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SULPHATE RESISTANCE OF MORTAR, CONTAINING GROUND BRICK CLAY CALCINED AT DIFFERENT TEMPERATURES

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ABSTRACT

The sulphate resistance of mortar containing ground calcined brick clay (GCBC) calcined at different tempertaures (600-1100°C) and ground sand (GS) as cement replacement materials is investigated. Also the porosity, pore size distribution and strength of a selection of these mortars are determined. Mortars containing GCBC calcined at a temperature higher than 900°C show superior sulphate resistance to those containing GCBC calcined at temperatures below 900°C. Although the intruded pore volume is higher at early ages of curing, the inclusion of GCBC in the mortars leads to refinement of pore structure and its contribution to strength is significant after a curing period of 90 days. The influence of the incorporation of GCBC (calcined at different temperatures) on the sulphate resistance of mortar, is discussed in terms of fundemental mechanisms. © *1997 Elsevier Science Ltd*

Introduction

Sulphate attack of mortars and concretes made with ordinary Portland cement (OPC) and their subsequent degradation is a highly complex process. There is no single universal mechanism involved, and the mode of failure depends on a wide range of different factors which include type of sulphate, curing environment and cement composition. High resistance to sulphate attack is normally associated with a fine discontinuous pore structure and low levels of calcium hydroxide (CH) (1,2). This is because the former inhibits transport of reactive species into the cement paste, and the latter limits the levels of ettringite and gypsum produced, which are the principal components implicated in the expansion and disruption of the cement paste matrix. However in particular environments (e.g. exposure to magnesium sulphate) low levels of CH have been associated with a reduced resistance to sulphate attack (3,4) resulting from decalcification of the C-S-H gel.

Cement Replacement and Sulphate Resistance. One effective method of increasing resistance to sulphate attack is to partially replace the OPC with pozzolanic materials such as condensed silica fume (CSF) (5) and fly ash (PFA) (1) or with latent hydraulic materials such as ground granulated blast furnace slag (GGBS) (6,7). All these mineral replacements produce pore refinement and reduce the permeability of the binder matrix although the curing time necessary to provide significant reductions in permeability depends on the initial mix composition and the activity of the particular mineral replacement. For example with highly active CSF, in general the total porosity of the paste is reduced with increase in CSF content (5) and a finer pore structure rapidly develops (8). GGBS has a similar effect but the refinement of the pore structure occurs much more slowly. With PFA the total porosity of the paste increases with increase in PFA content although there is also clear evidence (5,8) for the development of a finer and less permeable pore structure at advanced ages.

Although permeability plays an important role in limiting the extent of attack from sulphates the principal controlling factor is undoubtedly a chemical one. For example the work by Torrii and Kawamura (1,4) on mortars containing different levels of PFA exposed to Na_2SO_4 solution showed that although at 6 months, sulphate penetration in some mortars was equal to or greater than the control, these mortars still showed superior performance to the control. This is interpreted as being due to reduced CH levels which were observed (from thermal analysis measurements) to systematically decline with increasing PFA content. Consequently less ettringite and gypsum were able to form and therefore expansion decreased systematically with increase in PFA content. Thus due to its greater efficiency in reducing CH and also in promoting pore refinement, CSF is (at the same replacement level) more effective than PFA in reducing expansion of mortar exposed to Na_2SO_4 solution. A similar conclusion was reached by Al-Amoudi et al. (9) in their studies of plain and blended cements in sodium sulphate solution. They observed lower strength reductions in blended cement mortar than in plain cement mortar for mortars exposed to Na_2SO_4 solutions. Also mortars made with CSF blended cement showed smaller expansions and smaller strength reductions than mortars made with PFA blended cements.

In addition to the role of CH, Gollop and Taylor (10) have also emphasised (in work on sulphate attack of slag blended pastes) the importance of the availability of alumina in controlling ettringite formation, and consider this a major factor in influencing resistance to sulphate attack in Na_2SO_4 solutions. For example pastes containing slag were found to have increased sulphate resistance as the alumina content of the slag decreased. Also increased sulphate resistance was obtained by providing additional gypsum in the mix. This effect was attributed to the formation and retention of ettringite, formed in the early stages of hydration prior to external exposure to sulphates. Taylor also observed some decalcification of the C-S-H gel in Na_2SO_4 solutions.

Calcined Clay as Cement Replacement. Although each type of cement replacement material considered, contributes to sulphate resistance in a particular way, there are important features, principally CH reduction and pore refinement, which are common to all of these materials. It might be expected therefore that other, less well established pozzolans, will also provide sulphate resistance. One material recently shown by Wild et al.(11) to exhibit significant pozzolanic activity, equivalent to that of PFA, is GCBC. In this work Lower Oxford clay was calcined at temperatures between 600 and 1100°C and was used to partially replace cement (10 and 20% replacement) in mortar. The performance of the mortars, with regard to compressive strength development, was observed to fall into two distinct classes. Mortars containing clays calcined at temperatures between 600 and 800°C showed good initial (28 day) strength relative to the control, but poor long-term (90 day) strength. Mortars containing GCBC calcined above 800°C but below 1100°C showed poor early strength but good long term-strength. The optimum clay firing temperature to give maximum beneficial effect was around 1000°C which is the approximate firing temperature for brick production. In addition Wild (12) demonstrated that concrete, containing ground waste brick made from this clay gave 90 day strengths similar to or in excess of that of the control for replacement levels of up to 20%.

X-ray analysis of the clays fired between 600 and 800°C showed substantial clay phase (illite) still remaining and also strong reflections from anhydrite ($CaSO_4$). X-ray analysis of clays fired above 900°C showed the disappearance of illite, a marked reduction in anhydrite and quartz and growth of plagioclase feldspar. It was suggested that the poor long term-strength of mortars containing GCBC at 600-800°C, where pozzolanic activity derives from the activated clay, was due to the excessive amount of anhydrite present. At the higher firing temperatures (900-1100°C), where pozzolanic activity almost certainly derives from amorphous glassy phase, the amount of residual anhydrite was much lower and does not therefore impair the long term strength development of the mortar. The object of the current study is to assess the sulphate resistance of mortars containing these clays fired at the various temperatures, and to establish whether the trends in performance observed for strength are reflected in performance in respect of sulphate resistance.

In addition, in order to assess the influence of pore structure on these properties, porosity and pore size distribution data are reported for some compositions. It should be noted that the mortar bars used for sulphate resistance, porosity and pore size distribution measurements, are from the same mixes that were used to produce mortar bars for the determination of compressive strength reported in [10].

Experimental

Materials. The clay samples consisted of lower Oxford clay which had been calcined at 600, 700, 800, 900, 1000 and 1100°C. They were supplied in crushed form by Hanson Brick Company Ltd, UK. The chemical analysis of lower Oxford clay is given in given in [11]. Table 1 gives the sulphate content (SO_3) of the clay at the different calcining temperatures as supplied by Hanson Brick Ltd.

The cement used was ordinary Portland cement (OPC), the composition of which is given in Table 2. The sand used in the mortar mixes was a quartz sand with particles ranging from 0.25-0.71 mm. The same sand was also used in a finely ground form as an inert filler material for partially replacing the cement.

Grinding. The fired clay samples and a portion of the quartz sand were ground to approximately cement fineness using a HERZOG HSM/100 grinding machine for a period of two minutes. Although the particle size is bound to show some variation between the different samples, the grinding energy input was the same for all the samples.

Mixing, Specimen Preparation and Curing. The mortar mixes had proportions of 1 binder: 2.5 sand. The binder consisted of cement and GCBC, or cement and GS. The water to binder

TABLE 1

Sulphate Content for the Clay Calcined at Different Temperatures

Calcining Temperature, °C	600	700	800	900	1000	1100
SO_4-Water Soluble, wt %	4.0	4.4	4.1	3.5	2.4	1.3
SO_4-Acid (HCl) Soluble, wt %	5.3	5.6	5.6	4.4	2.8	1.0
SO_4-Total (HF) Soluble, wt %	5.3	5.6	5.7	4.4	2.7	1.2

TABLE 2

Composition of Cement

OXIDE	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	Na_2O	K_2O	TiO_2	L.O.I
%	20.2	4.2	2.0	63.9	2.1	3.0	0.14	0.68	----	2.81

ratio was kept constant at 0.55. The cement was partially replaced by 0, 10 and 20% of GCBC calcined at the various temperatures, or GS. Mortar bars of dimensions 25mm × 25mm × 285mm were used for these mixes. After casting, the moulds containing the specimens were covered with cling film to prevent loss of water by evaporation. After 24 hours the specimens were demoulded and wrapped with a few layers of cling film and placed in polythene bags. The bags were placed in a large plastic tank, covered with damp hessian and plastic sheeting and a lid was placed on the tank. The temperature of curing was maintained at 20 ± 2°C. This curing regime was adopted for these relatively small specimens to avoid leaching of $Ca(OH)_2$, carbonation and moisture loss. The specimens were used for compressive strength, porosity, pore size distribution and sulphate resistance.

Testing. The bars which were used for sulphate resistance studies had stainless steel inserts cast into their ends to allow the changes in length to be accurately monitored. Specimens were moist cured for 28 days and then immersed in a 5% sodium sulphate solution. The sulphate solution was replenished every two months. The changes in length of the specimens were then monitored at approximately two month intervals for a period of more than two years or until the specimens failed. An expansion of 0.5% was considered to be the failure criterion of mortar bars, although specimens were continued to be monitored up to an expansion of 1.25%.

Compressive strength measurements were made at ages of 7, 14, 28, 90 and 365 days. Only the strengths of mortars at 28 and 365 days are reported in this study. The other strength values are reported elsewhere (11) as is the testing procedure for compressive strength determination. After specimens were tested for compressive strength, samples from the broken specimens (about 2 g in weight) were taken and dried at 40°C under silica gel until a constant weight was achieved. Most of the weight loss (~80%) occurred in the first 24 hours. The dry samples were used to conduct the porosity and pore size distribution measurements using the mecury intrusion porosimetry (MIP) technique. Two Fisons (Italy) instruments were used for MIP, the Macropore Unit 120 and the Porosimeter 2000WS. Details of the procedure are given in (13). Only selected mixes were considered for MIP. These are the control mix which contained no GCBC and no GS, mixes containing GCBC calcined at 1000°C (which is the approximate firing temperature for brick production) and mixes containing GS.

Results and Discussion

Sulphate Expansion. Figures 1 to 3 show the expansion of mortar bars in 5% Na_2SO_4 solution for a period up to two years (720 days). Figure 1 compares the expansion of mortar bars containing 10 and 20% of GS with the control. The control failed (>0.5% expansion) at about 460 days, but when the cement was replaced by GS the bars failed at shorter times, the failure being earlier at higher replacement levels. However some bars including the control, continued to expand well above the 1.3 percent expansion level shown.

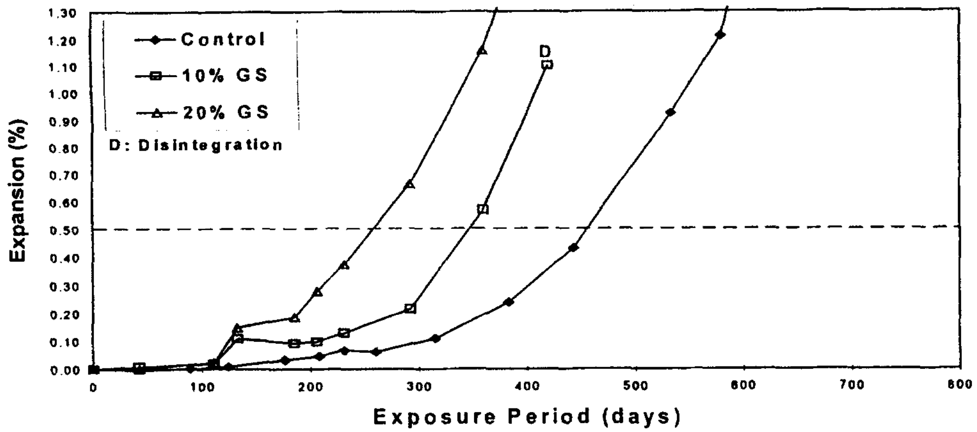

FIG. 1.

Sulphate expansion vs exposure period for mortar bars containing 0, 10 and 20% GS immersed in 5% Na_2SO_4 solution.

The expansions of mortar bars containing GCBC (0, 10 and 20%) calcined at 600, 700 and 800°C are shown in Figures 2a to 2c and those calcined at 900, 1000 and 1100°C are shown in Figures 3a to 3c. For bars containing GCBC calcined at 600, 700 and 800°C, the lower the calcining temperature the shorter the time period before the bars fail and also these bars tended to disintegrate at relatively low levels of expansion. For example all the bars containing ground brick calcined at 600°C disintegrated within 220 days, after expanding by less than 0.6%. Also there is a tendency for bars containing the lowest amount of GCBC replacement to expand more prior to failure than those containing larger amounts of ground brick.

There is a dramatic improvement in sulphate resistance for bars containing GCBC calcined at above 800°C (see Figures 3a-c) especially for calcining temperatures of 1000 and 1100°C. All the expansion values are well below 0.5% and after 720 days of exposure to sodium sulphate solution no signs of cracking or disintegration are apparent. Also sulphate resistance is higher at higher replacement levels. In particular for bars containing 20% GCBC calcined at either 1000 or 1100°C expansion is negligible.

Porosity and Pore Size Distribution. Figures 4a and 4b show the total intruded pore volume against curing period (up to one year) for the control mix and mixes with 10 and 20% replacement of cement with GS (Fig. 4a) and GCBC calcined at 1000°C (Fig. 4b). Partial replacement of cement by both GS and GCBC produces an increase in intruded pore volume relative to that of the control and the increase tends to be somewhat greater for GS replacement. Also the total intruded pore volume increases with increasing replacement level and as might be expected, decreases with increase in curing time, although there is quite a wide scatter in the data. The percentage of the total intruded pore volume which is made up from pores of radii less than 0.05μm was taken as measure of pore refinement. This is plotted against curing period, in Figure 5a for mortar containing GS, and in Figure 5b for mortar containing GCBC calcined at 1000°C. The data in both cases are compared with the control mortar. In this case there is a clear difference in behaviour relative to the control between mortar containing GCBC and mortars containing GS. In both cases in the early stages of curing (up to 28 days) the percentage of fine pores is less than in the control mortar and

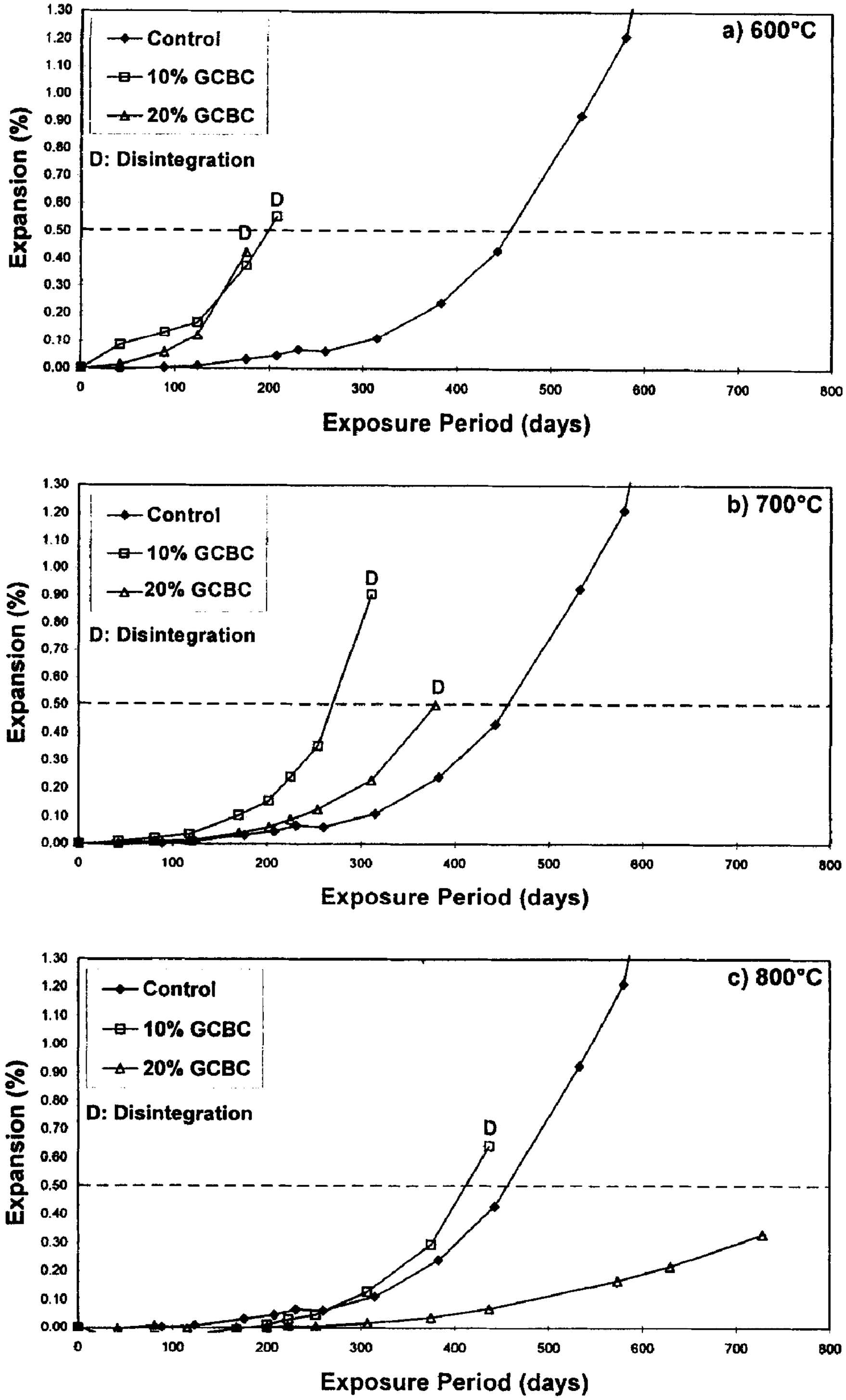

FIG. 2.

Sulphate expansion vs exposure period for mortar bars containing 0, 10 and 20% GCBC calcined at a) 600°C, b) 700°C and c) 800°C immersed in 5% Na_2SO_4 solution.

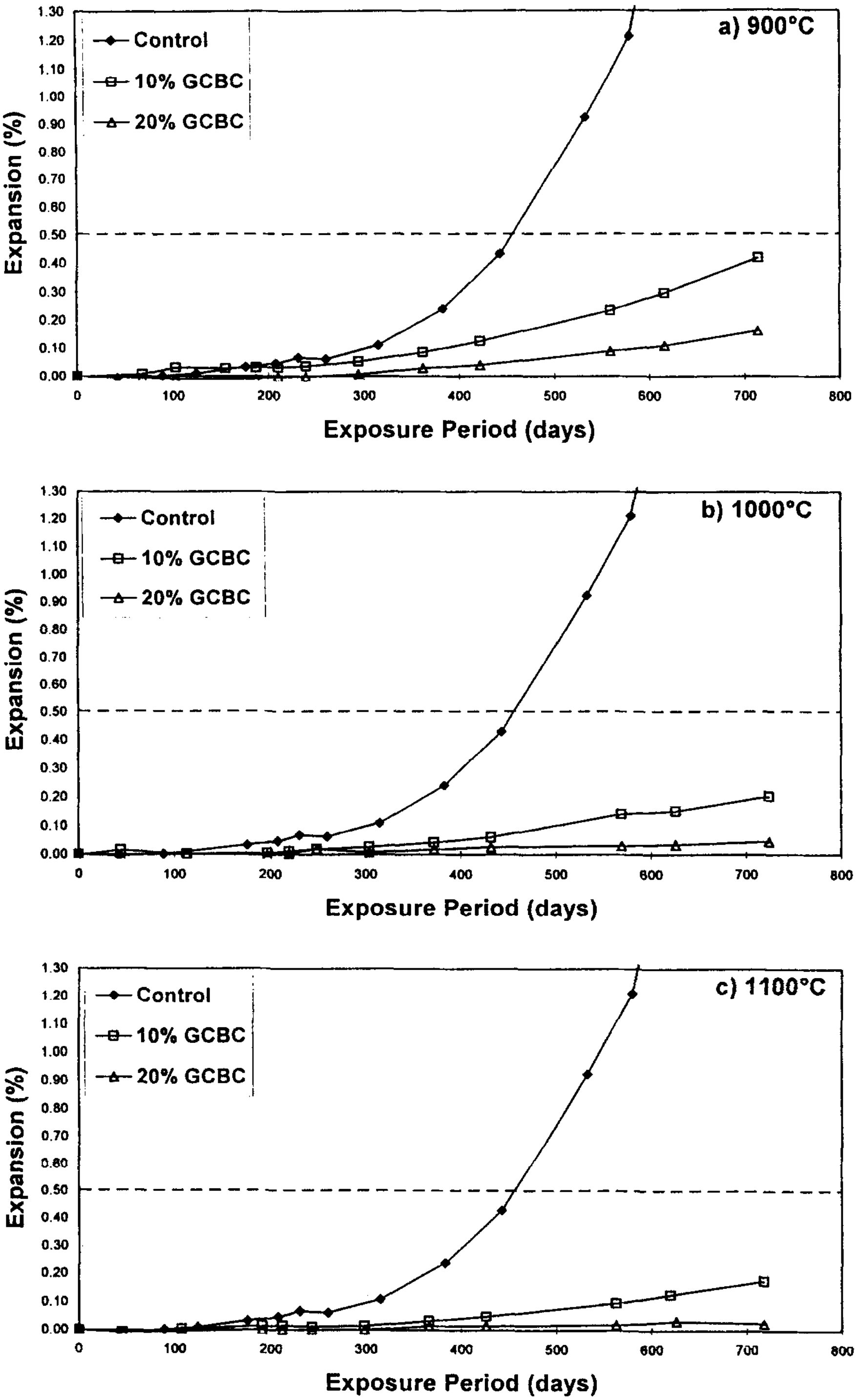

FIG. 3.

Sulphate expansion vs exposure period for mortar bars containing 0, 10 and 20% GCBC calcined at a) 900°C, b) 1000°C and c) 1100°C immersed in 5% Na_2SO_4 solution.

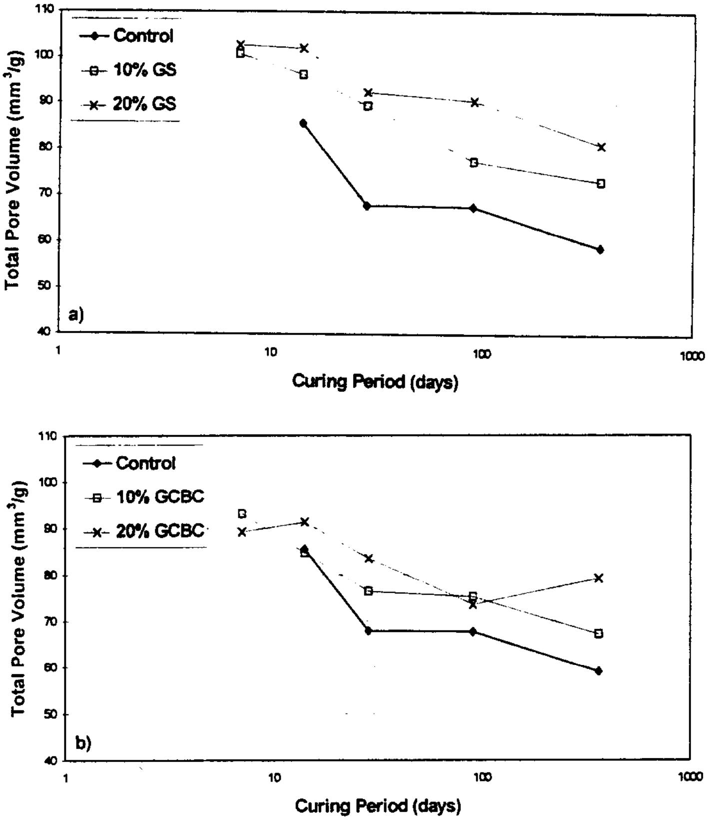

FIG. 4.

Total induced pore volume vs curing period for mortars containing a) 0, 10 and 20% GS and b) 0, 10 and 20% GCBC.

tends to decrease with increase in replacement level although less so with GCBC than with GS. However beyond 28 days the proportion of fine pores in mortar containing GCBC increases to levels in excess of the control (i.e. above 70%) whereas in the case of mortars containing GS the percentage of pores continues to show levels less than the control. This demonstrates that replacing cement with GCBC produces additional pore refinement at later curing periods (i.e. beyond 90 days) which indicates pozzolanic activity.

Strength. Figures 6a and 6b compare the development of compressive strength with curing time for respectively mortar containing GS (0, 10 and 20% replacement) and mortars containing GCBC calcined at 1000°C. At all curing times the strengths of mortars containing GS (Figure 6a) are lower than the control and progressively decrease with increase in replacement level. This corresponds to a coarsening of pores as illustrated in Figure 5a. For mortars containing ground brick clay (Figure 6b) the strengths are initially lower than the control and also decrease with increasing replacement level although less so with ground brick clay than with ground sand. However at late curing times the strengths exceed that of the control. This clearly reflects the refinement in pore structure observed in Figure 5b.

Figure 7a compares the 28 day strengths of mortars containing10 and 20% of GCBC with those containing equivalent levels of GS, and Figure 7b presents similar data for a curing

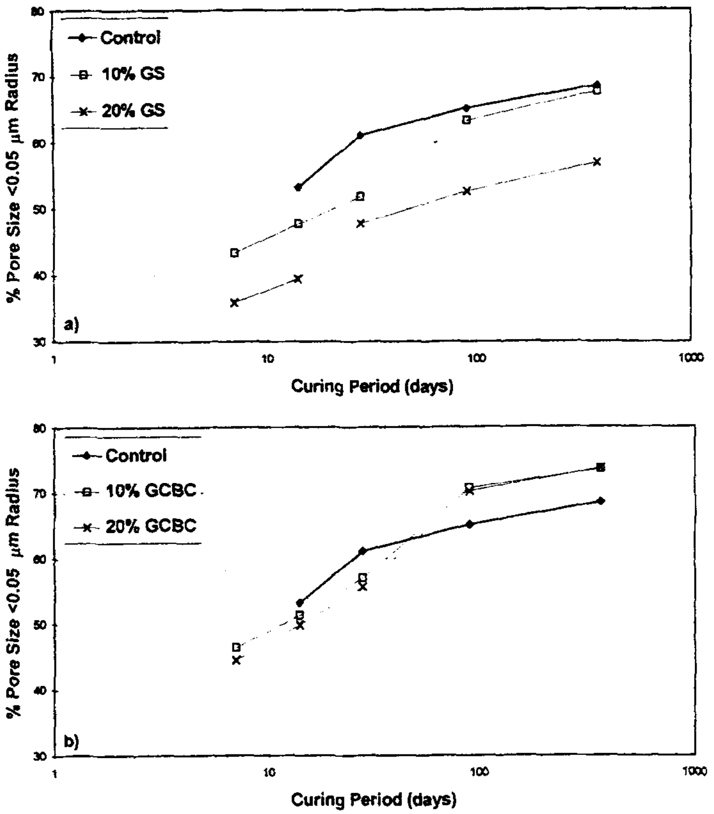

FIG. 5.

Percent pore volume occupis by pores <0.05 µm radius vs curing period for mortars containing a) 0, 10 and 20% GS and b) 0, 10 and 20% GCBC.

period of 365 days. These curing periods are selected because 28 days represents the curing period prior to immersion of the mortar bars in sulphate solution, and 365 days represents the long-term strength. The distinction in strength development between mortars containing GCBC calcined at above and below 800°C is clearly apparent from these figures.

Discussion. Both GS and GCBC produce an increase in total pore volume of mortar with increase in replacement level. However partial replacement of cement by GCBC produces significant pore refinement which does not occur with GS. Comparison of Figures 5a with 6a and Figures 5b with 6b demonstrate clearly the influence of that pore refinement on strength development. For the control and for mortars with GS there is a gradual and continuous but decelerating refinement in pore structure with time (Figure 5a) which corresponds with a similar gradual and continuous but decelerating increase in strength (Figure 6a). For mortar containing GCBC, beyond 28 days there is a marked increase in both the rate of pore refinement and the rate of strength gain and after one year both the compressive strength and the fineness of the pore structure are superior to that of the control even though the total pore volume remains above that of the control. This is clearly a result of the pozzolanic reaction of the GCBC with calcium hydroxide (CH), the reaction products of which are blocking and segmenting the capillary pore structure of the cement paste. This might be expected to in-

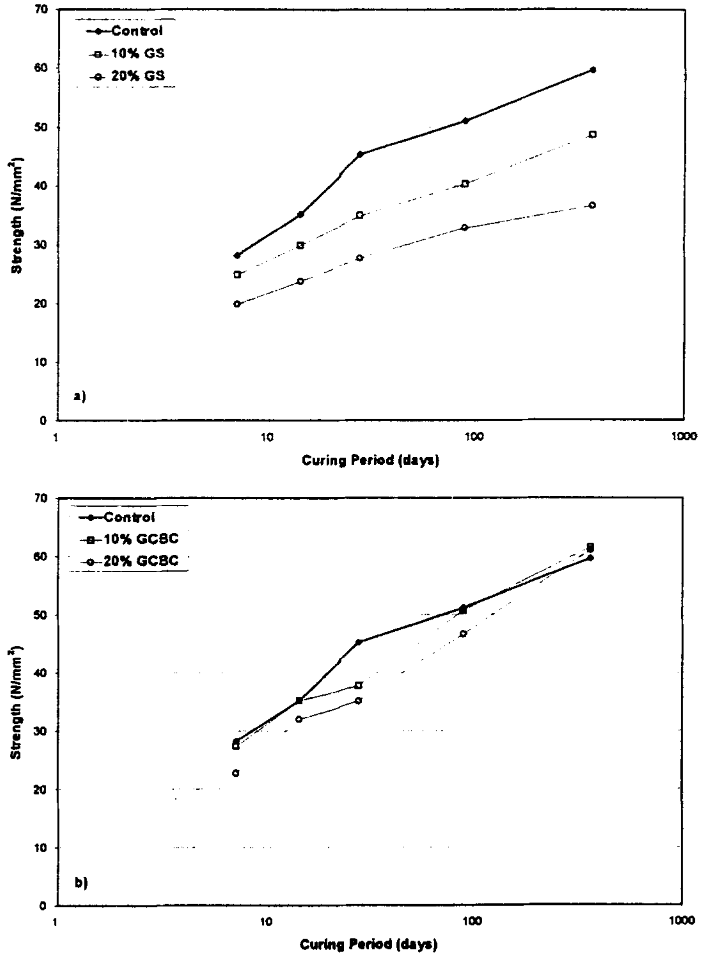

FIG. 6.

Compressive strength vs curing period for mortars containing a) GS and b) GCBC calcined at 1000°C.

crease the resistance to sulphates both by reducing the rate at which sulphates ingress the mortar and also by reducing its CH content, neither of which will occur for the GS mortars.

For the GS mortars (Figure 1) sulphate expansion begins earlier and is greater as the GS content increases, reflecting the increase in pore volume and the coarsening of the pore structure at higher GS content. This suggests that the increased volume available into which the reaction products can expand (and the reduced CH content due to the dilution effect) does not compensate for the increased ingress of sulphate into the enlarged coarse pore volume. In addition the lower strength of mortars with higher GS replacement will provide lower resistance to expansion.

For GCBC mortars (see Figures 2 and 3) expansion begins later and becomes smaller as the GCBC content increases, which is exactly opposite to that of GS mortars. This must clearly reflect the development of a finer pore structure which is indicated in Figure 5. Relative to the control the degree of pore refinement for GCBC does not exceed that of the con-

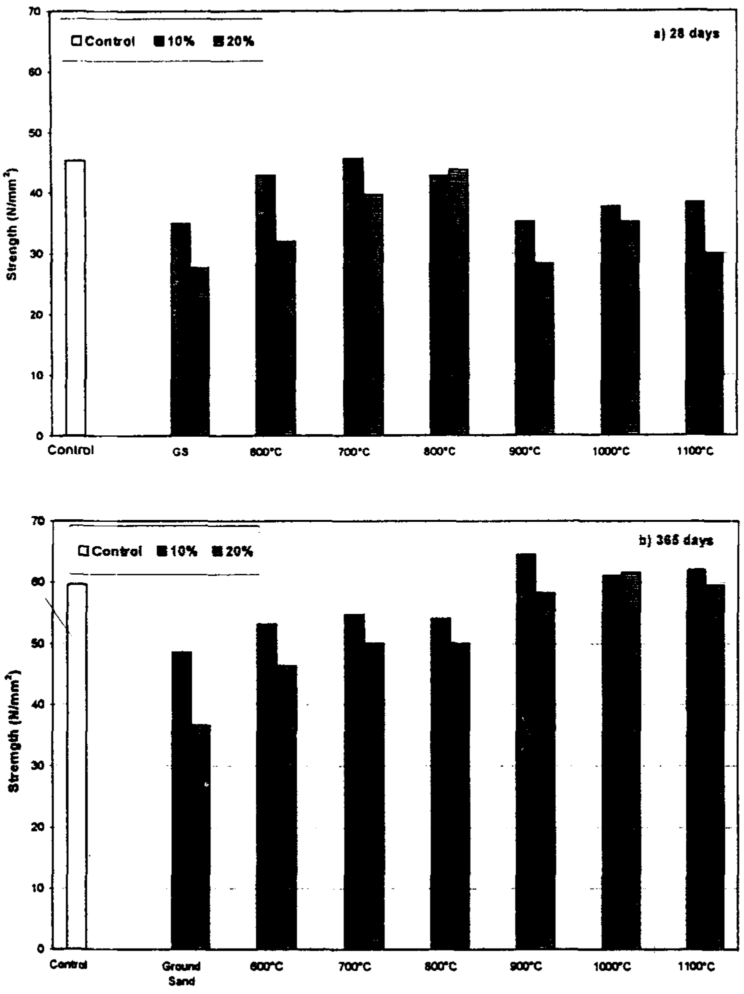

FIG. 7.

Compressive strength for mortars containing 0,10 and 20% replacement of either GS or GCBC calcined at 600-1000°C cured at a) 28 days and b) 365 days.

trol until quite a late age (between 28 and 90 days), but this is still well before either the control or the GCBC mortars begin to show any significant expansion. In addition, the dramatic effect that GCBC has on reducing expansion relative to the control and to the GS mortar, as the replacement level increases, also suggests that there is a significant chemical effect operating (i.e. reduction in CH content), however this still needs to be established by chemical analysis. No data were obtained for porosity and pore size distribution for the GCBC mortars at calcining temperatures other than 1000°C.

The performance of mortars containing GCBC calcined at 900, 1000 and 1100°C is very good in relation to both long-term strength development (Figure 7) and particularly sulphate resistance (Figure 3). The performance of mortars containing brick clay calcined at 600, 700 and 800°C is very poor with regard to long-term strength development and sulphate resistance. Wild et al. (11) have shown from X-ray analysis of the calcined clay and strength tests that the pozzolanic component is different over these two different temperature ranges (i.e.

activated clay over the low temperature range and amorphous glass phase over the high temperature range). Also the sulphate content (see Table 1) is much higher in the clay calcined at the lower temperatures. The combination of high initial sulphate content and a pozzolanic component consisting of activated clay appears to be very undesirable with regard to producing good long-term strength development and good sulphate resistance. Commercially this brick clay is fired at 1025°C, therefore this firing temperatures appears to be the ideal firing temperature to produce from this clay the most effective cement replacement material, with regard both to strength development and to sulphate resistance. Thus the potential exists for brick waste to be ground and utilised in mortar and concrete.

Conclusions

The following conclusions may be drawn from the observations:

i) The optimum calcining temperature for Lower Oxford clay (GCBC) in order to produce a pozzolan which imparts high sulphate resistance in mortar, is in the region of 1000-1100°C.
ii) Lower Oxford clay (GCBC) calcined at temperatures below 900°C produces a marked loss in sulphate resistance when used to partially replace cement in mortar.
iii) The porosity of mortar generally increases with increasing replacement levels of cement by GCBC calcined at 1000°C. In contrast the pore volume occupied by pores less than 0.05 μm radius increases rapidly between 28 and 90 days indicating significant pore refinement. This is reflected in the strength development of the mortar beyond 28 days.
iv) The poor long-term strength development and low sulphate resistance of GCBC mortar when the GCBC is calcined at temperatures between 600 and 800°C is probably due to the combined presence of activated clay and high initial levels of sulphate. In contrast the good-long term strength development and high sulphate resistance of GCBC mortar when the GCBC is calcined at temperatures between 1000 and 1100°C probably derives from the much lower initial sulphate levels and the presence of amorphous glass phase.
v) The results of the research suggest that some types of clay brick when ground to cement fineness could provide a valuable source of mineral replacement for cement. This is particularly so if the bricks are from demolished waste.

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