Effect of amorphous silica content in clay on mechanical properties of the mixture of clay and converter steelmaking slag

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ABSTRACT

A mixture of dredged soil and steelmaking slag solidifies owing to the pozzolanic reaction between the silica and alumina in the dredged soil and the calcium in the steelmaking slag. Previous studies have reported that, for the same steelmaking slag, the concentration of dissolved silica and the shear strength of a mixture of dredged soil and steelmaking slag increases as the content of amorphous silica in the clay increases. However, the relationship between factors that affect solidification strength, such as the ratio of amorphous silica content and the humic acid content, and the solidification strength of a mixture of clayey soil and steelmaking slag has not been clarified. In this study, focusing on the ratio of amorphous silica contents in clay, clays containing different ratios of amorphous silica content were prepared by mixing kaolin clay and metakaolin. The unconfined compressive strength s of the clay mixed with steelmaking slag were measured. For the same curing time and up to an amorphous silica content ratio of 15%, the strength increases with an increase in the ratio. In addition, the shear strength develops earlier for higher content ratios of amorphous silica. Compared with studies on dredged soils mixed with steelmaking slag, the amorphous silica content ratio of the clay in this study was higher than that of dredged soils. However, the shear strength in the dredged soil with amorphous silica from diatoms and minerals mixed with steelmaking slag developed earlier than that of the clay with amorphous silica from minerals mixed with steelmaking slag. The differences in the development of shear strength can be attributed to the difference of the amorphous silica from minerals or that from diatoms.

Keywords: steelmaking slag, amorphous silica, solidification, unconfined compressive test

1 INTRODUCTION

In recent years, Japan has annually produced approximately 14 million tons of steelmaking slag as a by-product of smelting steel (Horii et al., 2012). Steelmaking slag is often used as the base course material for road and ground improvements. In addition, the strength of dredged soil improves when it is mixed with steelmaking slag. Therefore, this mixture is used as an artificial geomaterial in ports.

This improvement in strength can be attributed to the pozzolanic reaction between the silica and alumina components in the dredged soil and the calcium component in the steelmaking slag (Kiso et al., 2008). In addition, the mixture of dredged soil and steelmaking slag becomes hard to solidify by containing humic substances (Kaneko et al., 2016).

Toda et al. (2018) reported that the concentration of dissolved silica in the pore water in dredged soil increases as the content ratio of amorphous silica increases, when using the same steelmaking slag. They also reported that the shear strength of mixtures of dredged soil and steelmaking slag correlated with the content ratio of amorphous silica in dredged soil. However, the detailed relationship between various factors that affect solidification strength, such as the amorphous silica content ratio and humic acid, and the solidification strength of a mixture of clayey soil and steelmaking slag has not been clarified.

Moreover, in mixtures of clayey soil and steelmaking slag, the strength development tendencies may vary according to the differences in the clayey soil. Kakihara et al. (2018) compared the tendency of shear strength development in a mixture of Kibushi clay and steelmaking slag to that in Kawasaki clay (i.e., marine...
clay), when using the same steelmaking slag. In the case of Kibushi clay, the unconfined compressive strength of curing, whereas in Kiso et al. (2018) and Kiso et al. (2008) measured the unconfined compressive strength of a mixture of dredged soil and steelmaking slag. They observed that the shear strength developed for 28 days of curing when using dredged soil and then gradually increased. The strength development tendencies when using dredged soil differs from those when using other clayey soils. However, the factors causing this difference have not been studied.

Considering this, this study was focused on the amorphous silica content ratio in clay. Amorphous silica includes inorganic amorphous silica and amorphous biogenic silica. Inorganic amorphous silica contains volcanic glass, metakaolin, and allophane, and amorphous biogenic silica contains diatoms. In this study, the authors focused on the amorphous silica content ratio in clay and investigated the relationship between the content ratio of inorganic amorphous silica in clay and the shear strength of the clay mixed with steelmaking slag. Metakaolin is used to control the content ratio of inorganic amorphous silica. The authors conducted an unconfined compressive test and examined the effect of the mixing ratio of kaolin clay and metakaolin on the characteristics of shear strength. Furthermore, the difference in the development of shear strength in the clay mixed with steelmaking slag due to the difference in the content ratio of the amorphous silica in clay was determined.

2 OUTLINE OF EXPERIMENTAL PROCEDURE

2.1 Experimental Materials

The kaolin clay used in this study was obtained from Indonesia (ρ = 2.61 g/cm³, wL = 71.4 %, wp = 44.1 %). Converter steelmaking slag A (ρ = 3.36 g/cm³) and B (ρ = 3.40 g/cm³) were used without aging treatment and obtained at different times. Furthermore, metakaolin (ρ = 2.66 g/cm³, wL = 67.4 %, wp = 47.8 %) was also used. Table 1 lists the chemical compositions of kaolin and metakaolin. Metakaolin is a phase produced by the dehydration of the OH ions in kaolinite at 500–650 °C, and it is industrially obtained via calcination of pure or refined kaolin clay at a temperature of 650–800 °C. It contains a significant amount of amorphous silica. Previous studies have focused on metakaolin as a material for partial cement replacement in mortar and concrete. It was proved that metakaolin is a very effective pozzolan (Sabir et al., 2001).

Figure 1 depicts the curve of particle size accumulation. Note that the accumulation in kaolin clay

![Graph](image)

Table 1. Chemical compositions of kaolin and metakaolin.

| Major element | Kaolin (%) | Metakaolin (%) |
|---------------|------------|----------------|
| SiO₂          | 46.15      | 34.48          |
| Al₂O₃         | 38.10      | 40.31          |
| Fe₂O₃         | 0.86       | 1.62           |
| TiO₂          | 0.19       | 1.98           |
| CaO           | 0.01       | 0.14           |
| MgO           | 0.04       | 0.09           |
| Na₂O          | 0.01       | 0.11           |
| K₂O           | 0.52       | 0.18           |

Table 2. Test conditions.

| No.   | Steelmaking slag | Mixing ratio (mass%) | Amorphous silica content ratio in clay | Curing Time (days) |
|-------|------------------|-----------------------|----------------------------------------|-------------------|
|       |                  | Kaolin Clay | Metakaolin                             |                    |
| MK0-A | A                | 100         | 0                                      | 9.40              | 3, 7, 14, 28      |
| MK5-A | A                | 95          | 5                                      | 9.94              | 3, 7, 14, 28      |
| MK10-A | A              | 90          | 10                                     | 10.47             | 3, 7, 14, 28      |
| MK20-A | A              | 80          | 20                                     | 11.54             | 3, 7, 14, 28      |
| MK40-A | A              | 60          | 40                                     | 13.68             | 3, 7              |
| MK50-A | A              | 50          | 50                                     | 14.75             | 3, 7              |
| MK75-A | A              | 25          | 75                                     | 17.43             | 3, 7              |
| MK100-A | A            | 0           | 100                                    | 20.10             | 3, 7, 14, 28      |
| MK0-B  | B               | 100         | 0                                      | 9.40              | 3, 7, 14, 28      |
| MK5-B  | B               | 95          | 5                                      | 9.94              | 3, 7, 14, 28      |
| MK10-B | B               | 90          | 10                                     | 10.47             | 3, 7, 14, 28      |
| MK20-B | B               | 80          | 20                                     | 11.54             | 3, 7, 14, 28      |
| MK100-B | B             | 0           | 100                                    | 20.10             | 3, 7, 14, 28      |
and metakaolin were measured using a laser diffraction/scattering particle size distribution analyzer, and these accumulation curves are expressed in volume percentage.

The amorphous silica content ratios in Kaolin clay and metakaolin were measured via selective dissolution experiments (Kodama et al., 1995). The amorphous silica content ratio in kaolin clay was 9.4 mass% calculated as SiO_{2}, and that in metakaolin was 20.1 mass% calculated as SiO_{2}.

2.2 Experimental conditions

The test conditions are listed in Table 2. Note that a mixture of kaolin clay and metakaolin is termed as clay hereinafter.

The process of preparing the specimens is as follows. The clay had a prescribed water content ratio. The water content ratio of clay was 1.65 w_{L} for kaolin clay. Artificial seawater was used as the pore water. The mixing ratio of clayey soil and steelmaking slag was clay:steelmaking slag = 7:3 by volume. The mixing ratio of clayey soil and steelmaking slag was defined by the mixing volume ratio of the clay and dry steelmaking slag. Note that the mass content ratio of the steelmaking slag in all samples was 64%. The mixture of clay and steelmaking slag was placed in a plastic mold to eliminate air. The specimens had a diameter of 50 mm and a height of 100 mm. The plastic molds containing the mixed soil were tightly sealed and cured at a constant room temperature of 20 °C for the prescribed duration. After curing, unconfined compressive tests on the specimens were conducted at an axial strain rate of 1%/min.

3 RESULTS AND DISCUSSIONS

3.1 Unconfined compressive strength

Figure 2 presents the relationship between unconfined compressive strength q_u and the metakaolin content ratio in the clay for steelmaking slag A at three and seven days of curing. As shown in this figure, for three days of curing and when the metakaolin content ratio in the clay was less than 75%, the q_u increases as the content ratio of metakaolin increases. The q_u for a metakaolin content ratio of 100% was almost identical to that for a metakaolin content ratio of 75%. For each metakaolin content ratio, the q_u for seven days of curing were higher than those for three days of curing. After seven days of curing, when the metakaolin content ratio in the clay was less than 75%, the q_u increases as the metakaolin content ration increases. The q_u at a metakaolin content ratio of 100% was almost identical to those for metakaolin content ratios of 50% and 75%.

Figure 3 presents the relationship between unconfined compressive strength q_u and the curing time up to 28 days for steelmaking slag A, for a metakaolin content ratio of 0%, 5%, 10% and 100%. Until 28 days of curing, at each curing time, the q_u increases as the metakaolin content ratio increases. In addition, at each metakaolin content ratio, the q_u increases as the curing time increases. For a metakaolin content ratio of 0%, the average q_u for 3, 7, 14 and 28 days of curing were 8.9 kN/m^2, 10.8 kN/m^2, 10.6 kN/m^2 and 59.6 kN/m^2, respectively. Therefore, for a metakaolin content ratio of 0%, the mixture containing clay and steelmaking slag solidifies between 14–28 days of curing. On the contrary, for a metakaolin content ratio of 100%, after 3 days of curing, the q_u was approximately 1300 kN/m^2 and thereafter the strength gradually increased.

![Fig. 2. Relationship between unconfined compressive strength q_u and metakaolin content ratio in clay for steelmaking slag A.](image)

![Fig. 3. Relationship between unconfined compressive strength q_u and curing time for steelmaking slag A.](image)

![Fig. 4. Relationship between unconfined compressive strength q_u and curing time for steelmaking slag B.](image)
Figure 4 depicts the relationship between the unconfined compressive strength $q_u$ and the curing time for the steelmaking slag B, up to 28 days of curing, for a metakaolin content ratio of 0%, 5%, 10%, 20% and 100%. Until 28 days of curing, similar to steelmaking slag A, at each curing time, the $q_u$ increases as the metakaolin content ratio increases. Furthermore, at each metakaolin content ratio, $q_u$ increases as the curing time increases. For a metakaolin content ratio of 100%, similar to steelmaking slag A, the shear strength developed early and thereafter the strength gradually increased.

Based on the abovementioned results, it was evident that, up to the predetermined content ratio of amorphous silica in clay, which was approximately 15% for steelmaking slag A, the shear strength of the mixture of clay and steelmaking slag increases as content ratio of amorphous silica increases, at each curing time. Moreover, when the content ratio of amorphous silica in the clay exceeded the predetermined amount, the shear strength of the mixture of clay and steelmaking slag can remain constant. It was also observed that until 28 days of curing, for the same curing time, up to 11.5% of amorphous silica content ratio in clay, the shear strength increases as the content ratio of the amorphous silica in the clay increases.

### 3.2 Shear strength development tendency

The effect of the content ratio of amorphous silica in the clay on the tendencies of shear strength development was determined. The ratios of the average $q_u$ at each curing time to the of strengths after seven days of curing, $q_u/q_{u,7}$, were calculated from Figure 3 and Figure 4.

Figure 5 shows the relationship between $q_u/q_{u,7}$ and the curing time for steelmaking slag A. For a metakaolin content ratio of 100%, the $q_u/q_{u,7}$ from three days of curing to seven days of curing was approximately 0.8–1.3. On the contrary, for the metakaolin content ratios of 5% and 10%, the value of $q_u/q_{u,7}$ increases as the curing time increases. After 14 days of curing, the value of $q_u/q_{u,7}$ for a metakaolin content ratio of 10% was higher than that for a metakaolin content ratio of 5%. Furthermore, after 28 days of curing, the value of $q_u/q_{u,7}$ for a metakaolin content ratio of 5% was higher than that for a metakaolin content ratio of 10%. For a metakaolin content ratio of 0%, the $q_u/q_{u,7}$ was approximately one up to 14 days of curing. After 28 days of curing, the $q_u/q_{u,7}$ was approximately 5.5. This indicates that, for a metakaolin content ratio of 0%, the mixture containing clay and steelmaking slag solidifies between 14–28 days of curing. Therefore, the shear strength of the clay mixed with steelmaking slag develops earlier with an increase in the metakaolin content ratio. However, the increase in the strength due to curing is lesser at higher metakaolin content ratios. This tendency was also observed at other metakaolin content ratios, for 3–7 days of curing.

Figure 6 presents the relationship between $q_u/q_{u,7}$ and the curing time for steelmaking slag B. For a metakaolin content ratio of 100%, similar to steelmaking slag A, the $q_u/q_{u,7}$ from three to seven days of curing was approximately 0.6–1.4. After 14 days of curing, for a metakaolin content ratio of 5%, 10% and 20%, the value of $q_u/q_{u,7}$ decreases as the metakaolin content ratio increases. For a metakaolin content ratio of 0%, similar to steelmaking slag A, the $q_u/q_{u,7}$ was approximately one up to 14 days of curing. After 28 days of curing, the $q_u/q_{u,7}$ was approximately 6. For steelmaking slag B, it was also observed that the shear strength of the mixture containing clay and steelmaking slag develops earlier as the content ratio of amorphous silica increases.

From the abovementioned observations, it evident that a higher content ratio of amorphous silica in the clay results in an earlier development of the shear strength of the mixture containing clay and steelmaking slag. However, the increase in the shear strength due to curing is lesser at higher content ratios of amorphous silica.

On comparing Figure 5 and Figure 6, for the same content ratios of the metakaolin in the clay, $q_u/q_{u,7}$ in
steelmaking slag A is higher than that in steelmaking slag B. This proves that the tendencies of shear strength development are different at the same amorphous silica content ratio, when the steelmaking slags are obtained at different times and have different particle size distribution.

To determine the tendencies of shear strength development in dredged soils mixed with steelmaking slag, the values of $q_u/q_{u,7}$ for each result obtained by Toda et al. (2018) and Kiso et al. (2008) were calculated.

Toda et al. (2018) measured the amorphous silica content ratio in volcanic glasses and diatoms for three dredged soils—dredged soils A, B, and C. They also conducted unconfined compressive tests on dredged soils mixed with steelmaking slag. The mixing ratio was dredged soil:steelmaking slag = 7:3, by volume. The amorphous silica content ratios of soils A, B, and C from the volcanic glasses were approximately 2.6%, 2.4%, and 1.1%, respectively. The amorphous silica content ratios of soils A, B, and C from the diatoms were approximately 5.2%, 4.7%, and 3.3%, respectively. Figure 7 presents the relationship between the unconfined compressive strength and the curing time. The $q_u$ of dredged soil A exhibited the highest values, followed by dredged soil B and C, respectively. In other words, higher content ratios of amorphous silica in the dredged soils resulted in higher shear strengths of the dredged soil mixed with steelmaking slag. However, the purified humic acid contents of the dredged soils were different.

Kiso et al. (2008) conducted an unconfined compressive test on the dredged soils, which had different flow values, mixed with steelmaking slag. Figure 8 depicts the relationship between the unconfined compressive strength $q_u$ and the curing time for the soils having the same mixing ratio, i.e., dredged soil:steelmaking slag = 7:3. The water content ratio of dredged soil decreased and the $q_u$ of the dredged soil mixed with steelmaking slag increased as the flow values of the dredged soil decreased.

Figure 9 presents the relationship between $q_u/q_{u,7}$, which is calculated using Figure 7 and Figure 8, and the curing time of 28 days. After seven days of curing, $q_u/q_{u,7}$ increased over time, and after 28 days of curing, the value of $q_u/q_{u,7}$ was approximately equal to 1.5–2.0. After three days of curing, the value of $q_u/q_{u,7}$ for all dredged soils was approximately 0.5. This indicates that, after three days of curing, the $q_u$ of the soil mixed with steelmaking slag was half of the strength achieved after seven days of curing. This indicates that the tendencies of shear strength development remained the same even when the flow values of the dredged soils were different. Therefore, when the same dredged soil was used, and its water content ratio was varied, the tendencies of shear strength development were the same; however, the shear strengths were different. In addition, on comparing Figure 9 to Figure 5 and Figure 6, the strengths of the dredged soil mixed with steelmaking slag developed as early as that of the amorphous silica content ratio of 20% in the clay in this study.

In comparison with the dredged soils used in Toda et al.’s study, the content ratios of the amorphous silica in the clays used in this study were higher. For instance, the content ratios of the amorphous silica in MK0 and MK10 were 9.40% and 9.94%, respectively. On the
contrary, the content ratio of the amorphous silica in dredged soil A used by Toda et al. was approximately 7.8%. However, the tendencies of the shear strength development in the mixtures used in this study were different from those of the mixtures used in Toda et al.’s study, as the steelmaking slag and the water content ratio of the mixtures were different in both studies. It was evident that the differences in the tendencies of shear strength development were caused by factors other than the content ratio of the amorphous silica in clay.

The differences between the clay used in this study and the dredged soil were discussed. The difference between amorphous silica is derived from minerals or diatoms was considered. The clays used in this study consisted of kaolin clay and metakaolin and do not contain diatoms. On the contrary, the dredged soils used in Toda et al.’s study included amorphous silica contents originating from volcanic glasses and diatoms. In Toda et al.’s study, 65~75% of the amorphous silica in the dredged soil was attributed to diatoms. Hence, the differences of the amorphous silica from the minerals or those of the amorphous silica from diatoms may affect the tendencies of shear strength development in the mixture containing clay and steelmaking slag.

From the abovementioned analysis, it is evident that when clays with different amorphous silica content ratios were mixed with steelmaking slag, the mixture of clay and steelmaking slag solidifies earlier as the content ratio of amorphous silica increases. However, even though the amorphous silica content ratio of the clays used in this study is higher than that of the dredged soil used in Toda et al.’s study, the shear strength development in the mixtures used in this study, up to 11.5% of the amorphous silica content ratio, was slower than that of the dredged soil used in Toda et al.’s study. For the amorphous silica content ratio of 20% in the clay in this study, the strength development was similar to that of the dredged soil used in Toda et al.’s study. Hence, the differences in the tendencies of the shear strength development can be attributed to the difference of the amorphous silica from minerals or that of the amorphous silica from diatoms.

4 CONCLUSIONS

In this study, the authors focused on the content ratio of the amorphous silica in clay and investigated the relationship between the content ratio of inorganic amorphous silica content in the clay and the shear strength of the clay mixed with steelmaking slag. Furthermore, the difference in the development of shear strength in the clay mixed with steelmaking slag, owing to the difference in the amorphous silica content ratio in clay, was determined.

The main conclusions are listed below.

• For an amorphous silica content ratio less than 11.5%, at the same curing time, the unconfined compressive strength increases as the content ratio of amorphous silica increases.
• The clay mixed with steelmaking slag solidifies earlier as the content ratio of amorphous silica increases. For a high amorphous silica content ratio, increase in the strength increasing was low even after seven days of curing.
• Compared with the studies on dredged soils mixed with steelmaking slag, the amorphous silica content ratio of the clay used in this study was higher than that of the dredged soils. However, the shear strength in the dredged soil with amorphous silica contents originating from the diatoms and the minerals mixed with steelmaking slag develops earlier than that of the clay with amorphous silica contents originating from the minerals mixed with the steelmaking slag. The differences in the tendencies of shear strength development can be attributed to the difference in the amorphous silica originating from minerals or that in the amorphous silica originating from diatoms.

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