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Strength and chemical resistance of mortars containing brick manufacturing clays subjected to different treatments

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Abstract

This paper presents the results of an investigation of the properties of mortar in which a calcined clay was employed as a pozzolan. Mortars were prepared using either heat treated clay or ground waste clay bricks (from the same clay subjected to 1000 °C calcining) as a pozzolanic partial replacement for cement at replacement levels of 10%, 20% and 30%. The compressive strengths of the mortars were monitored up to 90 days and the resistance to sodium sulphate solution and synthetic seawater was monitored up to 300 days. The specimens were also monitored for weight changes. Partially replacing cement by ground brick or heat-treated brick clay gives early strengths that are lower than that of the control. At 90 days, however, the strengths are the same as or are greater than that of the control. Heat-treated clay is effective in reducing expansion during exposure of the mortar to sulphate solution and synthetic seawater. The rapidly cooled clay gives better performance, in terms of strength development and resistance to harmful solutions, than the slow cooled clay.

Keywords: Ground brick; Heat-treated clay; Chemical resistance; Compressive strength

1. Introduction

Because of the technical, and sometimes economic, advantages that can be accrued by the use of pozzolans there has, over the last few decades, been increasing and widespread utilisation of fly ash, silica fume, natural zeolite and other pozzolans in concrete. There are compelling long-term environmental reasons for extending the practice of partially replacing cement in concrete with waste and other less energy intensive processed materials, which have pozzolanic properties. A possible source for a pozzolan is calcined clay. Natural pozzolans in the form of calcined earths blended with lime (calcium hydroxide) have been used to produce cementitious materials since ancient times. In the absence of a natural volcanic pozzolan, the Romans used ground waste bricks to manufacture hydraulic lime mortars. Recent years have seen revived interest in the use of such materials as pozzolans in concrete. For example a recent review [1] demonstrates the effectiveness of using metakaolin as a pozzolanic cement replacement in concrete in a range of applications such as the containment of hazardous wastes.

The continuing search for partial cement replacement materials has led the authors to investigate the utilisation of waste fired clay bricks as a pozzolan for concrete and mortar [2]. Use of crushed brick (surkhi) as a pozzolan has been practised in India for many years. When used as a partial cement replacement to produce mortar or concrete, crushed brick results in improved properties including reduction in permeability and improved resistance to sulphate attack and alkali-aggregate reaction [3]. The calcining temperature of clay has a great influence on its action as a pozzolan. The clay is in its most reactive state when the temperature of calcining results in the loss of hydroxyl and a collapsed and distorted clay structure [4].

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The calcining temperature required to produce this active state is usually in the range 600–900 °C [5,6]. Above this temperature crystallisation occurs and activity declines. However at even higher firing temperatures liquid phase forms which, on cooling, solidifies into an amorphous glass phase which also shows pozzolanic activity. In a previous study [2] the authors have demonstrated, by examining ground clay bricks fired at six different temperatures in the range 600–1100 °C, that the optimum firing temperature of Lower Oxford clay to produce the most effective pozzolan is approximately 1000 °C. This work has led to consideration of producing a low-cost manufactured pozzolan from the clay used for brick production. This paper reports the results of a study conducted on using the brick clay, subjected to different heat treatments, as a pozzolan in mortar.

2. Materials and methodology

2.1. Materials

The Portland cement (PC) used has the potential phase composition 50.9% C_3S, 20.7% C_2S, 11.6% C_3A and 6.4% C_4AF and complies with BS EN 197-1. The mineralogy of the clay is illite (23%), kaolinite (10%), calcite (10%), chlorite (7%), quartz (29%), gypsum (2%), pyrites (4%), feldspar (8%) and organics (7%). The sand used was 'Normensand', a standard European sand complying with BS EN 196-1.

Unlike brick production, where the clay is heated to temperatures in excess of 1000 °C, the clay used in the present investigation was heated in crucibles to 800 °C with a heating ramp pf 100 °C per hour. The furnace environment was kept constant at 800 °C for a further 2 h. After the heat treatment, one batch of calcined clay was allowed to cool to room temperature and a second was water quenched with a lid placed over the crucible. The heat-treated brick clays (HTC) were then used as partial cement replacement materials to produce mortar specimens for assessment of strength development and performance in salt solutions. Alongside the HTC specimens, samples in which the cement was partially replaced by ground waste clay bricks (GB) were also prepared ad subjected to the same tests. Table 1 gives the chemical compositions of PC and pozzolan used. The HTC and GB had the same composition and were approximately of cement fineness.

Table 1
Chemical composition of PC and HTC

	PC	HTC
Specific surface (Blaine) (m^2/kg)	350–500	320–350
Composition (%)		
SiO_2	20.6	54.8
Fe_2O_3	2.1	6.0
Al_2O_3	5.7	19.1
CaO	65.0	9.4
MgO	2.3	1.8
SO_3	3.3	2.9
Na_2O	0.14	0.5
K_2O	0.67	3.2
TiO_2	–	1.0
LOI	2.81	0.6

2.2. Mixture details

The mortar mixtures had proportions of 1:3:0.5 (binder: sand:water). This mix design is the standard mortar mix as stipulated in European Standards. The cementitious material consisted of PC and GB, PC and HTC or PC. Ten different mixtures compositions were examined in the present study. The PC was partially replaced by 0%, 10%, 20% and 30% GB or HTC. The designations used for the two heat-treated clays are QC (quenched) and SC (slow cooled). Mixture identification is made by the designation letters followed by the percentage replacement of PC by the pozzolan, e.g. QC20 and GB10 represent mixtures in which the PC was partially replaced by 20% quenched clay and 10% ground waste brick, respectively.

2.3. Specimen preparation, curing and testing

The compressive strength was determined by crushing 100 mm mortar cubes prepared in steel moulds. Mortar bars of dimension 20 mm × 20mm × 160 mm were used for the expansion and weight change measurements and the mortar was compacted into these moulds with the use of a vibrating table. After casting, the steel moulds containing the specimens were covered with plastic wrap to prevent loss of water by evaporation. After 24 h the specimens were stored in water at 20 ± 2 °C. The expansion bars had stainless steel inserts cast into their ends to facilitate accurate measurement of changes in length. After 28 days water curing, some bars were immersed in sodium sulphate solution (~2.4% concentration) while the remainder were immersed in synthetic seawater. Concentrations of the various salts used to manufacture the synthetic seawater can be found in Table 2. The monitoring of specimens subjected to sulphate solution and synthetic seawater was carried out in accordance with pr ENv 196-X [7]. The changes on length and mass of the specimens were monitored regularly for a period of 300 days. The salt solutions were renewed every 28 days. Failure, indicated by 'F' in Figs. 2 and 3, was taken as the point at which the specimen disintegrated or had expanded sufficiently so that it could no longer be measured with the comparator apparatus.

Table 2
Composition of synthetic seawater (from [7])

Salt	Quantity (g/l)
Sodium chloride	30.0
Magnesium chloride	6.0
Magnesium sulphate	5.0
Calcium sulphate	1.5
Potassium hydrogen carbonate	0.2

Each experimental measurement given in this paper is the average of those taken from three samples.

Table 3
Compressive strength of GB mortars (N/mm^2)

	7 d	28 d	90 d
CTRL	52.2	65.3	67.0
GB10	43.8	61.2	74.1
GB20	39.4	55.4	66.2
GB30	31.3	45.2	55.7

Table 4
Compressive strength of HTC mortars (N/mm^2)

	7 d	28 d	90 d
CTRL	39.6	52.5	61.3
QC10	38.7	52.5	62.1
QC20	32.2	46.8	59.3
QC30	24.9	39.1	53.1
SC10	38.2	52.5	58.1
SC20	32.1	46.7	52.1
SC30	25.1	40.8	48.7

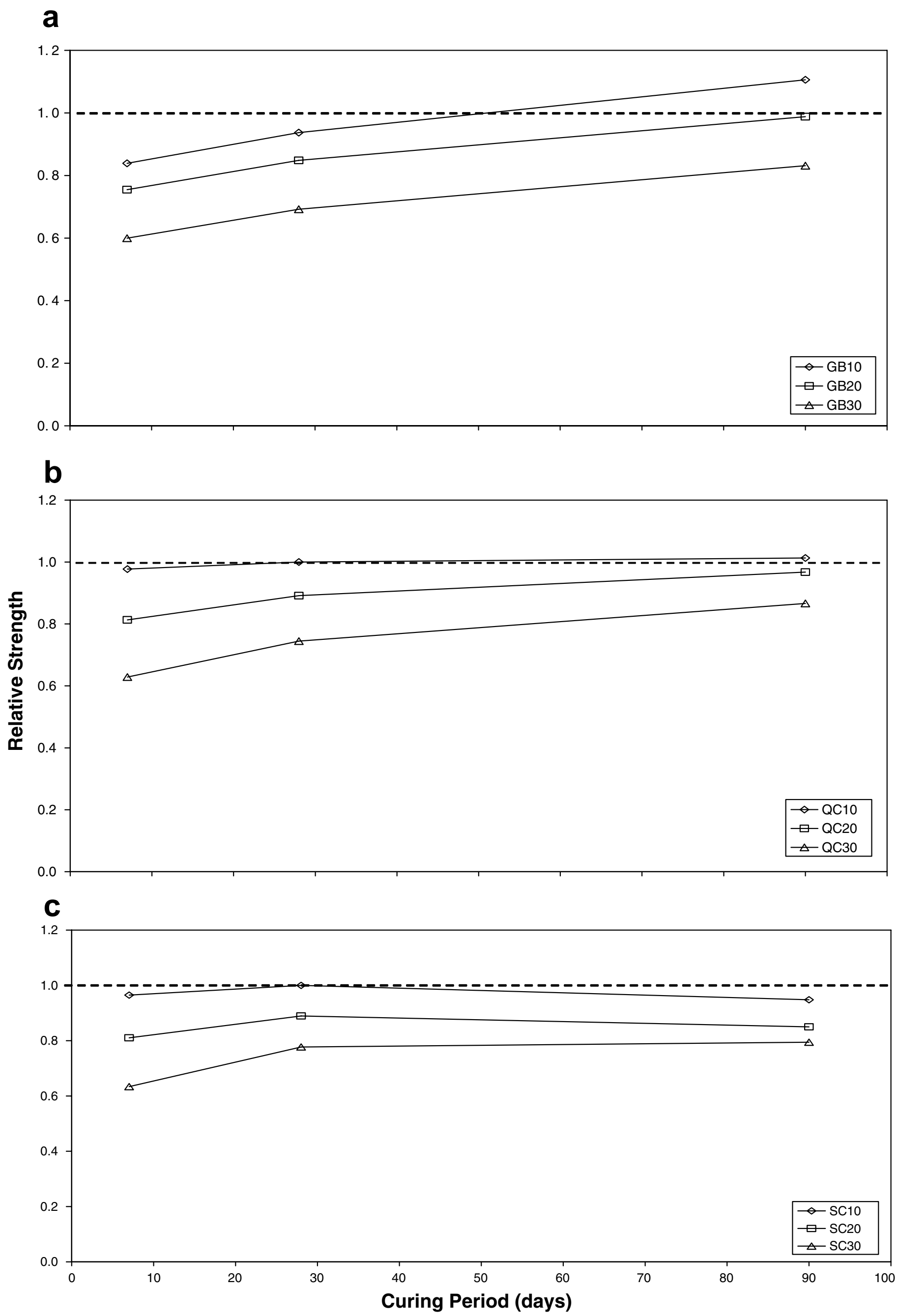

Fig. 1. Relative strength of mortar containing (a) GB, (b) QC (HTC) and (c) SC (HTC).

3. Results

3.1. Compressive strength

Tables 3 and 4 give the compressive strengths of mortars containing GB and the heat-treated clays QC and SC, respectively. All results shown are the average of those obtained from three tests. Partial PC replacement with GB or HTC results in compressive strengths at early ages that are considerably below those of the control concrete, but at 90 days the strengths are more or less unaffected. Fig. 1 gives the strength development in terms of relative strength, which is the strength at a particular age divided by the strength of the control concrete at the same age. Increasing replacement level results in decreasing relative strength. This is attributed to the dilution effect. As the PC hydrates pozzolanic activity occurs and strength increases with time such that at 90 days, with up to 20%

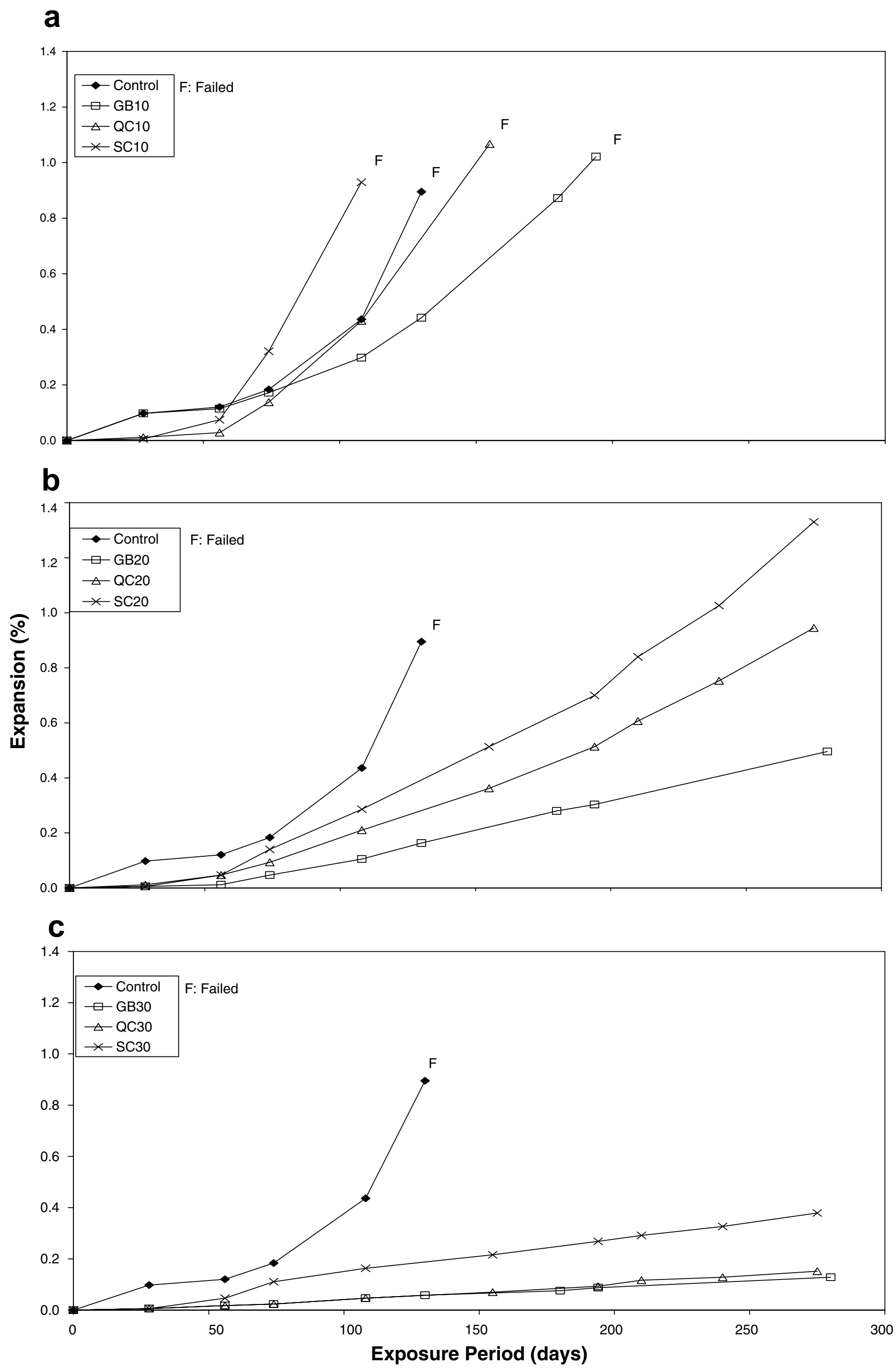

Fig. 2. Expansion of mortars exposed to sodium sulphate solution at replacement levels of (a) 10%, (b) 20% and (c) 30%.

PC replacements by GB or QC, strengths are the same, or in excess of that of the control. On comparing the performance of GB and HTC mortars it is apparent that at 7 days the relative compressive strengths of HTC mortars are generally greater than those for GB mortars. As curing time increases beyond 28 days, the rate of increase of relative strength of HTC mortar decreases considerably, whilst those of GB mortars continue to increase at approximately similar rates to those observed up to 28 days. The reduced rate of relative compressive strength increase at 28 days was a phenomenon observed in an earlier study [8] and attributed to an increased level of sulphate in clays calcined at lower temperatures. An analysis of the sulphate level was, therefore, conducted for all three clays. The acid (HCl) soluble sulphate contents for GB, QC and SC pozzolans were found to be 3.05%, 3.0% and 3.94%, respectively. The relatively higher level of sulphate in the SC pozzolan may be responsible for the decline in relative strength beyond 28 days. This behaviour, however, cannot be attributed to solely the sulphate level and other factors

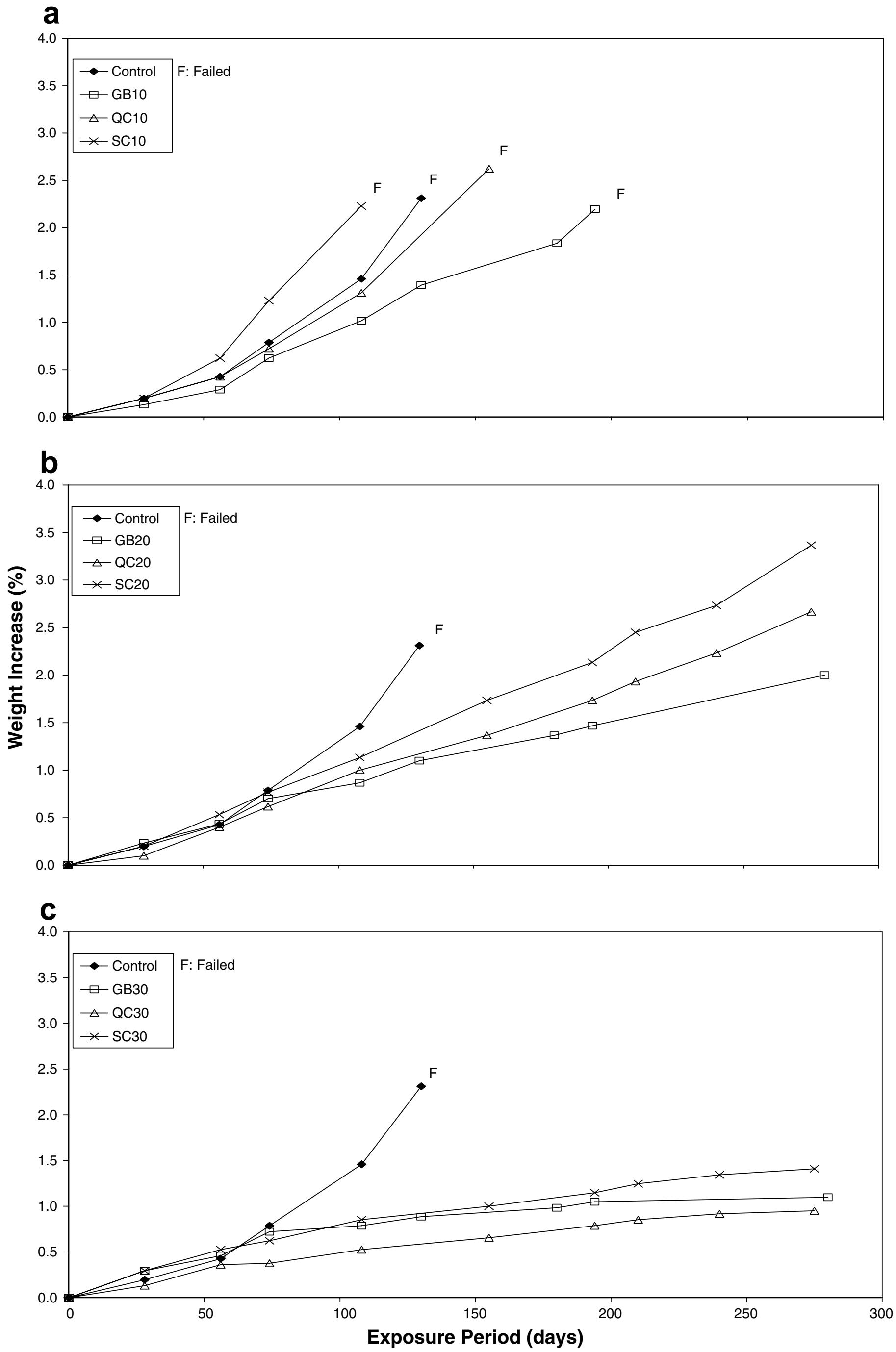

Fig. 3. Weight increase of mortars exposed to sodium sulphate solution at replacement levels of (a) 10%, (b) 20% and (c) 30%.

must be considered. For example it is established that pozzolanicity is very much affected by the glass content, which in turn is dependant on firing temperature. Vitrification (glass formation) of brick clay occurs at firing temperatures in excess of 900 °C and it can thus be deduced that HTC, which was fired at 800 °C, has negligible glassy phase relative to GB, which is fired at temperatures in excess of 1000 °C. Thus the pozzolanic activity must be a function of the distorted dehydroxylated clay. Quenching would be expected to 'freeze' in a more distorted structure with greater stored energy relative to slow cooling which promotes equilibrium and crystallisation. Therefore, this effect might be expected to give a more reactive material when quenching as opposed to slow cooling.

3.2. Chemical resistance

3.2.1. Sodium sulphate solution

Fig. 2 shows the expansion of the control (CTRL) mortar and GB and HTC (Qc and SC) mortars, with PC replacement levels of 10%, 20% and 30%, when exposed to sodium sulphate solution. In all cases, increasing replacement level gives increasing resistance to expansion and at 30% replacement both the GB and QC mortars show very small expansion relative to the control. In terms of providing resistance to expansion, particularly at low replacement levels, the GB mortar experiences the lowest expansion and the SC mortar the highest. In fact at 10% replacement, expansion of the SC mortar exceeds that of the control. This similar to strength development, the QC mortars generally perform better than the SC mortars, which again may be attributed to greater pozzolanic activity.

The increase in weight accompanying expansion was measured and the results are presented in Fig. 3. The weight increase shows very similar trends to those of expansion. Fig. 4 gives the relationship between weight increase and expansion in sulphate solution for all mortars investigated. The results show a strong direct correlation. The increase in weight that corresponds to very little or zero expansion (see Fig. 4(b)), represented by the intercept, is currently attributed to the filling of voids (pores or air voids) in the mortar by expansion products although this has not been verified by microscopy.

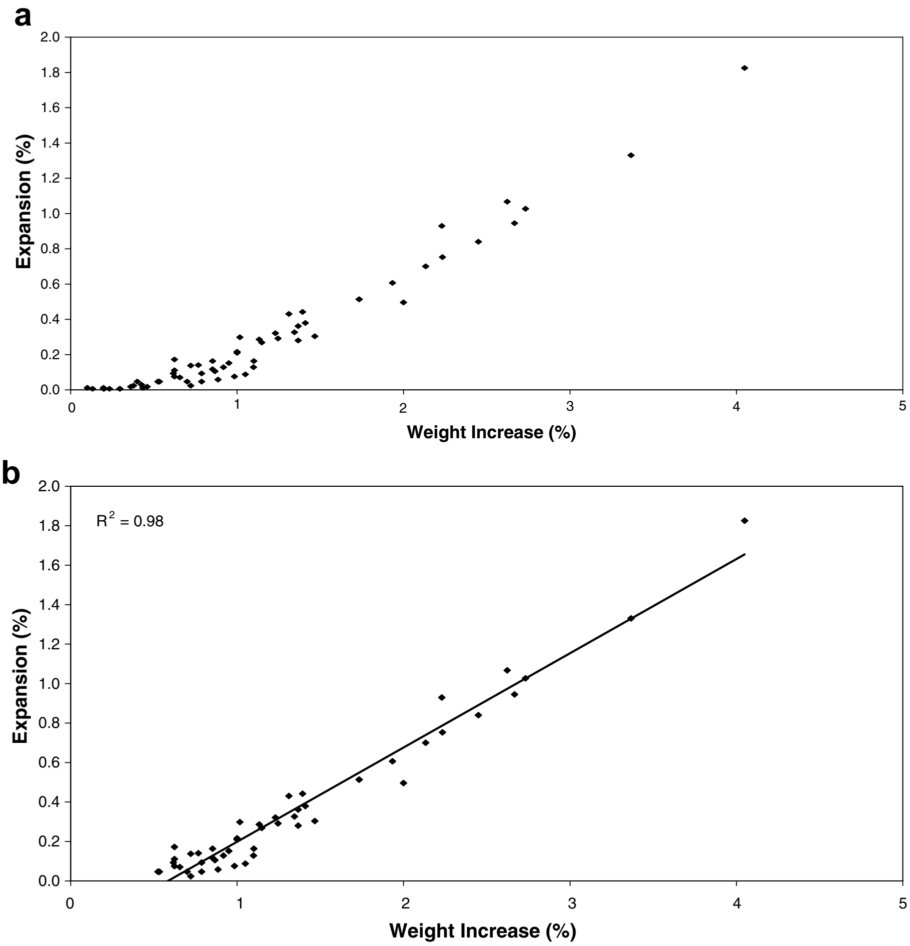

Fig. 4. Expansion versus weight increase of mortars (a) exposed to sodium sulphate solution and (b) the linear relationship between weight increase and expansion.

3.2.2. Synthetic seawater

Fig. 5 gives the expansions of the mortar bars subjected to synthetic seawater. Comparison with the results in Fig. 2 shows that the mortars expand much less than those subjected to sulphate solution. This agrees with observations by Lea who states that the lack of expansion in seawater can be attributed to the increased solubility of calcium hydroxide in seawater and that the presence of chlorides in the seawater inhibits the expansive reactions commonly associated with sulphate attack [9]. The low expansion rate may also be attributed in part to the formation of a skin of magnesium hydroxide (brucite), around the mortar prism, reducing the ingress of the aggressive seawater solution. GB and HTC mortars expand less than the control mortar and, as with exposure to sulphates, expansion is reduced as the percentage replacement increases. A significant observation is that the HTC mortars give expansions that are significantly smaller than those of the GB mortars, particularly at 10% and 20% replacements during early exposure. At 10% PC replacement, the QC mortars give smaller expansions than those of the SC mortars at all exposure periods. There seems to be little difference between the

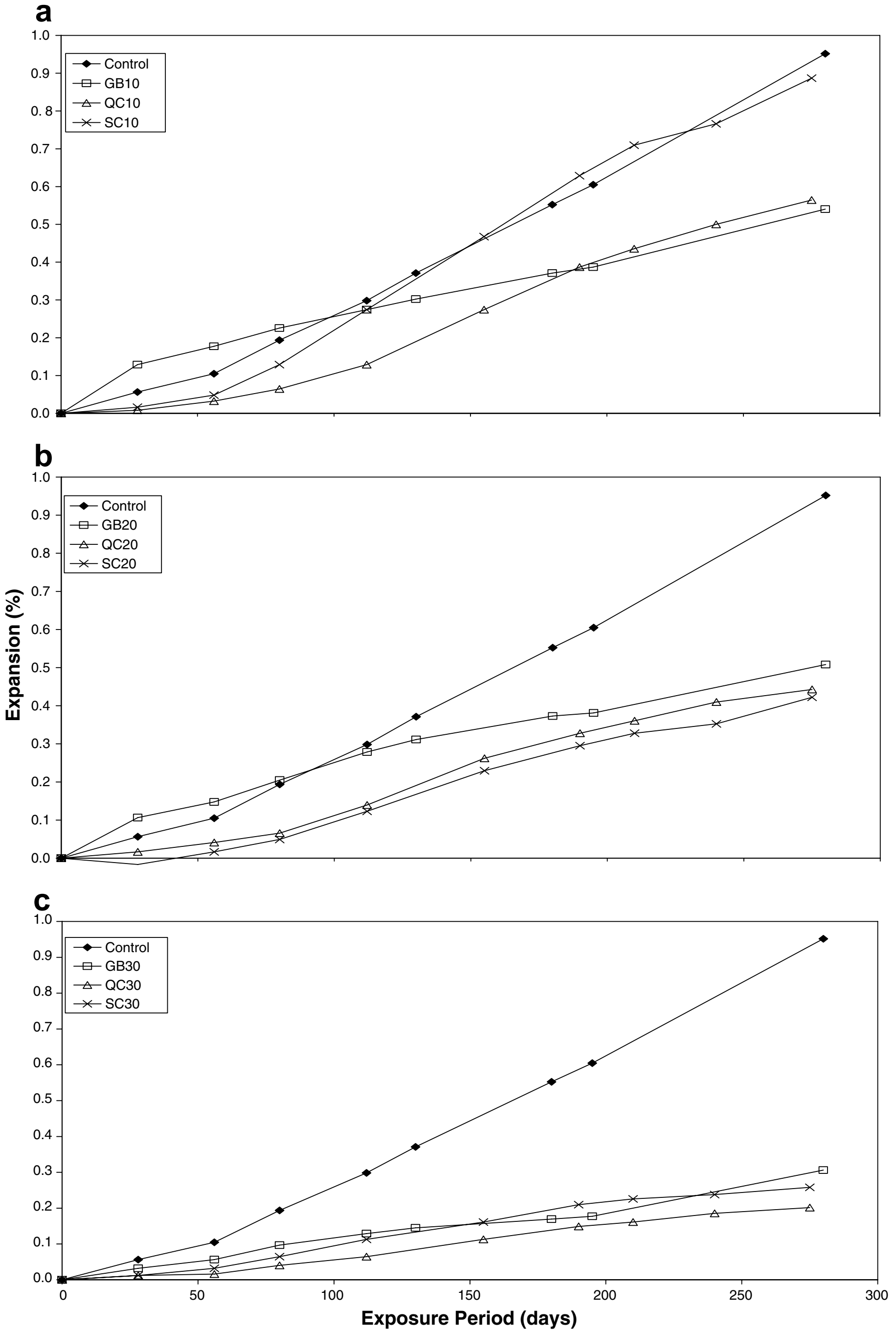

Fig. 5. Expansion of mortars exposed to synthetic seawater at replacement levels of (a) 10%, (b) 20% and (c) 30%.

performances of these two mortars as the percentage replacement increases. As with expansion, the weight increase reduces as the percentage replacement increases (see Fig. 6). Fig. 7 shows the relationship between weight increase and expansion. Again there is a distinct change in the gradient which, in this case, occurs at a weight increase of approximately 2.5%. This figure is about five times that obtained from mortars exposed to sulphate solution and is indicative of a much greater volume of reaction products being formed prior to expansion taking place. This suggests that the reaction products formed may be less expansive or may form extensively as surface deposits rather than in the internal pores (see Figs. 4 and 7).

4. Discussion

The HTCs examined in this investigation were manufactured from the same clay as that used in the production of bricks. Mortars containing HTC exhibited greater earlier relative compressive strengths than those of GB mortars.

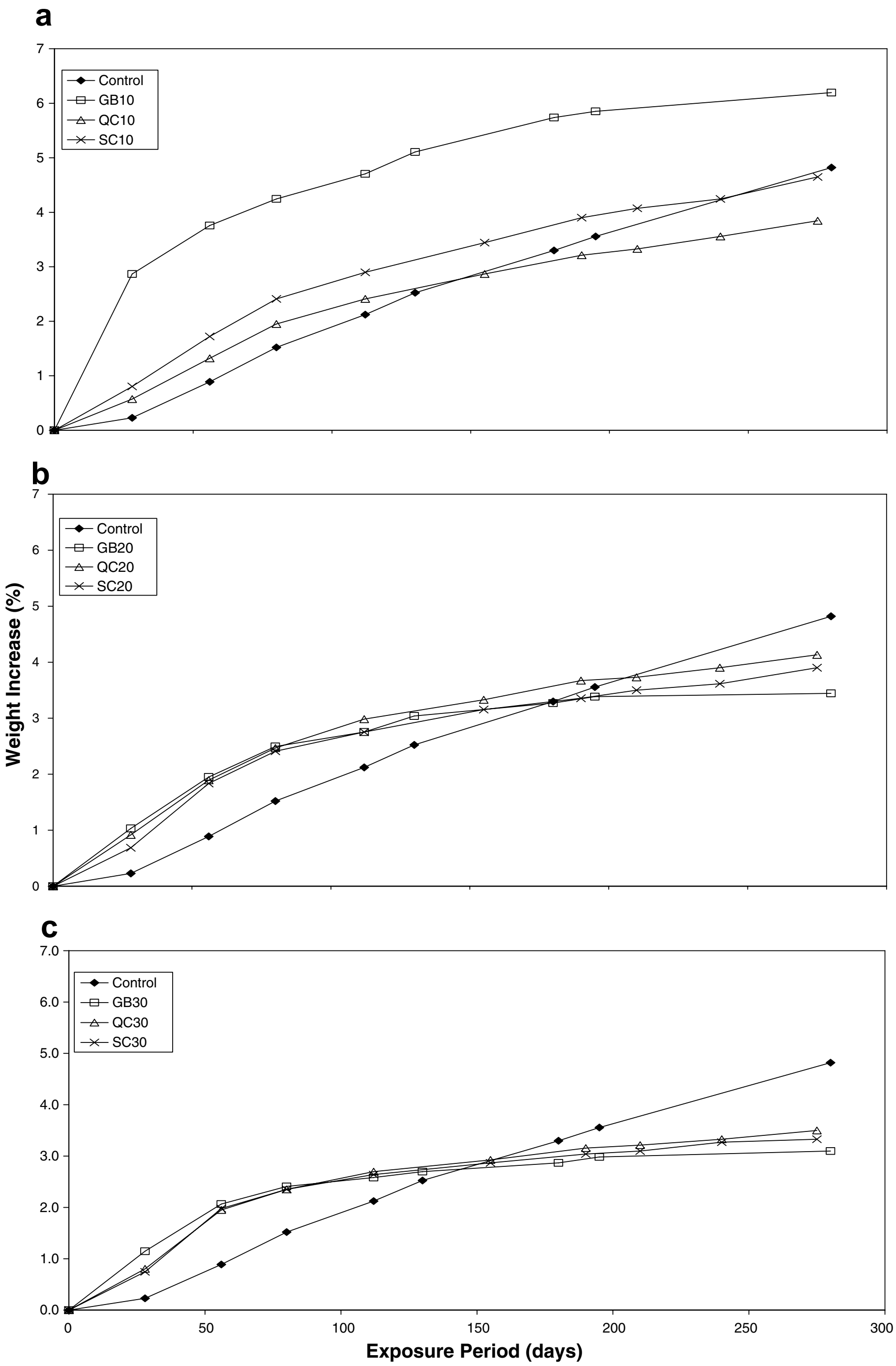

Fig. 6. Weight increase of mortars exposed to synthetic seawater at replacement levels of (a) 10%, (b) 20% and (c) 30%.

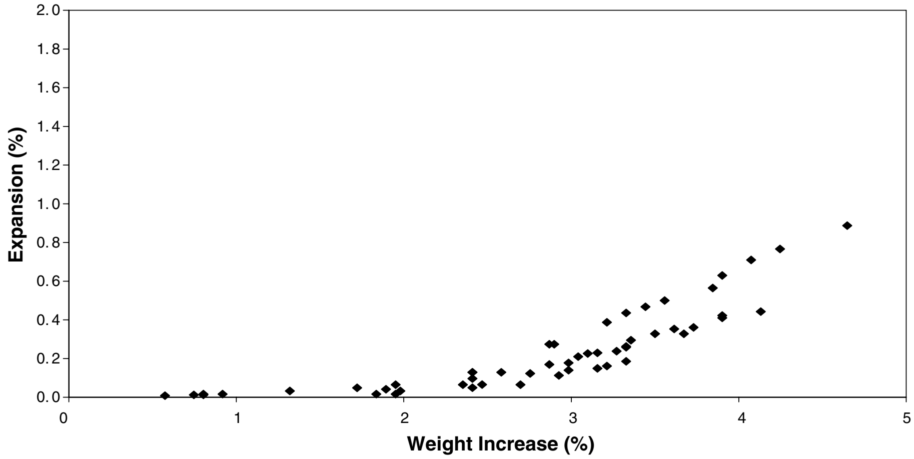

Fig. 7. Expansion versus weight increase of mortars exposed to synthetic seawater.

As curing time increases beyond 28 days, the rate of increase of relative strength of HTC mortars decreases considerably, whilst that of GB mortar continues to increase at similar rates to those observed up to 28 days. Analysis has shown that the QC (quenched cooled) HTC possessed a similar level of sulphate as that of GB, but the SC (slow cooled) HTC showed a higher level of sulphate. Although the higher level of sulphate in the SC pozzolan may be partly responsible for the decline in compressive strength beyond 28 days, this does not explain fully the general performance of TC observed here. Earlier work [8] has shown that the glass content of GB pozzolans appears to be the key factor in strength development, especially at curing times beyond 28 days. The firing temperatures experienced by the HTC (>800 °C) and by the GB (>1000 °C) lie on either side of the vitrification point of brick clay. Sintering and vitrification (glassy phase production) of brick making clay occurs at temperatures exceeding 900 °C. It is, therefore, reasonable to assume that the HTC will contain very little glassy phase. As the HTC has not undergone vitrification but was treated at temperatures exceeding those required for the bound mineral water to be removed (150–600 °C), its structure will be similar to that of an activated clay pozzolan such as metakaolin (MK). Metakaolin has been shown to enhance the early strength of mortar and its effects on strength at extended curing periods (>28 days) [10] also corroborates the trends observed for HTC mortars. This is evidence that the glass content of pozzolans is of primary importance with respect to long term strength development, most probably due to prolonged C–S–H gel production as a result of the glassy phase–calcium hydroxide (CH) interaction. The improvement in performance of QC mortars over that of SC mortars is attributed to the more distorted structure, due to quenching, resulting in a more reactive material.

Although the performance of HTC mortars in sulphate solution is superior to that of the control mortar, it is somewhat inferior to that of GB mortar. This is again attributed to glass content. Due to the differing firing temperatures of HTC and GB pozzolans, it is expected that GB would contain more of the glass phase. At all replacement levels the QC mortars showed better performance in sulphate solution to that of SC mortars.

It has previously been reported [11] that as the firing temperature of clay brick production decreases then so does its effectiveness at resisting sulphate induced expansion when used in a finely divided state as a pozzolan. It is considered that the moderate firing temperature of 800 °C experienced by HTC has the effect of producing a material similar, in its physical state, to MK. It has also been shown [12] that MK reduces expansion as the level of PC replacement increases and that this is attributed to reduction of the CH content [10] thus reducing the amount available for ettringite formation and growth. In acting as an active pozzolan, HTC consumes CH early in the hydration process resulting in less CH being available for gypsum and ettringite formation on exposure to sodium sulphate solution. Experience has shown that MK is considerably more active as a pozzolan than HTC. The difference in performance between HTC and MK is attributed to the type of clay used. The principal clay mineral in brick clay is illite (23%) whereas MK is derived from kaolinite. The temperatures that the HTC experienced were not sufficient to activate the illite, which requires temperatures in excess of 930 °C, and even then results in generally a poor pozzolan [13]. However lower Oxford clay also contains kaolinite (~10%) and it is the dehydroxylation of this phase that is considered to be the cause of the pozzolanic activity in the HTC mortars.

The more effective role played by GB, when compared to HTC, is attributed to the increased glass content of GB. Without the additional C–S–H gel from glassy phase dissolution, gel from hydration and initial reaction between HTC and CH will gradually decalcify due to the production of ettringite. With the decalcification of C–S–H gel, the strength of the HTC mortars will be somewhat reduced thus allowing more expansion than in the case of GB mortars.

5. Conclusions

1. Partially replacing Portland cement with ground brick or heat-treated brick clay results in early compressive strengths that are lower than that of the control. However, up to 20% replacements give strengths at 90 days that are the same as or greater than that of the control.
2. Relative strength decreases as the level of replacement increases. Although heat-treated clays give relative strengths at early ages that are greater than those of ground brick mortars, the latter provide better performance at extended ages. This is attributed to the higher glass content of ground brick.
3. Although the sulphate resistance of heat-treated brick clay mortars is somewhat less than that of ground brick mortar, heat-treated brick clays give superior performance to that of the control mortar, particularly at replacement levels of 20% or 30%. At all replacement levels the quenched clay results in better resistance than slow cooled lay.
4. Heat-treated clay mortars are effective in reducing the expansion due to exposure to synthetic seawater. At 10% and 20% replacements the heat-treated clay mortars give expansion at early exposure that are considerably lower than those of the ground brick mortars.

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