Development of porous lightweight heat-insulators using gypsum

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Besides natural gypsum, byproduct gypsum is always discharged from the desulfurization process in power plants and the neutralization process in chemical industry. In this study, a porous lightweight material was studied in order to develop a fundamental technology for recycling byproduct gypsum. First of all, several kinds of byproduct gypsiums were converted to hemihydrate type gypsiums by heating at 150 °C overnight, and their bending strengths were tested. Then, as next step, using one of the hemihydrates, porous materials were prepared at ambient temperature by the aid of an organic foaming agent and water. Two types of lightweight materials were obtained through adjusting the amounts of water and the forming agent. One is ordinary porous monolith having 96–183 kg/m³ of bulk density and 0.043–0.069 W/m K of thermal conductivity. Another is granule, of which bulk density was 69–137 kg/m³ and thermal conductivity was 0.047–0.050 W/m K. Hence, it is concluded that even using byproduct gypsum, high-performance porous heat-insulators could be produced, if the counterpart nonporous monolith has over 3 MPa of bending strength.

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1. Introduction

Gypsum available in Japan is classified into three categories, including byproduct gypsum, natural resource gypsum and recovered gypsum, which amount for 4.7 million tons in 2017.¹ The market shares of the 3 types of gypsum are 56.9, 35.6 and 7.5%, respectively.² Byproduct gypsum includes desulfurization gypsum and miscellaneous (guano, ilmenite, fluorite and copper ore processing). Natural resource gypsum is almost entirely depends on import from overseas. The recovered gypsum is recycled from used plaster board.³ In the plaster board industry, about 4.414 million tons of gypsum were consumed in 2018. If deposing waste gypsum, mainly plaster board, to landfill, hydrogen sulfide generates through micro-organism process. Hence, disposal of waste gypsum is a current environmental issue in Japan. On the other hand, waste soil with a high water content, such as construction sludge, is unsuitable for reclamation. Thus, some municipalities allow to add a small amount of waste gypsum to solidify the sludge, but this has not become a common countermeasure of recycling waste gypsum in large quantities. Incidentally, around 5 million tons of plaster board are discharged annually now in Japan. However, the gypsiums used now are desulfurization and natural resource gypsiums and only 5% is a recovered gypsum recycled from discarded plaster board.² Insulation materials used for roof and wall of buildings are roughly classified into the following three types.

First one is natural organic type using wool, flax, cork, cellulose (paper), etc. It is basically a natural material and is widely used because it can be supplied inexpensively in large quantities. However, although non-combustible treatment is applied in advance, it is still a material vulnerable to fire, and CO is emitted, which is a toxic gas.

The second type is organic foam using polystyrene, polyurethane, etc. It is an artificial material with high heat-insulation, but is somewhat expensive. Since it is organic, it is vulnerable to fire and ignites easily to emit toxic gas of CO as like the first type. Due to the deterioration over time, the gas yielded by the foaming agent is also liberated, and it is hard to say that artificial organic foam is durable and healthy.

The third type is inorganic fiber material using glass fibers, rock wool, etc. It is an artificial material with high heat-insulation, and is slightly inexpensive than the organic foam. It is often considered to be strong against fire because it is inorganic, but hydrocyanic acid gas is generated during fire because phenol resin or organic polymer is generally used to bundle the fibers. Furthermore, it has been pointed out that the resin deteriorates over time, resulting in that the heat insulation performance becomes lower and lower due to the sagging of fibers. Emission of CO gas is an issue too.

The porous gypsum material developed in present study is expected to solve the above-mentioned issues of the
conventional products. Since the porous gypsum is inorganic, it is extremely resistant to fire and completely incombusible so that almost no CO is emitted during fire. Also, since gypsum is inexhaustible material, it can be procured inexpensively in large quantities around the world. The manufacturing process of porous gypsum is also simple as described later. Then, it can be supplied inexpensively as a heat insulating material.

Energy saving has been advocated for a long time for suppressing global warming caused by CO₂ emissions. If focusing on the construction industry, the use of double glazing window and/or heat insulation is strongly recommended, but it is difficult to widely use them unless they can be supplied at low cost. The objective of the present study is to produce inexpensive and noncombustible porous heat insulating materials by using either virgin gypsum or waste gypsum.

2. Experimental

Prior to porous material preparation, several kinds of gypsum samples besides hemihydrate gypsum were collected. The gypsups except the hemihydrate gypsum were converted into hemihydrate type beforehand by heating at 150 °C overnight. Prismatic test-pieces were prepared by casting the hemihydrate into a 3-cell type mold of 40 × 40 × 160 mm dimension. Then, 3-point bending strength was measured at 1 week age under the conditions of 100 mm span and 0.5 mm/min cross-head speed, employing a tester (Orientec Tensiron RTC-1250A). The bending strength was obtained by an average of a set of 3 test-pieces.

Results are tabulated in Table 1. Hemi-
hydrates as received were used as it was, but other gypsups were converted to hemihydrate gypsups by heating at 150 °C overnight. It is noted that one of them was as received hemihydrate in α-form, which was produced by autoclaving. It is obvious that these gypsups can be classified into two groups in respect of bending strength, high strength group as high as 3 MPa or more, and low strength group as low as 1.5 MPa or less, disregarding the fineness of Blaine specific surface areas. As a result, hemihydrate for industrial use has been selected to prepare the porous materials mentioned later (See Table 1, specimen No.2), of which bending strength is markedly neither strong nor weak.

3. Results and discussion

3.1 Gypsum sources

Prior to making porous materials, the bending strengths of five kinds of gypsum of different sources were examined beforehand. Results are tabulated in Table 1. Hemihydrate gypsum as received was used as it was, but other gypsups were converted to hemihydrate gypsups by heating at 150 °C overnight. It is noted that one of them was as received hemihydrate in α-form, which was produced by autoclaving. It is obvious that these gypsups can be classified into two groups in respect of bending strength, high strength group as high as 3 MPa or more, and low strength group as low as 1.5 MPa or less, disregarding the fineness of Blaine specific surface areas. As a result, hemihydrate for industrial use has been selected to prepare the porous materials mentioned later (See Table 1, specimen No.2), of which bending strength is markedly neither strong nor weak.

3.2 Water-binder ratio and bulk density

Keeping the dosage of foaming agent constant, the change of bulk density with water-binder ratio, W/B, is shown in Fig. 1. The bulk density decreases with the increase of water. However, when the W/B exceeds 1.0,
the decrease of bulk density becomes slow and approaches to a constant. Furthermore, when W/B exceeds 1.0, granules tend to be formed as described in the next section. No discrimination was performed between granules and monoliths in bulk densities.

3.3 Bulk density and dosage of foaming agent

Figure 2 shows the change in bulk density with the dosage of foaming agent, keeping W/B to be 1.0. As the dosage of the foaming agent was increased from 0.15 to 0.40%, the bulk density dropped sharply, and then approached to a constant bulk density around 100 kg/m³. However, when the dosage of foaming agent was further increased, bubbles would be partially collapsed, and the bulk density of the solidified body turned upward.

When the dosage was around 0.3%, the foam inhibited the hydration of the hemihydrate gypsum so that the solid shape was barely maintained to form coarse body, which is easily granulated by scooping with a spoon, and so-called granules were obtained as indicated by black circles. The body obtained by adding the foaming agent around 0.15% was self-standing. If the dosage was 0.5%, the body was particularly rich in self-standing with enough strength for transportation in practical use.

Physical properties of the prepared porous body used for a heat insulating material are shown in Table 2 together with an example of granule type. The thermal conductivity is comparable or superior to commercially available perlite rock foam having 149 kg/m³ of bulk density and 0.063 W/mK of thermal conductivity, respectively, which were measured in our laboratory.

### Table 2. Physical properties resulted in comparison with commercial products

| No. | Bulk density [kg/m³] | Thermal conductivity [W/mK] | Thermal resistance [K/W] | Bending strength [MPa] |
|-----|----------------------|-----------------------------|--------------------------|------------------------|
| 1.  | 25                   | 0.035                       | 28.6                     | —                      |
| 2.  | 96                   | 0.043                       | 23.3                     | —                      |
| 3.  | 150                  | 0.065                       | 15.4                     | —                      |
| 4.  | 183                  | 0.069                       | 14.5                     | 0.111                  |
| 5.  | 389                  | 0.196                       | 5.1                      | 0.615                  |
| 6.  | 149                  | 0.063                       | 15.9                     | —                      |
| 7.  | 69                   | 0.047                       | 21.3                     | —                      |
| 8.  | 137                  | 0.050                       | 20.0                     | —                      |
| 9.  | Commercially available high performance heat insulators in average. | 0.063 | 16.0 | — |

Monolithic lightweight porous materials (Present study).

Perlite rock foam Granules (Present study).

3.4 Comparison to conventional porous materials

Figure 3 shows the relationship between the thermal conductivity and the bulk density of porous materials including present gypsum materials and some commercially available porous materials. Solid circles are the density and thermal conductivity of air (0.026 W/mK at 20 °C). Each point smoothly rides on a quadratic curve, thus the experimental data of present gypsum materials are reliable.
Figure 4 shows the data (open circles) of the products which are commercially available as heat-insulating materials regardless whether they are organic or inorganic, and the data (open squares) of the prototypes developed in present study.

So-called high-performance insulation materials generally have low bulk densities so that low thermal conductivity close to the air can be realized. However, for extremely lightweight materials there is a reversal phenomenon, of which thermal conductivity increases with the decrease of density. The reason is believed that heat transfer by convection becomes effective among conduction, convection and radiation of three elements of heat transfer. Thus, the bubbles or voids should be formed as small as possible. If it is impossible, the only option is to increase the material density, in other words reducing the void. For example, in the case of foamed styrene-based material, if the pore cells are made smaller, the thermal conductivity decreases. In the case of glass wool, when the vacancies are reduced in volume by compression, the thermal conductivity also decreases. The low coefficient of determination \( R^2 \) in Fig. 4 is due to this reversal phenomenon.

3.5 Materials strength and SEM images

As shown in Fig. 5(a), a monolithic lightweight body on the left, possessing 183 kg/m³ of bulk density, 0.069 W/mK of thermal conductivity exhibited 0.111 MPa of bending strength (Table 2, No.4). No marked chalking that is powdering of surface was observed and sufficiently resistant to transportation. Although other monolithic specimens were superior to this specimen in bulk density as well as thermal conductivity, marked chalking was observed so that surface passivation may be necessary for transportation. By the way, a monolith on the right had a high density.

On the other hand, the granule shown in Fig. 5(b) possessing 137 kg/m³ of bulk density and 0.050 W/mK of thermal conductivity was transportable in a bag. Therefore, it can be used as heat insulating material by filling it between the plates of walls. It is known that a back-injection vacuum cleaner is currently used for filling with flaky cellulosic insulation materials on site.

SEM images are shown in Fig. 6. The monolith, mentioned above, exhibited a globule pores around 500 μm or less, of which distribution was like as a densely packing
4. Conclusions

Conventionally, when a porous material is made by mixing foaming agent and inorganic binder, if its bulk density is less than 200 kg/m³, the material strength is rapidly decreased. So that, self-standing property becomes poor. By the way, air-dried box-form bread is self-standing and has a bulk density of about 200 kg/m³, which is convenient to imagine as a reference for lightweight porous materials.

Further, 300 and 260 kg/m³ are limits to cement and magnesian binder systems so far, respectively. By properly selecting the foaming agent, we succeeded in developing a series of porous materials that broke through the 200 kg/m³ border line using gypsum binder. Specifically porous monoliths and granules were obtained depending on mixing conditions. The bulk density and thermal conductivity of monoliths are 96–183 kg/m³ and 0.043–0.069 W/mK. Those of granules are 69–137 kg/m³ and 0.047–0.050 W/mK.

Present porous materials can contribute not only to the recycling of waste gypsums but also to the development of novel application to virgin gypsum. The criterion of practical application may be that bending strength of hemihydrate gypsum for raw material should exceed 3 MPa after solidification without adding the foaming agent. Eventually, present technology can contribute to the reduction of carbon dioxide emission to prevent global warming by applying the novel lightweight porous materials to buildings as heat insulation materials at low cost.

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