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Resistance to chemical attack of ground brick–PC mortar Part II. Synthetic seawater

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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 synthetic seawater solution and subsequent strength loss. The results indicate that the resistance of mortar to expansion is generally increased and the loss in strength reduced as the replacement level of cement with GB increases up to at least 30% replacement. However, different GB types, when used as partial cement replacement in mortar, were found to impart different degrees of resistance of the mortar to seawater. These differences are attributed to the variations in the chemical and phase compositions of the GB. Sulfate content, glass content, and oxide chemistry are the principal factors that determine the effectiveness of GB in resisting expansion. Small amounts of sulfate in GB do not have any deleterious effects on GB mortars and can be beneficial. © 2000 Elsevier Science Ltd. All rights reserved.

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

1. Introduction

Cementitious materials that are exposed to seawater can be subjected to various kinds of physical and chemical attack. The physical attack can take the form of freeze–thaw, salt weathering (exfoliation), and abrasion by sand in suspension. The chemical attack is due mainly to chloride ingress and sulfate attack. The physical attack and deterioration due to chloride ingress will not be dealt with here. The chemical attack that cementitious materials experience when exposed to seawater is also more complex than those exposed to sodium sulfate, due to the number of dissolved salts present. Seawater typically contains sodium chloride, magnesium chloride, potassium bicarbonate, and perhaps most significantly magnesium sulfate and calcium sulfate (gypsum). Not only do sulfates in solution combine with calcium hydroxide (CH) (produced as a consequence of cement hydration) and alumina (in the cement) to produce ettringite, but the presence of magnesium ions in the solution can also result in the formation of additional deleterious compounds. Expansion has been shown to be of only secondary importance in mortars exposed to seawater [1,2]. Of greater importance is the loss of strength experienced, which is attributed to the decalcification of C–S–H gel. In addition to the sulfate-induced decalcification of C–S–H gel [2], when a deficiency in CH arises, enhanced decalcification occurs by the reaction between Mg^{2+} ions in the seawater and C–S–H gel producing gypsum, non-cementing M–S–H phase, brucite, and hydrated silica gel [3]. As a result, decalcification of C–S–H gel is more severe than in sodium sulfate solution and leads ultimately to complete destruction of C–S–H and the formation of silica gel [2]. Perhaps the most significant product associated with exposure to magnesium sulfate solution is brucite ($Mg(OH)_2$). It has been observed that exposure to magnesium sulfate solution results in a composite layer of brucite and gypsum on the outside of concrete and mortar with the brucite being outermost [3–7]. Brucite has a very low solubility and remains intact at the surface of the cementitious material. It has a pore blocking effect and thus once formed limits the reaction between the cement matrix and magnesium sulfate solution.

Pozzolans, when used as partial cement replacement, are in general considered to improve the resistance of mortar or concrete to sulfate attack. The principal chemical effect of a pozzolan when present in mortar, is the removal of CH from

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the hydrating cement paste, leading to formation of additional cement gel. In the case of sulfate attack, on exposure to Na_2SO_4 solution CH depletion in the mortar is advantageous because the CH provides Ca^{2+} ions for ettringite and gypsum formation, leading to expansion and degradation of the mortar [8]. However, if the sulfate to which the mortar is exposed is $MgSO_4$, the reactions (as indicated above) are more complex. The CH reacts with MS to produce insoluble brucite (MH) which forms a protective layer on the surface of the mortar [3,4,9]. This layer is effective in blocking the pores and inhibiting penetration of Mg^{2+} and $SO_4{}^{2-}$ ions. For highly active pozzolans such as silica fume (SF), which accelerate cement hydration, a large proportion of the CH produced will be removed at a very early stage, particularly for high PC replacement levels. According to various authors [3,9,10] CH depletion promotes magnesium attack of the C–S–H gel, producing gypsum and non-cementitious M–S–H and this severely weakens the mortar. This suggests that to provide optimum effectiveness in resisting MS attack of cement, the pozzolan should be neither highly active nor present in large amounts, because rapid and wholesale removal of CH will promote attack of the C–S–H gel. For example, Torii and Kawamura [10] reported that mortar bars in 10% $MgSO_4$ solution showed decreasing expansion with increasing replacement of PC by SF and PFA up to SF and PFA levels of, respectively, 10% and 30% and expansion then increased at higher replacement levels. Also Al-Amoudi et al. [5] reported an increased strength loss of mortar exposed to Mg_2SO_4 solution when the SF content was increased from 10% to 20%. The pozzolan content should therefore be sufficiently active and present in appropriate amounts to reduce the CH to a level such that excessive amounts of expansive ettringite and gypsum are unable to form, while still being adequate to allow formation of an inhibiting layer of brucite on the mortar surface.

2. Experimental

2.1. Materials

The cement used was high C_3A (C_3A = 11.7%) 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 complying with EN 196-1 [11].

The brick types used derived from a variety of sources across Europe and are referred to as B, D, L, and P. Basic information on the oxide content and mineralogy of these brick types can be found in Tables 3 and 4. The mineralogical analysis was based on relative intensities of X-ray diffraction peaks and is therefore only semi-quantitative [12]. Thus, with respect to brick type B, the gypsum and anhydrite content (12% and 4%, respectively, Table 4) are clearly an overestimate in view of the SO_3 content (2.9%, Table 3) obtained. The bricks were ground to a specific surface of 320–350 m^2 kg^{-1} as determined by constant flow meter air permeability apparatus. Because subsequent results showed brick type D to be atypical of the types B, L, and P in influencing the properties of mortar, a further brick type L1 was selected which like D had a high CaO content, a low SO_3 content, and a relatively low glass content.

Table 1
Chemical composition of high C_3A (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.

Table 2
Minerological composition of high C_3A (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.

2.2. Mixing

The mortar mixes had proportions of 1:3 (binder/sand). The binder consisted of cement and ground brick (GB). The w/b ratio was kept constant at 0.5. In total, 25 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 unique 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. In order to assess the influence on expansion of initial sulfate content in GB nine special mixes were manufactured for GB type D (i.e., D10, D20, and D30 containing 2%, 3%, and 4% SO_3 in the form of gypsum).

2.3. Specimen preparation, curing, and testing

Mortar bars of dimensions 20 × 20 × 160 mm were used for testing. After casting, the moulds containing the specimens were covered in cling-film 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

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].

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

GB type	Quartz	Feldspar	Hematite	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].

of changes in length. After 28 days of water curing, the specimens were immersed in synthetic seawater in compliance with PR ENV 196-XM [13]. Concentrations of the various salts used to manufacture the synthetic seawater can be found in Table 5. The changes in length and mass of the specimens were then monitored over a period of 560 days. Each value given is the average of three measurements from three separate mortar bars. The synthetic seawater was renewed every 28 days. Failure (*F*) was taken as the point at which the specimen began to exhibit actual physical disintegration. After 560 days of exposure, GB mortar prisms B, L, and P (D having failed) were cut into 20 × 20 × 20 mm cubes and tested in compression. All values stated are the average of four readings. After 560 days of exposure small samples (≈4 mm in diameter) were taken from the interior of bars from selected mixes, dried at 40°C over silica gel and ground using a tungsten carbide mill. The resulting GB mortar powder was then subjected to qualitative X-ray diffraction (XRD) analysis using a Phillips diffractometer PW1965, a Phillips X-ray generator PW 1730 combined with a monochromator and the phases present identified.

3. Results

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

The expansion and weight increase of GB mortars B, D, L, and P versus time in synthetic seawater are shown in Fig. 1 together with those of the control mortar. The addition of GB to mortar dramatically influences seawater expansion. Expansion is lower than the control for all B, L, and P mortars and decreases with increasing replacement level. The opposite is true for GB mortar D in that expansion increases with increasing replacement level and is greater than the control at 20% and 30% replacement, suggesting that GB type D is introducing a component that is accelerating expansion and consequently decreasing the durability of the mortar. In fact, GB mortar D at replacement levels of 30% and 20% are the only two mortars to fail in this environment. After 560 days mortars containing GB types B, L, and P all show similar expansion values at 30% replacement (0.3–0.4%). As replacement levels decrease for these GB mortars, expansion increases by different amounts and GB mortar L exhibits the smallest spread of results (10% replacement exhibits only ≈0.6% expansion). The rate of expansion exhibited by the expansion versus time curves in Fig. 1 tends to decrease with increasing exposure time. This suggests that there is a reduction in the rates of reaction causing the expansion. The effect is opposite to that observed for identical bars immersed in sodium sulfate solution (see Ref. [14]) where expansion rate tends to increase with exposure time. The weight increase experienced by the mortar bars behaves in a similar manner to that of the expansion.

Table 5
Composition of synthetic seawater (from Ref. [10])

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

Fig. 2 shows the strength of the mortar prisms after 560 days of exposure to deionized water (a) and to synthetic seawater solution (b). Comparison of Fig. 2(a) and (b) shows that the effect of seawater on the compressive strength of mortar is very severe. In fact the control mortar in artificial seawater loses 76% of the strength it develops in pure water after 560 days. Fig. 2 also shows that, for the GB mortars that had not failed at 560 days (B, L, and P), increasing replacement of cement results in a reduction in the loss in compressive strength. This effect is very noticeable for GB mortars B and P. Therefore, the relatively low amount of expansion experienced by mortar bars in seawater does not necessarily mean less attack. For example, although brick type L at 20% and 30% replacement produces the smallest expansions it does not result in the smallest falls in compressive strength. The decrease in compressive strength observed is clearly due to a loss in bond strength [9,15,16] which could possibly be explained as resulting from decalcification of C–S–H gel which has previously been observed for mortars exposed to Mg_2SO_4 solutions [2,8].

With increase in exposure time, a crystalline layer was observed to develop on the surface of the control mortar and is shown, after 462 days, in Fig. 3(a). Underlying this layer

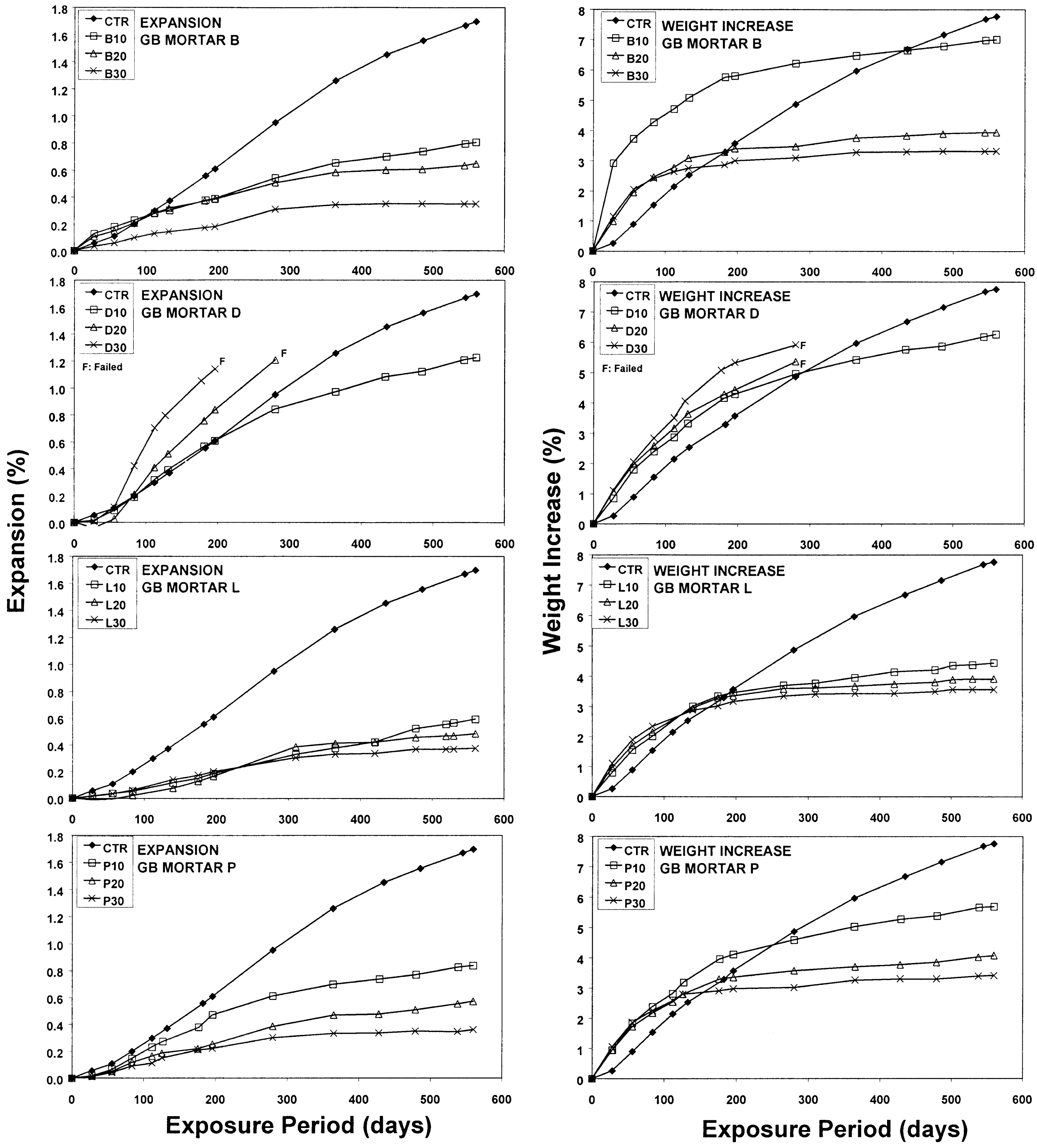

Fig. 1. Expansion and weight increase of GB mortars B, D, L, and P.

was another distinct layer of white material and underlying this was the surface of the mortar. The two layers were analyzed by XRD and were found to be brucite (Fig. 3(b)) and gypsum (Fig. 3(c)). This observation agrees with other researchers who observed that exposure to magnesium sulfate bearing solutions results in a composite layer of brucite and gypsum on the outside of mortar, with brucite being the outermost product [3–7]. Similar but less pronounced layers were observed to form on the GB mortars, becoming less apparent with increasing GB content. The decreasing expansion rate observed with increasing exposure time is in part attributed to the inhibiting effect of this

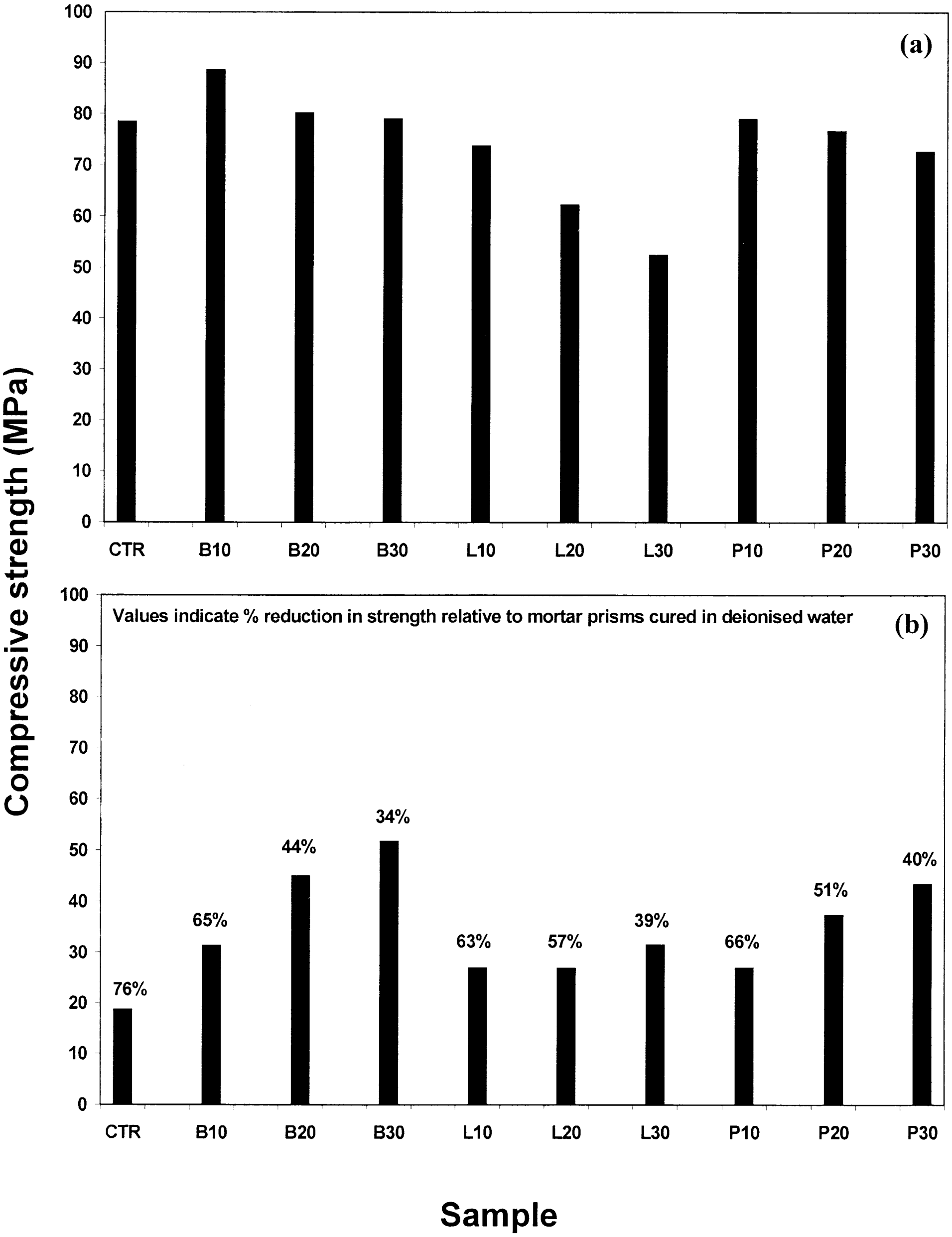

Fig. 2. Compressive strength of mortar (a) cured in deionized water and (b) exposed to synthetic seawater for 560 days.

surface brucite layer on the expansive reactions. This agrees with the consensus that the formation of brucite ($Mg(OH)_2$), which is itself an expansive process, is a self-limiting reaction and thus expansion over long periods is retarded [4]. For specimens taken from the interior of the mortar bars after 560 days of exposure, weak diffraction peaks due to portlandite were observed for the control. These peaks became weaker after 10% replacement of PC with GB and were not apparent at all at 20% and 30% replacement. At all replacement levels, including the control, weak peaks of ettringite, gypsum, and brucite were observed but there was no systematic variation in the height of those peaks between the different compositions.

3.2. GB type D with additional SO_3

The seawater expansion and weight increase of GB mortar D both with and without added sulfate are shown in Fig. 4. Dosing GB type D with sulfate has the effect of reducing significantly the amount of expansion and weight increase observed. The degree to which both expansion and weight increase are reduced tends to increase with increasing cement replacement level. Thus the lowest expansion is achieved for 30% replacement of cement by GB type D into which 4% SO_3 has been added. Surprisingly however, the lowest weight increase for all three replacement levels occurs when the GB is dosed with 3% SO_3. It is interesting

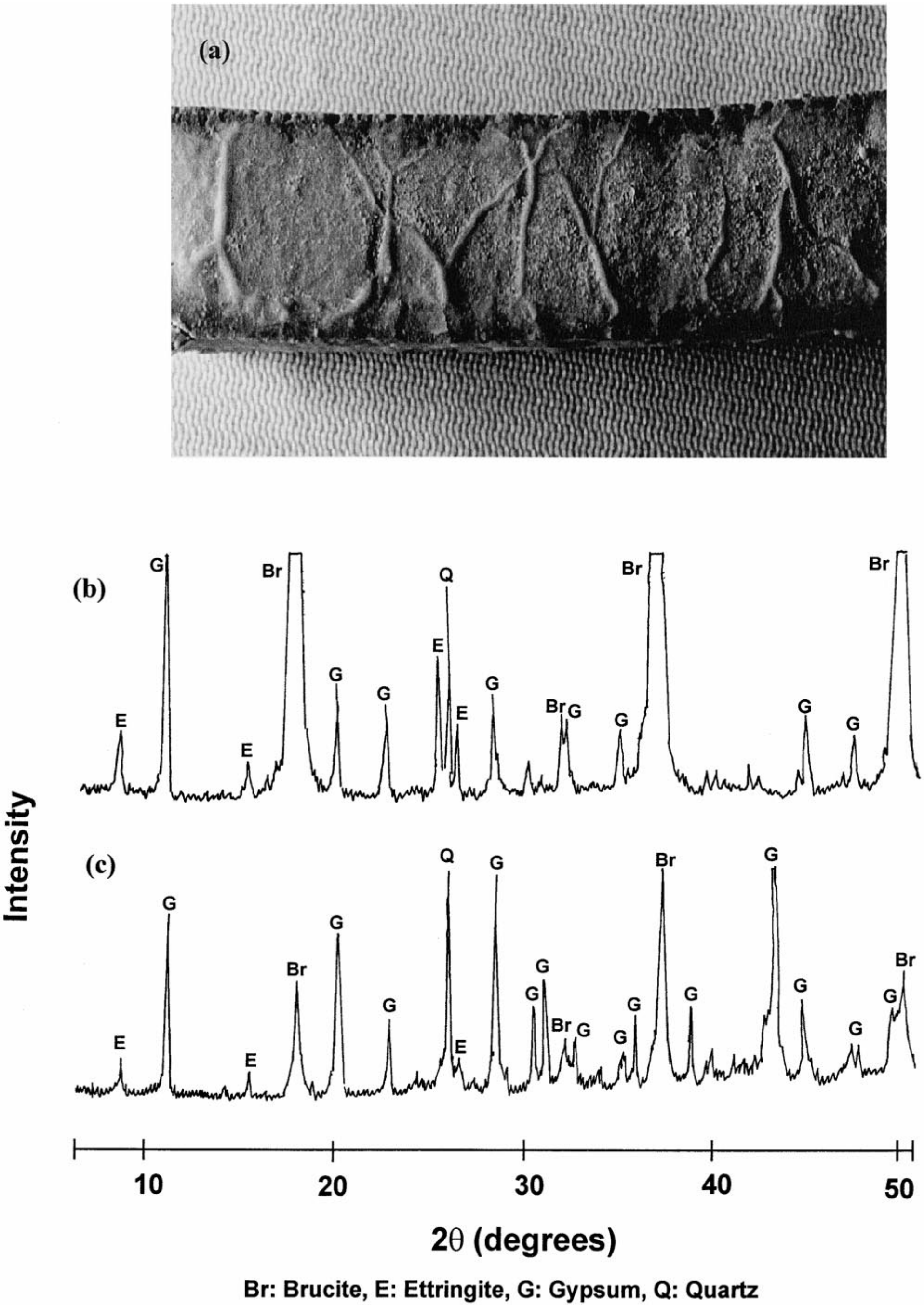

Fig. 3. (a) Crystalline deposit visible on the control mortar after 462 days of exposure, (b) XRD analysis of this deposit, and (c) the underlying white deposit after 560 days of exposure.

to note that all mortars dosed with SO_3 show marked reductions in the rate of expansion beyond about 200 days. The GB type D mortars with no additional SO_3 show expansion rates decreasing only slightly throughout.

3.3. GB type L1

The expansion and weight increase during exposure up to 280 days, for GB mortar containing brick type L1, are shown in Fig. 5. There are distinct similarities in the performance of this mortar with mortar containing brick type D in that:

(i) both expansion and weight increase are substantial up to 280 days,
(ii) increase in GB content produces an increase in expansion not a decrease (as it does for brick types B, L, and P).

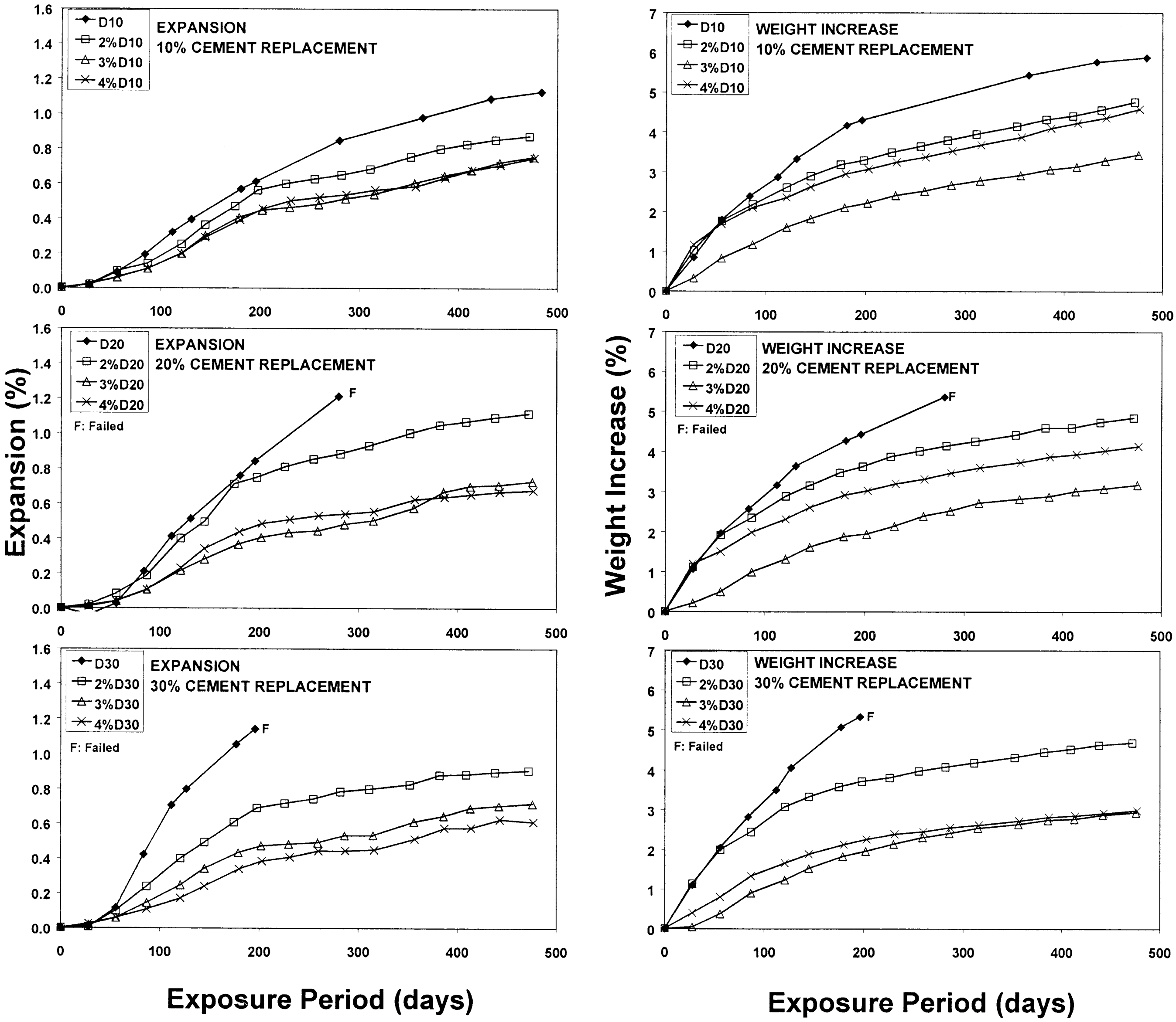

Fig. 4. Expansion and weight increase of GB mortar D with various amounts of additional SO_3.

In this case, however, the effect on expansion is slightly less severe in that expansion exceeds that of the control for 30% replacement, whereas for GB type D expansion exceeds that of the control for both 20% and 30% replacements.

4. Discussion

The expansion of mortars exposed to synthetic seawater is influenced significantly by the partial replacement of cement (10% to 30%) by GB (see Fig. 1). Mortars containing increasing amounts of GB types B, L, and P show progressively smaller expansions when exposed to synthetic seawater whereas mortars containing increasing amounts of GB types D and L1 show progressively larger expansions. Also GB types D and L1 accelerate expansion as the cement replacement level increases. However, deliberate addition of sulfate to GB type D reduces mortar expansion at all three GB replacement levels, relative both to expansion at that replacement level without added sulfate and expansion of the PC mortar control. A similar pattern of behavior (reported in Ref. [14]) was observed when mortar bars were exposed to sodium sulfate solution. This effect of added sulfate in reducing expansion is attributed to acceleration of the normally damaging expansive reactions, which are thus able to take place when the mortar is in its plastic state.

The rate of expansion observed involves an initial period of rapid expansion and as the exposure period increases the expansion rate decreases to a negligible value. This is very noticeable in GB mortar type D prisms with additional SO_3. The expansion experienced by mortars containing GB types

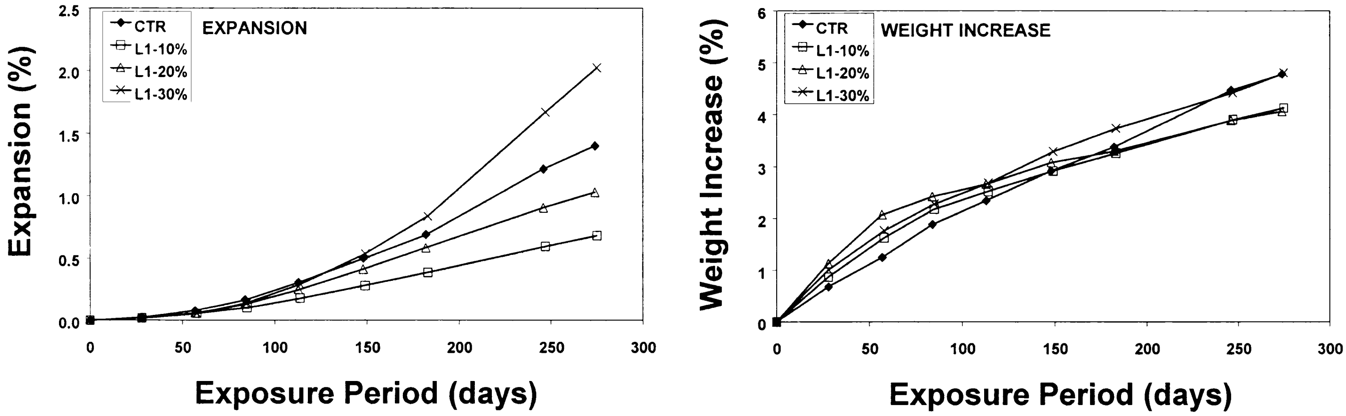

Fig. 5. Expansion and weight of GB mortar L1.

B, D, L, and P exposed to seawater produces less visible damage than when those same mortars (see [Refs. 14,17]) are exposed to sodium sulfate solution, with the majority of mortars remaining intact after 560 days of exposure. The trend of expansion observed for mortars exposed to synthetic seawater is attributed principally to the presence of Mg^{2+} ions, which are not present in sodium sulfate solution. The expansive products considered responsible for the deterioration of mortar exposed to sulfate ions in solution are ettringite and gypsum. The effect of Mg^{2+} ions on the expansion of both plain and blended cements is demonstrated clearly by the work of Al-Amoudi et al. [5] who exposed mortars to both sodium and magnesium sulfate solutions which had a sulfate concentration of 2.1%. Their data demonstrated that for a given amount of expansion, mortar prisms immersed in sodium sulfate solution showed a much smaller loss in strength than prisms immersed in magnesium sulfate solution. Magnesium sulfate solution on the other hand does not produce a highly expansive reaction but significantly damages the integrity of the mortar resulting in a reduced compressive strength. In the current work, although mortar prisms containing GB types B, L, and P exposed to artificial seawater (see Fig. 1) show less expansion with time than the equivalent prisms exposed to sodium sulfate solution (see Ref. [14]) and retain their integrity much longer before failing, they do experience substantial strength reductions (see Fig. 2). The difference in behavior between the two solutions is attributed to the formation of brucite, $Mg(OH)_2$, as a result of the interaction between Mg^{2+} ions in seawater and CH and C–S–H gel in mortar.

Due to its low solubility, brucite is considered to have a pore blocking effect, reducing the ingress of additional external solution and thus limiting the expansive reactions that occur. If considerable quantities of brucite are formed (in the presence of excess CH), a skin is formed on the surface of the mortar beneath which a layer of gypsum is commonly found [3–7]. This is exactly what is observed for the mortars investigated in the present work (see Fig. 3(a)). The exposure period before brucite is visually detected varies primarily with the quantity of GB pozzolan replacing PC in the mortar mix. Brucite is seen to have formed on the control mortar at exposure periods less than 56 days. As brucite formation is essentially a reaction between Mg^{2+} ions and CH, the reduced amounts or absence of observed brucite on the surfaces of mortars containing GB is attributed to reduction in available CH due to the dilution effect and to CH consumption by the pozzolanic reaction that results in additional cementing C–S–H gel. Thus, after 462 days of exposure to synthetic seawater, brucite is seen in decreasing quantities as the cement replacement level increases with no brucite visibly discernible at a replacement level of 30%. However, even up to 30% replacement, expansion is still decreasing with increase in GB content and the percentage loss in strength is also decreasing. This suggests that up to at least 30% replacement of PC by GB types B, L, and P decalcification of the C–S–H has not reached a level sufficient to totally destroy the cement bond. The mortars containing GB types D and L1 are thought to possess high-calcium glass and release high-calcium aluminates as the pozzolanic reaction proceeds [17]. This will contribute to ettringite and gypsum formation and thus in this case increasing the GB content makes available more calcium aluminates and hence results in greater expansion.

5. Conclusions

The following conclusions may be drawn from the above observations.

(1) The addition of GB to mortar as partial cement replacement influences significantly the expansion of the mortar when exposed to synthetic seawater. The type of GB has a marked effect on that expansion.

(2) GB that high has CaO content, low glass content, and low sulfate content (i.e., D and L1) reduces resistance of mortar to seawater and increases expansion and degradation.

(3) A layer of brucite forms on the surface of the mortar exposed to seawater and a layer of gypsum builds up below this. Formation of these surface layers is reduced as partial

replacement of PC with GB increases. The build up of these surface layers inhibits sulfate attack and retards expansion.

(4) The presence of GB (types B, L, and P) in mortar has the effect of limiting the strength loss experienced by mortar exposed to synthetic seawater. Strength loss is reduced as the GB content of the mortar increases up to a replacement level of 30%.

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