

alteration and reorganization of the C-S-H gel binder phase may have even more serious consequences. In many cases the groundmass C-S-H is reduced in calcium content over a wide area. Actually, the missing calcium may not be entirely removed from the system, but rather some of it may be concentrated in some areas of locally higher Ca/Si. Thus the 'decalcification' of C-S-H gel is not a uniform process over the concrete, but occurs in patches. A texture such as that shown in Fig. 6 often develops. In this 'salt and pepper' morphology the darker areas are virtually depleted of calcium, but show higher contents of other minor components; (magnesium, aluminum, and sulfur). The brighter areas have, in contrast, retained most of their calcium, and in a few areas may show higher Ca/Si than the original gel.

Sometimes extensive darker regions of C-S-H gel seen in backscatter SEM examinations represent a further alteration. Where magnesium is a significant component of the ground water much or all of the calcium from C-S-H gel may have been removed and replaced by magnesium, thus producing a magnesium silicate hydrate (MSH). Fig. 7 shows such an area. Extensive replacement of C-S-H gel by magnesium silicate hydrate, a non-binding phase, has been found in laboratory studies (5). Replacement of C-S-H gel by MSH results in significant deterioration of the affected concrete.

An unexpected feature of sulfate attack as seen in these concretes is the effect produced on residual unhydrated cement grains. As indicated previously, in most concretes these grains are preserved indefinitely without alteration. This is not the case in the present concretes. Passage of sulfate-bearing ground water through the concrete has produced major changes. Not only is the C_3A removed, but the alite and belite are decalcified, and may eventually be completely dissolved. The space thus produced may be filled by various secondary materials, including ettringite, monosulfate, brucite, Friedel's salt, and others. The C_4AF is resistant, and a frame of C_4AF generally remains and facilitates identification of the former cement grains. Fig. 8 shows one such instance, with the C_4AF identifiable as a narrow bright zone between two dark rounded grains, which originally seem to have been belite by their morphology. The calcium has been completely stripped away, leaving behind what is essentially a silica gel.

Fig. 9 shows another large cement grain in the process of alteration. Here the belite seems to have been dissolved, and the space left partly filled by monosulfate. For some reason the alite in the grain seems relatively unaffected. Fig. 10 records another instance, where the material deposited is ettringite rather than monosulfate.

DISCUSSION

The microstructural features of sulfate attack documented here provide only a rough overview and a sample of the many alterations found in the examination of affected concretes.

The responses are locally variable within a given concrete, and reflect variations in the access of the sulfate-bearing ground water over time, variations in concentration and composition of the ground water solution, variation in extent of carbonation, etc. The concretes studied here are not at the final stages of reaction, and do not necessarily display the full effects of changes that may eventually be produced. As indicated earlier, attack produces an irregular, but definite layering effect, with alterations most pronounced near the surface of ground water entry, and near the opposite surface where evaporation concentrates the penetrating solutions. A key indicator of the attack not easily documented is the dissolution and removal of the CH normally present in concrete; it is difficult to show the *absence* of a phase in pictures. In the normal examination of these concretes, the entire cross-section of the concrete member is specifically surveyed for the presence or absence of CH. In less advanced cases, some CH is often still present in the central portion of the cross section; in more advanced cases, no CH at all is usually found.

The fact that most of the concretes examined were made using ASTM Type V sulfate resisting cement requires some further discussion. Sulfate resistant cements are formulated with low C_3A contents to limit ettringite formation. However, If highly permeable concretes are produced and exposed to sulfate-bearing ground waters, the many other aspects of sulfate attack are not prevented or mitigated, and softening and eventual destruction of the concrete can be expected.

CONCLUSIONS

Sulfate attack on permeable high W/C concretes exposed to sulfate-bearing ground water results in fundamental alterations of the hardened cement paste. Formation of ettringite and deposition of gypsum within the paste are only more obvious symptoms of the destructive changes that take place. These changes also include dissolution of the CH, decalcification of C-S-H gel, and sometimes its complete replacement locally by magnesium silicate hydrate. Large cement grains, usually preserved unaltered in most mature concretes, are drastically altered, with alite and belite decalcified or completely removed by dissolution and partly or completely replaced by ettringite, monosulfate, or various other new substances. These changes result in deterioration or destruction of the

concrete despite the fact that the amount of ettringite produced may have been limited by the use of cements of low C_3A content.

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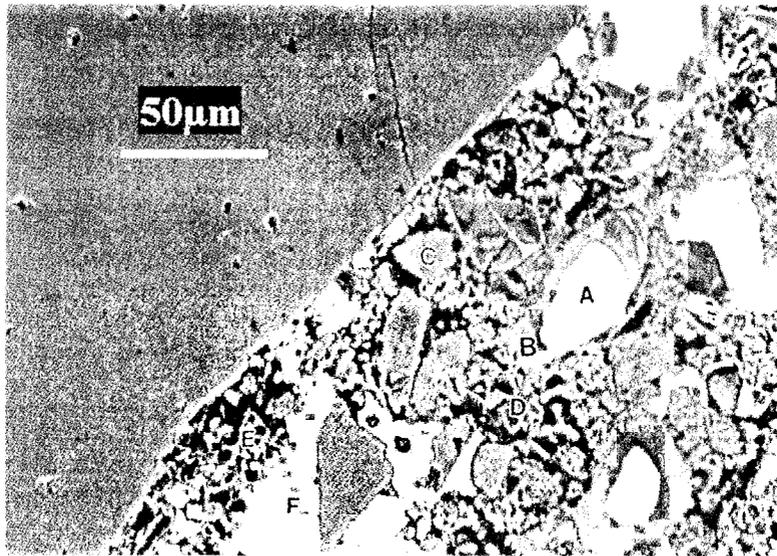


Fig. 1. Normal features of concrete not subject to sulfate attack. A is unhydrated cement; B and C are dense C-S-H gel; D shows hollow shells; E is C-S-H gel groundmass, and F is shows calcium hydroxide deposit around a small sand grain.

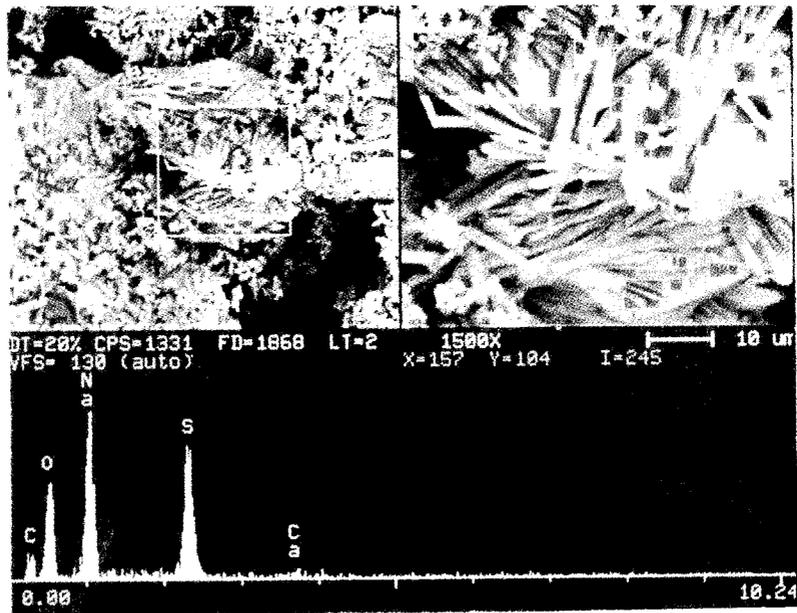


Fig. 2. Sodium sulfate efflorescence deposited on the upper surface of a garage slab.

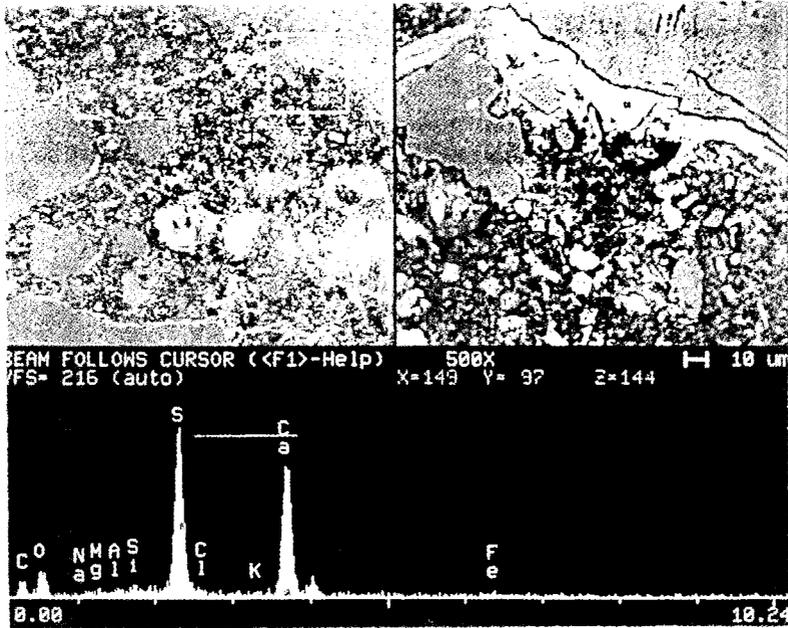


Fig. 3. Gypsum deposited in space around aggregate normally occupied by CH.

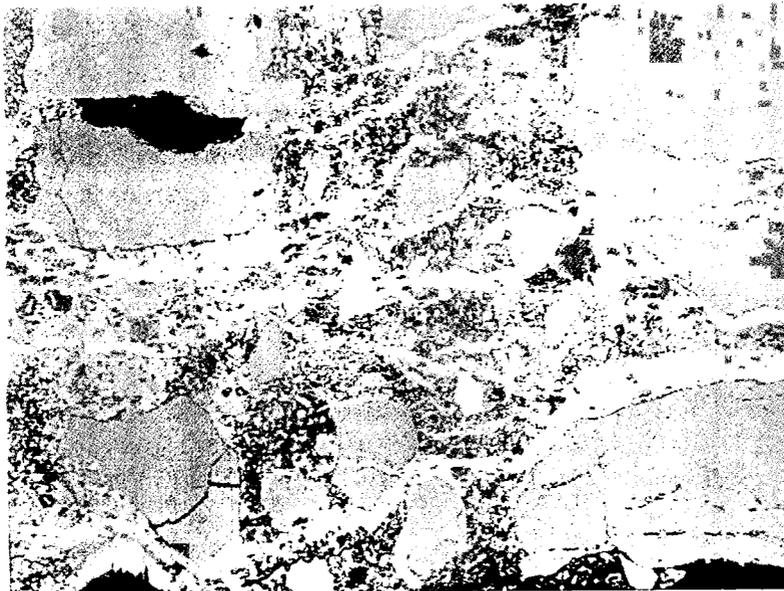


Fig. 4. Parallel bands of gypsum deposited near the surface of contact with ground water.

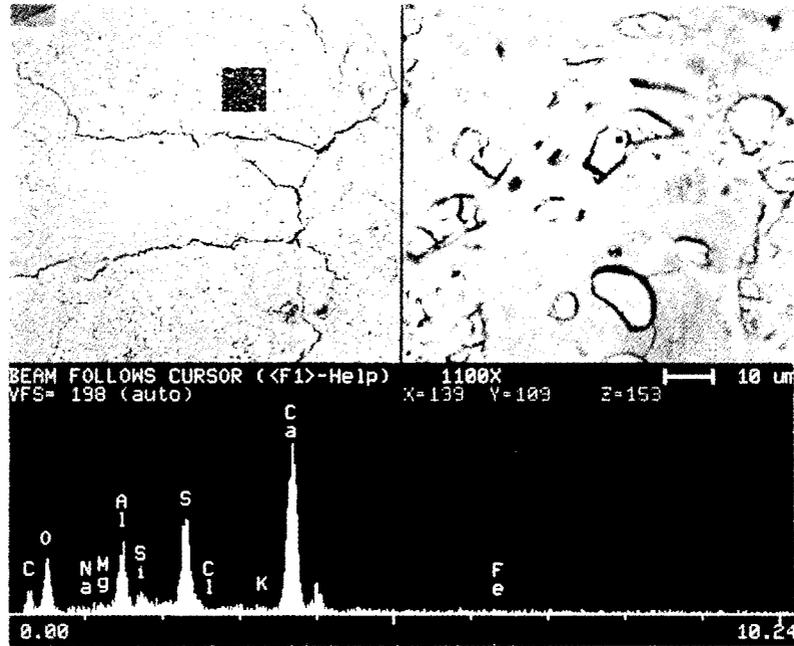


Fig. 5. Cracking associated with extensive ettringite deposition and local expansion.

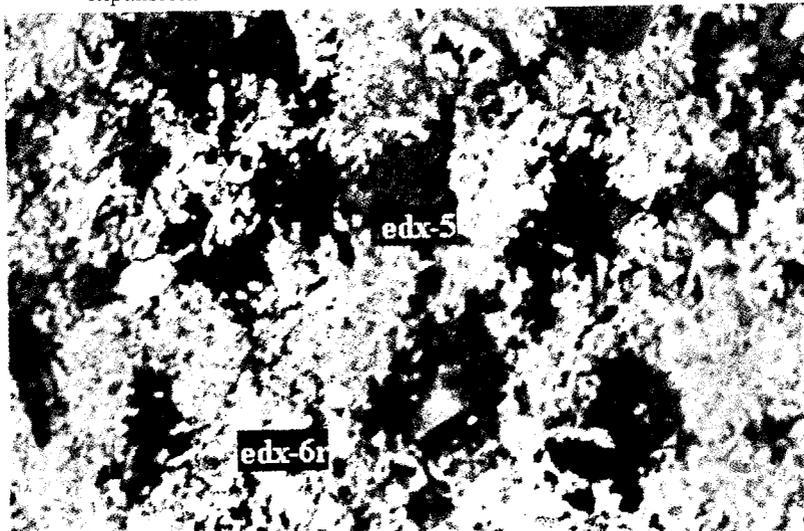


Fig. 6. "Salt and pepper" morphology developed in decalcified C-S-H gel. Dark areas show much lower Ca/Si ratios than normal C-S-H gel.

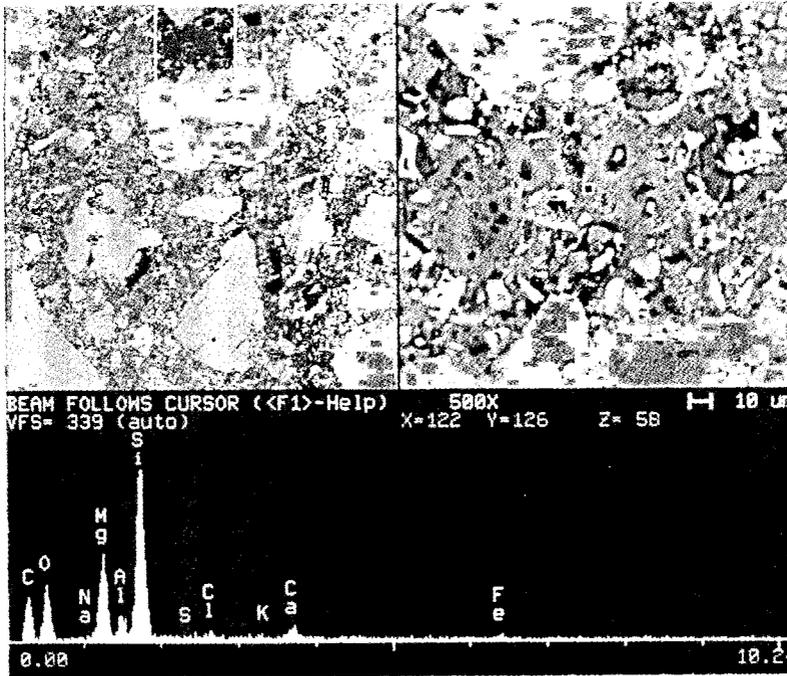


Fig. 7. Conversion of large areas of C-S-H gel to magnesium silicate hydrate.

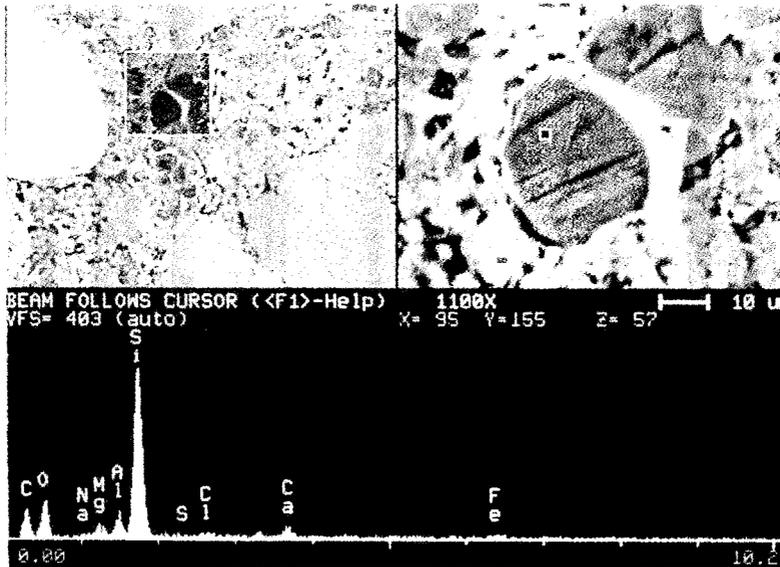


Fig. 8. Former cement grain with belite completely decalcified and converted to silica gel.

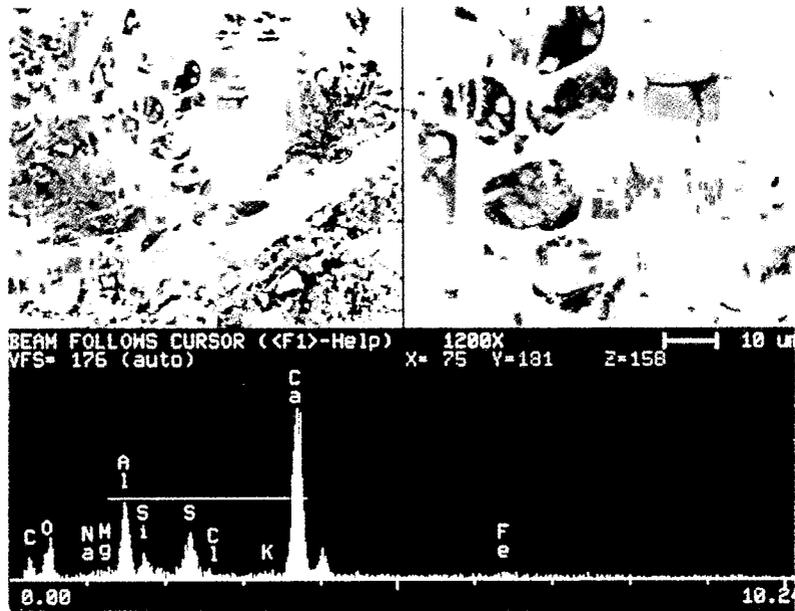


Fig. 9. Large former cement grain with belite dissolved and monosulfate deposited into the spaces created.

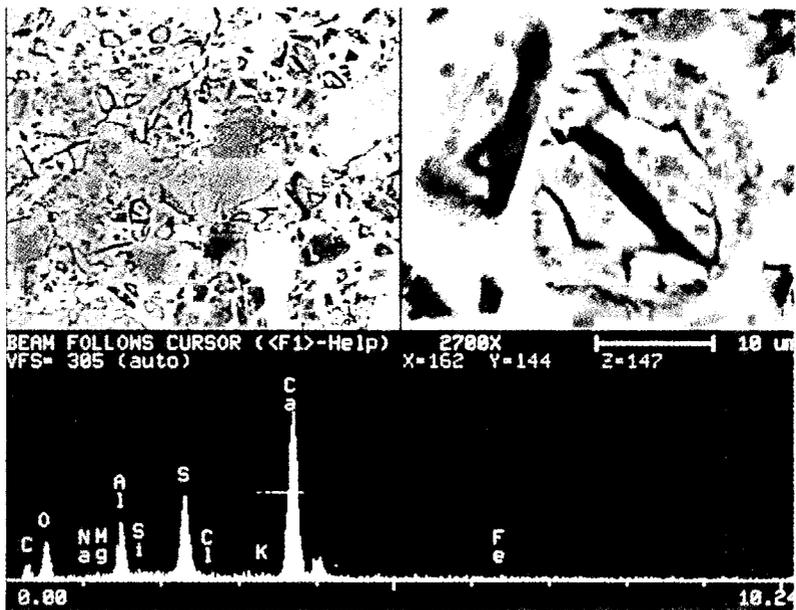


Fig. 10. Former cement grain with ettringite deposited in the space created by dissolution.

Sulfate Attack on Blended Portland Cements

by A. Borsoi, S. Collepardi, L. Coppola, R. Troli, and M. Collepardi

Synopsis: Paste and mortar specimens were manufactured by using ordinary portland cement (OPC), C₃A-free portland cement, slag cement and pozzolan cement. A carbonaceous or siliceous filler (10% by cement weight) was blended with each of the above portland cements. Limestone or quartz sands were used for mortar mixtures. Four different water-cement ratios (*w/c*) were adopted: 0.55, 0.50, 0.45, and 0.40.

After a 28-day wet curing, paste and mortar specimens were immersed in MgSO₄ aqueous solutions with a SO₄²⁻ concentration of 350, 750, and 3000 mg/l, corresponding to chemically aggressive exposures 5a, 5b, and 5c respectively, according to the European Norms (ENV 206).

The deterioration of cement paste specimens was studied by X-ray diffraction analysis to detect ettringite and/or thaumasite formation in relationship with the visual observation of sulfate attack.

The deterioration of mortar specimens was studied by measuring elastic modulus and compressive strength at different periods of aggressive exposure (from 1 month to 5 years).

After 5 years of exposure to the sulfate attack, paste and mortar specimens with slag and pozzolan cements were undamaged independent of the sulfate concentration, sand type, and *w/c*.

On the other hand, paste and mortar specimens with blended limestone-portland cements showed surface damage when exposed to the 3000 mg/l of SO₄²⁻ aqueous solution. However, they did not show loss of either compressive strength or elastic modulus in the 5 years of sulfate exposure. The surface damage was mitigated when OPC was replaced by the C₃A-free portland cement and completely eliminated when this cement was blended with a siliceous filler rather than with a limestone case.

Thaumasite and ettringite are responsible for the surface attack. The amount of thaumasite was a little higher in the presence of blended limestone portland cement.

Keywords: deterioration; durability; ettringite; limestone; sulfates

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INTRODUCTION

Concrete exposed to environmental sulfate can be damaged due to the formation of gypsum, ettringite, and thaumasite as a result of chemical interaction with the portland cement hydration products, such as calcium hydroxide (CH), monosulfate ($C_3A \cdot \bar{C}\bar{S} \cdot H_{12}$), calcium aluminate-hydrates (C-A-H), and calcium-silicate-hydrates (C-S-H):

