Research on durability and microscopic mechanisms of the portland slag cement stabilized soil under carbonation condition

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Abstract. In this study, physical-mechanical properties and microscopic characteristics of the slag Portland cement stabilized soil and the normal Portland cement stabilized soil after carbonization were investigated and compared through carbonization depth tests, unconfined compression tests, XRD and SEM tests. Results showed that carbonation depth of the slag Portland cement stabilized soil was lower than that of the normal Portland cement stabilized soil on each carbonization stage. Results of XRD and SEM tests showed that the normal Portland cement stabilized soil were decomposed into Cal after carbonization, which lead to loosened structure and strength retrogression.

1. Introduction
Anti-carbonation property is an important factor reflecting durability of cement stabilized soils. At home and abroad, some studies about carbonization effects on normal portland cements and portland slag cement and their mechanisms suggest that, anti-carbonation property of portland slag cement is poorer than that of normal portland cements[1][2][3], authors think that calcium content of portland slag cement is lower than that of normal portland cements, so calcium-silica ratio in the hydration product of portland slag cement is lower that of normal portland cements, thus content of calcium hydroxide in pore water of portland slag cement is lower than that of normal portland cements, under the same carbon dioxide corrosion condition, pH of portland slag cement decreases more rapidly, which accelerates decomposition of hydration products and causes reduction in concrete strength[1][3]. However, some other studies suggest that, strength decrease of portland slag cement concrete after complete carbonization is not obvious, anti-carbonization property of portland slag cement concrete is superior than that of normal portland cements[4]. For reinforcement treatment of highway subgrade, amount of cement added is less than amount of concrete added, so its anti-carbonization property should be further researched.

The main object of this study was to investigate strength characteristics and microstructure change mechanisms of hydration products of the portland slag cement stabilized soil and the normal portland cement stabilized soil under the carbon dioxide corrosion condition. The study mainly included (1) carbonation depth results of the two types of stabilized soils under the carbon dioxide corrosion condition were compared. (2) Strength change conditions of the two types of stabilized soils after complete carbonization were analyzed through unconfined compression tests, (3) Hydration mechanisms and microscopic characteristics of hydration products were analyzed through x-ray...
diffraction(XRD) and scanning electron microscope(SEM)test,(4)Anti-carbonization properties of portland slag cement stabilized soil were evaluated through the test results above.

2. Materials and methods

2.1. Materials
Kaolin was selected as the soil used for the experiment, which was purchased from a company in Zaozhuang city, natural moisture content of the soil was about 2%, specific gravity was 2.70g/cm3 and liquid limit was 30.1%, the portland slag cement used was 325# slag cement, which was manufactured by Taian cement plant. Main chemical components and content of all experimental materials were shown in table 1

| Chemical component          | CaO | SiO₂ | Al₂O₃ | SO₃ | Fe₂O₃ | MgO |
|----------------------------|-----|------|-------|-----|-------|-----|
| Kaolin                     | 0.41| 42.7 | 33.8  | 0.07| 5.13  | 0.06|
| The portland slag cement   | 31.2| 33.1 | 17.2  | 2.21| 1.05  | 11.1|
| The normal portland cement | 44.7| 27.4 | 13.1  | 3.96| 3.34  | 1.19|

2.2. Carbonation tests

2.2.1. Preparation of specimens
In this study, content of portland slag cement in portland slag cement stabilized soil was 30% of the dry soil, in order to compare, content of portland cement in normal portland cement stabilized soil was also 30% of the dry soil, moisture content was 60% of the dry soil. There were two kinds of specimen size, specimens for carbonation depth tests were test cubes with side length of 10cm, specimens for unconfined compression tests were cylinders with the size of Φ50mm*H100mm.

The prepared specimens were placed into the standard curing room (202℃, RH95%) for curing, after 28days’ curing, the specimens were used for carbonization tests.

2.2.2. Experimental method
Carbonization test method for concrete in 〈Standard for test methods of long-term performance and durability of ordinary concrete〉 was used for carbonization tests[5]. The carbonization test chamber used was CCB-70 carbonization test chamber for concrete, which manufactured by Shanghai Rongjida test instrument Co., Ltd, inner temperature of the carbonization test chamber was automatically controlled as 20℃, RH was 70 5% and CO₂ concentration was kept as 20 3%. One-dimensional carbonization method was used in the experiment, side surfaces and bottom of specimens were sealed with latex film, which made sure that CO₂ could only invade into specimens through top surface, specimens were respectively carbonized for 3 days, 7days, 14 days and 28days, 3 parallel specimens were prepared for each group, when required carbonization period of the specimens reached, latex films were removed, specimens were split along the midcourt line of the upper surface, scale mark was drawn on the profile. After that, the ethanol solution containing 1% phenolphthalein was dropped on the profile, the area where turned red was taken as the un-carbonized area, while the area with no color change was taken as the carbonized area, the distance from boundary to upper edge of the profile was taken as the carbonation depth, side surfaces of specimens might be slightly carbonized even under sealing condition, so carbonation depth on the midcourt line of the profile was taken as the carbonation depth of the specimen.

At the same time of the carbonation depth tests, 8 specimens (4 specimens per group) for unconfined compression tests with the size of Φ50mm*H100mm were placed into the carbonization test chamber for three-dimensional carbonization. Unconfined compression tests were performed when specimens were completely carbonized.
In order to identify hydration products of two types of stabilized soil after carbonization and analyze microstructure characteristics, pore distribution conditions, particle cementation degree and forms of hydration products, XRD and SEM tests were performed for the two types of stabilized soils after carbonization under standard curing conditions. XRD and SEM test specimens were sampled from inner fragments after unconfined compression tests.

Table 2. Carbonization test protocol presented in this study

| Test item                  | Related curing condition and stage                                      |
|----------------------------|------------------------------------------------------------------------|
| Carbonization depth        | Carbonization period of 3 days, 7days, 14 days                         |
| unconfined compression     | Standard curing period of 28days, 56days, carbonization period of 28days|
| strength                   |                                                                        |
| XRD                        | Standard curing period of 56 days, carbonization period of 28days      |
| SEM                        | Standard curing period of 28 days, 56days, carbonization period of 28days|

3. Analysis and discussion of test results

3.1. Carbonation depth test and mechanical test

3.1.1. Carbonization depth test
The two types of cement stabilized soil specimens were placed into the carbonization test chamber for carbonization of 3 days, 7 days, 14 days and 28 days, phenolphthalein color-developing method was used to detect carbonization depth on the profile when required carbonization period of the specimens reached [5]. The relationships between average carbonation depth and carbonation time for the two types of stabilized soil specimens were shown in Fig 1. The Figure showed that, carbonation depth of the normal portland cement stabilized soil during the entire carbonization period (28 days) was deeper than that of the portland slag cement stabilized soil, so it was intuitively shown that the portland slag cement had better anti-carbonization property.

3.1.2. Unconfined compression tests
When the two groups of specimens for unconfined compression tests (4 specimens per group, with the same charge ratio as that of carbonization depth test, the specimens were cylinders with the size of \( \Phi 50 \text{ mm} \times H100 \text{ mm} \)) were carbonized for 28 days, respectively take out 1 specimen from each group, specimens were split along the short transverse, phenolphthalein color developing method was used to detect carbonation depth, results showed that specimens were completely carbonized, the residual three specimens in each group were used for unconfined
Figure 1. Relationships between average carbonation depth and carbonation time

Compression tests, unconfined compressive strength of the two types of stabilized soils were obtained, the results were compared with that of the corresponding standard curing specimens which were cured for 56 days. Results were shown in Fig 2, results showed that, compression strength of the portland slag cement stabilized soil after complete carbonization was 450 kPa, while compression strength of the corresponding standard curing specimen was 1445 kPa, compressive strength reduced by 68.8%;

Figure 2. Unconfined compression strength comparison between completely carbonized stabilized soils and standard curing stabilized soils

Compression strength of the normal portland cement stabilized soil after complete carbonization was 230 kPa, compression strength of the corresponding standard curing specimen was 1356 kPa, compressive strength reduced by 83.0%. So the portland slag cement stabilized soil after complete carbonization had higher residual strength than that of the normal Portland cement stabilized soil.

3.2. Microcosmic test results

3.2.1. X-ray diffraction (XRD)

Results of unconfined compression tests showed that, compression strength of the two types of cement stabilized soils after carbonization had significant reduction, it might be caused by different hydration products produced between carbonized soils and standard curing soils. XRD test results further confirmed main hydration products produced after carbonization of the two types of stabilized soils, these hydration products were compared with those obtained from corresponding standard curing stabilized soils, results were shown in Fig 3.
Figure 3. The XRD spectrums of the completely carbonized stabilized soils and standard curing stabilized soils (5-70°)

XRD spectrums of the two types of completely carbonized stabilized soils showed that, calcium hydroxide (CH) was not detected, while a large number of calcium carbonate (Cal) was detected. When diffraction angle 2θ=29.0º and 2θ=43.1º, calcium carbonate (Cal) peak of the normal portland cement stabilized soil after complete carbonization was significantly more intense than that of the portland slag cement stabilized soil. This indicated that the normal portland cement stabilized soil after complete carbonization generated more calcium carbonate (Cal), the reason was that calcium oxide content in the normal portland cement was higher than that in the portland slag cement (see table 1), thus calcium ion content in pore water of the normal portland cement stabilized soil was higher than that of the Portland slag cement stabilized soil. Meanwhile, XRD spectrums of the two types of stabilized soils under standard curing condition and complete carbonization condition showed that, hydrated calcium silicate (C-S-H) was detected in all specimens, this indicated that the two types of stabilized soils after complete carbonization still contained undecomposed C-S-H, residual strength of the two types of stabilized soils after complete carbonization in Fig 2 was due to existence of undecomposed C-S-H. Fig 3 showed that: before and after carbonization, the most intense peak of ettringite (E) in the normal portland cement stabilized soil and the most intense peak of hydrotalcite (HT) in the portland slag cement had no significant variation, carbonization had no significant effect on hydration products of the two types of stabilized soils.

3.2.2. SEM test (SEM)

SEM results of the two types of cement stabilized soils after standard curing of 28 days were shown in Fig 4, Fig 4(a) was SEM results of the portland slag cement stabilized soil, Fig 4(b) was SEM results of the normal Portland cement stabilized soil, Fig 4(a) showed that C-S-H products in the portland slag cement stabilized soil under standard curing condition were mainly reticular, the structure was compact. Fig 4(b) showed that large volume product E was found in the normal Portland cement stabilized soil, this caused large pores between particles.
Results in Fig 4 showed that, hydration degree of the portland slag cement stabilized soil after standard curing of 28 days was more complete than that of the normal Portland cement stabilized soil, pores between particles were gradually filled and congealed, so the strength became higher macroscopically. Research on composite material cement slag concrete reported by Hadj-sadok [6] showed that structure compactness of the cement slag concrete was significantly increased under the water curing condition, they thought that was caused by formation of a large number of C-S-H during hydration process of the cement slag concrete. Some other literatures showed that, when aluminum oxide content in the portland slag cement was higher than 14%, 28-day compression strength was significantly increased[7], aluminum oxide content in the portland slag cement used in this study was 17.2% (See table 1).

Fig 5 was SEM results of the two types of cement stabilized soils after complete carbonization. Fig 5(a) was SEM results of the portland slag cement stabilized soil after complete carbonization, Fig 5(b) was SEM results of the normal Portland cement stabilized soil after complete carbonization. Fig 5(a) showed that a small amount of reticular C-S-H products still existed in the portland slag cement stabilized soil after carbonization, meanwhile, we observed that cubic CaO existed in the right side of the photo, as described above, 28-days hydration of the portland slag cement stabilized soil was complete, its pore compactedness was higher, so a part of C-S-H didn’t decomposed after carbonization due to not contacting with carbon dioxide, Fig 5(b) showed that, no reticular C-S-H products was found in the normal Portland cement stabilized soil, only loose white particles were found, this indicated that decalcified decomposition of the hydration product C-S-H occurred during the carbonization process of the normal Portland cement stabilized soil. The corresponding macroscopic behavior was sharp reduction of compression strength as shown in Fig 2.
4. Conclusion

4.1. Carbonization depth test showed that, carbonation depth of the portland slag cement stabilized soil was lower than that of the normal portland cement stabilized soil.

Unconfined compression tests showed that, compression strength of the two types of cement stabilized soils after carbonization was significantly reduced compared with the corresponding soils with the same charge ratio after standard curing, however, the portland slag cement stabilized soil had higher residual strength than that of the normal portland cement stabilized soil.

4.2. XRD results showed that, the hydration product C-S-H and CH in the two types of stabilized soils were decomposed into Cal after complete carbonization, which lead to loosened structure and strength retrogression.

SEM results further indicated that the portland slag cement stabilized soil before carbonization had more compact C-S-H reticular structure, which had good effects on anti-carbonization durability, so residual hydration products still existed after carbonization, which could improve strength.

4.3. All conclusions above shows that, carbonization has significant effects on the hydration products of the two types of cement stabilized soils, the macroscopical behavior is sharp reduction of compression strength, however, the portland slag cement stabilized soil has better anti-carbonization property than the normal portland cement stabilized soil.

References
[1] Bakharev T., Sanjayan J.G., Cheng Y.B., Resistance of alkali-activated slag concrete to carbonation[J]. Cement and Concrete Research, 2001, 31(9): 1277-1283.
[2] Puertas F., Palacios M., Vazquez T., Carbonation process of alkali-activated slag mortars[J]. Journal of Materials Science, 2006, 41(10): 3071-3082.
[3] Gruyaert E., Heede P.V.D., Belie N.D. Carbonation of slag concrete: Effect of the cement replacement level and curing on the carbonation coefficient – Effect of carbonation on the pore structure[J]. Cement and Concrete Composites, 2013, 35(1): 39-48.
[4] Pu Xincheng, Gan Changcheng, He Gui etal. Research on Durability of alkali activated slag concrete [J]. Concrete, 1991 (5): 13-21.
[5] PRC National Standard. GB/T 50082-2009. Standard for test methods of long-term performance and durability of ordinary concrete [S]. Beijing: Standards Press of China, 2009.
[6] Hadj-sadok A., Kenai S., Courard L., et al. Microstructure and durability of mortars modified with medium active blast furnace slag[J]. Construction and Building Materials, 2005, 25(2): 1018-1025.
[7] Barnes P, Bensted J. Structure and performance of cements[M]. CRC Press, 2002