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Stabilization of high water content clay using carbonized cow dung compost / calcined oyster shell and application of simple dry distillation gasifier

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ABSTRACT

This study proposes a geotechnical utilization of calcined waste oyster shells (COS) and carbonized cow dung compost (CC) instead of cement for stabilizing clay with high-water content. A comparison with commercial wood charcoal proved that CC with better adsorption capacity significantly improved high-water-content clay. COS has the potential to stabilize high water-content clay. Cone penetration tests was performed to investigate the mechanical property of the stabilized clay. Mixing of CC with a high-water absorption rate showed the improvement effect of COS-stabilized clay. The applicability of a mixture of cow dung and waste plastic by dry distillation gas generated from organic matter is also confirmed. When an appropriate amount of plastic is mixed with cow dung compost, it burns stably, the combustion temperature reaches 700℃ or higher, and a carbonized material with a temperature of around 600℃ is obtained. From the test results, it was confirmed that the carbonized material of cow dung compost will be used as good material in geo-environmental field.

Keywords: Calcined oyster shell, carbonized compost, high-water content clay, dry distillation gasifier

1 INTRODUCTION

Oyster shell can be converted into lime by calcination. Numerous studies have investigated the use of calcium oxide extracted from calcined oyster shells (COS) and considered the possibility of using COS as a cementitious material additive (Seo et al., 2019). However, the process of converting $CaCO_3$ into CaO by calcination usually occurs at a relatively high-temperature (about 1000 °C), and continuous high-temperature calcination brings extremely high production costs. Therefore, although COS is an excellent soil stabilizer, the amount of COS must be reduced.

The accumulation of domestic animal excrement is a public resource. In addition, there are many problems in the storage and use of raw manure, such as odor and emissions of harmful compounds, which poses a challenge to its effective treatment and application. It is expected that carbonized cow dung compost (CC) improves soil aggregates by utilizing its porous surface structure (Kameyama et al., 2021). Compared to COS, CC has lower costs owing to its low carbonization temperature and short carbonization time.

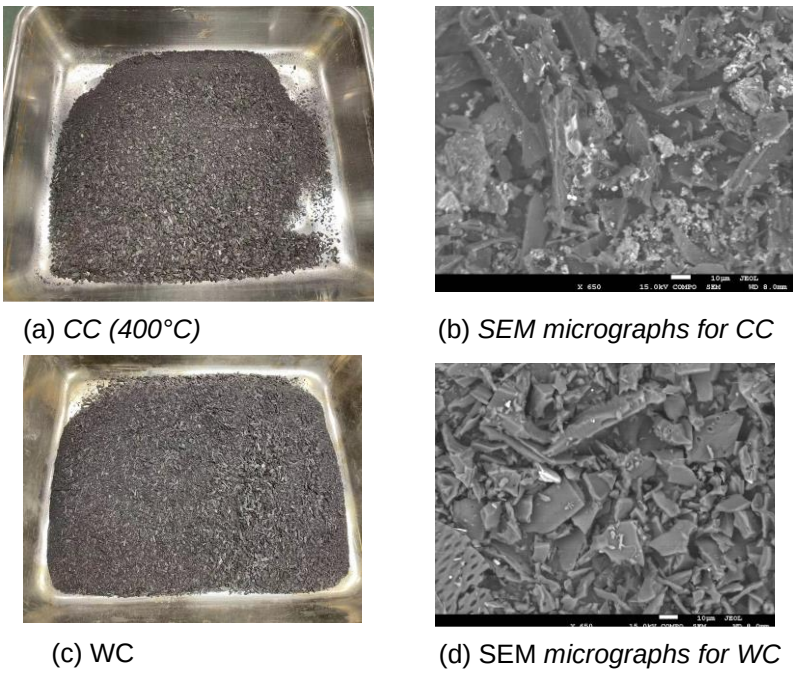
The objective of this research is to clarify whether recycled materials such as COS and CC can be used as solidifying agents for stabilizing clay with high water content and as substitute materials (Zhang et al., 2022). Based on a cone index test, the effect of COS on the clay improvement was compared. According to the mixing amount of carbonized material, the effect of carbonized materials replacing COS on stabilized clay was quantitatively investigated. Additionally, a simple dry distillation gasifier using its thermal energy is applied to a mixture of cow dung and waste plastic for obtaining low cost carbonized material.

2 UTILIZATION OF CARBONIZED COW DUNG COMPOST AND CALCINED OYSTER SHELL

2.1 Test procedure

2.1.1 Materials

The fermented cow dung compost was supplied by pastures in Kyushu, Japan. The cow dung compost was placed in an electric furnace at 110 °C for more than 24 h to obtain dry cow dung compost. Different calcination temperatures will affect the mesopore volume of carbides, thus affecting the adsorption capacity of carbides. In order to obtain the heating temperature for the best adsorption capacity, the heating temperature of the metal tank filled with dry cow dung compost (approximately 500 g) was set to 200–900 °C. A set of water absorption rate tests were carried out every 100 °C in this temperature range, and the sample was maintained under an isothermal condition for 30 min. The obtained carbonized cow dung compost (CC) was passed through a 2 mm sieve to remove coarse particles. The water absorption rate was determined according to the water absorption rate test method of JIS A 1110 and reflected the adsorption capacity of the carbide. To illustrate the effectiveness of the experiment, the wood charcoal (WC) obtained from NAFCO Co., Ltd. was used as the experimental control material. WC is crushed and passed through a 2mm sieve to obtain WC particles of the same size as CC. The particles of the WC and CC (400 °C) were observed using SEM, which illustrated that the particles have a smooth surface, sharp corners, and are non-uniformly shaped, as shown in Fig. 1.



(a) *CC (400°C)* (b) *SEM micrographs for CC*

(c) WC (d) SEM *micrographs for WC*

Figure 1. *Carbide in test and SEM micrographs for carbonized cow dung compost (CC: calcination temperature is 400 °C) and wood charcoal (WC)*

The waste oyster shells used in this study were from the southern coast of Japan. In order to remove salt and organic matter attached to the surface, the oyster shell (OS) surface is brushed and soaked in water for at least 7 days. The washed oyster shells were dried in an electrical furnace at 110 °C for 24 h. The temperature was lowered to room temperature and then pulverized to pass through a 2-mm sieve. The crushed oyster shell powder was calcined at 1000 °C for 2.5 h. The ignition loss (ignition loss = mass loss / mass before calcination × 100) of all COS powder was controlled at approximately 45 %.

The physical properties of the kaolin clay are Liquid Limit 44.4%, Plastic Limit 24.28%, Plasticity Index 20.12, particle density 2.62 g/cm^3 and fine particle content 84.6%..

2.1.2 Preparation of sample

To evaluate the contribution of carbides to the strength of COS-stabilized clay, COS of 30 kg/m^3 and carbide were added to the clay with an initial water content of 70 % at the same time in the test of mixed

carbide prepare the mixed sample. The content of COS (30 kg/m^3) and the initial water content of clay (70%) were constant in the test. To compare the difference in improvement effect caused by the mixing amount of two carbides (CC and WC), the mixed amounts of carbides were 30, 60, 90 and 120 kg/m^3, respectively. During specimen preparation, the clay was first uniformly mixed using a mortar mixer. The solidifying agent and water-absorbent materials were then added simultaneously to the clay and fully mixed until the entire sample attained uniform consistency. The test sample was sealed with macromolecular polyethylene to prevent evaporation and moisture absorption, and the sealed sample was placed at constant temperature (25 ± 3°C) and humidity (90% ± 3%). The stabilized clay samples were subjected to testing after 28 days of curing. A cone penetration test was performed on COS-stabilized clays to determine the cone index. In this study, the cone index was used as an important parameter to evaluate the improvement.

2.1.3 Testing procedure

Sample preparation is based on the standard of the Japanese Geotechnical Society's method of preparing samples by 'Practice for making and curing compacted stabilized clay specimens using a rammer'. After 28 days of storage, the sample was compacted in a mold with a height of 127 mm and diameter of 100 mm using a hammer mass of 2.5 kg and a drop height of 300 mm. The sample was pressed into the mold in three compaction layers. Approximately 40 mm intervals were set between compaction layers to press the sample into the mold three times. Each layer had 25 cycles of compaction (JIS A 1210 A-c method: compaction energy approximately 550 kJ/m^3), except that part of the weakly stabilized clay specimen was unable to compact. Subsequently, a cone penetration test (angle of 30°) was performed immediately. The penetration resistance of the test samples at 50, 75, and 100 mm was measured, and the average value divided by the cone bottom area was defined as the cone index.

2.2 Result and discussion

2.2.1 TG-DTA analysis of bulk oyster shell

The TG-DTA analysis of bulk oyster shell waste was performed. OS exhibits weight loss in two ranges: from 20 to 560 °C and from 560 to 750 °C. The primary endothermic reaction of OS between 560 and 750 °C is considered the thermal decomposition of $CaCO_3$. The actual mass change ratio attributed to CO_2 emissions was measured as 40.4 mass% for OS. The calcination of OS powder was considered to be the conversion of calcium carbonate to calcium oxide.

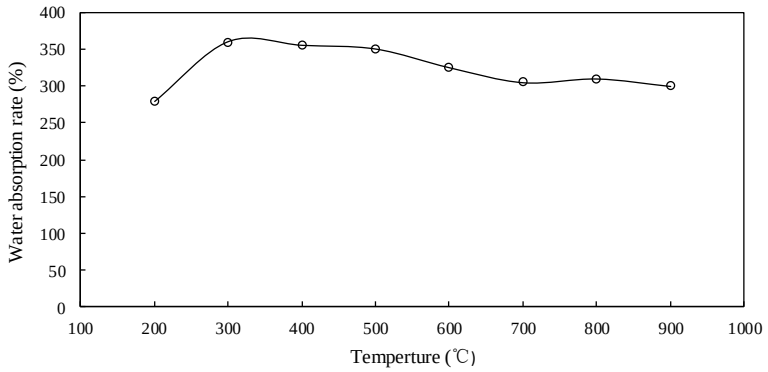
2.2.2 Improvement effect by mixing water absorbent materials

Figure 2 shows the effect of calcination temperature on the water absorption rate of the cow dung compost and the TGA (thermogravimetric analysis) results. When the temperature was maintained at 400 °C for 30 min, the water absorption rate peaked to 348% (water absorption rate is calculated as $(m_s/m_w) \times 100$, where, m_s is the mass that is in a saturated surface-dry condition after water absorption and m_w is the mass that is in an absolutely dry condition), which is more than twice that of WC (the water absorption rate of WC is 160%) as shown in Fig. 2 (a). Compared to other temperature conditions, cow dung compost has a larger average pore size and mesoporosity at 400 °C, which may lead to higher adsorption capacity (Qian et al., 2007). The results of the TGA in Fig. 2 (b) show that the yield decreased at higher pyrolysis temperatures because of carbon burning-off and tar volatilization. At 400 °C, the carbonized cow dung compost yield was 47% of the initial yield.

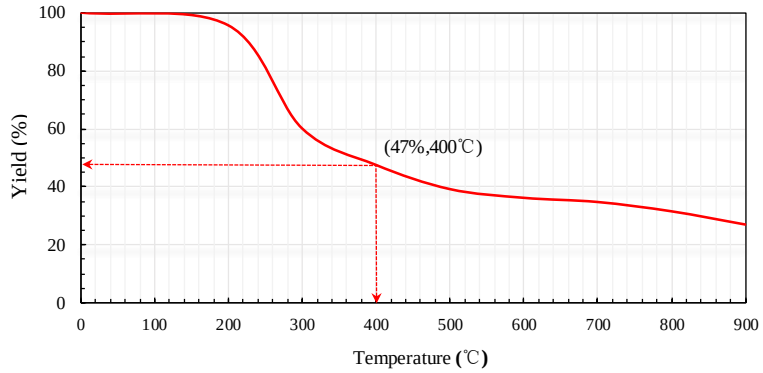
Although COS-stabilized clay improves the mechanical characteristics of clay, it has some limitations. Carbon dioxide (CO_2) is one of the main factors contributing to warming. COS manufacturing emits CO_2 via calcined oyster shells, burning fossil fuels, electricity, and transportation. Therefore, high-temperature calcination of oyster shell for a long time emits CO_2 in large amounts. For the above reasons, this study considered using carbides (CC and WC) to replace parts of COS to alleviate the environmental and cost problems caused by COS production.

The improvement effect within a curing time of 28 days with a 30 kg/m^3 of COS addition was used as a reference to determine the effectiveness of both carbides (CC and WC) in this study. Figure 3 presents the cone index (q_c) development for all stabilized clay specimens. The cone index increased slowly with increasing CC and WC contents in the initial range of 0–30 kg/m^3. The cone index increases rapidly when the CC content exceeds 30 kg/m^3. Compared with WC, the cone index development of CC was

large. When the mixing amount of CC was approximately 80 kg/m^3, the cone index was the same as that when the mixing amount of WC was 120 kg/m^3.



(a) *Effect of temperature on water absorption rate of CC*



(b) *Thermogravimetric analysis results (TGA)e of CC*

Figure 2. *Effect of temperature on CC; (a) effect of temperature on water absorption rate of CC, (b) Thermogravimetric analysis results (TGA) of CC*

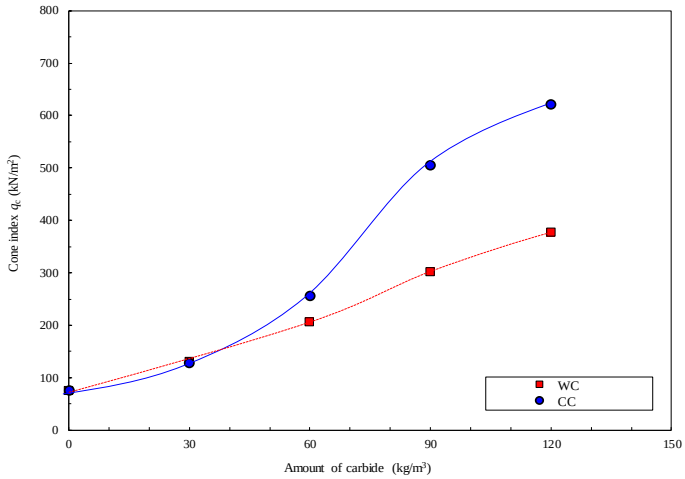


Figure 3. *Effect of carbide content on COS-stabilized clay*

3 APPLICATION OF SIMPLE DRY DISTILLATION GASIFIER FOR MAKING CARBONIZED MATERIAL

3.1 Apparatus and materials

A simple dry distillation gasifier was developed that can efficiently burn dry distillation gas generated by

pyrolysis of organic waste and carbonize samples in stainless steel pipes as shown in Fig.4. A stainless steel pipe with a diameter of 60 mm and a height of 600 mm is filled with a mixture of composted cow dung and waste plastic. A small hole was made in the lower part of the stainless steel pipe so that the dry distillation gas could leak out. Install an alcohol lamp for ignition at the bottom of the stainless steel tube. Cow dung compost cannot be carbonized well if its water content is high, so it was dried at 100°C for one day using a dryer. In the case of cow dung compost alone, carbonization gas was generated, but it did not burn well. On the other hand, when only plastic is pyrolyzed, the heating power is too strong and a large amount of soot is generated. A mixture of 300 g of cow dung compost, 15 g of PE (polyethene) and 15 g of PET (polyethylene terephthalate) is used as a sample. PET was shredded into small pieces, and PE was rounded to reduce its volume. In order to investigate the temperature change inside the stainless steel pipe, thermocouples were installed at the center and top of the pipe.

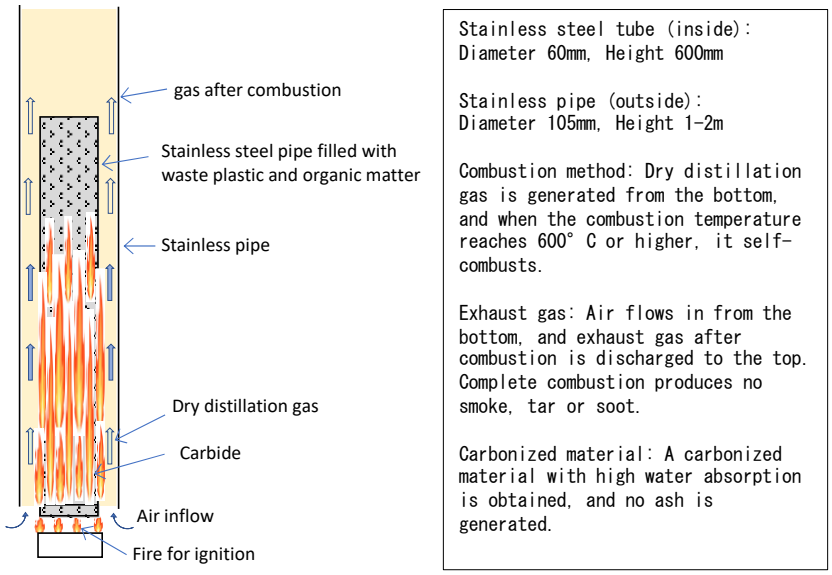


Figure 4. *Apparatus of dry distillation gasifier*

3.2 Experimental result and carbonized material

In the case of cow dung compost alone, carbonization gas was generated, but it did not burn well. On the other hand, if there is a lot of plastic, the heating power will be too strong and a large amount of soot will be generated. In the case of a mixture of waste plastic and woody biomass, by adding carbon and hydrogen-rich PE to woody biomass with a high oxygen content, the calorific value per unit weight and the amount of hydrocarbons in pyrolysis gas are improved. has been shown to be possible. Therefore, we used a sample of cattle dung compost mixed with PE and PET. When the alcohol stove installed at the bottom is burned, combustion occurs while carbonization gas is generated from the hole made under the stainless steel pipe.

Figure 5 shows temperature changes in the dry distillation gasifier. The temperature is higher in the lower part until 12 minutes, but after that, the temperature is higher in the upper part. The peak exceeds

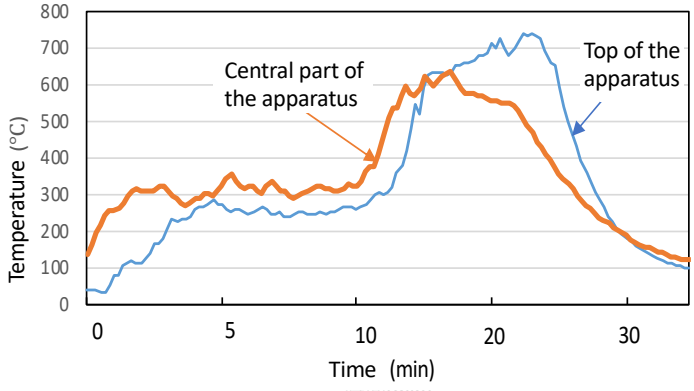


Figure 5. *Temperature change inside the apparatus*

700°C. After about 20 minutes, the temperature drops and remains almost the same. In the early stage when the temperature is low and the combustion is not complete, smoke is generated, but when the temperature reaches about 420 to 470°C when the carbonization gas is generated, the carbonization gas is sufficiently combusted and the amount of smoke decreases. Figure 6 is the sample after carbonization. In this way, if an appropriate amount of plastic is mixed with cow dung compost, charcoal can be obtained while burning stably.



Figure 6. *Carbonized material obtained by dry distillation gasifier*

4 CONCLUSIONS

In this study, calcined waste oyster shells (COS) and carbonized cow dung compost (CC) are used and the improvement effect of COS-stabilized clay using CC was investigated. Cone penetration tests was performed to investigate the mechanical property of the stabilized clay. Based on this investigation, the following conclusions were drawn:

1) Under 400 °C calcination temperature condition, the water absorption rate of CC was the highest, reaching 348%. A comparison with commercial wood charcoal proved that CC with better adsorption capacity significantly improved high-water-content clay.

2) COS has the potential to stabilize high water-content clay. Mixing of CC with a high-water absorption rate showed the improvement effect of COS-stabilized clay in the range of 0-120kg/m^3.

3) The applicability of a mixture of cow dung and waste plastic by dry distillation gas is confirmed. When an appropriate amount of plastic is mixed with cow dung compost, it burns stably, the combustion temperature reaches 700℃, and a carbonized material with a temperature of around 600℃ is obtained.

From the test results, it was confirmed that the carbonized material of cow dung compost will be used as good material in geo-environmental field.

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