Visualization of water adsorption/desorption phenomena in silica-gel particle by microfocus X-ray transmission imaging

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Received: 29 January 2018; Revised 7 February 2018; Accepted: 19 April 2018

Abstract
An adsorption heat pump system may make effective use of low-quality waste heat, but the system’s inadequate performance remains a critical issue. Improvements in efficiency and an understanding of the fundamental phenomena of water adsorption and desorption in a silica-gel particle are essential. X-ray transmission imaging was used to observe water adsorption/desorption phenomena in 3.7-mm-diameter silica-gel particles. Although previous studies did not conduct observations inside of the silica-gel particles, we were able to visualize the change in water distribution in silica-gel particles during adsorption and desorption using X-ray transmission imaging. When the silica-gel particles were cooled or heated, the adsorption or desorption proceeded gradually from the outer edge to the center, until the final equilibrium state of uniform water distribution was visible. A quantitative measurement of the water adsorbed in the silica-gel particles indicates that it took 20 min and 10 min to achieve adsorption and desorption equilibrium, respectively, in the silica-gel particle. In the silica-gel packed bed, all silica-gel particles desorbed at the same speed, but the adsorption slowed as the distance from the connection port increased.

Keywords: Adsorption heat pump, Silica-gel, Water adsorption/desorption, X-ray transmission imaging

1. Introduction

Energy challenges are an important global issue and many solutions have been proposed to address these. Waste-heat use is one solution to improve total energy efficiency (the ratio between primary and final energy consumption). The power-generation efficiency of thermal power plants is approximately 40%, and 60% of the energy is wasted as unutilized heat. High-temperature waste-heat can generate electrical power by using various thermodynamic cycles (Chung et al., 1997). However, most waste heat is at low temperature (less than 100°C), and there are many technical and economic issues associated with its use, such as the requirement for a cycle with a low-boiling-point working fluid.

An adsorption heat pump can be used to make effective use of low-temperature waste heat. The adsorption heat pump is a cooling device that uses the latent heat caused by the vapor adsorption/desorption phenomena related to the adsorbent, such as silica-gel (Ito et al., 1996a). In a system where silica gel particles and liquid water coexist, when silica gel adsorbs water vapor, liquid water evaporates to maintain the vapor pressure. At this time, as the liquid water temperature decreases owing to the latent heat of evaporation, it can be used for cooling and other applications. To regenerate the water-adsorbed silica gel, heating is necessary, and waste heat at ~80°C can be utilized at this time. The electricity consumption of an electric compressor used by a conventional air conditioner can be reduced by replacing the compressor with an adsorption heat pump. However, current adsorption heat pumps have a small output per unit volume (Ito et al., 1996b) compared with electric compressor-type air conditioners. To achieve high performance, a clarification of the adsorption/desorption efficiency in the silica gel and an improvement of its performance are...
required.

The silica-gel particle is a millimeter-scale bead that consists of nanometer-scale silicon dioxide. Water is adsorbed in the nanoporous structure of the silica gel. The adsorbed water content depends on the relative humidity, and the relationship is described by an adsorption isotherm (Ito et al., 1996a), a curve on a diagram relating amounts of water adsorbed on the surface of silica gel and pressure at a constant temperature. By measuring the temperature and water-vapor pressure under equilibrium conditions, the adsorbed water content in the silica-gel particle can be estimated. On the other hand, the adsorption heat pump repeats the heating and cooling of the silica-gel particle by utilizing the latent heat. The temperature profile inside the silica-gel particles is not uniform during heating and cooling. Thus, vapor adsorption proceeds inhomogeneously in the silica gel, and the adsorption isotherm cannot be applied to estimate the adsorbed water content under such a non-equilibrium state (Özdural et al., 2004).

In previous studies, temperature and mass changes that are caused by adsorption/desorption were measured by using a heat exchanger that was filled with many silica-gel particles (Chung et al., 1997, Ito et al., 1996a). This method allowed for an evaluation of the adsorption and desorption rates in the silica-gel packed bed. However, fundamental changes in the adsorbed water in the silica-gel particle and the spatial distribution of water during the adsorption/desorption process were not clarified. To explain the non-equilibrium water adsorption/desorption process in the silica-gel particle, the water distribution inside the silica-gel particle and a dynamic change in the amount of adsorbed water must be understood.

In this study, laboratory-scale microfocus X-ray imaging was used to investigate the water distribution in the silica-gel particle. X-rays can be used to visualize inside a sample non-invasively and non-destructively. Thus, X-ray transmission imaging was used to observe the unsteady water distribution in the silica-gel particles during adsorption/desorption. The variation in amount of adsorbed water with time was also measured quantitatively.

2. Experiments
2.1 Experimental apparatus to visualize the adsorption/desorption phenomena

Figure 1 shows the experimental apparatus that was used to visualize the water adsorption/desorption phenomena in the silica-gel particles. The main part of the adsorption heat pump consists of a silica-gel packed bed and a water-filled glass flask as an evaporator/condenser. Throughout the experiment, the main part of the apparatus was set on the table of an X-ray imaging system to achieve adsorption/desorption in the water-vapor atmosphere.

An RD (regular density) bead-type silica gel (Fuji Silysia Chemical Ltd., Japan) with a diameter of 3.7 mm and a density of 1.15 g/cm³ was used. The RD type silica gel has a microporous structure (with a pore diameter of approximately 2 nm). As shown in Fig. 2, several silica-gel particles were packed in a single layer between two aluminum laminate films to increase the heat transfer area (Ito et al., 1996a). A stainless steel tube for passing water vapor was attached to the end of the aluminum laminate film. The silica-gel packed bed was filled with the fluid, and temperature control (heating or cooling) was achieved by circulating hot (80°C) or cold (30°C) fluid from the two thermostatic baths. A glass flask was maintained at a constant temperature (20°C) by circulating cold fluid around it. During the experiment, the water vapor pressure in the system was determined by the water temperature in the glass-flask.

The heating/cooling cycle was performed only once. As a preliminary preparation, the vacuum pump was operated, valves 2 and 3 were opened, and air in the glass-flask was removed. Next, to desorb the water in the silica gel, valve 1 was opened and valve 2 was closed. Hot fluid was circulated around the packed bed and the inside of the packed bed was vacuumed with a vacuum pump to form an initial state in which water was desorbed. After 1 to 2 hours, an X-ray transmission image was obtained, which was used as the initial-state image.

When starting the adsorption experiment, after closing valve 3, the circulating fluid was switched from hot to cold. When the water temperature around the packed bed began to decrease, valve 2 was opened to connect the silica-gel packed bed and the glass-flask. At this time, X-ray transmission imaging was started, and the time was defined as the start of adsorption to the silica gel (t_{ad} = 0). Then, water vapor was adsorbed in the silica gel, and the same amount of water evaporated from the liquid water in the glass container. In the physical system, the latent heat caused in the glass container was used to cool the ambient fluid.

The adsorption experiment was carried out for 2 hours while obtaining X-ray transmission images. After that, in order to perform desorption experiment, circulating fluid was switched from cold to hot. The point at which the fluid...
temperature around the packed bed began to increase was defined as the desorption start time \( t_{de} = 0 \). Water that had adsorbed in the silica-gel particles desorbed and the same amount of water condensed in the glass container. The desorption experiment was carried out for 30 min.

Figure 3 show the results of the preliminary experiments for the temperature change in the packed bed when the temperature of the circulating fluid was switched. The temperature inside the packed bed increased or decreased significantly in approximately 2 to 3 min, and reached a steady state in approximately 15 min.
Fig. 3 Time-dependent temperature variation of silica-gel surface. Adsorption was caused by the packed bed cooling (left) and desorption was caused by its heating (right).

2.2 X-ray imaging system and analysis of obtained images

To visualize the water distribution in the silica-gel particles, a microfocus X-ray imaging system (inspeXio SMX-225CT, Shimadzu Corporation, Japan) was used. The imaging parameters are given in Table 1. Although the nanoscale structure inside the silica-gel particle cannot be resolved by microfocus X-ray imaging, the water content in the nanoscale pores can be detected with a micrometer-scale resolution (Özdural et al., 2004, Deevanhxay et al., 2013).

| Table 1 X-ray imaging system parameters. |
|------------------------------------------|
| X-ray tube voltage (kV) | 160 |
| X-ray tube current (µA) | 430 |
| Target material | W (Tungsten) |
| SID (X-ray source to image distance) (mm) | 1000 |
| SOD (X-ray source to object distance) (mm) | 205 |
| Image size (inch) | 8.0 × 8.0 |
| Effective pixels (pixel) | 1024 × 1024 |
| Exposure time of transmission imaging (sec) | 0.1 |
| Cumulated number | 100 |
| Transmission image resolution (µm/pixel) | 40 |

The luminance value at each pixel in the X-ray transmission image corresponds to the X-ray amount that reaches each pixel of the detector from the X-ray source. When X-rays penetrate the substance, they are absorbed according to the X-ray absorption coefficient and the substance thickness, and the X-ray intensity attenuates exponentially. The relationship between the irradiated and transmitted X-ray intensities is described by the Beer-Lambert law.

\[ I = I_\nu \exp(-\mu x), \]  

(1)

where \( I_\nu \) is the irradiated X-ray intensity, \( I \) is the transmitted X-ray intensity, \( \mu \) is the linear absorption coefficient of the substance, and \( x \) is the thickness of the substance. In Eq. (1), it is assumed that X-rays pass through a single substance. When X-rays pass through the water-adsorbed silica gel, temperature control fluid, and several walls of the container, the relationship between the X-ray intensity at each pixel in the obtained X-ray transmission image is given by Eq. (2).

\[ I_0 = I_\nu \exp\left(-\mu_s x_s - \mu_w x_{w0} - \mu_{cf} x_{cf} - \mu_{wa} x_{wa}\right), \]  

(2)

where subscripts \( s \), \( w \), \( cf \), and \( wa \) represent silica gel, adsorbed water, circulating fluid, and the walls of the container, respectively. Variables \( x_s \) and \( x_{w0} \) represent the total thickness of the solid part of the silica gel and the total thickness of the liquid water that is adsorbed in the nanoscale pores at the initial state, and which exists on the X-ray transmission path. The density of the circulating fluid changes owing to the temperature change, and the X-ray absorption coefficient \( \mu_{cf} \) also changes. To correct the variation in \( \mu_{cf} \), the transmitted X-ray intensity where silica gel does not exist (\( I_{corr} \)) is measured as shown in the Eq. (3).
By dividing $I_{0\text{corr}}$ by Eq. (2), the transmitted X-ray intensity that contains only the change in silica gel and adsorbed water was determined as shown in Eq. (4).

$$I_0' = I_0 / I_{0\text{corr}} = \exp(-\mu_s x_s - \mu_w x_{w0})$$

When water adsorbs onto or desorbs from the silica-gel particle, the amount of water in the nanoscale pore changes, and the transmitted X-ray intensity is as shown in Eq. 5.

$$I_x' = \exp(-\mu_s x_s - \mu_w x_{wt})$$

where $t$ is the arbitral time of the experiment. When Eq. (5) is transformed by dividing by Eq. (4), Eq. (6) is obtained:

$$\Delta x_w = x_{wt} - x_{w0} = \frac{1}{\mu_w} \ln \left( \frac{I_0'}{I_x'} \right)$$

where $\Delta x_w$ is the change in thickness of adsorbed water in the silica-gel particle. Therefore, by obtaining the X-ray transmission-intensity ratio from the experiment, it is possible to determine quantitatively the amount of water adsorbed and desorbed in the silica gel.

Although the X-ray linear adsorption coefficient of water $\mu_w$ is a known physical property, it differs depending on the X-ray energy, so it cannot be applied to analyze the visualization result created by mixed X-rays with various energies like those that were used in this experiment. Therefore, a calibration experiment was carried out and the transmitted X-ray intensity with respect to the amount of adsorbed water was examined to determine the X-ray absorption coefficient of water in the mixed X-ray.

In the calibration experiment, a container with water of a known thickness was placed on the X-ray optical path and the relationship with the natural logarithm of the transmitted X-ray intensity ratio was examined. The results of the calibration experiment are shown in Fig. 4. Under these experimental conditions, a linear relationship was resulted, and $\mu_w$ was set to 0.022 (mm$^{-1}$) from the gradient value of the approximate straight line.

The measurement uncertainty of the $\Delta x_w$ was evaluated as follows (BIPM et al., 2008). The standard uncertainty of the $\mu_w$ obtained by the calibration experiment was 0.98%. It includes uncertainty of the thickness of water in the container. The standard uncertainty of $\ln(I_0'/I_x')$ was 0.75%. It includes uncertainty of the irradiated X-ray intensity from the X-ray source, the sensitivity of the X-ray detector, and temperature of circulating fluid. Therefore, the combined standard uncertainty of the $\Delta x_w$ obtained by Eq (6) was 1.2%, and the expanded uncertainty was 2.4%. It was obtained by multiplying the combined standard uncertainty by a coverage factor $k=2$. Taking $k=2$ produces an interval having a level of confidence of approximately 95 percent.
3. Results and discussion

3.1 X-ray transmission imaging of adsorption/desorption process

As shown in Figs. 5 and 6, we observed the adsorption and desorption phenomena of water in silica gel. The color indicates the X-ray transmission intensity ratio of the initial image in the desorption state before the start of the experiment, and the visualized image at each time after the start of the experiment ($I_0/I_t$). A larger $I_0/I_t$ means that water was adsorbed.

The images at $t_{ad} = 1$ to 5 min show that water adsorption occurs at the outer edge of each silica-gel particle. After that, water adsorption progressed to the center with the passage of time. At $t_{ad} = 120$ min, the silica-gel particles appear to have reached a non-uniform water distribution (e.g., 1M and 3L). However, this occurs because the amount of water in the depth direction has accumulated as the spherical silica gels were observed with the X-ray transmission image. Fig. 5 includes a theoretical image assuming the uniform water adsorption in the spherical silica-gel particle, and it agrees well with the image obtained from the experiment. The closer to the center of the silica-gel particle, the greater the amount of water present on the X-ray transmission path, so that the $I_0/I_t$ increases.

The adsorption rate of silica gel varies depending on the location. Silica gel particles close to the connection port (1M and 1R) have almost reached equilibrium after approximately 20 to 30 min, because these images show similar...
water distribution. The adsorption of silica-gel particles furthest from the connection port (e.g., 5L, 5M and 5R) progressed very slowly. A comparison of $t_{ad} = 90$ min and $t_{ad} = 120$ min shows that a slight change is still underway in the water distribution, which suggests that the equilibrium state has not been reached in these silica-gel particles.

When the desorption experiment was started, desorption occurred from the outer edge to the inside, the same pattern as in the adsorption experiment. However, the desorption rate differs from that of the adsorption rate. All silica-gel particles showed the same change in water distribution, which means that the desorption rate was uniform regardless of the location. Finally, at $t_{de} = 10$ to $15$ min, $I_0/I_{tad}$ reached almost unity, which indicates that the water distribution in the silica-gel particles returns to the same state as the initial desorbed state.

### 3.2 Quantitative change of adsorbed water in silica gel

Relative changes in water content as associated with the adsorption and desorption were measured quantitatively for each silica-gel particle at the position indicated by the symbol in Figs. 5 and 6. The obtained water amount was divided by the mass of the silica-gel particles and was expressed as the adsorption amount per unit mass ($q$ (g/g)).

During the adsorption process, as shown in Fig. 7, the adsorption rate of silica gel 1M that existed near the connection port was rapid and equilibrium was almost reached in approximately 20 to 30 min. From the initial state to the adsorption equilibrium state, 0.25 g/g water was adsorbed in the silica-gel particles. These results agree well with the difference in adsorption amount ($\Delta q \approx 0.27$ g/g in the equilibrium state between 80°C and 30°C), which is obtained from the adsorption isotherm of the RD-type silica gel (Ito et al., 2000). This experimental method shows that the quantitative amount of water that is adsorbed in the silica-gel particles can be measured with high accuracy.

The adsorption rate became slower farther from the connection port, and even after 120 min, the silica-gel particles (4M) still adsorbed water. The mechanism by which the adsorption rate of the silica-gel particles varies depending on the location is unknown. In future studies, the influence of each silica-gel particle interaction on the water and heat transport phenomena must be studied.

During the desorption process, no difference existed between the desorption rate whatever the position. In all silica-gel particles, the amount of adsorbed water decreased, and they reached equilibrium in approximately 10 to 15 min. Compared with the time to reach equilibrium, the desorption rate was approximately twice the adsorption rate. When the equilibrium state was reached, the same water amount was achieved as in the initial state before the adsorption experiment.
4. Conclusions

A dynamic adsorption/desorption process in silica-gel particles was visualized by X-ray transmission imaging. The variation in the water distribution over time was visualized and a quantitative change in adsorbed water was obtained. When the silica-gel particles were cooled or heated, adsorption or desorption proceeded gradually from the outer edge to the center, and finally, an equilibrium state of uniform water distribution was achieved as visualized. We measured the quantity of water that was adsorbed in the silica-gel particles with a high accuracy. It took approximately 20 min for the adsorption process to reach equilibrium. The desorption process proceeded more rapidly, reaching equilibrium in approximately half the time (10 min). In the silica-gel packed bed, all silica-gel particles were desorbed at the same speed, but the adsorption process slowed as the distance from the connection port increased. These experimental results give important suggestions for optimizing the packed bed structure and operating conditions of adsorption heat pumps.

Acknowledgement

The researchers would like to thank Mr. Shozo YOSHIMURA, of the Tokyo Institute of Technology, for his invaluable assistance with the image analysis.

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