Fundamental study on the neutralization effect of grout using the carboxylate ester reactant

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ABSTRACT

The acid silica sol grouting material has been frequently used in the chemical grouting method. Recently, it has been recognized that the ground can contain high amounts of calcium carbonate (CaCO₃), which are formed by deposits of shell and corals (high CaCO₃ ground/soil). When using acid silica sol grout with a typical pH value of 2 to 4 in this type of ground, the chemical reaction of the excess acid in the grout reacts with the CaCO₃ in the ground to produce carbon dioxide gas with foaming. Consequently, this chemical reaction reduces the strength and permeability of the ground. On the other hand, alkaline-based grout does not produce CO₂ bubbles when there high levels of CaCO₃ are present in the ground, because there is no excess acid in the grout. However, the used of alkaline-based grout cannot be expected to improve durability after gelation because of the large amount of alkali components. Therefore, it is necessary to develop a grout that is more durable and does not cause CO₂ foaming in the high CaCO₃ ground. In this study, we investigated the physical properties of chemical grout agents mixed with a sodium silicate solution and acid carboxylic ester, controlling the duration of the gel time and CO₂ foaming. We compared the strength characteristics of sand-gel with sand-gel specimens using two sample soils: Tohoku silica sand No.6 and high CaCO₃ soil. Shrinkage and leaching tests were conducted to assess the durability of homo-gel.

Keywords: acid silica sol grouting agent, high calcium carbonate ground, carboxylic acid ester

1 INTRODUCTION

Chemical grouting is a soil improvement method. It has been used to improve strength and reduce the permeability of ground as well as to protect buried objects and underground structures. In comparison with other soil improvement methods, the chemical grouting method requires relatively simple preparation and small-scale equipment and can be applied in narrow and low spaces. Furthermore, it has a short construction time and fewer problems (such as vibration, noise, and transportation related issues) associated with construction.

In Japan, many major cities are located on the soft ground near estuaries, so most construction works require ground improvement processes. Thus, ground improvement techniques are quite advanced in Japan. We need to enhance the durability, workability, and strength of grouting materials.

The acid silica sol grouting material has been frequently used in the chemical grouting method[6]. Recently, it has been recognized that the ground can contain high amounts of calcium carbonate (CaCO₃), which are formed by deposits of shell and corals (high CaCO₃ ground/soil), especially in island areas. When using acid silica sol grout with a typical pH value of 2 to 4 in this type of ground, the chemical reaction of the excess acid H⁺A⁻ in the grout reacts with the CaCO₃ in the ground to produce carbon dioxide gas with bubbling/foaming:

\[ \text{CaCO}_3 + 2\text{H}^+ + \text{A}^- \rightarrow \text{Ca}_2\text{A}_2 + \text{H}_2\text{O} + \text{CO}_2 \uparrow \] (1)

Consequently, this chemical reaction reduces the strength and permeability of the ground.

On the other hand, alkaline-based grout does not produce CO₂ bubbles when there high levels of CaCO₃ are present in the ground, because there is no excess acid in the grout. However, we cannot expect to improve durability using alkaline-based grout after gelation because of the large amount of alkali components[7]. Therefore, we must develop a grout that is more durable and does not cause CO₂ foaming and can be
used when there is a high level of CaCO₃ in the ground. Here, durability is defined as the ability of homo-gel and sand-gel to resist external physical and chemical influences[9].

There are two methods to enhance the durability of alkaline-based grout. The first is to reduce the amount of alkali components in the primary agent. This method adds a small amount of the reaction material (reacting agent) to a silicic acid solution from which alkali components such as colloidal silica are removed. The second method is to neutralize the alkali component in the primary agent, with acids released from decomposing acid carboxylic ester (reaction material/reacting agent). For the first method, Sasaki et al. studied the effects of sandy soil and combinations of acidic reaction materials (reacting agents) on the characteristics of solidified sandy soils. Chemical grout easily gelates as close to neutral[9], and the grout cannot sufficiently penetrate the ground within a very short gelling duration (a few seconds of gel time).

When using the second method, acid carboxylic ester decomposes over a certain amount of time, so the chemical grout ensures a longer gel time to penetrate the ground. Furthermore, because the chemical grout is highly permeable, we can expect significant soil improvement for each grout injection, which reduces the number of grout injections and construction cost.

In this study, we investigated the physical properties of chemical grout agents mixed with a sodium silicate solution and acid carboxylic ester, controlling the duration of the gel time and CO₂ foaming. We compared the strength characteristics of sand-gel with sand-gel specimens using two sample soils: Tohoku silicic sand No.6 and high CaCO₃ soil. Shrinkage and leaching tests were conducted to assess the durability of homo-gel.

### 2 MATERIALS AND SPECIMENS

We used solution-type grout agents. We considered three types of grout agents (acid-based, alkaline-based, and mixed grout agents), which are special high molar water glass and colloidal silica with added acid carboxylic ester, as reacting agents that neutralize the alkaline components of the mixed grout agent.

Colloidal silica refers to colloid particles of silica or hydrated silica and is also called silica sol. A colloid has particles ranging from 1 to 100 nm and is a substance that remains evenly dispersed throughout a liquid, solid, and gas. In this study, we used colloidal silica with an average particle size of 20 nm, which was derived from metal silicon.

A total of six types of solution-type grout agents were considered in the laboratory experiments. Four types of grout agents (D-1HH, D-1H, D-1, D-1L) were used to control CO₂ foaming by neutralizing the alkaline component of the primary agent (hereafter referred to as the D series). For comparison, we considered acid-based grout agents with molar ratios of SiO₂ to Na₂O ([SiO₂]/[Na₂O]) equal to 3.1 (hereafter referred to as acid-based grout agent SL-1), and an alkaline-based grout agent (hereafter R-2). Onishi et al. reported that the unconfined compressive strengths of sand-gel specimens using these two grout agents with Tohoku silicic sand No.6 are similar to those of the D series. The materials and properties of each grout agent are listed in Table 1. The properties of the materials used in the grout agents are also listed in Table 2.

For the D series, the primary agents of the special high molar water glass and colloidal silica were mixed with the same ratio. Thus, for all four grout agents of the D series, the SiO₂ concentration of the primary agents and the molar ratio of the grout agents were 8 (w/v) % and 10, respectively.

| Grout type | Primary agent | Silica concentration (w/v)% | Molar ratio | Reacting agent | Neutralization ratio |
|------------|---------------|-----------------------------|-------------|----------------|---------------------|
| D-1HH      | Special high molar water glass Colloidal silica | 8 | 10.0 | Carboxylic acid ester 75wt% sulphuric acid | 179% |
| D-1H       | Special high molar water glass Colloidal silica | 8 | 10.0 | Carboxylic acid ester 75wt% sulphuric acid | 139% |
| D-1        | Special high molar water glass Colloidal silica | 8 | 10.0 | Carboxylic acid ester 75wt% sulphuric acid | 116% |
| D-1L       | Special high molar water glass Colloidal silica | 8 | 10.0 | Carboxylic acid ester 75wt% sulphuric acid | 82% |
| SL-1       | Water glass No.3 | 5 | 3.1 | 75wt% sulphuric acid | 110% |
| R-2        | Special water glass | 11 | 4.0 | Carboxylic acid ester | 44% |
The differences within the D series are because of the amount of acid carboxylic ester added as a reacting agent, which is determined as the neutralization rates shown in Table 1. For the D series, the neutralization ratios of D-1HH, D-1H, D-1, and D-1L were 179%, 139%, 116%, and 82%, respectively. Only the neutralization ratio of D-1L was less than 100%. The neutralization rate is defined as:

\[
\text{Neutralization ratio} = \frac{\text{Acid equivalent of reacting agent}}{\text{Molar equivalent of basic contained in grout agent}} \times 100 \quad (2)
\]

The basic molar equivalent is the sum of the amount of sodium oxide (Na₂O) in the water glass and colloidal silica. The acid equivalent of the reacting agent is the sum of the amount of sulphuric acid and the amount of carboxylic acid decomposed from acid carboxylic ester. When preparing the D series grout agents, we obtained a pH value of 11.4 and assumed that the acid carboxylic ester did not decompose.

For the unconfined compressive test, we used Tohoku silica sand No.6 and high CaCO₃ soil to make sand-gel specimens. Table 3 summarizes the properties of the high CaCO₃ soil used in this study.

### Table 3. Soil properties of the high CaCO₃ soil samples.

| Property               | Value |
|------------------------|-------|
| Soil particle density  | 2.769 |
| Wet density [g/cm³]    | 1.769 |
| Wet content [%]        | 43.80 |
| Grain size             |       |
| Gravel [%]             | 1.90  |
| Sand [%]               | 85.13 |
| Silt [%]               | 12.97 |
| Calcium content [%]    | 53.80 |

### 3 EXPERIMENTS

#### 3.1 Leaching and shrinkage test for homo-gel

When using a solution-type grout agent in the chemical grout method, we can expect improvements in the water retention and strength of the ground because of its high permeability. However, an aqueous dispersion of the solution-type grout agent can cause several problems such as groundwater contamination and eluviation of the grout agent. Thus, we require a very durable grout agent. Furthermore, its application to high CaCO₃ ground requires no formation of CO₂ gas.

We ran leaching and shrinkage tests to investigate the durability of homo-gel using the solution-type grout agent. We poured 125 ml of each grout agent into a polypropylene volumetric flask and cured it at 20 °C (Fig. 1(a)). Seven days later, purified water was added to increase the volume to 250 ml after ensuring the gelation of the grout agent (homo-gel) (Fig. 1(b)) and measuring the initial weight of the homo-gel. After seven more days, the water in the flask was sampled and the silica concentration was analyzed using inductively coupled plasma-atomic emission spectrometry. The purified water was added to the flask and the weight of the homo-gel was measured. These processes were repeated for 14, 28, 60, 120, 180, 240, and 360 days to evaluate the volume change of the homo-gel and silica eluviation.

For D series grout agents, the alkaline components of the primary agent are neutralized, with acids released by hydrolysis of the carboxylic acid ester, which can also be observed using pH indicators (thymol blue and methyl red). Several drops of 1% thymol blue and methyl red solutions were added to the grout agents to detect the internal and surface pH of the homo-gel. The pH values were measured for curing periods of 1, 3, 7, 14, and 28 days. The pH colour change ranges are shown in Fig. 2 for thymol blue and methyl red.

![Fig. 1. Homo-gel specimen preparation.](image)

![Fig. 2. Range of pH and colour for thymol blue and methyl red.](image)
3.2 Unconfined compressive test for sand-gel

Sand-gel specimens were made using Tohoku silica sand No.6 with six types of grout agents. All sand-gel specimens were wet-cured at 20 °C. After 28 days of wet curing, the unconfined compressive test was conducted in accordance with JIS A 1216. Each grout material was first placed into a cylindrical acryl pipe with a diameter of 5 cm and a height of 15 cm. Then, a soil sample was filled and compacted in the pipe. After removing it from the pipe, the specimen was reshaped and was adjusted to 10 cm high.

Similarly, for the high CaCO₃ soil, sand-gel specimens were made with three types of grout agents (D-1HH, SL-1, and R-2). We used high CaCO₃ soil (Table 3) that was passed through a 2 mm sieve.

When high CaCO₃ soil was filled with an acid-based grout agent (SL-1), it caused CO₂ gas foaming, as shown in Fig. 3(a). The mixture quickly hardened, as shown in Fig. 3(b). We anticipated the excess acid of the grout agent to be neutralized by CaCO₃. Therefore, sand-gel specimens for SL-1 were prepared by lowering the pH of the grout agent and lengthening the gel time by increasing the amount of reacting agent. Their sand-gel densities were smaller and more brittle compared with sand-gel specimens using Tohoku silica sand No.6.

![Fig. 3. High CaCO₃ soil mixing with acid-type grouting agent during preparation of sand-gel specimens.](image)

4 TEST RESULTS

4.1 Results of leaching and shrinkage test for homo-gel

Figure 4 shows the relationship between the volume change of homo-gel and the curing time for each grout agent. Similarly, Fig. 5 shows the relationship between a reduction of the silica concentration in the homo-gel and the curing time.

For R-2, the volume of the homo-gel significantly reduced during the early curing time, and there was far more leaching of silica than the other six grout agents (Fig. 6(a)). Further shrinkage and leaching occurred when the curing time increased. This shows that the homo-gel is durable. For SL-1, the leaching of silica was very small compared that for R-2. However, the volume consistently decreased with the curing time, and after 120 days of curing, the volume reduced more than those for the other six grout agents.

However, for D-1HH, D-1H, and D-1 (which have neutralization ratios over 100%), the volume changes and leaching of silica were relatively small compared with those of R-2. D-1HH (which has the highest neutralization ratio) was more stable in terms of volume and silica leaching than any of the other grout agents. For D-1L (which has a neutralization ratio less than 100%), the volume expansion and silica leaching processes were very fast, and the homo-gel collapsed after only 180 curing days (Fig. 6(b)). The homo-gel absorbs water, so the D-1L homo-gel absorbed a significant amount of water, could not retain its shape, and collapsed.

![Fig. 4. Relationship between volume changes of the homo-gel specimen and the curing time.](image)

![Fig. 5. Relationship between the reduction in the silica concentration and the curing time.](image)

Figure 7 shows the changes in the pH of the homo-gel over time to verify the neutralization of the alkaline components in the grout agents. Because the gelation of SL-1 was confirmed after seven curing days, this was used as the start time for the pH measurements for SL-1. For the D series, the pH values of the homo-gel pH for D-1HH, D-1H, and D-1 gradually decreased over time. This implies that the alkaline components of these homo-gels were neutralized.
Figure 8 shows the colour changes of the homo-gels over the curing time (at 0 (immediately after mixing), 7, and 28 days) using thymol blue for D-1 (Fig. 8(a)) and D-1L (Fig. 8(b)). The pH values for both D-1 and D-1L were 11.4 immediately after mixing. However, the pH of D-1 was less than 8.0 and the gel became yellow, whereas the pH of D-1L decreased to 9.7 after seven days and 10.1 after 28 days. The neutralization of D-1L was incomplete and the gel remained blue.

![Figure 6](image1)

(a) D-1HH (b) D-1H

Fig. 6. Example of the appearance of the homo-gel during the leaching and shrinkage tests.

![Figure 7](image2)

Fig. 7. Relationship between the homo-gel pH and the curing time.

4.2 Results of unconfined compressive strength test for sand-gel

The results for the 28 days cured unconfined compressive strength of sand-gel specimens using Tohoku silica sand No.6 for each grout agent are summarized in Table 4. The unconfined compressive strength ranges from 250 to 300 kN/m² for all grout agents. Apparently, the strengths are generally similar for all grout agents.

A strength range of 250–300 kN/m² was selected because the design strength for mitigating liquefaction hazards requires 50–100 kN/m² when local sand is used with a chemical grout agent to control CO₂ foaming by neutralizing the alkaline in the primary agent. In practice, we consider a ratio of the in-situ laboratory strength of sand-gel of 2. Therefore, we require a strength of 100–200 kN/m². When using Tohoku silica sand No.6 (which does not contain fine particles), the strength appears to be 1.5–3 times larger than local sand, and thus the unconfined compressive strength of sand-gel ranges from 250 to 300 kN/m².

| Specimen | $q_u$ [kN/m²] | $\rho_i$ [g/cm³] |
|----------|---------------|-----------------|
| D1-HH    | 277.0         | 2.057           |
| D-1H     | 292.3         | 2.068           |
| D-1      | 284.3         | 2.065           |
| D-1L     | 277.3         | 2.066           |
| SL-1     | 274.8         | 2.079           |
| R-2      | 283.7         | 2.047           |

The results of the unconfined compressive strength of sand-gel specimens using high CaCO₃ soil are summarized in Table 5. The unconfined strengths and wet densities for any grout agents were smaller than those of Tohoku silica sand No.6. This could be because of the difficulties when compacting the preparation of sand-gel specimens and the better strength characteristics of sand-gels using Tohoku silica sand No.6 than local sand.

R-2 was the strongest of the considered grout agents, but it is not durable (as mentioned in Sec. 4.1). D-1HH was stronger than SL-1. Furthermore, the acid-type grout agent SL-1 was weaker and has a smaller wet density in comparison because of CO₂ foaming. In this experiment, CO₂ gas escaped through the mould opening, but when the grout agent is injected into the ground the strength and density of the sand-gel would be even smaller.

| Specimen | Gel time [sec] | $q_u$ [kN/m²] | $\rho_i$ [g/cm³] |
|----------|---------------|---------------|-----------------|
| D1-HH    | 15 to 20      | 120.3         | 1.889           |
| SL-1     | 2             | 102.3         | 1.819           |
| R-2      | 30 to 35      | 177.7         | 1.908           |
5 CONCLUSION

For the application of alkaline-based and high durable grout agents to the ground with high levels of CaCO_3, we verified the effectiveness of acids released by the decomposition of acid carboxylic ester to neutralize the alkaline in the primary agent.

We reconfirmed that the alkaline-based grout agent is not durable, whereas acid-based agents are very durable. However, when using acid-based grout agents in the ground with high levels of CaCO_3, we found that the grout agent immediately gelates with the sand, resulting in poor strength and durability. To control the immediate gelation, we must add more acid-based reacting agent, but this reduces the strength and durability and increases CO_2 foaming.

However, D-1HH, D-1H, and D-1 (which have neutralization ratios over 100%) enhanced the durability, as demonstrated by our leaching and shrinkage tests. D-1L (which has a neutralization ratio below 100%) resulted in a collapse of the homo-gel.

An effective compaction method for sand-gel using soil with high levels of CaCO_3 must be developed, and we should then re-evaluate the strength characteristics of the sand-gel. Strength tests for sand-gel and durability tests for homo-gel using seawater are also required, so that this work can be applied to mitigate liquefaction hazards and for bulkhead wall construction. In addition, we must measure the long-term durability.

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