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Resistance to chemical attack of ground brick-PC mortar
Part I. Sodium sulphate solution

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Abstract

The partial replacement of high C_3A cement blended with ground brick (GB) is investigated in terms of resistance of GB mortar to sodium sulphate (Na_2SO_4) solution. The results indicate that the sulphate resistance of mortar is generally increased as the replacement level of cement with GB increases up to at least 30% replacement. However, the GB types investigated exhibit varying resistance to sulphate expansion when used as partial cement replacement and this is attributed to their chemical and phase composition. Sulphate content, glass content, and oxide chemistry are the principal factors that determine the effectiveness of GB in resisting sulphate expansion. Small amounts of sulphate in GB do not have any deleterious effects on GB mortars and can be beneficial. Bricks with high-calcium glass or a low proportion of glassy phase should not be used as pozzolans. Bricks with a high proportion of low-calcium glass make very effective pozzolans. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Sulphate attack; Expansion; Pozzolan; Mortar; Ground brick

1. Introduction

In hardened cement-based materials the effect of external sulphate-bearing solutions can lead to intense internal stresses and ultimately to failure. The sulphates in solution combine with calcium hydroxide (CH, produced as a consequence of cement hydration) and alumina (in the cement) to produce ettringite, the formation of which can in particular chemical environments produce expansion and disruption. Numerous mechanisms have been proposed for this expansion [1–3] and no single mechanism has been unequivocally identified as the principal cause. One way of reducing the potentially deleterious components responsible for the expansion is the use of pozzolanic cement replacement materials. Not only do pozzolanic cement replacement materials reduce the amount of alumina and lime that are available for reaction by the "dilution effect," but also consume CH as a result of the pozzolanic reaction that produces additional cementing C-S-H gel. The use of pozzolans in mortar with respect to increased sulphate resistance has been widely investigated. Pulverized flyash (PFA) [4,5], condensed silica fume (CSF) [4,6], and metakaolin (MK) [7] have all been shown to increase resistance to sulphate attack when used to partially replace cement in concrete and mortar. Recently the use of ground calcined brick clay as a pozzolanic material has also been investigated [8]. Wild et al. [8] demonstrated that the calcining temperature of a particular brick clay had a significant effect on the performance of mortar exposed to sodium sulphate solution when the calcined clay was used as a pozzolan in the mortar. The importance of the phase composition of pozzolans is highlighted in work on PFA [9–11]. For example, high-calcium-glass fly ashes release calcium aluminates in a high pH environment that readily form expansive products in the presence of sulphate [10], whereas low-calcium-glass fly ashes undergo a long-term pozzolanic reaction that produces additional C-S-H gel and low-calcium C-A-H phases [12]. The detrimental effect of high-calcium-glass fly ash to concrete sulphate resistance has been demonstrated [11] as has the beneficial effect of low-calcium-glass fly ash [11,13]. However, the type of aluminate-bearing compound present in the cementitious material prior to sulphate exposure is also a key factor. It has been shown that prior to exposure to sulphate solutions, PFA-cement pastes with ettringite as their primary aluminate compound exhibit greatly increased resistance to deterioration relative to PFA-cement pastes whose primary aluminate compounds are monosulphate and C-A-H [9]. This has been attributed to the fact that in the former case, ettringite formation occurs while the paste is still plastic when it is able to accommodate the associated volume increase. In the latter case, ettringite originates from monosulphate and

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Table 1
Chemical composition of high C_3A (11.6%) PC[a]

SiO_2	Al_2O_3	Fe_2O_3	CaO	SO_3	Free lime
20.6	5.7	2.1	65.0	3.3	1.6

[a] Data provided by Blue Circle Industries plc.

C-A-H within the hardened paste, which itself imbibes sulphate and water.

2. Methods

2.1. Materials

The cement used was high C_3A (C_3A = 11.6%) Portland cement (PC), the composition of which is given in Tables 1 and 2. The sand used in the mortar mixes was “Normensand,” a standard European sand. Eight brick types were chosen initially from a variety of sources across Europe. Four were selected for detailed investigation (referred to as B, D, L, and P). Subsequently another brick type (referred to as L1) was also selected for detailed investigation. Basic information on the oxide content and mineralogy of these brick types can be found in Tables 3 and 4 [14]. The bricks were ground to a specific surface of 320 to 350 m^2kg^{-1} as determined by a constant flowmeter air permeability apparatus.

2.2. Mixing

The mortar mixes had proportions of 1 binder:3 sand. The binder consisted of cement and ground brick (GB). The water:binder (w/b) ratio was kept constant at 0.5. Thirteen different mortar mixes were investigated. The cement was partially replaced by 0, 10, 20, and 30% of the various GB types. Each mix was assigned a code (e.g., B10 represents 10% partial replacement of cement by GB type B). In all cases 0% replacement of cement in mortar is referred to as the control.

2.3. Specimen preparation, curing, and testing

Mortar bars of dimensions 20 × 20 × 160 mm were used for these mixes. After casting, the 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 for initial curing. The bars had stainless steel inserts cast into their ends to facilitate accurate monitoring of changes in length. After 28 days of water curing the specimens were immersed in sodium sulphate solution (2.1% concentration). The changes in length and mass of the specimens were then monitored every 28 days for a period of 560 days. The sodium sulphate solution was also renewed every 28 days. Further details of the testing procedure can be found elsewhere [15]. Failure was taken as the point at which the specimen lost its structural integrity (i.e., it disintegrated).

Table 2
Mineralogical composition of high C_3A (11.6%) PC[a]

C_3S	C_2S	C_3A	C_4AF
50.9	20.7	11.6	6.4

[a] Data provided by Blue Circle Industries plc.

Table 3
Composition of GB types B, D, L, P, and L1[a]

GB type	SiO_2	Al_2O_3	Fe_2O_3	CaO	SO_3	TiO_2	MgO	Na_2O	K_2O	P_2O_5
B	54.83	19.05	6.00	9.39	2.90	0.97	1.77	0.50	3.15	0.20
D	69.99	10.62	4.02	8.86	0.038	0.55	1.39	1.02	2.61	0.11
L	68.79	15.23	6.28	1.79	0.127	0.85	2.02	0.26	3.71	0.07
P	72.75	15.89	4.97	0.87	0.07	0.84	1.20	0.27	2.17	0.10
L1	58.02	15.28	6.26	8.07	0.139	0.77	3.80	0.71	4.12	0.15

[a] Data provided by the Danish Technical Institute [14].

3. Results

3.1. GB types B, D, L, and P

Fig. 1 shows the expansion of GB B, D, L, and P mortars exposed to sodium sulphate solution for up to 560 days. The amount of GB incorporated in the mortar significantly influences the expansion, as does the type of GB utilised. Expansion of mortar with GB types B (Fig 1a) and L (Fig. 1c) is lower than that of the control at all cement replacement levels. Expansion of GB mortar type P (Fig. 1d) is greater than the control at the 10% replacement level, and expansion in mortar containing GB type D (Fig. 1b) is greater than the control at all compositions. GB B, L, and P mortars show a distinct trend of decreasing expansion with increasing replacement level in the range 10 and 30%. GB D mortar, however, shows the reverse trend in that expansion becomes greater with increasing replacement level. At the termination of the experiment (560 days exposure) only two mortars did not fail (i.e., GB B and L mortars, both at a replacement level of 30%). GB B mortar exhibits the greatest level of resistance to expansion, showing an expansion less than a quarter that of GB L mortar.

Fig. 2 shows that the weight increase vs. exposure time for mortar exposed to sodium sulphate solution exhibits the same trend as that of expansion vs. exposure time. In fact, apart from the scale, the curves for expansion (Fig. 1) and weight increase (Fig. 2) are almost identical. There appears, therefore, to be a very close correlation between expansion and weight increase over time. Fig. 3, which shows expansion against weight increase for all binder compositions and for all GB types, clearly confirms that there is indeed a strong correlation between expansion and weight increase. This close correlation provides very strong evidence that the component producing the weight increase is also causing the expansion. Also, it should be noted from Fig. 3 that up to a weight increase of $\simeq$1%, the percentage expansion is very small indeed ($<$0.1%). This can be attributed to the initial filling of existing pore space (i.e., the capillary porosity that develops within the mortar and residual air voids re-

Table 4
Mineralogy of GB types B, D, L, P, and L1 normalised on a scale 0–100[a]

GB type	Quartz	Feldspar	Haematite	Cristobalite	Gypsum	Anhydrite	Glass content (%)
B	35	4	7	9	12	4	28
D	53	20	5	11	–	trace	12
L	35	19	16	11	–	trace	19
P	70	2	4	3	–	–	21
L1	52	14	10	8	–	trace	16

[a] Data provided by the Danish Technical Institute [14].

sulting from incomplete compaction) by the developing expansive product. For larger weight increases there is a marked increase in the rate of expansion, and there is also a strong linear relationship between weight increase and expansion. The fact that the increase in weight per unit increase in length (and hence volume) is constant indicates that the product or products formed from the components taken up by the mortar bars from the surrounding solution are directly responsible for the volume increase.

3.2. GB type D with additional SO_3

The very different expansions observed for GB type B and D mortars indicates that the type of GB used can result in significant differences in performance. Table 2 confirms that there is a large difference in the SO_3 contents of these GB types. To establish the effect that the SO_3 present in the GB has on expansion, additional SO_3 (in the form of gypsum) was mixed with GB type D at levels of 2, 3, and 4% of weight of GB. The resulting GB-SO_3 mix was then used as partial cement replacement (at 0, 10, 20, and 30% replacement) in mortar.

It is apparent from Fig. 4 that the presence of SO_3 in the GB alters the behaviour of the GB mortar significantly when exposed to sodium sulphate solution. At all replacement levels and for all amounts of added SO_3 the mortars now exhibit expansion that is less than that of the GB type D mortars without added SO_3. The reduction in expansion relative to the GB type D mortars with no added SO_3 also

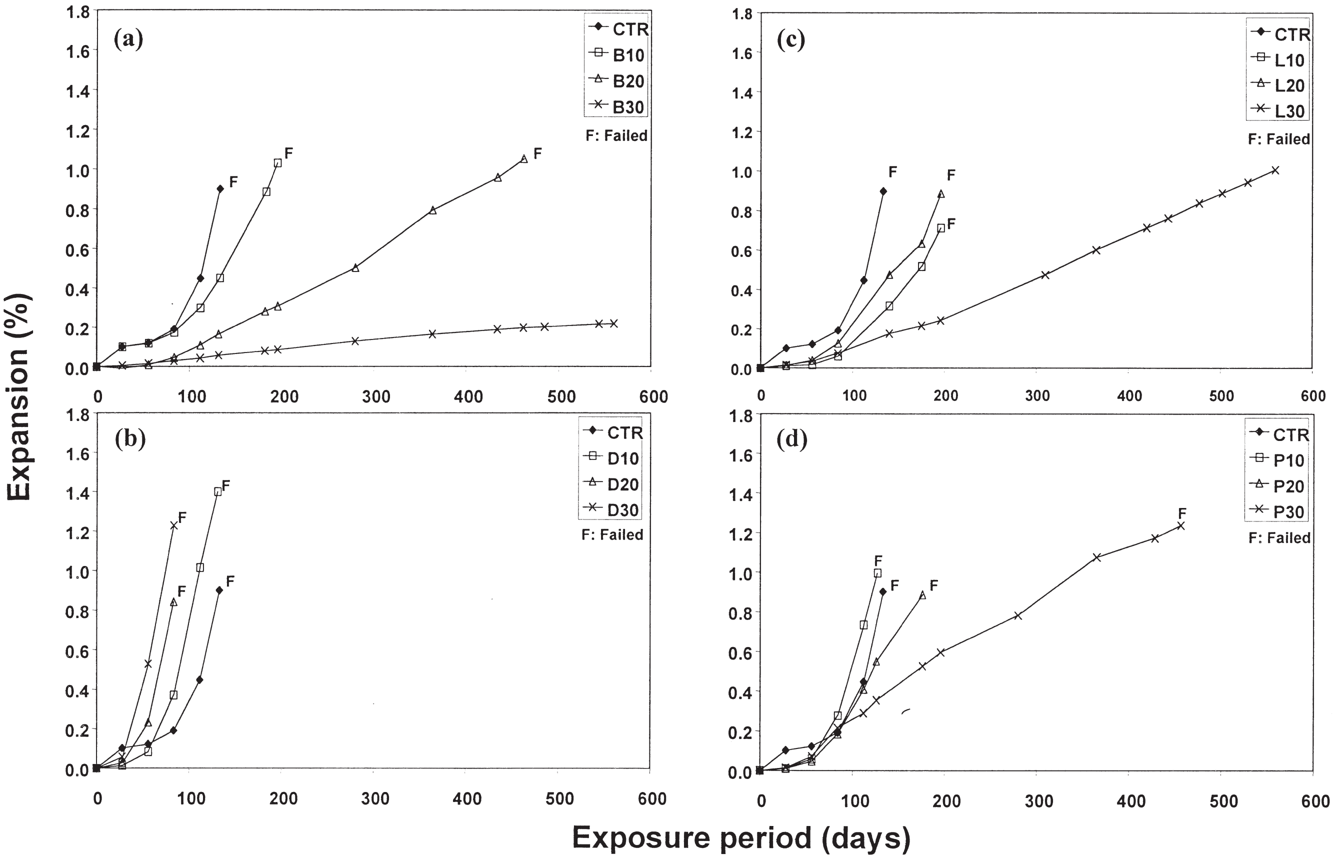

Fig. 1. Expansion of GB type (a) B, (b) D, (c) L, and (d) P mortars exposed to sodium sulphate solution.

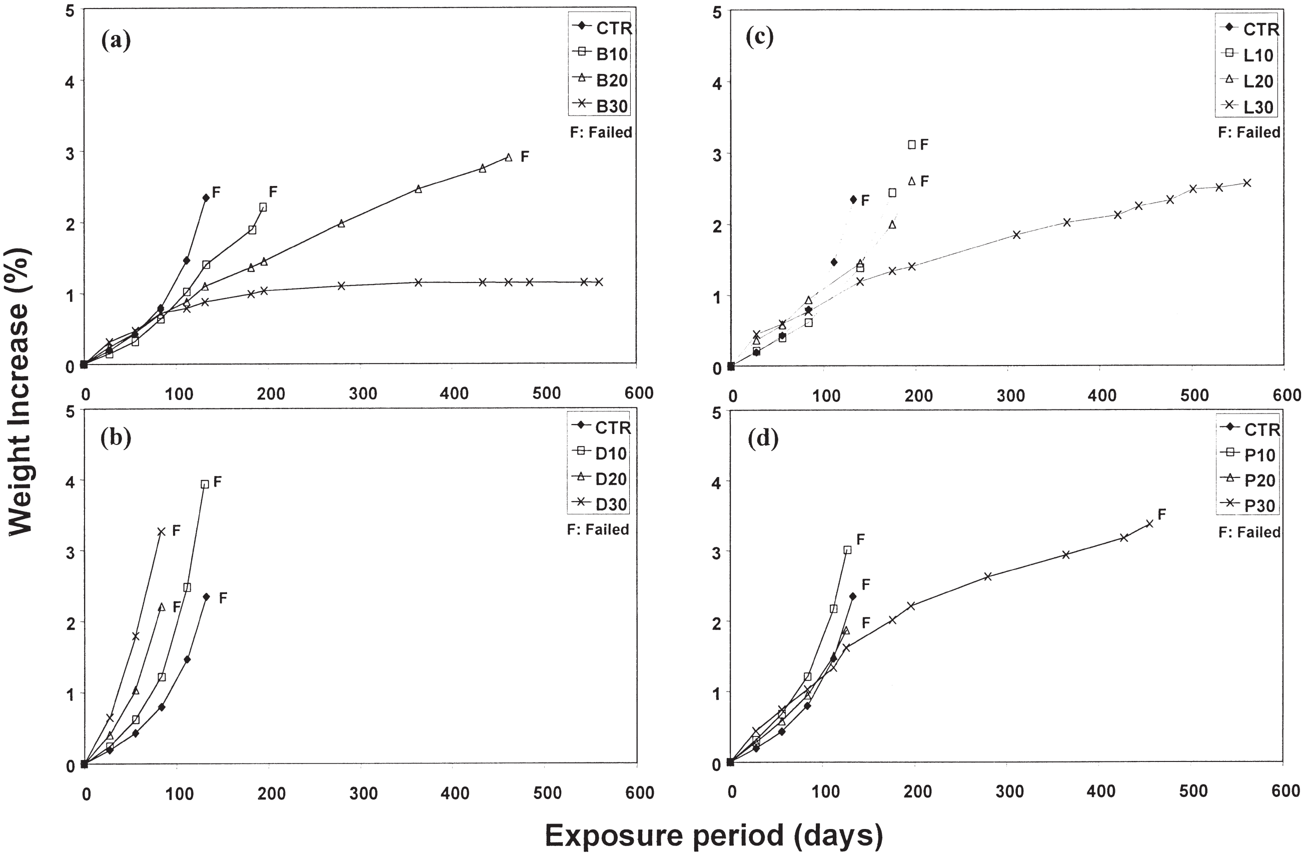

Fig. 2. Weight increase of GB type (a) B, (b) D, (c) L, and (d) P mortars exposed to sodium sulphate solution.

increases with increasing GB replacement level. This is the reverse of what is observed for GB mortar D with no added SO_3 when exposed to sodium sulphate solution (Fig. 1b).

In particular when 30% cement is replaced with GB type D containing added SO_3 (Fig. 4c), the expansion of the mortar is reduced from 0.6% at 2% SO_3 addition to 0.46% at 3% SO_3 addition and to 0.32% at 4% SO_3 addition. In contrast to GB D mortar with no added SO_3, which exhibits greatest expansion at the highest level of cement replacement (Fig. 1b), mortars containing GB type D exhibit the lowest expansion at the highest level of cement replacement with added SO_3. This is very strong evidence that the additional SO_3 is in some way retarding the expansion of these mortars, as the presence of various quantities of SO_3 in the pozzolan is the only variation between the two cement replacement materials.

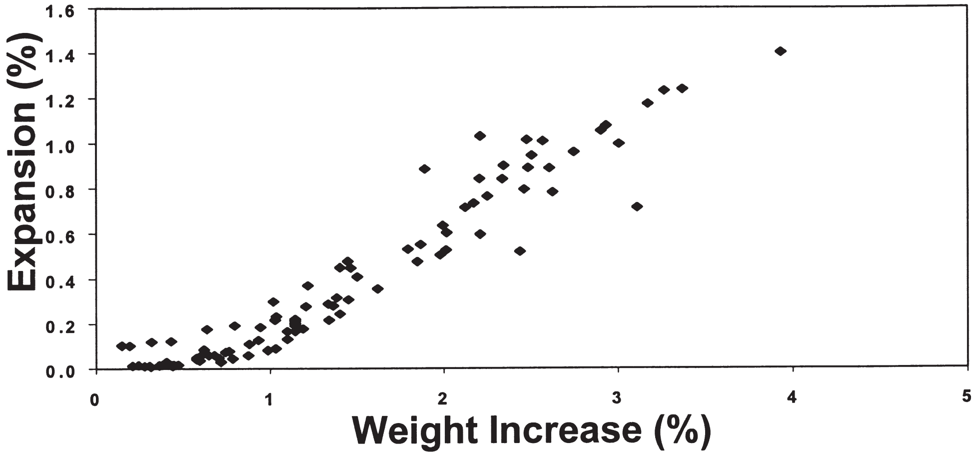

Fig. 3. Expansion vs. weight increase of GB type B, D, L, and P mortars exposed to Na_2SO_4 solution.

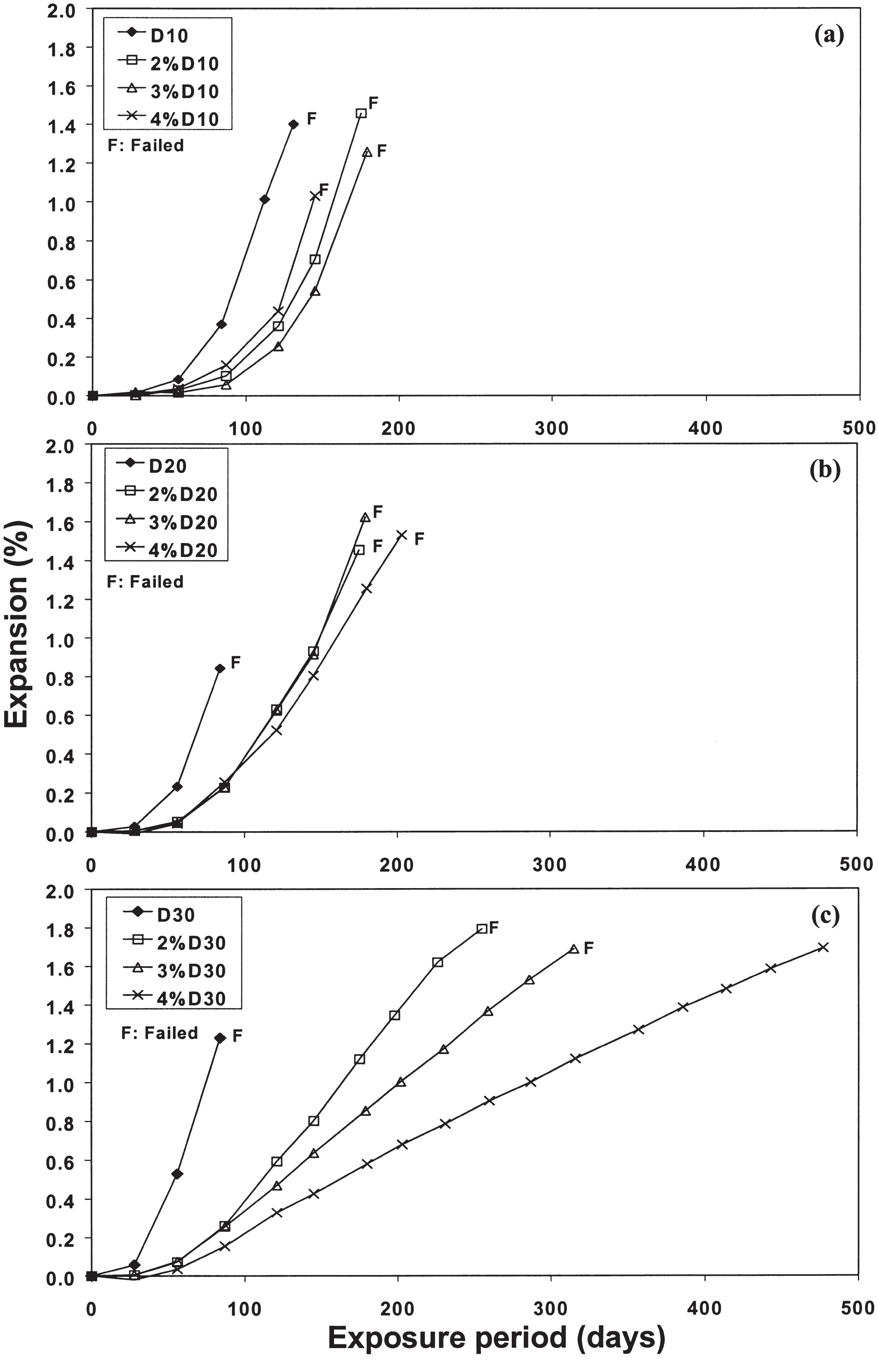

Fig. 4. Expansion of GB type D-SO_3 mortar exposed to Na_2SO_4 solution at cement replacement levels of (a) 10%, (b) 20%, and (c) 30%.

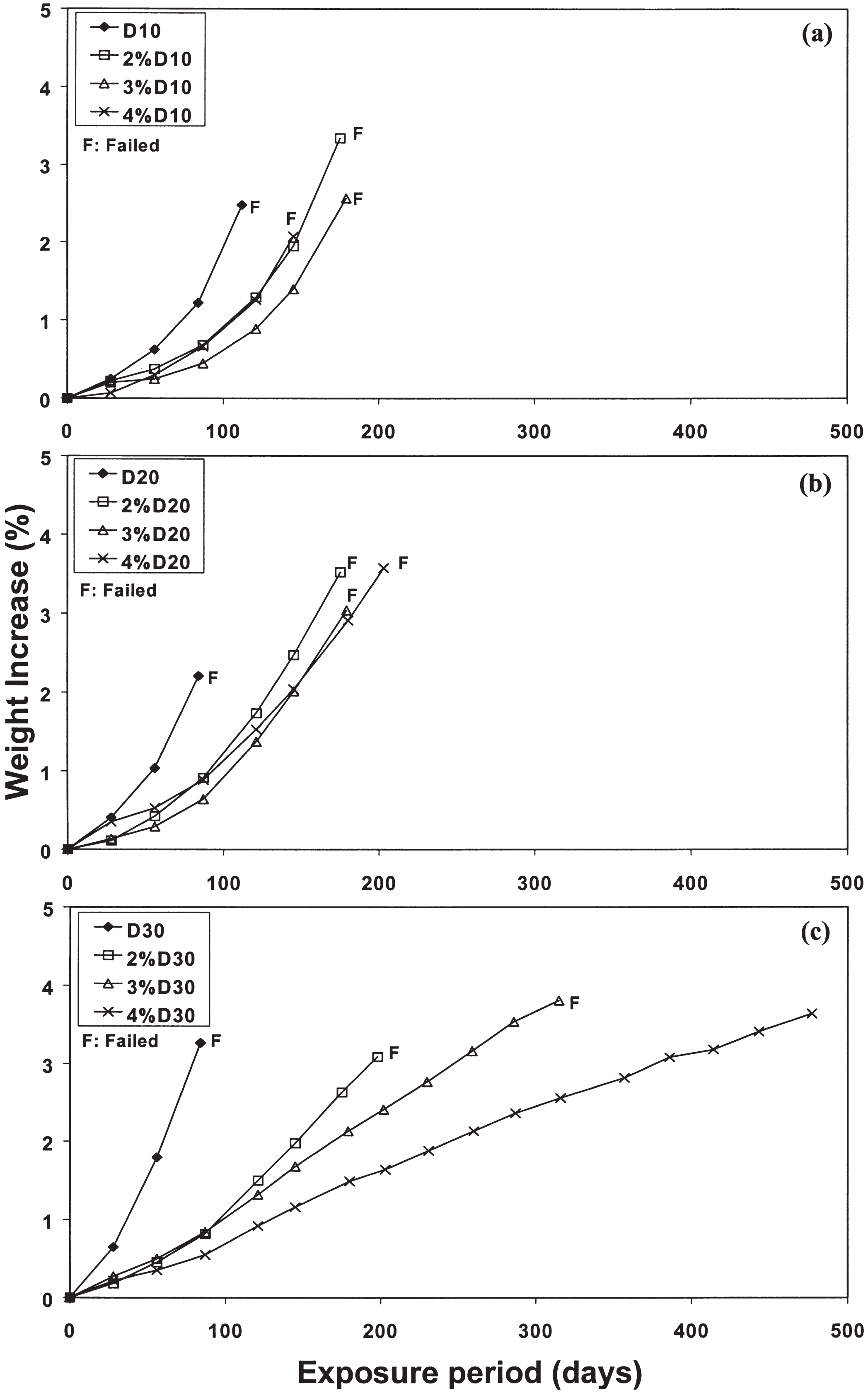

Fig. 5. Weight increase of GB type D-SO_3 mortar exposed to Na_2SO_4 solution at cement replacement levels of (a) 10%, (b) 20%, and (c) 30%.

The added SO_3 also has the effect of reducing substantially the weight increase of GB mortar during exposure, which becomes progressively smaller relative to GB mortar D without added SO_3 as replacement level increases (Fig. 5). There is, in agreement with the previous data (Fig. 3), a very close correlation between expansion and weight increase of mortar containing GB type D with added SO_3 (Fig. 6). The more linear relationship observed in this investigation can be attributed to the fact that only one GB type is being utilised as a cement replacement material. The correlation observed in Fig. 3 is for mortars containing four chemically diverse brick types and thus a greater degree of scatter would be expected. The intercept with the weight increase axis (i.e., zero expansion) is, however, much smaller when the ground brick is dosed with additional SO_3 (Fig. 6). Again, this intercept represents the weight increase for which expansion is negligible, that is, the stage during which the void spaces in the mortar (pores or air voids) are being filled with expansive product.

3.3. GB type L1

The results reported above confirm that increasing the SO_3 level of GB type D has a significant influence on reducing expansion of GB mortar. However, brick types L and P, as with GB type D, also have low sulphate levels, but the expansion characteristics that they impart to mortar are totally opposite to those imparted by brick type D and are similar to those imparted by brick type B (which has a high SO_3 content). Thus the low SO_3 content of brick type D cannot on its own be responsible for the effect that brick type D has on the expansion characteristics of the mortar.

The distinctive features of GB type D, in addition to low sulphate content, are that it has a low-glass content and high-CaO content. If these are the characteristics of a potentially detrimental GB when used as a cement replacement material, then a trend of increasing mortar expansion with increasing cement replacement would be expected. To test this hypothesis GB type L1 (which possesses these characteristics; see Table 2) was selected for detailed investigation.

Fig. 7a, which shows the expansion of GB type L1 mortar when exposed to sodium sulphate solution, clearly establishes the development of this expected trend. Similar to GB D mortar, increasing cement replacement level with brick type L1 results in increasing expansion, but in this case although mortars with 20 and 30% cement replacement exhibit expansion in excess of the control at 10% cement replacement the expansion is slightly less than the control. The weight increase (Fig. 7b) exhibits the same trend as that observed for expansion and again establishes the close correlation between expansion and weight increase, which is illustrated in Fig. 7c. All the mortars failed at the same exposure time and the expansions exhibited for the 20 and 30% cement replacement levels are greater than those for brick types B, L, and P, but similar to those for mortars containing brick type D.

4. Discussion

The partial replacement of cement by GB (0 to 30%) greatly influences the expansion of mortar in sodium sulphate solution (Fig. 1). In most cases the expansion is reduced but in some cases it is increased. In particular, brick type D has a wholly detrimental effect on the resistance of mortar to expansion. It accelerates expansion and failure, and the greater the level of replacement, the more rapidly that failure occurs. Brick types B, L, and P, however, retard expansion significantly. The amount of expansion produced systematically decreases as the amount of replacement of cement by GB (types B, L, and P) in the mortar increases.

The very marked increase in the expansion of mortar-containing brick type D is attributed to its chemical and mineral phase composition. Comparison of the chemical compositions of the four GB types used in the initial investigation (B, D, L, and P) shows that the greatest difference is

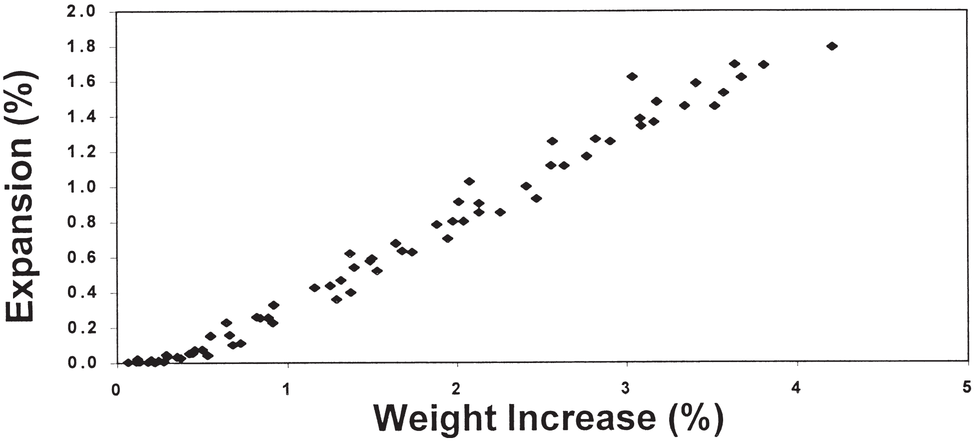

Fig. 6. Expansion vs. weight increase of GB type D-SO_3 mortars exposed to Na_2SO_4 solution.

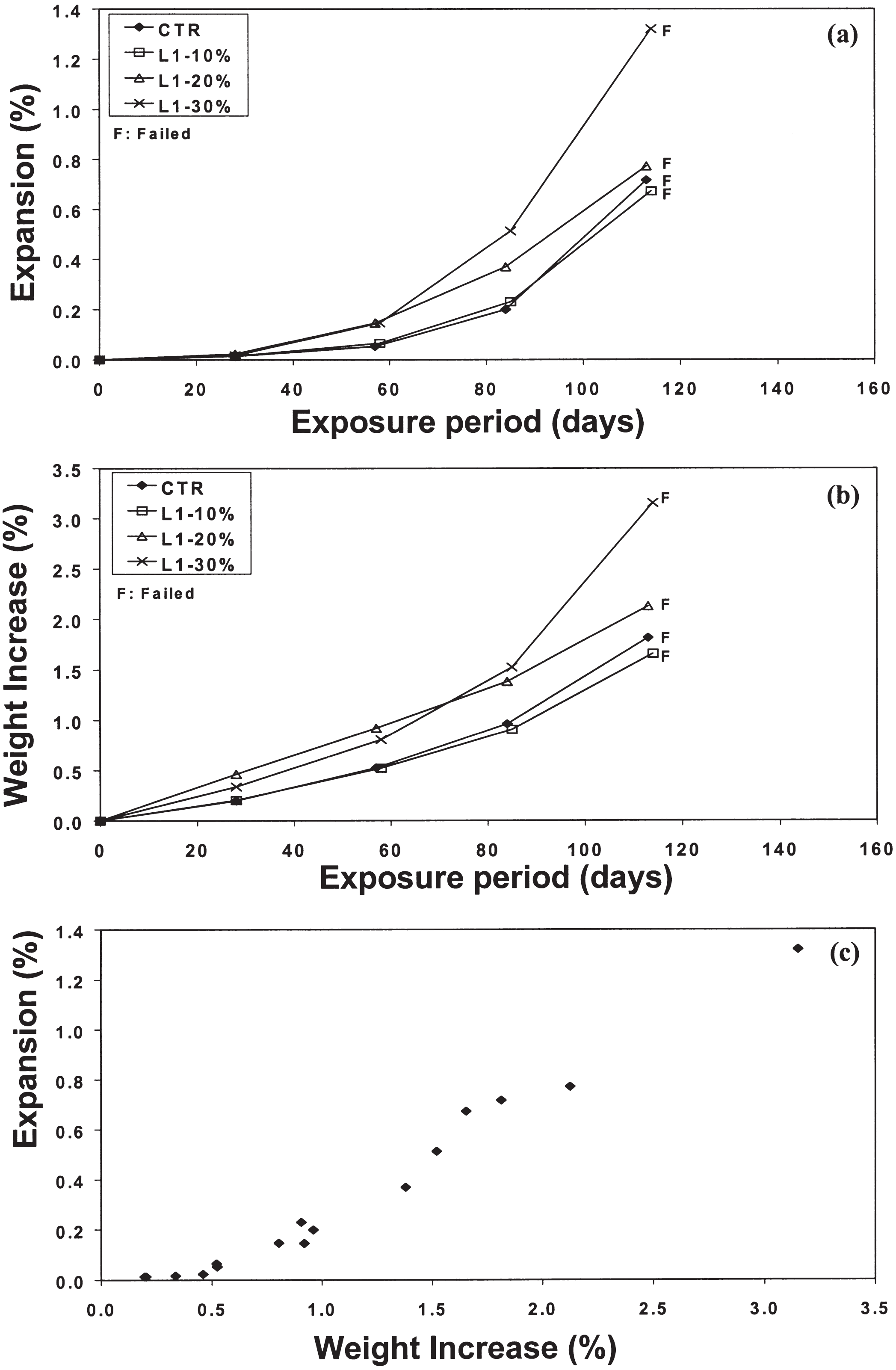

Fig. 7. (a) Expansion vs. time, (b) weight increase vs. time, and (c) expansion vs. weight increase for GB type L1 mortar exposed to sodium sulphate solution.

in calcia (CaO) content. GB types L and P have very low-calcia contents (1.79 and 0.87%, respectively), while GB types B and D have very high-calcia contents (9.39 and 8.86%, respectively). From the chemical and mineralogical analysis (Tables 3 and 4, respectively) it is apparent that in GB type B, part of the CaO is fixed as gypsum and anhydrite, which is not the case in GB type D. Some CaO will go into solution in crystalline feldspar and some will be incorporated in the vitreous alumino-silicate component of the brick. The Na_2O and K_2O components in the brick will also be incorporated in both the feldspar phase and the vitreous phase. Without detailed microprobe analysis of the vitreous phase it is not possible to quantitatively determine the CaO content of the phase, although it is reasonable to assume that as the CaO:glass ratio in the system (excluding the CaO combined with sulphate) increases, it will also increase in the glass phase. The CaO:glass ratio in the five brick types is given in Table 5, which shows that this ratio is very much greater for brick types D and L1 than for brick types B, L, and P. It is particularly large for brick type D.

Work by Tikalsky and Carrasquillo [11] on the sulphate resistance of fly ash concrete has established that if the glassy phase in fly ash contains a high level of CaO (above about 10%), then the fly ash accelerates the expansion of concrete exposed to sodium sulphate solution, and increasing amounts of fly ash increase the deterioration rate. If, however, the glassy phase contains a low level of CaO then the fly ash increases resistance to expansion and high levels of fly ash reduce the deterioration rate. This is exactly what is observed for GB: high levels of types D and L1 (high CaO:glass ratio) increase expansion and accelerate deterioration and high levels of types B, L, and P (low CaO:glass ratio) reduce expansion and inhibit deterioration. According to Tikalsky and Carrasquillo [11], the amount of calcium in the glass determines both the glass dissolution rate by CH and the nature of the reaction products. Fly ash containing low-calcium glass undergoes a long-term pozzolanic reaction that produces C-S-H gel and low-calcium aluminate hydrates, whereas fly ash containing high-calcium glass releases calcium aluminates, which are readily available to form expansive calcium sulphoaluminates in the presence of sulphates.

Although the CaO content of the glass in GB type B is probably much less than in GB type D, the high gypsum (and anhydrite) content of GB type B might be expected to increase the deterioration rate of mortars in which it is incorporated, since these have a natural inbuilt SO_3 content. However, mortar that contains GB type B shows the highest resistance to sodium sulphate solution. Deliberate addition of SO_3 to GB type D at equivalent SO_3 concentrations to that in GB type B was also found to improve the resistance of mortar to expansion on exposure to sodium sulphate solution. In both cases the increased initial SO_3 content will promote and accelerate the normally damaging expansive reactions, which are thus able to take place at a very early stage (i.e., in the period during and immediately after mixing when the mortar is in a highly plastic state). This effect has been reported by Gollop and Taylor [16] in work on sulphate attack of slag-blended pastes. Thus small levels of SO_3 (up to 4%) in the brick can be advantageous in enhancing resistance to expansion when exposed to a sulphatic environment.

Table 5
CaO:glass ratio of GB types B, D, L, P, and L1

B	D	L	P	L1
0.19	0.73	0.08	0.04	0.49

From the current investigations, it is not possible to determine the limits inside which the chemical and phase composition of the GB pozzolan should fall if it is to improve sulphate resistance and not accentuate sulphate attack. The key components appear to be CaO and glass content with SO_3 content also being significant. It is suggested that bricks that have high-calcium content, particularly if coupled with low-glass content and low-sulphate content, impair the chemical durability of mortar; the damaging component is probably a high-calcium glass.

The findings discussed above are reinforced by the additional work done on high-CaO content GB, L1. Unlike GB type L, type L1 has the effect of increasing the deterioration of mortar with increasing GB content when exposed to a sulphatic environment (Fig. 7). GB types L and L1 both have broadly similar SO_3 (0.127 and 0.139%, respectively) and glass (19 and 16%, respectively) contents. However, the CaO content of GB types L and L1 vary significantly (1.79 and 8.07%, respectively) and therefore the CaO concentration in the glassy phase of GB type L1 is expected to be much greater than for GB type L. This provides further evidence that (similar to PFA) the concentration of CaO in the glassy phase present in the GB is a key factor in its resistance to sulphate attack.

5. Conclusions

1. The addition of GB to mortar as partial cement replacement influences significantly the sulphate expansion of the mortar. The type of GB has a marked effect on that expansion.
2. Glass content, oxide chemistry, and sulphate content are key factors to the effectiveness of GB in resisting sulphate expansion.
3. GB of high CaO:glass ratio (excluding the CaO combined with sulphate) increases sulphate expansion of mortar and should not be used as a pozzolan. GB of low CaO:glass ratio (excluding the CaO combined with sulphate) reduces sulphate expansion of mortar and provides an effective pozzolan, particularly if the glass content is high.

4. Small amounts of sulphate in GB do not have any serious deleterious effects on GB mortars and can be beneficial.

Acknowledgments

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