天然メソポーラス材料を用いた低コスト吸着式ヒートポンプの研究開発
その 20　吸着材充填熱交換器テストピースを用いた吸着/脱着速度に関する実験
Research and Development of Low-Cost Adsorption Heat pump using Natural Mesoporous Material
20th: Experiment on Adsorption-Desorption Rate using Test Piece of Adsorber

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The purpose of this research is to study the performance of adsorption desorption rate. In this work, WSS + 20wt. % LiCl was used as the adsorbent, and adsorption was performed at 30 ℃, RH33 %. The experimental results were compared under different desorption conditions to obtain the ideal desorption conditions. Desorption was carried at 60 ℃, RH5 % desorption conditions, and the respective material mass translate coefficients were calculated to results of the adsorption rate and desorption rate.

1.　Introduction

From the viewpoint of energy saving and low environmental load, research on an adsorption heat pump (AHP) that can generate cold heat of about 7 to 15℃ using low-quality heat of 80 ℃ or less has been advanced. However, due to cost reasons, it has not spread widely. In previous studies, Porous materials, such as those that support chlorides in silica gel pores to ensure low cost and high moisture adsorption performance [1]. Previous study [2] shows that WSS functions well as a supported substance for lithium chloride. In our laboratory, we have started to develop low cost AHP by using lithium chloride supported on Wakkanai siliceous shale (WSS) as an adsorbent. A prototype of a slurry-type WSS adsorbent was prepared by adding mainly 20 wt. % lithium chloride to WSS (hereinafter referred to as WSS + 20 wt. % LiCl). Last year, our laboratory also did corresponding research on the mass mass coefficient and adsorption diffusion coefficient [3]. Due to insufficient control of the adsorption time, this update made a moving chamber in order to better calculate the material mass coefficients. However, due to the difficulty of manufacturing vacuum conditions, this experiment was performed in chambers under atmospheric pressure.

In this study, we use this kind of adsorption material to evaluate the adsorption and desorption. Based on the experimental data and the calculated material mass coefficient, we judged the change of the adsorption and desorption rate.

2.　Materials and methods

2.1 Materials-coated Test Pieces

Wakkanai siliceous shale is a natural mesoporous material abundantly abundant in the Soya district of Hokkaido. It can absorb and release a large amount of moisture especially at a relative humidity of 70 % or more, and the maximum adsorption amount reaches 270 mg/g. When impregnated in an aqueous solution of chloride and supported in the pores for the purpose of improving its moisture absorption capacity, if the amount supported is excessive, the aqueous solution generated by deliquescent of the adsorbed water and the supported substance under high humidity will be removed from the pores. There is a problem that it elutes and the surface becomes wet. In our previous work on adsorption heat pumps, we considered salt loading on WSS in order to increase the amount of adsorption in the operating relative vapor pressure range (0.1-0.3) of adsorption heat pumps. Was proposed. By supporting lithium chloride on WSS, sufficient adsorption performance was exhibited even in the range of the operating relative vapor pressure of the adsorption heat pump, and it was found that WSS also functions as a support for deliquescent lithium salts.

The mainstream adsorbents are synthetic zeolite-

based adsorbents, mainly silica gel or AQSOA-FAM. Since these adsorbents are made by chemical synthesis, the problem that the production cost of the adsorbent itself is high has become apparent. Due to this problem, the introduction cost of the adsorption heat pump remains high. For example, Invensor's 10 kW adsorption heat pump costs about 3 million yen. Therefore, our laboratory proposed a new porous material, the Wakkanai siliceous shale, which is a natural porous material abundantly found in the Soya district of Hokkaido. This shale is 100-150 yen / kg even if it is processed into fine powder, which is very advantageous in terms of price. In other words, if we are conducting research and development on an adsorption heat pump using Wakkanai siliceous shale, and will be able to market an adsorption heat pump with the same or better performance as the products currently on the market,

Actually an adsorbent heat pump (AHP) using a material in which lithium chloride (LiCl) is supported on the Wakkanai siliceous shale (WSS), a natural mesoporous material, as an adsorbent. It has been in progress for years. In previous studies, WSS+20 wt. % LiCl was used as an adsorbent, and research is being carried out using lab-scale to actual-scale test machines for social implementation. After filling the adsorption material on the heat exchanger pieces, and perform the drying operation to get the test piece required for the experiment.

In this research we use The Linear Driving Force (LDF) model to analyze the mass transfer characteristics. LDF model is usually applied to analysis of adsorption column dynamic data and for adsorptive process designs due to its simple, analytic, and physically consistent.

2.2 Moving Chamber

According to the previous research of this laboratory, the change of the adsorption amount can be obtained through experiments, however the experimental time cannot be controlled, therefore the numerical calculation of the adsorption and desorption rates cannot be obtained. In order to calculate both the adsorption and desorption rate, this time we used the Dual Moving Chamber which is developed by our laboratory for experiments. The appearance of the device is shown in Figure 1. The great thing about this device is its fully automatic stage. The schematic diagram of the Dual Moving Chamber is shown in Figure 2. The characteristics of the device are that

adsorption and desorption are performed in two chambers separately. In this experiment, we set the left chamber as the adsorption chamber and the right as the desorption chamber.

The device has three major features. One is that the conditions of the two chambers are different, and they can work independently, and the air at different temperatures and humidity will not mix with each other. The second is that the entire process of work stages is automated and does not require human action. There are two shutters between the two chambers. When the test piece needs to move between the two chambers, the two shutters in A chamber and B chamber automatically open and close to complete the movement of the substance between the chamber A and chamber B. The third is that he can dynamically test the moisture change of the test piece in units of one second. So according to the amount of adsorption by the weight change of the test piece in the experiment, and then calculate the adsorption rate of the substance mass coefficient based on the cycle time.

Figure1. Outward appearance of Dual Moving Chamber
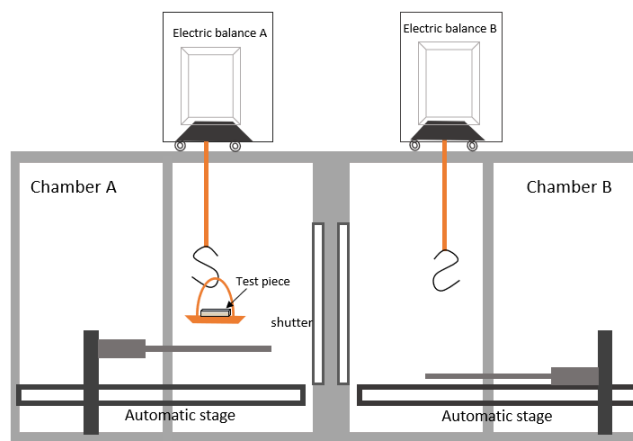

Figure2. Schematic diagram of Dual Moving Chamber

3. Experimental Results and discussions

3.1 Experimental results

Figure 3. shows the change of the adsorption capacity of the adsorbent according to time under the same adsorption conditions and different desorption conditions. Figure 3. shows a comparison of the amount of adsorption under two conditions, and Figure 4. shows a comparison of the amount of desorption under different conditions. The first group adopts adsorption conditions of 30 °C and 33 % humidity and the second group adopts adsorption conditions of 30 °C and 5 % humidity.

It can be seen from Figure 3. at under the same adsorption conditions, due to the different desorption conditions, the adsorption amount also changes to a certain extent. Under the desorption conditions of the second group (60 °C, RH5 %), the adsorption amount is also slightly higher than the first group. According to Figure 4., the desorption amount of the second group is significantly larger than that of the first group under different desorption conditions. Due to the good desorption performance of the second group, we take the conditions of the second group as the experimental conditions for subsequent experiments. The test piece is placed in the second set of conditions described above, and this experiment has ten cycles. The change in the adsorption amount of the test pieces according to the time pasts is shown in Figure 5.

In the ten test cycles, three groups at the beginning, middle, and end were selected, and the average material mass coefficient was calculated by the LDF calculation model, and the adsorption and desorption rates were compared. Figure 6. shows the adsorption comparison of the three groups of cycles, and Figure 7. shows the comparison of the desorption of the three groups of cycles.

From Figure 5., the weight change of the test piece shows an upward trend, which indicates that the adsorption amount of the adsorption piece is greater than the desorption amount during the entire experiment. A set of cyclic adsorption and desorption was performed for 15 minutes each, and the total adsorption amount was greater than the desorption amount. We can consider that the adsorption rate was greater than the desorption rate in this experiment.
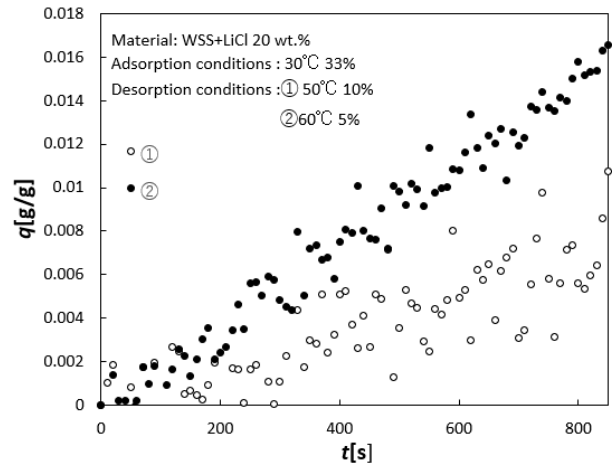

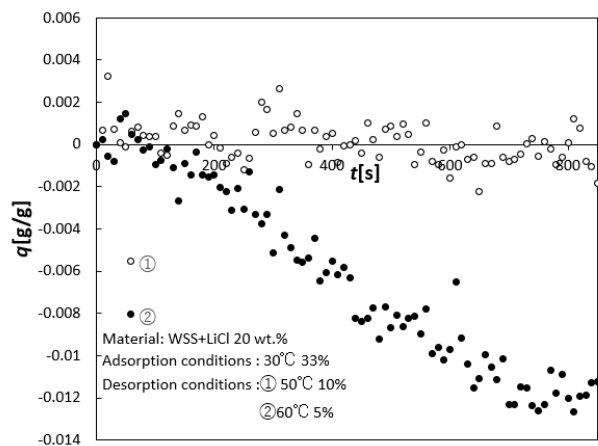**Figure3. Changes in adsorption amount under different desorption conditions**

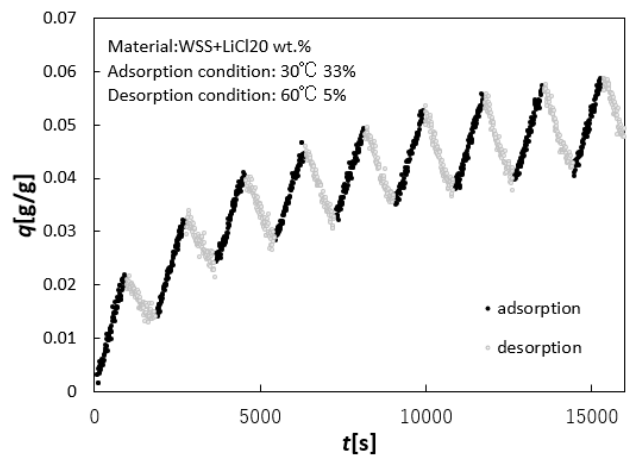**Figure4. Changes in desorption amount under different desorption conditions**

Figure5. Change in adsorption amount of test piece in one experimental period
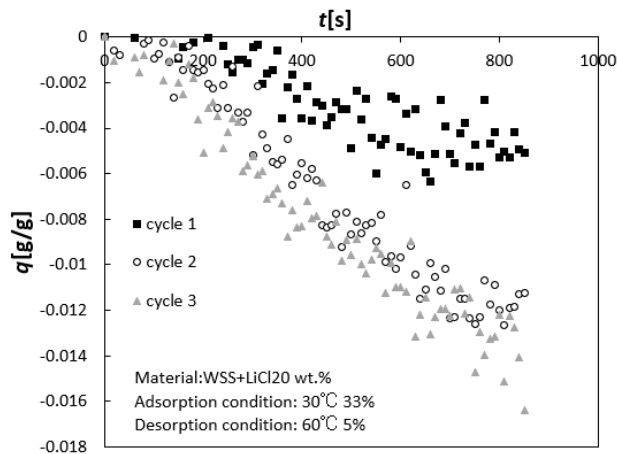
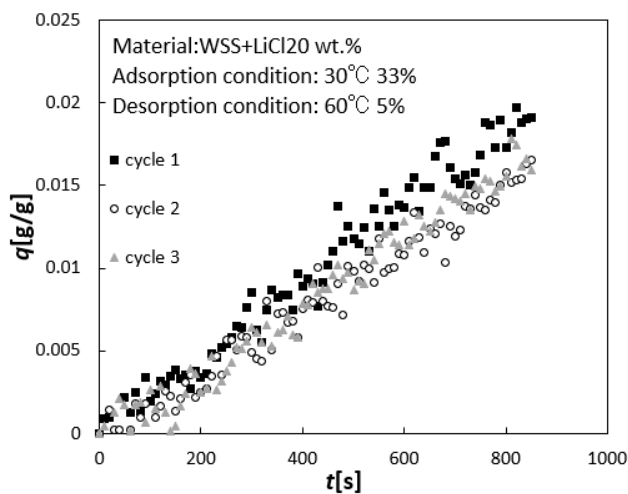**Figure6. Changes in adsorption capacity in different cycles**

Figure7. Changes in desorption capacity in different cycles

Calculate the overall material mass coefficient through LDF model

$$\frac{dq}{dt} = K_{\mathrm{m}}(q^* - q) \qquad (1)$$

Table 1. shows the adsorption and desorption mass transfer coefficient calculated in this experiment. The overall desorption substance mass coefficient is 4.23×10^{-4}, the overall adsorption substance mass coefficient is 7.68×10^{-5}, and the desorption substance movement coefficient is about 5.5 times that of adsorption. In previous studies, the overall mass transfer coefficient of desorption that is generally 3-4 times that of adsorption under the same temperture. Considering the influence of the adsorption characteristics of the material, we believe that 5.5 times is within a reasonable range.

Table 1 mass transfer coefficients

Km,ads	Km,des
7.68×10^{-5}	4.23×10^{-4}

3.2 Discussions

In general, both the adsorption and desorption values of the material mass coefficient obtained in this experiment are too small. For this phenomenon, we speculate that there are two possible reasons. First, the experiment was conducted under atmospheric pressure, and atmospheric pressure has a certain effect on the adsorption. The second is that the temperature at the beginning of the experiment did not reach the temperature required by the experiment, which resulted in the actual saturation adsorption amount being smaller than the data used for calculation.

In order to solve this problem, the possibility of conducting the same experiment under vacuum conditions will be explored in the future, and the measurement of the surface temperature of the material will also be carried out step by step.

Nomenclature

q	Water sorption amount [g/g]	K_{m}	Overall mass transfer coefficient [s^{-1}]
t	Time [s]	q^*	Saturated Water sorption amount [g/g]
$K_{\mathrm{m,ads}}$	Adsorption mass transfer coefficient [s^{-1}]	$K_{\mathrm{m,des}}$	Desorption mass transfer coefficient [s^{-1}]

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