Study on Effect of Chemical Composition of Geopolymer to Improve Sludge by Using Fiber Materials

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Abstract: Geopolymer, an environmentally friendly alternative to ordinary Portland cement, is currently receiving increased attention in academic and industrial communities for its ability to produce fly ash based geopolymer material in several applications. Geopolymer material is known as an inorganic-polymer composite and is synthesized by the aluminosilicate compound materials with alkali hydroxide and alkali silicate. Current researches on geopolymer are mainly focused on geopolymer concrete properties such as mechanical properties, paste properties and durability properties in laboratory. However, few specific publications are available concerning the feasibility of geopolymer modified soft soil (sludge) in the actual landslide area which is mainly due to earthquake and heavy rainfall. This paper presents the details of studies carried out on strength of sludge improved with various geopolymer contents. The composition of sludge is 60% silt, 40% clay and water content is 70%. Sodium hydroxide (NaOH) 12 Molar and sodium silicate solution (Na2SiO3) were prepared. The test specimens were made of 50 x 100 mm cylindrical mold and 20°C temperature curing condition. By adding paper debris, the specimens were made immediately after mixing by compaction, in contrast without adding paper debris, after 24 hours the specimens were made with same condition to compare. Compressive strength after 12 and 18 hours was measured. The results showed that the modified soil with paper satisfied the target (125 kN/m²) with geopolymer content nearly 9% after 12 hours and all of them obtained enough strength after 18 hours. Moreover, modified soil without paper reached target after 12 and 18 hours but revealed lower strain performance.

Keywords: Geopolymer, Sludge, Fly ash, Unconfined compressive test

1. Introduction

During the past 100 years, landslide has considerable impact, causing structural damage and loss of life. The landslide disaster occurs frequently for complex natural condition and becomes major factors hindering the social and economic development in loess regions [1]. The incidences of landslides have been increasing in recent years due to rapid pace of developments in hilly regions and climate change [2]. Furthermore, Japan is known as a nation that suffered huge damage by earthquake and seismic activity. Moreover, landslide generates a huge volume of sludge blocking road, supply lines (telecommunication, electricity, water, etc.) and waterways. Furthermore, almost the recovery disaster activities are done by human, heavy machine cannot move to this area because of soft soil. For prompt recovery, improvement of sludge that has enough strength quickly for heavy machine can fast move to that area is required.

In previous researches, Portland cement was predominantly used as adhesive to improve the characteristic of sludge. Surely, it has many advantages but a long time is necessary to reach enough strength for heavy machines to move on the modified sludge. Ordinary Portland Cement (OPC) is most popular adhesive in the construction in the world. The cement industry is known as significant contributor releasing greenhouse gasses into the atmosphere [3]. Carbon dioxide (CO2) as a by-product of cement manufacture is emitted during burning fossil fuels in the kiln, chemical conversion of calcinating calcium carbonate (CaCO3) in production of clinker, as well as from power generation. Annually, cement production exhausted about 1.5 billion tons and 7% of total greenhouse gas emission to the environment [4,5] Due to the exponential use of concrete, cement production has increased at a much higher speed than atmospheric CO2 concentration, i.e. than all major CO2 emission caused by human activities, such as energy and transportation. Thus to overcome this issue, a new technology should be innovated to decrease adverse impact to environment or civil engineering industry researches alternative binder to substitute or supplement Portland cement.

Geopolymer Cement is novel alternative cement to traditional Portland cement. The term “geopolymer” was created by J. Davidovits in 1979 to describe the chemical properties of inorganic polymers based on aluminosilicates [6]. Geopolymers have been the subject of intense study because they are environmentally friendly cementing agents, with low energy consumption and low toxicity, are stable at high temperature and have high durability [7]. Geopolymers present cementitious properties and, therefore, great potential for use in the construction industry. Geopolymers can be synthesized from a variety of silica and alumina rich materials [8,9] such as metakaolin, steel furnace slag and fly ash. The recycled waste silica and alumina rich materials are thus of interest for sustainability research and practice. By the way, we have already developed a new recycling method for high water content mud such as construction sludge by using paper debris (fragments of old newspaper) and cement to increase the recycling rate of construction sludge [10]. This method is called “Fiber-cement-stabilized soil method”. This method shows several features on modified soil: high failure strength and failure strain, high durability for drying and wetting as well as high dynamic strength [11]. But a long time is necessary to reach enough strength value. As the first step of this research, the utilization of geopolymer proposed instead of Portland cement. In this paper, the influence of chemical
composition of geopolymer on failure strength and strain characteristic of modified sludge is investigated.

2. The Principle of Fiber-cement-stabilized Soil Method
The principle of the Fiber-Cement-Stabilized soil method is as follows:
1) The initial high water content cause soil particles move freely in the water as “fluid” (Figure. 1a).
2) When paper debris is added to the sludge, they absorb the water and decrease the superficial water content in sludge (Figure. 1b).
3) Finally, geopolymer cement is added and mixed with the sludge. Then, the geopolymeric occurs and strength of the modified soil is increased. (Figure. 1c)

3. Materials and Experimental Procedure

3.1 Materials
The imitation sludge was made by mixing of Kasaoka clay (Kasanen Kogyo Company) and silt (Marunaka Shirato Company). The mass ratio of silt and clay is 3:2, the grain size distribution of imitation sludge and 2 samples which obtained in landslide area was shown in Fig. 2. Physical and mechanical properties of imitation sludge were shown in Table 1. Fly ash (FA), from Tohoku Hatsuden Kogyo Company, was used as the main source of aluminosilicate material for making geopolymer cement. CaO content is 5.51, therefore, it is classified as Class F according to ASTM C 618 (ASTM 2012a). Table 2 shows Chemical composition of clay, silt and fly ash. A mixture of sodium hydroxide (NaOH) and sodium silicate (Na₂SiO₃) solution was used as the alkaline activator solution. Sodium hydroxide and sodium silicate were collected from a local commercial producer. The concentration of sodium hydroxide solution was kept constantly at 12 molars for all mixtures. The mass ratio of SiO₂ to Na₂O of sodium silicate was 3 with chemical compositions of 29.53% of SiO₂, 10.56% of Na₂O and 59.91% water.

3.2 Experimental procedure
Procedure to make specimens is as follows.
1) The water content of sludge is adjusted by adding water into the sludge (70% by weight) and mixed for 5 minutes.
2) Paper debris, fly ash and alkaline activator solution are poured gradually in the mixer and the mixing was continued for further 8 - 10 minutes to achieve a uniform mixing. A. Palomo [12] stated that activator solution-to-fly ash ratio was not a relevant parameter on the compressive strength of geopolymer binder. But another research shows a contradictory result, whereby activator-to-fly ash ratio has influence over the compressive strength of geopolymer mortar. So that, in my research the constant activator solution-to-fly ash ratio was used at 0.4 following the result from [13] that shows the optimum ratio between fly ash and alkaline solution on compressive strength of geopolymer binder. In this experiment, the removal of heat treatment means that there was no acceleration of the hardening process of geopolymerization. This means the ratio of sodium silicate to sodium hydroxide is an important factor for destruction of solid particles and the hydrolysis of dissolved Al³⁺ and Si⁴⁺ ions. If the OH⁻ concentration is high enough, more water will accelerate the dissolution and hydrolysis, but excess alkalinity will cause the micro-crack on fly ash particles due to strong base concentration. That why in this experiment, the ratios of sodium silicate to sodium hydroxide are designed with varying as 9:1, 8:2, 7:3 and 5:5 as previously suggested by [14] to investigate the
effect of the ratio of Na$_2$SiO$_3$ to NaOH. As the mention before, paper debris, a fragment of old newspaper, which is necessary to improve the rheology of the mixture by reducing the water was kept constant at 3% and its size is about 15 mm square.
d) Specimens are made by using the cylindrical steel mold, 50 mm in diameter and 100 mm in height. Each specimen is compacted with the same amount of compaction energy. In particular, the rammer of 1.5 kg is allowed to free-fall to the soil surface from the height of 0.2 m; the amount of free-fall of each layer is five times for the first layer, 10 times for the second and third layer, and 20 times for the fourth layer.

![Fig. 3 Relationship between Na$_2$SiO$_3$:NaOH ratio and failure strain of modified sludge (condition A) ](image)

![Fig. 4 Relationship between Na$_2$SiO$_3$:NaOH ratio and failure strain of modified sludge (condition A) ](image)

4. Experimental Results and Discussion

4.1 Effect of ratio Na$_2$SiO$_3$ to NaOH on failure strength of modified sludge

Prior to the unconfined compression test, the target values for failure strength and failure strain of were set to determine the optimum ratio of geopolymer chemical composition for improvement the characteristic of sludge. Specially, brittle fracture is unfavorable applied for ground materials. That’s why they were specified as follows referring to previous our research about the factor of safety [15]:

(a) Failure strength: more than 125 kN/m$^2$
(b) Failure strain: more than 5%

Furthermore, the target value should be achieved after hours because the modified sludge in this research will be applied for disaster site. Figure 3 and Figure 4 show the effect of ratio of Na$_2$SiO$_3$ to NaOH on failure strength and failure strain after 12 hours and 18 hours. The failure strength of modified sludge is significantly governed by the Na$_2$SiO$_3$ and NaOH ratio. Alkali concentration is a significant factor in controlling the leaching of alumina and silica from fly ash particles, subsequent geopolymerization and mechanical properties of hardened geopolymer. The sodium hydroxide solution (NaOH) dissolves silica and alumina oxide from FA and enhances the geopolymerization reaction with sodium silicate solution (Na$_2$SiO$_3$). The low amount of NaOH is not enough to dissolve silicon and aluminum atoms in raw materials, but high amount of NaOH causes the micro-crack on the FA particles due to strong base concentration [3,16]. The test result (Fig. 3) shows that the highest failure compressive strength is obtained at the condition A2 after 18 hours. After 12 hours, condition A1 shows the highest failure strength because initial temperature of alkaline solution in condition A1 when it was made is higher than greater ratio that means the environmental reaction is more workable than another ratio, hence early failure strength can be improved. At the low temperature (20°C), the dissolution of FA particles was slowly, the geopolymer gels grew slowly and modified sludge specimens were still moist. But with the fibrous paper inside the structure, the connection between soil particles and geopolymer is improving, that made the specimens is ductility with the compressive test. Figure 5 shows the fibrous paper intertwined with soil particle to improve the ultimate failure strain. So that, increasing the curing time, the amount of Al$^{3+}$ ion dissolved from amorphous phase in FA were sufficient to polymerize with Si$^{4+}$ ion in alkaline activator. This trend is in agreement with the result in Fig. 3 and Fig. 4. From that results, all specimens satisfied failure strength target value after 18 hours and failure strain after 12 hours. But the value
strength of modified should be achieved after 12 hours curing time. In that case, Na$_2$SiO$_3$/NaOH ratio of 5:5 and 7:3 are chosen to investigate the effect on failure compressive strength and failure strain when increasing geopolymer content.

4.2 Effect of geopolymer content on mechanical strength of modified sludge

Figure 6 to Figure 9 show the influence of Na$_2$SiO$_3$:NaOH ratio 5:5 and 7:3 on the failure strength and strain of modified sludge. As shown in Fig. 6 and Fig. 7, from condition B1 to B3, the failure compressive strength decreases with an increase in the amount of geopolymer content while failure strain also increased. This is because when increasing amount of geopolymer content, the moisture which is supplied by the water in alkaline activator solution increased in each specimen. If the geopolymerization reaction doesn’t occur effectively, the specimens at high geopolymer content are weaker than the low ones with the same moisture content of sludge. In the formation of three-dimensional alumino-silicate network, NaOH was strongly influenced on the dissolution of silica and alumina from fly ash. In the condition B, as increasing geopolymer content, the amount of NaOH was also increasing. It was expected that would lead to greater the dissociation of the active species of raw material and yielding formation of more geopolymer gel network. However, too high NaOH concentration may disrupt the geopolymerization process due to the excessive quantity OH$^-$ ions which lead to inefficient reaction. Although condition B has high initial temperature of alkaline activator solution, it’s not enough for acceleration the dissolution of Al$^{3+}$ and Si$^{4+}$ ions from FA particles and also prevents the polycondensation (releasing water). It leads to reduce the failure strength of modified sludge in spite of increasing amount of geopolymer binders. In the contrast, failure compressive strength increases when increasing amount of geopolymer content at condition C while the failure strain decreased as shown in Fig. 8 and Fig. 9. It can be indicated that condition B is insufficient to stimulate the geopolymerization whereas the condition C may cause the immediate decrease of liquid sample and induce structural creaks on the samples [13]. The concentrations of Na and Si.
determine the type of hydrolyzed ion and the path of the condensation process, and hence the chemistry and properties of the resulting geopolymer [8]. From condition C1 to C3, the geopolymer content was increasing that means the concentration of Na₂SiO₃ as well as Si⁴⁺ ion concentration was increasing. In a system with a high Si⁴⁺ ion concentration and enough OH⁻ environmental, condensation starts with the formation of oligomeric silicates, leading to [poly(sialate–siloxo) and poly(sialate–disiloxo)] 3D rigid polymeric structures that were shown in Eq. (1) and Eq. (2).

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\text{SiO}_2 + H_2O + OH^- \rightarrow [\text{SiO(OH)}_3]^-
\]  

(1)

\[
\text{SiO}_2 + 2OH^- \rightarrow [\text{SiO(OH)}_2]^2-
\]  

(2)

4.3 Effect of geopolymer content on failure strength and strain of modified sludge without adding paper debris

The experimental results by using the mixture condition D are discussed. Figure 10 and Figure 11 show the relationship between failure strength, failure strain and geopolymer content on modified soil without adding paper debris. As shown in Fig. 10, the failure strength increases with increasing the geopolymer content and all results satisfy the target value while failure strain decreases and the values are lower than target value. As mention before, in the first stage of the main reaction, water is indispensable reactant for hydrolysis (consuming water). But in the second stage, too much water will hinder the polycondensation kinetically.

After 1 day curing at 20°C in the oven, lots of amount of water in treated sludge is significantly evaporated. That means the polycondensation, as well as geopolymerization reaction, is also increasing. Furthermore, cause the reduction of moisture in modified-sludge, the compaction power is more effective than the modified sludge that immediately compacted after mixing. But in the case of failure strain, the result of condition D didn’t satisfy the target value. As shown in Fig. 12, the specimen was quickly broken than other conditions.
Figure 13 and Figure 14 show the compression stress–strain curves of all conditions after 12 and 18 hours curing, respectively. It is clearly to see that condition D had unstable mechanical property while the other conditions can maintain the strength after reaching the peak strength. From previous research [15], the paper debris added to the sludge can increase the compressive strength as well as reinforcing agent, the deformability of specimens was better than normally stabilized sludge. This conclusion was in agreement with the result in Fig. 13 and Fig. 14. As the cracks are growing, paper debris hindered relative slippage of damaged sections and prevented sludge block deformation, thus restraining crack development and improving the ultimate strain (Fig. 5, Fig. 12).

5. Conclusions
This research investigated the effect of chemical composition of geopolymer on failure strength and failure strain of sludge improved by Fiber-cement-stabilized soil method instead of Portland cement. The following results were obtained:

1. For early failure strength of modified–soil, Na₂SiO₃: NaOH ratio 5:5 and 7:3 shows good results after 12 hours and 18 hours, respectively. All samples achieved failure strain target values.
2. At Na₂SiO₃: NaOH ratio 5:5, failure strength decreased and failure strain increased with an increase of geopolymer content. In contrast, failure strength increased and failure strain decreased with an increase of geopolymer content at ratio 7:3. Furthermore, value of geopolymer content nearly 9 % at ratio 7:3 achieved the target value on failure strength after 12 hours.
3. Modified-soil without adding paper debris need cures in oven 1 day at 20°C, then specimens can be made by compaction. After 12 hours and 18 hours, failure strength was significantly higher than target value but failure strain was not satisfied. Furthermore, specimens without adding paper debris showed unstable mechanical property, they achieved the peak strength very quickly but couldn’t maintain the strength property and collapsed suddenly. The fiber is important factor for modified sludge. The effect of amount of paper debris should be considered.

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References