

Development of an Autonomous Humidity Controlling Building Material by Using Mesopores

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In order to improve the deterioration of moisture circumstances have been brought by Japanese weather of which sultry in summer and biting in winter and the prevalence of high airtight and heat insulation without energy, the investigation of autonomous humidity controlling building materials has been done. The capillary condensation phenomenon was utilized for obtaining the autonomous humidity control ability. The relation between the pore size and the relative humidity was expressed by Kelvin's equation. From this equation, it was important that the capillary condensation occurs in the pores around 10nm in diameter from 40 to 70% relative humidity in which human being felt comfortable. The humidity controlling abilities of allophane, the silica gel and gibbsite which had mesopores were investigated and it was clarified that the mixture of gibbsite and clay minerals was appropriate for the interior wall building materials.

Therefore the plate sample was prepared from the mixture of gibbsite and clay minerals and studied the humidity control ability. As a result, it showed superior performance.

Key words; humidity control, capillary condensation phenomenon, mesopore, gibbsite

1. INTRODUCTION

Japan is located at the northern east end of the Asia monsoon area, so it is very sultry in the summer and biting cold in the winter. This is the reason why the houses are open to the outside and made of the moisture breathing natural materials such as woods, papers and soils.

In recent years, energy consumption at public welfare is growing because of wishing an amenity life by people whereas the consumption at industries is saved because of much effort by enterprises^[1]. Under such circumstances, current houses are highly airtight and energy saving. But the indoor air tends to be very wet or dry on account of using artificial materials which cannot breath moisture. Furthermore problems of allergic mold/tick or dew condensation sometimes arise in the houses. And the release and build-up of formaldehyde and other injurious volatile organic compounds (VOCs) from them has led to new health-related problems, now well known as the "Sick House Syndrome"^{[2],[3]}. To solve these problems without energy, it is proposed that autonomous humidity controlling building materials are used indoors.

In this paper, the mechanism of the autonomous humidity controlling material using mesopores and the humidity controlling ability of the prepared samples were investigated.

2. EXPERIMENTAL

2-1. Sample Preparation

As the humidity control material, allophane, silica gel and gibbsite were used. The reason why they were selected

was because they contain many meso-pores in their structure, so it was expected to have high humidity control ability. Allophane is a natural mineral mined from Kanuma in Ibaraki prefecture, Japan, it is an amorphous clay material included in volcanic ash soil, and constructed from poorly ordered Si-O-Al structure. Its morphology is an aggregate of micro midair particles that have many mesopores^[4]. The silica gel was industrial grade from Fuji Silysia Chemical, Ltd. Fujita reported that the silica gel prepared under special conditions, adsorbed 80% moisture of its own mass at a 50 to 80% relative humidity^[5]. Gibbsite was obtained from TOSTEM Corporation. It was a by-product generated from producing aluminum ware, but its purity was similar to a virgin material. Okada et al. reported that γ -alumina had a high moisture adsorption capacity which has a high surface area widely used as a catalyst support^[6]. The gibbsite generated γ -alumina by heat treatment was used in this study.

The test samples were prepared as follows. 20% of the mesoporous materials and 80% of the plastic clay materials from Aichi prefecture located in the center part of Japan were mixed and crushed for 4 hours in a pot mill with water. Their slips were then dried at 120°C for 12 hours and obtained granules with a moisture content of 7% by passing through a screen of 8mesh and adding water. The test samples with dimensions of 150x150x5mm were formed by a uniaxial press at a pressure of 21MPa and then fired at from 600 to 1000°C for 1 hour in an electric furnace.

2-2. Evaluation Items

The pore size distribution, specific surface area,

moisture adsorption/desorption behavior and adsorption ability of harmful gases were measured and the constituent phases were identified by XRD (RIGAKU RAD-IIA). The pore size distribution was measured by a PoreMaster-33P (Quantachrome Instruments) and an Autosorb-1-MP/VP (Quantachrome Instruments). The specific surface area was measured by an Autosorb-1-MP/VP (Quantachrome Instruments).

The moisture adsorption behavior was measured as follows. The samples were saturated at 25°C and 50% in an incubator, then placed in another incubator at 25°C and 90% and the amount of moisture adsorption measured. After 24 hours, they were returned to the incubator at 25°C and 50% and the amount of moisture desorption measured.

The desiccators, which had volume were 12 liters, were used for the closed vessel and 56 cm² of the test sample were sealed on the back and side with aluminum tape was placed in the desiccators. The desiccators without cover were placed in an incubator, and kept at 25°C and 60%RH for 24 hours. The covers were added, and the temperature of the incubator was varied from 25 to 5°C in 12 hours and heated to 25°C in 12 hours. This cycle was then repeated. At that time, the relative humidity in the vessel was measured by a temperature & humidity meter (ESPEC Corporation) with and without the test sample.

3 RESULTS AND DISCUSSION

3-1. Development of Humidity Controlling Materials

The moisture adsorption/desorption behaviors of the test samples fired at 900°C between 50 to 90% relative humidity at 25°C are shown in Fig.1. The silica gel and gibbsite showed similar moisture adsorption/desorption behaviors and allophane showed one half of them. When the samples were returned to the incubator at 50% relative humidity, every sample desorbed moisture which was adsorbed at 90% relative humidity even with a small hysteresis. Furthermore, it was clarified that the moisture adsorption/desorption rate of single was faster than that of the coexisting of clay minerals from a change in the moisture adsorption behaviors with time.

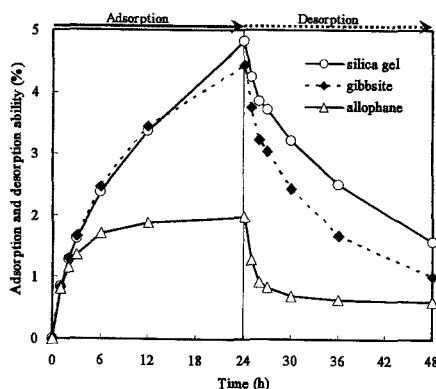


Fig.1 Adsorption and desorption behavior.

It was clarified that the moisture adsorption behaviors did not reach the saturated values even after 24 hours in Fig.1. Therefore, in order to estimate the saturated values

of each sample, the following equation was applied to the moisture adsorption behaviors in Fig.1.

$$C = C_0(1 - e^{-\alpha t}) \quad (1)$$

, where C is the adsorption amount at time t , α is the moisture adsorption ratio at time t , and C_0 is the saturated adsorption amount. Equation (1) was converted to equation (2) by a logarithmic transformation. If a correlation between left side and right side of the equation (2) exists, the moisture adsorption behavior can be expressed by this equation.

$$\ln(C_0) - \ln(C_0 - C) = \alpha t \quad (2)$$

Fig.2 shows the relation between left and right side of the equation(2). By transforming to equation (2), there were good correlations between them. The values of C_0 and α were similarly obtained in case of silica gel and allophane as shown in Table I. The moisture adsorption rate, α in case of the coexisting clay minerals is higher than for it alone except for the gibbsite fired at 600 and 800°C, so it was thought that the moisture adsorption rate was controlled by the clay minerals.

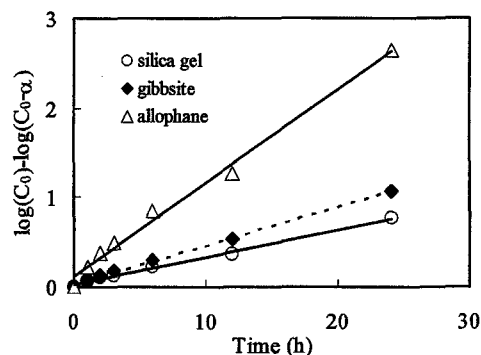


Fig.2 Relation between $\log(C_0) - \log(C_0 - C)$ and time.

Table I C_0 and α for moisture adsorption.

| Temperature (°C) | gibbsite | | silica gel | | allophane | |
|---------------------|--------------|--|--------------|--|--------------|--|
| | C_0 (%) | α (10 ² t ⁻¹) | C_0 (%) | α (10 ² t ⁻¹) | C_0 (%) | α (10 ² t ⁻¹) |
| 600 | 3.9 | 5.9 | 5.7 | 4.5 | 3.5 | 4.6 |
| 800 | 4.8 | 3.8 | 6.5 | 3.7 | 3.6 | 3.0 |
| 900 | 4.6 | 2.4 | 5.5 | 3.0 | 2.2 | 4.0 |
| 1000 | 1.3 | 6.7 | 1.6 | 8.2 | 0.3 | 8.5 |

Fig.3 shows a change in the saturated moisture adsorption amount for the test samples versus firing temperature. The saturated moisture adsorption of silica gel decreased gradually up to 900°C, but it decreased drastically at 1000°C. In case of allophane it kept up to 800°C and then decreased drastically. On the other hand, gibbsite generated mesopores by dehydrating the structure water. The saturated moisture adsorption amount of gibbsite increased to 800°C, and gibbsite did not keep much of the adsorbed moisture at 1000°C. Therefore, it was thought that the gibbsite mesopores had the highest

heat resistance. This fact was also recognized for the clay mixture system. The moisture adsorption amount of gibbsite did not decrease up to 900°C. It was clarified that the mixture of gibbsite and clay minerals had a good moisture adsorption amount even at 900°C.

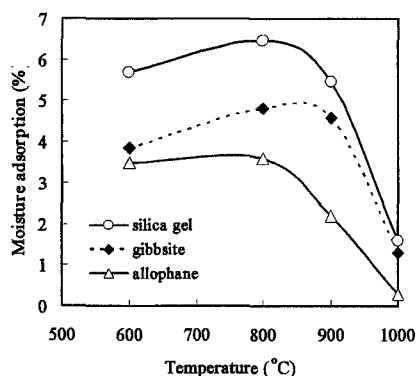


Fig.3 Saturated moisture adsorption with temperature for gibbsite, allophane and silica gel.

The capillary condensation phenomenon on the surface of the mesoporous materials provides the autonomous moisture adsorption/desorption ability. The relation between the pore size, r and relative humidity, P/P_0 is expressed by Kelvin's equation^[7].

$$r = -(2V\gamma\cos\theta) / (\rho RT \cdot \ln(P/P_0)) \quad (3)$$

, where γ is the surface tension of the liquid, M is the molar volume, θ is the contact angle of the liquid on the surface of the capillary vessels, ρ is the density of water, R is the gas constant and T is the absolute temperature. This equation indicates that as the relative humidity becomes higher, the pore size becomes bigger which produces the capillary condensation phenomenon. When the thickness of the adsorbed water on the surface of the capillary vessels is compensated, the relation between the pore size and relative humidity becomes more accurate^[8].

$$r^2 = r + t \quad (4)$$

$$t^{2.3} = -0.132 / \{\ln(P/P_0) - 0.08\} \quad (5)$$

Applying equations (3), (4) and (5), the pore radius adsorb moisture vapor at 50 (90) in relative humidity are 2 (11) nm. Therefore, for the exerting humidity control ability, from several to dozens of nm of the volume of mesopores is important.

The pore size distributions are shown in Fig.4. The horizontal axis is the pore diameter and the longitudinal axis is the frequency of the pore volume. Two kinds of pores were observed, one was mesopore from 1 to 10nm and the other was macro pore over 10nm. The mesopores of the silica gel had a narrow distribution centered at 6nm. They gradually decreased with the higher temperature and almost disappeared at 1000°C. In the case of allophane, the mesopores were smaller and the distribution was wider than in the case of silica gel. A similar change with temperature was observed and also disappeared at 1000°C. On the other hand, the diameter of mesopores increased from 4nm at 600°C to 7nm at 900°C and the distribution became broader with the higher temperature in the case of gibbsite.

The macro pores from 10 to hundreds nm were attributed to clay minerals, and it was assumed that they were connected to the rate of the moisture adsorption/desorption behavior.

The relation between the volumes of the mesopores related to the adsorption/desorption behavior from 50 to 90% in relative humidity and the saturated moisture adsorption amount are shown in Fig.5. It was clarified that a good correlation existed between the two.

Gibbsite dehydrates and forms mesopores at around 400°C, by heating, gibbsite then changes to κ -type alumina. Furthermore as the temperature increases, the pore size becomes bigger. The mesopores around 10nm were lost and changed to the χ -type alumina at 1000°C. In this study, γ -alumina was not identified by XRD. The humidity control ability of the mesoporous material reached a maximum value at 800°C. At higher than 800°C, the mesopores rapidly decreased. The strength is very important as well as the humidity control effect of the tile, so heat stability is necessary for obtaining a higher strength. The coexistence of clay minerals is effective for heat stability of the mesopores. A gibbsite-clay mixture was less subject to temperature from 800 to 900°C than only

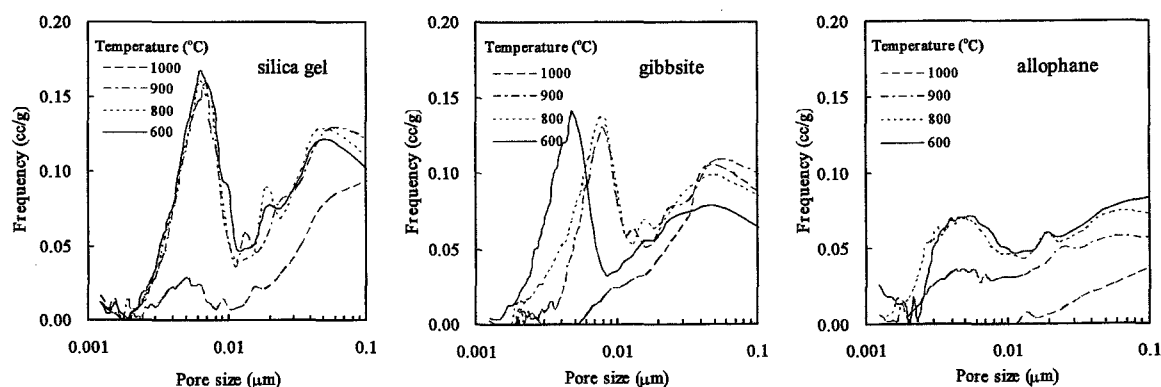


Fig.4 Pore size distributions for silica gel, gibbsite and allophane.

gibbsite. There were not big changes in XRD for the silica gel and allophane.

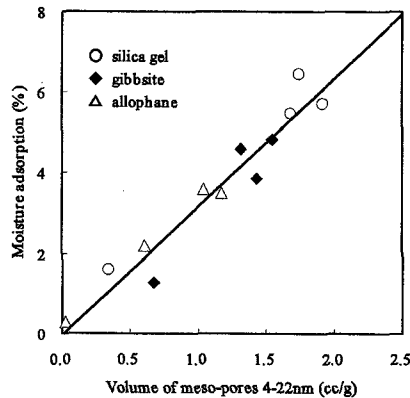


Fig.5 Relation between volume of mesopores from 4 to 22nm and moisture adsorption.

3-2. Evaluation of Humidity Controlling Material

Based on the results, the tiles with a size of 303x303x5.5mm were prepared by using a mixture of gibbsite and clay minerals and fired at 900°C for application as interior wall coverings. The physical properties of the test samples are as follows: bulk density: 1.7g/cm³, flexural strength: 5MPa and porosity: 40%.

Fig.6 showed change in relative humidity with and without the test sample in desiccators. Without the test sample, relative humidity in desiccators increased and reached dew point. Even though putting the test sample in the desiccators, relative humidity was kept the range 60 to 70%RH. When humidity in desiccators rose, the pores adsorbed extra moisture. Conversely, when the humidity went lower, the pores released the moisture they had adsorbed. Thus, the test sample had the function of preventing the room becoming excessively humid or dry so as to maintain a comfortable humidity range (40% to 70%) which was gentle to the skin and throat. In terms of moisture adsorption/release performance, the test sample was more than 15 times better than vinyl wallpaper. Thus, it maintained a comfortable humidity range (40 to 70%) which was gentle to the skin and throat.

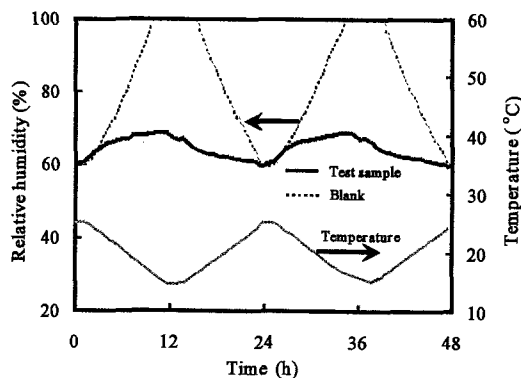


Fig.6 Change in relative humidity in closed vessel.

Dew condensation occurrence was facilitated in the winter season because of big difference between indoor and outdoor temperatures and the large amount of water formed by the use of room heaters. This is particularly so in the case of modern houses, which are airtight and prevent the escape of water vapor. In houses where dew condensation is severe, dew is formed even on the walls. The use of the test sample as an indoor wall finishing material will prevent such dew formation.

4. CONCLUSION

Ceramic mesoporous materials were prepared from silica gel, gibbsite and allophane with clay minerals. They had mesopores sized from 4 to 20nm and macro-pores around 100nm. The mixture of gibbsite and clay minerals was appropriate for the interior wall building material. Its behavior of moisture adsorption and desorption was discussed and it showed good performance and was expected to improve the quality of indoor air when it was applied to interior wall of a room.

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