Strength Developed from Carbonate Cementation in Silica-Carbonate Base Course Materials

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Strength increases resulting from carbonate cementation in compacted sands and cemented coquina highway base course materials of variable quartz-calcite composition were investigated through the use of limerock-bearing-ratio (LBR) testing. Quartz and calcite sands were mixed in various proportions, compacted into LBR molds, soaked for time periods from 2 days up to 60 days, and tested to determine strength increase with time. For comparison, cemented coquina highway base course materials of variable quartz-calcite composition were also compacted, soaked, and tested. In addition, duplicate sets of specimens were tested that had 1 percent $Ca(OH)_2$ (hydrated lime) mixed with the dry materials before compacting and soaking. This was done to provide a source of Ca^{2+} ions for formation of additional calcium carbonate cement. Results of the LBR testing program showed that more strength developed as the calcium carbonate composition of both the quartz-calcite sand mixes and the cemented coquina samples increased. Addition of $Ca(OH)_2$ to the samples enhanced carbonate cementation effects, with large strength increases occurring in high-carbonate materials. Scanning electron microscopic examinations of the tested LBR materials, base course materials cored from in-service highways, and naturally occurring calcite-cemented quartz sandstones and limestones revealed different bonding characteristics between calcite cement-calcite particle and calcite cement-quartz particle systems, which would explain the strength development patterns observed in LBR testing.

Highway base courses in Florida constructed with crushed-limestone materials have been observed to increase in strength with time after construction. The Florida Department of Transportation (FDOT) has conducted studies, both in the laboratory (*1, 2*) and on satellite road projects, investigating the strength increase of high-carbonate-composition (60 to 100 percent) base course materials. The research indicated that the strength increases were due to a slight drying of the base course (*2*) and to dissolution and reprecipitation of fine carbonate particles, which serve as a cementing agent within the base course (*1*).

High-carbonate-composition base course materials have traditionally been preferred for construction of state highways in Florida. However, as the sources of these materials are depleted, new sources must be found to accommodate the transportation needs of the state's rapidly expanding population. Materials obtained from the newer quarries often have a different mineralogical composition because of the great variability of geologic conditions affecting their deposition.

This has been the case with cemented coquina base course materials in Florida (*3*). Currently mined cemented coquina contains abundant quartz sand, often resulting in carbonate compositions below the 50 percent required by FDOT. The quartz occurs in two forms. Some is incorporated into cemented limestone rock, but most exists as unconsolidated quartz sand. Field observations in operating quarries indicated that the quartz sand occurs in layers of variable thickness interbedded within the cemented limestone rock material. The rock and quartz sand become mixed during mining and processing operations, resulting in a final product that often has a high silica composition.

Several instances of deterioration have occurred in county-built roads when low-carbonate materials were used for the base course. Therefore, research is being conducted to determine the effects of high silica composition on the engineering behavior of highway base courses in Florida. This project has focused on the role of quartz particles in the carbonate cementation process and the resulting strength development.

PARTICLE CEMENTATION

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

The strength behavior of sands and gravels is considered to be purely frictional in nature, and therefore they are termed "cohesionless" materials. Cementation of the particles provides a cohesive component to the system (*5, 6*),

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thereby increasing the overall strength of the soil mass. Therefore, natural cementation of particles, such as carbonate cementation in limestones, within a highway base course could cause an increase in strength of the material with time as cementation progresses.

STRENGTH-TESTING METHODS

The objective of this research has been to evaluate strength development with time due to carbonate cementation in highway base course materials consisting primarily of quartz and calcite particles. The testing program involved the use of limerock-bearing-ratio (LBR) tests (*7*) on materials of varying quartz-calcite composition in order to determine strength changes as a function of composition and time.

The standard LBR test method involves compacting the material into 6-in. molds at modified AASHTO compactive efforts and soaking the compacted material in water for 48 hr. The material is then removed from the water and penetrated by a loading device with an LBR value calculated as follows:

$$\text{LBR} = \frac{\text{unit load (psi) at 0.1-in. penetration}}{\text{800 (psi) (value for standard limerock)}} \times 100 \qquad (1)$$

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 a LBR value of 100 corresponding to a CBR value of 80.

Sand Mixes

Quartz and calcite sands were mixed in various proportions, resulting in percent-quartz-to-percent-calcite compositional 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°) for time intervals of 2, 7, 14, 30, and 60 days before testing.

In Figure 1, LBR values for 7-, 14-, 30-, and 60-day soaking periods for sand mixes are shown relative to the standard 2-day-soak LBR values for the various mix compositions. LBR values for the extended soaking periods are plotted as percent increase over the 2-day reference LBR for each compositional mix. Figure 1 shows the differences in strength development as composition varies. Low-carbonate sands (0 and 25 percent) show no strength increase up to 60 days' soaking, whereas higher-carbonate sands (40 to 100 percent) showed strength increases, with more strength developing as carbonate content increases. Maximum increase was obtained after 14 days' soaking, with no additional strength developing for 30- and 60-day soaking periods. This may be related to the small amount

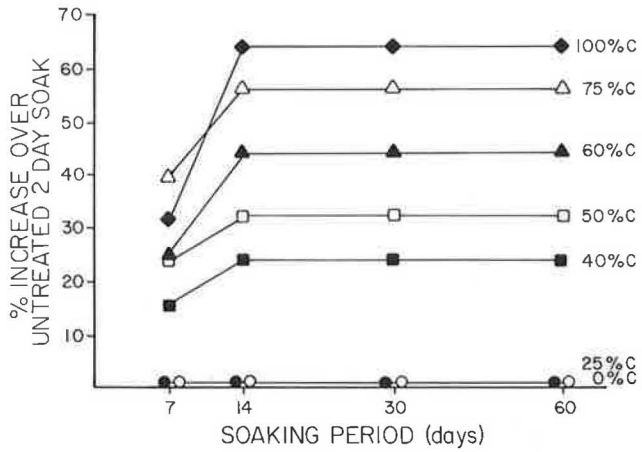

FIGURE 1 Strength development in quartz-calcite sand mixes.

(<2 percent) of fine-grained material (< No. 200 sieve) in the carbonate sand. Dissolution is likely to be more efficient for small carbonate particles than for coarser particles because of the 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. However, it is suspected that over longer periods of time, cementing material would be provided by coarser carbonate particles but at a slower rate because there is less available surface area for dissolution and a smaller amount of water held by large particle contacts.

Cemented Coquina

Cemented coquina base course materials were also compacted, soaked, and tested to be compared 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 were 2, 7, 14, and 30 days; the 60-day soaking periods were 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 varies.

Figure 2 shows percent increase in strength of each composition for soaking periods of 7, 14, and 30 days compared with the standard 2-day-soak LBR value. More strength 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 the two materials are compared. Cemented coquina materials continued to increase in strength up to 30 days' soaking, whereas quartz-calcite sand mix strength did not increase after soaking 14 days. This is thought to be due to slightly more carbonate fines (< No. 200 sieve) occurring in the cemented coquina materials than in the sand mixes.

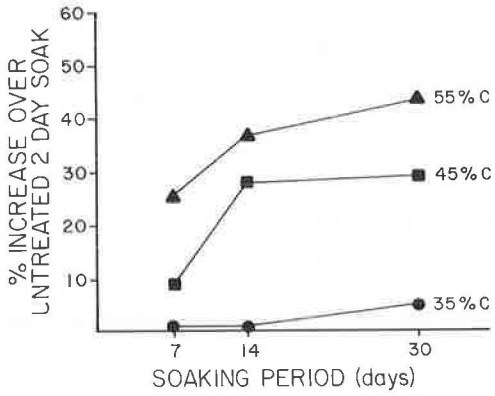

FIGURE 2 Strength development in cemented coquina materials.

$Ca(OH)_2$ Treatment

Another portion of the LBR testing program involved the addition of 1 percent $Ca(OH)_2$ (hydrated lime) to the dry materials before compaction for each sample composition and soaking period. 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. In Figure 3, LBR values after 2-, 7-, 14-, 30-, and 60-day soaking periods for sand mixes treated with 1 percent $Ca(OH)_2$ before compaction are compared relative to the standard 2-day soak for untreated sand mixes. The effects are shown of an additional source of carbonate cement on strength increase with time and compositional variation of the mixes. It may be seen that $Ca(OH)_2$ treatment significantly enhanced strength development and variational patterns observed in LBR data for the untreated sand mixes. Very large increases (>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 contents decreased. Quartz sands developed no additional strength after 30 days' soaking and only a slight increase (30 percent) after 60 days' soaking.

Treatment of cemented coquina materials with $Ca(OH)_2$ also resulted in enhanced cementation effects as shown in Figure 4. Strength increases for each composition after soaking periods of 2, 7, 14, and 30 days relative to the standard untreated 2-day-soak LBR values have been plotted. More strength was developed when cemented coquina materials were treated with $Ca(OH)_2$; the trend of more strength developing with increasing carbonate composition persisted in these experiments.

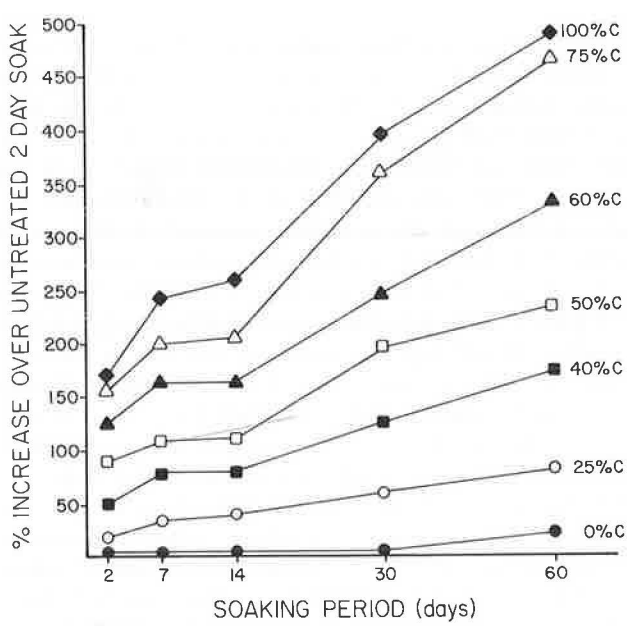

FIGURE 3 Strength development in quartz-calcite sand mixes treated with 1 percent $Ca(OH)_2$.

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. In addition, cemented coquina base course materials cored from in-service highways and some naturally occurring calcite-cemented quartz sandstones and limestones were also examined with the SEM to further investigate cementation characteristics.

LBR Materials

Samples of the LBR materials were removed from the molds after soaking and testing, dried, and prepared for SEM examination. The micrographs presented are images of broken surfaces of the cemented materials. Figures 5 and 6 show the different characteristics between carbonate cementation of quartz and calcite particles in the sand mixes. In Figure 5, the carbonate cement (C_c) has not bonded to the quartz particles (Q), as shown by the clean

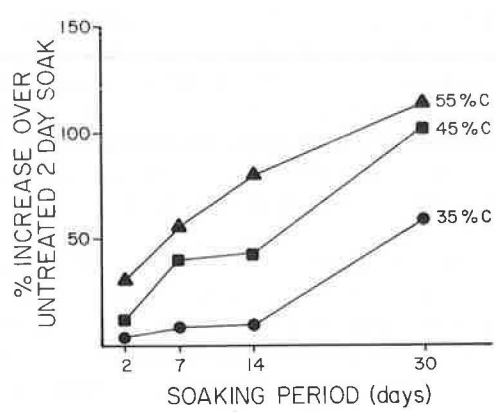

FIGURE 4 Strength development in cemented coquina materials treated with 1 percent $Ca(OH)_2$.

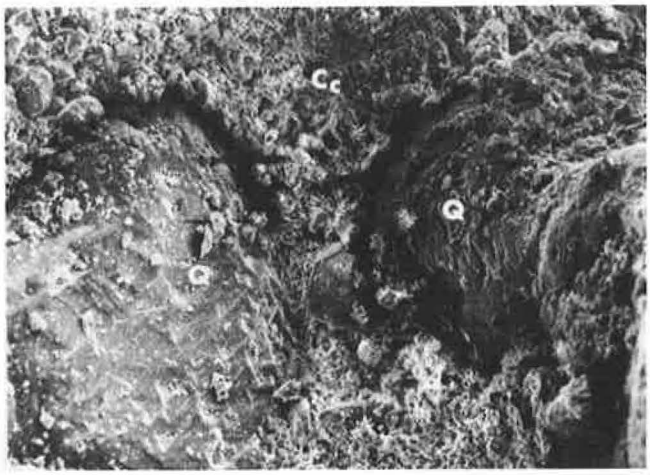

FIGURE 5 Sand mix, 75 percent carbonates, 1 percent $Ca(OH)_2$, 14-day soak (×308).

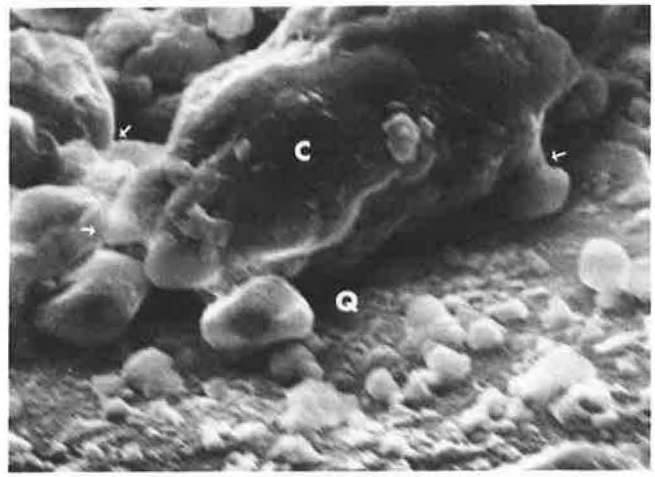

FIGURE 7 Sand mix, 25 percent carbonates, 7-day soak (×1,800).

quartz particle surfaces and the large void separating the particles and the cement. In contrast, Figure 6 shows a calcite particle (C_p) that 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, unlike the cement in Figure 5, which is separated from the quartz particles by a large void.

Higher-magnification micrographs of cement-particle contact for quartz and calcite 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 indicating 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

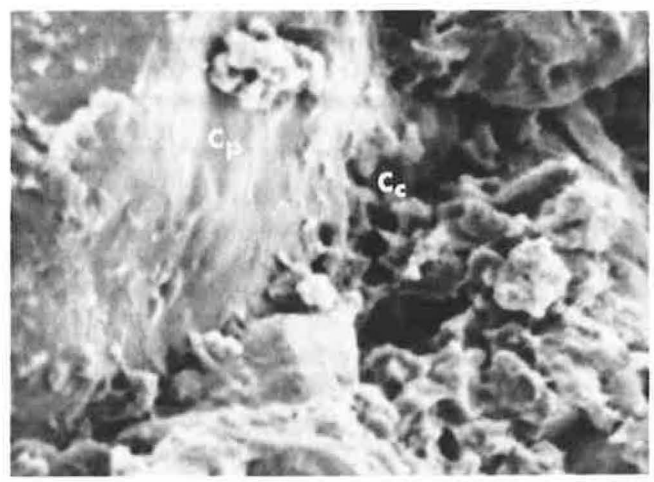

FIGURE 8 Sand mix, 100 percent carbonates, 1 percent $Ca(OH)_2$, 30-day soak (×2,400).

FIGURE 6 Sand mix, 100 percent carbonates, 1 percent $Ca(OH)_2$, 14-day soak (×143).

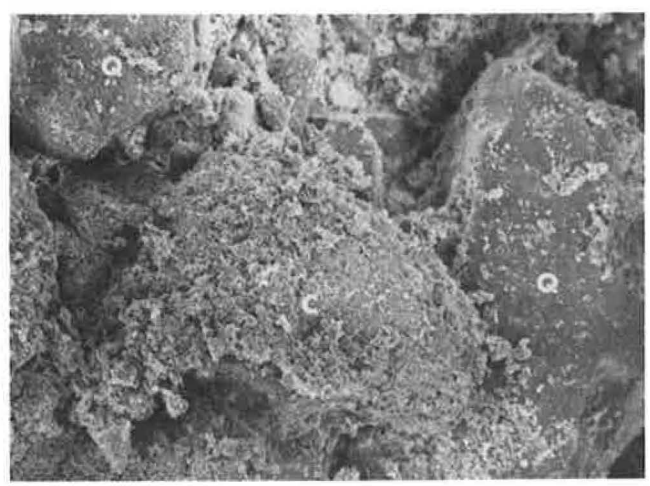

FIGURE 9 Cemented coquina, 45 percent carbonates, 1 percent $Ca(OH)_2$, 30-day soak (×113).

FIGURE 10 Cored cemented coquina highway base course, 59 percent carbonates (×218).

well cemented, whereas quartz particles (Q) exhibit clean particle surfaces, free of carbonate cement.

Highway Cores

Cemented coquina base course materials of variable carbonate composition (35 to 60 percent) were cored from highways in service from 3 to 5 years. These materials were examined with the SEM to provide field evidence of cementation for comparison with observations from laboratory experiments.

Cementation characteristics observed in these materials were very similar to those from soaked LBR materials. Figure 10 shows carbonate particles that have been well cemented in a 50 percent carbonate highway core sample. In Figure 11, carbonate particles (C) have been well cemented, whereas quartz particles (Q) exhibit clean particle surfaces. Small amounts of cement can be seen filling some pore spaces around the quartz particles, but close examination reveals voids at cement-particle contact.

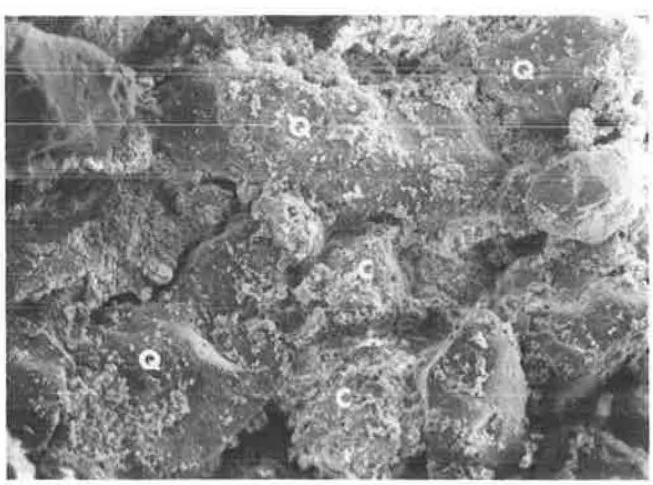

FIGURE 11 Cored cemented coquina highway base course, 37 percent carbonates (×75).

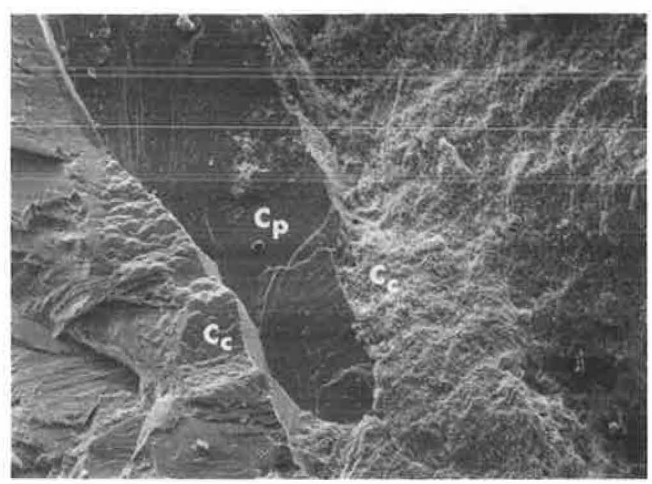

FIGURE 12 Calcite-cemented quartz sandstone, Badlands, South Dakota (×113).

Sandstones and Limestones

Naturally occurring calcite-cemented quartz sandstones from the Badlands of South Dakota and limestones from the Anastasia formation in Florida were examined to observe cement-particle contact of some materials in more advanced stages of cementation. The South Dakota sandstones are unique in that the calcite cement has grown as large scalenohedral crystals, incorporating quartz particles into the crystal structure as it developed. Figure 12 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 cement-particle contact.

In contrast to the lack of carbonate cement-quartz particle bonding observed in the sandstone, Figure 13 shows a carbonate particle (C_p) surrounded by carbonate cement (C_c) in the Florida limestone. Note that the fracture has occurred through the carbonate particle rather than around it, as was the case for the quartz particles in Figure 12. The cement appears to be bonded to the carbonate par-

FIGURE 13 Cemented coquina, Anastasia formation, Florida (×94).

ticle, as shown by the lack of any voids at the cement-particle contact.

DISCUSSION

The high susceptibility of calcium carbonate to dissolution and reprecipitation under normal physical and chemical conditions operating at the earth's surface was demonstrated 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°) 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 water, which is the main controlling factor over carbonate dissolution and precipitation (*8, 9*). Field evidence of the ability of calcium carbonate to form cementing material under surface conditions was obtained from microscopic examinations of in-service cemented coquina highway base course materials.

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 idea of "compatible" and "incompatible" cements as put forth by Dapples (*10*) and others (*11–13*). Carbonate cementation of carbonate particles (compatible system) exhibited much better cement-particle bonding than carbonate cementation of quartz particles (incompatible system). This was revealed in the LBR testing program by the higher strength increases for high-carbonate samples as compared with high-silica samples.

Microscopic examinations supported LBR testing data by revealing 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 compared with the carbonate cement-quartz particle system, in which the cement seems to precipitate from solution into pore spaces without nucleation and bonding to the quartz particle surfaces. Examination of the fractured surfaces of the various materials demonstrated this well; quartz particles exhibited clean surfaces, free of adhering cement, and voids existed between cement and particles at cement-particle contact. This was in contrast to carbonate cementation of calcite particles, which appear to be well bonded to the cement as shown by cement-covered particle surfaces and absence of voids at cement-particle contact.

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 calcium carbonate cementing material, which resulted in larger and more rapid strength increases than in untreated materials. These experiments also enhanced the effects of cement-particle composition, with more strength developing 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 in the pore water during soaking. Calcium hydroxide has a solution pH of 12.4 at 25°C (*14*), which would increase the CO_3^{2-} species of dissolved carbonate in the pore water of the sand mixes (*15*). The Ca^{2+} ions and CO_3^{2-} 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 suggest that this procedure may be useful for strength improvement of high-carbonate foundation materials and as a testing method for determination of self-cementation potential of foundation materials. A suggested method of test would be as follows:

1. Mix 1 percent $Ca(OH)_2$ with 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 with the standard 2-day-soak LBR (or CBR) value for the untreated materials to determine a percent 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. However, one problem with the test is that the soaking interval required for the treated samples may vary among different materials because of differences in particle size and distribution. This may affect the amount of strength developed because of differences in compacted density between various materials.

The results of the research project indicate that the strength of cemented coquina base course materials will be affected by their mineralogical composition. High-carbonate cemented coquina materials should cement much better than high-silica cemented coquina materials, providing a stronger and more stable base course from increased cohesion provided by strong bonding of precipitated carbonate cement to carbonate particles. High-silica cemented coquina materials would be less stable because of several factors. Lack of bonding between carbonate cement and quartz particles would result in decreased strength and stability derived from carbonate cement precipitating in the base course. In addition, less carbonate cementing material would be produced in the high-silica materials because the base course serves as its own source of cement; that is, fewer carbonate particles would be available for dissolution to provide precipitated carbonate cement. Silica cement would not be expected to precipitate in these materials because quartz particles are very stable under the earth's surface conditions (*15*), thus prohibiting a source of dissolved silica for precipitation.

Because large amounts of quartz sand are present in the high-silica materials, larger carbonate aggregate particles may effectively "float" in the sandy material. This would reduce material stability by decreasing the number of large aggregate contacts. In addition, the large areas of quartz grains are not likely to cement together because of the lack

of carbonate cement-quartz particle bonding and reduced supply of carbonate cement, as discussed earlier. High-carbonate cemented coquina materials have less quartz sand, resulting in more large aggregate contacts. Quartz grains "floating" in the matrix of carbonate materials would tend to be bound by the carbonate materials, thereby preventing their movement.

CONCLUSIONS

1. Laboratory soaking of compacted quartz-calcite sand mixes and cemented coquina base course materials continuously in plain water resulted in strength increases with time except for samples with high silica composition.
2. Higher strengths were developed in proportion to increasing 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 carbonate cement through carbonation of Ca^{2+} ions.
4. Treatment of high-carbonate materials with 1 percent $Ca(OH)_2$ greatly increased their strength after extended soaking periods (30 to 60 days), whereas 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 determine the self-cementation potential of quartz-carbonate soils.
5. SEM examinations of soaked quartz-calcite sand mixes and cemented coquina base course materials, with and without $Ca(OH)_2$ treatment, 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 because of a lack of bonding between carbonate cement and quartz particles.
6. Field evidence of cementation characteristics observed in laboratory samples was obtained from microscopic examinations of naturally occurring calcite-cemented sandstones and cemented coquina base course materials cored from in-service highways. These materials provided good field correlation of laboratory results, with similar cement-particle bonding characteristics being observed.

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