

Effect of Sulfates on Cement-Stabilized Clay

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

This paper describes an investigation into the effect of sulphates on the strength of cement-stabilized clays. It is found that sulphates have a detrimental effect on clay-cement mixtures, similar to that on concrete, which, in extreme cases, results in the complete disruption of the material. Sulphate contents up to 7 percent (as SO_3) of the dry weight of the clay had little effect on the compressive strength of the clay-cement when cured at constant moisture content but when more than 1.0 percent (as SO_3) of either magnesium or calcium sulphate was present in the clay, clay-cement mixtures disintegrated on immersion in water. The effect was even more pronounced when sulphate-free clay-cement was immersed in aqueous sulphate solutions; as little as 0.2 percent of sulphate in the surrounding water reduced the strength by more than 50 percent.

It is concluded that damage to cement-stabilized clay would not be less severe than that which would be experienced by an average quality concrete in the same circumstances.

● IN GREAT BRITAIN granular and light clay soils have been successfully stabilized with portland cement for the construction of road bases but few heavy clays have been so treated because of difficulties in mixing. The development in recent years of improved mixing machinery suggests that this limitation may soon be overcome, in which case it will be necessary to know whether there are in clays any chemical constituents affecting the hardening of cement, such as there are in some granular soils.

By analogy with the behaviour of concrete it might be expected that sulphates, which are widely distributed in British clays, would also have an adverse effect on soil-cement and that these would present a problem in the cement-stabilization of heavy clays.

This paper describes work which was undertaken at the Road Research Laboratory in Great Britain to find the effect of sulphates on the compressive strengths of hardened clay-cement mixtures.

OCCURRENCE OF SULPHATES IN SOILS

Sulphates usually occur in British soils in the form of the sparingly soluble calcium sulphate (gypsum) although sodium and magnesium sulphates are also encountered in certain areas. Bessey and Lea (1) have reviewed the distribution of sulphates in Great Britain and have noted that they usually occur only in clay soils, since gravels and sands are leached free from soluble constituents by percolating waters. For this reason the concentrations of sulphates in the surface soil layers are often lower than those in the subsoil so that concrete placed near the surface on a well-drained soil is likely to be free from attack. They also point out that the sulphate contents of soils and ground-water are subject to wide seasonal fluctuations and vary considerably over quite small areas; because of this measurements of the total sulphate content are of only limited value. The distribution of sulphates in a British clay is illustrated in Figure 1, which shows the variation with depth of the sulphate and calcium contents of a profile of Oxford clay; the top 4 ft has been leached free from calcium sulphate, which has accumulated in the middle layer. Tests have shown that only the sulphate-free layer can be successfully stabilized with cement.

WATER SOLUBLE CALCIUM (CaO) AND SULPHATE (SO_3)
per cent

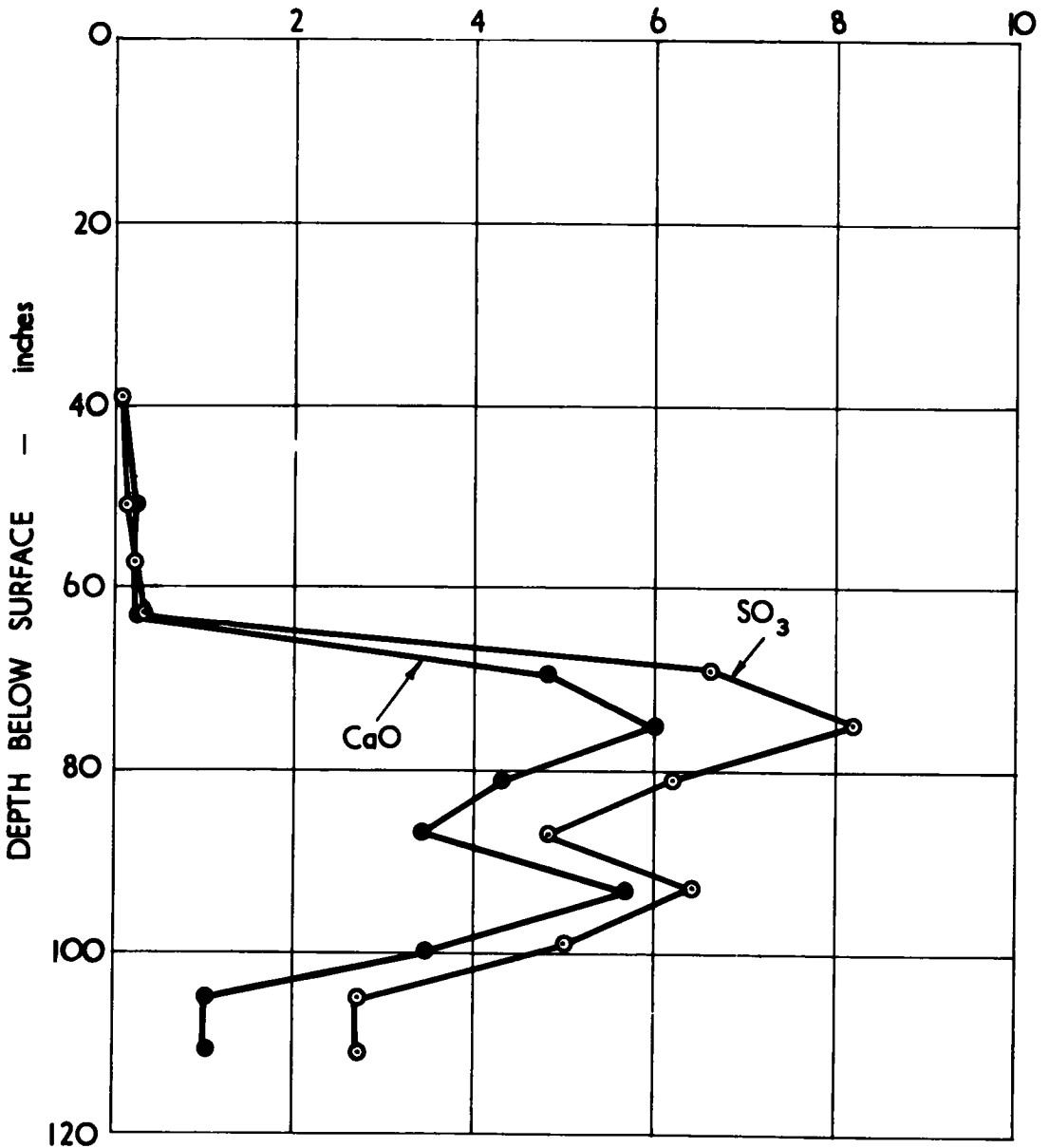


Figure 1. Variation with depth of sulphate and calcium contents for soil from an Oxford clay profile.

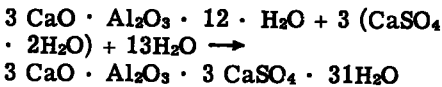
Under other climatic conditions the occurrence of sulphates may not be limited to clays and the lower soil strata. Moisture may percolate downwards during periods of heavy rainfall, but due to evaporation there will also be an appreciable upward movement of moisture in the dry season, with a resulting increase in the salt concentration in the surface strata. These conditions characterize the areas in which the Solonetz

and Solontchak alkaline soils occur (2); e.g. Central Europe, the Southern United States of America and the Middle East.

POSSIBLE EFFECTS OF SULPHATES ON SOIL-CEMENT

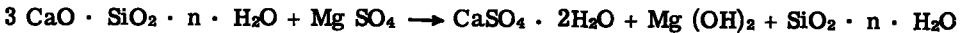
There are three ways in which sulphates might be expected to affect the strength of soil-cement:

1. If sulphate-bearing ground-water flows through a soil-cement mixture, calcium sulphate can combine with the tri-calcium aluminate in the hydrated cement, producing calcium sulpho-aluminate according to the equation:



(1)

This reaction is accompanied by a considerable increase in the volume of the solid material, and in concrete and mortar this has been shown to lead to the destruction of the hydrated cement matrix, and to loss of strength. The action of magnesium sulphate is even more marked in that it can also attack the calcium silicates in the hydrated cement, according to the equation:



(2)

This reaction is also accompanied by a large increase in volume of the solid constituents, and the calcium sulphate formed is free to attack the tricalcium silicate according to equation 1. Since the reactants in equations 1 and 2, with the exception of magnesium sulphate, are only sparingly soluble in water, it would be expected that the action of sulphates would be more apparent when excess water can have access to the system and that the attack would result in a considerable expansion of the soil-cement. The effect of calcium (but not magnesium) sulphate can be partly overcome by increasing the ferric oxide content at the expense of the aluminium oxide content during the manufacture of cement, the product being known as "sulphate-resistant cement."

2. If a high proportion of water-soluble salts is present in a hardened soil-cement mixture two possibilities arise, both of which could lead to a reduction in strength when the soil-cement is immersed in water. In the case of a sparingly soluble salt the solid material will gradually dissolve leaving water-filled voids in the structure resulting in a reduction in the strength of the soil-cement. If the salt present is already in solution an osmotic pressure could be set up between the stronger salt solution in the soil-cement and the surrounding water; this pressure might be sufficient to cause some disruption of the soil-cement. The possibility of these circumstances occurring in practice is debatable, but cannot be completely ignored.

3. In arid areas it is known that a considerable upward movement of moisture can occur in soils. Soluble salts may be transported with this moisture and concentrated in the surface where the salts crystallize and disrupt the soil structure, creating what are known as "salt boils."

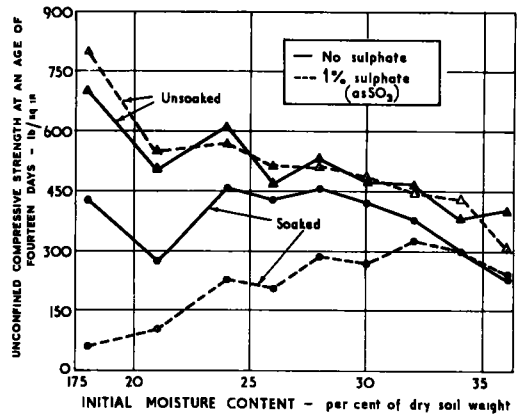


Figure 2. Effect of moisture content, sulphate content and immersion in water on the strength of a clay stabilized with ordinary portland cement.

EXPERIMENTAL WORK

The experiments were devised to determine the effects of calcium and magnesium sulphate on cement-stabilized clay and to find in what manner and under what conditions these effects became apparent. This was done by comparing the strengths of the clay-cement when subjected to different forms of attack by the sulphates with the strengths of the clay-cement when unaffected by such attack. The strengths of the clay-cement mixtures were measured by the British Standard procedure (3) for determining the effect of immersion in water on the unconfined compressive strength of

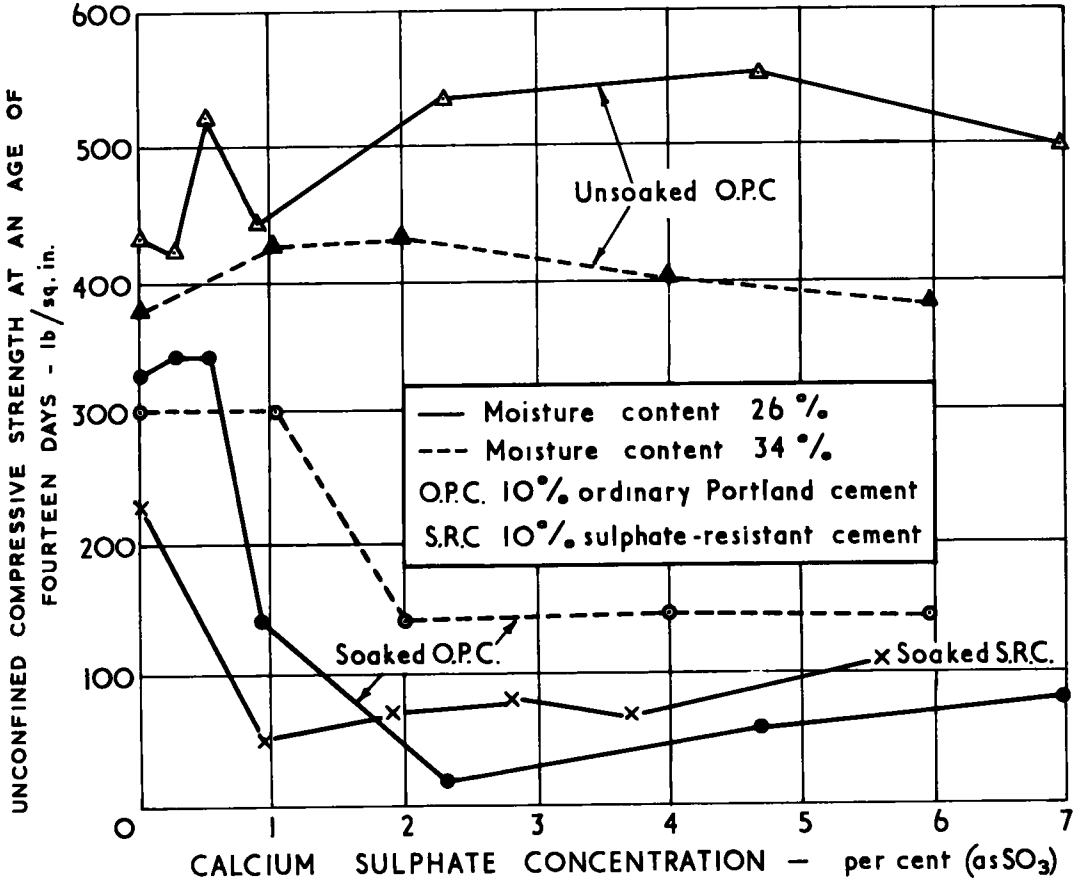


Figure 3. Effect of moisture content and calcium sulphate concentration on the strength of a clay stabilized with ordinary portland cement and sulphate-resistant cement.

cylindrical specimens, 4-in. long and 2-in. diameter, of cement-stabilized soil. The British Standard test is a modification of the unconfined compressive strength test in which two identical specimens are prepared and cured at constant moisture content and temperature by coating them with paraffin wax and storing them at a temperature of 25 C. One specimen is left for 14 days; the other is left for 7 days after which time its wax coat is removed and the specimen is completely immersed in water for 7 days. The strengths of both specimens are determined at the end of the 14-day period.

The clay used for the work was a sample of sulphate-free boulder clay with a clay content of 30 percent (particles less than 0.002 mm in diameter), a liquid limit of 45 percent and a plastic limit of 26 percent. Soil-cement specimens were prepared by mixing the clay with the cement for 5 minutes and then mixing for a further 10 min-

utes with sufficient water to bring the mixture to the appropriate moisture content. The material was then compacted to an air-voids content of 5 percent.

To study the effect of the presence of sulphate in soil-cement mixtures the following investigations were made.

Effect of Sulphate and Moisture Contents

A study was first made of the effect of the presence of calcium sulphate in clay on the strength of the cement-stabilized clay when cured both normally and after immersion

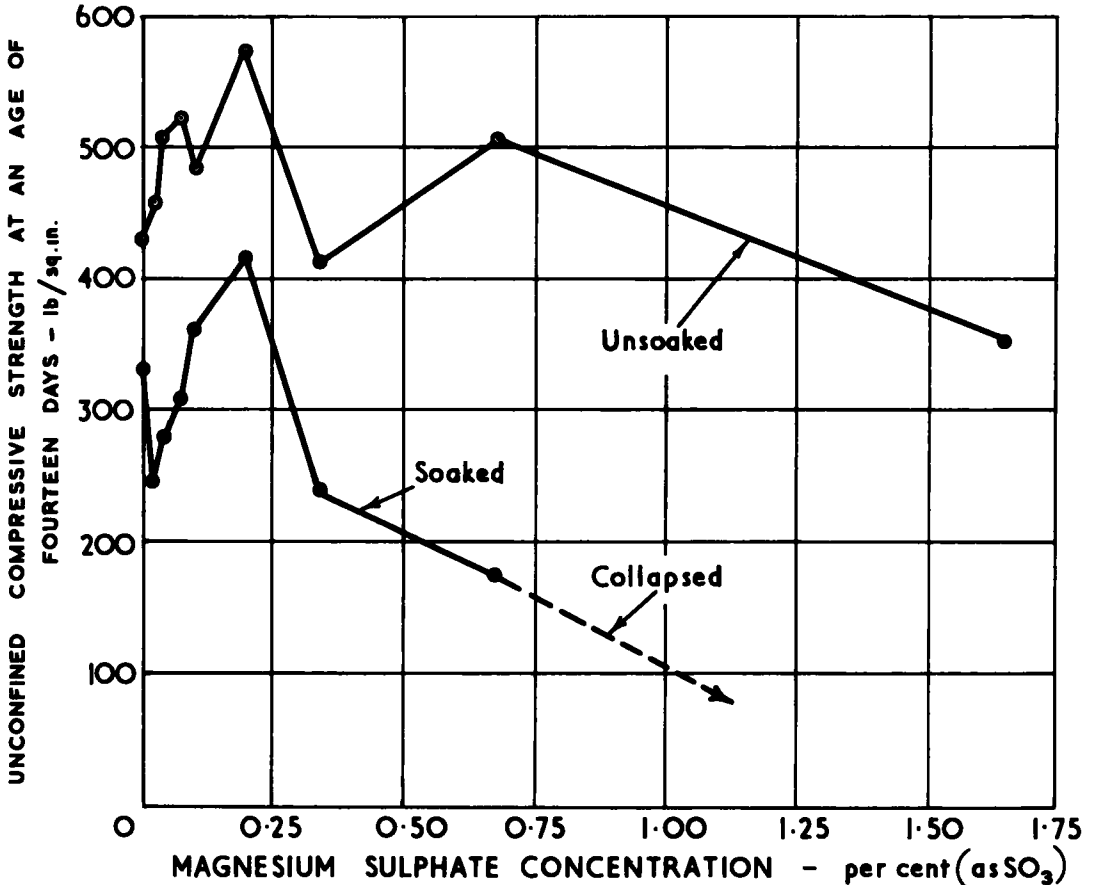


Figure 4. Effect of magnesium sulphate concentration on the strength of a clay stabilized with ordinary portland cement.

in water. Specimens for the water-immersion test were prepared from samples of the boulder clay at moisture contents ranging from 18 to 36 percent; 10 percent of ordinary portland cement was added and the specimens were compacted to an air-voids content of 5 percent. A similar set of specimens containing, in addition, 1 percent of calcium sulphate (as SO₃) was also prepared. The strengths of the specimens were measured either after normal curing for 14 days or after normal curing for 7 days plus immersion in water for 7 days.

The results (Fig. 2) show that as the moisture content increased the strength of the normally cured soil-cement both with and without sulphate decreased and that the presence of the sulphate had no significant effect. Immersion in water, however, reduced the strengths at all moisture contents although to a smaller extent at the higher moisture contents. The presence of the sulphate resulted in significantly lower strengths than

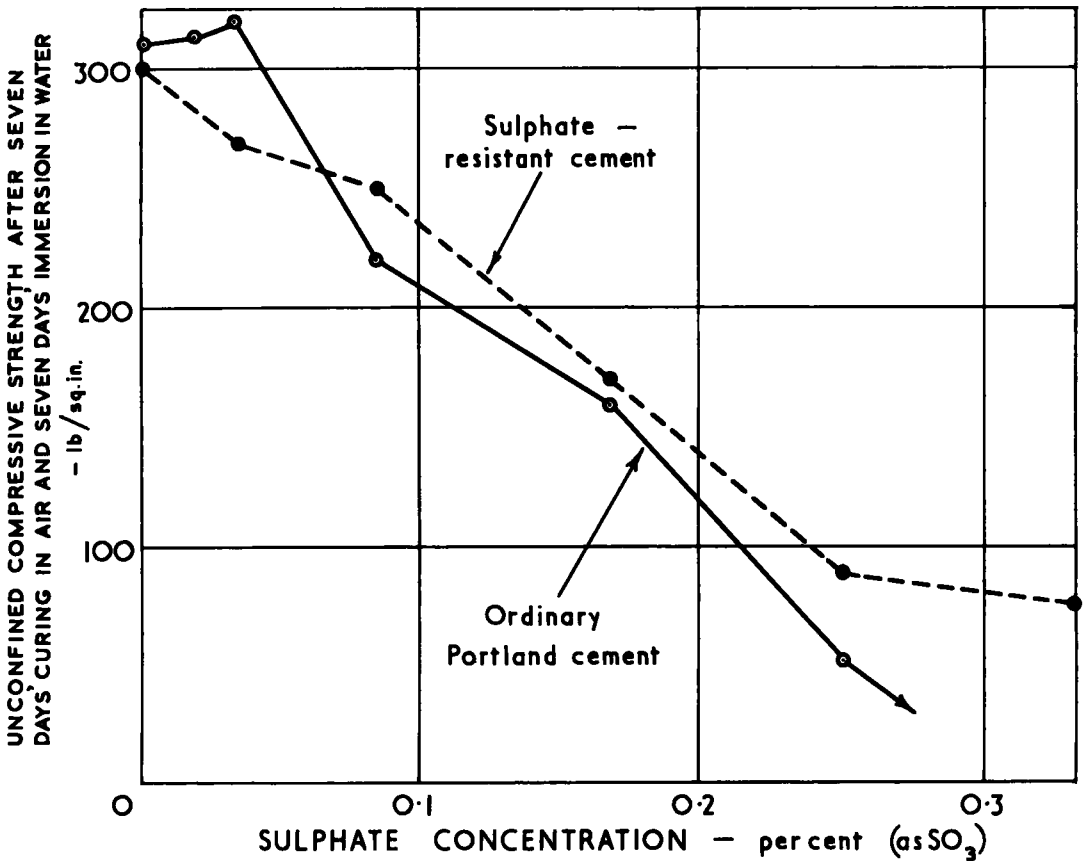


Figure 5. Effect of immersion in magnesium sulphate solution on the strength of boulder clay stabilized with ordinary portland cement and sulphate-resistant cement.

were obtained when it was absent, except when the moisture content of the clay was above 32 percent (i. e. some 6 percent above the plastic limit) (4).

Since an increase in the initial moisture content of the clay-cement appeared to have a beneficial effect, a series of tests was made in which two sets of specimens were prepared at moisture contents of 26 and 34 percent. The former is the moisture content at which the boulder clay would normally be stabilized (2 percent below the plastic limit of the clay-cement) while the latter is the highest moisture content at which it was found that specimens could be handled without deformation. Calcium sulphate in concentrations ranging from 0 to 7 percent (as SO₃) and 10 percent of ordinary portland cement were added.

The results (Fig. 3) confirm that at both moisture contents the presence of calcium sulphate in concentrations up to 7 percent (as SO₃) had little effect on the strengths of the normally cured specimens but after immersion the strengths of the specimens were greatly reduced at concentrations above 0.5 and 1.0 percent of SO₃ for initial moisture contents of 26 and 34 percent, respectively. Together with the previous results (Fig. 2) this suggests that as the sulphate content increases more moisture is required in the mixture to minimize the decrease in strength. However, the extent to which the moisture content of the mix can be increased is limited and, moreover, it seems likely that sulphate concentrations of the order of those measured in the profile would lead to loss in strength of the soil-cement mixture even if the moisture content of the mix was high.

In a further test to determine whether the effect of the calcium sulphate on the compressive strength of the clay-cement was reduced by the use of sulphate-resistant cement, specimens were prepared which were identical with the foregoing except that sulphate-resistant cement replaced ordinary portland cement. The 14-day strength of this set of specimens was measured only after immersion. The strengths (Fig. 3) were not significantly higher than when ordinary portland cement was used. However, as sulphate-resistant cement has a lower content of tricalcium aluminate than ordinary portland cement and as this constituent is mainly responsible for early strength, higher strengths might possibly have been obtained if the specimens had been tested at a greater age.

A limited number of tests similar to those described above was carried out on specimens stabilized with 10 percent of cement but in which magnesium sulphate replaced calcium sulphate. The results (Fig. 4) show that the effect of the magnesium salt was more marked, in that the immersed specimens containing more than 0.7 percent of the salt (as SO_3) completely disintegrated.

Effect of Immersion of Soil-Cement in Magnesium Sulphate Solution

In practice it is possible that a stabilized sulphate-free clay might be constructed on a sulphate-bearing foundation. Experiments were therefore made to determine the destructive effect on a clay-cement mixture of contact with a sulphate-bearing solution.

Unconfined compressive strength specimens were prepared from samples of the boulder clay mixed with 10 percent of ordinary portland cement and 26 percent of water compacted to an air-voids content of 5 percent. After curing for 7 days at

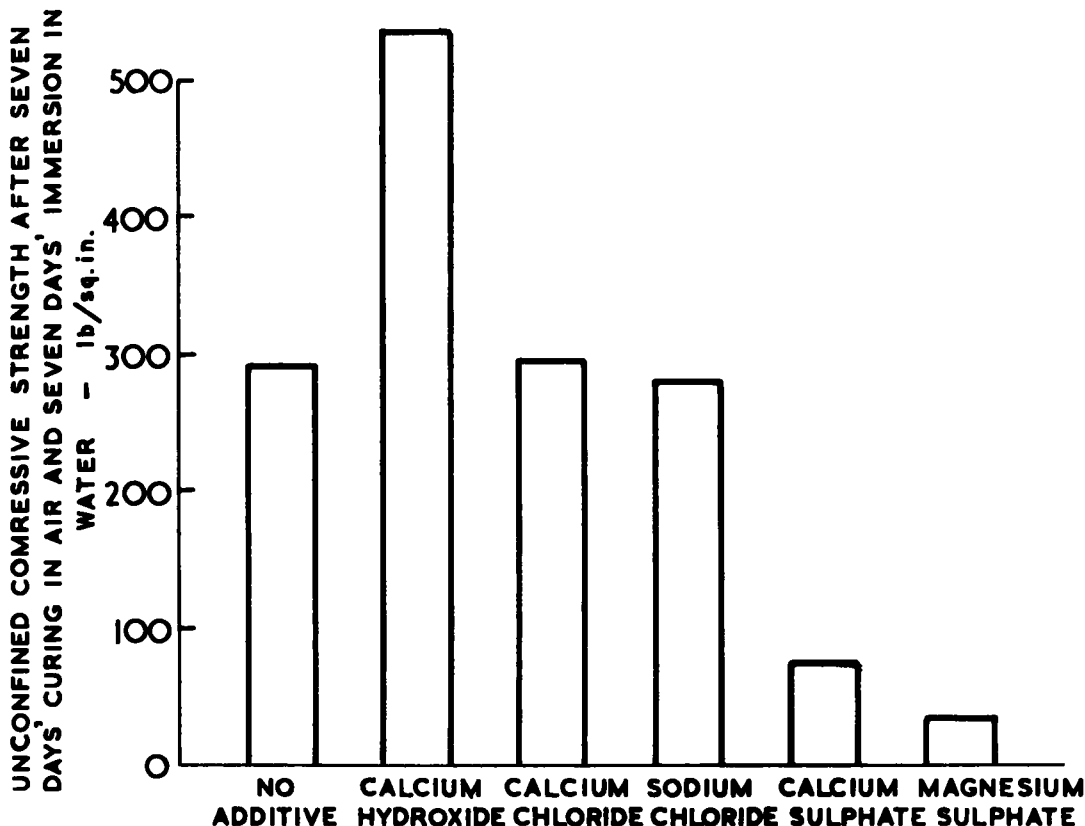


Figure 6. Effect of salts at equivalent concentrations on the strength of boulder clay stabilized with ordinary portland cement.

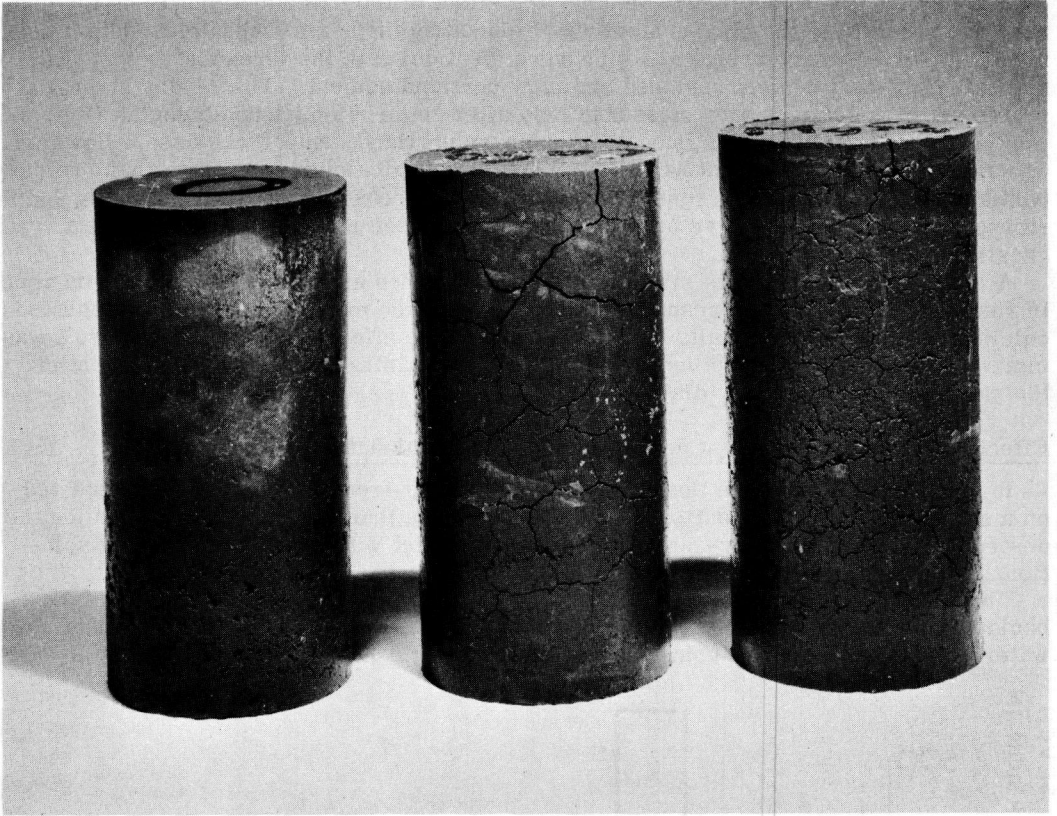


Figure 7. Effect of sulphates on soil-cement after immersion in water for seven days. (Left to right, control specimen, specimen + calcium sulphate, specimen + magnesium sulphate.)

constant moisture content and temperature these specimens were immersed in solution of magnesium sulphate of different concentrations for a further 7 days, and their compressive strengths were then determined. A parallel experiment was made using sulphate-resistant cement. The results (Fig. 5) showed that when the concentration of sulphate in the water exceeded 0.05 percent of SO_3 significant reductions in strength were obtained, and when 0.20 percent was present the strength was reduced by 50 percent. In four out of the six specimens the sulphate-resistant cement gave significantly higher strengths after immersion in water than did ordinary portland cement.

Investigation of a Possible Osmotic Pressure Effect

Clay-cement specimens were prepared using boulder clay with 10 percent of ordinary portland cement and admixtures of calcium hydroxide, calcium chloride, calcium sulphate, magnesium sulphate and sodium chloride. The specimens were then subjected to the immersion test. The amount of salt added was sufficient to provide the equivalent weight in grams per litre of water in the soil-cement. With the calcium chloride, sodium chloride and magnesium sulphate all the salt present would be in solution and, as they were at equivalent concentrations and are all strong electrolytes, they would give rise to equal osmotic pressures. In the case of the sparingly soluble calcium hydroxide and calcium sulphate insufficient water was present for the salts to go into complete solution, and a large proportion of the salts would be present in the solid form; loss in strength would therefore be more likely to arise from replacement

of the solid material by water than by osmotic pressure. The results show that only the specimens containing sulphates had lower strengths (Fig. 6) and exhibited signs of expansion and cracking (Fig. 7). It is concluded therefore that reduced strength is not due to internal stresses caused by osmotic pressures.

Effect of Partial Immersion in Water on Soil-Cement Containing Soluble Salts

To examine the effect on the strength of soil-cement of the crystallization of salts in the surface, caused by the capillary rise of moisture through a soil containing soluble salts, a soil-cement specimen was prepared from a soil from Abadan, Persia, by mixing with 10 percent of ordinary portland cement. This soil was chosen because it comes from an area where such crystallization effects are known to occur and also because it contained 1.2 percent of calcium sulphate (as SO_3) and 1.5 percent of sodium chloride (as Cl). The soil-cement specimen was allowed to cure at constant moisture content and temperature for 7 days and was then placed in water to a depth of a half-inch for several weeks during which time moisture was absorbed through the base of the cylinder and evaporated from the upper surfaces, causing a concentration of the soluble salts in the top of the specimens. Figure 8 shows the appearance of a specimen after two weeks; the upper surface had disrupted owing to crystal formation and had become so loose that the surface layers of the soil-cement could be easily scraped off with a penknife.

DISCUSSION OF THE EFFECT OF SULPHATES ON SOIL-CEMENT

The deleterious effect of sulphate-bearing ground-water on structures containing cement is well known, although cases where concrete road slabs are attacked are not of frequent occurrence in the United Kingdom. In the case of concrete building structures below ground level the problem has been dealt with in a publication from the Building Research Station (5), which classifies clay soils and ground-waters into the following three groups with respect to the risk of sulphate attack:

1. Sites with low sulphate content:

Ground-water	30 parts per 100,000 of SO_3
Clay	0.2 percent SO_3

2. Sites of moderate severity with regard to sulphate attack:

Ground-water	30 - 100 parts per 100,000 of SO_3
Clay	0.2 - 0.5 percent SO_3

3. Sites with high risk of sulphate attack:

Ground-water	100 parts per 100,000 of SO_3
Clay	0.5 percent SO_3

The results obtained in the investigations described in this paper indicate that

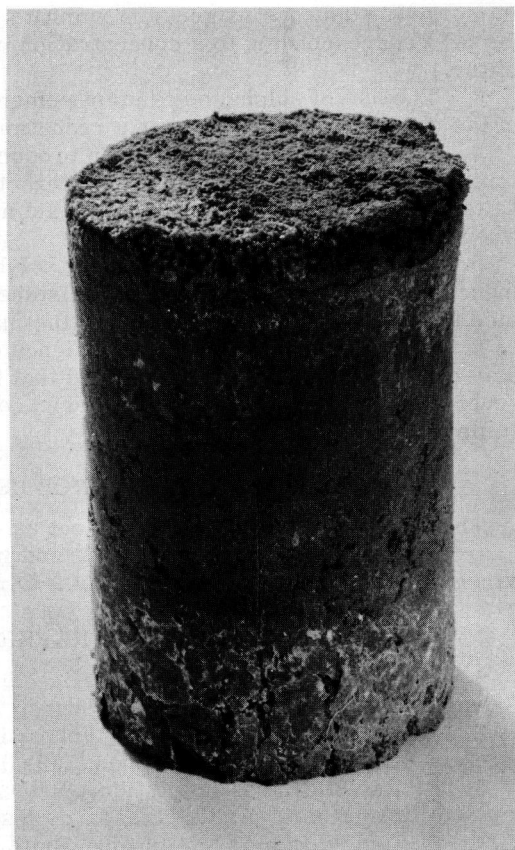


Figure 8. Specimen of soil-cement made from soil containing soluble salts, showing disruption of the top surface caused by crystal formation.

there is a serious risk of the deterioration of clay-cement mixtures in contact with contaminated clay or ground-water if sulphate is present in concentrations of the same order as those in groups 2 and 3 of the above classification. Sufficient site experience is not yet available, however, to indicate whether the numerical values quoted are directly applicable to sites where clay-cement road bases are to be used, and further research is required on this problem.

Damage arising from the crystallization of salts would be expected wherever salts (not necessarily sulphates) were present and the climatic conditions were such (i. e. long dry periods) as to cause the salts to move with the moisture into the surface and crystallize. The damage caused by this action can be minimized by sealing the surface so that excessive evaporation losses do not occur.

CONCLUSIONS

The following conclusions have been drawn from the work described:

1. In experiments in which calcium and magnesium sulphates were added to salt-free clay, the presence of magnesium sulphate in the clay in concentrations above 0.75 percent (as SO_3) by weight of the soil resulted in disintegration when the cement-stabilized clay was immersed in water. Calcium sulphate in concentrations greater than 1 percent (SO_3) considerably reduced the compressive strength, but the reduction was lessened by increasing the moisture content of the mix.
2. The strength of a clay-cement mixture was reduced by more than 50 percent when immersed in aqueous magnesium sulphate solutions of 0.20 percent concentration (as SO_3) corresponding to a concentration of 2,000 parts per million of SO_3 in ground-water.
3. The use of sulphate-resistant cement instead of portland cement as the stabilizer of the clay soil did not result in a reduction in the action of the sulphates.
4. The effect of the sulphates in producing a loss in strength of the clay-cement on immersion in water was due to the interaction of the sulphate and the cement, and salts which did not react with cement did not seriously affect the strength of soil-cement when it was totally immersed in water.
5. In the case of a clay containing soluble salts a loss in strength was obtained by inducing an upward movement of moisture so that the salts were deposited in the surface where they caused disruption of the material.
6. There is little practical experience of the attack by solutions of sulphates on soil-cement, but it would be expected that the damage to soil-cement would be not less severe than that which would be experienced by an average quality of concrete in the same circumstances.

ACKNOWLEDGMENTS

The work described was carried out as part of the programme of the Road Research Board of the Department of Scientific and Industrial Research, United Kingdom. The paper is published by permission of the Director of Road Research.

REFERENCES

1. Bessey, G. E., and Lea, F. M., "The Distribution of Sulphates in Clay Soils and Ground-Water." Proc. Inst. Civ. Engrs, 2 (1), 159-81 (1953).
2. Jenny, H., "Factors of Soil Formation: A System of Quantitative Pedology, McGraw-Hill, New York and London (1941).
3. British Standards Institution, British Standard 1924, 1957. "Methods of Test for Stabilized Soils." British Standards Institution, London (1957).
4. British Standards Institution, British Standard 1377, 1948, "Methods of Test for Soil Classification and Compaction." British Standards Institution, London (1948).
5. Building Research Station, "Concrete in Sulphate Bearing Clays and Ground-Waters." Building Research Station, Digest No. 31, H. M. Stationery Office, London (1951).