Expansion of Cement-Stabilized Minestone due to the Oxidation of Pyrite

M. D. A. Thomas, R. J. Kettle, and J. A. Morton

Despite the successful use of cement-stabilized minestone (CSM) in road construction, some CSM pavements have suffered deformation attributed to the expansion of the CSM layer. Three sites where deformation has occurred are described, and evidence from field samples is presented. Chemical analyses of the retrieved samples showed that the materials had reduced iron sulfide and increased sulfate contents when compared with reported values for the raw minestones. Examination of thin sections suggested that much of the distress within the CSMs was associated with deteriorating pyritic minestone particles. In addition, sulfate minerals were frequently found in close association with both the pyritic minestone and the products of cement hydration. X-ray diffraction analysis and scanning electron microscopy produced further evidence of sulfate minerals in the cracks of the CSMs. It is concluded that the long-term expansion of CSM is due to the oxidation of pyrite, a component of the raw minestone, to form sulfate minerals. Not only does the ongoing sulfate production increase the potential for sulfate attack on the products of cement hydration, but the reduced mineral density of the sulfate products generates crystallization pressures within the CSM.

Minestone, or unburned colliery shale, is the by-product of the coal mining industry and is principally composed of the shales, mudstones, and seatearths closely associated with the coal seam. The mineralogy is dominated by quartz and a variety of clay minerals (1), commonly kaolinite, illite, chlorite, and a mixed-layer illite-montmorillonite.

In the United Kingdom, minestone is currently produced at the rate of 60 Mtonnes a year with existing stockpiles totaling 3000 Mtonnes (2). Approximately 5 Mtonnes are used each year through a variety of outlets (3), many of which are within the construction industry.

Early studies (4) of cement-stabilized minestone (CSM) indicated its potential as a structural pavement layer. Subsequent field trials (5,6) also met with some success and, following improvements in the availability of suitable mix-in-place and continuous-mixing plant, CSM has been used as the main structural layer in many applications within British Coal including hardstandings, coal stacking areas, and haul roads (6–8). CSM has also been used in the construction of public roads (9), particularly in southeast England where the supplies of traditional road-building aggregates are limited.

M. D. A. Thomas, Department of Materials, Imperial College of Science and Technology, c/o Building Research Station, Garston, Werts WD2 9JR, United Kingdom. R. J. Kettle, Department of Civil Engineering, and J. A. Morton, Department of Geological Sciences, University of Aston, Birmingham B4 7ET, United Kingdom.

The design of pavements incorporating CSM is usually carried out in accordance with Road Note 29 (10) and the construction is controlled by the requirements of the Department of Transport (11). CSM is required to achieve a 7-day crushing strength of 3.5 MPa for cubic specimens. Durability requirements include proven resistance to a British Standard immersion test (12) and the Transport and Road Research Laboratory frost heave test (13). In addition, the raw minestone must satisfy grading and plasticity criteria and must not have an acid-soluble sulfate content in excess of 1 percent (as SO_4).

Despite the rigorous testing employed before use of CSM, some CSM structures have suffered considerable disruption due to swelling (14,15). The most dramatic case occurred within a few days of compaction of the CSM layer (14) and was due to short-term swelling mechanisms inherent in mudrocks (16,17). In other cases, failure occurred following reasonable periods of satisfactory performance; the examination of three such pavements forms the subject of this study.

SITES EXAMINED

Three failed cement-stabilized pavements were made available for detailed examination, one in northeast England, the other two in Kent. All three pavement structures had performed adequately for the first year. Distress was first noticed during the summer between 1 and 2 years after construction.

Lorry Park

A lorry park was constructed in 1981 using minestone from the Wardley Colliery in northeast England both as a compacted unbound layer to achieve grade and as a 150-mm cement-stabilized base layer. The Wardley minestone had been extensively examined (18) and was considered suitable for use as a cement-stabilized material. The cement content of 8 percent produced a mean 7-day crushing strength of 5.75 MPa for the test cubes made at the site (8). This value is in excess of the minimum 3.5 MPa required by the Department of Transport (11).

Despite the apparent suitability of the material, the parking area showed some distress at a construction joint after 12 to 18 months of service. Excavation at the location of the distress showed that movement of one or both of the CSM layers had occurred adjacent to the construction joint. Although the distress may have been exacerbated by a poorly finished con-

struction joint, the movement was undoubtedly the result of CSM expansion. An intact slab from either side of the joint was removed for laboratory examination.

Car Park

A large industrial car park was constructed in two distinct phases using minestone from the Snowdown Colliery in southeast England. Although comprehensive construction details are not available, it is known that the minestone was blended with 30 percent waste sand before cement stabilization. A cement content of 8 to 10 percent was used throughout.

The suitability of Snowdown minestone has been well reported (9). However, after approximately 12 months, the second phase suffered visible disruption in the form of asphalt ridges, often 50 mm high, in the wearing course. When cores were cut through the ridges, a discontinuity was found extending from the ridge through the CSM layer at a slope of approximately 45° (Figure 1). Evidence of matching fractured particles on each side of a discontinuity suggested that the problem stemmed from shear failure of the CSM rather than a poorly formed construction joint. The shear stresses were produced by the horizontally constrained expansion of the CSM layer. Cores were also taken from the failure zone, and these appeared to be intact.

The first phase was still performing adequately with no visible signs of distress. Nevertheless, cores were taken from this phase to compare them with those from the second phase.

School Playground

The material used to surface a school playground was again obtained from the Snowdown Colliery and also contained 30 percent waste sand and a cement content of 8 percent. Eighteen months after construction, visible deterioration of the structure occurred in the form of asphalt override at the site of concrete drains that subdivided the playing areas into smaller bays. The drains were fractured in many places. The cause of distress was again attributed to the expansion of CSM (Figure 2). An intact slab of CSM was removed for laboratory investigation. It is noteworthy that as the slab dried following excavation, it developed a white crystalline efflorescence. A similar but less pronounced effect was noted for the samples taken from the other sites.

In a few isolated cases, disintegrating aggregate particles were detected in the samples removed from the Kent sites. The disintegration took the form of crumbling and splitting along laminae. On one occasion, yellow deposits were evident in the laminations of such particles.
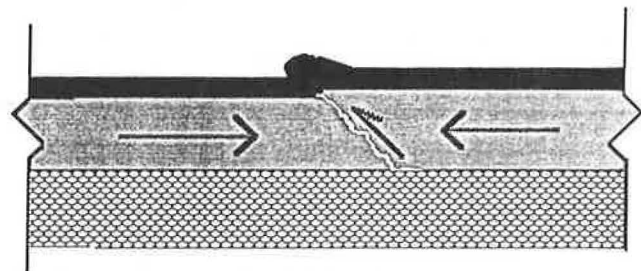

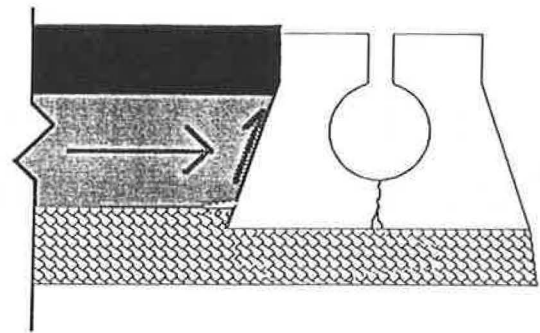FIGURE 1 Mode of failure in Snowdown CSM: car park.

FIGURE 2 Mode of failure in Snowdown CSM: school playground.

TABLE 1 EQUIVALENT CUBE STRENGTHS AND SULFUR CONTENTS FOR COLLECTED CSM SAMPLES.

Site	Equivalent Cube Strength (MPa)	Forms of Sulfur (% SO_3)		
		Total	Pyritic	Sulfate
Lorry park	4.56	1.21	0.65	0.40
Car park, Phase 1	3.01	2.10	1.45	0.45
Car park, Phase 2	2.38	3.64	2.70	0.63
School playground	2.65	2.80	2.05	0.58

LABORATORY EXAMINATION OF CSM SAMPLES

In the laboratory the following tests were employed to assess the CSM samples:

1. Compressive strength;
2. Total, pyritic, and sulfate sulfur contents;
3. X-ray diffraction analysis of CSM and, where possible, crack infill material and efflorescence;
4. Preparation and examination of thin sections; and
5. Examination of crack surfaces by scanning electron microscopy.

Specimen preparation and test methods are described elsewhere (17). Table 1 shows the results of the strength tests and gives the sulfur values.

DISCUSSION OF RESULTS

Strength

The CSM sampled from the lorry park recorded compressive strength in excess of the specified 3.5 MPa. However, the equivalent cube strength of the CSM was considerably lower than the reported 7-day strength of 5.75 MPa for site-prepared cubes (8).

The compressive strengths of the cores taken from the three CSM sites using Snowdown minestone were all below the required 3.5 MPa. Although no strength data are available from site-prepared cubes, previous field trials have reported 7-day strengths in excess of 7 MPa for Snowdown CSM cubes compacted at the average field density (19). In addition, blending 30 percent waste sand can increase the compressive strength of Snowdown CSM by at least 20 percent (20).

At all three sites, the CSM remote from the area of disruption was intact. However, evidence based on compressive strength determinations would suggest a degree of strength loss in this CSM as well.

Chemistry

The sulfur chemistry of Wardley minestone was determined before its use at the lorry park (*18*):

Form of Sulfur	Percent SO₃
Total	1.4
Pyritic	0.96
Acid-soluble	<0.1
Water-soluble	<0.1

The main anomaly between these data for the raw minestone and the determinations made for the CSM (Table 1) is the distribution of the total sulfur between pyritic and sulfate sulfur. Allowing for a typical sulfate content of 2 percent for cement (*21*) and for a cement content of 8 percent as used at the lorry park (*8*), the sulfate contribution of the Wardley minestone in the CSM increased to 0.24 percent (or 0.27 percent by mass of raw shale). Conversely, the measured pyritic sulfur content decreased to 0.65 percent, which is equivalent to 0.70 percent by mass of raw shale.

Chemical analyses of the raw Snowdown minestones used in the Kent sites are not available. An examination of the chemical data for the Snowdown CSM shows disparities between the sulfur contents (total, pyritic, and sulfate) for the CSM used in the two phases of the car park—the Phase 1 material having less sulfide or sulfate-bearing minerals. All three Snowdown CSMs have higher levels of sulfide and sulfate than the Wardley CSM. This is in spite of the considerable dilution due to the sand addition in the Snowdown CSMs.

X-ray Diffraction Analysis

The x-ray diffractometer traces of the three CSM sites are similar, and the trace from the CSM used in the construction of the second phase of the car park is shown in Figure 3. The principal peaks can be assigned to the quartz and the various clay minerals normally associated with minestone (*1*) and also to calcite ($CaCO_3$). The majority of the calcite is undoubtedly the result of the carbonation of the portlandite [$Ca(OH)_2$] released during the hydration of cement. The absence of a portlandite trace would suggest that little portlandite remains after 12 to 18 months' exposure. The fairly broad peak at an angle of 32° may be due to a combination of siderite ($FeSO_4$) and cement clinker minerals.

The only discernible differences between the sample traces for the Snowdown and Wardley CSMs were enhanced quartz peaks and subsequently reduced clay peaks for the Kent materials (resulting from the addition of a waste sand to the minestone before stabilization). A comparison between the relative peak heights of quartz and clay minerals for the two phases from the car park suggests an increased quartz content for the first phase.

During the preparation of thin sections from the intact samples of Snowdown CSM, cracks were detected in the cut surfaces. In many cases, a white crystalline infill material was found. Where possible, this material was removed from the cut face opposite that used for the thin section and analyzed by x-ray diffraction. A typical diffractogram trace of material removed from a crack in the CSM from the car park is shown in Figure 4. Some of the peaks correspond to those shown in Figure 3, because it was impossible to avoid removing some of the main body of material. The most noticeable differences between the two traces are the additional peaks associated with gypsum ($CaSO_4 \cdot 2H_2O$) and ettringite ($3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 31H_2O$) and the increased heights of
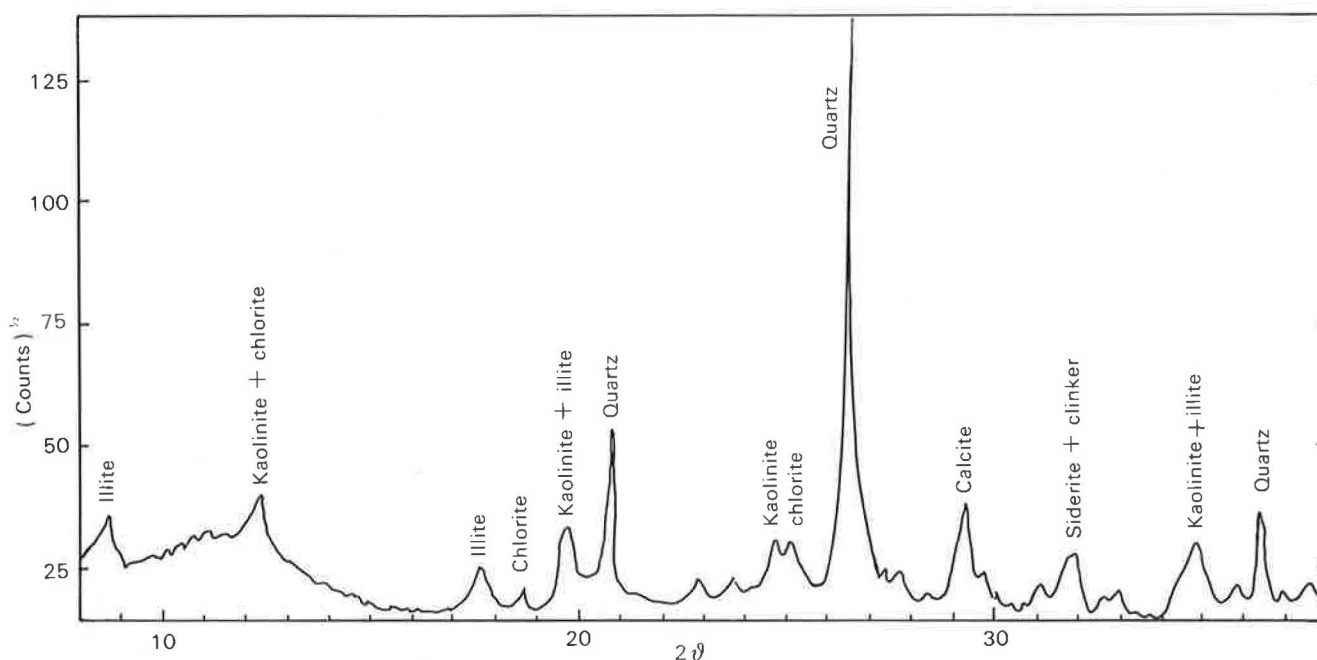

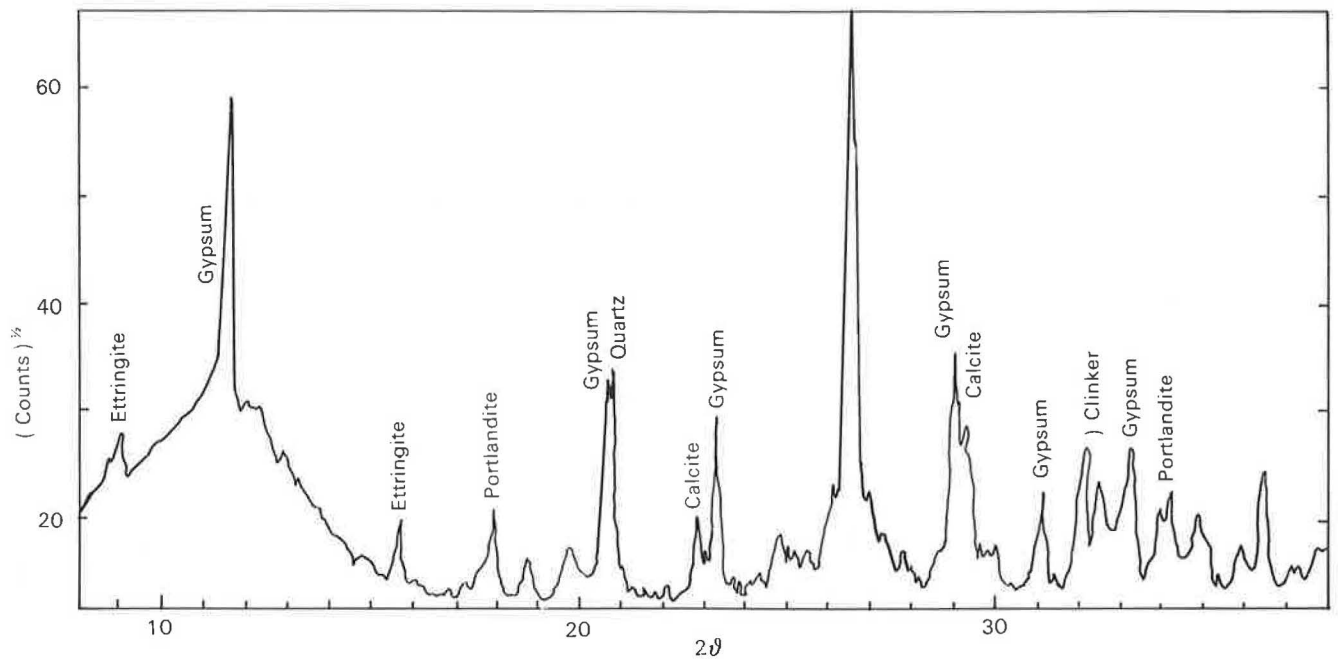**FIGURE 3 Diffractogram for CSM from car park, second phase.**

FIGURE 4 Diffractogram for crack infill material taken from car park, second phase.
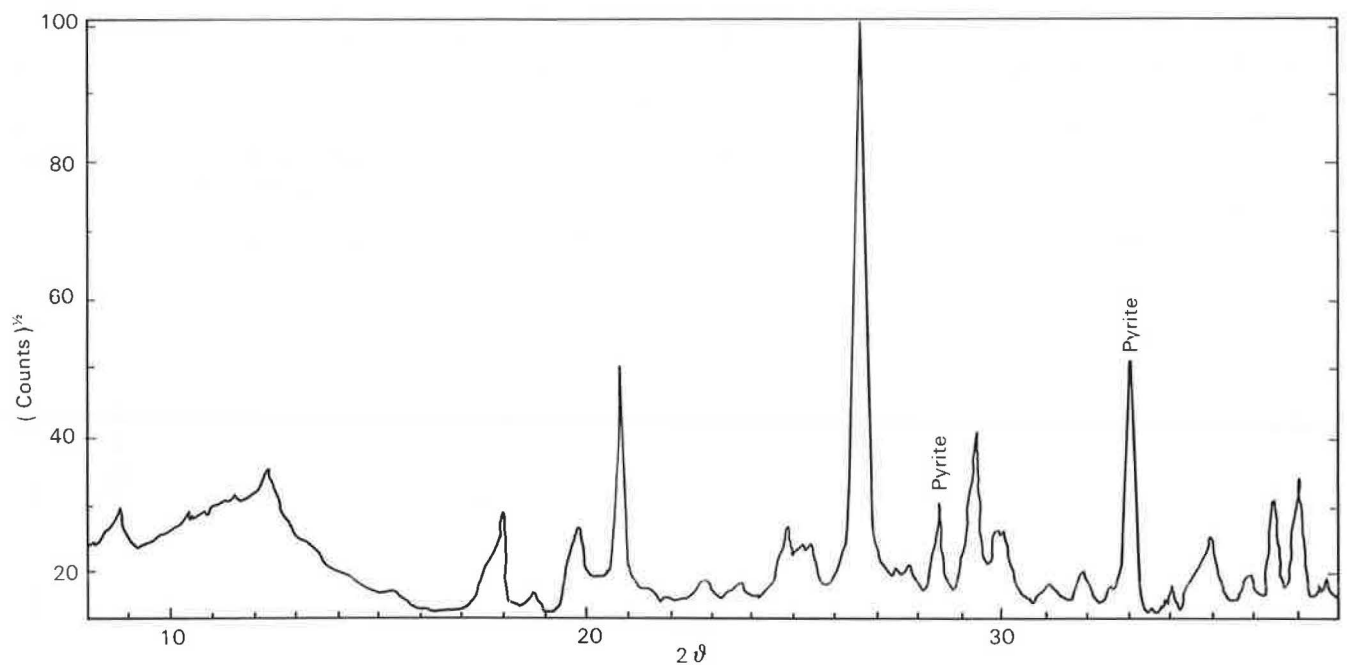

FIGURE 5 Diffractogram for disintegrated shale particle taken from school playground CSM.

the calcite and clinker mineral peaks. The minerals gypsum and ettringite were not always identified in association with one another, both minerals being separately identified in crack infill material.

The efflorescence from the Snowdown CSMs was also successfully removed and analyzed, the diffraction peaks corresponding mainly to the mineral thenardite (Na_2SO_4). Where disintegrating aggregate particles were detected, these were removed for analysis, and they invariably gave traces corre-

sponding to highly pyritic shales (Figure 5). Attempts were made to remove the material between the laminations, and although no positive identification could be made, the presence of the mineral jarosite $[KFe_3(SO_4)(OH)_6]$ is tentatively indicated in Figure 6. The peak around 29° in Figure 6 may not be assigned to gypsum in the absence of the principal gypsum peak at 11.7°. Many peaks on this trace are difficult to interpret, especially the large peak at 32°, although this may be partially due to siderite ($FeCO_3$).
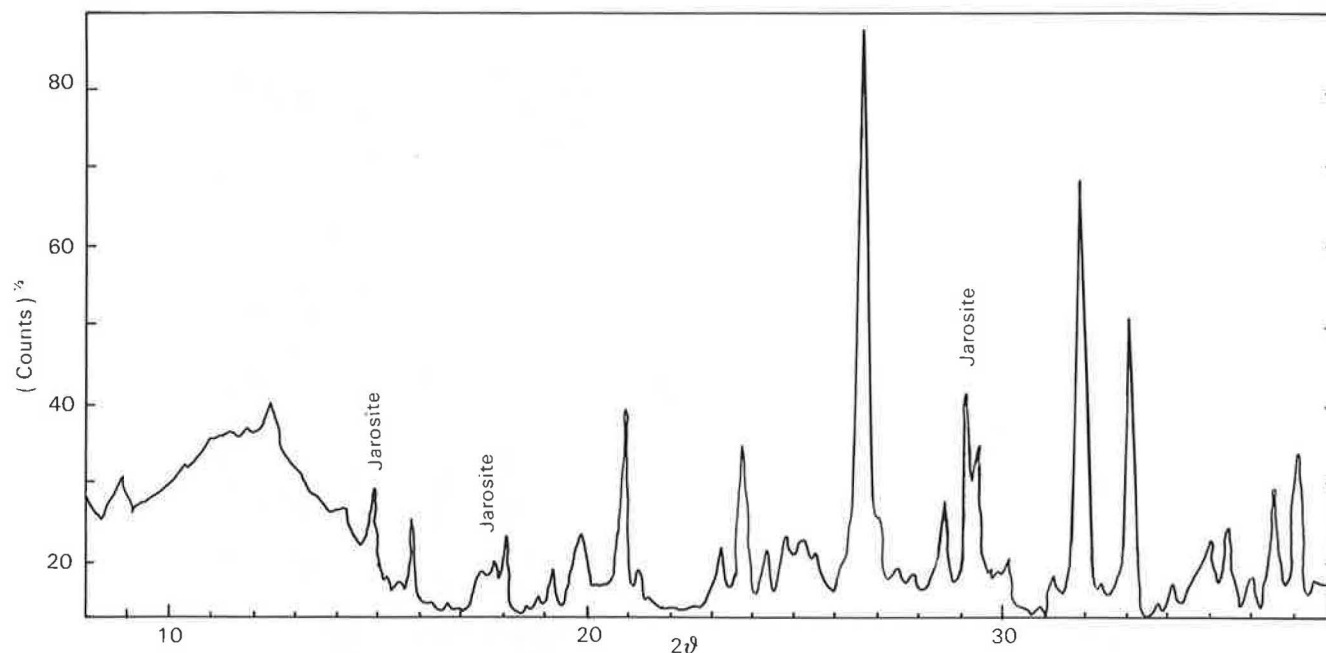
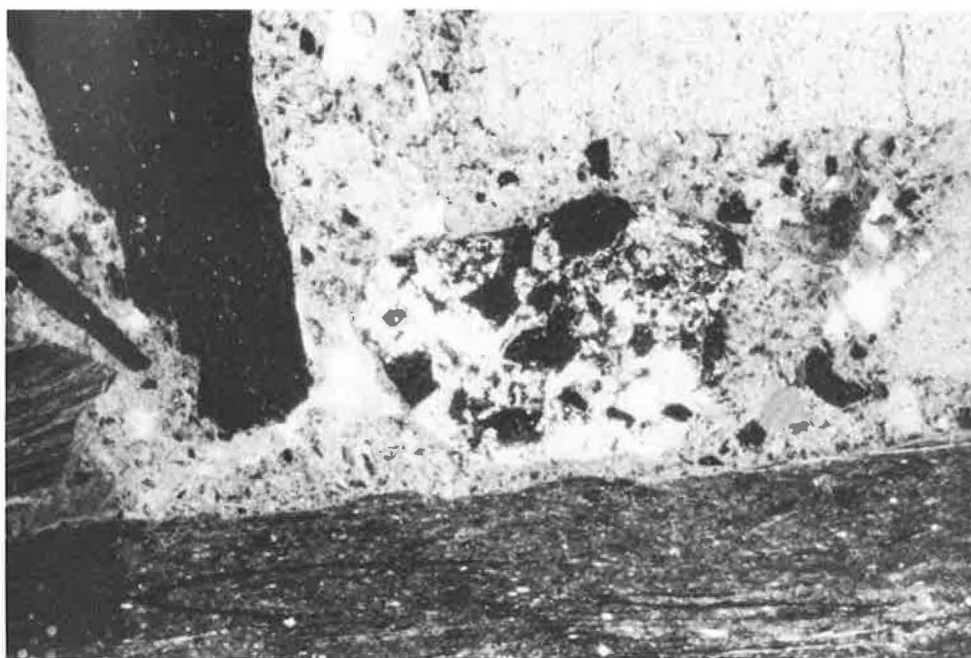**FIGURE 6   Diffractogram for material taken from between laminations of disintegrated shale particle.**

FIGURE 7   Photomicrograph of CSM from school playground (width of view 13 mm).

Examination of Thin Sections

Examination of petrographic sections taken from all three sites showed the materials to be extensively cracked. Because the preparation of material for thin sectioning requires it to be dried before resin impregnation, many of the cracks surrounding aggregate particles may result from the shrinkage of the aggregate. This suggests that much of the material in colliery shale is moisture sensitive. Coal was also identified in the CSM matrix.

Examination by reflected light revealed that many of the aggregate particles contained finely grained pyrite. In many cases these particles had undergone considerable deterioration and internal cracking. Figure 7 is a photomicrograph of a section through the CSM from the school playground, the center of which is dominated by a disaggregated particle of pyritic shale. The void spaces are a result of material loss during specimen preparation. However, there is some evidence of secondary mineral formation within the smaller cracks and surrounding some of the remaining shale particles. A

FIGURE 8   SEM photomicrograph (× 5,000) of pore infill material in Snowdown CSM.

small fraction of this mineral was resolved to be gypsum but the larger part remains unidentified.

Virtually no portlandite was detected in any of the sections. There was, however, an abundance of calcite as a result of the carbonation of portlandite. Gypsum was often found in association with the calcite. Hydrated cement minerals and cement clinker minerals were also present. In a few isolated cases, ettringite could be identified in close association with these minerals.

A comparison of the sections from the Wardley CSM and the three Snowdown CSMs showed the principal difference to be the abundance of quartz particles in the sections from Kent due to the addition of sand. These additional quartz particles tended to be in the size range of 150 to 425 microns. A point count was undertaken for the materials from the two phases of the car park. The first-phase material recorded approximately 10 percent more counts for quartz.

Scanning Electron Microscopy

Where crack infill material was removed for x-ray diffraction analysis, the associated crack surfaces were examined by scanning electron microscopy. Figure 8 shows such a crack surface taken from the CSM used in the construction of the school playground. The needle-shaped crystals are ettringite, which was confirmed by a dispersive x-ray analysis that measured calcium, sulfur, and aluminum as the most predominant elements (these being the elemental oxides of ettringite).

EXPLANATION OF IN SITU BEHAVIOR

At all three sites where failure of the pavement had occurred, the mode of failure was consistent with the expansion of the

CSM layer. The expansion resulted in an overall strength loss throughout the CSM, with the materials from Kent failing to retain sufficient strength to satisfy the 7-day strength requirement specified by the Department of Transport (*11*) at the time of construction.

The examination of mineralogical slices suggests that much of the minestone fraction is susceptible to certain volume changes when subjected to fluctuations in moisture content. In particular, the expansive clay minerals and any residual coal may generate expansive movements. However, in view of the time scale and season during which the pavements failed (the CSM was in a dry state at all three sites), it seems unlikely that the disruption can be attributed to moisture movements.

The decrease in the pyritic sulfur content and the corresponding increase in the total sulfate content of the Wardley CSM imply that the oxidation of the pyrite present in minestone continues beyond cement stabilization and compaction. Although no such comparisons are available for the Snowdown minestone, the presence of deteriorated, sulfide-rich particles in the Snowdown CSM would suggest that similar geochemical changes are prevalent. These particles must have been intact at the time of mixing to avoid dispersion of the deteriorated fragments throughout the CSM matrix.

The oxidation of pyrite is initiated by contact with moist air, and the first products formed are ferrous sulfate and sulfuric acid:

$$2FeS_2 + 2H_2O + 7O_2 \longrightarrow 2FeSO_4 + 2H_2SO_4 \qquad (1)$$

Further oxidation of the ferrous sulfate produces ferric sulfate:

$$4FeSO_4 + O_2 + 2H_2SO_4 \longrightarrow 2Fe_2(SO_4)_3 + 2H_2O \qquad (2)$$
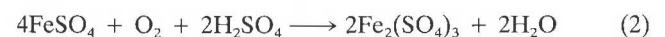
The ferric sulfate, a strong oxidizing agent, may reduce further pyrite:

$$7Fe_2(SO_4)_3 + FeS_2 + 8H_2O \longrightarrow 15FeSO_4 + 8H_2SO_4 \qquad (3)$$

Reaction 2 cannot proceed chemically in the acidic environment normally associated with this process (*22*), and at low pH, the reaction is thought to occur because of the action of autotrophic bacteria of the *Ferrobacillus-Thiobacillus* type (*23*). Because of the presence of cement, the pH of CSM pore fluid is likely to remain alkaline, and thus the oxidation of ferrous sulfate may occur abiotically.

These reactions are common in coal mines (*24*) and on colliery spoil tips, although the extent to which they occur in CSM is not known. The oxidation of pyrite, even due to the occurrence of Reaction 1 alone, has serious engineering implications for CSM.

First, the production of sulfate salts of significantly lower density than pyrite leads to an increase in the volume of solids. If the crystallization of these minerals is confined, then considerable pressures are produced. These crystallization pressures are sufficient to degrade minestone particles and would undoubtedly lead to expansion of CSM.

The volume increase associated with the conversion of pyrite to jarosite, a process identified in the Snowdown CSM, is reported to be 115 percent and that of pyrite to ferric sulfate is 170 percent (*22*). The conversion of calcite to gypsum by reaction with the sulfuric acid released during pyrite oxidation is a known cause of heave in pyritic shale fills (*25,26*). With the exception of some of the Staffordshire minestones, most minestones contain insufficient calcite for this mechanism to prevail (*17*) in unbound minestone.

The second consequence of pyrite oxidation is the increase in the sulfate content of the CSM, which increases the potential for sulfate attack on the minerals of cement hydration. The combination of sulfate minerals with tricalcium aluminate to form ettringite and with calcium hydroxide to form gypsum is well established in concrete technology (*21*). The abundance of sulfuric acid that results from pyrite oxidation exacerbates the problem of sulfate attack. The acid will combine with either calcium hydroxide or calcite (resulting from the carbonation of calcium hydroxide) to form further gypsum. The formation of both ettringite and gypsum leads to considerable volume increase.

Both ettringite and gypsum have been detected in cracks in CSM. Gypsum often forms in association with calcite in CSM. This may result from the simultaneous action of sulfate ions and carbon dioxide on the calcium hydroxide released during cement hydration, forming gypsum and calcite, respectively. Alternatively, the gypsum may result from sulfuric acid attack on the calcite following carbonation.

Distress due to both pyrite oxidation and sulfate attack was detected in all the CSM samples tested, but was far more prevalent for the Snowdown CSM. The increased distress for these CSMs is due to the higher level of sulfur present, both as sulfide and sulfate minerals, in the constituent raw minestone. The survival of the CSM from the first phase of the Pfiser car park may be due to a combination of its reduced sulfur chemistry and increased sand addition. Continuing action of the sulfur-bearing mineralogy may eventually lead to failure.

It is worth noting that the Wardley CSM failed only at the site of a construction joint and that the CSM remote from this joint retained considerable strength. Other studies, both of site applications (*8*) and of laboratory-produced specimens (*17*), have shown Wardley CSM to be a durable material. There is little doubt that the presence of pyrite and sulfates in the raw minestone leads to an expansion of the CSM, but it is improbable that this expansion would have led to disruption without the assistance of a poorly finished construction joint.

The criteria currently used to assess the suitability of a particular minestone source for use in CSM make no allowance for its pyritic sulfur content. Many minestones have tolerable levels of sulfur-bearing mineralogy and can produce strong, durable CSMs (*17*). The need to establish effective criteria capable of identifying these minestones cannot be overemphasized.

REFERENCES

1. R. J. Collins. A Method for Measuring the Mineralogical Variation of Spoil from British Collieries: *Clay Materials*, Vol. 2, 1976, pp. 31–50.
2. *Report of Aggregates and Waste Materials*. Working Group, CP31/73, Building Research Establishment, 1973.
3. A. K. M. Rainbow, ed. *International Symposium on the Reclamation, Treatment and Utilization of Coal Mining Wastes*. National Coal Board, London, 1984.
4. R. J. Kettle and R. I. T. Williams. Preliminary Study of Cement Stabilised Unburnt Colliery Shale. *Roads and Engineering Construction*, Vol. 47, No. 559, 1969, pp. 200–206.
5. R. J. Kettle and R. I. T. Williams. Colliery Shales as a Construction Material. *Proc., International Conference on Use of By-Products and Wastes in Civil Engineering*, Vol. 2, Laboratoire Central des Ponts et Chaussées, Paris, 1978, pp. 475–481.
6. D. A. Tanfield. Construction Uses for Colliery Shale. *Contract Journal*, Jan. 1978, pp. 141–143.
7. A. K. M. Rainbow. Colliery Spoil—Its Production, Properties, and Use in a Cement Stabilized Form. Seminar on Waste Materials in Concrete. *Cement and Concrete Research*, 1982.
8. W. Sleeman. Practical Application of Cement Bound Minestone within the British Coal Mining Industry. In *Proc., International Symposium on Reclamation, Treatment, and Utilisation of Coal Mining Wastes*, National Coal Board, London, 1984, pp. 53.1–19.
9. R. J. Kettle. The Improvement of Colliery Spoil. *Quarterly Journal of Engineering Geology*, Vol. 16, 1983, pp. 221–229.
10. *A Guide to the Structural Design of Pavements for New Roads*. Road Note 29. U.K. Transport and Road Research Laboratory, Crowthorne, Berkshire, England, 1970.
11. *Specification for Road and Bridge Works*. Department of Transport, London, 1977.
12. *Methods of Test for Stabilised Soils*. BS1927. British Standards Institution, 1975.
13. D. Croney and J. Jacobs. *The Frost Susceptibility of Soils and Road Materials*. Report LR90. U.K. Transport and Road Research Laboratory, Crowthorne, Berkshire, England, 1970.
14. T. V. Byrd. The Sad Canterbury Tale. *New Civil Engineer*, Nov. 1980.
15. J. A. Morton, R. J. Kettle, and M. D. A. Thomas. Some Experimental Observations on the Potential Expansion of Cement Bound Minestone. In *Proc., International Symposium on Reclamation, Treatment, and Utilisation of Coal Mining Wastes*, National Coal Board, London, 1984, pp. 56.1–8.
16. A. T. McNulty. *Durability Criteria for Cement Bound Minestone.* Ph.D. thesis. University of Aston, England, 1985.
17. M. D. A. Thomas. *The Performance of Cement Stabilised Minestone.* Ph.D. thesis. University of Aston, England, 1986.
18. G. Berry. *Report on an Investigation into the Cement Stabilisation of Unburnt Spoil and Tip Washery Discard from the Former Wardley*

Colliery, Northeast Area. Report No. YRL13461. National Coal Board, London, 1981.

19. R. J. Kettle. The Use of Colliery Shale in Highway Construction. In *Proc., International Conference on Materials of Construction for Developing Countries*, Thailand, 1978.

20. M. D. A. Thomas. *Swelling Phenomena in Cement Stabilised Minestone*. Interim Report B. University of Aston, England, 1985.

21. A. M. Neville. *Properties of Concrete*, 3rd ed. Pitman Books Ltd., London, 1981.

22. E. Penner, J. E. Gillot, and W. J. Eden. Investigation of Heave in Billings Shale by Mineralogical and Biochemical Methods. *Canadian Geotechnical Journal*, Vol. 7, 1970, pp. 333–338.

23. K. L. Temple and E. W. Delchamps. Autotrophic Bacteria and the Formation of Acid in Bituminous Coal Mines. *Applied Microbiology*, Vol. 1, No. 5, 1970, pp. 255–258.

24. S. I. Kuznetsov, M. V. Ivonov, and N. N. Lyalikova. *Introduction to Geological Microbiology* (C. H. Oppenheimer, ed.), McGraw-Hill, New York, 1963.

25. A. B. Hawkins and G. Pinches. Timing and Correct Geochemical Testing of Soils/Weak Rocks. Presented at Engineering Group of the Geological Society 20th Regional Meeting on Site Investigation Practice: Assessing, University of Surrey, 1984.

26. P. J. Nixon. Floor Heave in Buildings Due to the Use of Pyritic Shales as Fill Material. *Chemistry and Industry*, Vol. 4, March 1978, pp. 160–164.