

# Discussion

on paper published in the  
*Magazine of Concrete Research*

Volume 37, Number 131 : June 1985

---

## **The use of beams with a single edge notch to study the sulphate resistance of OPC and OPC/pfa pastes\***

D. C. Hughes and T. Grounds

### **Contribution by B. Marchese**

*Dipartimento di Ingegneria dei Materiali e della Produzione, Facolta di Ingegneria,  
Universita' di Napoli, 80125 Piazzale Tecchio, Naples, Italy*

Correlation between material strength and microstructural changes is a study area of primary interest and considerable difficulty. Microstructural analysis of the mature cement paste becomes even more difficult mainly because of its latent reactivity roused by contact with aggressive solutions.

I well agree with the following deductions of the authors: the sulphate resistance of OPC/pfa and other blended cement pastes is strongly dependent upon the degree of curing and reactivity of the pozzolan; the precured specimen's surfaces react differently from the bulk paste; the field conditions could give results different from those in an accelerated laboratory test; the microstructure is strongly dependent on the zone. As a consequence, particularly regarding the last point, interpolation of the microscope analysis results must be made with extreme caution.

Dr Hughes and Dr Grounds have found that some areas of the fracture surfaces of the notched beams of OPC paste (cured for 1 week) show massive deposits of ettringite and calcite at later ages, i.e. after about 35 days of immersion, Figure 9. Then, "after further immersion, the formation of gypsum was noted, Figure 10". Actually, referring to the Figure 10 caption, only 3 days seem necessary to obtain gypsum

formation. An explanation is required, bearing in mind also that the large polyhedral forms in Figure 10 seem to be unreacted material. For a better understanding of the second generation products of cement pastes I should like to submit some unpublished morphologies I have obtained studying the sea water attack on mature blastfurnace cement paste<sup>(1)</sup>. The specimens, reinforced with steel fibres, were precured in tap water for six months, microcracked in flexure and then immersed in non-flowing sea water for three years.

Figure I shows part of the internal surface of a crack. On the left is the cross-section of superficial patina formed by granular masses. At higher magnifications, Figures II(a) and (b), they may be recognized as slag relicts covered with a layer of other material identified from XRD as calcite. Some areas, such as S and R, are easily attributable to a slag grain and to a replica of another grain, respectively.

A nearby region, slightly further in, shows quite different morphologies, Figure III(a), with fibrous and microgranular forms, Figure III(b). The bunched forms are attributed to freely-grown aragonite<sup>(2)</sup>. They reveal a high content of Ca from energy dispersion X-ray spectrometry (EDXRA) data.

The other forms appear as heaps of lamellae, Figure

---

\*Pages 67 to 74 *MCR* 131.

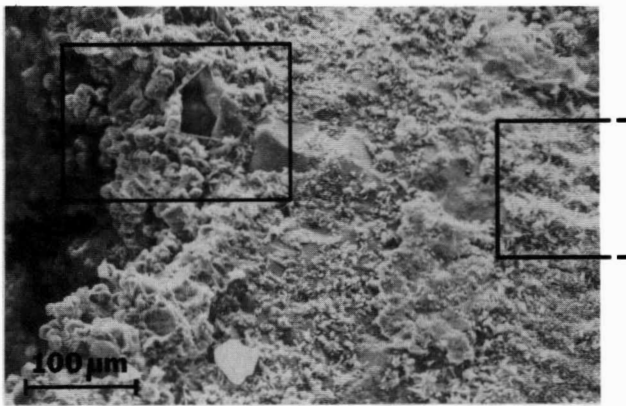


Figure I: SEM micrograph of a crack internal surface of a mature blastfurnace slag cement paste in contact with sea water. Areas marked are shown enlarged in Figures II and III.

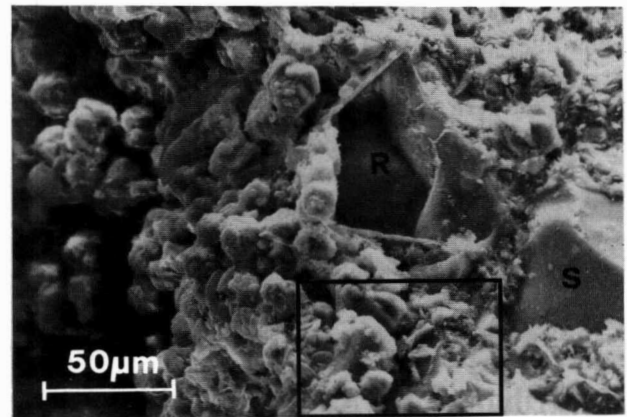


Figure II(a): Enlargement of area marked in Figure I. S = slag grain; R = replica of a slag grain.

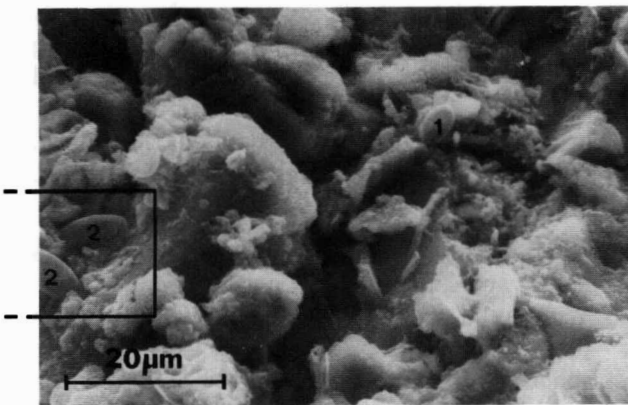


Figure II(b): Enlargement of area marked in Figure I. 1, 2 = ovoidal forms.

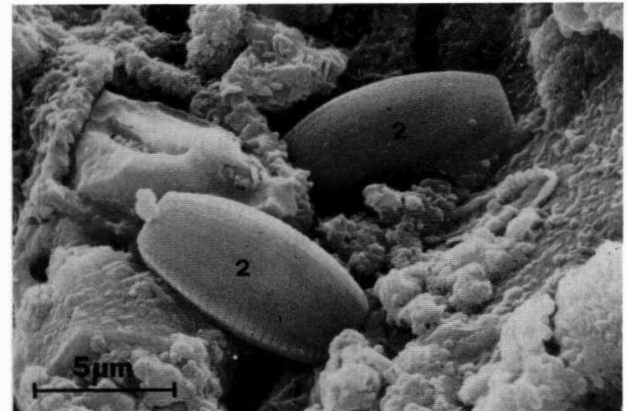


Figure II(c): Enlargement of area marked in Figure II(b).

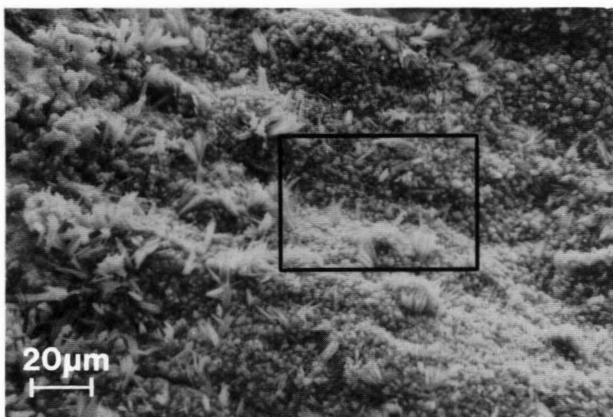


Figure III(a): Enlargement of area marked in Figure I.

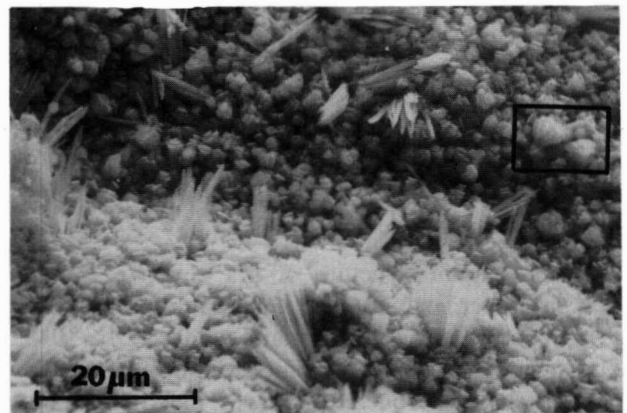


Figure III(b): Enlargement of area marked in Figure III(a).

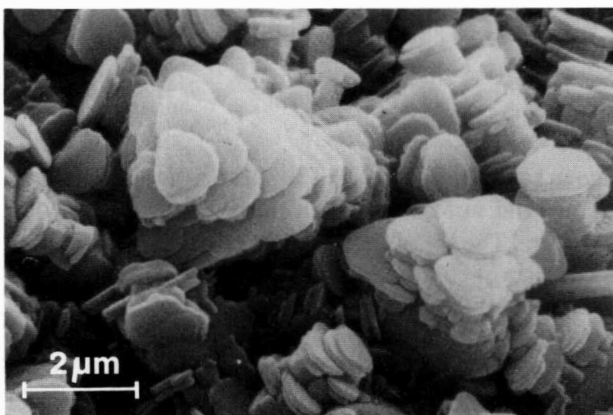


Figure III(c): Enlargement of area marked in Figure III(b).

III(c), with a very high content of Mg and minor quantities of Si and Cl. They were attributable to brucite<sup>(3)</sup>. Very unusual forms, considered to be artefacts, were present in superficial layers, Figures II(b) and (c). In ovoidal forms, as 1 in Figure II(b), and also with truncated edges, as 2 in Figures II(b) and (c), with longitudinal and transverse grooves, they revealed a high content of Si. Their constitution should be organic in nature.

## Contribution by R. Amtsbüchler

*D & H Ash Resources Pty (Ltd), Randburg, South Africa*

We found this paper very interesting, but one must bear in mind that all the investigations were conducted on pastes with a fixed water/cement ratio. Further, one must be careful not to translate the results on pastes to those for concrete and in particular under field conditions.

Fly ash concrete (using a blended cement of 30% pfa with good water-reducing capability and pozzolanic reactivity) can be designed to have the same early strength as an OPC control concrete. Some of the factors which contribute to (early) strength can have an influence on sulphate resistance too. These factors are:

- (1) reduced water demand for a given workability (improved water/cementitious ratio, therefore a better pore structure with less capillaries and voids);
- (2) 'fine filler effect' (physical presence of pfa spheres), which stimulates cement hydration;
- (3) pozzolanic reaction (further refinement of the pore structure due to ongoing growth of calcium-silicate-hydrates).

The better pore structure of pfa concrete can be proven by permeability tests e.g., water-permeability tests in accordance with German Standard DIN 1048. Our own extensive permeability testing programme, using 30 N/mm<sup>2</sup> concrete, showed clearly a better impermeability of 30% pfa concrete compared to OPC concrete. Even under dry curing conditions

## Reply by the authors

We would like to thank Dr Marchese and Mr Amtsbüchler for their contributions and agree that the interpretation of materials properties and microstructural features is fraught with difficulties.

The brief SEM observations indicated very little morphological change to the fracture surfaces of the notched beams until sometime *after* the beam was seriously weakened by the formation of a flaw or flaws

## REFERENCES

1. MARCHESE, B. Interfacial microstructural alterations of mature blastfurnace cement pastes. Tenth International Congress on the Chemistry of Cement, Rio de Janeiro, September 1986.
2. REGOURD, M. Physico-chemical studies of cement pastes, mortars, and concretes exposed to sea water. *Performance of concrete in marine environment*. Detroit, American Concrete Institute, 1980. Publication SP-65. pp. 63-82.
3. CONJEAUD, M. L. Mechanism of sea water attack on cement mortar. *ibid.* pp. 39-41.

(3 days wet, 25 day dry), pfa concrete was less adversely affected than OPC concrete. This must have a bearing on the sulphate resistance of concrete under field conditions.

Further, we refer to research undertaken by Prof. Dr. Blaschke, University Münster, West-Germany<sup>(2)</sup>. Some of his findings are:

- (1) After 7 days of hydration, fly ash pastes shows hardly any capillary pores, just gel pores.
- (2) Within the *first days* of hydration, a reaction product between cement gel and the 'glassy' pfa spheres is formed on the surface of the fly ash particles. This product is a potassium-stabilized alumo-silicate-hydrogel with a high absorption rate, which most probably contributes to the sulphate resistance of fly ash concrete.

Therefore we do not agree with the statement in the Introduction that the potential benefits of a concrete with a cement/pfa blend are realized after long curing times only. As pointed out above, sulphate resistance of fly ash concrete does not depend only on the rather slow pozzolanic reaction.

## REFERENCES

1. WISCHERS, G. and RICHARTZ, W. *Einfluss der Bestandteile und der granulometrie des zements auf das gefüge des zementsteins*. Dusseldorf, Beton-Verlag, 1982.
2. 25 Jahre beton mit flugasche. VG8-TB203, 1984.

due to sulphate action. This is not to say that chemical change did not occur, albeit unseen, within the pore structure. The use of the thermogravimetry revealed the formation of ettringite at immersion times prior to the formation of flaws and confined to the 2 mm thick slice cut from the surface of the samples. This behaviour was common to both OPC and OPC/pfa pastes. Interestingly, the distribution of ettringite in an SRPC

paste was much more widespread, occurring in the deepest slices examined at 10–12 mm from the surface.

With regard to Dr Marchese's comment on the polyhedral forms in Figure 10 of the original paper it should be said that these were not observed until an immersion time greater than that necessary to cause flaw formation. XRD analysis of scrapings from the fracture surfaces of companion samples of that shown in Figure 10 indicated substantial calcite and gypsum peaks and little calcium hydroxide. The forms are ascribed to calcite.

Mr Amtsbüchler implies that we have attempted to directly correlate our paste samples immersed in an artificial solution with concrete subject to field conditions. This is not so and would be unwarranted. The examination of the durability of materials is an awkward subject. Whilst the use of real time experiments is more closely related to field conditions than accelerated testing, the latter is used to generate adequate data within a realistic time scale. This dictates the use of small samples, which are therefore often pastes, together with a concentrated aggressive environment. It is known that the pozzolanic reaction of pfa is slow, producing field conditions which may be broadly summarised as slow hydration occurring *simultaneously* with a relatively mild aggressive attack. In contrast, the laboratory regime is an independent two phase system comprising an accelerated curing *followed* by a highly aggressive attack. The two regimes are thus quite different. It was this point to which we were drawing attention when stating that an appropriate curing regime needs to be specified for the laboratory evaluation of the sulphate resistance of blended cements.

## REFERENCES

1. MONTGOMERY, D. G., HUGHES, D. C. and WILLIAMS, R. I. T., Fly ash in concrete—a microstructure study. *Cement and Concrete Research*. Vol. 11, 1981. pp. 591–603.
2. TAYLOR, H. F. W., MOHAN, K. and MOIR, G. K. Analytical study of pure and extended Portland cement pastes: II, Fly

A well designed OPC/pfa concrete is not simply an OPC concrete with a direct 30% replacement of OPC by pfa. It is a different material and should be recognised as such. The incorporation of ash not only alters the water demand but also acts as nucleation sites for hydration products<sup>(1)</sup> whilst altering the chemistry of that hydration<sup>(2)</sup>. The combination of these factors will affect the properties of the concrete in addition to the pozzolanic reaction and should be accounted for in order to realise the full potential of the material. The defined limits of the reported investigation did not encompass such a broad spectrum.

Unfortunately Mr Amtsbüchler does not give any details to support his statements and it may be worth summarising our findings. From our work on OPC, OPC/pfa and SRPC pastes, it was found that the sulphate resistance of the OPC/pfa was sensitive to the period of curing prior to sulphate immersion, whilst that of the OPC was not. Despite 12 weeks curing at 35°C the OPC/pfa was outperformed by an SRPC similarly cured for 4 weeks<sup>(3)</sup>. There was no simple correlation between sulphate resistance and water permeability<sup>(3)</sup>. The sulphate attack within the pore structure appeared to be selective. The sulphate resistance of pastes may be a function of:

- (1) the ability of the sulphate ion to diffuse through the pore structure, i.e. related to permeability;
- (2) the ability of the sulphate ion subsequently to gain access to the susceptible minerals, determined by the entry size of the pores associated with them; and
- (3) the quantity of  $\text{Ca}(\text{OH})_2$  present.

ash- and slag-cement pastes. *Journal of the American Ceramic Society*. Vol. 68, 1985. pp. 685–690.

3. HUGHES, D. C. Sulphate resistance of OPC, OPC/fly ash and SRPC pastes: pore structure and permeability. *Cement and Concrete Research*. Vol. 15, 1985. pp. 1003–1012.