

Fig. 4—Swelling of mortar prisms as a function of the surface/volume ratio of the test specimens during exposure in synthetic seawater and in saturated lime-water, at a pressure of 10 MPa

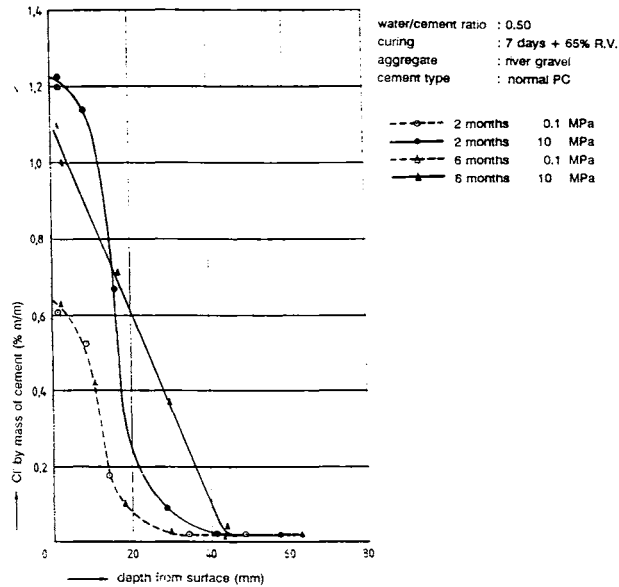


Fig. 5—Chloride-ion concentration profiles in normal portland cement concrete with $w/c = 0.50$

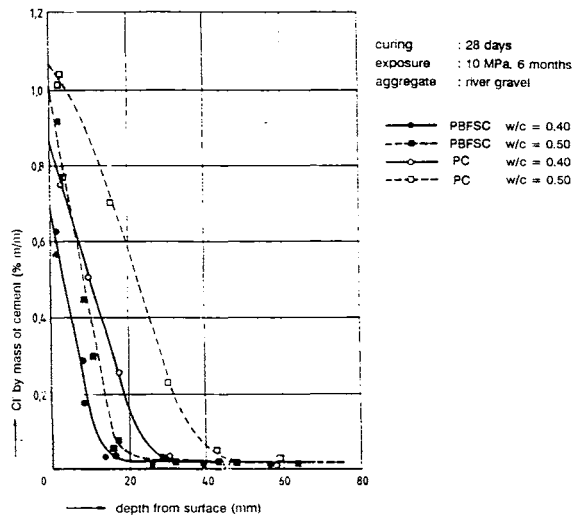


Fig. 6—Chloride-ion concentration profiles for normal portland cement concrete and blast furnace slag cement concrete with $w/c = 0.40$ and 0.50

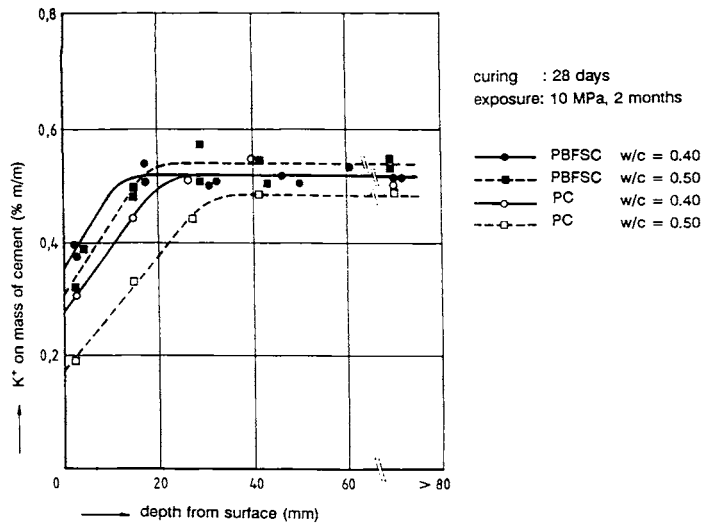


Fig. 7—Potassium-ion concentration profiles after 2 months at 10 MPa pressure

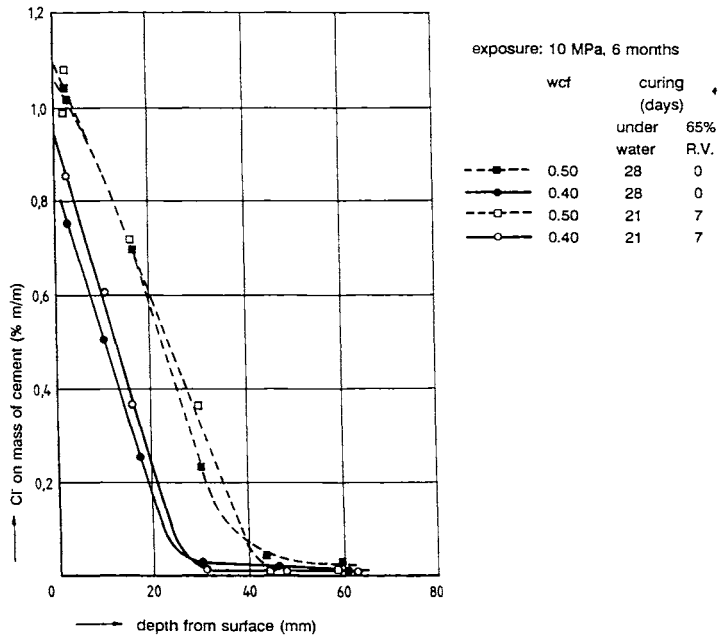


Fig. 8—Effect of drying on chloride penetration

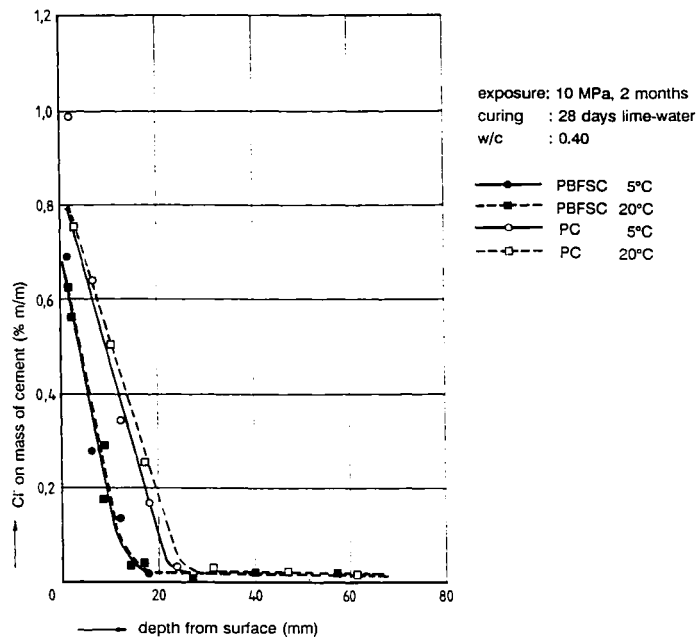


Fig. 9—Effect of temperature on chloride penetration

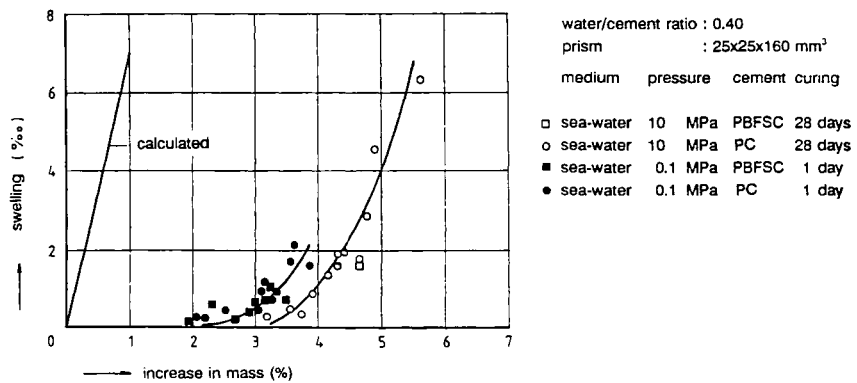


Fig. 10—Relation between swelling and increase in mass

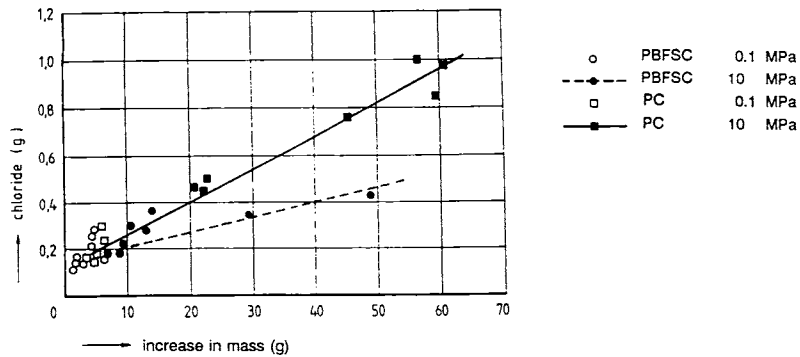


Fig. 11—Relation between penetrated chloride and increase in mass

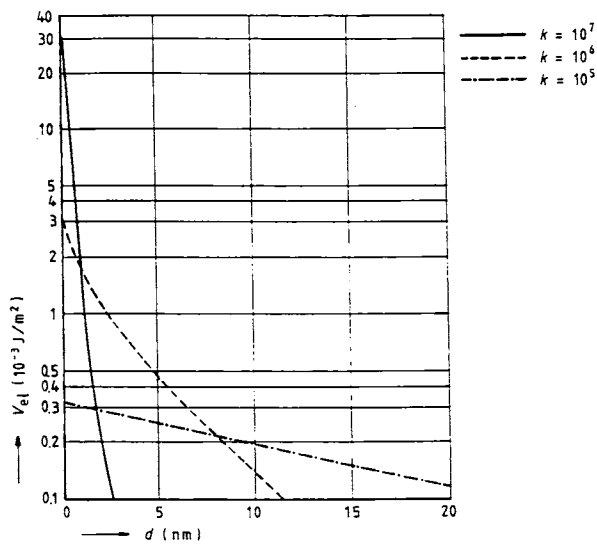


Fig. 12—Electro static repulsion potential as a function of half the distance between two plates for different concentrations of the electrolyte

Durability of High Alumina Cement Mortars for the Marine Environment

by N.C. Baker and P.F.G. Banfill

Synopsis: High Alumina Cement (HAC) mortars, made at 5°, 20° and 40°C, were mixed using seawater, de-ionised water and reconstituted seawater. The admixtures used were: an accelerator, a superplasticiser, anti-washout, air-entraining and water-proofing admixtures, and an ethylene-vinyl acetate (EVA) polymer latex dispersion. Results on short term (one year) durability against freezing and thawing and wetting and drying in all three waters are presented and compared to the performance of the same combinations over three years at a marine exposure site. The samples with polymer latex performed poorly in most tests, while the control and samples with accelerator and superplasticiser performed well in both laboratory exposure conditions and on the marine site. Temperature of mixing and curing is very important in both the early and long term performance of HAC, but the interactions between the effects of admixtures and conditions mean that it is obligatory to carry out durability tests on any proposed combination before a decision is taken regarding materials selection.

Keywords: Admixtures; durability; high alumina cements; marine atmospheres; mortars (material); seawater; temperature; tests

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INTRODUCTION

HAC is known to have superior qualities in resisting attack by seawater and many other hostile chemical environments. HAC is widely recommended as being more durable than ordinary portland cement in seawater (1,2). The conversion process does continue but is usually very slow (as little as 15% in 34 years) except in the tidal zone or in warm waters (3). HAC is also recommended for use in cold environments. HAC made with $W/C < 0.4$ has been found to be particularly resistant. Whereas there may be situations where it is necessary to mix HAC with seawater, especially offshore where fresh water is in short supply, and where there will be no embedded metal in the material, for example for repair work or for mass concrete in sea walls, there is disagreement as to the benefits or otherwise of this. Some research shows that it might be better than with fresh water (1) and some suggests that the possibility of the formation of chloroaluminates precludes its use (4). For instance, Halse and Pratt (5) found that although there was early retardation with seawater and HAC, the later microstructure was very similar to that with fresh waters.

A research programme was set up to investigate the durability of HAC mortars mixed with sea and fresh waters plus various admixtures. The aim was to provide information on the effectiveness of a range of admixtures when exposed to simulated and field exposure conditions. As well as short-term laboratory tests, a long-term field trial was set up. Information on the effects on fresh properties (6) and early properties of the hardened mortars (7) has already been reported; this paper reports results on durability tests in the laboratory and the field.

EXPERIMENTAL PROGRAMME

Materials

HAC (Ciment Fondu) from a single batch supplied by Lafarge Aluminous Cement Co Ltd, with the chemical and physical properties shown in Table 1, was used throughout with a siliceous sand conforming to a French standard grading used widely in work at Lafarge, which was achieved by combining separate particle size fractions as shown in Table 2. Three different mixing waters were used: de-ionised water (DI), Irish Sea water, which was allowed to settle but was not filtered

(SW), and a reconstituted seawater made up from a corrosion test mixture - BDH Chemicals (RSW)), see Table 3. To simulate the effects of using unwashed marine sand, each mixture was also repeated using additional sea salts (SS), giving mixtures designated DI + SS, SW + SS and RSW + SS. The amount of corrosion test mixture needed to achieve this was 6.6g total solids per kg of sand in the mortar.

The total W/C was 0.4 throughout (being the usually recommended maximum W/C for HAC) and the cement:sand ratio was 1:2. Admixtures were chosen to represent a range of types such as might be used in marine work, whether for bulk work or for repairs. The admixtures and their dosage rates were:

- lithium citrate accelerator at 0.025% by weight of cement (Accel)
- superplasticiser (FEB SP3) at 0.6% by weight of cement (SP)
- anti-washout (Conplast UW) at 1% by weight of cement (AWO)
- air-entrainer (Cormix AE1) at 45ml/50kg of cement (AEA)
- water-proofer (Palace "Intrapruf") at 1:30 in the mixing water (WP)
- EVA dispersion polymer (Vinamul 3281) at 5% solids by weight of cement (EVA).

The dosage rates were the maxima recommended by the manufacturers, with the aim of emphasising any effects. Prior information on the compatibilities of the accelerator and superplasticiser with HAC was available (8,9) but no formal data were available for the other admixtures. The range of mixtures was repeated at three temperatures: 5, 20 and 40°C, in order to cover the extremes which material might experience in the field. Hence, including the control mixture without admixtures (Nil), this programme resulted in a factorial design of 126 mixtures (7 admixtures x 6 water types x 3 temperatures).

Mixing and curing

The materials, except admixtures, for each batch were pre-heated or pre-cooled to the temperature (5, 20, 40°C) at which they would eventually be cured. Each batch was made in two halves in a Kenwood Chef domestic mixer, with one minute's dry mixing at 120 rev/min, followed by addition of the mixing water and admixture as appropriate over a period of one minute with hand mixing. At the end of this process the mortar was given final mixing for one minute at 250 rev/min. Each mixture was used to make cubes (75mm) for compression testing, cylinders (40mm diameter, 100mm long) for chloride diffusion and permeability tests and prisms (40 x 40 x 160mm) for the durability tests. All specimens were cured in temperature-controlled fresh water tanks at 5, 20 and 40°C for 7 days after demoulding.

Test methods

A laboratory programme of wetting and drying and freezing and thawing was carried out in DI, SW and RSW waters (i.e. 6 prisms from each mixture). After 7 days fresh watercuring, each specimen was subjected to 120 cycles spread over a 12 month period, during which it stood in the testwater to alternating depths of 25mm and 100mm (wetting and drying) or a constant depth of 100mm (freezing and thawing). Freezing and thawing specimens were alternately frozen at -5°C and thawed at 20°C.

During this one-year durability trial the samples were tested for ultrasonic pulse velocity (UPV) with the PUNDIT instrument, for length change by a 100mm gauge length Demec instrument and for weight changes. At the end of the year each specimen was tested in three point bending (100mm between support points) to determine the flexural strength.

In addition, one specimen from each mixture has been installed in a long-term exposure trial since January 1989. These specimens are secured in wire baskets at the mid-tide level on a rocky beach on the Irish Sea coast. They are being tested at intervals for UPV, weight change and length change as well as being visually inspected.

RESULTS

A large amount of data has been accumulated and space permits only selected significant features to be presented here. Analysis of Variance has been used to assess the significance of the factors involved and only those factors found to be statistically significant will be reported here. In this context, significant means that there is a less than 1% probability that the effect mentioned is due to chance.

Laboratory durability

Flexural strength-- Four-way Analysis of Variance (which included exposure regime type as an extra factor) showed that the effects of the various factors on flexural strength are complex. Admixture, temperature, water and exposure regime were all significant, as were all the two- and three- factor interactions except for mixing water/exposure regime and admixture/ mixing water/ exposure regime. Tables 4 and 5 show the effect of freezing and thawing and wetting and drying, respectively, on the flexural strength of specimens mixed with water types DI and SW+SS after one year. The 20°C specimens were not always the strongest and 40°C specimens performed surprisingly well, particularly when mixed with the water type SW + SS. Unfortunately, there are no flexural strength results for unexposed prisms so it is not possible to assess changes in strength as a result of freezing and thawing or wetting and drying.

Weight change-- Admixture, mixing water and various interactions were significant. All specimens gained in weight during wetting and drying and only those containing accelerator lost weight through spalling under freezing and thawing in SW and RSW.

UPV-- Most UPV levels were continuing to rise at one year but for the 50°C specimens made with EVA and WP this rise ceased at 6 months. Rises were continuing but slight for 20°C and steeper for 40°C (Fig. 1-3).

Spalling-- Visual inspection of specimens showed spalling of 50°C groups in freezing and thawing at one year, except for those containing anti-washout admixture. Some specimens from the nil, accelerator and superplasticiser groups at 20°C also showed spalling. 40°C groups generally showed spalling, except for those with superplasticiser, air-entrainer and waterproofer, which remained very good at one year.

Length change-- A large number of demec spots came off the specimens during the course of the durability trial and so explicit statistical analysis of length change has not been possible.

Exposure Site Durability

The samples on the exposure site have, at the time of writing, been in place for three years, so the results reported here are for a longer period than the laboratory trial. All three winters have included at least one period of very cold weather with snow and temperatures below 0°C.

UPV-- Admixture and temperature and the interaction between them were significant as at early ages. Velocities have mostly stopped rising or are rising very slowly, indicating that strength development has virtually ceased (Figs. 1-3).

Weight change-- Admixture and temperature and the interaction between them were significant, unlike the results from the laboratory durability tests, where temperature was not a significant factor but mixing water was. Most samples showed an increase in weight from exposure, with the exception of 20 samples (just under half) from the groups made at 40°C. Weight loss was not always a perfect match with spalling, most notably with the group made at 40°C containing waterproofer: they all showed weight loss but not spalling. The largest weight losses in the 40°C samples were from the anti-washout and accelerator groups and the lowest were from the superplasticiser and air-entrainer groups (see Fig. 4).

Expansion and contraction-- Complete statistical analysis was impossible because of the lost Demec spot problem, but inspection of the data showed that most 50°C samples had expanded since exposure and all except one of the 40°C samples had contracted, with the 20°C samples variable. On this basis it was assumed that temperature and admixture would be significant effects and missing data was replaced with the mean value of the whole temperature group and of the whole admixture/temperature group as appropriate and Analysis of Variance carried out on the data so produced. In both cases the analysis suggests that admixture, water and temperature may be significant.

Visual inspection-- All the severe spalling occurred within the 40°C group and was particularly severe in the samples made with accelerator and anti-washout, with many samples showing clear signs of an expansive chemical reaction as the cause of the spalling. Conversion seems to accelerate spalling as 20°C samples (with low levels of conversion) showed less spalling even though they were exposed to the same freezing and thawing in the field site. Only the samples made with air-entrainer and waterproofer completely escaped spalling. One 40°C sample made with accelerator had broken in two across the width. Interestingly some specimens showed clear spalling without any weight loss, having presumably absorbed further seawater into porous converted regions.

No biological changes had been evident after 18 months but over the interval between the 18 month and 3 year inspections 64 specimens acquired growths of barnacles and eight grew small seaweeds. The effects are not statistically significant, although inspection indicates that the 20°C group was far more affected