Improved Characteristics in Sulfate Soils Treated with Barium Compounds Before Lime Stabilization

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Some sulfate-bearing soils stabilized with calcium hydroxide (lime) have developed heave over periods of time. This heave is thought to result from reactions of soluble sulfates, calcium hydroxide, and free aluminum in the soil or groundwater, or both, to form ettringite ($3\ CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 32H_2O$), a highly water-expansive mineral. Laboratory testing, using the California bearing ratio (CBR) method, has indicated increased bearing strength values and decreased swell when barium hydroxide or barium chloride was added to sulfate-rich soils before lime application. A California soil containing sodium sulfate had increased strength values when either barium compound was used with lime as compared with specimens with lime only. A barium hydroxide treatment followed by lime application to a Texas soil containing sodium sulfate was successful, showing increased CBR values and a decrease in percent swell. Potential volume change tests were conducted on a Colorado soil and the California and Texas soils using lime only and lime added to soils treated with barium hydroxide or barium chloride. The barium hydroxide plus lime treatment showed a marked decrease in swell pressure when compared with lime-only treatment. The mix of barium chloride plus lime decreased in swell pressure, but not as significantly as the mix of barium hydroxide plus lime. The presence of ettringite in the treated soils was determined using scanning electron microscopy. Ettringite formation was not detected in the California or Colorado soils for either combination of barium hydroxide or barium chloride plus lime. The Texas soil contained an abundance of ettringite in the mix of barium chloride plus lime, and it was present, but sparse, in the mix of barium hydroxide plus lime.

Soluble sulfates react with calcium hydroxide and free aluminum to form ettringite ($3CaO \cdot Al_2O_3 \cdot 3CaSo_4 \cdot 32H_2O$) (*1*). Expansion caused by the growth of ettringite in sulfate soils treated with calcium hydroxide (lime) may produce severe problems in the construction and performance of pavement foundation systems (*2*). The amount and type of sulfates present, sodium sulfate or calcium sulfate, and the amount and type of clay material are properties believed to play key roles in the poststabilization expansion developed over time in lime-treated sulfate soils. The formation of ettringite also is responsible for the deterioration of concrete by sulfate attack (*3,4*).

The sulfate content is clearly the most important property to consider when evaluating such soils for construction purposes. The quantity of sulfates present generally dictates the extent to which ettringite will form. Simply, the greater the content of soluble sulfates in a soil, the greater the potential for the growth of ettringite.

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That sodium sulfate and calcium sulfate (gypsum) have different solubilities suggests that the form of sulfates present in a soil plays an active role in the degree to which ettringite will form. Gypsum is approximately 100 times less soluble than other sulfate minerals normally found in soils (*5*). Calcium and sodium sulfate commonly form evaporite minerals in arid to semiarid regions, because of little or no leaching, crystallizing when their concentrations exceed their solubility limits. Gypsum is the most common sulfate mineral found in soils because of its relatively low solubility.

The percentage and type of clay minerals present in a soil generally dictate the amount of lime required for stabilization. Soils with a high clay content or an initial high plasticity index (PI) and swell require greater amounts of lime to effectively reduce the plasticity, eliminate the swell, and stabilize the soil (*6*). The addition of lime to a sulfate-bearing soil provides calcium, which reacts with the sulfates to form gypsum, which may react with aluminum to form ettringite (*7*).

The type or types of clay present also are believed to be major factors in determining the strength and swell potential in lime stabilization (*8*). Smectites are three-layered clays that are highly expansive. Thus, a soil containing large amounts of smectite will require more lime to become stabilized (*9*). However, the two-layered structure of kaolinite may allow it to be a greater source of aluminum needed for the formation of ettringite in sulfate-bearing soils.

Tests have been conducted to determine if reactions that form ettringite could be minimized in sulfate-bearing soils by pretreating them with barium hydroxide or barium chloride in an effort to reduce the soluble sulfates before lime stabilization. Barium compounds should react to form less-soluble barium sulfates (*10*), thereby reducing the availability of calcium sulfates for ettringite formation. Another method involving a double-lime treatment of sulfate soils also was investigated in an effort to reduce detrimental sulfate reactions.

MATERIALS AND METHODS

Three soils were studied in this research project because of their high sulfate content and expansive nature. Soils from Orange County, California, Central Texas, and Denver, Colorado, were used in various aspects of the testing procedures. The soils vary in composition with the amount and type of sulfates, the amount and type of clay components, swell, and plasticity. The lime used in all tests was a calcium hydroxide [$Ca(OH)_2$] obtained through Fisher Scientific.

Initial properties that influence lime stabilization were determined by analyzing untreated soil samples. Soil mineral compositions were determined using X-ray diffraction (XRD) procedures (*11*) and microscopic techniques. Clay percentages were determined using a standard hydrometer test (ASTM D422). The plasticity indices were determined by a standard Atterberg limits test (*12*).

California Bearing Ratio (CBR) Testing

The optimum water contents for compaction of the soils were determined by a modified Proctor density test (ASTM D698). The soils were then compacted, using a standard CBR method (ASTM D1557), into 6-in.-diameter molds at their optimum water contents and soaked in water for periods of 4, 14, 40, and 60 days. After the soaking periods, the compacted soils were measured for percent swell and tested to determine bearing strength values.

Three types of treatment methods were conducted on the soils. Untreated soils and soils treated with 6 percent lime were tested for swell and strength values after 4-day soaking periods.

A double application of lime (*7*) was conducted where 3 percent lime was added followed by an uncompacted wet curing period of 7 days before the application of an additional 3 percent lime before compaction. The samples were then soaked for 60 days before being tested for swell and strength characteristics.

In the barium compound treatment method, soils were pretreated with 3 percent barium hydroxide or 3 percent barium chloride, compacted at their optimum water contents, soaked in water for 14 days, and tested for strength and swell values. The soils were then dried at 50°C, disaggregated, treated with 6 percent lime, compacted at their optimum water contents, and soaked for periods of 14 and 40 days before being tested for strength and swell values.

Potential Volume Change (PVC) Testing

The soils were compacted into 2.75-in. molds at their plastic limits and at 2.5 times standard Proctor compactive efforts and measured for swell pressures exerted against the restraining force of a proving ring over periods of 7 days using a PVC meter. The meter is used to perform swell index tests to determine the expansive nature of a soil and to give it a rating of either noncritical, marginal, critical, or very critical, depending on the amount of swell that is developed (*13*).

Two soil treatment methods were investigated in the PVC testing. In the first method, 6 percent lime was added to each soil, followed by mixing, compacting, and monitoring of swell pressures developed during 7-day soaking periods.

In the second method, 3 percent barium hydroxide or 3 percent barium chloride was added to each soil, followed by wet curing for 7 days, and drying at 50°C. They were then disaggregated, treated with 6 percent lime, compacted, and monitored for swell pressures developed during 7-day soaking periods.

RESULTS

Initial properties that influence lime stabilization and control the behavior of sulfate soils are the soluble sulfates content, clay percentage, plasticity index (Table 1), and soil mineral composition (Table 2). The Texas and Colorado soil properties were almost identical, except that the Colorado soil contained more kaolinite (Figure 1). The California soil had a soil mineral composition similar to that of the Texas soil, but the soluble sulfates content and clay percentage were much lower.

CBR Testing

Testing after a 4-day soaking period resulted in an increase in CBR values and a decrease in percent swell for both soils when 6 percent lime was added compared with the untreated soils (Table 3). Testing after a 14-day soaking period of soils pretreated with the two barium compounds indicated an increase in CBR values with the addition of lime to the pretreated soils (Table 3). The mix of barium hydroxide plus lime appeared to control the swell more effectively than the mix of barium chloride plus lime in the Texas soil. Comparing these data with tests previously conducted using lime only and untreated samples, the mix of barium hydroxide plus lime increased in CBR values for both soils and decreased in percent swell for the Texas soil (Table 3, Figure 2). Percent swell for the California soil may be considered negligible in all cases. The mix of barium chloride plus lime increased in CBR values for the California soil but had little to no improvement in CBR values or percent swell for the Texas soil (Table 3). The California soil was retested using an extended soaking period of 40 days. When both barium compounds were used, CBR values increased over those of the previous 14-day soaking test (Table 3).

The double application of lime using the California and Texas soils was relatively successful (Table 3). The results were somewhat improved over those for the mix of barium chloride plus lime but were not as successful as those for the mix of the barium hydroxide plus lime.

TABLE 1 INITIAL SOIL PROPERTIES

Soil Type	Soluble Sulfates	Clay %	Plasticity Index
Texas	8,870 ppm	67%	41
California	3,850 ppm	27%	13
Colorado	10,000 ppm *	80%	44

*-value from (14).

TABLE 2 ORIGINAL SOIL MINERAL COMPOSITION

Soil Type	Mineral Composition
Texas	Smectite, Illite, Kaolinite, Gypsum, Quartz
California	Smectite, Illite, Kaolinite, Gypsum, Quartz
Colorado	Smectite, Illite, Kaolinite, Gypsum, Quartz

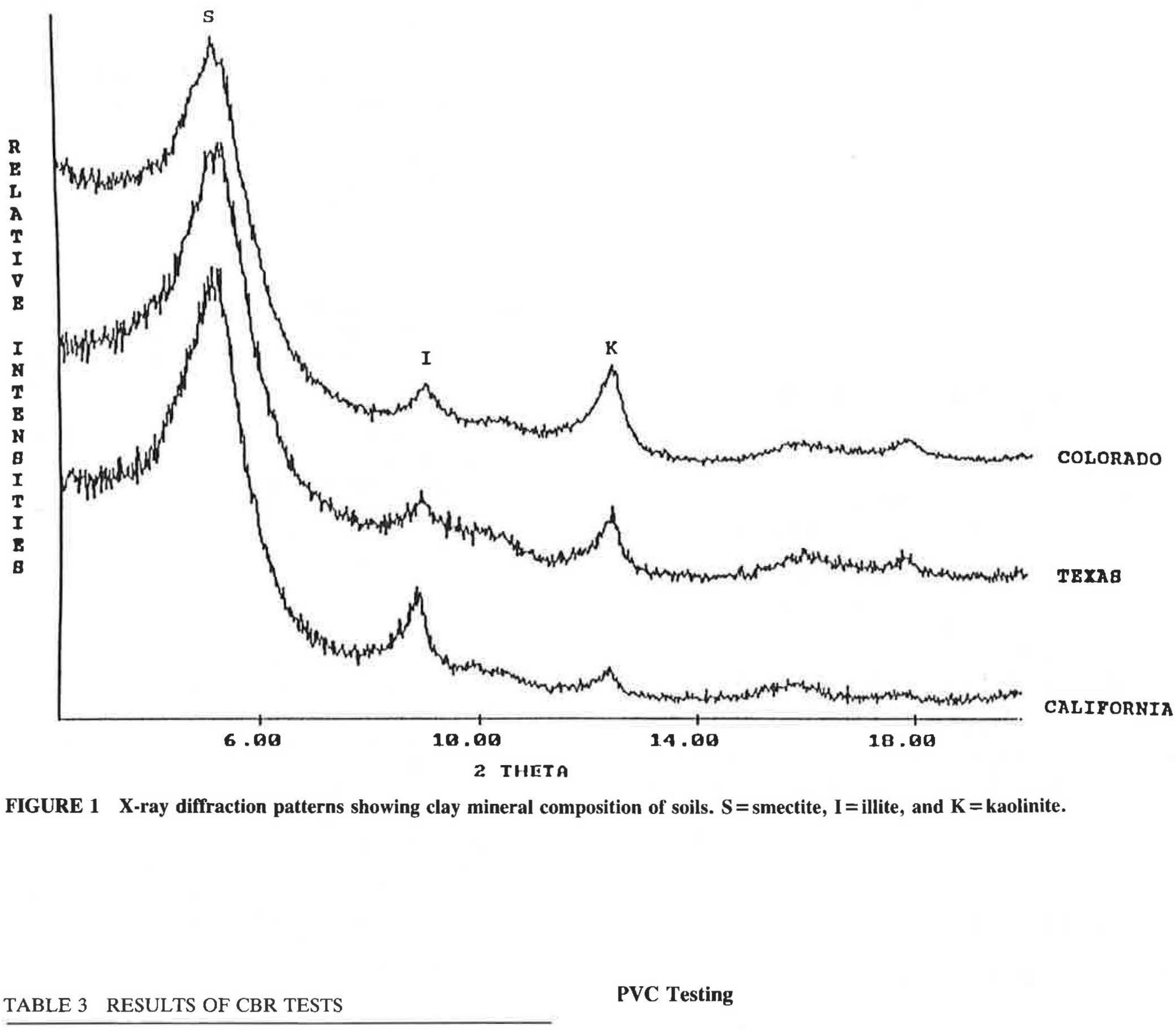

FIGURE 1 X-ray diffraction patterns showing clay mineral composition of soils. S = smectite, I = illite, and K = kaolinite.

TABLE 3 RESULTS OF CBR TESTS

Soil Type	Treatment	Length of Soak	CBR Value	% Swell
Texas	Untreated	4 Days	0.7	12
Texas	6% Ca(OH)2	4 Days	5.1	5.7
Texas	3% Ba(OH)2	14 Days	3.5	1.9
Texas	3% Ba(OH)2 + 6% Ca(OH)2	14 Days	21.2	3.2
Texas	3% Ba(OH)2 + 6% Ca(OH)2	40 Days	•	•
Texas	3% Ba(Cl)2	14 Days	•	•
Texas	3% Ba(Cl)2 + 6% Ca(OH)2	14 Days	4.3	11.6
Texas	3% Ba(Cl)2 + 6% Ca(OH)2	40 Days	•	•
Texas	Double Application of Lime	60 days	21.5	5
California	Untreated	4 Days	4.2	.7
California	6% Ca(OH)2	4 Days	10.4	0.02
California	3% Ba(OH)2	14 Days	5.1	0.24
California	3% Ba(OH)2 + 6% Ca(OH)2	14 Days	20.6	0.17
California	3% Ba(OH)2 + 6% Ca(OH)2	40 Days	48.7	-0.24
California	3% Ba(Cl)2	14 Days	3.2	1.5
California	3% Ba(Cl)2 + 6% Ca(OH)2	14 Days	24.8	0.08
California	3% Ba(Cl)2 + 6% Ca(OH)2	40 Days	36.9	-0.06
California	Double Application of Lime	60 days	45.7	0.65

• -- Data not available

PVC Testing

Testing of the Texas and Colorado soils using the PVC meter confirmed the CBR test results. For all soils, the mix of barium hydroxide plus lime significantly decreased in swell pressure compared with the lime treatment only (Table 4). The mix of barium chloride plus lime exhibited some improvement over the mix of lime only but not as significantly as that of the mix of barium hydroxide plus lime (Table 4).

Scanning Electron Microscope (SEM) Analysis

Samples were taken from the 14-day-soak soils pretreated with the two barium compounds and analyzed using SEM to determine if the formation of ettringite was being controlled. The California soil treated with the double application of lime had an abundance of ettringite, an elongated, needle-like mineral (*1*) (Figure 3a), as did the Texas soil. Ettringite was not detected in the California soil treated with either barium chloride or the mix of barium hydroxide plus lime (Figures 3b and 3c). By adding 15 percent barium hydroxide to the California soil, barium sulfate crystals were formed over a 2-

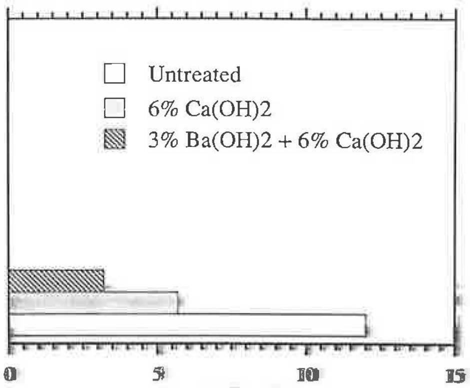

FIGURE 2 Percent swell from CBR tests on Texas soil.

month soaking period (Figure 3d). In the Texas soil, ettringite was found to be relatively abundant in the mix of barium chloride and lime (Figure 4a) and was present, but sparse, in the mix of barium hydroxide and lime (Figure 4b). Barium sulfates were formed in the Texas soil when treated with 15 percent barium hydroxide and 15 percent barium chloride (Figures 4c and 4d, respectively). Samples from the PVC tests also were analyzed with the SEM. Ettringite (Figure 5a) and barium sulfates (Figure 5b) were observed in the Texas soil treated with 3 percent barium hydroxide and 6 percent lime. Barium sulfate crystals (Figure 5c) were observed in the Colorado soil treated with 3 percent barium hydroxide and 6 percent lime. Although ettringite was observed in some treated samples by SEM analysis, it was not detected by XRD procedures.

DISCUSSION OF RESULTS

California Bearing Ratio Testing

The pretreatment of sulfate soils with barium compounds before lime application was most successful with the California soil. In these soils, the formation of ettringite was deterred and strength values were increased using both barium compounds. This may be because of the soils' relatively low soluble sulfate content, low clay content, and low plasticity. The Texas soil, which has a higher soluble sulfate content, greater clay content, and is more plastic, improved in strength and swell values under the barium hydroxide pretreatment but not under the barium chloride pretreatment. The higher content of sulfates in the Texas soil explained the formation of ettringite despite pretreatment methods. The barium ions are believed to be more available in the mix of barium hydroxide plus lime than in the mix of barium chloride plus lime. Pretreatment with larger amounts of barium hydroxide might be more effective in controlling ettringite formation in high-sulfate soils. However, these tests have not yet been conducted in the current study.

The increase in CBR values observed for the 40-day soaking period in the California soil is believed to be caused by cementitious effects of lime treatment forming calcium silicate hydrates and calcium aluminate hydrates through dissolution of Si and Al in the clay mineral structures. This can account for strength improvement over time, which has been demonstrated in other lime-treated soils (*15*). The barium compound are thought to react with the sulfates, forming less soluble barium sulfates, leaving a lesser amount of sulfates available to react with calcium hydroxide and aluminum to form ettringite. Reduction of ettringite formation leaves more free lime, keeping the pH above 12.4, allowing for more dissolution of the clay fraction to produce additional cementing materials during lime stabilization.

The double application of lime had improved strength values both for the Texas and California soils and a decrease in swell for the Texas soil over that of a single lime treatment. The soils in the double application study were soaked for longer periods of time, yet their CBR values increased and swell in the Texas soil was controlled to a degree. It is believed that the lime from the first application reacts with the sulfates to form gypsum and ettringite. The second application, which can be better mixed with the flocculated soil produced by the initial application, redistributes the sulfate minerals already formed. This second application of lime will furnish the calcium and high pH necessary to form calcium silicate hydrates and calcium aluminate hydrates in and around the pores, reducing the permeability and available water to the ettringite crystals.

PVC Testing

The lime-only treatment rated as a critical swell value for soil expansion. Lime added to soils treated with barium hydroxide reduced swell pressures in volume change tests, keeping the swell in the noncritical range. Lime added to soils treated with barium chloride controlled the swell to some degree and rated as marginal.

TABLE 4 RESULTS OF PVC TESTS WITH 7-DAY SOAKING PERIODS

Soil Type	Treatment	Pressure exerted (lb./sq. ft.)
Texas	6% Ca(OH)2	7,600
Texas	3% Ba(Cl)2 + 6% Ca(OH)2	3,700
Texas	3% Ba(OH)2 + 6% Ca(OH)2	1,000
California	6% Ca(OH)2	5,400
California	3% Ba(Cl)2 + 6% Ca(OH)2	1,900
California	3% Ba(OH)2 + 6% Ca(OH)2	700
Colorado	6% Ca(OH)2	5,400
Colorado	3% Ba(OH)2 + 6% Ca(OH)2	700

CONCLUSIONS

1. The amount and type of sulfates present, and the amount and type of clay material, are properties believed to play key roles in the poststabilization expansion of lime-treated sulfate soils.
2. The test results indicate that the swell resulting from lime treatment of sulfate soils may be controlled, and strength values increased, by pretreating them with barium compounds before lime application. Barium sulfates with low solubilities

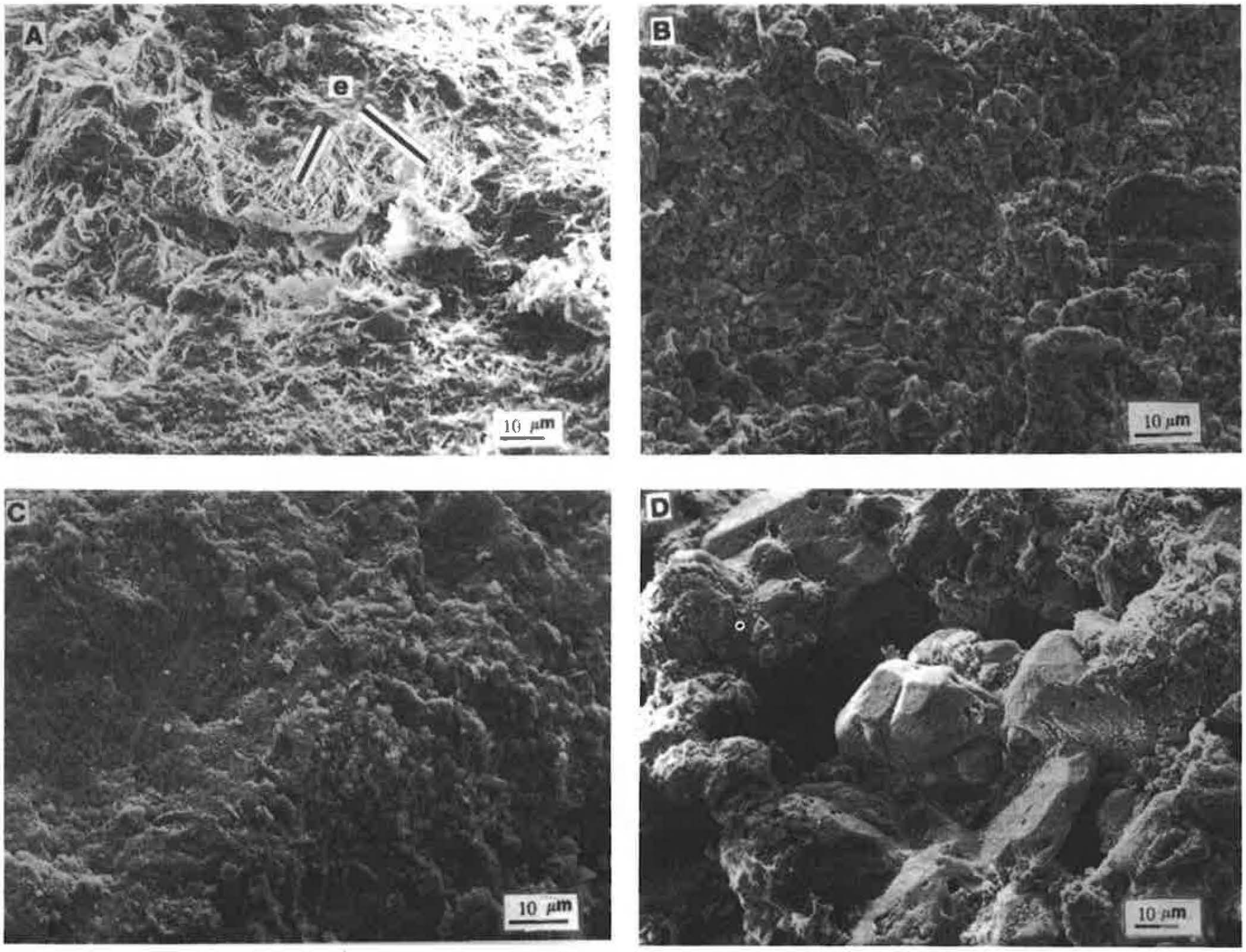

FIGURE 3 California soil: (A) double application of 3 percent lime + 3 percent lime CBR test with 60-day soak, showing ettringite, 720 ×; (B) 3 percent $Ba(OH)_2$ + 6 percent lime treatment, CBR test with 14-day soak, 1,050 ×; (C) 3 percent $Ba(Cl)_2$ + 6 percent lime treatment, CBR test with 14-day soak, 1,150 ×; (D) 15 percent $Ba(OH)_2$ treatment, 2-month soak, 730 ×.

are formed, removing the sulfate ions so that they are not free to react with the lime to form gypsum. If the sulfate availability is eliminated, the water-sensitive mineral ettringite cannot form. Barium hydroxide proved to be a more effective pretreatment compound than barium chloride.

3. Soils with low sulfate contents may be stabilized by applying the lime in two applications (double treatment). It is believed that the reactions forming gypsum and ettringite occur after the first application of lime and that the mixing of the second application breaks up the crystals and supplies more lime, which allows for the formation of cementing agents, increasing strength values and decreasing swell.

4. Because the use of barium compounds has never been applied to field studies, their impact on the surrounding environment, primarily groundwater, is unknown. Also, barium compounds are considerably more costly to use than lime. Therefore, future studies should concentrate on the method involving the double application of lime because it is more practical to use.

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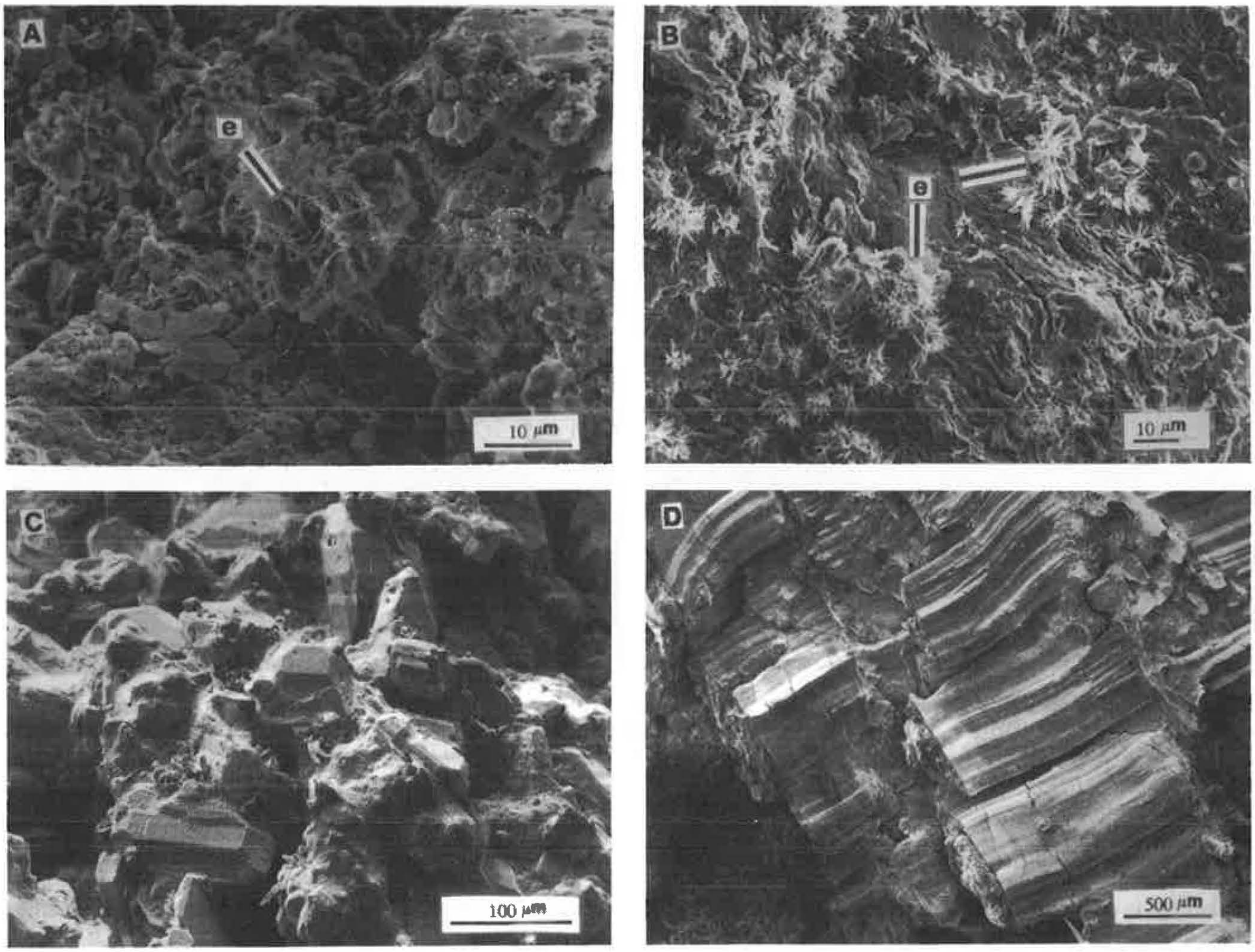

FIGURE 4 Texas soil: (A) 3 percent $Ba(OH)_2$ + 6 percent lime treatment, CBR test with 14-day soak, showing ettringite, 1,550 ×; (B) 3 percent $BA(Cl)_2$ + 6 percent lime treatment, CBR test with 14-day soak, showing ettringite, 790 ×; (C) 15 percent $Ba(OH)_2$ treatment, 2-month soak, 200 ×; (D) 15 percent $Ba(Cl)_2$ treatment, 2-month soak, 35.7 ×.

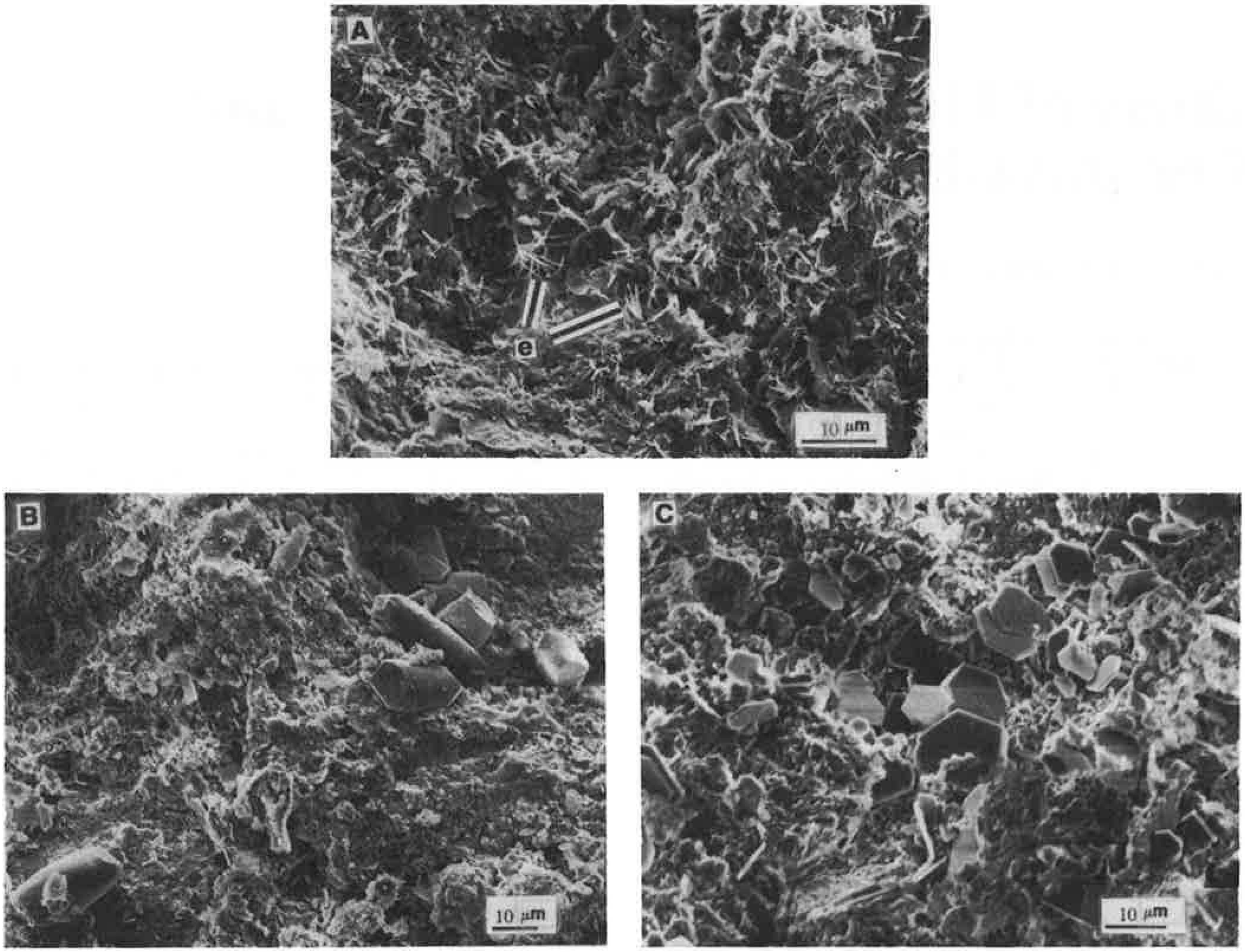

FIGURE 5 (A) Texas soil treated with 3 percent $Ba(OH)_2$ + 6 percent lime, PVC test with 7-day soak, showing ettringite, 1,350 ×; (B) Texas soil treated with 3 percent $Ba(OH)_2$ + 6 percent lime, PVC test with 7-day soak, 700 ×; (C) Colorado soil treated with 3 percent $Ba(OH)_2$ + 6 percent lime, PVC test with 7-day soak, 1,180 ×.

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