Effect of Sulfates on Cement- and Lime-Stabilized Soils

P. T. SHERWOOD, Road Research Laboratory, Department of Scientific and Industrial Research, United Kingdom

This paper describes the results of a laboratory investigation made to determine the effect of the presence of sulfate ions in soils on the durability of cement- and lime-stabilized soils. The method of investigation consisted of observing the behavior of specimens of stabilized soil when totally immersed in water. When tested in this way cement- or lime-stabilized clay mixtures containing calcium, magnesium, or sodium sulfates disintegrated within a few days of being immersed, whereas cement-stabilized sand mixtures containing the same proportions of sulfate were unaffected even after being immersed for one year. This suggested that the effect was related to the clay content of the soil, and differential thermal analysis and X-ray analysis showed that, at the high pH values encountered in cement and lime-stabilized soils, a reaction occurs between the clay fraction and any sulfates present.

It is proposed that sulfate attack on cement-stabilized soils is due principally to this reaction and that the relatively slow combination of the sulfates with the cement is of secondary importance. This explains why lime-stabilized clay soils are similarly affected by the presence of sulfates and also why the severity of the action of sulfates cannot be reduced by using sulfate-resistant cement in place of ordinary portland cement.

It is concluded that under certain conditions sulfates present in a cement- or lime-stabilized soil can lead to its disintegration. These conditions are most likely to occur when the soil contains an appreciable clay fraction and when the moisture content of the soil is liable to increase above that at which it was compacted. Because under other circumstances sulfates may appear to have a beneficial effect, it is suggested that it is inadvisable to make use of these beneficial effects unless all possibility of deleterious effects on the durability of the material can be excluded.

ONE OF THE MAIN problems that arise from the use of cement-stabilized soil as a road base material is the presence of chemical compounds in the soil which can either inhibit the normal hardening of the cement or lead ultimately to a loss of durability of the hardened material.
The effects of organic compounds in preventing the hardening of soil-cement are now well understood but the effects of sulfate ions in the soil are still in some doubt. Experimental work carried out by Lambe and his co-workers (1) has shown that the strength of soil-cement can often be increased by the use of small proportions of metal sulfates as secondary additives. On the other hand, the action of sulfate ions in causing disintegration of hardened concrete would lead one to expect a similar effect with soil-cement. However, the two cases are not entirely analogous, because with concrete sulfate ions external to the concrete are reacting with hardened cement that has been mixed with a sulfate-free aggregate, whereas with soil-cement an additional problem arises from the presence of naturally occurring sulfates within the soil mass. Further, with soil-cement there is the added complication of the presence of clay.

Earlier work by the author (2) suggested that the presence of sulfates in cement-stabilized clay soils would result in a loss of durability under conditions where the soil-cement was subject to an increase of moisture content. Further research has now been carried out on this problem in which the investigation has been extended to soils having different clay contents and to soils stabilized with hydrated lime.

PREVIOUS WORK

Lambe, Michaels, and Moh (1) carried out extensive laboratory studies on the effect of small percentages (of the order of 1 percent) of alkali metal salts as secondary additives to cement-stabilized soils. In this investigation it was found that with many soils, particularly those containing organic matter, the addition of sodium sulfate resulted in a considerable increase in the strength of the stabilized soil, although with a few soils a reduction in strength was observed. Kozan (3) confirmed the ability of small proportions of sodium sulfate to increase the strength of some cement-stabilized soils.

Evidence for the detrimental effect of sulfate ions on the strength of cement-stabilized soil has been given by Mehra Chadda and Kapur (4), Cordon (5), and the author (2). These investigations showed that a loss in strength usually occurred when cement-stabilized soils were immersed in solutions containing sulfate ions or when cement-stabilized, sulfate-bearing soils were immersed in water. The sulfate attack on the soil-cement was more rapid than that on concrete, and Cordon suggested that the speed of reaction might be associated with the fact that soil-cement was less dense, so that diffusion of the sulfate solutions or water could occur more easily. Cordon found that stabilized soils made with coarse-grained soils, high cement contents, and sulfate-resistant cement produced the most resistant material.

Figure 1, which is taken from the author's previous paper (2), shows the effect of immersion in water on the strength of a cement-stabilized clay containing calcium sulfate. The presence of calcium sulfate had little effect on the compressive strength when the stabilized soil was cured at constant moisture content, but the same material suffered a considerable loss in strength when immersed in water. Substitution of sulfate-resistant cement for ordinary portland cement did not reduce the disintegrating effect of the calcium sulfate.

Other tests (Fig. 2), in which cement-stabilized clay, free of sulfate, was immersed in solutions of magnesium sulfate, showed that as little as 0.2 percent (as SO₃) of magnesium sulfate could reduce the strength by more than 50 percent.

An instance has been recorded in South Australia (6) where the presence of calcium sulfate in soil resulted in the disintegration of a soil-cement road.

SCOPE OF PRESENT INVESTIGATION

It is clear from the previous investigations of this problem that different effects can result from the action of sulfate ions on cement-stabilized soils and that the mechanism of the action depends on factors not fully understood. The investigations described in this paper have as their object the elucidation of this mechanism.

In view of the considerable knowledge of the reactions of sulfate ions with the cement in concrete it would be expected that similar reactions would take place with granular soils stabilized with cement and that with stabilized cohesive soils the clay
fraction would be the principal factor introducing new features in the reactions involved. The primary object of the present investigation was therefore to explore the effect of the clay content of soil on the resistance of the stabilized soil to sulfate attack. Five artificial soils with different clay contents and having the particle-size distributions shown in Figure 3 were used for this study. They were prepared by mixing London clay (clay content 62 percent, liquid limit 80 percent, plastic limit 28 percent as measured by B.S. procedures (7)) and a pure silica sand in proportions (by weight) of 100:0, 75:25, 50:50, 25:75, 0:100.

The investigations involved tests on specimens of these soils, stabilized with cement, some of which contained calcium sulfate and some of which were free of sulfate but subject to external attack by sulfate ions, with the object of differentiating between the effects obtained in the two cases.
Because in cement-stabilized soils chemical reactions take place at high pH values induced by the calcium hydroxide released during the hydration of portland cement, the investigations were subsequently extended to include a study of the resistance of lime-stabilized soil to sulfate attack in the hope that this would help to explain the reactions involved.

The ordinary portland cement used in the investigations had the chemical and physical properties given in Table 1. The hydrated lime that was used was of general reagent grade and contained 92 percent calcium hydroxide. The calcium, magnesium, and sodium sulfates that were used were all of analytical reagent grade.

TEST PROCEDURE

In the author's previous paper (2) it was shown that cement-stabilized soils containing sulfate ions were subject to a reduction in strength only when their moisture contents were increased by the immersion of specimens in water. In practice, however, there will be circumstances in which the stabilized soil does not increase in moisture content, as well as other circumstances in which an increase takes place. It is therefore

<table>
<thead>
<tr>
<th>TABLE 1</th>
</tr>
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<tbody>
<tr>
<td>PHYSICAL AND CHEMICAL PROPERTIES OF ORDINARY PORTLAND CEMENT USED</td>
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</table>

<table>
<thead>
<tr>
<th>Property</th>
<th>Value (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemical analysis (%):</td>
<td></td>
</tr>
<tr>
<td>CaO</td>
<td>66.08</td>
</tr>
<tr>
<td>SiO₂</td>
<td>22.54</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>1.91</td>
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<tr>
<td>Al₂O₃</td>
<td>4.39</td>
</tr>
<tr>
<td>MgO</td>
<td>0.83</td>
</tr>
<tr>
<td>SO₃</td>
<td>2.01</td>
</tr>
<tr>
<td>Na₂O</td>
<td>0.17</td>
</tr>
<tr>
<td>K₂O</td>
<td>0.35</td>
</tr>
<tr>
<td>TiO₂</td>
<td>0.27</td>
</tr>
<tr>
<td>P₂O₅</td>
<td>0.24</td>
</tr>
<tr>
<td>Mn₂O₇</td>
<td>0.11</td>
</tr>
<tr>
<td>Loss on ignition (%):</td>
<td></td>
</tr>
<tr>
<td>0 - 105 C</td>
<td>0.16</td>
</tr>
<tr>
<td>105 - 590 C</td>
<td>0.81</td>
</tr>
<tr>
<td>590 - 1,000 C</td>
<td>0.52</td>
</tr>
<tr>
<td>Calculated compound composition (%):</td>
<td></td>
</tr>
<tr>
<td>3CaO·SiO₂</td>
<td>58.0</td>
</tr>
<tr>
<td>2CaO·SiO₂</td>
<td>20.0</td>
</tr>
<tr>
<td>3CaO·Al₂O₃</td>
<td>8.6</td>
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<tr>
<td>4CaO·Al₂O₃·Fe₂O₃</td>
<td>5.8</td>
</tr>
<tr>
<td>CaSO₄</td>
<td>3.4</td>
</tr>
<tr>
<td>CaO</td>
<td>1.4</td>
</tr>
<tr>
<td>Setting time (min):</td>
<td></td>
</tr>
<tr>
<td>Initial</td>
<td>145</td>
</tr>
<tr>
<td>Final</td>
<td>275</td>
</tr>
<tr>
<td>Specific surface (sq cm/g)</td>
<td>3,790</td>
</tr>
<tr>
<td>Specific gravity</td>
<td>3.14</td>
</tr>
<tr>
<td>Strength tests on 2.78-in. mortar cubes (lb/sq in.):</td>
<td></td>
</tr>
<tr>
<td>At 3 days</td>
<td>3,240</td>
</tr>
<tr>
<td>At 7 days</td>
<td>4,850</td>
</tr>
</tbody>
</table>
apparent that the laboratory test procedure should permit determinations to be made separately, both of the strength of the stabilized soil when cured at constant moisture content and of the loss of strength due to an increase of moisture content. Both these requirements are satisfactorily met by the B.S. resistance to immersion test (8). This test is a modification of the unconfined compressive strength test in which two identical sets of specimens are prepared, kept at constant moisture content by coating them with paraffin wax, and cured at a constant temperature of 25°C. One set of specimens is allowed to cure for 14 days; the other is allowed to cure for only 7 days, after which time the wax coatings are removed and the specimens are completely immersed in water for the next 7 days. The strengths of both sets of specimens are determined at the end of the 14-day period. The resistance to immersion of the stabilized soil (R_i) is given by

\[
R_i = \frac{\text{Strength of specimens immersed in water}}{\text{Strength of control specimens}} \times 100
\]

In addition to the presence of the sulfate ions, the resistance of cement-stabilized soil to immersion is affected by the texture of the soil; e.g., stabilized sandy soils are much less affected by immersion in water than stabilized clayey soils. It is possible to isolate this effect from the effect of the presence of the sulfate ions, by also determining the resistance to immersion of the stabilized soil in the absence of sulfates; a measure of the effect of the presence of sulfates on the durability of the material is given by

\[
\text{Resistance to sulfate attack} = \frac{\text{Resistance to immersion of stabilized soils containing sulfates}}{\text{Resistance to immersion of stabilized soil free from sulfates}} \times 100
\]

Although the preceding procedure is suited to the study of the effects of sulfates when they occur in the soil, it has to be modified in studying the effect of immersing stabilized soil in solutions containing sulfate ions. In this case the equation is

\[
\text{Resistance to immersion in sulfate solutions} = \frac{\text{Strength of specimens immersed in sulfate solution}}{\text{Strength of specimens immersed in water}} \times 100
\]

**EXPERIMENTS WITH CEMENT-STABILIZED SOILS**

**Immersion in Magnesium Sulfate Solution**

The previous work showed that sulfate attack was most severe when specimens of cement-stabilized soil were immersed in solutions containing sulfate ions (cf., Figs. 1 and 2) and as a preliminary investigation the effect on the strength of the cement-stabilized sand-clay mixtures of immersion in magnesium sulfate solution was studied.

Sets of specimens of each of the five soil mixtures, stabilized with 10 percent of ordinary portland cement, were prepared at moisture contents corresponding to a value of 2 percent below the plastic limit of each mixture and at densities corresponding to an air content of 5 percent. (Unconfined compressive strength specimens are normally prepared at the optimum moisture content and maximum dry density obtained by the B.S. compaction tests on the stabilized soil. In this instance insufficient quantities of the soil were available for compaction tests to be made; a moisture content of 2 percent below the plastic limit of the stabilized soil has been found to approximate to the optimum moisture content as found in the B.S. compaction test). All the specimens were cured at constant moisture content for 7 days and then immersed in solutions of magnesium sulfate for 7 days. At the end of this period they were removed and measurements made of their unconfined compressive strengths.

The resistance of the specimens to immersion in solutions containing sulfate ions was dependent on the clay content (Fig. 4). Although 0.5 percent of magnesium sulfate
was sufficient to cause the complete disintegration of the stabilized clays, the strength of the stabilized sands was unaffected. Figure 5 shows that the disintegration of the cement-stabilized clay specimen was due to cracking brought about by a large increase in volume; it also shows a white incrustation of magnesium hydroxide that formed on the cement-stabilized sand specimens. It was at first thought that this incrustation on the sand specimens formed an impenetrable skin which prevented ingress of magnesium sulfate; however, as will be seen later, this was not the case.

Effect of Presence of Calcium Sulfates In the Soil

Although it is possible that soil-cement might be attacked by water containing sulfate ions it is more likely that sulfate attack would originate from the presence of sulfates (usually calcium sulfate) in the soil itself. Different proportions of calcium sulfate were therefore added to each of the sand-clay mixtures and sets of

![Figure 4. Effect of immersion in magnesium sulfate solution on strength of London clay-sand-cement mixtures stabilized with 10 percent of ordinary portland cement.](image)

Figure 5. Specimen of cement-stabilized clay immersed in 2 percent solution of magnesium sulfate. Specimen of cement-stabilized sand immersed in 2 percent solution of magnesium sulfate. Large volume increases of clay specimen and white incrustation on sand specimen shown.
Figure 6. Effect of calcium sulfate on strength of cement-stabilized London clay-sand mixtures.

cement-stabilized specimens were prepared from each of these mixtures. One-half of each set of specimens was subjected to the B.S. resistance to immersion test, and the other half was tested by a modified form of the immersion test in which an immersion period of 3 months was used in place of the specified 7 days. The effect of immersion for both periods of time is shown in Figure 6, and the appearance after 7 days of immersion of clay specimens with and without calcium sulfate is shown in Figure 7.

The resistance to attack by calcium sulfate, as for magnesium sulfate, was found to be related to the clay content of the mixtures (Fig. 6). A comparison of Figure 6a with Figure 6b shows that the attack occurred within a short period after immersion in water and that except for the 75:25 sand-London clay mixture no further attack took place. The sand specimens containing no clay were not affected even after immersion for 1 year.

The rate of attack and its dependence on the clay content suggested that the main reason for the sulfate attack was not, as had been previously thought, due to combination of the sulfate ions with the cement as is the case with sulfate attack on concrete. The fact that soil stabilized with sulfate-resistant cement is equally liable to attack also suggests that combination of the sulfates with the cement is not the primary cause of sulfate attack on cement-stabilized soil. It has been suggested that in the presence of lime (or cement) calcium sulfate can combine directly with clay minerals and it seemed more likely that this was the cause of sulfate attack. Further experiments were therefore made to examine this possibility.

EXPERIMENTS WITH LIME-STABILIZED SOILS

If sulfate attack is due to a reaction between the clay fraction and the sulfate, then lime-stabilized soils should be affected in a similar manner to cement-stabilized soils. To find if this was the case experiments were made in which specimens of a heavy clay (London clay) stabilized with 10 percent of lime and cured at constant moisture content for one week were immersed in solutions of either sodium sulfate or magnesium sulfate, at concentrations ranging from 0 to 1.5 percent (as SO₃). Figures 8 and 9 show the appearance of the two sets of specimens at the end of the immersion period. In all cases, cracking and swelling of the specimens immersed in the sulfate solutions had occurred, making them too weak for unconfined compressive strength tests to be performed.

Further experiments were made in which different proportions of calcium, sodium, and magnesium sulfates were incorporated in specimens of the heavy clay stabilized with 10 percent of lime. Two sets of specimens were made for each sulfate concentration, and were cured at constant moisture content. At the end of 7 days the wax coating was removed from one set and the specimens immersed in water. After a further 7 days the unconfined compressive strengths of both the immersed and control sets of specimens were determined. Figure 10 shows that provided the lime-stabilized clay remained at constant moisture content calcium sulfate had a marked beneficial effect, whereas sodium sulfate and magnesium sulfate were without significant effect. However, a considerable loss of strength due to expansion and cracking occurred when the specimens were immersed in water.
Figure 7. Effect of calcium sulfate (gypsum) on expansion of cement-stabilized clay.

Figure 8. Specimens of London clay stabilized with 10 percent of lime after immersion in solutions of sodium sulfate for 7 days. (Figures on tops of specimens give concentrations of sodium sulfate as percent SO$_3$.)

Figure 9. Specimens of London clay stabilized with 10 percent of lime after immersion in solutions of magnesium sulfate for 7 days. (Figures on tops of specimens give concentrations of magnesium sulfate as percent SO\(_3\)).

Cured at constant moisture content for 14 days
Cured at constant moisture content for 7 days and then immersed in water for 7 days

Figure 10. Effect of sulfates on strength of London clay stabilized with 10 percent of hydrated lime.

The experiments with lime clearly show that lime-stabilized soils are affected by sulfates in a similar manner to cement-stabilized soils. In the case of lime there can be no question of it reacting directly with calcium sulfate and the sulfate attack must be a result of a reaction between the sulfate and the clay fraction.

INVESTIGATION OF LIME-CLAY-SULFATE-REACTION

Mineralogical analyses, using X-ray diffraction and differential thermal methods of samples of lime-stabilized London clay containing 2 percent (as SO\(_3\)) of calcium sulfate, revealed that the calcium sulfate had disappeared from the specimens that had been immersed in water. As there was insufficient water present for the calcium sulfate to have been completely leached from the specimen sampled, this can only mean that it had reacted with the clay. There was also some evidence that ettringite (calcium sulfo-aluminate) had been formed as a result of this reaction.

Ettringite is the product formed when sulfate ions attack concrete; it occupies a greater volume than the reactants from which it is formed and this results in expansion of the concrete. It seems probable that the formation of ettringite is also responsible for the disintegration of cement-
and lime-stabilized soils except that in these cases the ettringite is derived, primarily
in the case of cement and exclusively in the case of lime, from a reaction between cal­
cium sulfate and the clay. Further experiments are to be made to confirm this find­
ing.

RESULTS

It is evident from this work that the disintegration of soil-cement due to sulfate ions
is brought about, primarily, by a chemical reaction that is different from that involved
in sulfate attack of concrete. The degree of disintegration was proportional to the
amount of clay present in the soil and this is attributed to a reaction that occurs between
clay and sulfate ions in the presence of lime and excess water. Although the sand-
cement specimens were more permeable than those containing clay they were not af­
fected by sulfate ions in the period of test, and the fact that soil-cement is more rapidly
attacked than concrete by sulfate ions cannot therefore be attributed to its greater per­
meability. The main reason for the disintegration of soil-cement by sulfate ions is
thus the clay-sulfate reaction which is clearly much more rapid than the cement-sulfate
reaction that brings about the sulfate attack of concrete. Cement-stabilized sands
cannot be affected by the sulfate-clay reaction; this explains why they have been found
to be much less susceptible to sulfate attack than cement-stabilized clay soils. So far,
tests have not been carried out for sufficiently long to enable any conclusions to be
drawn about the long-term susceptibility of cement-stabilized sands to sulfate attack
but there is no reason to suppose that it would be very different from that of concrete.
The sulfate-clay reaction helps to explain reported effects of sulfates on cement-
stabilized soils which appeared to be anomalous. In their studies with sodium sulfate,
Lambe and his co-workers (1) found that it had beneficial effects on some soils and
detrimental effects on others, and it is significant that the detrimental effects were ob­
tained with the soils that had the highest clay contents. The fact that the use of sulfate-
resistant cement does not lessen the degree of sulfate attack (Figs. 1 and 2) is also
readily explained.

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