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Hydrothermal Synthesis of Meso-porous Materials using Diatomaceous Earth

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Abstract. In order to sustain the inherent properties of diatomaceous earth (DE), a low-temperature synthesis of meso-porous material from DE was carried out using a hydrothermal processing technique under saturated steam pressure at 200 °C for 12 h. The experimental results showed that the most important strength-producing constituent in the solidified specimens was tobermorite formed by hydrothermal processing, and the addition of slaked lime was favorable to tobermorite formation. At Ca/Si ratio around 0.83 in the starting material, tobermorite appeared to form readily. A high autoclave curing temperature (200 °C), or a longer curing time (12 h) seemed to accelerate the tobermorite formation, thus leading to a higher strength development.

Keywords: Hydrothermal synthesis, Meso-porous material, Diatomaceous earth; Tobermorite, Strength

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INTRODUCTION

Diatomaceous earth (DE) is a chalk-like, soft, friable, earthy, very fine-grained, siliceous sedimentary rock. It is very finely porous, very low in density, and essentially chemically inert in most liquids and gases, which is being used principally as filter aid, absorbent as pet litter, insulation materials etc.

Due to the porous property and low density, DE has a high potential application in the manufacture of meso-porous ceramic materials. The meso-porous materials have capability of humidity-regulating, i.e., making the water vapor in the atmosphere to condense with the capillary pores that exist on their surface when the humidity is high; while when the humidity is low, they should function to vaporize the condensed water. The DE ceramics is manufactured at a lower temperature (800 °C) so as to sustain the porous property [1], which, undoubtedly, results in a low strength for these meso-porous materials. Ishida [2] reported that the temperature of manufacture of earthen products must be lower than 500 °C to sustain the inherent properties and performance of earthen materials (pore distribution).

A hydrothermal processing method has been applied to the field of building materials [2] and recently, it has been also used to solidify wastes into building materials [3-5] The hydrothermal processing method is carried out at 150-200 °C in saturated steam pressure, and therefore it is considered to be suitable to manufacture DE meso-porous materials.

In hydration of Portland cement, tobermorite has been shown to be the most important strength-producing constituent of hydrated cement [6,7]. In the hydrothermal processes of calcium silicate products and insulating materials, the strength development has been proven to be due to the formation of tobermorite and calcium silicate hydrate (CSH) [8,9]. In our previous researches, municipal incineration ash [3] and coal fly ash [4] have also been solidified hydrothermally with the formation of tobermorite. The DE meso-porous materials, therefore, may be synthesized hydrothermally with tobermorite formation.

To the best of our knowledge, however, the hydrothermal solidification of DE with tobermorite formation has not been reported extensively in the literature.

In this study, the DE was used as a raw material for hydrothermal synthesis of meso-porous materials. In order to obtain the DE meso-porous materials with a high strength, we investigate how to solidify DE using a hydrothermal synthesis method. The aim of this study is to investigate the condition of tobermorite formation, and then evaluate the effects of the tobermorite formation, curing time and temperature on the strength development of the solidified specimens. The results are expected to provide useful information on the manufacture of building materials from DE.
EXPERIMENTAL PROCEDURE

The DE used in this study was obtained from Showa Chemical Industry Co. Ltd. in Japan. The BET specific surface area of DE measured by Autosorb-1 (Quantachrome) is 34.6 m²/g. The particle size distributions as determined by laser diffraction technology (X100, Microtrac), and composition by x-ray fluorescence (XRF, RIX3100, Rigaku) of DE are shown in Fig. 1 and Table 1. In order to form tobermorite, the DE mixed with slaked lime at different mixing ratio was used as starting material. The starting material (20 g) was first mixed with 15 mass% distilled water (3.0 ml) in a in a mortar, and then the mixture was compacted by compaction pressure of 20 MPa in a disc-shaped mould (ø30mmxθ120mm). The demoulded specimens were subsequently autoclaved under the saturated steam pressure (1.56 MPa) at 120 - 200 °C up to 24 h. After autoclaving, all the solidified specimens were dried at 80 °C for 24 h before testing.

![Particle size distribution of DE](image)

**FIGURE 1.** Particle size distribution of DE.

**TABLE 1.** Composition of DE used (mass%).

<table>
<thead>
<tr>
<th>Element</th>
<th>Mass%</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>86.4</td>
</tr>
<tr>
<td>CaO</td>
<td>0.9</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>9.2</td>
</tr>
<tr>
<td>TiO₂</td>
<td>0.3</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>2.5</td>
</tr>
<tr>
<td>K₂O</td>
<td>0.7</td>
</tr>
</tbody>
</table>

The solidified disc-shaped specimens (ø30mm×H20mm) were used to measure the tensile strength employing the Brazilian testing method [10]. The Brazilian tests were conducted in an Instron universal testing machine (M1185) at a crosshead speed of 0.2 mm/min. Three specimens were tested for each hydrothermal processing condition, and the experimental results presented in this study are the averaged data. After the strength testing, the crushed specimens were investigated for phase analysis by an X-ray diffraction (XRD, MiniFlex, Rigaku) and for microstructure by a scanning electron microscope (SEM S-4100, Hitachi).

RESULTS AND DISCUSSION

Figure 2 and 3 indicate the XRD pattern and SEM photograph of the DE used. For the XRD pattern of the DE, main phases corresponding to cristobalite (SiO₂), hematite (Fe₂O₃), quartz (SiO₂) and kyanite (Al₂SiO₅) are confirmed, and disk-shaped diatom frustules are well preserved in the photograph (Fig. 3). Because SiO₂ content in the DE occupies more than 85 mass%, slaked lime should be added so as to form tobermorite.

![XRD pattern for DE](image)

**FIGURE 2.** XRD pattern for DE.

![SEM photograph of DE powder](image)

**FIGURE 3.** SEM photograph of DE powder.

Figure 4 shows the effect of slaked lime content on the tensile strength of the solidified specimens. The strength increases with increasing slaked lime content until 50 mass%, and then decreases for a larger slaked lime content, suggesting that an optimum slaked lime
content exists for the hydrothermal synthesis of the DE meso-porous materials. The tensile strength at 50 mass% slaked lime added is more than 10 MPa, which is higher than ordinary concrete. It should be noted that the molar ratio of CaO/SiO₂ (Ca/Si) of the starting material for 50 mass% slaked lime added is about 0.91, which is close to the Ca/Si of tobermorite (0.83). This suggests that the strength development may be due to the tobermorite formation.

![FIGURE 4. Effect of slaked lime content on the strength.](image)

![FIGURE 5. XRD patterns for different content of slaked lime.](image)

XRD patterns for the solidified specimens with different slaked lime content are shown in Fig. 5. Without slaked lime added, the main phases of cristobalite (SiO₂), Hematite (Fe₂O₃), quartz (SiO₂) and kyanite (A1₂SiO₅) are confirmed. New phases corresponding to 1.1 nm tobermorite (Ca₅Si₆H₂O₁₈·4H₂O) and portlandite (Ca(OH)₂), however, become distinct for slaked lime content of 40-60 mass%. Comparison of the results with the strength results shown in Fig. 4 suggests that the strength development is believed to be due to tobermorite formation because the portlandite should come from the slaked lime added. It is notable that with 60 mass% slaked lime added, the peak intensity of portlandite becomes very high and tobermorite peak appears to become low. Compared with the strength result shown in Fig. 4, this excessive slaked lime added appears to cause a reduction in tobermorite formation and thus leads to a decrease in the strength development. This result agrees with that reported by Jing et al., who studied the hydrothermal solidification of coal fly ash [4].

![FIGURE 6. Effect of curing temperature on the strength.](image)

![FIGURE 7. Effect of curing temperature on the strength.](image)

The influences of the autoclave temperature and time on the tensile strength of the solidified specimen synthesized with 50 mass% slaked lime added are presented in Figs 6 and 7. In Figs 6 and 7, the data points plotted at room temperature and zero curing time, respectively, indicate the results for as-compacted specimens (without hydrothermal processing). It is clear that the hydrothermal processing usefully increases the tensile strength of solidified...
specimens. For instance, the tensile strength at 3 h (200 °C) is about 6 times higher than that of the as-compact specimen. The similar trend observed for the curing temperature effect can be seen in Fig. 7.

Figures 8 and 9 show the XRD patterns for the effects of the curing temperature and time discussed in Fig. 6 and 7 respectively. Figure 8 confirms xerothalite, Hematite, quartz, kyanite and portlandite in the as-compact specimen, and with increasing curing time, however, the peak intensities of portlandite and xerothalite tend to decrease, suggesting that the added portlandite appears to have been acted with xerothalite in the DE to form calcium silicate hydrate (CSH). Because the trace of CSH formed, it might fail to be detected by XRD. At 12 h, however, the 1.1 nm tobermorite forms, and this also results in the highest strength shown in Fig. 6. This suggests that a longer curing time is favorable to tobermorite formation. The XRD patterns for different curing temperature is shown in Fig. 9. It is clear that higher curing temperature (200 °C) accelerates the tobermorite formation, thus leading to the highest strength development (Fig. 7).

CONCLUSIONS

A hydrothermal processing technique has been developed for synthesis of meso-porous material from DE so as to sustain the inherent properties of DE. The experimental results can be summarized as follows:

1. DE could be synthesized hydrothermally at 200 °C for 12 h, at which the tensile strength was more than 10 MPa.
2. The most important strength-producing constituent in the solidified specimens was shown to be tobermorite formed by hydrothermal processing, and the addition of slaked lime was favorable to tobermorite formation. At Ca/Si ratio around 0.83 in the starting material, tobermorite appeared to form readily.
3. A high autoclave curing temperature (200 °C), or a longer curing time (12 h) seemed to accelerate the tobermorite formation, thus leading to a higher strength development.

REFERENCES