Ca(OH)₂ Treatment of Crushed Limestone Base Course Materials for Determination of Self-Cementation Potential

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Highway base course materials composed of crushed limestone aggregates have been observed to increase in strength with time under both field and laboratory conditions. Studies have shown that this is due primarily to the movement of Ca^{2+} and CO_3^{2-} ions, which produces a natural cementation process in these materials. Testing of materials with variable silica-carbonate compositions indicated that the amount of strength developed from the carbonate cementation process is a function of the mineralogic composition of the materials, with more strength developed as calcium carbonate composition increased. Scanning electron microscopic studies suggest that this is due to differences in bonding characteristics between calcite cement–calcite particle and calcite cement–quartz particle systems. Treatment of the silica-carbonate materials with $Ca(OH)_2$ (hydrated lime) before testing enhanced strength development by furnishing Ca^{2+} ions, which carbonate to form an additional source of calcium carbonate cement. This treatment allows for a more rapid test method to determine the potential strength development in silica-carbonate materials from natural cementation processes.

The Florida Department of Transportation has investigated the strength increase observed in highways constructed with crushed limestone base course materials through both laboratory studies (1–3) and satellite road projects. The research has indicated that the strength development occurs because of a slight drying of the base course (2) and dissolution and reprecipitation of fine carbonate particles, which serve as a cementing agent within the base course (1,3).

Calcium carbonate is a very common cementing agent in natural geological materials due to its high susceptibility to dissolution and precipitation under the range of physical and chemical conditions encountered on and within the earth (4). Since highways are constructed at the earth's surface, they are subjected to fluctuating environmental conditions such as temperature and atmospheric pressure. Therefore, the engineering behavior of base courses composed of calcium carbonate materials may be influenced by cementation processes operating within them.

Cementation of the particles provides a cohesive component to the system (5,6), thereby increasing the overall strength of the soil mass. Therefore, natural cementation of particles within a highway base course could cause an increase in strength of the material with time as cementation progresses.

High-carbonate-composition base course materials have traditionally been preferred for construction of state highways in Florida. However, as sources of these materials are depleted, new sources must be found to accommodate the transportation needs of the state's rapidly expanding population. This often results in a change in mineralogical properties and performance. Materials currently obtained from the newer quarries sometimes contain abundant unconsolidated quartz sand, and several instances of deterioration have occurred in county-built roads that used the high-silica materials for the base course.

Research was conducted to determine the effects of high silica composition in these materials on the carbonate cementation process and the resulting strength development (3). From this research, a test method has been devised involving $Ca(OH)_2$ treatment of silica-carbonate materials that enables a more rapid evaluation of potential strength development from natural cementation processes.

STRENGTH TESTING METHODS AND MATERIALS

The testing program utilized Limerock Bearing Ratio (LBR) tests (7) on materials of varying quartz-calcite composition in order to determine strength changes as a function of sample composition and time. The standard LBR test method involves compacting materials into 6-in. molds at modified AASHTO compactive efforts and then soaking the compacted materials in water for 48 hr. The materials are then removed from the water and penetrated by a loading device, with an LBR value calculated as follows:

$$LBR = \frac{\text{Unit load (psi) at 0.1-in. penetration}}{800 \text{ psi}} \times 100 \qquad (1)$$

The test is performed at different water contents, and the maximum LBR value is taken. The LBR test is similar to the more commonly used California Bearing Ratio (CBR) test. An approximate correlation has been established between the two methods, with an LBR value of 100 corresponding to a CBR value of 80.

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Sand Mixes

Quartz and calcite sands were mixed in various proportions, resulting in compositional quartz-to-calcite ratios of 0:100, 25:75, 40:60, 50:50, 60:40, 75:25, and 100:0. The various mixes were compacted into LBR molds at maximum Modified Proctor densities and continuously soaked in water at room temperature (70° ± 2°F) for time intervals of 2, 7, 14, 30, and 60 days before testing. Continuous soaking of the samples was performed, because a previous study (*1*) showed that this method is more efficient for producing carbonate cementation in the laboratory than using wetting and drying cycles.

Figure 1 shows the LBR values for 7-, 14-, 30-, and 60-day soaking periods, relative to the standard 2-day soak, for the various sand mix compositions. LBR values for the extended soaking periods are plotted as percentage increases over the 2-day reference LBR for each compositional mix. The graph illustrates the differences in strength development as composition varied. Low-carbonate sands (0 and 25 percent calcite) show no strength increase up to 60 days soaking, while higher carbonate sands (40 to 100 percent calcite) showed strength increases, with more strength developed as carbonate content increased.

Maximum increase was obtained after 14 days soaking, with no additional strength developed for 30- and 60-day soaking periods. This may be related to the small amount (less than 2 percent) of fine-grained material (passing Number 200 sieve) in the carbonate sand. Dissolution of small carbonate particles is likely to be more efficient than coarser particles due to higher surface area available in fine-grained materials. It is possible that the fine carbonate particles have been "used up" in the cementation process after 14 days and that the coarser particles are not providing cementing material as efficiently. It is suspected that coarser carbonate particles would provide cementing material over longer periods of time, but at a slower rate due to less available surface area for dissolution and the smaller amount of water held by large particle contacts.

Cemented Coquina

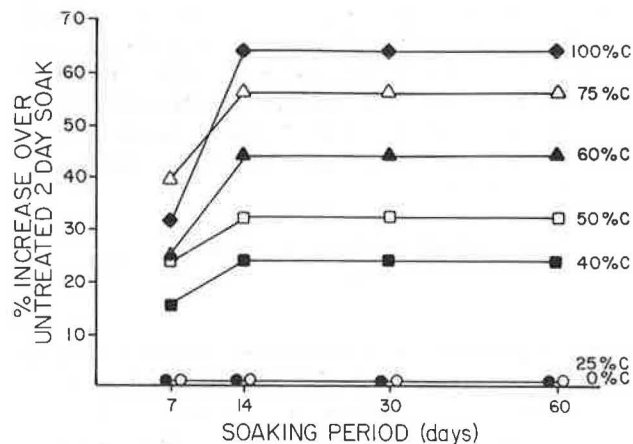Cemented coquina base course materials mined from the Anastasia Formation on the east coast of Florida were also compacted, continuously soaked, and tested to compare with sand mix data. Compositional variation was more limited in these materials, with quartz-to-calcite ratios of 45:55, 55:45, and 65:35 used for testing. Soaking periods of 2, 7, 14, and 30 days were used, with the 60-day soaking periods omitted because of a limited amount of sample material.

LBR data for soaked and tested cemented coquina materials also indicate differential strength development as composition varied. Figure 2 shows percentage increase in strength of each composition for soaking periods of 7, 14, and 30 days relative to the standard 2-day soak LBR value. More strength was developed in the cemented coquina materials as carbonate content increased, as was the case for the quartz-calcite sand mixes. However, differences in the pattern of strength development can be seen when comparing the two materials. Cemented coquina materials continued to increase in strength up to 30 days soaking, while quartz:calcite sand mixes did not increase after soaking 14 days. This is thought to be due to slightly more carbonate fines (passing Number 200 sieve) occurring in the cemented coquina materials than in the sand mixes.

Ca(OH)₂ Treatment

Another objective of the research was to develop a test method for prediction of potential strength development in silica-carbonate materials. Previous work (*1*) using NaCl and CO_2 treatments showed that these methods did not significantly increase cementation in the laboratory over that derived from soaking in plain water. Therefore, another treatment method was investigated by mixing 1 percent $Ca(OH)_2$ (hydrated lime) to the dry materials before compacting and soaking. This was done in an attempt to enhance carbonate cementation and, therefore, strength development. Carbonation of additional Ca^{2+} ions furnished by the $Ca(OH)_2$ should provide an additional source of calcite cement, thereby enhancing cementation effects.

Figure 3 shows the LBR values for 2-, 7-, 14-, 30-, and 60-day soaking periods on the quartz-calcite sand mixes treated with 1 percent $Ca(OH)_2$ before compacting, compared to the standard 2-day soak on untreated sand mixes. The graph illustrates the effects of an additional source of carbonate cement on strength increase with time and compositional variation of the mixes. It indicates that $Ca(OH)_2$ treatment significantly

FIGURE 1 Strength increase of untreated quartz-calcite sand mixes.

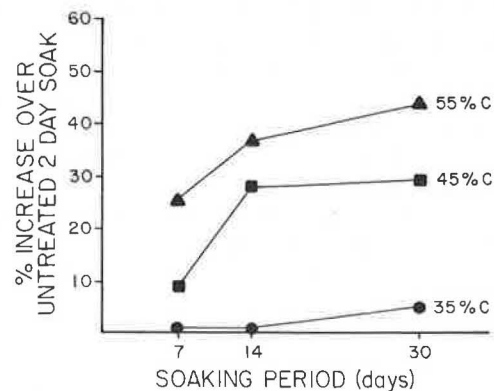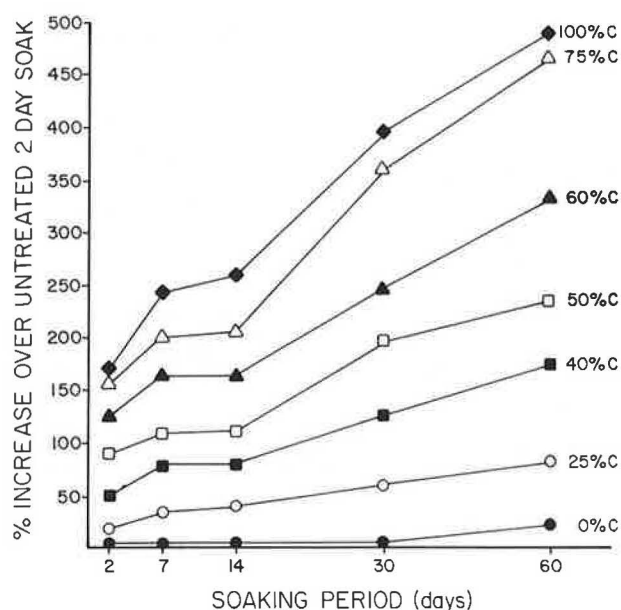**FIGURE 2 Strength increase of untreated cemented coquina materials.**

FIGURE 3 Strength increase of quartz-calcite sand mixes treated with 1 percent Ca(OH)$_2$.

FIGURE 4 Strength increase of cemented coquina materials treated with 1 percent Ca(OH)$_2$.

enhanced strength development and variational patterns observed in LBR data for the untreated sand mixes. Very large increases (more than 450 percent) in strength occurred for high-carbonate sands, with strength developed continuously up to 60 days. Less strength was developed in the sand mixes as carbonate content decreased. Quartz sands developed no additional strength after 30 days soaking and only a slight increase (30 percent) after 60 days soaking.

Treatment of the cemented coquina materials with 1 percent Ca(OH)$_2$ also resulted in enhanced cementation effects. Figure 4 shows strength increase for each composition after soaking periods of 2, 7, 14, and 30 days, relative to the standard untreated 2-day soak LBR values. More strength was developed when cemented coquina materials were treated with Ca(OH)$_2$, with the trend of more strength developed with increasing carbonate composition persisting in these experiments.
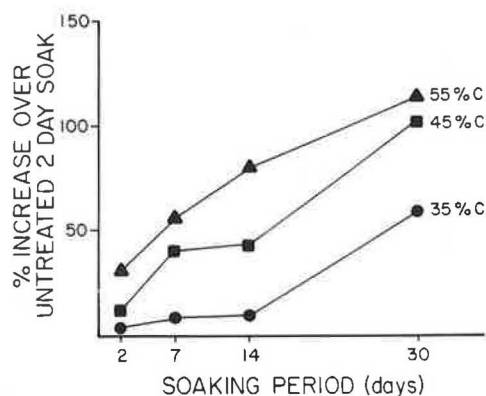
SEM EXAMINATIONS

Scanning electron microscope (SEM) examinations were conducted on tested LBR materials to aid in explanation of strength testing data by observing cementation characteristics. Samples of the LBR materials were removed from the molds after soaking and testing, dried, and prepared for SEM analysis.

The micrographs presented in Figures 5 and 6 show the different characteristics between carbonate cementation of quartz and calcite particles in the quartz-calcite sand mixes. In Figure 5, the carbonate cement (C$_c$) has not bonded to the quartz particles (Q), as evidenced by the clean quartz particle surfaces and the large void separating the particles and cement. In contrast, Figure 6 shows a calcite particle (C$_p$) which seems to be well bonded to the carbonate cement (C$_c$). Carbonate cementing material has adhered to the particle surface during fracture, and the cement is in good contact around the calcite particle edges.
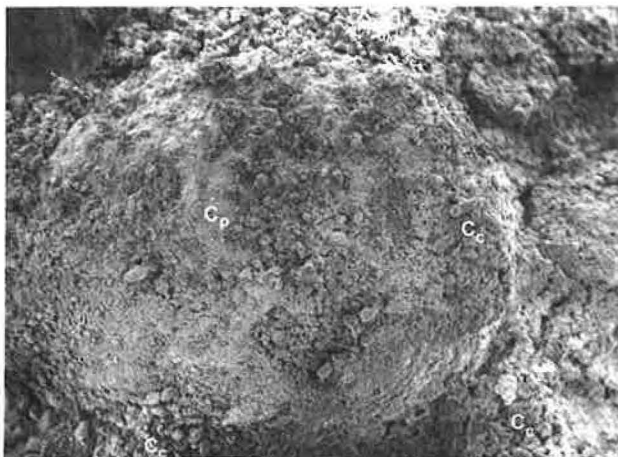

FIGURE 5 Sand mix, 75 percent carbonates, 1 percent Ca(OH)$_2$, 14-day soak (303×).

FIGURE 6 Sand mix, 100 percent carbonates, 1 percent Ca(OH)$_2$, 14-day soak (141×).

Higher magnification micrographs of cement-particle contacts for quartz and calcite particles are shown in Figures 7 and 8. The carbonate cement (C) and quartz particle (Q) are separated by a void in Figure 7. Note the arrows where small carbonate particles have been cemented together. Figure 8 shows carbonate cement (C_c) bonded to a large carbonate particle (C_p).

Similar cementation characteristics were observed in examination of cemented coquina LBR materials after soaking and testing. In Figure 9, calcite particles (C) are well cemented, while quartz particles (Q) exhibit clean particle surfaces, free of carbonate cement.

Naturally occurring calcite-cemented quartz sandstones from the Badlands of South Dakota were also examined to observe cement-particle contacts of materials in more advanced stages of cementation. Figure 10 is a micrograph of a fractured surface of the material showing the quartz particles (Q) in a calcite cement matrix (C). The cement has pulled away, leaving clean quartz particle surfaces, and large voids exist at the cement-particle interface.
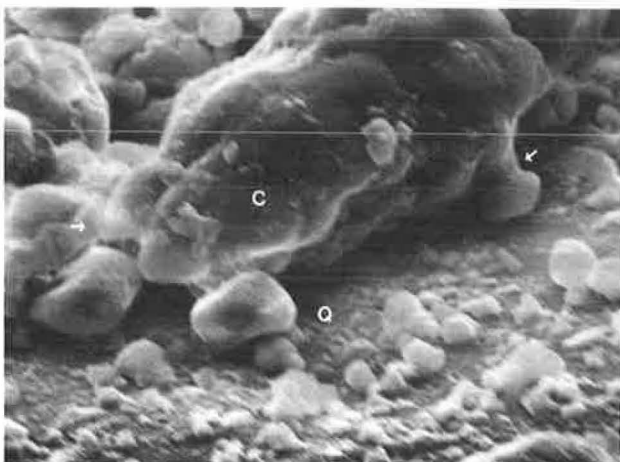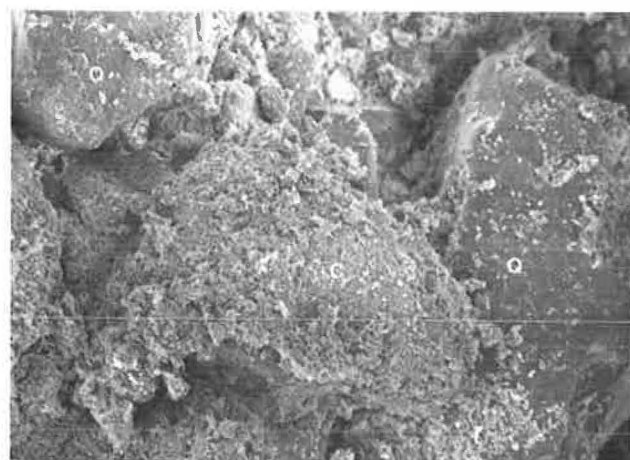

FIGURE 9   Cemented coquina, 45 percent carbonates, 1 percent $Ca(OH)_2$, 30-day soak (111×).
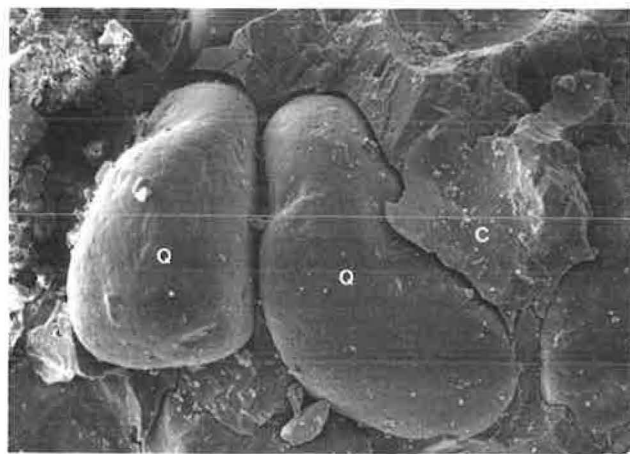
FIGURE 10   Calcite cemented quartz sandstone, Badlands, South Dakota (111×).

FIGURE 7   Sand mix, 25 percent carbonates, 7-day soak (1776×).

FIGURE 8   Sand mix, 100 percent carbonates, 1 percent $Ca(OH)_2$, 30-day soak (3552×).

DISCUSSION OF RESULTS

The high susceptibility of calcium carbonate to dissolution and reprecipitation under normal physical and chemical conditions operating at the earth's surface was illustrated in the LBR testing program by the strength increases occurring in the laboratory samples after extended soaking in water. Because the samples remained at constant temperature (70° ± 2°F) during soaking, the cementation process operating within the samples is thought to be controlled by variations in atmospheric pressure. This would cause changes in the CO_2 content of the pore waters, which is the main controlling factor over carbonate dissolution and precipitation (8,9).

Differential strength gains as a function of mineralogical composition in the tested LBR materials, along with microscopic observations of the different bonding characteristics of carbonate cement to calcite and quartz particles, support the ideas on "compatible" and "incompatible" cements as put forth by Dapples (10) and others (3,11,12). Carbonate cementation of carbonate particles (compatible system) exhibited

much better cement-particle bonding than carbonate cementation of quartz particles (incompatible system). This was evidenced in the LBR testing program by the larger strength increases for high-carbonate samples as compared to high-silica samples.

Microscopic examinations supported LBR testing data by illustrating the different cement bonding characteristics as a function of cement-particle composition. Carbonate cement appears to nucleate directly onto calcite particle surfaces, creating a strong cement-particle bond. In the carbonate cement–quartz particle system, the cement seems to precipitate from solution into pore spaces without nucleation or bonding to the quartz particle surfaces. Examination of fractured surfaces of these materials illustrated this, with quartz particles exhibiting clean particle surfaces free of adhering cement, and voids existing between cement and particles at cement-particle contacts. This was in contrast to carbonate cementation of calcite particles. These particles appear to be well bonded to the cement, as evidenced by cement-covered particle surfaces and absence of voids at cement-particle contacts.

Treatment of both quartz-calcite sand mixes and cemented coquina materials with 1 percent $Ca(OH)_2$ before compacting and soaking the samples proved to be very effective in providing an additional source of carbonate cementing material, resulting in larger and more rapid strength increases than in untreated materials. These experiments also enhanced the effect of cement-particle composition, with more strength developed as carbonate composition of the samples increased. As discussed previously, the $Ca(OH)_2$ provides an additional source of Ca^{2+} ions, which form carbonate cementing material through carbonation of the Ca^{2+} ions during soaking. Calcium hydroxide has a solution pH of 12.4 at 25°C (*13*), which would increase CO_3^{2-} species of dissolved carbonate in the pore waters of the samples (*14*). The Ca^{2+} ions and CO_3^{2-} ions combine and precipitate as calcium carbonate cement, thus increasing the strength of the soaked materials.

The large strength increases obtained from $Ca(OH)_2$ treatment of high-carbonate samples suggests that this procedure may be useful for strength improvement of high-carbonate foundation materials and as an accelerated testing method for determination of potential self-cementation of silica-carbonate foundation materials. A suggested method of test would be as follows:

1. Mix 1 percent $Ca(OH)_2$ to dry materials before compaction into LBR (or CBR) molds at optimum water content.

2. Soak the compacted sample in water for 2 to 7 days.

3. Test the sample and compare to the standard 2-day soak LBR (or CBR) value for the untreated materials to determine a percentage increase in strength.

The strength developed in the treated sample should be indicative of the strength that would be developed in untreated materials soaked for 30 to 60 days. This treatment would greatly reduce the required soaking time, allowing for a more rapid test method for determination of potential strength development.

One problem with the test is that the soaking interval required for treated samples may vary among different types of materials because of differences in particle size and distribution. This may affect the amount of strength developed as a result of differences in compacted density and the amount of carbonate fines between various materials. Therefore, initial trial tests comparing treated and untreated materials may be required on a case-by-case basis for different types of materials in order to develop empirical relationships. Once a strength relationship has been developed for a particular type of material, the $Ca(OH)_2$ treatment method could be used routinely, thus avoiding the extensive soaking periods required to determine strength development in untreated silica-carbonate materials.

CONCLUSIONS

1. Continuous laboratory soaking of compacted quartz-calcite sand mixes and cemented coquina base course materials in plain water resulted in strength increases with time, except for samples of very high silica composition.

2. Higher strengths were developed in proportion to increasing calcium carbonate composition for both quartz-calcite sand mixes and cemented coquina base course materials.

3. Treatment of quartz-calcite sand mixes and cemented coquina base course materials with the addition of 1 percent $Ca(OH)_2$ before compacting and soaking proved to be an effective method of enhancing cementation effects on strength development by furnishing a more soluble source of Ca^{2+} ions, which form calcium carbonate cement through carbonation of the Ca^{2+} ions.

4. Treatment of high-carbonate materials with 1 percent $Ca(OH)_2$ greatly increased the rate and amount of their strength development, while treatment of high-silica materials resulted in little or no strength increase. This suggests that $Ca(OH)_2$ treatment might be effectively used to improve strength of high carbonate composition materials and as a testing method to provide a more rapid determination of the self-cementation potential of silica-carbonate soils.

5. Scanning electron microscopic examinations of the soaked and tested materials showed that the observed strength gain variations were due to the different cement-particle bonding properties of carbonate cement–calcite particle and carbonate cement–quartz particle systems. Strength increases were more pronounced in high-carbonate materials because of good bonding of carbonate cement to calcite particles. In contrast, high-silica materials developed little or no strength increase because of a lack of bonding between carbonate cement and quartz particles.

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