps for over 48 hour at 100 °C.



Fig. 4 aluminum heat exchanger and the WSS-20wt%LiCl filled heat exchanger

2.4. Description of the experimental setup

Schematic drawing of the experimental setup is illustrated in Fig. 5. Main component consist of three vessels of the adsorber, evaporator and condenser, which are made by the stainless steel. The adsorber is connected to the evaporator and condenser. Heat exchanger with adsorbent is placed in the adsorber, which has volume of 4 L. Hot water for the regeneration and cold water for the cooling were alternately supplied into the heat exchanger by using three way valves.

Heat exchanger for evaporator, the size of which is 80mm × 90mm × 20mm, is placed in the bottom of the evaporator (2L in volume). For the evaporation of water, 80ml distilled water previously is put in the vessel. The decreased water by the evaporation, the amount of which is estimated by the heat of evaporation, is directly supplied into the vessel by using a 20ml syringe during the regeneration period. To take the cold water from the evaporator, the constant temperature of 20 °C is supplied into the heat exchanger from the cold water bath controller.

A spiral coil tube made by the stainless steel convoluted flexible tube (1/4 inches in diameter and 96 inches in length) is used for the condenser. The constant temperature of 30 °C is supplied into the coil. The flow rate of

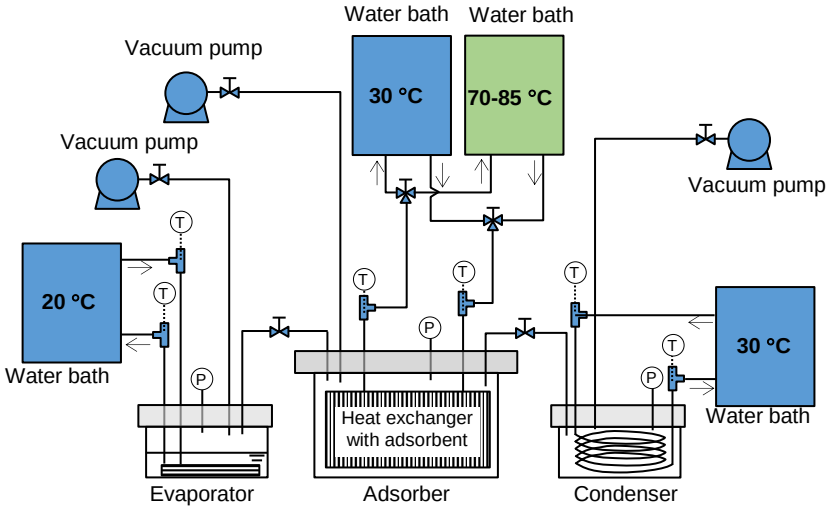


Fig. 5 Schematic drawing of the experimental setup for cooling test in this study

supplied water is measured by the flow sensor, and the inlet and outlet temperature are measured by PT100 platinum resistance thermometers. All of data is recorded by the data logger.

2.5. Evaluation of the cooling power and COP cooling

The cooling power (P_c) was calculated by the difference of water temperature between the inlet and outlet of the heat exchanger in evaporator and the flow rate of water according to Eq. 1. t_{evp} indicates the operation time of evaporation period. The regeneration power (P_h), which was contains the heat of preheating ($P_{p.h}$) for the heat exchanger with adsorbent and desorption heat (P_{des}) of adsorbed water by the heating, was calculated by the Eq. 2. t_{reg} indicates the operation time of preheating and desorption periods by heating. The cooling COP was obtained by the ratio of the cooling power to the heating power, as shown Eq. 3.

$$P_c = \int_o^{t_{evp}} q_{evp}\rho_w c_w\left(T_{in,evp} - T_{out,evp}\right)dt \quad (1)$$

$$P_h = P_{p.h} + P_{des} = \int_0^{t_{reg}} q_{reg}\rho_w c_w\left(T_{in,reg} - T_{out,reg}\right)dt \quad (2)$$

$$COP = \frac{P_c}{P_h} \quad (3)$$

The specific cooling power is calculated by the adsorbent amount and total cycle time as shown in Eq 4.

$$\mathrm{SCP} = \frac{P_C}{m_{dry} \cdot t_{cycle}} \quad (4)$$

3. Results and discussion

3.1. Evaluation of water sorption isotherms

The water vapor sorption isotherms of the composite materials were evaluated at the 25 °C by using the water vapor sorption analyzer of a Hydrosorb (Quantachrome instruments). The sorption isotherms of WSS + LiCl and WSS + LiBr composites were plotted in the Fig.6, respectively. In the AHP system, as the desired evaporation temperature is from the 7 to 15 °C, it is desirable that the sorption amount of water vapor shows higher values between 1.0 and 1.7 kPa of the saturated vapor pressure, which corresponding to the evaporate temperature. The

shape of the each isotherm curves at the same amount of chloride component was very similar. However the sorption amount of WSS + LiCl was two times higher than the WSS + LiBr at the water vapor pressure range of 1.0 -1.7 kPa. The maximum sorption amount (Q_{max}) of WSS + 40 wt% LiCl and WSS + 20wt % LiCl at 1.7 kPa gave 0.94 and 0.48 g/g, respectively. From this result, WSS + LiCl was chosen as the composite material for the adsorbent in the AHP system.

In addition, to evaluate the residual amount (Q_{res}) of adsorbed water at the regeneration condition, the water vapor sorption isotherm at 80 °C was measured as shown in Fig. 7, compared with the results of 30 °C. The sorption amount was decreased compared with the low temperature condition. If it was assumed that the residual amount after the regeneration was identical with the sorption amount at the high temperature, the Q_{res} of WSS + 40 wt% LiCl and 20 wt% LiCl, gave 0.17 g/g and 0.11 g/g, respectively.

Theoretical sorption amount in AHP system might be estimated by the differential value between the Q_{max} and the Q_{res}. When the AHP operation was performed by a following condition, the evaporation temperature (T_{evp}) = 15 °C, condensation temperature (T_{con}) = 30 °C, sorption temperature (T_{sor}) = 30 °C and regeneration temperature (T_{reg}) = 80 °C, the theoretical sorption amounts (Q_{the}) of WSS + LiCl 40wt% and WSS + LiCl 20wt% were estimated as 0.77 and 0.37 g/g, respectively.

As mentioned in the introduction, the composite materials have the problem of the corrosion of chloride. The excess sorption induced by the deliquescence of LiCl would not be desirable. In the composite materials, the porous material acts as the vessel to keep the adsorbed water in the mesopore and macropore. Taking into the account of the total pore volume (0.64 cm^3/g) and the Q_{max}, it was decided that the WSS + 20 wt% LiCl (Q_{max} = 0.48 g/g) was suitable as the adsorbent, compared to the WSS + 40wt% LiCl (Q_{max} = 0.96 g/g).

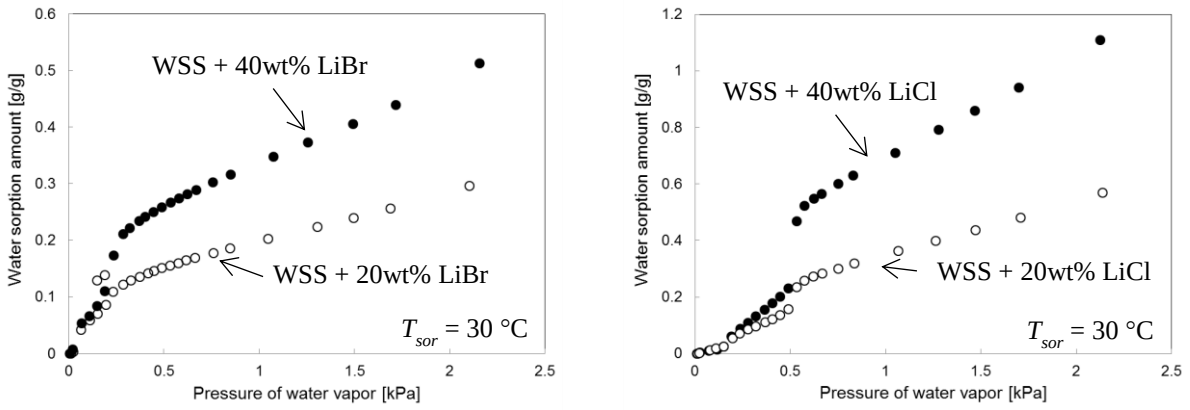


Fig. 6 Water sorption isotherms of the prepared composite materials at 30 °C.
The left graph is for the WSS + LiBr and the right graph is for the WSS + LiCl.

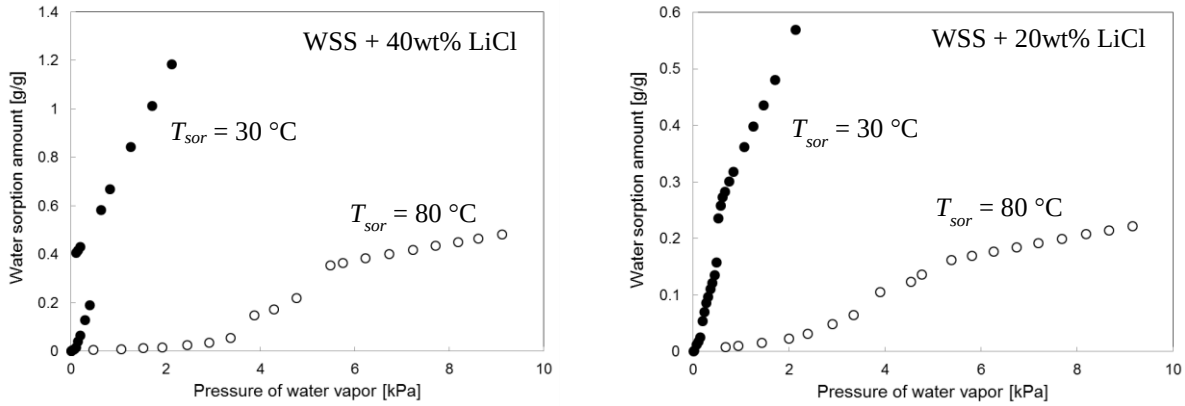


Fig. 7 Water sorption isotherms of the prepared composite materials at 25 °C and 80 °C.
The left graph is for the WSS + 40wt% LiCl and the right graph is for the WSS + 20w% LiCl.

3.2. Cooling effect of WSS-LiCl composite materials

Cycle test of the sorption and regeneration to evaluate the cooling effect was performed at the following temperature conditions, T_{reg}=80 °C, T_{con}=30 °C, T_{sor} = 30 °C, and the temperature of water supply to the heat exchanger in the evaporator is 20 °C. The flowrate of regeneration (q_{reg}) and cooling for the heat exchanger with adsorbent was 1.5 L/min.

Fig. 8 showed the cooling power and water temperature in inlet and outlet from the heat exchanger in evaporator. The flow rate of supply water (q_{evp}) was 0.26 L/min. The inlet temperature showed a constant temperature of 20 °C, and outlet temperature reached to 14 – 16 °C by the evaporation. The heat of cooling (P_c) obtained by the accumulation of the cooling power curve was 25.0 kJ and average cooling power was 83.3 W. The SCP showed 0.378 kW/kg. From the P_c and the latent heat of water vaporization (2501 J/(g·K)), the water evaporation amount was estimated as 10.0 g. The water sorption amount over the adsorbent weight gave 0.09 g/g, and the ratio of sorption amount against the Q_{the} showed 24.3%.

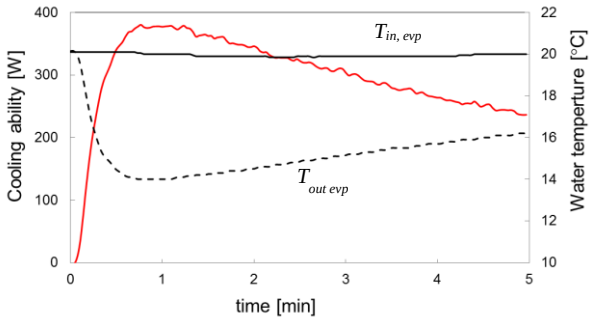


Fig. 8 Water temperature and cooling power

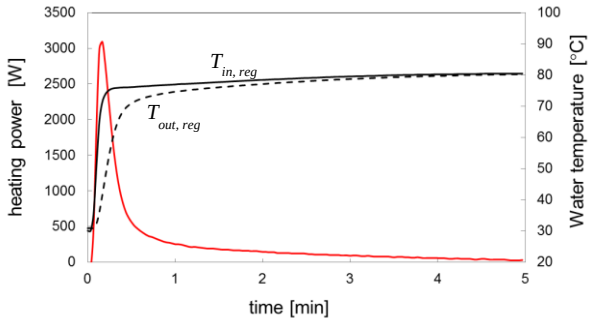


Fig. 9 Water temperature and heating power

The heating power and the temperature change of the inlet and outlet in the adsorber were as shown in Fig. 9. The heating power, which including the preheating and regeneration, was rapidly increased at the few second. After that, the heating power gradually decreased with increasing the time. The heating of regeneration (P_h) and average heating power for the regeneration were 78.5 kJ and 262 W. The COP obtained by the ratio of *Ph* to *Pc* showed 0.32.

3.3. The regeneration temperature dependency

Fig. 10 showed the SCP and COP and the average evaporation temperature (T_{evp}) obtained by the outlet of heat exchanger in the evaporator against the regeneration temperature. All of data was the average values from the 6 times cycle test. The SCP was increased with the increasing the regeneration temperature. The COP and

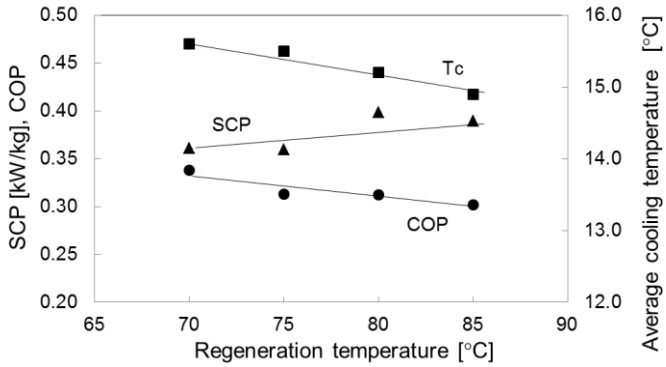


Fig. 10 SCP, COP and cooling temperature as a function of regeneration temperature.

T_{evp} showed decrease tendency against the regeneration temperature. These values of SCP, COP and T_{evp} data were summarized in Table 1, compared to the reference values of AQSOA [2]. The SCP showed 1.5 -1.6 times

higher than that of AQSOA. However, the COP of our results showed lower values of 0.3 - 0.34. The COP depends on the many factors, such as thermal conductivity and activation energy of the composite materials, heat capacity of heat exchanger and heat loss from the vessels. From our previous results [10], the activation energy of water desorption for the adsorbent of WSS with LiCl were estimated as 100 - 105 kJ/mol from the TG/DAT measurement, and the values slightly higher than that of conventional adsorbent. This COP difference may be caused by the difference of the activation energy of desorption. In addition, the heat capacity of heat exchanger and thermal conductivity of adsorbent influences the COP. To enhance the sorption performance and COP, the determination of the optimal cycle time and improvement of the thermal conductivity and water transfer in the adsorbent should be considered in future work.

Table 1 SCP, COP and average cooling temperature

Regeneration temperature [°C]	SCP [kW/kg]	COP [-]	T_e [°C]	t_{cycle} (t_{evp} - t_{reg}) [min]
70	0.335	0.34	15.6	10 (5-5)
75	0.340	0.31	15.5	10 (5-5)
80	0.360	0.31	15.2	10 (5-5)
85	0.390	0.30	14.9	10 (5-5)
80 [1]	0.235	0.44	15.0	7 (2-5)

4. Conclusions

For reducing the cost of AHP adsorbent, the composite materials with the natural mesoporous materials and LiCl has been used as the adsorbent in this study. From the evaluation of the water sorption isotherms at the low temperature and high temperature, the theoretical sorption amount were 0.77 for WSS + 40wt% LiCl and 0.37 for WSS + 20wt% LiCl, respectively. From the comparison of the maximum sorption amount and pore volume of WSS, WSS + 20wt% LiCl was chosen as the adsorbent in this study. To evaluate the cooling performance of composite adsorbent, the adsorbent filled small heat exchanger was prepared. From the cyclic test of evaporation and regeneration (80 °C) using the small heat exchanger, the SCP and COP showed 0.36 kW/g and 0.31, respectively. From the temperature dependency test, SCP was increased with the increasing the regeneration temperature.

Acknowledgements

This work was partially supported by New Energy and Industrial Technology Development Organization (NEDO).

Nomenclature

Symbols

m_{dry} : quantity of dry adsorbent [g]
C_w : specific heat of water [J/(g·K)]
P_c : heat of cooling [J]
P_h : heat of regeneration [J]
$P_{p.h}$: heat for preheating for the heat exchanger with adsorbent
P_{des} : desorption heat of adsorbed water from the adsorbent
Q : sorption amount [g/g]
q : flow rate of water supply into the heat exchanger [cm^3/min]
T : temperature [K]
t : time [s]

ρ_w : density of water [g/cm^3]

Follows subscript is for the temperature (T)
max : maximum sorption amount
res : residual sorption amount
the : theoretical sorption amount
in : inlet of heat exchanger for the evaporator / adsorber
out : outlet of heat exchanger for the evaporator / adsorber
evp : evaporation
con : condensation
sor : sorption
reg : regeneration

Follows subscript is for the time (t)
evp : time of the evaporation period
reg : time of the regeneration period
cycle : total time of evaporation and regeneration periods

References

[1] Sapienza A., Santamaria S., Frazzica A. and Freni A., Influence of the management strategy and operating conditions on the performance of an adsorption chiller, *Energy*, 2011;**36**:5532-5538
[2] Sumi H., Kurachi S., Hiroyama T., Umeda Y., Oshima K. and Kakiuchi H, Evaluation of Water-warming Characteristics of an Integrated Adsorption Heat Pump with Zeolite Absorbent, *Kagaku Kogaku Ronbun-shu* 2009;**35**:312-317.
[3] Freni, A., Dawoud, B., Bonaccorsi, L., Chmielewski, S., Frazzica, A., Calabrese, L., Restuccia, G, Characterization of Zeolite-Based Coatings for Adsorption Heat Pumps, 1st ed.; Springer; 2015
[4] Restuccia G., Freni A, Vasta S., Aristov Y.I., Selective water sorbent for solid sorption chiller: experimental results and modelling, *Int. J. Refrig*. 2004;**27**:284-293.
[5] Freni A., Russo F., Vasta S., Tokarev M., Aristov Y.I., Restuccia G., An advanced solid sorption chiller using SWS-1L, *Appl. Therm. Eng*. 2007;**27**:2200-2204.
[6] Freni A, Sapienza A, Glaznev I.S., Aristov Y.I., Experimental testing of a labscale adsorption chiller using a novel selective water sorbent "silica modified by calcium nitrate", *Int. J. Refrig*. 2012;**35**:518-524.
[7] Y.I. Aristov Y.I., Sapienza A., Ovoshchnikov D.S., Freni A., Restuccia G., Reallocation of adsorption and desorption times for optimisation of cooling cycles, *Int. J. Refrig*. 2012;**35**:525-531.
[8] Kurokawa A., Togawa J., Nabeshima Y., Nagano K., The evaluation of the moisture sorption mechanism of chloride-impregnated Wakkanai Siliceous Shale, *Kagaku Kogaku Ronbunshu* 2011;**37**:394-399.
[9] Nakabayashi S., Nagano K., Nakamura M., Togawa J., Kurokawa A., Improvement of water adsorption ability of natural mesoporous material by impregnating with chloride salts for development of a new desiccant filter, *Adsorption* 2011;**17**:675-686.
[10] Liu H., Nagano K.,Morita A., Togawa J. and Nakamura M., Experimental testing of a small sorption air cooler using composite material mate from natural siliceous shale and chloride, *Appl. Therm. Eng* 2015;82:68-81.