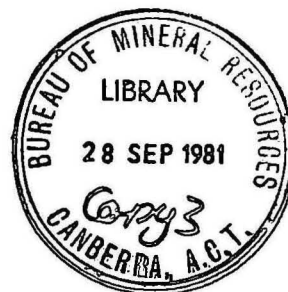


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BUREAU OF MINERAL RESOURCES, GEOLOGY AND GEOPHYSICS

RECORD 1981/42

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RECORD

Report on pyritic aggregate and the
cause of warping in concrete paving
flags, Parkes Place,
Canberra, A.C.T.

by

A.D. Haldane

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SUMMARY

The investigation reported herein arose from a request from the Department of Housing and Construction for advice on the possible adverse effects of the use of pyritic aggregate in concrete and whether such usage could be related to the warping of concrete paving that had occurred at Parkes Place, A.C.T.

The construction of the paved area, and the nature of the pavement warping are described briefly. Samples taken from paving flags, bedding mortar, concrete base and salt encrustation were subjected to chemical, X-ray, electron microscope, optical thin section, and physical examination.

The paving flags were found to contain noticeably higher levels of total sulphate, water (above 105⁰) and carbonate than the bedding mortar or concrete base. The salt encrustation was identified as ettringite and its microscopic distribution is described.

A prior suggestion that sulphate impurity in the aggregate used for the concrete base had leached upward into the paving slabs, where it formed ettringite thus causing warping by differential expansion, is shown to be untenable.

It is concluded that the use of clean pyritic aggregate in concrete mixes is not likely to cause failure of the resulting concrete by the ettringite reaction, and that the cause of warping of the concrete flags of Parkes Place was the use of a high proportion of sulphate-rich cement in the manufacture of the paving flags, combined with water-logging resulting from the lack of adequate drainage.

INTRODUCTION

In March 1979, BMR was approached by the Department of Housing and Construction (DHC) for advice on the effect of the use of pyritic aggregates in concrete, and its possible relation to the warping of concrete paving flags that had occurred at Parkes Place, Parkes, A.C.T. Advice was requested on the general question of concrete deterioration caused by sulphates derived from pyritic rocks, and specifically on the behaviour of the paving flags at Parkes Place.

Previously BMR had investigated a similar problem for DHC relating to the extensive failure of bituminous concrete road paving in the suburbs of Hackett, Watson and Downer. The cause of the failures was identified as accumulations of pickeringite ($\text{Mg Al}_2 (\text{SO}_4)_4 \cdot 24 \text{H}_2\text{O}$) with minor epsomite ($\text{Mg SO}_4 \cdot 7\text{H}_2\text{O}$) and gypsum ($\text{Ca SO}_4 \cdot 2\text{H}_2\text{O}$). These are all water-soluble sulphates formed during the natural oxidation or weathering of pyrite. The source of these sulphates was traced to the ABM quarry, off the Federal Highway. Examination of the quarry in 1969 showed an abundance of encrusted sulphates at the quarry work face, and around the scalping stockpile in particular. Re-examination late in 1979 showed a similar pattern of the presence of sulphates in joints and fractures in the walls of the quarry and in crushed rock. Other quarries in the ACT contain pyrite and other metallic sulphides, but no salt accumulations have been observed.

As aggregate from the Federal Highway quarry had been used in the construction of the concrete base slab at Parkes Place, DHC suggested that there may be some connection between sulphates and the paving flag failures.

PARKES PLACE PAVING FAILURE

The paved area covers approximately 10,000 m² and is situated in Parkes Place directly in front of Parliament House. The paving had been constructed from precast concrete flags, 600 mm square by 38 mm thick, bedded on cement mortar 25 to 30 mm thick. The mortar layer is supported on a base slab of reinforced concrete approximately 125 mm thick. Joints between flags were filled with red tinted mortar. The pavement included some flags of natural granite for decorative effect.

Failure of the paving flags was confined to the precast concrete flags only, and could be seen as a general up-warping of the peripheral zone of each flag, resulting in dishing with fracture of the flag in some cases. Associated with this, parting of the bond between the flag and underlying mortar had occurred with the deposition of a white laminar encrustation in the voids so formed. Fracture of the grouting mortar between flags was also evident.

Expansion of the flags had occurred at some earlier stage and had been relieved by joints sawn in the paving flags. Inspection of the area during stripping of the flags and bedding mortar did not reveal any defects in either the bedding mortar or the concrete base. However, there was a clear correlation between the amount of encrustation and the degree of dishing.

Samples of paving flag, bedding mortar and encrustation were collected during the stripping operation, and a 10 cm core sample of the concrete base was provided by DHC. Samples of salt encrustation were also obtained from the Federal Highway quarry.

RESULTS

X-ray diffraction analysis of the encrustation from the flag/mortar interface identified the material as ettringite, a hydrated calcium aluminium sulphate, virtually insoluble in water and with the formula $\text{Ca}_6\text{Al}_2(\text{SO}_4)_3(\text{OH})_{12} \cdot 24\text{H}_2\text{O}$. The salt encrustation from the Federal Highway quarry was identified as pickeringite, a hydrated magnesium aluminium sulphate, very soluble in water and with the formula $\text{Mg}_2\text{Al}_2(\text{SO}_4)_4 \cdot 22\text{H}_2\text{O}$. Other sulphates such as those of iron, aluminium, calcium and magnesium may also be found in the Federal Highway material depending on the sampling procedure used.

The results of chemical analysis of sampling of paving flag, mortar and concrete base are as follows

	Paving flag %	Bedding mortar %	Grouting mortar %	Concrete base %
Water soluble SO_3	0.03	0.02	-	0.02
Total SO_3	0.76	0.39	0.48	0.22
Aggregate	58.0	68.0	64.6	80.0
Moisture (105°C)	6.9	7.7	-	3.1
Water above 105°C	4.6	3.4	-	2.6
Carbon Dioxide	1.8	1.3	-	1.5
Loss on ignition (1100°C)	6.5	4.9	-	4.2
<hr/>				
Bulk density (g/cm^3)	2.2	2.0	-	2.3

All results except bulk density are expressed as percent of air-dry sample.

Low-power optical examination of hand specimens of the paving flag and two mortar materials showed vesicles lined, or partly filled, with acicular crystals identified morphologically and by electron probe analysis as ettringite. The ettringite crystals were most abundant at the flag/bedding mortar interface. Ettringite was far less abundant in the concrete base section, and some cavities in this section were lined with deposits of calcite.

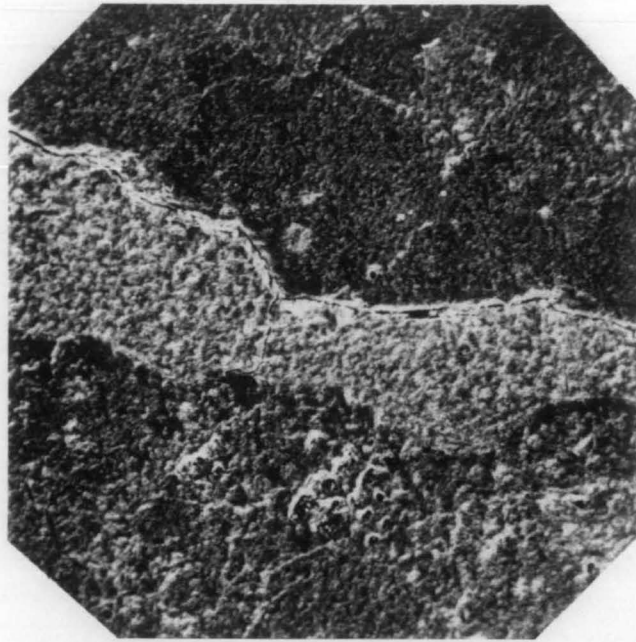


Fig 1(a) Fracture line, in paving flag along cement matrix (light grey)- aggregate (dark grey) boundary. Magnification 47X.

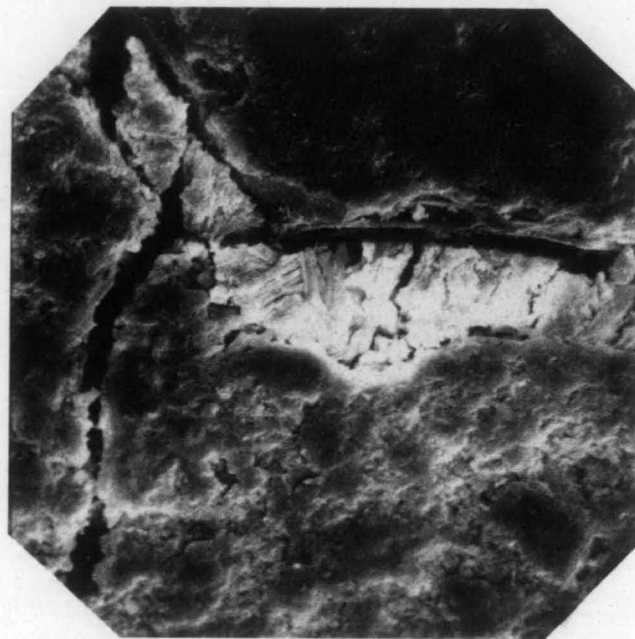
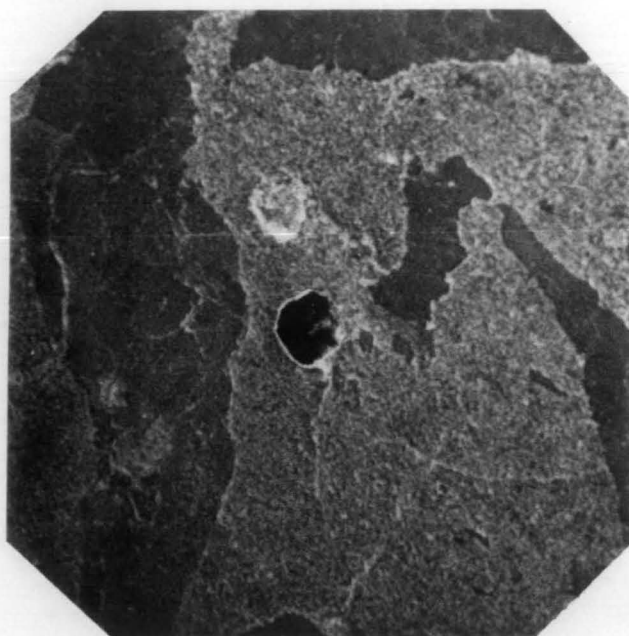
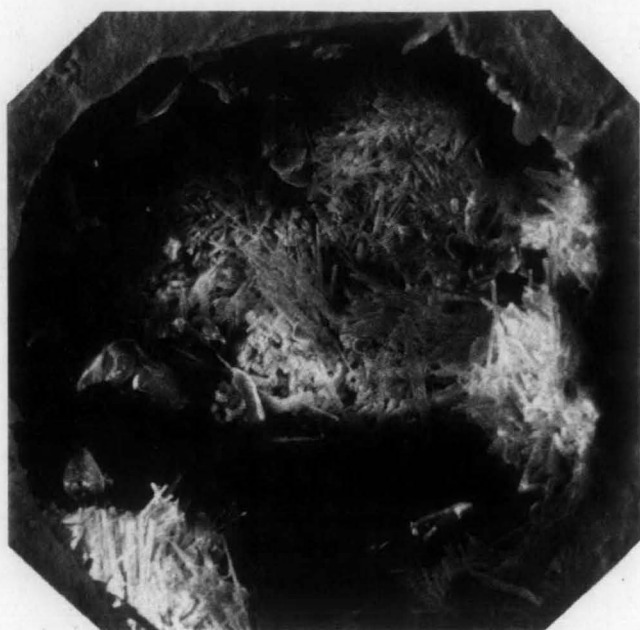


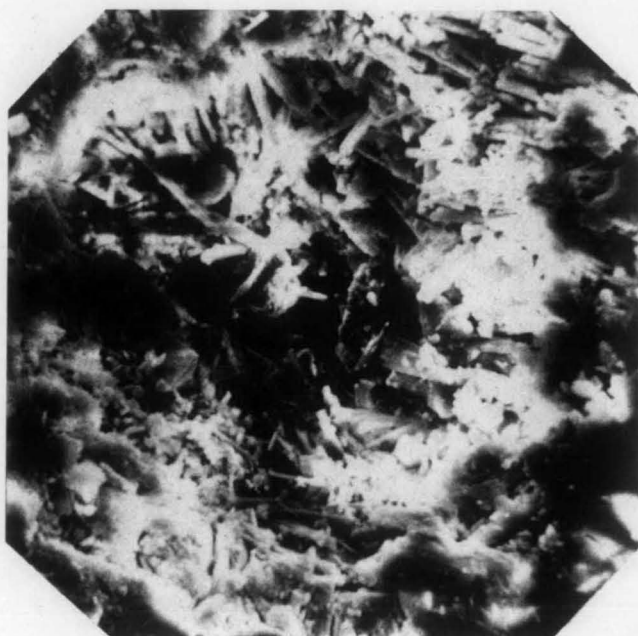
Fig 1(b) Central section of fracture in fig 1(a) showing filling of fracture by ettringite crystals. Magnification 470X.



(a)



(b)



(c)

Fig 2 (a) Paving flag showing filled vesicle (white) and partially-filled vesicle (black) in cement matrix (light grey). Aggregate is dark grey. Magnification 20 X.
 (b) Ettringite crystals in partially-filled vesicle visible in fig 2(a). Magnification 200 X.
 (c) Dense mass of ettringite crystals in filled vesicle visible in fig 2(a). Magnification 430 X.

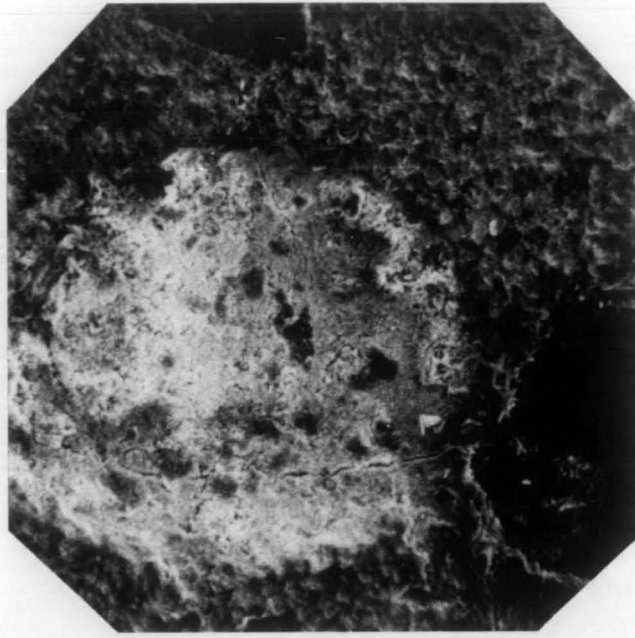


Fig 3(a) Paving flag showing filled vesicle (white) in cement matrix (light grey). Magnification 80X.

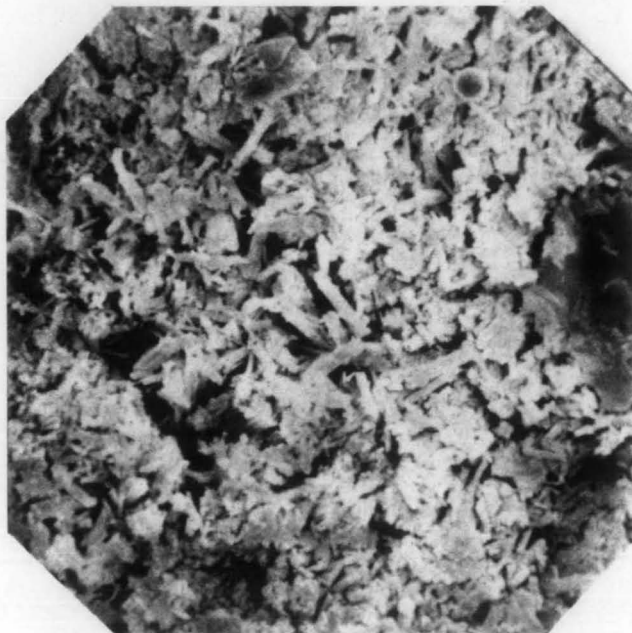


Fig 3(b) Central area of fig 3(a) showing filled vesicle (white) in cement matrix (light grey). Magnification 80X.



Fig 3(c). Central area of fig 3(b). Magnification 2000 X

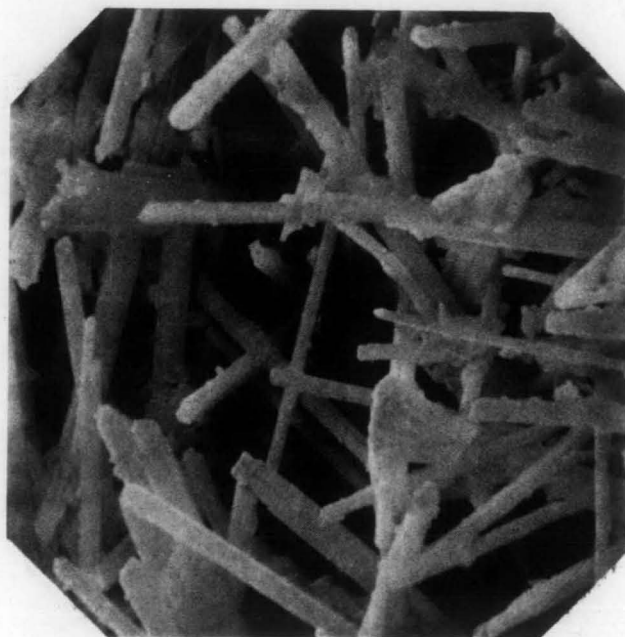


Fig 3(d) Partially filled vesicle in fig 3(a) (black area, lower right hand corner of 3(a)) showing detail of ettringite crystals. Note generally larger crystals than in filled vesicle (fig 3(c)) and absence of cement particles. Magnification 2000 X.

Microscopic examination of thin sections of the paving flags showed crystals of ettringite lining, and in places filling, cavities and cracks (Figures 1-3). In some instances crystals of ettringite could be traced from one vesicle along fractures running through the cement matrix or along aggregate grain boundaries to another vesicle. In thin sections of bedding mortar, ettringite occurs as vesicle-filling only, no fractures were observed. No ettringite was observed in thin sections of the concrete base which is free of fractures and small vesicles. Thin sections which include the flag/mortar boundary show an abundance of ettringite along the interface where parting has occurred.

Figures 1(a & b), 2(a-c), and 3(a-d) contribute a series of scanning electron micrographs taken to illustrate vesicle and fracture filling found in the paving flags. The body of the flags exhibits a network of microscopic cracks filled with ettringite (Fig. 1). These cracks occur in the cement matrix and along aggregate grain boundaries. Spherical voids, filled to various degrees of completeness with well-developed ettringite crystals, occur throughout (Figs 2 & 3). Other inclusions are a felted mass of ettringite, unidentified crystals and remnants of other material. An examination of the base of a piece of paving flag showed a thin skin approximately 1 mm thick of soft, white, altered cement matrix. X-ray diffraction analysis of this material and the adjacent grey cement matrix gave the following approximate composition:

	Soft white layer %	cement matrix %
Calcite	65	30
Ettringite	25	5
Quartz, etc.	10	65

DISCUSSION

It was suggested during preliminary discussions with DHC that deterioration of the paving flags had been caused by sulphate, presumably introduced in aggregate from the Federal Highway quarry which is known to contain water soluble sulphates. DHC had been advised that sulphates in solution had migrated from the base through the mortar into the lower part of the overlying flags. This in turn, it was claimed, led to the formation of hydrated calcium sulphotoaluminate, resulting in differential expansion and warping. This explanation can only be correct if the quantity of added sulphate impurity was in excess of that required by the tricalcium aluminate in the cement to form ettringite.

Sulphate, in the form of gypsum, is added during cement manufacture to control the rate of initial set. Calcium sulphate reacts with the tricalcium aluminate phase of cement in the presence of water to form colloiddally dispersed calcium sulphotoaluminate hydrate (ettringite, if crystalline). This reaction proceeds throughout the water-curing stage until either all calcium sulphate or all tricalcium aluminate is consumed; it only occurs in the presence of liquid water. Any calcium sulphate remaining in excess would be available for leaching and could then migrate to the upper layers under conditions of saturation with water. It is important to recognise that for the proposed leaching to be effective the net water movement must be upward, implying a potentiometric surface above the paving flags. There is no evidence for this. Saturation of the flags and base by rain water would result in downward leaching to an extent dependent on the permeabilities of the flag, mortar, concrete base and underlying soil.

A further consideration is the quantity of gypsum required to provide an excess of calcium sulphate. This depends on the tricalcium aluminate (C_3A) content of the cement. American portland cements contain 10 - 15% C_3A for Type I, Australian cement contains approximately 5% C_3A . On the basis of the lesser figure it would be necessary to add more than 9.6% of gypsum to the cement during manufacture or later to provide excess calcium sulphate. This is equivalent to 4.5% SO_3 , which is in excess of the standard specification for Australian cement, and most probably would result in the failure of any concrete in which it was used.

From the analyses of the various materials it is possible to estimate the sulphate content of the cement used in each material. The values are

	Paving flag	Bedding mortar	Concrete base
%SO ₃	2.7	2.0	1.7

and may be compared with an average value of 1.6% SO₃ for Australian Type I cement (equivalent to 3.4% gypsum). If the sulphate in the paving flags and bedding mortar in excess of the normal content of say 1.6% SO₃ is transferred to the concrete base, the resultant sulphate level in the cement would be 2.5% SO₃, which is lower than the sulphate level required to provide leachable calcium sulphate. It is concluded, on the grounds of both the probable direction of leaching and the quantity of sulphate in the system, that the sulphate now apparent as ettringite crystals in the paving flags and mortar could not have originated from the concrete base.

It will be noted from the foregoing that the sulphate content of the base concrete, 0.22% SO₃, is in close agreement with the value of 0.20% calculated for a Type 1 cement, and clearly indicates that there has been no significant addition of sulphate to the concrete base at any time. In view of the foregoing conclusion, an alternate explanation for the failure of the paving flags is required.

It is immediately apparent from the chemical analyses that the paving flags contain the highest sulphate levels relative to both the concrete and its contained cement, 0.76% and 2.7% SO₃ respectively, so that attention was directed to the paving flags themselves as the source of ettringite.

The paving flags consist of a mixture of crushed granite aggregate and cement in the ratio 2:1 with almost complete absence of fines (only a little rock dust from the crushed granite). The flags are relatively porous (bulk density 2.2 g/cm³) and in section show zones of high porosity 2 - 3 mm deep on the upper and lower faces of the slabs. The cement matrix has been appreciably altered in these zones; the upper surface by weathering, and the lower surface by the accumulation of ettringite and calcite.

The microscopic features described earlier are interpreted as evidence of extensive leaching under water-logged conditions since it is only possible for ettringite to crystallise in voids and connecting fractures if there are filled with liquid water. The source of ettringite is by dissolution of the calcium sulphoaluminate hydrate gel formed during setting and curing of the flag concrete.

Reallocating all sulphate in excess of the normal content in the bedding mortar and concrete base to the paving flags gives a value of 3.0% SO_3 for the cement used in the flags. This is at the specified limit for sulphate in ordinary cement but well below the value of 5% SO_3 for Type K expanding cement. It is unlikely that a sulphate content of 3.0% SO_3 alone could be responsible for the observed dishing of the paving flags. In any case the expansion caused by the ettringite reaction would have occurred during setting and curing and would be uniform throughout the flag, as would any possible subsequent expansion.

Some additional factor is needed to localise the deposition of ettringite crystals at the flag/bedding mortar interface, and this is considered to be the water-logging referred to above. Normally, paving flags are laid on a bed of sand on the ground and consequently are able to drain freely. The type of construction used at Parkes Place places the flags on a 125 mm thick concrete slab effectively sealing off all drainage except perhaps by lateral movement. This has led to water-logging during wet weather, particularly as both the paving flags and bedding mortar are reasonably porous: having 20% and 28% voids respectively.

The high cement content of the paving flags is a further compounding factor as, although the flags represent only 25% of the total concrete structure, they initially would have contained 49% of the total sulphate. The flags would have an abundant supply of calcium sulphoaluminate hydrate (calculated as 15% ettringite) for dissolution, and subsequent crystallisation as ettringite.

With regard to the use of pyritic aggregate in concrete generally, there is no evidence to suggest that the pyrite would undergo oxidation releasing sulphate which could then react with the cement matrix to form ettringite. The high pH resulting from the solution of calcium hydroxide

(portlandite) in saturated concrete completely inhibits the growth of Thiobacillus responsible for the accelerated oxidation of pyrite. The main danger associated with the use of pyritic aggregate is the unwitting inclusion of soluble sulphate formed by pre-oxidation of pyrite in the quarry proper or in stock-piles. However it would require substantial quantities to raise the sulphate content of the concrete to a level where the ettringite reaction would cause failure. Cement can contain up to 4% SO_3 equivalent to 8.6% gypsum or 10.7% pickeringite before it exhibits any expansion.

It should be noted that in the case of contaminated aggregate the sulphate is present during the mixing and setting of the concrete. In this case there is an immediate series of reactions between the tricalcium aluminate of the cement, water and sulphate to form a calcium sulphotoaluminate gel resulting in uniform expansion during the curing stage.

Sulphate added to concrete after curing, by the penetration of sulphate-bearing water is a completely different case; as little as 200 ppm SO_4 can produce positive attack and 2000 ppm severe attack leading to failure.

CONCLUSIONS

1. It is considered that the failure of the paving flags at Parkes Place is due to a combination of an unfavourable aggregate: cement ratio in the flags together with a higher than normal level of sulphate, and poor mechanical design which has resulted in water-logging by rainwater through lack of adequate drainage. These two factors have enabled the slightly soluble calcium sulphotoaluminate hydrate gel to leach from the flags and crystallise as ettringite. Formation of ettringite has occurred preferentially near the edges of the flags by lateral movement of water towards the joints as drying out occurred after water-logging. The accompanying volume changes have resulted in differential stress, causing warping.

As the paving flags are not made of local materials, their failure has no direct implications regarding the use of local materials by the ACT construction industry. The problem, however, underlines the need for drainage below pavements of flags.

More generally, because sulphate is associated with some local quarries:

1. Assuming that a concrete mix has been formulated for maximum density, the only problem likely to occur with the use of pyritic aggregate (even if some associated sulphate impurity is included) is iron-staining which would result from the oxidation of pyrite in aggregate exposed at the surface. However, care should be taken with small batches of concrete that excessive pickeringite (hydrated magnesium aluminium sulphate) or epsomite (hydrated magnesium sulphate) is not present, as the inhibiting effect of the chemical environment of curing concrete may not be sufficient to prevent subsequent failure.
2. The use of pyritic aggregate in porous concrete placed in locations subject to prolonged water saturation should, as a precautionary measure, be avoided.
3. Pyrite in aggregate used in a road base where water saturation occurs will tend to oxidise to pickeringite. The acidity and volume change resulting from the crystallisation of pickeringite at the bituminous concrete-base grade interface is known to cause spalling of the bituminous concrete.