

## Hydrothermally Solidified Waste Soil

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Increased environmental concerns, such as shortage of the natural resources, environmental pollution, global warming and wastes disposal, highlight the need to build up a new society based on recirculation of our limited natural resources. In order to build up the recirculation society, the input (e.g. raw materials, fossil fuels) and the output (e.g. waste materials, exhaust gases) of the natural system should be reduced by recirculation of materials and energy. Based on this point of view, the authors have been studying hydrothermal processing for conversion of inorganic wastes into the useful materials with very low energy, at the waste heat level. In the hydrothermally solidified waste soil, the strength development by the formation of hydrogarnet was recognized, resulting in flexural strengths between 15 to 20 MPa. It was believed that the formation of mesopores (size=0.04 $\mu$ m approx.) that accompanied with the formation of hydrogarnet is related to the strength development. Simultaneously the hydrothermally solidified waste soil was a human friendly material with a humidity control property caused by the above mentioned mesopores in the range of 0.01 - 0.1  $\mu$ m. From these results, it was clarified that the hydrothermally solidified waste soil was a low environmental impact and human friendly material.

Key words: waste soil, hydrothermal processing, flexural strength, humidity control, mesopore

### 1. INTRODUCTION

Increased environmental concerns, such as shortage of the natural resources, environmental pollution, global warming and wastes disposal, highlight the need to build up a new society based on recirculation of our limited natural resources. In order to build up the recirculation society, the input (e.g. raw materials, fossil fuels) and the output (e.g. waste materials, exhaust gases) of the natural system should be reduced by recirculation of materials and energy. Based on this point of view, the authors have been studying hydrothermal processing for conversion of inorganic wastes into the useful materials with very low energy, at the waste heat level.<sup>1)-4)</sup>

The present work is an attempt to solidify the waste soil which is a by-product in the mining industry and is dumped in large amount. The waste soil contains much amount of clay minerals. It is known that the wall made from clay has a superior property of humidity control. It is also expected that the hydrothermally solidified waste soil has a humidity control property.

However, in the general calcium silicate materials for which hydrothermal treatment is available, such as sand lime bricks and ALC, the raw materials need to have 90mass% or higher purity of SiO<sub>2</sub>.<sup>5)</sup> Therefore, there are few studies in which the raw materials contained much amount of clay minerals were used for hydrothermal solidification. In this paper, using kaolinite as the source of Al<sub>2</sub>O<sub>3</sub>, which is typical clay mineral, the behavior of strength development and humidity control was investigated in hydrothermally treated bodies belonging to the kaolinite-quartz-lime

system. Using actual waste soil as raw material, the application of the hydrothermally treated waste soil to the building material was also investigated.

### 2. HYDROTHERMALLY SOLIDIFIED KAOLINITE-QUARTZ-LIME MIXTURE

#### 2.1 Experimental Procedure

Quartz (Indian quartz, Tatsumori Ltd., CMC-12-S, mean particle size 6.8 $\mu$ m, specific surface area 1.85m<sup>2</sup>/g) as the Si source and kaolinite (Georgia kaolin, Dry Branch Kaolin Company, Hydrate PXN, mean particle size 1.7 $\mu$ m, specific surface area 15.8m<sup>2</sup>/g) as the Al source were used as the starting materials. Their chemical compositions are shown in Table I. Lime (CaO) was used as the Ca source. It was obtained by calcining CaCO<sub>3</sub> (Wako Pure Chemicals Industries, Ltd., reagent grade) at 1000° C for 5 h.

Table I. Chemical Composition of Starting Materials

elements	Indian quartz	Georgia kaolin
SiO <sub>2</sub>	>99.5	45.4
Al <sub>2</sub> O <sub>3</sub>	—	39.2
Fe <sub>2</sub> O <sub>3</sub>	—	0.6
CaO	—	<0.1
MgO	—	<0.1
K <sub>2</sub> O	—	0.1
Na <sub>2</sub> O	—	<0.1
TiO <sub>2</sub>	—	1.4
L.O.I.#	—	13.9

# Loss on ignition

The quartz, kaolinite and lime were weighed to obtain mixtures with kaolinite/(quartz+kaolinite) mass ratios ( $K/(Q+K)$ ) of 0, 0.1, 0.5, 0.9 and 1.0 with the lime/(quartz+kaolinite) ratio being kept constant at 0.21. The amount of lime added was decided on the criterion that, for  $K/(Q+K)=1.0$ , the Ca/Si atomic ratio was 0.5. After weighing, distilled water was added and mixed in sufficient quantity for slaking the lime, followed by an additional amount of water for forming (10 mass% of the powder mix). Rectangular test specimens of  $10\text{mm} \times 15\text{mm} \times 40\text{mm}$  were formed by uniaxial pressing (30MPa) and hydrothermal treatment under saturated steam pressure at  $200^\circ\text{C}$  for periods ranging from 2 to 20 h.

After hydrothermal treatment, the test specimens were dried at  $80^\circ\text{C}$  for 2 d. The dried specimens were tested for flexural strength (TENSILON RTM-500, A&D, Japan, 3 point flexural strength test, span 30mm, cross-head speed 0.5mm/min, no. of specimens 5) and their bulk density was measured (calculated from the mass and dimensions). The phases that constitute the specimens were identified by XRD analysis (RAD-B, Rigaku, Japan). The pore size distribution was determined by mercury intrusion porosimetry (Autoscan-33, Quantachrome). The amount of the moisture adsorption and desorption was measured between 40% R.H. (relative humidity) and 80% R.H. at  $25^\circ\text{C}$  for the specimens which were cut into halves (size of  $10\text{mm} \times 15\text{mm} \times 20\text{mm}$ ) and whose five faces were sealed with aluminum sheet.

## 2.2 Results and discussion

### 2.2.1 Strength development

The variation of flexural strength and phases formed with curing time was shown in Fig. 1.

Formation of calcium silicate hydrate, such as C-S-H, tobermorite ( $\text{Ca}_5(\text{Si}_6\text{O}_{18}\text{H}_2) \cdot 4\text{H}_2\text{O}$ ) and gyrolite ( $\text{Ca}_8(\text{Si}_{12}\text{O}_{30})(\text{OH})_4 \cdot 7\text{H}_2\text{O}$ ), was observed for the quartz rich specimen, i.e. those with  $K/(Q+K)=0, 0.1$ . On the other hand, for the kaolinite rich specimen, i.e. those

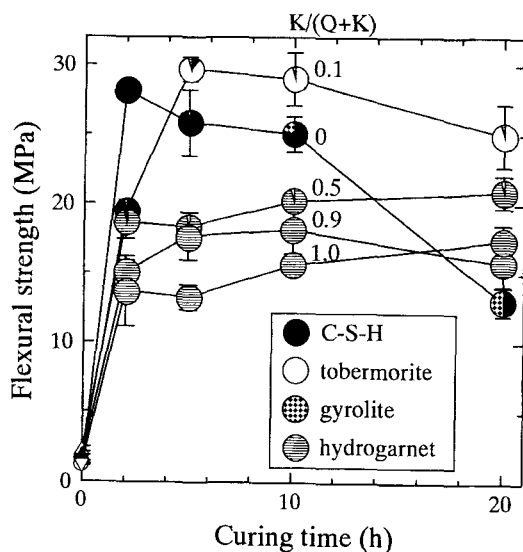


Fig. 1 Variation of flexural strength and phases formed with curing time.

with  $K/(Q+K)=0.5$  to 1.0, hydrogarnet ( $\text{Ca}_3\text{Al}_2(\text{SiO}_4)(\text{OH})_8$ ) was mainly formed. For all compositions, it was clear that hydrothermal treatment led to an increase in strength. Even kaolinite rich compositions could be solidified by hydrothermal treatment. In the case of specimens with  $K/(Q+K)=0$  and 0.1, where calcium silicate hydrates were the main phase, the maximum flexural strength, which was about 30MPa, was reached for curing times of 2 to 5 h. However, after reaching the maximum value, the strength decreased for longer curing times. This trend was particularly clear for  $K/(Q+K)=0$  and is thought to be caused by the formation of gyrolite.<sup>6),7)</sup> In the case of the kaolinite rich specimens with  $K/(Q+K)=0.5$  to 1.0, the flexural strength was 15 to 20MPa after 2 h treatment, tending to increase very slightly for longer curing times.

The relation between strength development and the microstructure of the solidified bodies was investigated by measuring the pore size distribution (Fig.2).

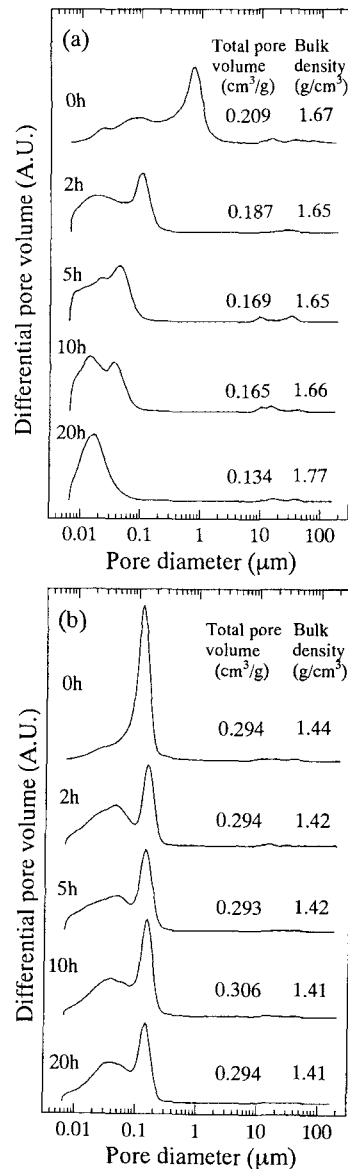


Fig.2 Pore size distribution of the specimen with (a)  $K/(Q+K)=0.1$  and (b) 1.0.

Before hydrothermal treatment, the pore size distributions show peaks at  $1\mu\text{m}$  and  $0.1\mu\text{m}$  for  $K/(Q+K)=0.1$  and  $1.0$ , respectively. It was observed that the peaks tended to shift towards finer diameters with increasing  $K/(Q+K)$ . These peaks correspond to the spaces existing between the raw material particles at the time of forming the bodies, suggesting that the pore diameters become finer with the increase in the amount of kaolinite ( $1.7\mu\text{m}$ ) in the composition. In the case of specimens with  $K/(Q+K)=0.1$ , where calcium silicate hydrates were the main phase, these peaks which correspond to the interparticle spaces shift towards finer diameters up to about  $0.01\mu\text{m}$  with increasing curing time. The reason for the observed strength development in the quartz rich specimens is the formation of fine pores of size  $0.01\mu\text{m}$  accompanying the precipitation of C-S-H and tobermorite.<sup>1),2),7)-9)</sup> In contrast to the specimens with  $K/(Q+K)=0.1$ , shifting of the pore diameter peaks towards finer diameters was not recognized in the specimens with  $K/(Q+K)=1.0$ . The pore diameter peak heights at  $0.1\mu\text{m}$  decreased to about  $1/2 - 2/3$  of their original values after 2 h of treatment, while the decrease was slight in longer treatment than 2 h. These peaks remained even after 20 h of treatment. Fresh peaks were observed to form at about  $0.04\mu\text{m}$  as the curing time increased. Since hydrogarnet is the only phase formed by hydrothermal treatment, the pore formation behavior is thought to result from the precipitation of hydrogarnet, and there is a possibility that the formation of these pores influenced the strength development.

### 2.2.2 Humidity control performance

The humidity control property of the specimens autoclaved at  $200^\circ\text{C}$  for 10h were estimated. It is generally said that the humidity control property increase with the amount of moisture adsorption and desorption. The behavior of moisture adsorption and desorption between 40% R.H. and 80% R.H. at  $25^\circ\text{C}$  was shown in Fig. 3. It was recognized that the humidity control property of the hydrothermally solidified kaolinite-quartz-lime mixtures. Especially, in the case of specimens with  $K/(Q+K)=0$ , where C-S-H were the main phase, and  $K/(Q+K)=0.9$  and  $1.0$ , where much amount of kaolinite were contained, much amount of moisture adsorption and desorption was observed. It is considered that these behaviors of humidity control are influenced by the mesopores in the range of  $0.01 - 0.1\mu\text{m}$ .<sup>10)</sup>

### 3. APPLICATION TO BUILDING MATERIAL

Using actual waste soil as a raw material, the application of the hydrothermally treated waste soil to the building material was investigated.

The waste soil (from a smashed rock plant in Tochigi, Japan,  $\text{SiO}_2$  81.1mass%,  $\text{Al}_2\text{O}_3$  8.5mass%, mean particle size  $32.6\mu\text{m}$ ), slaked lime ( $\text{Ca}(\text{OH})_2$ ) and water were used as the starting material and mixed at the ration of waste soil : slaked lime : water = 80 : 20 : 10 (mass ratio). The specimens having  $200\text{mm} \times 200\text{mm} \times 20\text{mm}$  were formed by uniaxial pressing (30MPa) and autoclaved at  $180^\circ\text{C}$  for 6 h.

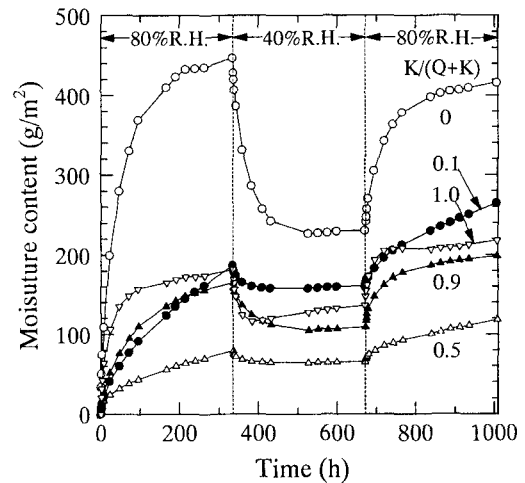


Fig. 3 Behavior of the moisture adsorption and desorption of the specimen autoclaved at  $200^\circ\text{C}$  for 10h between 40% R.H. and 80% R.H. at  $25^\circ\text{C}$ .

The flexural strength of hydrothermally solidified waste soil was about 8MPa and greater than that required for the building materials such as tile or brick. Because of the low treatment temperature, it is possible to add straw or some organic materials for improving appearance. Although production of conventional ceramics is low energy material synthesis process, the energy required for the hydrothermal soil solidification process is even lower, being only about  $1/6$  compared to that required for chinaware.<sup>11)</sup> It is clear that the hydrothermally solidified waste soil is an extremely low environmental impact material.

The comparison of the humidity control property among the hydrothermally solidified waste soil, wood and wallpaper was shown in Fig. 4. The amount of moisture adsorption and desorption of hydrothermally solidified waste soil was indicated almost similar value with wood which was a natural humidity control material.

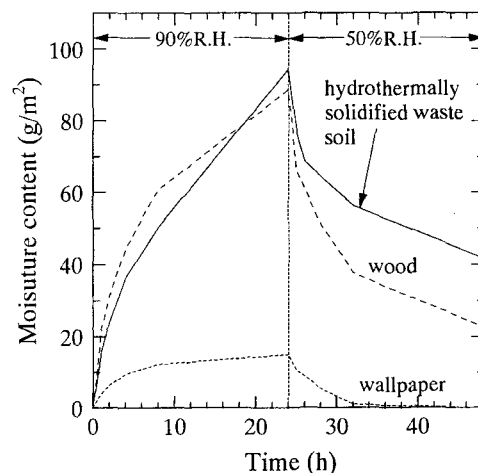


Fig. 4 Behavior of the moisture adsorption and desorption of various building materials between 50% R.H. and 90% R.H. at  $25^\circ\text{C}$ .

The hydrothermally solidified waste soil was used as the flooring material for the living room (35m<sup>2</sup> area) in an apartment and the changes in temperature and humidity were measured under normal living conditions over a one year period.<sup>12)</sup> Compared with other apartments, changes in temperature and humidity of the hydrothermally solidified waste soil floored apartment were smaller (Fig. 5). The hydrothermally solidified waste soil is considered to be a human friendly material which can supply us an amenity and healthy circumstance and also to be an energy saving material which can control without inputting energy instead of air-conditioner.

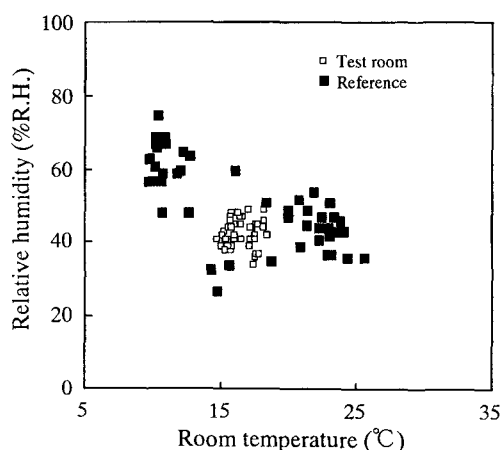


Fig. 5 The influence of hydrothermally solidified waste soil on the room temperature and relative humidity for 1 month in winter.

#### 4. CONCLUSIONS

(1) In the case of the kaolinite rich specimens with  $K/(Q+K)=0.5$  to 1.0, the strength development by the formation of hydrogarnet was recognized, resulting in flexural strengths between 15 to 20 MPa. It was believed that the formation of mesopores (size=0.04 $\mu$ m approx.) that accompanied with the formation of hydrogarnet is related to the strength development.

(2) It was recognized that the humidity control property of the hydrothermally solidified kaolinite-quartz-lime mixtures. Especially, in the case of specimens with  $K/(Q+K)=0$ , where C-S-H were the main phase, and  $K/(Q+K)=0.9$  and 1.0, where much amount of kaolinite were contained, much amount of moisture adsorption and desorption was observed. It is considered that the behavior of humidity control is influenced by the mesopores in the range of 0.01 - 0.1  $\mu$ m.

(3) Using actual waste soil as a raw material, the flexural strength of hydrothermally solidified bodies was about 8MPa and greater than that required for the building materials such as tile or inter rocking block. The energy required for the hydrothermal soil solidification process is even lower, being only about 1/6th compared to that required for chinaware. And it was recognized that the hydrothermally solidified waste soil had the superior property of humidity control. From these results, it was clarified that the hydrothermally solidified waste soil was a low environmental impact and human friendly

material.

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