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Water-retention properties of porous ceramics prepared from mixtures of allophane and vermiculite for materials to counteract heat island effects

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Abstract

Porous ceramics for anti-heat island effect were prepared from mixtures of allophane and vermiculite (VA samples). Allophane and vermiculite which had been ground for 0.5–2 h was mixed in various mass ratios, formed into pellets by uniaxial pressing at 40 MPa, and heated at 600–800 °C to form porous ceramics. The large thermal expansion of the vermiculite upon explosive dehydration of interlayer water causes cracking of the pellets with higher vermiculite contents. However, this can be controlled by grinding the vermiculite prior to heating. Grinding the vermiculite for ≥2 h suppresses its expansion, enabling pellet samples with high vermiculite contents to be prepared without cracking. The bulk densities of samples prepared at 800 °C from vermiculite ground for 2 h decrease from 1.72 to 0.94 with increasing allophane content. The pore size distribution in these samples shows a distinct peak at about 1 μm irrespective of the mixing ratio. The number of smaller pores (<50 nm) increases with increasing allophane content while the number of larger pores (20–40 μm) increases with increasing vermiculite content. The compressive strengths of the samples range from 1 to 3 MPa except for samples containing a high proportion of vermiculite ground for 1 h. The water absorption (W_a) of the samples increases from 37 to 63% with increasing allophane content. This absorption rate is fast enough to absorb >90% of the W_a within 1 min for samples of 10 mm Ø × 5 mm^3 size. By contrast, the release of the absorbed water is very slow, with 50% of the W_a retained for ≥30 h in the VA samples at a relative humidity of 55% at 20 °C; this is slower than in pure allophane and much slower than in a reference sample of foamed glass (about 4 h). All these properties make the VA samples useful as water-retaining materials to combat ‘‘heat island’’ effects.

Keywords: Water-holding property; Allophane; Vermiculite; Porous property; Anti-heat island material

1. Introduction

In the large cities of industrial countries, most of the ground surface is covered by artificial pavement materials and many large buildings. The materials generally used are of low thermal conductivity and absorb solar energy rather effectively due to their dark color. Furthermore, exhaust heat from automobiles and air conditioners is increasing with increased population, economic activity and the adoption of modern lifestyles. The reduction of cooling by vapor evaporation from the ground surfaces and increases in the generated heat is causing large cities to become hotter. Cities heated by sunlight retain their high temperature up to midnight, especially in the summer season. The number of nights on which the minimum temperature is greater than 25 °C (called tropical nights) is increasing; for example, the average number of tropical nights in Tokyo has increased from a few to more than 40 over the past 100 years, reflecting an average temperature increase of about 4 °C [1]. This phenomenon has recently been termed a ‘‘heat island’’. Such changes in the ground surfaces of big cities also causes another climate change effect in winter, namely the lowering of the relative humidity to an over-dried state similar

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to a desert environment, leading to the spread of diseases such as influenza.

Many materials with water-retention properties have been developed for use in various types of functional pavement systems. In these pavements, a particular cooling effect arises from vapor evaporation occurs from the surface of pavements containing water-retention materials and/or water-retaining porous ceramics. Candidate water-retaining materials include slag [2], bentonite [3] and diatomite [4]. Water-retaining porous ceramics have also been prepared using various wastes, e.g., blast furnace slag [5] and Kira (the waste generated from the benefication process of silica sand and plastic clay [6]). However, it is difficult to maintain this effect for any length of time without supplying water because the water-retaining materials developed so far have a rather poor ability to release the retained water continuously since little consideration has been given to the importance of this slow release property. Water-retaining materials for use in pavements should therefore have a fast rate of water-absorption, high water absorption capacity and a slow release rate of the adsorbed water.

Soil used for agriculture may contain the clay minerals vermiculite and allophane which are well-known for their water-retention properties. If they are used as powders, their outer surfaces do not present many adsorption sites. For this reason, vermiculite is heat-treated to create spaces between the layers of the particles and allophane is used in a granular form to utilize the spaces between the agglomerated nano-particles. We, therefore, considered that more spaces might be made available for water adsorption if these powders were mixed and lightly sintered to form necks between the contacting grains. The mixing of platy particles should not only enhance slow water release by a shielding effect [7] but also increase the mechanical strength [8].

This paper describes the preparation of porous ceramics by heating mixtures of vermiculite and allophane at relatively low temperatures. The effect of changing the mixing ratios, grinding times of the vermiculite and the heating temperature was investigated. The water absorption rate, amount of water absorbed and its release rate was determined for these materials and compared with a foamed glass sample.

2. Experimental

2.1. Preparation of the samples

The starting materials were vermiculite from Phalaborwa, South Africa (0 grade, Vermitech Co.) and allophane from Kanuma pumice (Lead Co.). The vermiculite (4 g) was ground in a planetary ball mill (Itoh Co.) at 300 rpm using Si_3N_4 balls (Ø10 mm) for 0.5, 1 and 2 h. The allophane was obtained by sieving (#200) the Kanuma pumice. The two clays were mixed in various ratios using an agate mortar and pestle, then uniaxially pressed at 40 MPa to form 10 mm Ø × 5 mm pellets. The pellets (designated VA samples) were heated at 600–800 °C at a heating rate of 10 °C/min. Foamed glass prepared by heating waste glass powder at about 900 °C with a small amount of SiC as a foaming agent was used as a reference material when cut to similar size and shape as the VA samples.

2.2. Characterization of samples

The expansion of the VA samples upon heating was determined from the diameter and thickness of the pellets, measured using a micrometer. The bulk densities of these samples were calculated by the conventional method. The microstructures of the VA samples were observed by SEM (JSM-5310, JEOL) at an accelerating voltage of 15 kV. The compressive strengths of the VA samples were measured using a universal testing machine (Autograph DCS-R-10TS, Shimadzu) with a 500 kg load cell and a head speed of 0.5 mm/min. The pore size distributions of the VA samples were determined by Hg porosimetry (Pascal 140 and 240, CE Instrument).

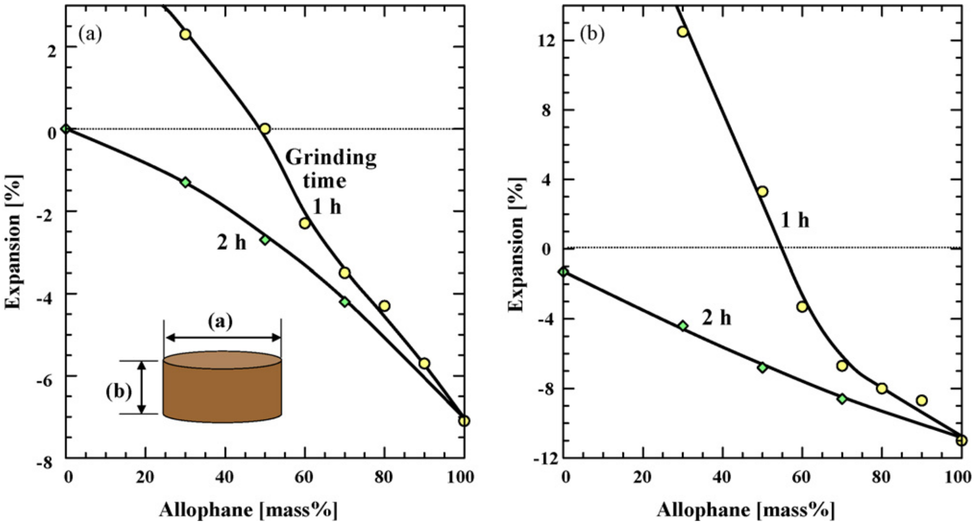

Fig. 1. Expansion of the VA samples prepared at 800 °C from 1 and 2 h ground vermiculites as a function of the allophane content.

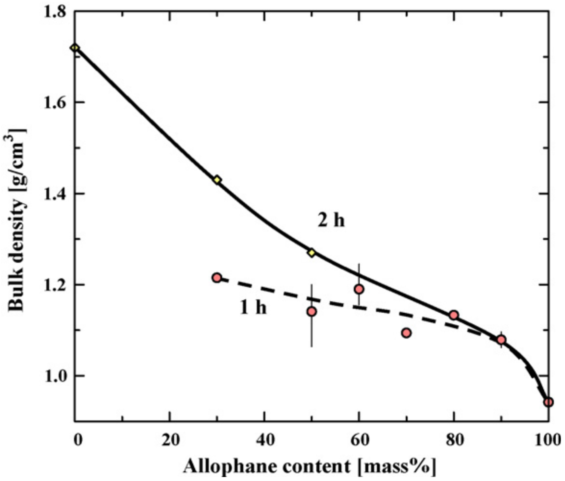

Fig. 2. Bulk density of the VA samples prepared at 800 °C from 1 and 2 h ground vermiculites as a function of the allophane content.

2.3. Water-retention properties

The water absorption of the VA samples was determined by immersing them in water at 20 °C and weighing after predetermined time intervals up to 24 h. The water absorbed after 24 h was defined as the water absorption (W_a (%)). Release of the absorbed water was measured in an atmosphere with the relative humidity controlled at 55% using a saturated $Mg(NO_3)_2 \cdot 6H_2O$ solution. The water release rate was then evaluated from the time at which half the absorbed water was lost ($t_{1/2}$ (h)).

3. Results and discussion

3.1. Effect of preparation conditions

The VA samples prepared from the as-received vermiculite powder showed many cracks after heating, due to the abrupt expansion of the vermiculite particles. This expansion and cracking of the samples was suppressed by grinding the vermiculite. Although the VA samples prepared from vermiculite ground for 0.5 h still show evidence of expansion and cracking, this is largely suppressed by grinding $\geq$1 h. Changes in the expansion of the VA samples prepared from vermiculite ground for 1 and 2 h and heated at 800 °C are shown in Fig. 1 as a function of the allophane content in the samples. In the case of the samples prepared from 1 h ground vermiculite, the pellet size increases with increasing allophane content, especially <50% allophane. By contrast, the VA samples prepared from 2 h ground vermiculite show no expansion after heating, with no cracks observed even in the sample containing 100% vermiculite. However, the bulk density clearly increases with increasing vermiculite content (Fig. 2), reflecting the reduced porosity of those samples. Thus, the allophane-rich VA compositions are preferable if 1 h ground vermiculite is used, whereas, usable vermiculite-rich compositions require vermiculite ground for 2 h to avoid cracking.

The effect of heating temperature was investigated using samples containing 90% allophane and 10% of vermiculite ground for 1 h. Fig. 3 shows the water absorption (a) and compressive strength (b) of these samples as a function of heating temperature. The W_a values are about 63% at heating temperatures of 600 and 700 °C but decrease on heating above 700 °C, becoming 57.5% at 800 °C. By contrast, the compressive strengths show the opposite trend to W_a, and increase with increasing heating temperature from about 1 MPa at 600 °C to >2 MPa at 800 °C. Thus, there is a trade-off between W_a and compressive strength with heating temperature, leading to our adoption of 800 °C for the remainder of this study.

3.2. Characterization of the 800 °C samples

The SEM microstructures of the VA samples are shown in Fig. 4 together with the reference foamed glass sample. The

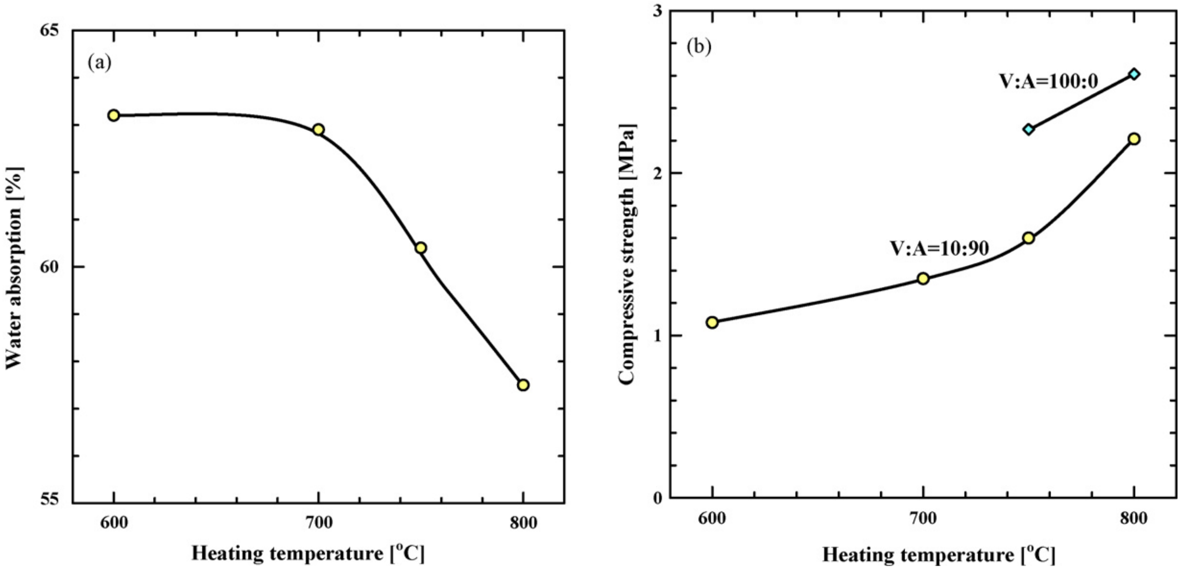

Fig. 3. Effect of the heating temperature on the water absorption (a) and compressive strength of VA samples (V:A = 10:90) prepared at 800 °C from 1 h ground vermiculite (b).

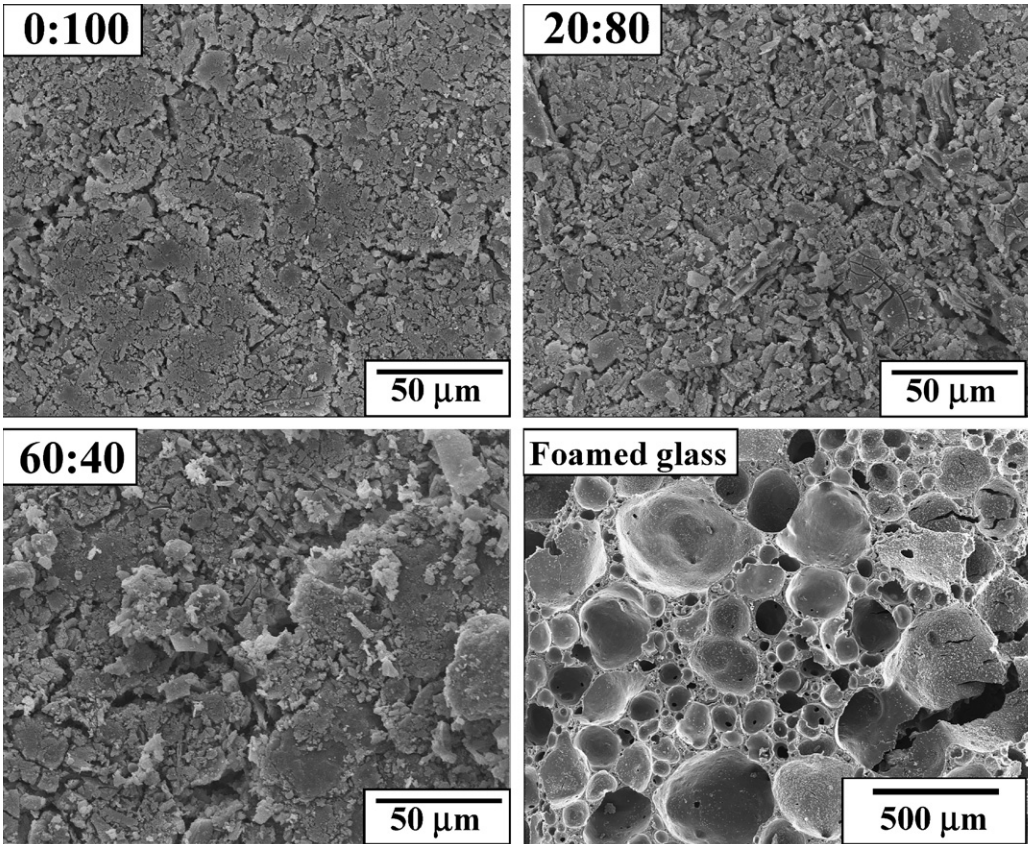

Fig. 4. Microstructures of the VA samples prepared at 800 °C, and of the foamed glass reference material.

microstructures of the VA samples show pores of visible size and crack-like shape in a dense-looking matrix. The platy particles with smooth surfaces correspond to the ground vermiculite. The appearance of all the VA samples is similar, but the microstructure of the foamed glass is quite different, with large spherical pores ranging in size from several tens to hundreds of μm.

The pore size distributions of the VA samples (Fig. 5) all show a distinct peak at about 1 μm irrespective of the allophane content and the use of 1 h ground vermiculite. Increasing the allophane content increases the number of small pores

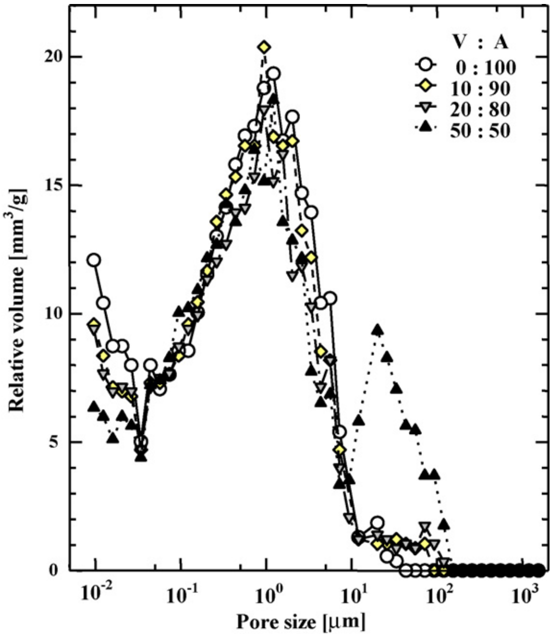

Fig. 5. Pore size distributions of the VA samples prepared at 800 °C from vermiculite ground for 1 h.

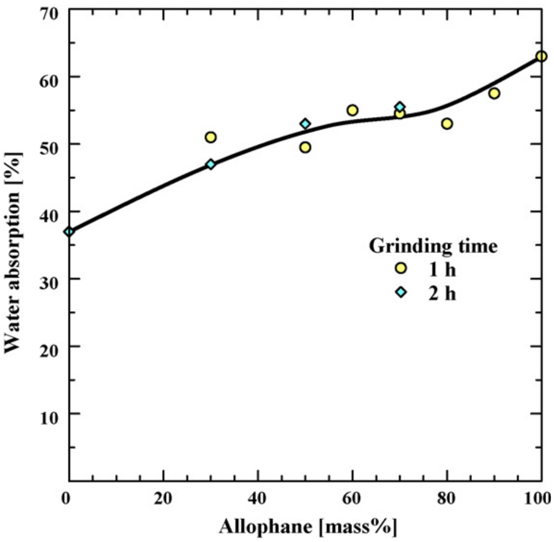

Fig. 6. Water absorption of the VA samples prepared at 800 °C from 1 and 2 h ground vermiculites as a function of allophane content.

(<0.1 μm), thought to be formed by the agglomeration of spherical ≈5 nm nano-particles of allophane [9]. On the other hand, larger pores (>10 μm) are also observed, especially in the V:A = 50:50 sample. These pores are related to the expansion of vermiculite upon heating [10], suggesting that the various pore sizes can be controlled by mixing allophane with ground vermiculite, and that this is a very good strategy for enhancing the water-retention properties of the VA samples.

3.3. Water-retention properties

The water absorption data of the VA samples prepared from vermiculite ground for 1 and 2 h are shown in Fig. 6 as a function of the allophane content. The samples show a gradual decrease of W_a with decreasing allophane content irrespective of the grinding time of the vermiculite, reflecting the higher W_a of allophane than of vermiculite. Since the minimum W_a requirement for water-retaining materials used in pavements is 40% [11], most of the present samples satisfy this condition.

The weight loss curves of VA, allophane, vermiculite and foamed glass are shown in Fig. 7 as a function of heating time. All the samples show initial steep weight losses which become more gradual at longer water-release times. These weight loss curves can be divided into two parts, approximated by straight lines. We define the water-release parameter ($t_{1/2}$) by the time taken for half the water to be released from the samples. Fig. 8 shows these $t_{1/2}$ values as a function of the allophane content of the samples. The samples prepared using 1 h ground vermiculite have $t_{1/2}$ values of about 30 h; these are larger than for the allophane sample (20 h). The $t_{1/2}$ values increase slightly with increasing allophane content up to V:A = 10:90, increasing even further in the samples prepared using the vermiculite ground for 2 h. Dispersion of the thin platy particles of ground vermiculite in the allophane matrix is effective in preventing vapor evaporation from the porous ceramics. A maximum value of $t_{1/2}$ value of about 38 h was recorded for the sample with V:A = 30:70. Since the $t_{1/2}$ value of the foamed glass reference sample is only about 4 h, the present VA samples show excellent slow water release properties, probably due to the smaller pores compared with those in the foamed glass. The low throat/pore ratios of the VA samples also facilitate slow water release, giving good water-retention properties.

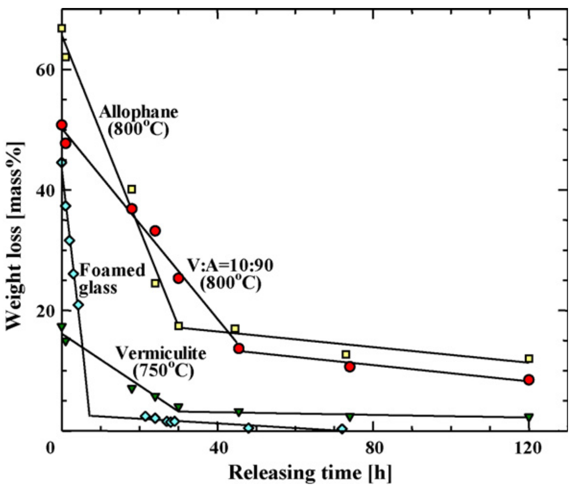

Fig. 7. Weight loss curves of VA, allophane, vermiculite and foamed glass as a function of the water-release time.

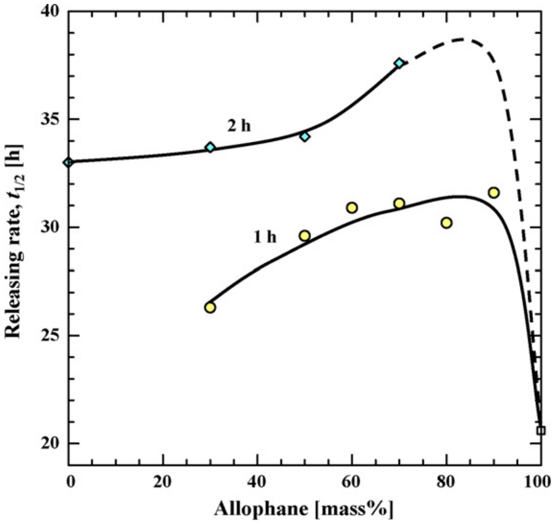

Fig. 8. Water-release rate ($t_{1/2}$) of the VA prepared at 800 °C from 1 and 2 h ground vermiculites as a function of allophane content.

The compressive strengths of the VA samples are shown in Fig. 9. The samples prepared using vermiculite ground for 1 h show strength increases with increasing allophane content up to V:A = 10:90. The maximum recorded strength (2.2 MPa) is much higher than that of the foamed glass (0.43 MPa), and is also higher than the minimum strength required for pavement filler materials (0.5 MPa) [11]. However, the strength decreases significantly at allophane contents <30% due to the expansion of the vermiculite (Fig. 1). The samples with higher allophane contents are therefore preferable as water-retaining prepared using vermiculite ground for 1 h. By contrast, the compressive strength increases with lower allophane contents in samples

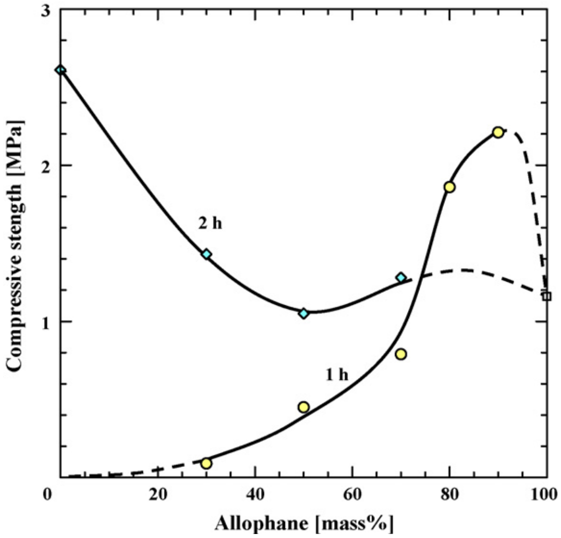

Fig. 9. Compressive strength of the VA samples prepared at 800 °C from 1 and 2 h ground vermiculites as a function of allophane content.

prepared using vermiculite ground for 2 h. With vermiculite ground for longer times, the mixing ratio necessary for good water-retaining properties increases greatly.

4. Conclusions

Porous ceramics with good water-retention properties were prepared from mixtures of ground vermiculite with allophane, heated at 600–800 °C. The following observations were made:

(1) Grinding of the vermiculite is necessary to suppress cracking of the ceramics caused by the abrupt expansion of the vermiculite particles.
(2) Heating the ceramics at 800 °C produces adequate mechanical strength but a small decrease in their water absorption properties.
(3) Water absorption by the VA samples increases from 37 to 63% with increasing allophane content.
(4) Water release by the samples (defined in terms of their $t_{1/2}$ value) is slowed down by mixing allophane with the ground vermiculite, due to the synergy effect of high water absorption by the allophane and the shielding effect of the vermiculite. The $t_{1/2}$ values of the VA samples are about one order of magnitude better than in the foamed glass used as the reference material.
(5) Increasing the grinding time of the vermiculite from 1 to 2 h increases the water-retention properties of the resulting VA samples.
(6) The compressive strengths of the VA samples other than the vermiculite-rich materials containing 1 h ground vermiculite range from 1 to 3 MPa.

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