

# Effect of carbonation on strength development of cement-treated Toyoura silica sand

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#### Abstract

It is well known that the strength of cement-treated soil increases over the course of several years. In general, the long-term increase in strength is attributed to the pozzolanic reaction between the cement paste and the soil. The carbonation of cementitious material can also increase its strength. In this study, the effect of carbonation of cement-treated sand on its strength was investigated. Specimens of cement-treated Toyoura silica sand were cured under three conditions: sealed, natural, and accelerated carbonation. The  $CO_2$  concentrations under the three curing conditions were 0%, 0.03%, and 5%, respectively. The measured strengths of the specimens cured under sealed conditions were almost constant after 28 days, whereas those of the specimens cured under the natural and accelerated conditions increased beyond 28 days because of carbonation. These results indicate that carbonation is one of the main reasons for the long-term increase in the strength of cement-treated sand. Based on thermal analysis, the effect of the  $CO_2$  concentration on the strength and elastic modulus can be explained by the formation of CaCO<sub>3</sub>. © 2015 The Japanese Geotechnical Society. Production and hosting by Elsevier B.V. All rights reserved.

Keywords: Cement-treated sand; Carbonation; Strength; Elastic modulus; Calcium carbonate; Cement; Silica sand

## 1. Introduction

The cement treatment of soils to create cement-treated soil—also called cement-stabilized soil, soil cement, etc.—has been widely used to improve the properties of soil foundations (Kézdi, 1979; Bell, 1993; Kitazume and Terashi, 2013). Cement stabilization/ solidification has also been used to immobilize heavy metals in contaminated soils (United States Environmental Protection Agency, 1989; Malviya and Chaudhary, 2006; Chen et al., 2009). Cement-treated soils contain cement, water, soil, and air, just like concrete and mortar. However, due to their different constituent ratios and materials, cement-treated soils have several

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unique properties. For example, cement-treated soils have relatively small amounts of cement and large amounts of soil and air.

One of the unique properties of cement-treated soils is their tendency to increase greatly in long-term strength beyond 28 days. Many studies have reported that after a few years, cement-treated soils have strengths that are 2–6 times higher than their strengths at 28 days (Mishima et al., 1995; Saitoh, 1988; Shibuya et al., 2001; Hayashi et al., 2003; Horpibulsuk et al., 2003; Kongsukprasert et al., 2007, Seng and Tanaka, 2011). The design strength of a cement-treated soil is usually determined based on its strength at 28 days, in a manner similar to concrete. The large gap between the design strength at 28 days and the actual long-term strength beyond 28 days has both advantages and disadvantages in practice. The development of long-term strength serves to increase the stability of foundations and immobilize heavy metals; however, the development of excessive strength could prevent the re-excavation

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of the stabilized foundation. To develop rational designs, therefore, it is essential to clarify the mechanism of long-term strength development.

Kongsukprasert et al. (2007) investigated data for both cement-treated soils and concrete and found that the ratio of strength increase depends on the strength at 28 days. However, the detailed discussion of the mechanism based on physico-chemical aspects is necessary to adequately explain the ultimate strength of cement-treated soils.

In general, the mechanism of strength development of cementtreated soils is explained by a combination of the following: (1) the original strength of the cement-free soil, (2) the improvement in basic soil properties owing to the decrease in water content and ion exchange, (3) the cement hydration, and (4) the pozzolanic reaction, as shown in Fig. 1 (Express Highway Research Foundation of Japan, 1978; Kézdi, 1979; Kitazume and Terashi, 2013). While the short-term increase in the strength of cement-treated soils up to 28 days is mainly due to cement hydration, the long-term increase in the strength beyond 28 days is mainly due to the pozzolanic reaction between soils and cement paste under the high-alkalinity conditions created by the cement. Kézdi (1979) noted that the pozzolanic reaction plays a significant role in the strength of cement-treated clay; however, several studies have reported that cement-treated sand also exhibits a large increase in long-term strength. These findings suggest the existence of another factor that is responsible for increasing the long-term strength of cement-treated sand.

The carbonation of cement-treated soil warrants further discussion as it, too, leads to an increase in strength. Carbonation is a process by which carbon dioxide (CO<sub>2</sub>) in ambient air penetrates cementitious materials and reacts with cement hydrates such as calcium hydroxides (portlandite, Ca(OH)<sub>2</sub>) and calcium–silicate–hydrate (C–S–H) gel in the cement paste matrix to form calcium carbonates (CaCO<sub>3</sub>). These chemical reactions are expressed as follows:

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O \tag{1}$$

 $(CaO)_{x}(SiO_{2})(H_{2}O)_{y} + xCO_{2} \rightarrow xCaCO_{3} + (SiO_{2})(H_{2}O)_{t}$  $+ (y-t)H_{2}O$ 



Fig. 1. Typical explanation of mechanism of increase in strength of cement-treated soils.

Unhydrated cement also reacts with  $CO_2$ , as expressed by the following reaction equations:

$$(CaO)_{3}(SiO_{2}) + (3-x)CO_{2} + yH_{2}O \rightarrow (3-x)CaCO_{3} + (CaO)_{x}(SiO_{2})(H_{2}O)_{y}$$

$$(3)$$

$$(CaO)_{2}(SiO_{2}) + (2-x)CO_{2} + yH_{2}O \rightarrow (2-x)CaCO_{3} + (CaO)_{x}(SiO_{2})(H_{2}O)_{y}$$

$$(4)$$

In the field of concrete engineering, carbonation is one of the main causes of the corrosion of steels embedded in reinforced concrete structures, and therefore, it has attracted considerable research attention (Leber and Blakey, 1956; Papadakis et al., 1991, Neville, 1996). Carbonation significantly lowers the alkalinity of concrete via the consumption of  $Ca(OH)_2$ . This decrease in alkalinity destroys the passive protective oxide film around steel, causing it to start corroding. Simultaneously, the generation of carbonates by carbonation changes the pore structure of concrete, often increasing the density of the pore structure and thereby increasing the concrete strength.

Studies on the carbonation of cement-treated soils have mainly aimed to improve cement-based solidification/stabilization of heavy metals by accelerated carbonation techniques (Fernández Bertos et al., 2004; Nishi et al., 2004; Chen et al., 2009). Accelerated carbonation techniques supply carbon sources such as gaseous  $CO_2$  or sodium carbonate (Na<sub>2</sub>CO<sub>3</sub>) during soil mixing. These carbon sources can activate the reaction of unhydrated cement, increase the early strength of the mixture, and reduce the leaching of heavy metals and alkalinity. However, few studies have investigated the effect of carbonation on the long-term strength of cement-treated soils, although this topic is very important to the understanding of the mechanism of long-term strength development.

In the present study, the effect of carbonation on the strength of cement-treated sand was investigated. Toyoura silica sand, which was used as a standard sand in Japan, was used as a chemically stable soil to eliminate the effect of the pozzolanic reaction that would occur with clay. This study also did not address the solidification/stabilization of heavy metals but rather was focused on the effect of carbonation on strength development in cement-treated soils. In the experiments conducted in this study, cement-treated Toyoura silica sand specimens were prepared and then cured under sealed, natural, and accelerated carbonation conditions. Their strength development and carbonate contents were then analyzed.

## 2. Materials and methods

#### 2.1. Specimens

(2)

Cement-treated specimens were prepared by mixing Toyoura silica sand, ordinary Portland cement, and tap water, based on the JGS 0811-2000 standard. The densities of the sand and cement were  $2.63 \times 10^3$  kg/m<sup>3</sup> and  $3.15 \times 10^3$  kg/m<sup>3</sup>, respectively. Tables 1 and 2 show the chemical compositions of the sand and cement, respectively. The designed cement contents

(ratios of cement to dried sand by weight), the water contents of the sand, and specimen densities were 8 mass%, 8 mass%, and  $1.7 \times 10^3$  kg/m<sup>3</sup>, respectively. Based on these values, the design water content of the specimens was calculated to be 7.4 mass%.

The materials were mixed using a mixer. First, air-dried sand and water were mixed for 1 min to control the water content. Then, the cement was added and mixed for 1 min. Finally, the materials were mixed again for 1 min after hand mixing to remove material attached to the mixer.

After mixing, cylindrical specimens 100 mm in diameter and 200 mm high were prepared by compaction with a weight of 2.5 kg from the height of 300 mm, applied 25 times for each of three layers of each specimen. Table 3 shows the three conditions under which the specimens were cured: natural, accelerated carbonation, and sealed. Under the natural and accelerated conditions, the specimens were cured under sealed conditions for six days after casting and then cured in water for one day. They were then stored in a room or chamber in which the temperature and relative humidity (RH) were maintained at 20 °C and 60%, respectively. Under the natural curing conditions, the average measured  $CO_2$  gas concentration in the room was  $\sim 0.03\%$ , and under the accelerated carbonation conditions, the  $CO_2$  concentration in the chamber was maintained at 5% to promote the carbonation of the specimens. Under the sealed conditions, the specimens were sealed and cured in a room at a constant temperature of 20 °C to investigate their strength development in the absence of the carbonation effect. To this end, the specimens were sealed using aluminum tape, and the constancy of their weight during curing was confirmed to ensure that sealed conditions were maintained throughout.

## 2.2. Measurements

#### 2.2.1. Unconfined uniaxial compressive test

After the prescribed curing periods, the unconfined compressive strengths of the specimens were measured through uniaxial compressive tests conducted in accordance with the JIS A 1216 standard. Gypsum was used to fill the gaps

Table 1

Chemical	composition	of	Toyoura	silica	sand	(%)
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Ignition loss	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	CaO	MgO
0.5	92.6	3.7	0.7	0.5	0.2

Table 2					
Chemical	composition	of ordinary	Portland	cement (%).	

Chemical composition	Ignition loss	$\mathrm{SiO}_2$	$Al_2O_3$	Fe <sub>2</sub> O <sub>3</sub>	CaO	MgO	$SO_3$
Cement for specimens	cured under s	sealed c	ondition	ns			
	2.19	20.62	5.16	2.98	64.38	1.23	2.13
Cements for specimens	s cured under	natural	or acce	elerated	conditi	ons	
	2.11	20.50	5.23	3.01	64.40	1.25	2.00
	2.08	20.59	5.24	3.00	64.32	1.24	2.14

between each specimen and the loading plates of the test machine. The specimen displacement during compressive testing was measured using local displacement transducers (LDTs). The specimens cured under natural and accelerated conditions were tested without any treatment of their water content; in other words, the strengths of air-dried specimens were measured. In contrast, the specimens cured under sealed conditions were tested after saturation for 24 h to compare the results with those of the other study. In general, an increase in water content leads to a decrease in measured strength. In our preliminary experiments using similar specimens and minor differences in the curing conditions, the strength decreased from 3.57 N/mm<sup>2</sup> without saturation to 3.07 N/mm<sup>2</sup> with saturation. However, because the focus of this study is on the strength development over time, the difference in the pretreatment of the water content of the specimens does not alter the conclusions of this study.

## 2.2.2. Measurement of carbonation depth

After the compressive strength tests, the carbonation depths of the specimens cured under natural and accelerated conditions were measured from their cross sections at a height of 45 mm from the bottom to avoid a fractured surface. A 1% phenolphthalein alcoholic solution was used as a visual indicator to detect the carbonated area based on the JIS A 1152 standard.

#### 2.2.3. Thermal analysis

The amounts of calcium hydroxide (Ca(OH)<sub>2</sub>) and calcium carbonate (CaCO<sub>3</sub>) were measured by thermogravimetric and differential thermal analysis (TG-DTA). A powdered sample for TG-DTA was obtained by taking a disk sliced  $\sim$  50 mm from the bottom of each cylindrical specimen after compressive testing and then crushing it to a maximum size of 90 µm. The TG-DTA of each sample was conducted at temperatures ranging from room temperature to 1000 °C in a nitrogen gas atmosphere. The rate of temperature increase was set to 10 °C/min. The amounts of Ca (OH)<sub>2</sub> and CaCO<sub>3</sub> were determined from the mass losses between 400 and 450 °C and 650 and 800 °C, respectively. The specific temperature ranges were selected based on the DTA results. In this study, they were modified based on the chemically bound water measured between 105 and 1000 °C to consider the various compositions of cement paste and sand in the powdered samples. The modification method is explained in detail later.

## 3. Results and discussion

#### 3.1. Carbonation depth

Table 4 shows cross sections of the specimens after the supplying of phenolphthalein and the measured carbonation depths. The red-colored area (dark-colored area in Table 4) in each cross section indicates the uncarbonated zone. The images show that all of the specimen areas were carbonated by the age of 180 days under the natural conditions (exposed to the air) or by the age of 91 days under the accelerated conditions. The progress of carbonation in the cement-treated sand was much faster than that in normal

Table 3 Curing conditions of specimens.

Curing condition	After casting to 5th day	6th day	From 7 to 27th day	From 28th day
Natural (CO <sub>2</sub> $\cong$ 0.03%) Accelerated (CO <sub>2</sub> =5%) Sealed (CO <sub>2</sub> =0%)	Sealed ( $T=20$ °C) Sealed ( $T=20$ °C) Sealed ( $T=20$ °C)	Water ( $T=20$ °C) Water ( $T=20$ °C) Sealed	Room ( $T=20$ °C, RH=60%, CO <sub>2</sub> $\cong$ 0.03%) Room ( $T=20$ °C, RH=60%, CO <sub>2</sub> $\cong$ 0.03%) Sealed	Room Chamber ( $T=20$ °C, RH=60%, CO <sub>2</sub> =5%) Sealed

Table 4 Measured carbonation depth of cross sections.



concrete because of the coarser pore structure and lower  $Ca(OH)_2$  content of the cement-treated sand.

## 3.2. Unconfined compressive strength

Fig. 2(a)–(c) shows the measured stress–strain relations of the representative specimens cured under natural, accelerated, and sealed conditions, respectively. The strain is taken as the average of two axial strains measured using LDTs. Table 5 shows the water contents, unconfined compressive strengths,  $q_{max}$ , and elastic moduli,  $E_{50}$ , of the specimens. These are the average values of each of three test results obtained under the same conditions. However, in some cases, data were not obtained because of experimental errors. In the case of the specimen cured under accelerated conditions, at an age of 180 days, only one specimen was tested, and the strain could not be measured. The standard deviations of the strengths and elastic moduli were calculated, and the average coefficients of variation were found to be 9.3% and 13.7%, respectively. The long-term strength increase ratio beyond 28 days was also calculated for each curing condition. Figs. 3 and 4 show the changes in the compressive strength and elastic modulus, respectively, over time. Fig. 5 shows the relationship between the compressive strength and the elastic modulus.

Under natural conditions, the specimen strength increased steadily over the course of the measurement period. The strength at 365 days was approximately 1.7 times that at 28 days and was the highest strength measured in this study. The trend of the strength development was consistent with trends observed in previous studies of long-term strength development. The elastic modulus also increased over time; however, its growth ratio was not significant. As discussed later, the strength development that occurred under the natural curing conditions can be explained by the carbonation. Under accelerated carbonation, the strength increased rapidly up to 56 days and remained almost constant thereafter. The maximum strength measured at 56 days was approximately 1.3 times that at 28 days. The elastic modulus increased greatly from 56 days to 91 days and became approximately twice that at 28 days. As discussed later, carbonation of C–S–H gel rather than Ca(OH)<sub>2</sub> is believed to have reduced the increase in strength and increased the elasticity due to carbonation.

Under the sealed curing conditions, the strength and elastic modulus of the specimen remained almost constant during the measurement period. This indicates that the specimen remained stable in the absence of  $CO_2$ .

With regard to the relationship between the compressive strength and the elastic modulus, shown in Fig. 5, it was observed that the strengths of specimens cured under sealed conditions were lower than those of specimens of the same strength level cured under natural and accelerated conditions. The reason for this is the increase in water content resulting from the saturated treatment of specimens cured under sealed conditions, as explained previously. The elastic moduli of all of the specimens cured under natural conditions and some of the specimens cured under accelerated conditions increased with strength in a manner similar to that typically observed for normal concrete. On the other hand, the elastic moduli of specimens cured under accelerated conditions increased rapidly after 56 days, even for the same strength level, and therefore, the corresponding plots differed from those for the other data. This may be attributed to carbonation of C-S-H gel rather than Ca(OH)<sub>2</sub>. The details are discussed later based on the generation of CaCO<sub>3</sub>.

### 3.3. Amounts of $Ca(OH)_2$ and $CaCO_3$

Fig. 6 shows examples of the thermogravimetric analysis (TGA) results. These results show changes in the sample weight with increasing temperature. Fig. 7 and Fig. 8(a) and (b) show the TG–DTA results for the amounts of Ca(OH)<sub>2</sub> and CaCO<sub>3</sub> in the cement paste of the samples cured under the natural and accelerated conditions, respectively. Ca(OH)<sub>2</sub> is generated by cement hydration and consumed by carbonation, whereas CaCO<sub>3</sub> is mainly produced from cement hydrates, such as Ca(OH)<sub>2</sub> and C–S–H gel, by carbonation (Eqs. (1) and (2)). We calculated the amounts of Ca(OH)<sub>2</sub> and CaCO<sub>3</sub> in the cement paste to examine the change in the structure of the cement paste. In these calculations, we needed to take the constituent ratios of sand and cement in the measured values into consideration because the TGA results include the effect of sand in a sample. That is, the existence of stable sand in a



Fig. 2. Stress–strain relation. (a) Results for specimens cured under natural conditions (CO<sub>2</sub>  $\cong$  0.03%). (b) Results for specimens cured under accelerated conditions (CO<sub>2</sub>=5%). (c) Results for specimens cured under sealed conditions.

Table 5 Measured unconfined compressive strengths and elastic moduli.

Curing condition	Age (days)	Water content (%)	Compressive strength, $q_{max}$ (N/mm <sup>2</sup> )	Standard deviation (N/mm <sup>2</sup> )	Strength/strength at 28 days	Elastic modulus, $E_{50}$ (kN/mm <sup>2</sup> )	Standard deviation (kN/mm <sup>2</sup> )	Elastic modulus/elastic modulus at 28 days
Natural	28	2.0	3.69	0.34	1	3.71	0.23	1
$(\text{CO}_2 \cong 0.03\%)$	56	1.2	4.42	0.58	1.20	6.24	1.80	1.68
	91	1.1	4.42	0.46	1.20	5.13	0.97	1.38
	180	0.8	5.12	0.66	1.39	5.85	1.10	1.58
	365	0.9	6.28	0.34	1.70	5.53*	_	1.49
Accelerated	28	2.0	3.69	0.34	1	3.71	0.23	1
$(CO_2 = 5\%)$	35	1.1	4.16	0.73	1.13	6.16	1.93	1.66
	42	1.1	4.46	0.30	1.21	5.38	0.75	1.45
	56	1.0	4.79	0.33	1.30	5.17	0.36	1.39
	91	1.1	4.60	0.72	1.25	9.80	0.47	2.64
	180	1.0	4.20*	_	1.14	-**	_	_
	365	**	4.81	0.63	1.30	8.38	1.17	2.26
Sealed	28	23.0	3.59	0.06	1	5.66	0.55	1
$(CO_2 = 0\%)$	180	22.8	3.29	0.17	0.92	5.51	0.35	0.97
	365	23.7	3.48	0.10	0.97	5.96	0.67	1.05

\*Data were obtained from only one specimen because of the experimental errors associated with the other two specimens.

\*\*Data were not obtained because of experimental errors.



Fig. 3. Changes in strength under different curing conditions.



Fig. 4. Changes in elastic modulus under different curing conditions.



Fig. 5. Relationship between compressive strength and elastic modulus.



Fig. 6. Examples of changes in weight according to thermogravimetric analysis.



Fig. 7. Changes in amount of Ca(OH)2 under different curing conditions.

sample decreases the mass ratios of  $Ca(OH)_2$  and  $CaCO_3$  measured by TGA. Although the constituent ratios in the sample may be calculated from the chemical composition analyzed by a dissolution method, in this study, they were

calculated from the thermal analysis results. First, the amount of chemically bound water in each sample was measured from the mass reduction from 105 to 1000 °C in TG–DTA. In parallel, the amount of chemically bound water in the cement paste, shown in Fig. 9, was calculated by numerical simulation (Maekawa et al., 1999, 2003; Nakarai et al., 2006, 2007). Then, the amounts of Ca(OH)<sub>2</sub> and CaCO<sub>3</sub> in the cement paste as normalized values were calculated using the following equations:

$$CH_{cp\_exp} = CH_{sp\_exp} \times \frac{Wch_{cp\_cal}}{Wch_{sp\_exp}}$$
(5)

$$CC_{cp\_exp} = CC_{sp\_exp} \times \frac{Wch_{cp\_cal}}{Wch_{sp\_exp}}$$
(6)

In these equations,  $CH_{cp\_exp}$  and  $CC_{cp\_exp}$  are the amounts of Ca(OH)<sub>2</sub> and CaCO<sub>3</sub> in cement paste, respectively;  $CH_{sp\_exp}$  and  $CC_{sp\_exp}$  are the amounts of Ca(OH)<sub>2</sub> and CaCO<sub>3</sub> in a sample as measured by TG–DTA, respectively;  $Wch_{cp\_cal}$  is the amount of chemically bound water in the cement paste, as calculated by numerical simulation; and  $Wch_{sp\_exp}$  is the amount of chemically bound water in the sample, as measured by TG–DTA (% in mass).

The origin of CaCO<sub>3</sub> was also calculated on the basis of the TG–DTA results in this study. The amount of CaCO<sub>3</sub> from Ca  $(OH)_2$  was calculated based on the reduction in Ca $(OH)_2$ , whereas the amount of CaCO<sub>3</sub> from C–S–H gel, other hydrates, and unhydrated cement was calculated using the following equations:

$$CC_{CH} = \left(CH_{cp\_cal} - CH_{cp\_exp}\right) \times \frac{M_{CC}}{M_{CH}}$$
(7)

$$CC_{CSH} = CC_{cp\_exp} - CC_{CH}$$
(8)

In these equations,  $CC_{CH}$  is the amount of CaCO<sub>3</sub> generated by the carbonation of Ca(OH)<sub>2</sub>;  $CH_{cp\_cal}$  is the amount of Ca(OH)<sub>2</sub> calculated by numerical simulation, neglecting the effect of carbonation;  $M_{CH}$  is the molar mass of Ca(OH)<sub>2</sub> (=74.093 g/ mol);  $M_{CC}$  is the molar mass of CaCO<sub>3</sub> (=100.87 g/mol); and  $CC_{CSH}$  is the amount of CaCO<sub>3</sub> generated by the carbonation of C–S–H gel and other hydrates, except Ca(OH)<sub>2</sub>.

Regardless of differences in the atmospheric CO<sub>2</sub> concentration, the amounts of Ca(OH)<sub>2</sub> and CaCO<sub>3</sub> decreased and increased, respectively, with time because of carbonation. The changes that occurred under the accelerated conditions were faster and greater than under the natural conditions. The amount of Ca(OH)<sub>2</sub> remaining became almost constant after 91 days under the accelerated conditions, and that under the natural conditions reached the same level at 365 days. The reason for this was that the high CO<sub>2</sub> concentration accelerated the progress of carbonation. With regard to the origin of the CaCO<sub>3</sub> generated, under the natural conditions, the increase in CaCO<sub>3</sub> after 28 days can be explained by the carbonation of Ca(OH)<sub>2</sub>. In contrast, under the accelerated conditions, the increase in CaCO<sub>3</sub> between 28 and 91 days can be explained by the carbonation of Ca(OH)2, whereas the generation of CaCO<sub>3</sub> after 91 days was dominated by the carbonation of other hydrates such as C-S-H gel.



Fig. 8. Changes in amount of CaCO<sub>3</sub> under different curing conditions. (a) Natural conditions. (b) Accelerated conditions.



Fig. 9. Numerical results for amounts of chemically bound water and Ca(OH)2.



Fig. 10. Relationship between unconfined compressive strength and CaCO<sub>3</sub>.

Fig. 10 shows the relationship between the unconfined compressive strength and the amount of  $CaCO_3$ . Under the natural curing conditions, the strength increased almost constantly with increasing  $CaCO_3$  content as a result of carbonation. This means that carbonation contributes to the large increase in the long-term strength of cement-treated sand, as well as the pozzolanic reaction in cement-treated clay. Under the accelerated curing conditions, up to 56 days, the strength increased in the same manner as under the natural curing



Fig. 11. Relationship between elastic modulus and CaCO<sub>3</sub>.

conditions. Beyond 56 days, the strength decreased slightly with increasing CaCO<sub>3</sub>. Fig. 11 shows the relationship between the elastic modulus and the amount of CaCO<sub>3</sub>. Under the natural and accelerated conditions, up to 56 days, the elastic modulus also gradually increased with increasing CaCO<sub>3</sub>, in a manner similar to that observed for the strength. However, under the accelerated conditions, beyond 56 days, the elastic modulus increased rapidly with a slight increase in the amount of CaCO<sub>3</sub>. These results suggest that the effects of carbonation on the strength and elastic modulus depend on the  $CO_2$  concentration. The progression of carbonation at low  $CO_2$ concentrations effectively increases the strength, whereas at high CO<sub>2</sub> concentrations, carbonation largely increases the elastic modulus. The particular changes that occur at high CO<sub>2</sub> concentrations might be caused by the increase in CaCO<sub>3</sub> from carbonation of C-S-H gel, as shown in Fig. 8. A decrease in strength due to carbonation of C-S-H gel has been suggested in previous studies that focused on the carbonation of concrete and mortar (Kobayashi, 1991; Cahyadi and Uomoto, 1995). The elastic moduli reported in the literature for Ca(OH)<sub>2</sub>, C-S-H gel, and  $CaCO_3$  (calcite) are 35–50, 18–36, and 86 GPa, respectively (Constantinides and Ulm, 2004; Valentinia et al., 2014). These studies also considered the possibility that the formation of CaCO<sub>3</sub> from C-S-H gel due to carbonation

contributes to the large increase in elasticity more than does the formation of  $CaCO_3$  from  $Ca(OH)_2$ .

## 4. Conclusions

The effect of carbonation of cement-treated Toyoura silica sand on its strength development was investigated in this study using specimens cured under three conditions: sealed (CO<sub>2</sub>=0%), natural (CO<sub>2</sub>  $\cong$  0.03%), and accelerated carbonation (CO<sub>2</sub>=5%). The following results were obtained from the experiments.

Under the sealed conditions, the strength remained almost constant after 28 days. This means that the specimen in this study cured under sealed conditions was stable in the absence of  $CO_2$ .

Under natural and accelerated curing conditions, carbonation of the cement-treated sand specimens rapidly progressed. Under natural curing conditions, carbonation steadily increased the strength and elastic modulus of the specimens. Under accelerated curing conditions, carbonation initially increased the strength and elastic modulus and then the strength slightly decreased.

Under natural conditions, the strength and elastic modulus increased almost constantly as the amount of CaCO<sub>3</sub> produced by carbonation increased. This indicates that carbonation contributes to the large increase in the long-term strength of cement-treated sand. This can be explained by the carbonation of Ca(OH)<sub>2</sub> at low CO<sub>2</sub> concentrations. Under accelerated curing conditions up to 56 days, the strength and elastic modulus initially increased in the same manner as that observed under natural conditions. Beyond 56 days, the strength decreased slightly and the elastic modulus increased rapidly as the amount of CaCO<sub>3</sub> increased. This might be due to carbonation of C–S–H gel at high CO<sub>2</sub> concentrations. This mechanism should be examined in future research.

In conclusion, the results of this study show that the commonly held notion that pozzolanic reaction is responsible for the long-term strength development of cement-treated sand is somewhat erroneous: carbonation is the main factor in the strength development of these sands. This is due to the porous structure of cement-treated sand, which permits the deeper penetration of  $CO_2$  gas.

In future research, the combined effects of carbonation and pozzolanic reaction on the long-term strength development of cement-treated soils, including clays, will be examined. In this study on cement treated sands, the effect of the pozzolanic reaction was negligible.

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