CORROSION OF LOW-POROSITY MATERIALS PREPARED WITH THE USE OF GYPSUM-FREE PORTLAND CEMENT

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The differences in the resistance to corrosion GF cement and ordinary portland cement are due to different microstructural characteristic, above all significantly lower porosity of hardened GF cement pastes and concretes. The hardened GF cement pastes and concretes are corroded by the same mechanism (corrosion of the 2nd and 3nd types) as the corresponding PC materials. The difference between GF cement and PC is based on the corrosion rate, which is much lower with the GF cement materials.

INTRODUCTION

The resistance of concrete structures to aggressive effects has never ceased to be a topical issue, as there are always outstanding problems associated with the durability of concrete in roads, highways and airport runways in connection with the effects of deicing salts, polluted atmosphere, and others.

The elementary possibility of increasing the durability of building materials, in particular concrete, is based on reducing their porosity. In the case of concrete, this can be most easily achieved by reducing the water-to-cement ratio. This reduction has become one of the most topical problems in the technology of building materials. A reduction of the water-to-cement ratio of cement pastes, mortars and concrete (while maintaining the desired workability) can be achieved by optimizing the cement grain sizes distribution or the concrete mix composition, or by using additives. At present, plasticizers based on lignine or naphtahalene sulphonated derivatives are frequently used as such additives.

Very satisfactory results are obtained with simultaneous application of plasticizing additives (highly efficient naphthalene sulphonated derivatives) and amorphous silica fune (a by-product of metallurgy) [1, 2]. This combination allows the water-to-cement ratio of concrete to be cut down to 0.25 and even less. Another possibility is provided by using concrete mixes based on gypsum-free cement (hereafter GF cement, GFC), GF cement is based on ground Portland cement clinker, in which the regulating effect of gypsum has been replaced by the synergically acting effect of a mixture of a sulphonated polyelectrolyte (such as sulphonated lignine or sulphonated polyphenolate) and a salt of an alkali metal (such as carbonate). The GF cement allows the water-to-cement ratio of pastes, mortars and concrete to be substantially reduced without impairing the workability. The properties and the course of hydration of GF cements have been described in a number of studies, such as [3 through 6].

The present account is concerned with the corrosion of low-porosity cementitious materials (pastes and mortars) of GF cement. The respective research is closely related to the comercial production of GF cements in the Czech Republic, at CEVA Prachovice a. s. (a part of the Holderbank Group).

EXPERIMENTAL

For the experimetal pastes and mortars, the GF cement was prepared by grinding a standard Portland cement clinker to a specific surface area of $580 \ m^2/kg$ in the presence of a grinding aid. The clinker had the following composition: 66.5% CaO, 21.8% SiO_2, 4.49% Al_2O_3, 2.76% Fe_2O_3, CaO_{free} 1.0%, 1.05% SO_3. In the comparison experiments, use was made of a mark 400 cement made from clinker from the same locality.

Pastes of identical workability (apparent viscosity), having a free-flowing character, were prepared from the GF cement and the conventional Portland cement. Owing to the different rheological behaviour of the GF cement and the Portland cement pastes [6], the water-to-cement ratio of the former was 0.25 and that of the latter 0.36. The GF cement pastes were prepare with additions of 0.4% Kortan FM (a sulphonated polyphenolate) and 1% Na_2CO_3. The pastes were formed into specimens $20 \times 20 \times 20$ mm in size, whose compressive strength was determined at the respective time intervals.

The mortars (1:3) were prepared so as to show an approximately equal workability (mortar spread to EN): mortars with the GF cement and the conventional Portland cement had water-to-cement ratios of 0.30 and 0.50 respectively. The GF cement mortars were prepared with additions of 0.6% Kortan FM and 1.6% Na_2CO_3 and formed into specimens $40 \times 40 \times 160$ mm in size, likewise then tested for compressive strength at the time intervals specified.

Following 24 hours of hydration, the mortar specimens were placed in water at +20° C, in an Na_2SO_4 solution (100 g/l), in an NaCl solution (150 g/l) and in 5% H_2SO_4. The concentrations of the aggressive solutions were regularly checked and whenever the concentration fell by 5–10 rel.%, it was adjusted to the original value.

The fragments from the destructive tests on pastes were used to study the pore size distribution (Autopore Micromeritics, Hg porosimetry) and the morphology of the fracture surfaces by the JEOL scanning electron microscope. The composition of the individual formations on the fracture surfaces was determined by EDAX, using the ZAF corrections. The morphology and the composition were likewise determined by the EDAX method on fragments obtained from compressive testing of cement mortar specimens.

THE RESULTS AND THEIR DISCUSSION

The results of measuring the porosity of hardened GFC and Portland cement pastes are plotted in Figs 1, 2 and 3. They indicate a significant difference in the development of microstructure between the two cements. In consequence of the lower water-to-cement ratio (at the same workability), the hardened GFC pastes exhibited a lower porosity and a smaller mean pore size. There was a significant difference in pore size distribution: Both GFC and PC pastes showed a decrease in mean pore size and total porosity in the course of hydration. However, this decrease was relatively smaller with GF cement that with Portland cement, which is indicative of the creation of a relatively stable porous structure in GFC pastes already in the early stages of hydration. These results
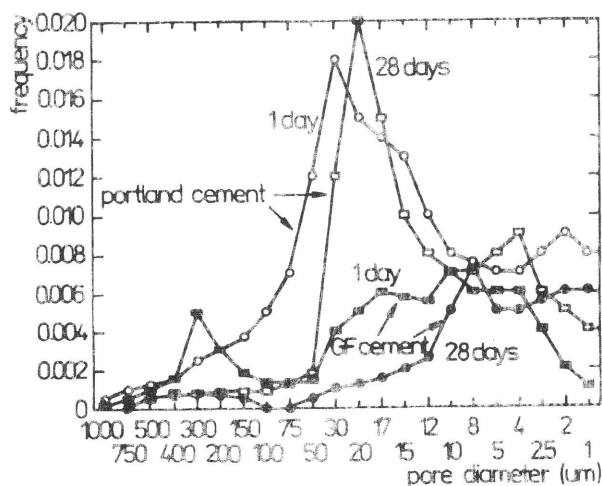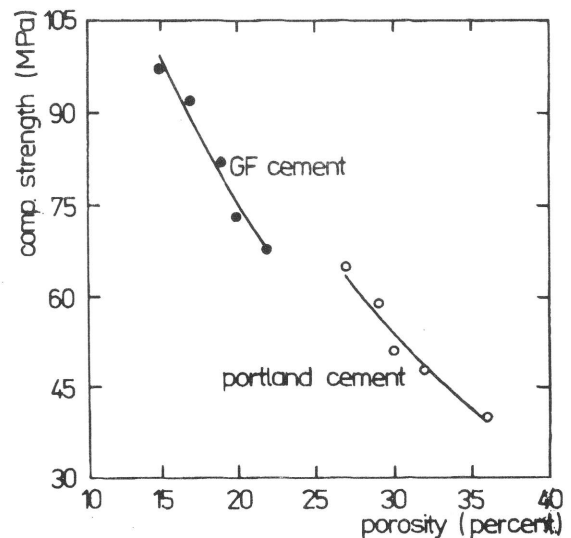
Fig. 2. *Compressive strength of hardened PC and GFC pastes vs. their total porosity. The PC and GFC pastes had the same workability.*

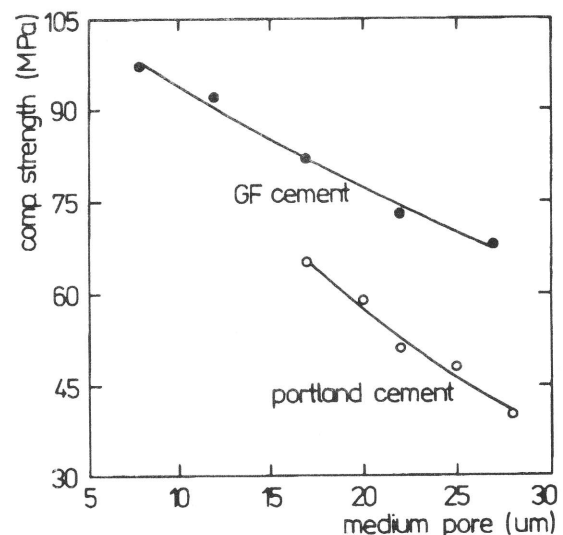Fig. 3. *Compressive strength of hardened PC and GFC pastes vs. their nean pore size. The PC and GFC pastes had the same workability.*

Fig. 1. *Pore size distribution in hardened PC (w = 0.36) and GFC pastes (w = 0.25) after 1 and 28 days. The pastes of Portland cement and the gypsum-free cement had the same workability.*

established for GF cement are in agreement with the findings by Jambor [7], who studied the porosity of Portland cement specimens with very low water-to-cement ratios (prepared by compression moulding). The strength vs. total porosity curves for GF and Portland cements (Fig. 2) are in fact mutually linked, following the same trend. There is a certain gap in the strength vs. mean pore size relationships which indicates (in agreement with the EDAX measurement results) that in addition to the difference in the structure of porosity, there is also a difference in the com-

position ("bonding potential", [7]) of GF cement hydration products compared to those of the Portland cement.

The microstructure of hardened GF cement (Fig. 6) differs from that of hardened Portland cement in particular by the absence of crystalline portlandite formations of high compactness and uniformity. The structure of hardened GF cement was not proved to contain any of the characteristic portlandite crystals; only the EDAX measurements revealed some variations on the CaO/SiO_2 ratio in the hardened material, at micron distances.

Figs. 4 and 5 show the time courses of the strength of GFC and PC mortars exposed to the effects of the various media. It should be noted that the conditions of exposure to the aggressive environments were highly demanding (a concrete structure may be exposed to aggressive effects as soon as after 24 hours of hydration). The results indicate that exposure of Portland cement specimens to Na_2CO_3 and NaCl solutions at first brings about an increase in strength, followed by a decline in strength after a certain period of time (as corresponds to the third type of corrosion). The pressure of new crystalline formations comes into effect more in the sulphate solution than in the chloride one. The sulphate corrosion brings about a considerable expansion which eventually leads to complete disintegration of the specimens.

With GF cement, the storage of specimens in water produced a much higher strength than with Portland cement specimens. The course of strength of GFC in terms of time during exposure to aggressive solutions was analogous to that of Portland cement specimens,
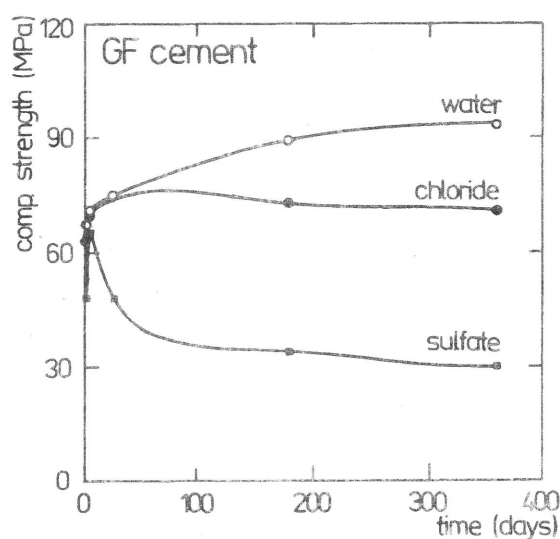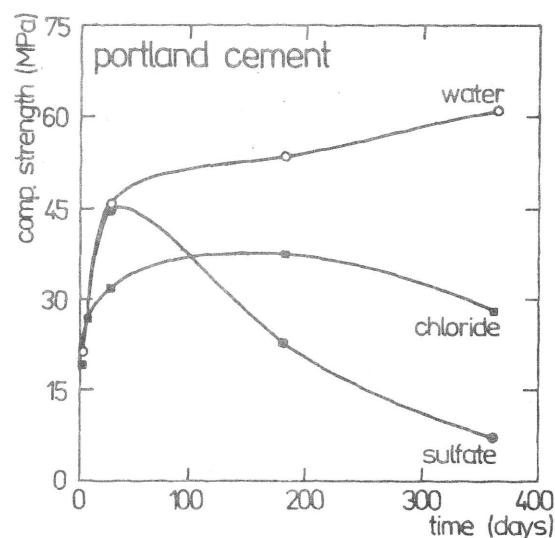

Fig. 5. The time course of compressive strength of Pc mortars (w = 0.30) placed in various media (water, Na_2SO_4 solution 100 g/l, NaCl solution 150 g/l).

likewise corresponding to corrosion of the 3rd type. However, the loss in strength of the GF specimens was both absolutely and relatively lower than that of the PC ones. The strength of GF cement specimens after long-term aggressive exposure was significantly higher. In the case of sulphate corrosion, there was another important difference, namely in the mechanism of corrosion. With the GFC specimens, the sulphate corrosion proceeded solely at the surface, producing the typical white surface corrosion layer (cf. the boundary between the corroded and uncorroded layer in Fig. 7) and there was no expansion and no disintegration. EDAX measurements revealed that the surface corrosion layer formed on GFC mortar specimens during exposure to the sulphate solution was composed for the most part of $CaSO_4$, and there was an only small increase in the content of S in the interior of the specimens. Similarly, exposure to the NaCl solution resulted in positive determination of corrosion products in the interior of the GF specimens (by EDAX) only after one year, while this occurred much earlier with PC specimens. The corrosion products due to exposure of GF specimens to NaCl solution (Fig. 8) were identified as a mixture of $CaCl_2$ with $CaCO_3$. This did not conform to the assumption that chloroaluminate hydrates are formed.

The corrosion by H_2SO_4 of mortars of both GF and Portland cement had the character of dissolution whose rate was again much lower with the GF specimens. Fig. 9 illustrates the character of the surface layer of the GF cement mortar after 3 months of exposure to H_2SO_4. The surface layer contained for the most part $CaSO_4$ (according to EDAX) and the inte-

Fig. 4. The time course of compressive strength of GFC mortars (w = 0.30) placed invarious media (water, Na_2SO_4, solution 100 g/l, NaCl solution 150 g/l).

rior was not affected by any corrosion, nor did it show any significant increase in S concentration (EDAX measurements). Control experiments with Portland cement showed a distinctly higher rate of dissolution.

CONCLUSION

1. The character of hardened GF cement pastes and mortars differs from that of hardened Portland cement ones. The differences are not only due to total porosity, but also to pore size distribution. The significantly lower porosity of hardened GF cement pastes and mortars compared to those with Portland cement are due to the possibility of processing GF cement at low water-to-cement ratios.

2. The hardened GF pastes, mortars and concerte are corroded by the same mechanism as the corresponding PC materials (corrosion of the 2nd and 3rd types). The difference between the two types of cement is based on the corrosion rate, which is much lower with the GF cement materials. The pressures of crystallization of the secondary corrosion products are significantly less effective owing to the higher strength of GF cements.

3. The gypsum-free cement being manufactured in the Czech Republic provides the possibility of producing mortars and concrete with a resistance to chemically aggressive environments significantly superior to that of materials made with Portland cement.

References

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Translated by K. Němeček

KOROZE NÍZKOPORÉZNÍCH HMOT Z BEZSÁDROVCOVÉHO PORTLANDSKÉHO CEMENTU

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Základní cestou pro získání stavebních hmot s vysokou odolností vůči působení agresivního prostředí je snížení vodního součinitele a tím snížení pórovitosti. Touto možností je příprava stavebních hmot z bezsádrovcového portlandského cementu (dále jen GF cementu). GF cement je založen na semletém slínku portlandského cementu, kde je regulační účinek sádrovce nahrazen synergicky působící směsí sulfonovaného polyelektrolytu (na př. ligninsulfonanu nebo sulfonovaného polyfenolátu) a soli alkalického kovu (na př. uhličitanu). U kaší, malt i betonů z GF lze výrazně snížit vodní součinitel beze ztráty zpracovatenosti. Charakter zatvrdlé hmoty GF a portlandského cementu je při stejném výchozím slínku odlišný. Rozdíly v zatvrdlé hmotě jsou dány nejen v celkové pórovitosti, ale i v rozdělení velikostí pórů. Znatelný posun k nižší pórovitosti zatvrdlých hmot z GF cementu ve srovnání s portlandským cementem je dán možností zpracování GF cementu při nízkém vodním součiniteli.

Zatvrdlé hmoty z GF cementu jsou korodovány stejným způsobem jako hmoty z běžného PC (koroze 2. a 3. druhu). Rozdíl mezi GF a PC spočívá v rychlosti této koroze, kdy koroze u hmot z GF cementu probíhá výrazně pomaleji. Krystalizační tlaky sekundárních korozních produktů se zřejmě projevují podstatně méně v důsledku vyšší pevnosti zatvrdlé hmoty u GF cementů.

GF cement vyráběný v České republice dává možnost přípravy speciálních hmot s vyšší odolností vůči agresivnímu prostředí než je tomu u běžného PC.

Obr. 1. Rozdělení velikostí pórů zatvrdlých kaší portlandského (w = 0.36) a GF cementu (w = 0.25) po 1 a 28 dnech. Kaše portlandského a GF cementu se stejnou zpracovatelností.

Obr. 2. Závislost pevnosti v tlaku kaší portlandského a GF cementu na celkové pórovitosti. Kaše portlandského a GF cementu se stejnou zpracovatelností.

Obr. 3. Závislost pevnosti v tlaku kaší portlandského a GF cementu na střední velikosti pórů. Kaše portlandského a GF cementu se stejnou zpracovatelností.

Obr. 4. Závislost pevnosti v tlaku malt GF cementu (w = 0.30) na čase při uložení v různém prostředí (voda, roztok Na₂SO₄ 100 g/l, roztok NaCl 150 g/l).

Obr. 5. Závislost pevnosti v tlaku malt portlandského cementu (w = 0.50) na čase při uložení v různém prostředí (voda, roztok Na₂SO₄ 100 g/l, roztok NaCl 150 g/l).

Obr. 6. Struktura lomové plochy kaše (w = 0.25) GF cementu po 28 dnech hydratace.

Obr. 7. Struktura maltového tělesa GF cementu po 1 roce uložení v roztoku Na₂SO₄ (100 g/l). Rozhraní mezi korozní vrstvou (A) a neporušeným vnitřkem tělesa (B).

Obr. 8. Struktura korozních produktů uvnitř maltového tělesa z GF cementu po 1 roce uložení v roztoku NaCl (150 g/l).

Obr. 9. Struktura povrchové vrstvy maltového tělesa z GF cementu vystavené po dobu 3 měsíců působení 5% roztoku H₂SO₄.
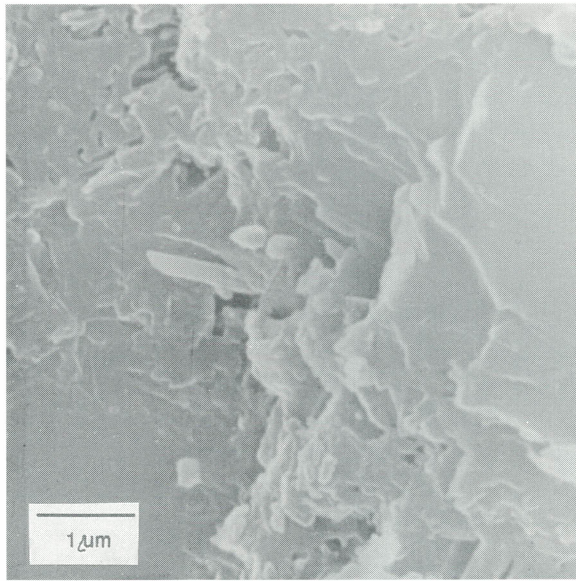
Fig. 6. *The structure of a fracture surface of a hardened GF coment paste (w = 0.25) after 28 days of hydration.*
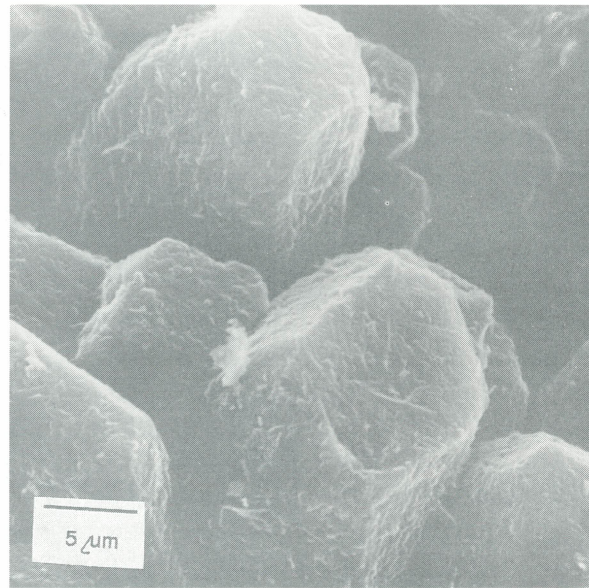

Fig. 8. *The structure of corrosion products inside a GFC mortar specimen after 1 year of exposure to NaCl solution (150 g/l).*
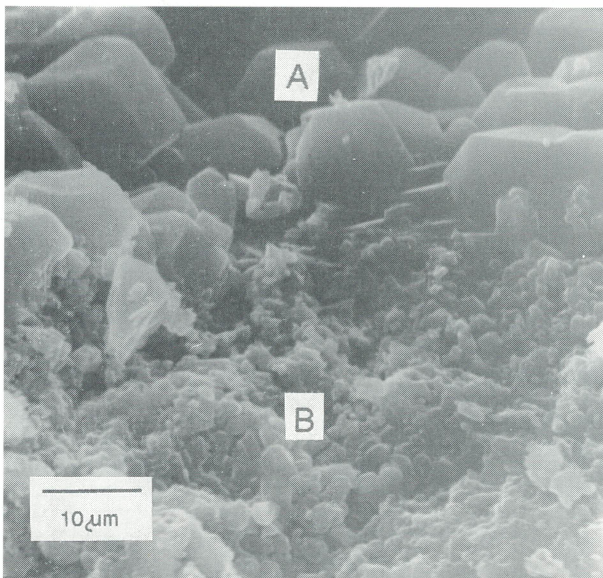

Fig. 7. *The structure of a GFC mortar specimen after 1 year of exposure to Na_2SO_4 solution (100 g/l). Interface between the corroded layer (A) and the intact specimen interior (B).*
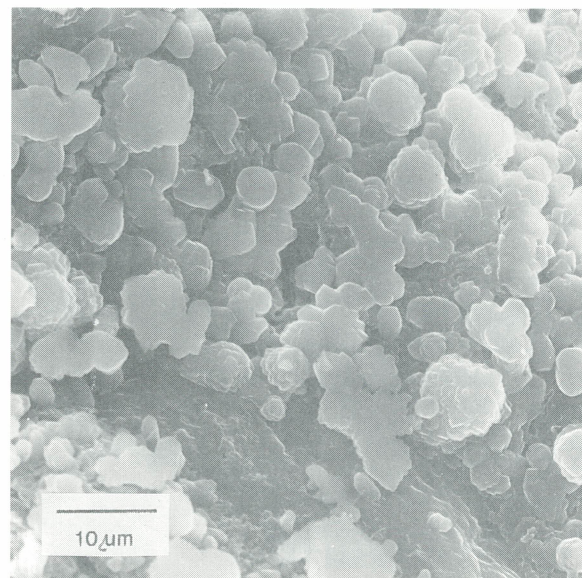

Fig. 9. *The structure of the surface layer of a GFC mortar specimen exposed for 3 months to a 5% Na_2SO_4 solution.*