DEVELOPMENT OF AN AUTONOMOUS HUMIDITY CONTROLLING BUILDING MATERIAL BY USING MESOPORES

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ABSTRACT

The investigation of autonomous humidity controlling building materials has been conducted In order to improve the deterioration of moisture circumstances brought about by Japanese weather which is sultry in summer and biting in winter and the prevalence of high airtight and heat insulation without energy. 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 and the adsorption behaviour for formaldehyde which is one of the allergens of the sick house syndrome. As a result, it showed superior performance for both properties.

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. Current Japanese houses are highly airtight and thermally insulated in order to save energy. As a result, problems related to increased moisture in the indoor air have occurred, for example, excessive dew formation, etc. To solve these problems without energy, it is proposed that autonomous humidity controlling building materials are used indoors.

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, the authors have developed interior wall tiles which control the indoor humidity and introduced them to the Japanese market ten years ago. The name of product is "ECOCARAT". We have also presented them at CERSAIE (International Exhibition of Ceramic Tile and Bathroom Furnishings) in Italy three years ago, and have proposed their use in countries in which there are similar problems of indoor moisture in Europe, North America and Asia.

In this paper, the mechanism of the autonomous humidity controlling material using mesopores and the characteristics of the humidity controlling and the adsorption behaviour of represented by formaldehyde 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 meso pores[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.

They were fired from 600 to 1000ºC for 1hour in an electric furnace and also mixtures with 20% of each humidity control material and 80% clay mineral were fired.

The test samples were prepared as follows. 20% of the meso-porous materials and 80% of the plastic clay materials from Aichi prefecture located in the centre part of Japan were mixed and crushed for 4 hours in a pot mill with water. Their slips were then dried at 120ºC 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 around 900ºC for 25mintes using a roller hearth kiln.

2.2. EVALUATION ITEMS

The pore size distribution, specific surface area, moisture adsorption/desorption behaviour and adsorption ability of harmful gases were measured and the morphology of the samples observed by SEM (JSNM-5400, JEOL Ltd.). 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 behaviour was measured as follows. The samples were saturated at 25ºC and 50% in an incubator, then placed in another incubator at 25ºC and 90% and the amount of moisture adsorption measured. After 24hours, they were returned to the incubator at 25ºC and 50% and the amount of moisture desorption measured.

The moisture adsorption isotherm of the test sample was measured using the BELSORP-18 (BEL JAPAN, Inc.) at 25ºC. The samples were pretreated for 13 hours at 110ºC under 10^{-2} torr before measurement. The measurement was done from 0.10 to 0.96 relative pressures.

The desiccators, which had volume were 12liters, were used for the closed vessel and $56cm^2$ 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 25ºC and 60%RH for 24 hours. The covers were added, and the temperature of the incubator was varied from 25 to 5ºC in 12 hours and heated to 25ºC 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.

The ability of adsorption for formaldehyde representative VOCs of the test sample was measured by small scale chamber method[7]. Two pieces of the test sample sized 0.15m x 0.15m were mounted in the chamber which volume was $0.02m^3$, so loading factor was $2.2m^2/m^3$. Ordinary wallpaper was also measured for comparison.

The air including formaldehyde with $120\mu g/m^3$ was introduced into the chamber with rate $0.01m^3/h$ and formaldehyde including in the outlet air from the chamber was trapped by DNPH (2,4-dinitrophenylhydrazine) cartridge passing $0.01m^3$ of the air. This cartridge was extracted by $5x10^{-6}m^3$ of acetonitrile and then measured the concentration of formaldehyde by HPLC (high performance liquid chromatography, LC-10, SHIMADZU CORPORATION). Mixture of distilled water and acetonitrile as solvent and Discovery TM RP-Amide C16 column keeping at 40ºC were used for measurement.

The adsorption ability of harmful gases was estimated as follows. A bag with a volume of $0.003m^3$ made of polypropylene was used. Plate-like materials were sealed on the back and side surface by thin aluminium tape. Five kinds of harmful gases were used, i.e., ammonia, a representative odour of rest rooms, hydrogen sulfide, which a constituent in cigarette smoke, methyl mercaptan, which is an excrement, trimethylamine, which is from garbage, and ethyl alcohol, which is a representative odour in hospitals. The concentrations of these gases were 10, 10, 50, 35, 1000ppm, respectively. The materials were placed in a bag and the gas introduced. After starting the adsorption, the concentration of the gas in the bag was measured by a detector tube.

3. RESULTS AND DISCUSSION

3.1. DEVELOPMENT OF HUMIDITY CONTROLLING MATERIALS

The moisture adsorption/desorption behaviours of the test samples fired at 900ºC between 50 to 90% relative humidity at 25ºC are shown in Fig. 1. In case of the stand-alone, the silica gel showed the highest moisture adsorption/desorption behaviour, gibbsite showed one half of that silica gel and allophane showed less than one third of the silica gel. In case of multiple of clay minerals, the silica gel and gibbsite showed similar moisture adsorption/desorption behaviours and allophane showed one half of them. When the samples were retuned 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 behaviours with time.

It was clarified that the moisture adsorption behaviours 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 behaviours 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 behaviour can be expressed by this equation.

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

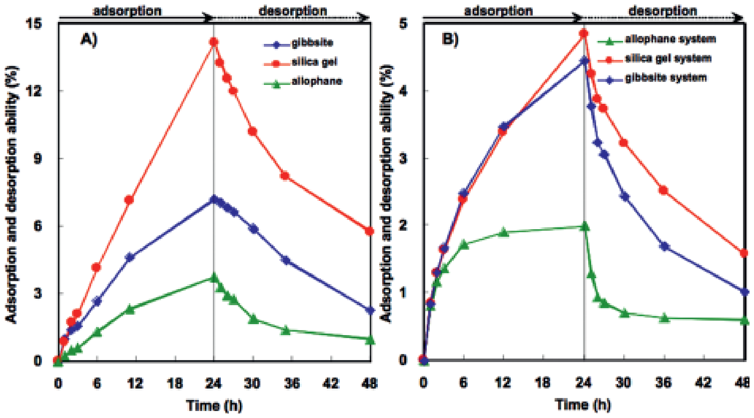

Figure 1. Adsorption and desorption behavior for A) stand alone and B) clay mixture system.

Fig. 2 shows the change in the moisture adsorption amount with time of gibbsite stand-alone fired from 600 to 1000ºC. By transforming to equation (2), there were good correlations between the left side and right side of equation (2) (Fig. 3). The values of C_0 and α were similarly obtained in case of silica gel and allophane as shown in Table 1. 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 800ºC, so it was thought that the moisture adsorption rate was controlled by the clay minerals.

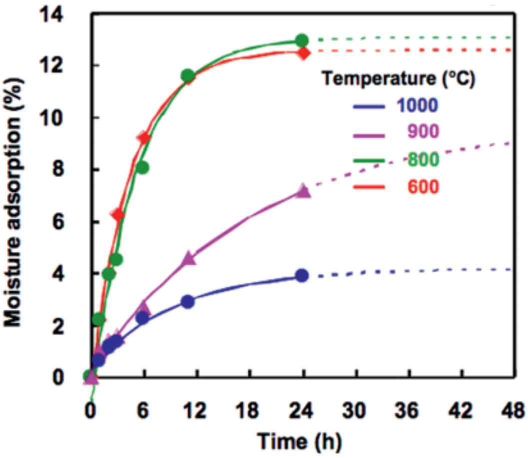

Fig.2 Change in moisture adsorption of gibbsite stand alone as a function of time.

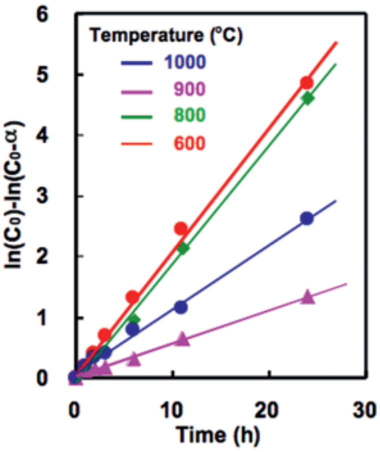

Fig.3 Change in log(C_0)-log(C_0-α) as a function of time.

TEMPERATURE (ºC)	GIBBSITE		SILICA GEL		ALLOPHANE	
	C_0 %	$\alpha(10^2t^{-1})$	C_0 %	$\alpha(10^2t^{-1})$	C_0 %	$\alpha(10^2t^{-1})$
STAND ALONE						
600	13	9.7	66	1.1	7.4	2.4
800	13	8.4	57	0.7	4.7	2.9
900	9.7	2.4	48	0.6	5.2	2.3
1000	4.2	4.6	0.6	0.9	0.3	5.3
CLAY MIXTURE						
600	3.9	5.9	5.7	4.5	3.5	4.6
800	4.8	3.8	4.6	3.6	3.6	3.0
900	4.6	2.4	3.9	2.6	2.2	4.0
1000	1.3	6.7	1.6	8.2	0.3	8.5

Table 1. C_0 and α for moisture adsorption.

Fig. 4 shows a change in the saturated moisture adsorption amount for the stand-alone and mixture with clay minerals versus firing temperature. In case of the stand-alone, silica gel kept more than 50% of its own mass of the moisture adsorption amount up to 900ºC, but it completely lost the capacity at 1000ºC. Allophane also showed a similar tendency. In other words, the saturated moisture adsorption amount did not change up to 900ºC, but was all lost at 1000ºC. On the other hand, gibbsite generated mesopores by dehydrating the structure water. The saturated moisture adsorption amount of gibbsite increased to 800ºC, and gibbsite did not keep much of the adsorbed moisture at 1000ºC. 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 900ºC. It was clarified that the mixture of gibbsite and clay minerals had a good moisture adsorption amount even at 900ºC.

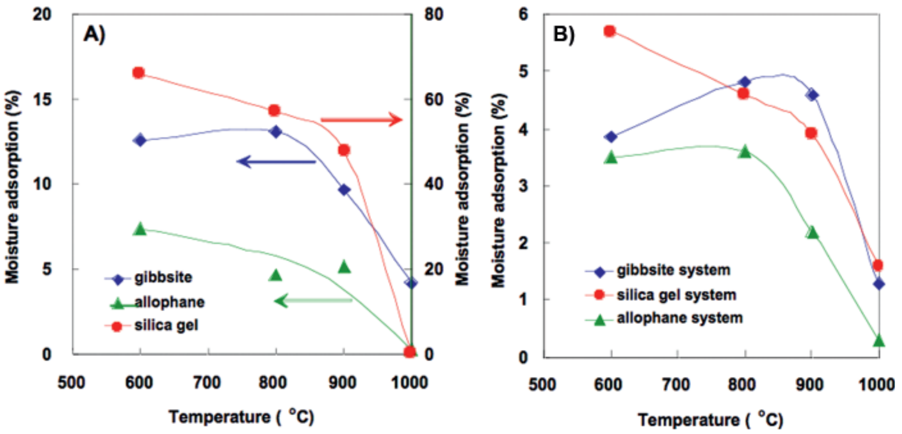

Figure 4. Saturated moisture adsorption with temperature for gibbsite, allophane and silica gel system, A) stand alone, B) clay mixture.

The capillary condensation phenomenon on the surface of the meso-porous 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[8].

$$r=-(2V\gamma\cos\sigma)/(\rho RT\bullet\ln(P/P_0)) \qquad (3)$$

where: γ is the surface tension of the liquid, M is the molar volume, σ 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[9].

$$r'=r+t \qquad (4)$$

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

Applying equations (3), (4) and (5), the pore radius adsorb moisture vapour 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 for the stand-alone and mixture with clay minerals are shown in Figs. 5 and 6, respectively. The horizontal axis is the pore diameter and the longitudinal axis is the frequency of the pore volume. The mesopores of the silica gel alone had a narrow distribution centred at 6nm. They gradually decreased with the higher temperature and disappeared at 1000ºC. 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 1000ºC. On the other hand, the diameter of mesopores increased from 4nm at 600ºC to 30nm at 1000ºC and the distribution became broader with the higher temperature in the case of gibbsite.

For the mixture of clay minerals, the variation in the mesopores showed a similar tendency but other pores from 10 to hundreds nm also existed. They were attributed to clay minerals, and it was assumed that they were connected to the rate of the moisture adsorption/desorption behaviour.

The relation between the volumes of the mesopores related to the adsorption/desorption behaviour from 50 to 90% in relative humidity and the saturated moisture adsorption amount are shown in Fig. 7. It was clarified that a good correlation existed between the two.

Gibbsite dehydrates and forms meso-pores at around 400ºC, by heating. Gibbsite then changes to κ-type alumina. Furthermore as the temperature increases, the pore size becomes bigger. The meso-pores around 10nm were lost and changed to the χ-type alumina at 1000ºC. The humidity control ability of the meso-porous material reached a maximum value at 800ºC. At higher than 800ºC, the meso-pores 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 meso-pores. A gibbsite-clay mixture was less subject to temperature from 800 to 900ºC than only gibbsite. There were not big change in X-ray diffraction patterns for the silica gel and allophane.

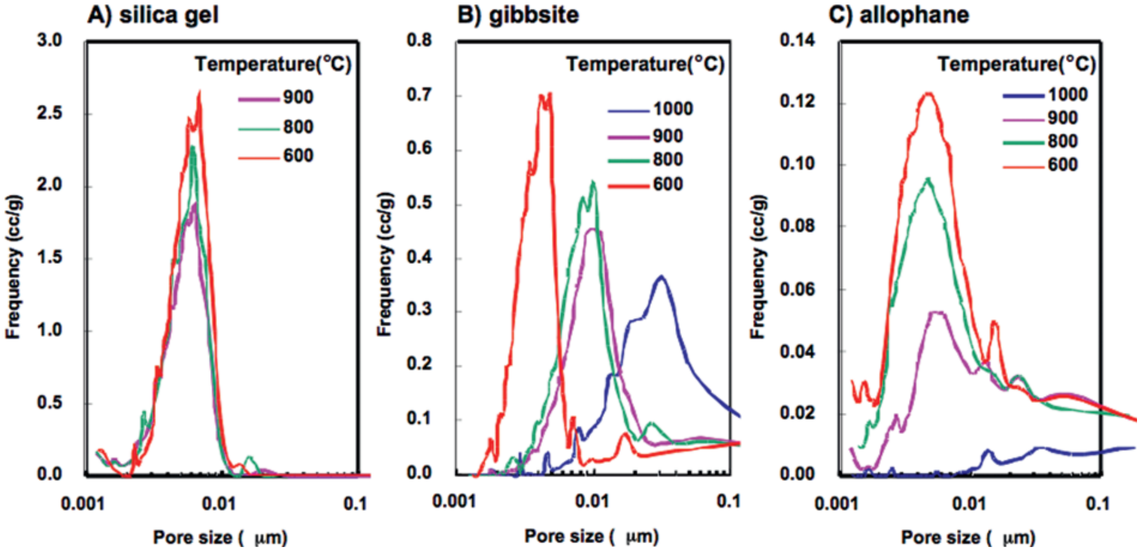

Figure 5. Mesopore size distributions for A) silica gel, B) gibbsite and C) allophane.

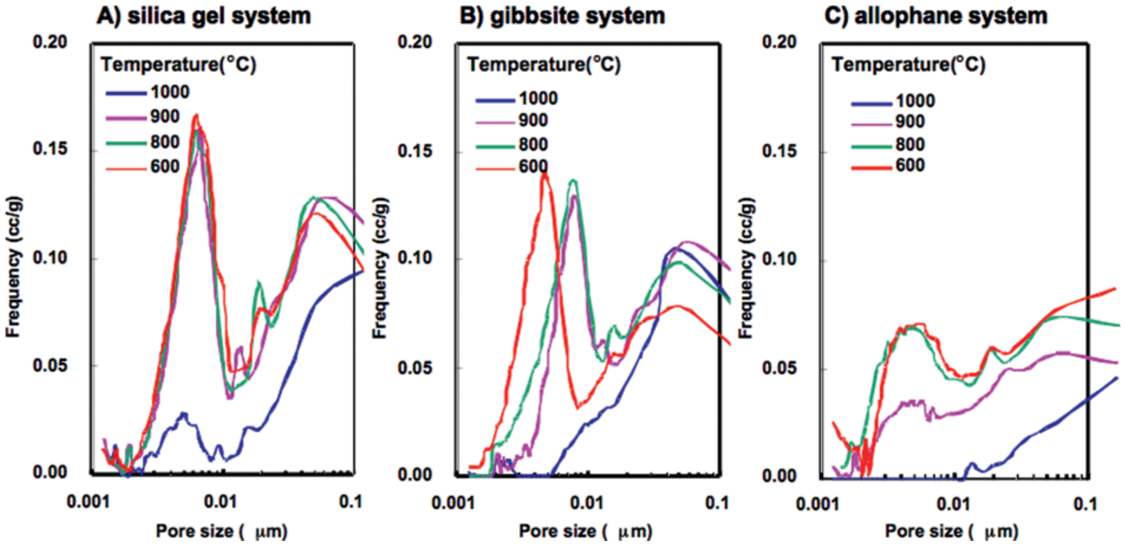

Figure 6. Mesopore size distributions for clay mixture system, A) silica gel, B) gibbsite and C) allophane.

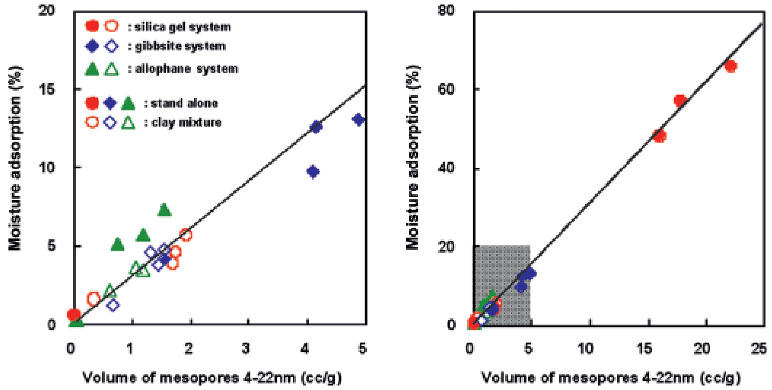

Figure 7. Relation between volume of mesopores from 4 to 22nm in diameter and moisture adsorption from 50 to 90% relative humidity.

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 900ºC for application as interior wall coverings. The physical properties of the test samples are as follows: bulk density: 1.7g/cm^3, flexural strength: 5MPa and porosity: 40%.

Fig. 8 showed moisture adsorption isotherm of the test sample. The test sample adsorbed much moisture more than 60% moisture pressure and amount of moisture adsorption was about 650g/m^2 under increasing the partial pressure of humidity in air from 50 to 90%. In contrast, moisture adsorbed on the test sample desorbed easily with decreasing moisture pressure.

Fig. 9 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.

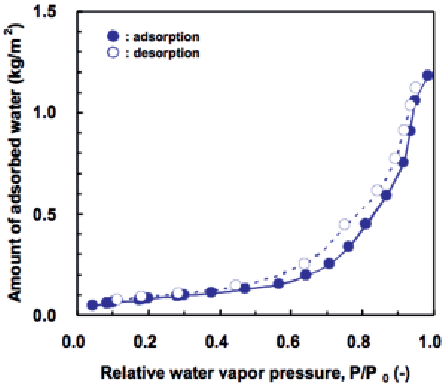

Figure 8. Adsorption-desorption behavior as a function of relative humidity, P/P$_0$ at 25ºC.

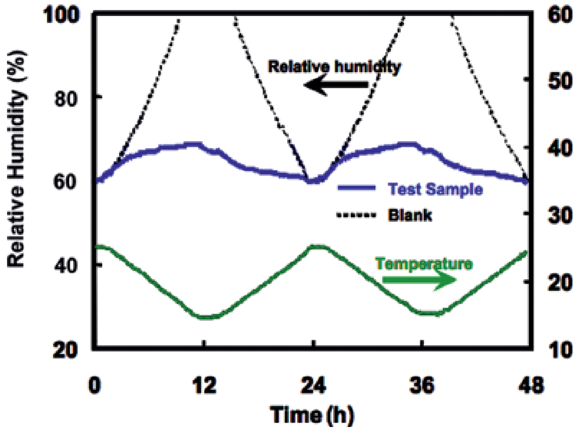

Figure 9. Change in relative humidity in closed vessel.

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 vapour. 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.

Fig. 10 shows the variation of formaldehyde concentration in the presence of wallpaper or the test sample in the small chamber. Wallpaper did not decrease a formaldehyde concentration, but the test sample reduced a formaldehyde concentration two to three times higher than specified in the guideline of the Ministry of Health, Labour and Welfare (MHLW) of Japan to a level much lower than the specified level in only one day. The effect of the test sample continued at least one week under this condition.

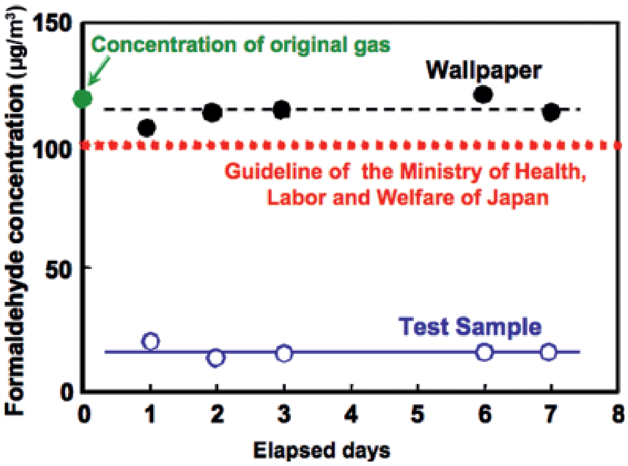

Figure 10. Effects of the test sample on the adsorption of formaldehyde.

Fig. 11 shows the deodorization rate of plaster board, wallpaper and the test sample in the small bag. The test sample reduces these smells by adsorbing ammonia, hydrogen sulphide, methyl mercaptan, trimethylamine and toluene which are the superior to that of plaster board and wallpaper. The smells of toilets, cigarettes, pets, and decayed household garbage are among the most offensive smells that occur in our everyday life.

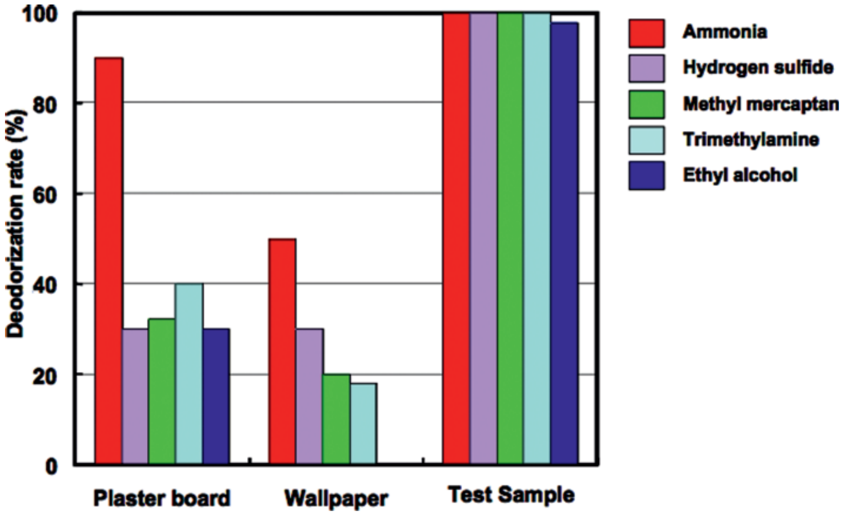

Figure 11. Effects of the test sample on reducing unpleasant smell.

4. CONCLUSION

Ceramic porous material was prepared from allophone and other clay materials. It had mesopores sized from 1 to 10nm and macro-pores from 100 to 500nm. It's behaviour of moisture adsorption and desorption, formaldehyde adsorption of odour materials was discussed. It showed good performance for either measurement and was expected to improve the quality of indoor air when it was applied to interior wall of a room.

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