Pergamon

Cement and Concrete Research, Vol. 26, No. 1, pp. 35-40, 1996
Copyright © 1996 Elsevier Science Ltd
Printed in the USA. All rights reserved
0008-8846/96 $15.00 + .00

0008-8846(95)00185-9

THE PERCOLATION OF PORE SPACE IN THE CEMENT PASTE/AGGREGATE INTERFACIAL ZONE OF CONCRETE

Karen L. Scrivener
Department of Materials, Imperial College
London SW7 2BP, England

Kamran M. Nemati
Department of Civil Engineering, University of California
Berkeley, U.S.A.

(Communicated by D. Sorrentino)
(Received November 2, 1995)

ABSTRACT

The cement paste in the interfacial transition zone (ITZ) around aggregate particles has a significantly higher porosity than bulk cement paste. This elevated porosity will effect the transport properties of concrete. The penetration of Wood's metal into concrete samples indicates that the porosity in the interfacial zone is permeated preferentially to the bulk paste. This technique also indicates the width of the interfacial zone in which the porosity is interconnected.

Introduction

The interfacial zone between cement paste and aggregate in concrete has long been considered as a zone of weakness, both in terms of strength and in terms of the permeation of fluids. However relatively little is known about the quantitative differences between the properties of this zone and those of the 'bulk' cement paste.

The microstructure of the interfacial zone is determined by the packing of the anhydrous cement grains against the much larger aggregate particles. The well known 'wall effect' leads to a depletion of anhydrous cement in the interfacial zone, approaching zero at the aggregate surface. As a result of the anhydrous distribution there is an increase in the amount of porosity in the interfacial zone. Scrivener and co-workers (1,2,3,4,5) have measured the microstructural gradients in concretes by analysis of backscattered electron (BSE) images. This work indicates that the thickness of the zone affected by the packing of the cement grains extends to at least to the size of the largest cement particles, which may be up to 100 μm. However, the migration of ions results in preferential deposition of hydration products in the more open interfacial zone, which ameliorates the effects of cement packing. Consequently the distance over which there is a significant increase in the porosity is only around 35-45 μm, Figure 1. In this experimental technique the distances measured are those in the plane of the section, which will rarely cut the

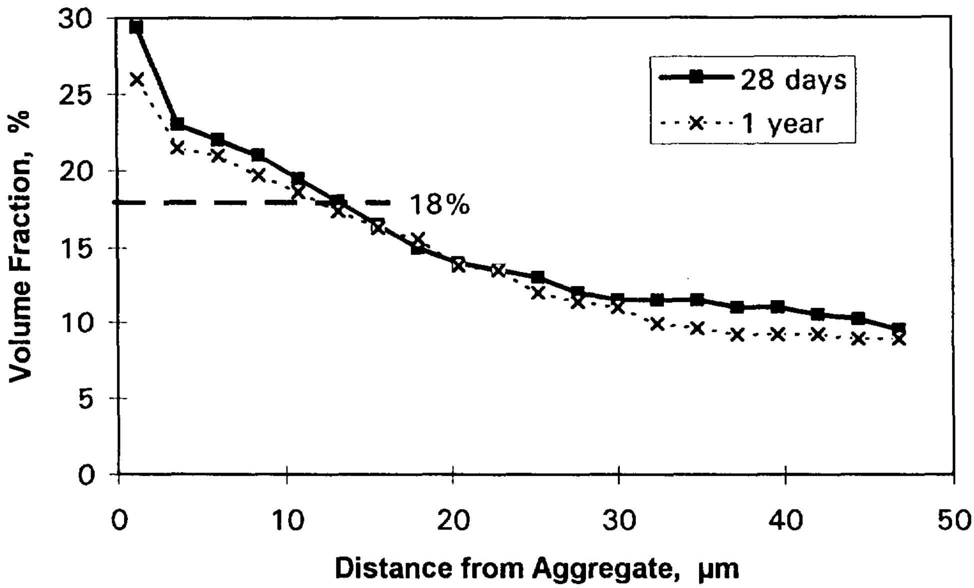

FIG. 1.
Average distribution of porosity in the interfacial transition zone around aggregate particles in a concrete with w/c 0.4, from 5.

aggregate particles equatorially. Thus the distances measured will generally be greater than the perpendicular distance to the aggregate surface. The correction factor for this effect has been estimated to be 0.81 (i.e. 35 μm in the plane of the section is on average equivalent to a perpendicular distance of 28.35 μm) (5).

The effects of the interfacial zone on the permeability of concrete are not clearly established. Many aggregates have a lower permeability than cement paste, so their addition to cement paste might be expected to result in concrete with a lower permeability than cement paste, despite the introduction of the more porous interfacial zones. Also, as pointed out by Laugesen (6) the effect of the anhydrous cement packing at the aggregate surfaces means that there is a higher effective water to cement ratio in the interfacial zone, which must result in a lower w/c for the bulk cement paste in concrete than for a plain cement paste having constant w/c throughout.

A most illuminating piece of work in this area is that of Winslow and co-workers (7,8). In this work a series of mortars were made with increasing volume fractions of sand, but other mix parameters held constant. These mortars were examined by mercury Intrusion porosimetry (MIP) and it was found that above a threshold sand content of about 45% there was a disproportionate increase in the volume intruded at pressures corresponding to pore neck sizes between 0.1 and 10 μm. It was conjectured that above this critical sand content the interfacial zones became linked together or percolated. Comparison of these experimental results with a simulation model of non overlapping 'hard cores' representing aggregate particles with 'soft shells' representing the interfacial zones, Snyder et al (8) found that an interfacial zone of 15 -20 μm best explained the MIP data.

This estimate of 15-20 μm for the thickness of interfacial zones in mortars is considerably less than the distance of about 30 μm over which higher porosities were measured by Scrivener et al.. The main reason for this discrepancy is that porosity will only contribute to the ingress of fluid (e.g. mercury) if it is interconnected. Simulations of cement microstructures generated by Bentz and Garboczi (9) indicate that the pore structure of cement paste becomes disconnected at volume fractions below about 18%. Referring to the curves shown in Figure 1, in a mature paste the porosity exceed 18% out to a distance of some 10-12 μm (corrected for sectioning effect) from the aggregate. This value is slightly lower than that estimated by Snyder et al. However, the resolution of the images used for analysis was only about 0.25 μm, this may lead to an underestimation of the total porosity of up to 3% in comparison with measurements by methanol adsorption (10).

In the light of the probable importance of the interfacial zone in the penetrability of concrete, it would be very desirable to be able to examine directly the extent to which transport occurs preferentially through the interfacial zone. Fortunately such an opportunity has arisen through the study in the SEM of concretes impregnated under load with Wood's metal. The results of which are described in this paper.

Experimental Technique

The equipment used for this experiment was specially designed and developed at the University of California at Berkeley to study the cracks in concrete samples as they exist under load. It is described in detail elsewhere (11,12). Whilst under load the concrete is intruded with Wood's metal* under a pressure of 10.3 MPa (1,500 psi), which should penetrate pores and cracks down to 0.08 μm. After intrusion the metal is allowed to solidify before unloading. The findings presented here refer to a reference sample which was only subjected to a restraining pressure of 10.3 MPa.

A normal-strength concrete cylinder (strength ~ 52 MPa), 203 mm (8 inches) long by 102 mm (4 inches) in diameter, was cast and cured at 100% RH for about 1 year. The concrete cylinder ends were ground parallel to one another with water used as the cooling fluid during cutting and grinding before testing. It was then dried in an oven at a temperature of 45°C, until reaching constant weight, to remove the moisture in the concrete, before placing in the vessel for the intrusion of the molten metal. The vessel was heated to 96°C with the top cap left open. Wood's metal was poured into the vessel to a level above the top end of the concrete cylinder to form a molten metal reservoir with the concrete cylinder totally submerged inside. The top cap was then immediately closed. A ceramic heater was placed around the vessel to liquefy the metal inside and to maintain a constant temperature throughout the experiment. This temperature was, in turn, monitored by a thermocouple that was attached to the side of the top cap. With the internal temperature thus established and maintained at 96°C, a vacuum was applied to the vessel and kept constant for at least 30 minutes. The vacuum removed any air that had become trapped in the concrete cylinder when it was assembled into the vessel. The

*Wood's metal, whose commercial name is Cerrosafe®, is a fusible alloy and in the liquid phase it is nonwetting, with an effective surface tension of about 400 N/m. It consists of 42.5% Bi, 37.7% Pb, 11.3% Sn, and 8.5% Cd. It has a melting range from 71.1°C to 87.8°C (160°F to 190°F) below the boiling point of water, and is solid at room temperature. Wood's metal has a Young's modulus of 9.7 GPa and a density of 9.4 g/cm^3.

vacuum was then removed and a nitrogen pressure of 10.3 MPa applied to the top of the vessel, to saturate the connected pores and cracks in the sample. This condition was maintained for 2 hours to allow the liquid metal to penetrate into pores and fractures. Afterwards, fans were used to cool the vessel down to room temperature and to expedite solidification. Approximately 3 hours lapsed between the time pore pressure was applied and the metal was allowed to solidify. After the experiment, specimens were extracted from the concrete cylinder and polished for the SEM study.

Results and Discussion

Figure 2 shows a view of the sample at low magnification. The bright areas are the intruded Wood's metal. It can be seen that most of the areas intruded with Wood's metal lie in the interfacial transition zones around aggregate particles, although not all these zones have been intruded. Figure 3 shows an intruded ITZ at higher magnification. There is a marked contrast between the pores in the ITZ which are filled with Wood's metal and those further from the aggregate which remain dark. The width to which the pores are filled is highly variable extending from about 30-100 μm into the paste. Also in this micrograph a crack can be seen running across the upper half of the image. This crack has not been filled with Wood's metal, which suggests that it formed during specimen preparation and was not present during intrusion.

The fact that groups of pores, which appear discrete on the two dimensional sections, become filled with the intruded metal, suggests that the pores are interconnected in three dimensions. And it is apparent that the tendency for pores to be connected is much greater in the vicinity of aggregate particles. It is possible that microcracks could have formed during the conditioning of the specimens or during the heating phase of the experiment. However, the temperature used

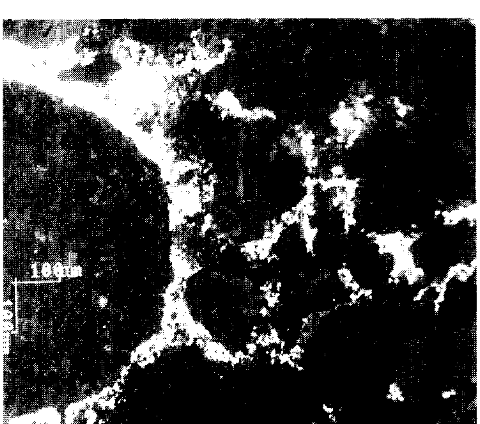

FIG. 2.
Low magnification view of microstructure. Areas intruded with Wood's metal appear bright and are concentrated around the aggregate grains.

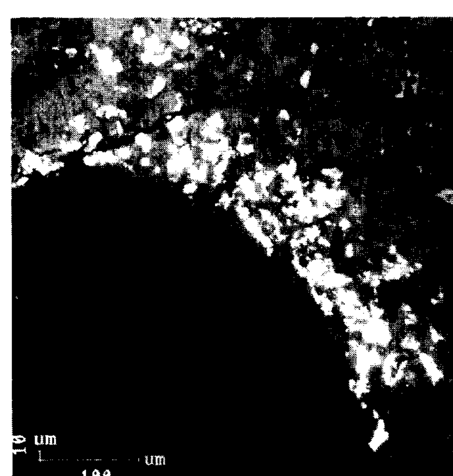

FIG. 3.
ITZ around an aggregate particle at higher magnification. (Crack probably formed during specimen preparation).

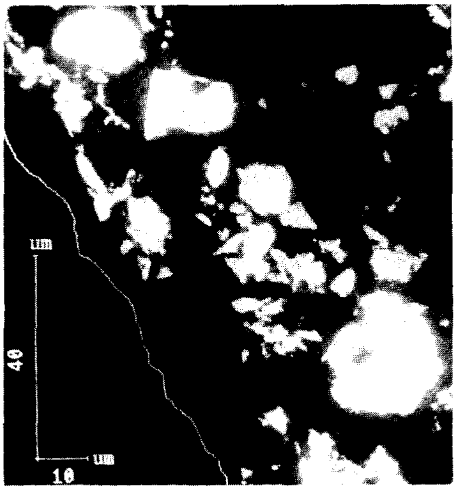

FIG. 4.
Even at higher magnifications there is no evidence of cracks linking intruded areas.

during conditioning was only 45°C. Even at high magnification, Figure 4 there is no evidence of interconnecting microcracks between the pores.

The apparent width of the ITZ in which the porosity is interconnected observed here, of 30 - 100 μm, appears to be considerably wider than the value of 10 - 20 μm discussed in the introduction. Considering just this one example, the sectioning effect cannot be corrected for and it was not possible to make enough measurements to give an average width, but general observation suggested that the interconnected width was probably at least 20 μm. If the aggregate and ITZ in concrete behave as a 'hard core/soft shell' system, this higher width would mean that the ITZs in concrete could be percolated at quite low aggregate contents. This study gives direct evidence for the fact that the higher porosity in the ITZ results in this porosity being more interconnected and confirms that the ITZ has an important effect on the transport properties of concrete.

References

1. Scrivener, K.L., Bentur, A. and Pratt, P.L., "Quantitative characterisation of the transition zone in high strength concretes" Adv. Cem. Res. 1, (1988), 230-237.
2. Scrivener, K.L. and Gartner, E.M., "Microstructural gradients in cement paste around aggregate particles" in Bonding in Cementitious Composites, 77-86. (Proc. Mat. Res. Soc. Symp., 114, 1988).
3. Scrivener, K.L., Crumbie, A.K. and Pratt, P.L., "A study of the interfacial region between cement paste and aggregate in concrete" in Bonding in Cementitious Composites, 87-88. (Proc. Mat. Res. Soc. Symp., 114, 1988).
4. Scrivener, K.L. and Pratt, P.L., "Characterisation of Interfacial Microstructures" Ch. 1 in State of the Art Report, RILEM Committee 108 ICC, Maso, J.C. ed (F.N. Spon,) 1992, to be published.
5. A.K. Crumbie, PhD Thesis, University of London 1994.
6. P. Laugesen, presentation at 4th Euroseminar on Microscopy of Building Materials, Visby, Sweden, May 1993.

7. D.N. Winslow & D. Liu, "The pore structure of cement paste in concrete"; Cem. Concr. Res., **20**, 227-235, 1990.
8. K.A. Snyder, D.N. Winslow, D.P. Bentz & E.J. Garboczi, "Effects of interfacial zone percolation on cement based composite transport properties"; Mat. Res. Soc. Symp. Proc., **245,** *Advanced Cement Based Systems: Mechanisms and Properties,* 265-270, 1992.
9. Bentz, D.P. & Garboczi, E.J. (1992), "Percolation of phases in a three-dimensional cement paste microstructural model" Cem. Concr. Res. **21,** 325-344 (1991).
10. Scrivener, K.L., Patel, H.H., Pratt, P.L. and Parrott, L.J., "Analysis of phases in cement paste using backscattered electron images, methanol adsorption and thermogravimetric analysis" in Microstructural Development During the Hydration of Cement, 67-76. (Proc. Mat. Res. Soc. Symp., 85, 1987).
11. K.M. Nemati, pp 12-32 in 'Generation and interaction of compressive stress-induced microcracks in concrete', Ph.D. Thesis, University of California, Berkeley (1994).
12. K.M. Nemati, P.J.M. Monteiro, submitted to Materials and Structures (1995).