JOURNAL OF MATERIALS SCIENCE **32** (1997) 4109–4116

Acid attack on pore-reduced cements

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Because the durability of high-performance cements is as important as their strength, the performance of pore-reduced cement (PRC) in aggressive media such as sulfuric, hydrochloric and ethanoic acids, was studied and compared with that of ordinary Portland cement (OPC). The effects of exposure to these media on these cements were monitored by periodic visual inspection and sample weighing. Specific interactions with regard to interconnected porosity were addressed and the corrosion products characterized. PRC is less susceptible than OPC against hydrochloric and ethanoic acids. However, sulfuric acid damages PRC and OPC to almost the same extent. It is shown by electron microprobe analysis that the hydrochloric and ethanoic acids quickly penetrate the interior of normal cement pastes by acid leaching of the interconnected porosity. The reduced porosity of PRC reduces the susceptibility to attack by this mechanism. Sulfuric acid exposure causes extensive formation of gypsum in the cement surface regions, which results in mechanical stress and ultimately leads to spalling. Thus fresh surfaces are exposed regularly and therefore the relatively closed microstructure of PRC is no hindrance to this kind of attack.

1. Introduction

The relative brittleness and low tensile strength of traditional unreinforced cements, compared to other building materials, had led to intensive research into the improvement of mechanical performance over the past twenty years. Consequently, several cement-based materials, such as macro-defect free (MDF) [1, 2] and densified small particle (DSP) cements [3], or the hot- and cold-pressed products of Roy *et al.* [4, 5] have been developed and show significant improvements in tensile strength and flexural strength. Pore-reduced cement (PRC) [6] is a more recent development. It is obtained by the compaction of immature cement pastes mixed at normal water/cement ratios, in a press which permits the partial removal of water not yet absorbed by cement hydration. The resulting water/cement ratio can be reduced to a value of approximately 0.1. The enhanced mechanical properties [6], the mineralogy and microstructure [7], and the substantially decreased porosity [8] of PRC have already been reported.

Research on high-performance cements has resulted in considerable improvements of mechanical performance, but a knowledge of long-term stability (i.e. dimensional stability, freeze–thaw resistance and durability in aggressive environments) is needed, before the potential for practical applications of these cements can be fully assessed. Preliminary results on the durability of pore-reduced cement have been reported elsewhere [8]. This paper concentrates particularly on the resistance of PRC to aggressive solutions, such as hydrochloric, sulfuric and ethanoic acids.

Acid attack on cement causes decalcification and formation of more or less soluble degradation products, which have no binding properties and are therefore leached away [9–14]. This process naturally commences on the external faces, but it also acts internally via the interconnected porosity of the cement. The latter effect is self-accelerating, because the internal degradation leads to increased porosity and, consequently, enhanced intrusion of the aggressive media [12, 13, 15]. The close relation between the transport of cement-degrading species into the cementitious matrix and the porosity of the cement has been explored by Garboczi [16] and Struble *et al.* [17] who confirm that the interconnected porosity governs the transport of material and therefore the kinetics of the cement degradation [13, 15, 18, 19].

It has been shown elsewhere [8] that the manufacture of PRC not only decreases the level of porosity, but also changes the nature of the pores. At the lower volume porosities, which are characteristic for PRC, isolated pores predominate. These pores are not connected to the outer boundaries of the product and therefore are sealed from intrusion and leaching. Hence the resistance of PRC to acids is expected to be higher than in ordinary cement.

2. Experimental procedure

Ordinary Portland cement (OPC) (Table I) was mixed with water at room temperature at a water/cement ratio of 0.35 and cast into perspex moulds (80 mm high and 40 mm diameter). After an initial set of 3–4 h, the pastes were demoulded and pressed as described in

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TABLE I Composition of OPC (wt%)

SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	Na_2O	K_2O
20.08	5.01	3.26	64.48	2.60	2.82	0.06	0.52

TABLE II Initial concentrations and pH of the applied acids

Acid	Concentration ($mol\,l^{-1}$)	pH
Sulfuric acid	0.20	0.9
Hydrochloric acid	0.27	0.5
Ethanoic acid	0.05	3.0

detail by Macphee [6]. Immediately after pressing, the post-pressed density of each cylinder (approximate height 55 mm and 45 mm diameter) was measured using a displacement method, with hexane as the displaced liquid. The cylinders were then stored either in water or in a desiccator conditioned by a saturated solution of copper sulfate pentahydrate (98% relative humidity) at room temperature for a period of 28 d before they were horizontally cut into halves and completely immersed into the acids. The concentrations of the acids and their initial pH are shown in Table II and were chosen to match those used in the existing literature on acid attack on cement [9–11, 20–22]. The acids were replaced weekly. Visual inspections and weight recordings of the cement samples were made every month. Prior to weighing, the samples were washed under running tap water and loosely adhering corrosion products were brushed away from the cylinder surfaces. Microstructural analysis was carried out on polished sections of the cement specimens on a scanning electron microscope (ISI-SS40) fitted with a Tracor Northern TN 2000 Microanalyser. Microanalytical studies were undertaken with a Cameca SX51 Probe Microanalyser. X-ray diffraction (XRD) was carried out using a Philips PW1710.

3. Results and discussion

3.1. Sulfuric acid

All cylinders start to deteriorate considerably after 14 d exposure, with the formation of circular layers of gypsum, which spall off spontaneously. The weight changes of the samples pre-stored under water as a function of time and density are shown in Fig. 1. Cylinders pre-stored in moist air showed a similar trend and are therefore not shown here. A gain in the weight of unpressed samples (densities around 2000 $kg\,m^{-3}$) was noted within the first month of exposure. This has also been reported by Torii and Kawamura [21] and by Metha [9] during similar studies, and can be explained by the deposition of corrosion products in the relatively open pore structure. The higher density samples, with their more closed pore structure, do not show this behaviour. Apart from the initial weight gain of the unpressed specimens, there is a steady weight loss from all the samples. After 1 y exposure, up to almost 60% of the initial weight is lost from the cylinders, regardless of curing condition, with no sign of slowing down of the degradation process. There is no apparent dependence of the degradation rate on the paste density.

Microstructural studies of the cylinders exposed to sulfuric acid for a period of 1 y (Fig. 2a) reveal features similar to those reported elsewhere [8] for an exposure time of 6 mon. A layer of gypsum has formed on the surface of the cement (1), containing silica-rich grains (2), which are probably silica gel originating from decalcified cement. The core of the specimen still seems unaffected and therefore dense, although a reaction zone of approximately 50 μm depth is observed (3). As can be seen from X-ray mapping (Fig. 3), calcium is depleted and sulfur is considerably enriched in this region. There is no further sulfur penetration beyond this zone.

The gypsum layer and the cement core are only loosely connected, as is evidenced by the macroscopic cracking at the interface, and this is presumably the region from where the spalling proceeds. This area is slightly enriched in aluminium. A magnification of the intermediate region (Fig. 2b) shows cement grains depleted of calcium (1). The growth of gypsum around cement grains is observed. Gypsum formation is associated with a volume increase, which in this case may have resulted in the disconnection of the gypsum rim from the now silica-rich cement grain relict (2). This feature possibly represents the primary stage of

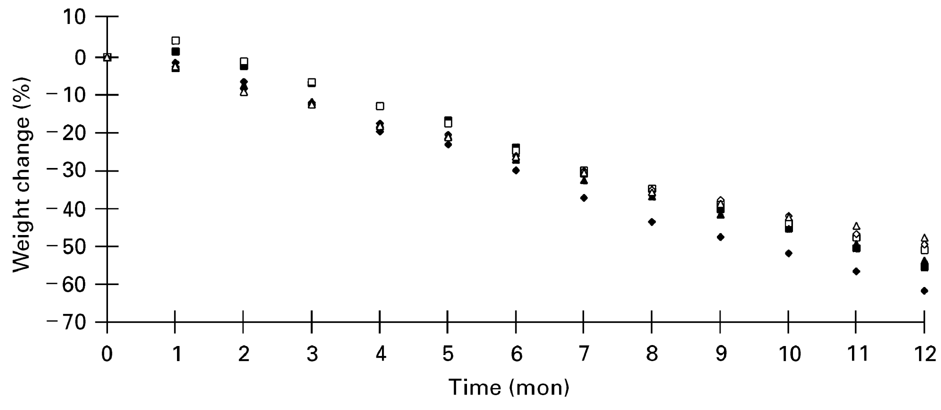

Figure 1 Effect of 0.2 M sulfuric acid exposure on OPC and PRC products. Density: (■) 2089, (□) 2123, (◆) 2242, (◇) 2430, (▲) 2567, (△) 2583 $kg\,m^{-3}$.

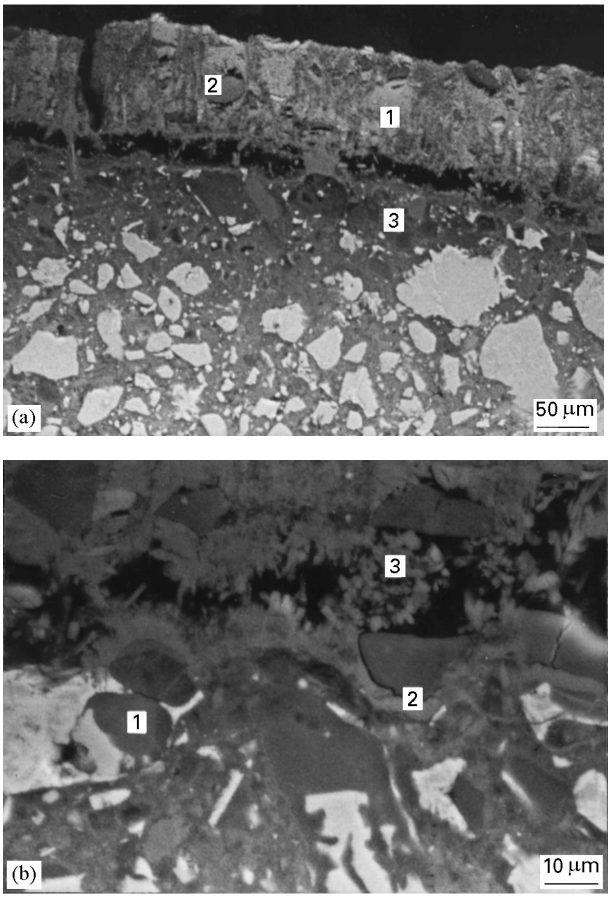

Figure 2 (a) BSE micrograph of a polished section of the edge of a PRC cylinder exposed to sulfuric acid for 1 y. (b) Higher magnification image of the same sample showing the transition zone between the outer layer and the cement core.

mechanical failure, leading to the spontaneous spalling of the gypsum layer. There are also formations in that particular zone, which contain calcium, sulfur and aluminium (Fig. 3), so that the existence of ettringite ($3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 32H_2O$) cannot be excluded. These observations are made for unpressed samples, too. Apparently, the more closed microstructures of pressed cements does not decrease their susceptibility to sulfuric acid relative to the unpressed cements. That the reaction is restricted to surfaces is supported by the rapid establishment of a constant pH upon immersion. Within the first week, the pH rose to 3.5. Even at the end of the immersion experiment (1 y) the pH rose to only 4.7 within 1 wk, suggesting that the reservoir of alkalinity within the cement core is still not affected. This indicates that there is only a surface reaction between the acid and the cement, i.e. the acid does not penetrate very far into the cement.

Although the formation of gypsum as a result of sulfuric acid attack on cement or concrete has been reported frequently, there is no agreement on its consequences. Some authors claim that the relative insolubility of gypsum leads to formation of a protective layer on the cement surface, which slows down further attack [9, 10, 20]. However, the spontaneous spalling of this layer observed in this study is in line with results reported by Torii and Kawamura [21]. Lawrence [23] had found that substantial deposits of gypsum in concrete can cause expansion similarly Wang [24] and Gollop and Taylor [25] report cracking and expansion in the gypsum layer formed in cements exposed to sulfate solutions. Cohen and Mather [26] dismiss expansion effects in the gypsum layer, arguing that gypsum forms via a through-solution mechanism, and crystals precipitated in this way do not cause expansion. They claim that expansive gypsum only forms by a topochemical mechanism. In this study, there are clear indications for expansive gypsum having formed via through-solution; however, evidence for gypsum having formed topochemically also exists. The authors believe that there is no need to discuss both mechanisms exclusively.

It is also possible that the formation of ettringite is responsible for the spontaneous separation of the corrosion layer from the cement core. The ample supply of sulfate, accompanied by the intrusion of the acid front, may also have resulted in the formation of ettringite, whose expansive nature is well known [23, 27–29]. When the pH drops below 10.7, ettringite would decompose into aluminium hydroxide and gypsum [14, 30], and therefore its only temporary existence may explain the only occasional appearance of ettringite in the exposed microstructures.

3.2. Hydrochloric acid

The weight changes of the cylinders pre-stored under water and exposed to hydrochloric acid as a function of time and density are shown in Fig. 4. Results obtained for pre-storage in moist air are nearly identical and therefore they are not shown here. It can be seen that after 1 y immersion, the pressed cements show better resistance than the unpressed ones. Although the concentration of the hydrochloric acid is slightly higher than that of the sulfuric acid, there is a lower weight loss for all the samples.

The cylinders appeared to be mechanically stable, i.e. they do not spall. However, they appeared more porous than unexposed samples, indicated by the longer time required for degassing for electron microscopy; the unpressed controls even sounded hollow when tapped with a metallic object. A brown to yellow gel-like surface layer formed, of which the major component was an amorphous material identified as an impure silica gel. At the early stage of 1–3 mon exposure, Friedel's salt ($3CaO \cdot Al_2O_3 \cdot CaCl_2 \cdot 10H_2O$), ettringite and calcite could also be detected in the degradation products; the latter probably having formed due to atmospheric carbon dioxide. However, these phases are not abundant and disappear after longer times of exposure as a result of the decreasing pH of the leachant. Owing to the reaction between the fresh, weekly replenished acid and the cement, the pH of the leachant undergoes changes during the course of the experiment. Within the first week of exposure the pH of the solution increased to 12. After 7 mon it rose only to 9.5 within 1 wk. After 12 mon the pH increased to only 3.3 after 1 wk exposure, indicating the deteriorating alkalizing power of the cement with time. This reflects the increasing depths to which the acid has to penetrate in order to react with hydroxyl ions.

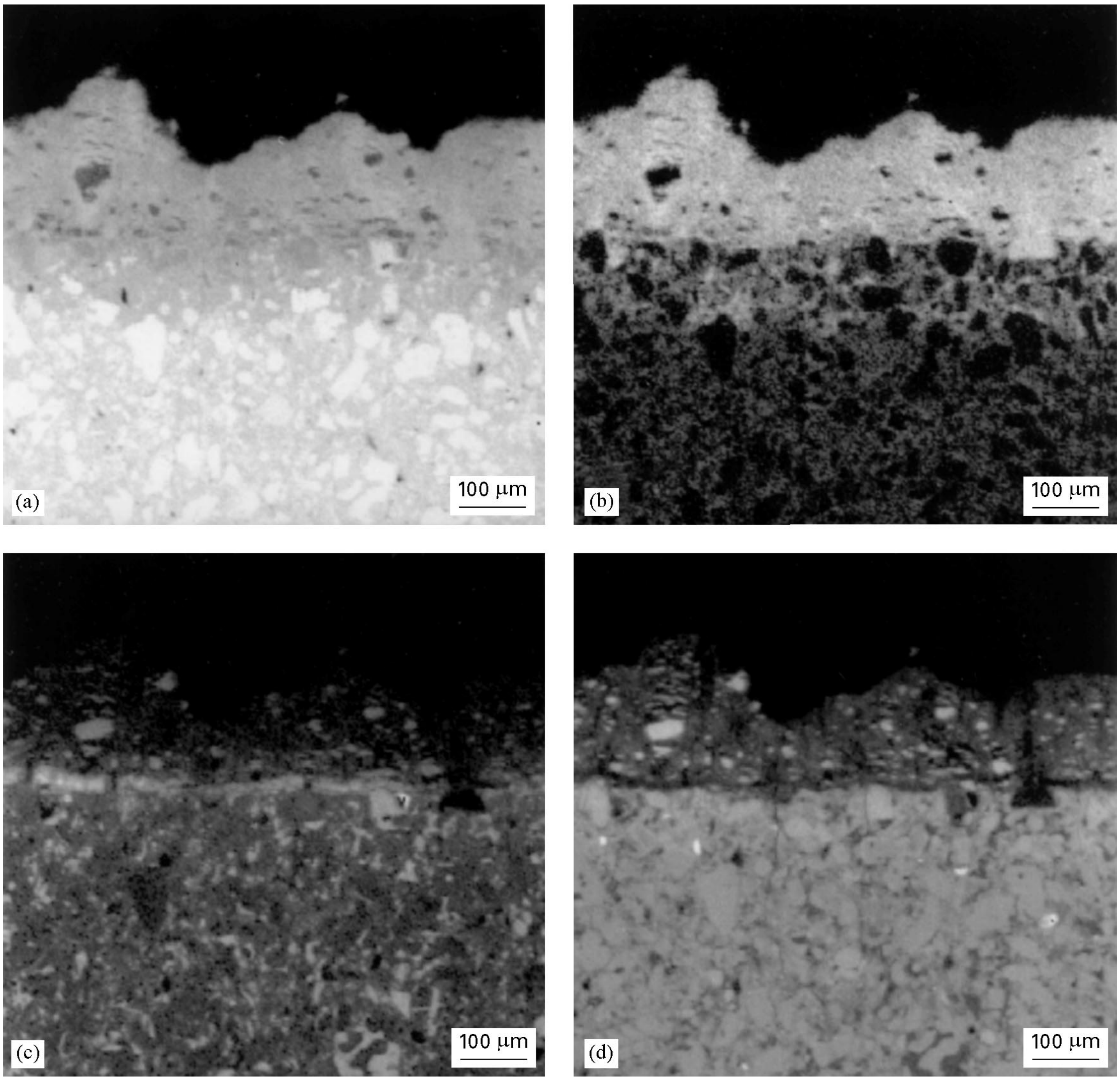

Figure 3 Electron probe microanalysis element maps from a PRC sample exposed to sulfuric acid for 1 y (bottom part of the images: cement core; upper part: gypsum layer). Maps are: (a) Ca, (b) S, (c) Al, (d) Si.

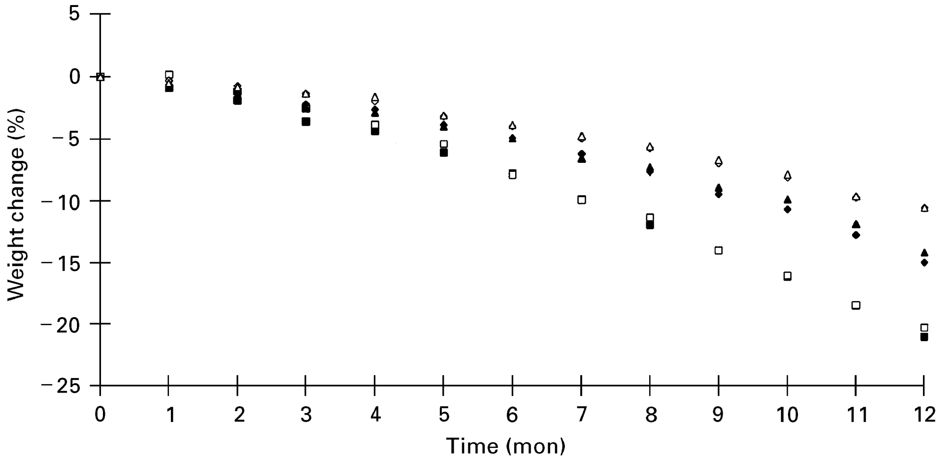

Figure 4 Effect of 0.27 M hydrochloric acid exposure on OPC and PRC products. Density: (■) 2089, (□) 2099, (◆) 2416, (◇) 2440, (▲) 2554, (△) 2573 kg m^{-3}.

Apart from the porous microstructure, micrographs of the surfaces of PRC samples exposed to hydrochloric acid for 1 y (Fig. 5a) show clear layering effects, resembling those reported by Pavlík in a similar study on hardened ordinary Portland cement pastes [10, 11]. The outermost layer (1) does not contain any calcium and is rich in silicon and aluminium, whereas the latter element is especially concentrated in a band parallel to the cylinder surface (2), which is also slightly enriched in iron (Fig. 6). The depletion of

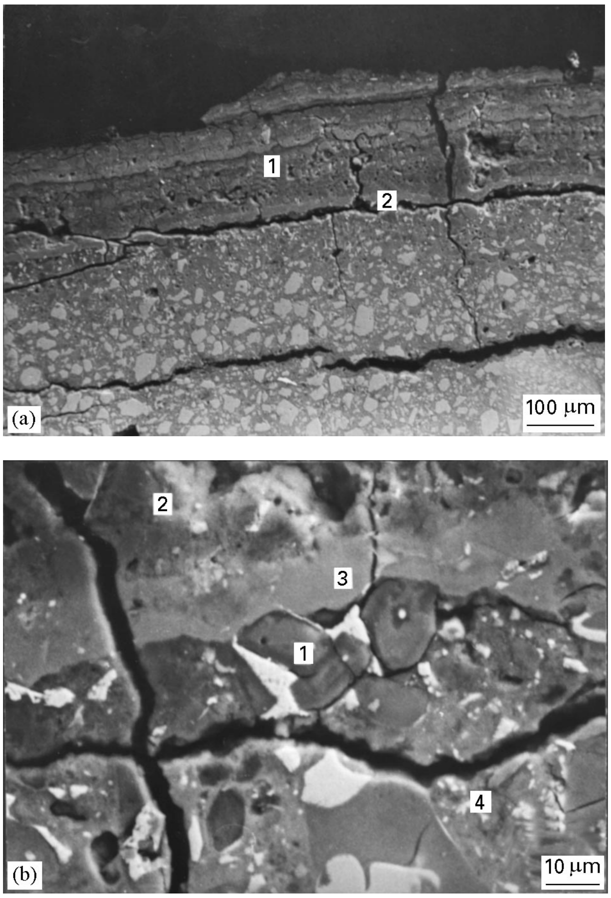

Figure 5 (a) BSE micrograph of a polished section of the edge of a PRC cylinder exposed to hydrochloric acid for 1 y. (b) Higher magnification image of the same sample showing the transition zone between the outer layer and the cement core.

calcium underneath the surface layer is due to decalcification of the cement grains, also illustrated in a higher magnification back-scattered electron (BSE) image (Fig. 5b, 1) of the transition zone between the outer silica-rich layer (2), the aluminium-rich band (3) and the cement core (4). These layering effects are typical for both pressed and unpressed samples and are due to the deposition of the less-soluble products of cement degradation (hydroxides of silicon, aluminium and iron) according to their solubilities at different pH levels, whereas calcium chloride is leached out easily [10–13]. The microprobe map (Fig. 6) also shows that chloride is penetrating the cement. It was observed that its concentration in the pressed cylinders was slightly higher than in the unpressed ones. This might be due to the higher availability of portlandite in the unpressed cement, which is the most vulnerable cement phase for acid attack [10]. The resulting calcium chloride is leached very quickly from the cement. The lower portlandite content in the pressed samples [7] allows the chloride to undergo reactions with other cementitious phases. The formation of Friedel's salt following chloride penetration into cement has been reported [12, 31–33], and this phase was detected in the present study also, by XRD of material taken from the region directly below the amorphous surface layer. Formation of other calcium chloro-aluminates and solid solutions between those chloro-aluminates and hydrated aluminate phases [34, 35] are possible too, and their formation cannot be excluded in the present study. Chloride ions are also known to be absorbed in the calcium silicate hydrate gel (C–S–H) [31, 32, 36], and this may contribute to the appearance of chloride in the X-ray maps. That the amount of chlorine detected in the surface layer is lower than in the cement core can be accounted for by the pH, which, in the corrosion layer is low enough to dissolve the chloride containing phases.

Phase investigations at the centre of the exposed cylinders yielded a mineralogy identical to that of unexposed cements, i.e. predominantly portlandite and hydrated calcium silicates for the unpressed controls, but unreacted cement phases with some portlandite for the PRC [7]. However, visual inspection of exposed unpressed cement cylinders revealed the presence of a light-grey zone at the outer edge of the cement core, and XRD of this region showed a diffuse pattern consistent with amorphous C–S–H, but without portlandite. Small amounts of ettringite were identified in this region, too. Such a zone was also observed by Pavlík in a study on the corrosion of cement paste by acetic acid and nitric acids [11] and referred to as "core layer", a zone, where the H^+ concentration is high enough to dissolve portlandite, but not sufficiently high to decalcify the C–S–H. For PRC, which contains only a small amount of portlandite in general, such a distinctive portlandite-free zone cannot be seen, even after 1 y hydrochloric acid exposure. However, a slight increase in sulfur was observed at the outer edge of the cement core (Fig. 6), as was reported by Pavlík also [11].

Another microstructural characteristic of PRC cylinders exposed to hydrochloric acid is the cracks proceeding parallel to the surface (Fig. 5a). These cracks are connected with perpendicular fissures. Horizontal cracking in OPC pastes exposed to acidic environments has also been reported by Revertégat *et al.* [13], and these authors suggest that cracks, appearing in the sound part of the cement, could be due to weak points enlarged by desiccation. The present study implies that these cracks are rather a sign for internal acid attack than artefacts of the sample preparation, because higher magnifications of the microstructure around such cracks (Fig. 7) show altered paste around them. This is visualized by the calcium-depleted cement grains (1) in the areas around such cracks. The rims of the crack in Fig. 7 (2) are rich in silicon and magnesium, but also contain calcium, aluminium and chlorine in a smaller quantity. It is assumed that these are silicon-rich gels of varying composition, similar to the corrosion products observed at the external faces of the cement. Naturally, internal acid attack preferentially commences in areas easy to access, such as interconnected pores or fissures. As the attack progresses, these flaws are widened by the removal of reaction products and further degradation of the cement. The compositional alterations of the cement paste around the cracks caused by internal attack are evidence of the existence of the cracks before sample preparation. Their width, however, might have been enlarged whilst the specimens were prepared for

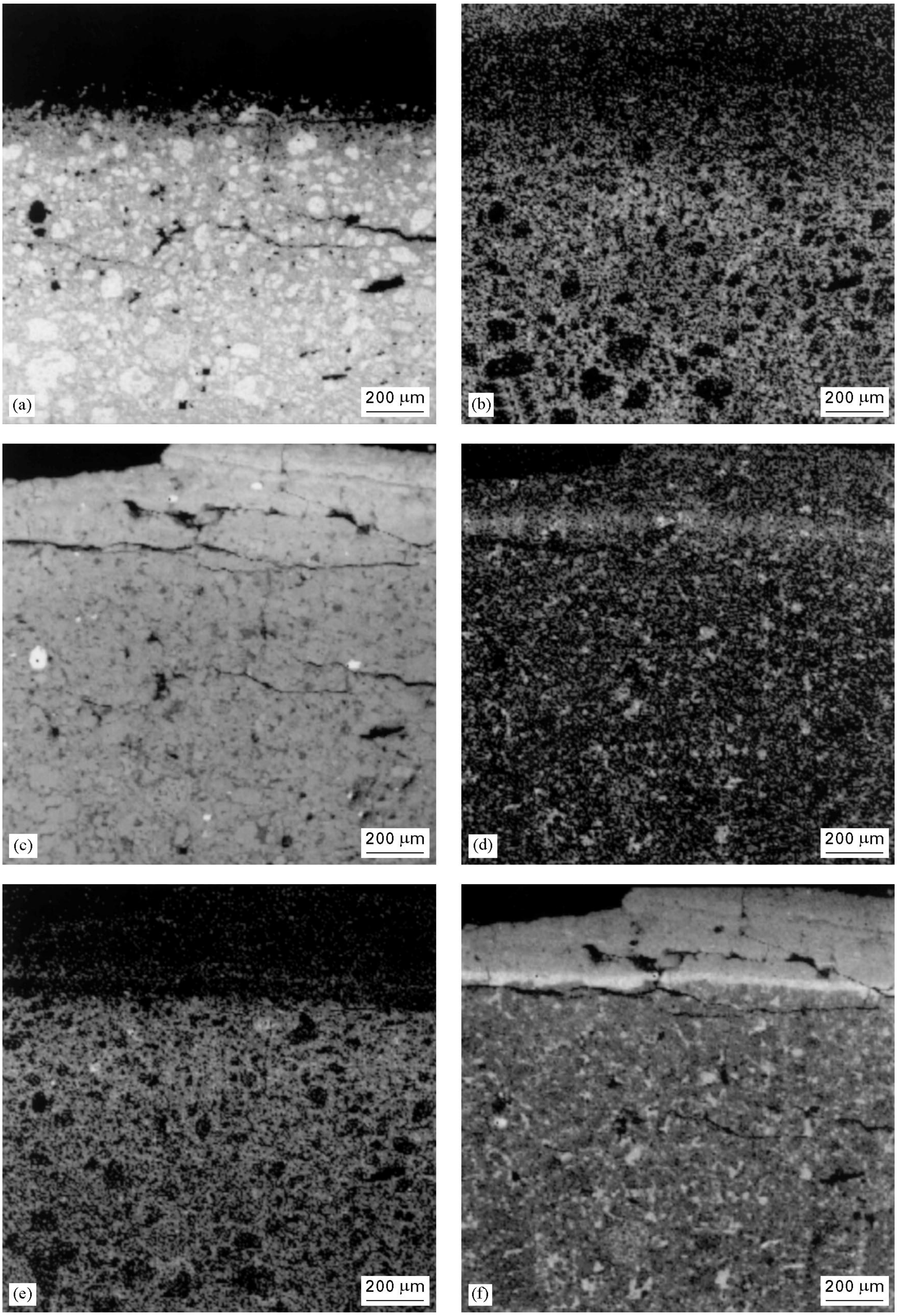

Figure 6 Electron probe microanalysis element maps from a PRC sample exposed to hydrochloric acid for 1 y (bottom part of the images: cement core; upper part: corrosion layer). Maps are: (a) Ca, (b) Cl, (c) Si, (d) Fe, (e) S, (f) Al.

electron microscopy, because the gels, which have formed as a consequence of the attack, can be subject to drying shrinkage.

3.3. Ethanoic acid

Exposure of cements to ethanoic acid had effects very similar to hydrochloric acid exposure; therefore, a detailed discussion of these observations seems unnecessary. The pressed samples are less sensitive to the acid solution than the unpressed ones. However, due to the lower concentration of the ethanoic acid, all cements lose less weight than under hydrochloric acid exposure.

Visually the exposed cylinders appeared to be unaffected and mechanically intact. A whitish layer was

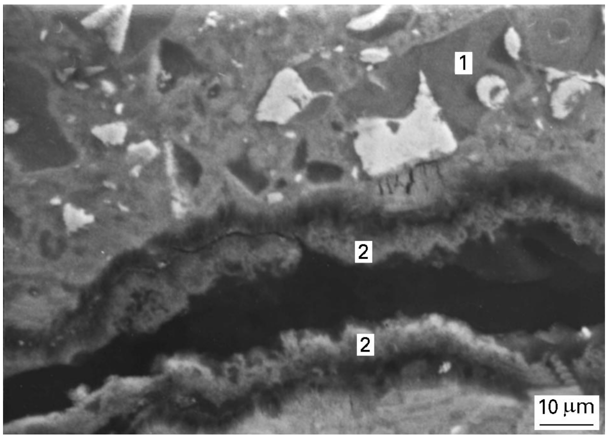

Figure 7 BSE micrograph of a polished section of a PRC cylinder exposed to hydrochloric acid for 1 y showing a crack proceeding through the core of the cement.

found floating on the surface of the solution and was analysed as calcite. The pH of the ethanoic acid solution rose from 3 to 12 within a week at the beginning of the experiment, and still went up to 11 within 1 wk after an overall exposure time of 1 y.

Microstructural investigations revealed calcium depletion in the cement grains close to the surface of the specimen, leaving behind silica-rich relicts. However, a distinctive deposition of corrosion products, as was reported for the hydrochloric acid exposure, could not be observed. This is probably due to the low concentration of the ethanoic acid, which is not strong enough to attack the cement paste as a whole and therefore preferentially reacts with the calcium hydroxide and alite.

A similar kind of "core layer", as was described in the hydrochloric acid section, was found in the unpressed samples. Cracks similar to those observed in the cements exposed to hydrochloric acid appeared in the matrix. Again, the chemical alterations in the paste around them give reason to assume that they have formed due to internal acid attack and might have been widened under sample preparation.

3.4. General remarks on the mechanism of attack

Owing to their different concentrations, a direct comparison of the acids in terms of their effect on PRC is inappropriate. Nevertheless, the enhanced deterioration of both PRC and OPC in sulfuric acid cannot merely be explained by concentration differences. It appears that the mechanism of attack is different. The formation of the gypsum layer as the low solubility reaction product does not protect the cement from further attack, because it spalls off spontaneously. Thus fresh cement surface is continually exposed for attack. Significant penetration of sulfuric acid does not occur, and hence there are hardly any microstructurally related differences in the resistance of the different cements against sulfuric acid attack.

Although hydrochloric and ethanoic acid attack naturally starts on the surface, these acids diffuse to a much greater extent into the cement and react with the cementitious matrix. The changes in pH thus occurring are reflected in alterations within the cement, most obvious in the leaching of calcium, and the deposition of reaction products according to their solubility under a certain pH. These deleterious reactions inside the cement matrix lead to an increased porosity. Because the initial level of interconnected porosity in PRC is low, its deterioration process is delayed, which is illustrated in a higher resistance against these acids.

When the resistance of PRC to acids is to be related to data available on OPC it must be taken into account that the cylinders in this study were lightly brushed before weighing and weight loss–time relations as reported by Revertégat [13] and Grube and Rechenberg [37] for cements with undisturbed corrosion layers cannot be directly compared with our data. The formed corrosion layers are partly destroyed and thus their protective potential is diminished. Owing to the increased porosity and the formation of cracks, which provide new sites for the attack of the replenished acid, the weight loss is accelerated. The brushing of the samples, however, cannot be responsible for the enhanced physical damage of the cylinders stored in sulfuric acid, because the spalling of the gypsum layer took place spontaneously.

Furthermore, the present study does not confirm a direct relation between the solubility of the calcium salt of the attacking acid and the rate at which deterioration occurs.

4. Conclusion

The resistance of pore-reduced cements compared to ordinary Portland cements in sulfuric, hydrochloric and ethanoic acid has been investigated. It has been shown that sulfuric acid has a highly deleterious effect on both pressed and unpressed cements. In the case of hydrochloric and ethanoic acid attack, PRC is more resistant than OPC. The difference between sulfuric acid and hydrochloric and ethanoic acids is the nature of the degradation products formed as a consequence of the acid attack. In the case of hydrochloric and ethanoic acids, the attack predominantly proceeds via penetration into the interconnected porosity and the weight loss of the cement is only caused by leaching of soluble reaction products. This process is hindered in PRC with its closer microstructure and is therefore responsible for its better resistance against this type of attack.

The extensive gypsum precipitation on the cement surfaces occurring with sulfuric acid attack tends to cause mechanical stresses in the surface layers and ultimately leads to loss of adhesion. The consequence is spalling, and thus the loss of material seems to keep up with the penetrating acid front. Because this kind of attack predominantly happens on the external surface, the dense microstructure of PRC is of no benefit. Owing to the poor penetration of sulfuric acid, chemical changes in the core of the cement are restricted to the region close to the surface, whereas the penetration of hydrochloric and ethanoic acids causes changes within the cement core.

Acknowledgements

The authors gratefully acknowledge the advice and assistance of Dr A. Coats. The financial support of the Engineering and Physical Science Research Council for Dieter Israel and EPMA is also gratefully acknowledged.

References

1. J. D. BIRCHALL, A. J. HOWARD and K. KENDALL, *Nature* **289** (1981) 388.
2. K. KENDALL, A. J. HOWARD and J. D. BIRCHALL, *Philos. Trans. R. Soc.* (*Lond.*) **A310** (1983) 139.
3. L. HJORTH, *ibid.* **A310** (1983) 167.
4. G. R. GOUDA and D. M. ROY, *J. Amer. Ceram. Soc.* **59** (1976) 412.
5. S. O. OYEFESOBI and D. M. ROY, *Cem. Concr. Res.* **7** (1977) 165.
6. D. E. MACPHEE, *Adv. Cem. Res.* **3** (1990) 135.
7. D. E. MACPHEE, E. E. LACHOWSKI, A. H. TAYLOR and T. J. BROWN, in "Proceedings of the Materials Research Society Symposium", edited by F. P. Glasser, G. J. McCarthy, J. F. Young, T. O. Mason and P. L. Pratt (Materials Research Society, Pittsburgh, PA, 1992) Vol. 245, p. 303.
8. N. M. GESLIN, D. ISRAEL, E. E. LACHOWSKI and D. E. MACPHEE, in "Proceedings of the Materials Research Society Symposium", edited by S. Diamond, F. P. Glasser, L. D. Wakely, S. Mindess, J. Skalny and L. Roberts (Materials Research Society, Pittsburgh, PA, 1995) Vol. 370, p. 237.
9. P. K. METHA, *Cem. Concr. Res.* **15** (1985) 969.
10. V. PAVLÍK, *ibid.* **24** (1994) 551.
11. *Idem*, *ibid.* **24** (1994) 1495.
12. S. CHANDRA, *ibid.* **18** (1988) 193.
13. É. REVERTÉGAT, C. RICHET and P. GÉTOUT, *ibid.* **22** (1992) 2159.
14. E. J. REARDON, *ibid.* **20** (1990) 175.
15. A. DELAGRAVE, M. PIGEON and É. REVERTÉGAT, *ibid.* **24** (1994) 1433.
16. E. J. GARBOCZI, *ibid.* **20** (1990) 591.
17. L. STRUBLE, E. J. GARBOCZI and J. CLIFTON, in "Proceedings of the Materials Research Society Symposium", edited by F. P. Glasser, G. J. McCarthy, J. F. Young, T. O. Mason and P. L. Pratt (Materials Research Society, Pittsburgh, PA, 1992) Vol. 245, p. 329.
18. F. P. GLASSER, *Adv. Ceram.* **3** (3rd Meeting) (1988) 139.
19. K. BYFORDS, *Cem. Concr. Res.* **17** (1987) 115.
20. N. I. FATTUHI and B. P. HUGHES, *ibid.* **18** (1988) 545.
21. K. TORII and M. KAWAMURA, *ibid.* **24** (1994) 361.
22. P. NISCHER, *Z. Straßenforsch.* Nr. 793 B 883/2 Widerstand gegen chemischen Angriff (1993) 1.
23. D. LAWRENCE, *Mag. Concr. Res.* **42** (1990) 249.
24. J. G. WANG, *Cem. Concr. Res.* **24** (1994) 735.
25. R. S. GOLLOP and H. F. W. TAYLOR, *ibid.* **25** (1995) 1581.
26. M. D. COHEN and B. MATHER, *ACI Mater. J.* **28** (1991) 62.
27. P. K. METHA, *Cem. Concr. Res.* **3** (1973) 1.
28. K. OGAWA and D. M. ROY, *ibid.* **11** (1981) 741.
29. F. P. GLASSER, D. DAMIDOT and M. ATKINS, *Adv. Cem. Res.* **7** (1995) 57.
30. A. GABRISOVÁ, J. HAVLICA and S. SAHU, *Cem. Concr. Res.* **21** (1991) 1023.
31. J. J. BEAUDOIN, V. S. RAMACHANDRAN and R. F. FELDMANN, *Cem. Concr. Res.* **20** (1990) 259.
32. H. G. MIDGLEY and J. M. ILLSTON, *ibid.* **14** (1984) 546.
33. O. S. B. AL-AMOUDI, M. RASHEEDUZZAFAR, M. MASLEHUDDIN and S. N. ABDULJAUWAD, *Mag. Concr. Res.* **46** (1994) 113.
34. L. HELLER and M. BEN-YAIR, *J. Appl. Chem.* **16** (1966) 223.
35. U. BIRNIN-YAURI, PhD thesis, University of Aberdeen (1993).
36. K. BYFORDS, *Cem. Concr. Res.* **17** (1987) 115.
37. H. GRUBE and W. RECHENBERG, *ibid.* **19** (1989) 783.

Received 19 April
and accepted 19 December 1996