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Cement and Concrete Composites 21 (1999) 129–137

Cement &
Concrete
Composites

Performance of Portland limestone cements in mortar prisms immersed in sulfate solutions at 5°C

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Abstract

The results of a test programme to investigate the sulfate resistance of mortars, immersed up to 12 months at 5°C in magnesium sulfate and sodium sulfate solutions, is described. The mortars were prepared from four cements; a Portland cement, a sulfate-resisting Portland cement and two Portland limestone cements containing 15% by mass of an oolitic limestone and a carboniferous limestone. The mortar specimens were subject to BS 5328 Class 4A and 4B sulfate exposure conditions. These are the highest classes for concretes prepared using sulfate-resisting Portland cement (SRPC) before surface protection is required and are two and three classes higher than those recommended for concretes prepared using Portland cement (PC) and Portland limestone cement (PLC), respectively. Two free water–cement ratios were used, 0.5 and 0.75. Performance was monitored by visual assessment, expansion and changes in flexural and compressive strengths.

At a free water–cement ratio of 0.75, the PC mortars and PLC mortars exhibited visually very severe attack with the former showing expansion and reductions in strength, and the latter mainly reductions in strength. At a free water–cement ratio of 0.50 both the PC mortars and PLC mortars showed slight/moderate to severe visual attack, the degree of deterioration appearing slightly greater in the PLC mortars, more especially those made with oolitic limestone. The PLC mortars also exhibited reductions in compressive failure load. The SRPC mortars exhibited little visual deterioration, no expansion, a small increase in flexural strength and no significant reductions in compressive strength. At a free water–cement ratio of 0.75 substantial amounts of thaumasite, together with ettringite was present in the surface layers of the deteriorated PLC mortars whilst ettringite was present in the surface layers of the deteriorated PC mortars. It is concluded that mortars made with a PC with a C_3A content of about 10% by mass were broadly similar in their vulnerability to sulfate attack at 5°C as PLC mortars containing 15% limestone by mass, although the mode of attack was different.

Keywords: Portland cement; Portland limestone cement; Sulfate attack; Thaumasite attack; Expansion; Strength

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1. Introduction

In BRE Digest 363 [1], it has been stated that concretes containing finely divided calcium carbonate, exposed to wet, cold conditions, may be vulnerable to a form of sulfate attack due to thaumasite formation. In recent years, BRE has identified, from six field investigations, problems of sulfate attack of mortar and concrete in which thaumasite was present [2]. One case involved a concrete in which a sulfate-resisting Portland cement and an oolitic limestone aggregate had been used. Similar deterioration has also been reported under laboratory conditions using mortars and concretes prepared with various limestone aggregates and stored at 5°C in sulfate conditions ranging from Class 2 to 5 [2–4]. However, it has also been acknowledged [2] that deterioration in which thaumasite may be implicated is probably rate in practice.

The observations above are of some concern as Portland limestone cement to BS 7583: 1992 [5] which permits 6–20% of a selected limestone, may be manufactured in the UK in the future. However, it should be noted that Portland limestone cements are currently not recommended for concrete in ground water conditions above Class 1 for sulfate [5].

In a BRE/BCA/Cement Industry Working Party programme [6], it was shown that at 20°C the performance in sulfate solutions of Portland limestone cements containing 25% by mass of various limestones, was mostly dependent upon the C_3A content of the parent PC. Limestone additions produced no consistent effect, sometimes producing an improvement and sometimes a worsening performance.

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PII: S0958-9465(98)00009-2

The objectives of the work described in this paper were:

- to establish for a small range of cements, particularly those containing 15% of a limestone addition, the environmental conditions and mortar mix proportions under which thaumasite can be produced and under which disruption due to thaumasite formation may occur;
- to compare the relative performance, in sulfate solutions, of mortars prepared using a sulfate-resisting Portland cement, a Portland cement and two Portland limestone cements containing 15% by mass of a carboniferous and an oolitic limestone, respectively.

Tests were carried out at 5°C for periods up to 12 months, in either magnesium or sodium sulfate solutions on mortars with free water–cement ratios of 0.50 and 0.75 which, for the cements containing 15% by mass of limestone, correspond to free water–Portland cement ratios of 0.59 and 0.88, respectively.

2. Materials

Four cements were employed, a sulfate-resisting Portland cement (SRPC), a Portland cement (PC) with a C_3A content of approximately 10% by mass and two cements containing 15% by mass of a carboniferous and an oolitic limestone. The chemical and physical properties of the SRPC, PC and limestones are given in Table 1. The cements containing limestone were manufactured by inter-blending. No limestone was added to the SRPC. The sand used was German Normensand which is a CEN standard sand, as described in BS EN 196-1 [7].

3. Experimental

Mortars were mixed according to the BS EN 196-1 procedure [7] and mortar prisms, 40 × 40 × 160 mm in size, were cast with free water–cement ratios of 0.5 and 0.75 and with sand–cement ratios of 3:1 and 4.5:1, respectively. The mortar prisms were cured in a fog room at 20°C for 24 h, demoulded and stored under water at 20°C until an age of 28 days. The prisms were then transferred to a series of water and sulfate solution tanks in which the solution/water volumes were approximately five times the volume of the prisms accommodated. The prisms were stored at 5°C for periods of up to 12 months in the following solutions which were renewed each month:

- sodium sulfate solution — 0.35% as SO_3 (i.e. 4.2 g SO_4/l and 2.0 g Na/l) with and without air bubbling;
- magnesium sulfate solution — 0.35% as SO_3 (i.e. 4.2 g SO_4/l and 1.05 g Mg/l) with and without air bubbling.

Table 1
Chemical and physical properties of cements and limestone fillers

Chemical analysis %	SRPC	OPC	Oolitic limestone	Carboniferous limestone
SiO_2	21.7	20.2	2.0	2.4
Al_2O_3	3.3	5.3	0.5	0.1
Fe_2O_3	5.3	2.2	0.98	<0.01
Mn_2O_3	–	0.04	–	<0.02
TiO_2	–	0.23	–	<0.01
CaO	64.2	66.4	52.6	54.2
MgO	1.0	0.9	0.7	0.2
SO_3 (total)	1.9	2.5	0.5	0.10
CO_2	–	–		
K_2O	0.54	0.56	0.07	0.11
Na_2O	0.12	0.23	0.02	0.02
Free CaO	0.80	1.20	–	–
LOI	1.1	0.7	–	42.7
IR	–	0.5	–	–
Density (kg/m^3)	–	3140		2857
Surface area (m^2/kg)	420	344		469
%+45 μm	–	17.4		

Main analyses by XRF.

Total S by an automatic carbon/sulfur analyzer, alkalis by spectrometry.

The prisms (23 specimens) were positioned so that the solution/water was able to contact all sides of the prisms. Air was bubbled through some of the solutions to determine whether dissolution of carbon dioxide from the air could provide the carbonate necessary for thaumasite formation. The solutions used correspond, respectively, to Class 4A sulfate conditions (SO_4 3.1–6.0 g/l, Mg ≤ 1.0 g/l) and Class 4B sulfate conditions (SO_4 3.1–6.0 g/l, Mg > 1.0 g/l) in BS 5328 [8].

Periodically, the prisms were removed from the solutions/water and an assessment was made of performance from:

- visual assessment;
- length measurements (six prisms);
- flexural and compressive strength according to BS EN 196-1 procedure (a) [7] (four prisms).

For visual assessment the following scale was used:

- 0 no attack;
- 1 very slight attack;
- 2 slight attack;
- 3 moderate attack;
- 4 severe attack;
- 5 very severe attack;
- 6 partial disintegration;

- 7 total disintegration.

Qualitative X-ray diffraction analysis was carried out on friable material removed from the surface of prisms showing deterioration. Powdered samples (1 g) with a fineness of less than 53 microns were prepared from the material. X-ray measurements were made on a fully automated Siemens D500 diffractometer operating at 40 KV and 30 mA using copper $K\alpha$ radiation. Data were accumulated for scans between 5° and 50°2Θ and processed using Siemens DIFFRAC-AT 18 software.

4. Results

4.1. Visual assessment

The visual assessment of the prisms after 12 months immersion is summarized in Table 2. Prisms immersed in tap water exhibited no deterioration and are not included in Table 2. Photographs of a number of the deteriorating prisms are shown in Figs 1 and 2. Prisms with a water–cement ratio of 0.75 suffered a greater degree of attack than those with a w/c of 0.5. The overall degree of attack tended to be more severe in magnesium sulfate solution than sodium sulfate solution (Table 2). The SRPC prisms showed only very slight attack at 12 months, whilst the PC prisms and Portland limestone cement (PLC) prisms with a water–cement ratio of 0.75, showed deterioration ranging from very severe attack to 'total disintegration' at 12 months. Bubbling air through the sulfate solutions resulted in no significant differences in the visual appearance of the prisms (Table 2). At w/c 0.50 the PC and PLC mortars showed slight/moderate to severe visual attack, the degree of deterioration appearing slightly greater with the PLC mortars, especially those made with oolitic limestone.

4.2. Expansion

At 12 months, the expansions of all the prisms immersed in water and all the 0.5 w/c ratio prisms immersed in the various sulfate solutions were essentially zero.

Expansions of the 0.75 w/c ratio prisms are shown plotted against age in Figs 3 and 4 for prisms immersed in sulfate solutions, with and without air bubbling, respectively. The expansion behavior of the prisms immersed with and without air were broadly similar (compare Figs 3 and 4). The 12 month expansion behavior of the prisms allows the various cements to be ranked as follows:

- SRPC — a contraction of up to 0.010%;

Table 2
Visual assessment of condition of SRPC, PC and PLC mortars at 12 months

Cement type	w/c Ratio	0.35% SO_3 as $MgSO_4$		0.35% SO_3 as Na_2SO_4	
		With air bubbling	Without air bubbling	With air bubbling	Without air bubbling
SRPC	0.5	Very slight attack on edges 0–1	Very slight attack on edges 0–1	Very slight attack on edges 0–1	Very slight attack on edges 0–1
PC	0.5	Moderate attack on corners and edges 3	Moderate attack on corners and edges 3	Attack on corners and edges 2–3	Attack on corners and edges 2–3
PLC, carboniferous limestone	0.5	Moderate attack on corners and edges 3	Moderate to severe attack on corners and edges 3–4	Moderate attack on corners and edges 3	Moderate attack on corners and edges 3
PLC, oolitic limestone	0.5	Severe attack. Disintegration of surface layers 4	Severe attack. Disintegration of surface layers 4	Severe attack, some disintegration of surface layers 3–4	Moderate to severe attack on corners, edges and faces 3–4
SRPC	0.75	Very slight attack on corners and edges 1	Very slight attack on edges 0–1	Very slight attack on corners 1	Very slight attack on corners and edges 0–1
PC	0.75	Partial to total disintegration 6–7	Partial to total disintegration 6–7	Partial disintegration 6	Severe attack on corners and edges 5–6
PLC, carboniferous limestone	0.75	Very severe attack to partial disintegration 5–6	Partial to total disintegration 6–7	Very severe attack to partial disintegration of surface layers 5–6	Very severe attack on corners, edges and faces 5–6
PLC, oolitic limestone	0.75	Partial to total disintegration 6–7	Partial to total disintegration 6–7	Partial disintegration of corners, edges and faces 5–6	Very severe attack on corners, edges and faces 5–6

- PLC, carboniferous limestone — a small contraction of up to 0.004% in the sodium sulfate solution and a small expansion of up to 0.009% in the magnesium sulfate solution;
- PLC, oolitic limestone — a small expansion of up to 0.018% in the sodium sulfate solution and an expansion of up to 0.032% in the magnesium sulfate solution;
- PC — an expansion of up to 0.039% in the sodium sulfate solution and an expansion of 0.020% at 7 months and 0.163% at 6 months in the magnesium sulfate solution with and without air, respectively.

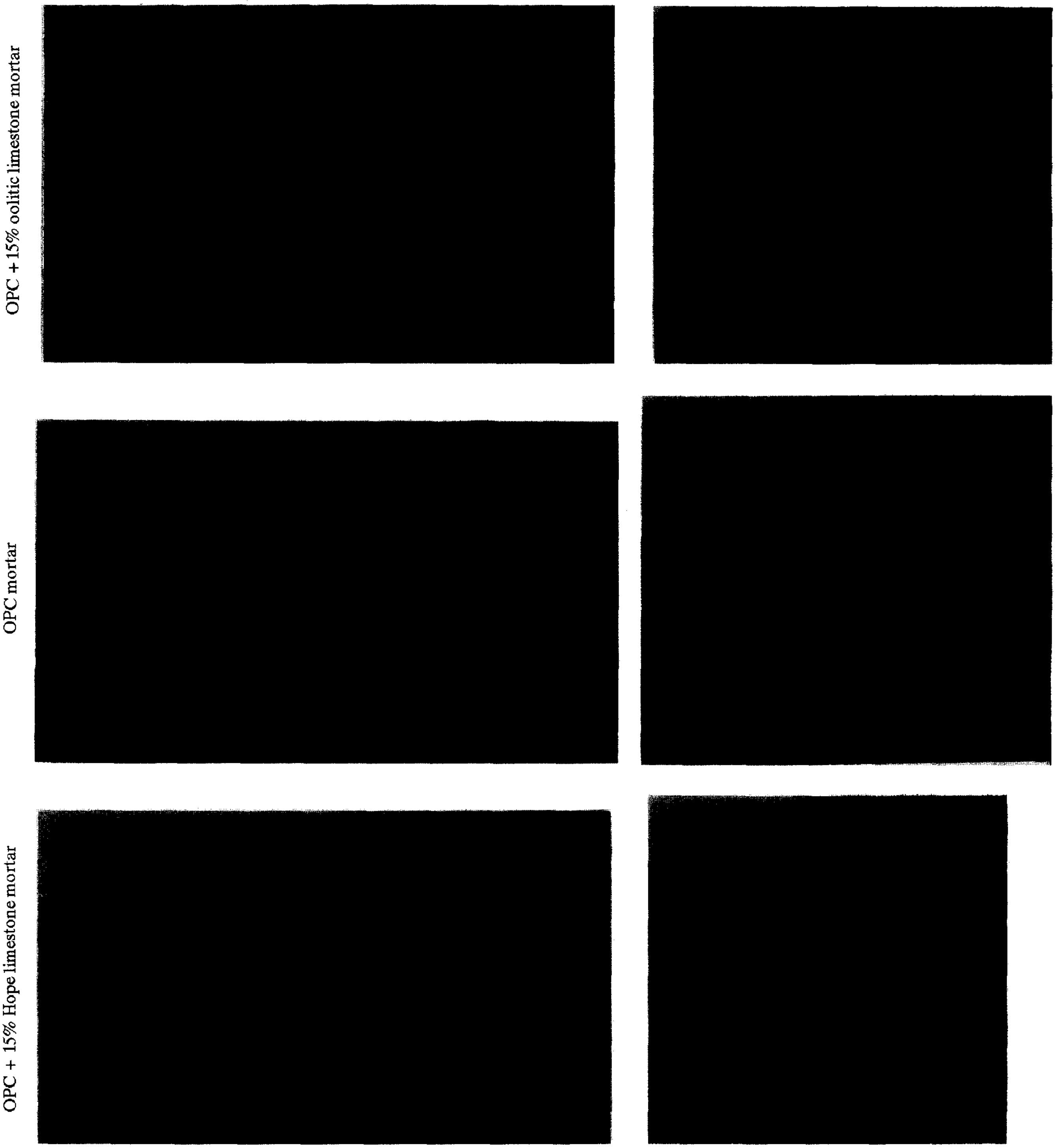

Fig. 1. Condition of PC and PLC mortars (w/c 0.5) following 12 months storage in $MgSO_4$ solution. PLC, oolitic limestone, 2–3; PC, 2–3; PLC, carboniferous limestone, 3–4.

Prisms made using PC, at 0.75 w/c, immersed in the magnesium sulfate solution, broke at 7 months. The corresponding prisms immersed in the same solution, but with air bubbling through, broke at 8 months.

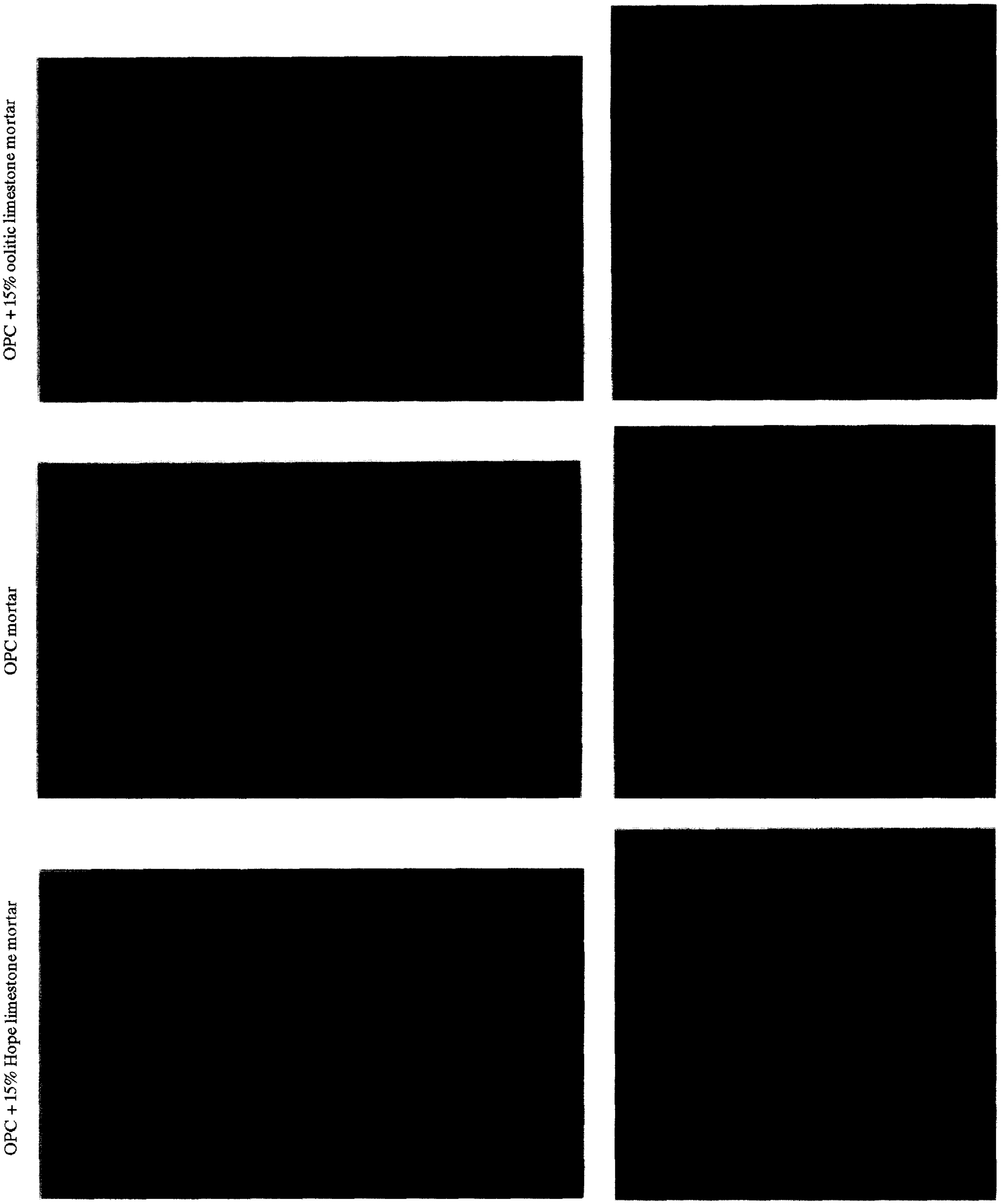

Fig. 2. Condition of PC and PLC mortars (w/c 0.75) following 12 months storage in Na_2SO_4 solution. PLC, oolitic limestone, 4; PC, 4–5; PLC, carboniferous limestone, 4.

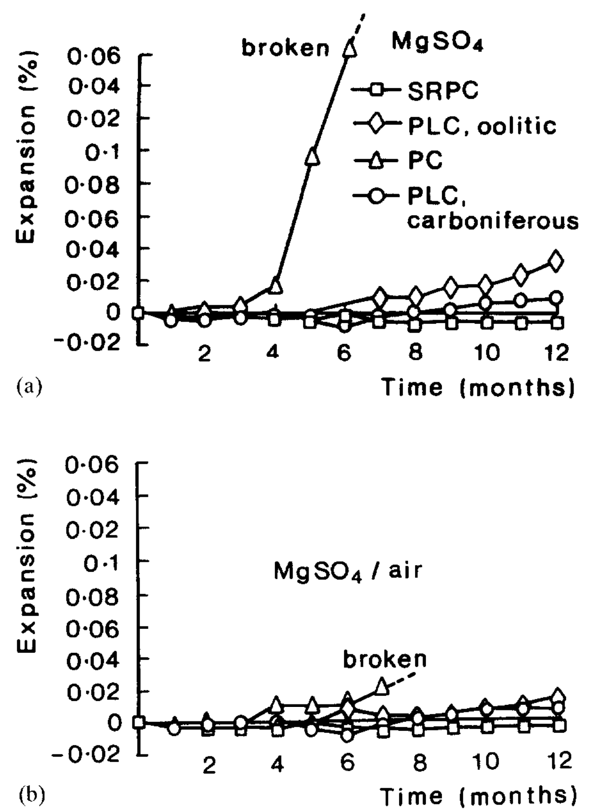

Fig. 3. Expansion data for 0.75 w/c mortars. Magnesium sulfate solution.

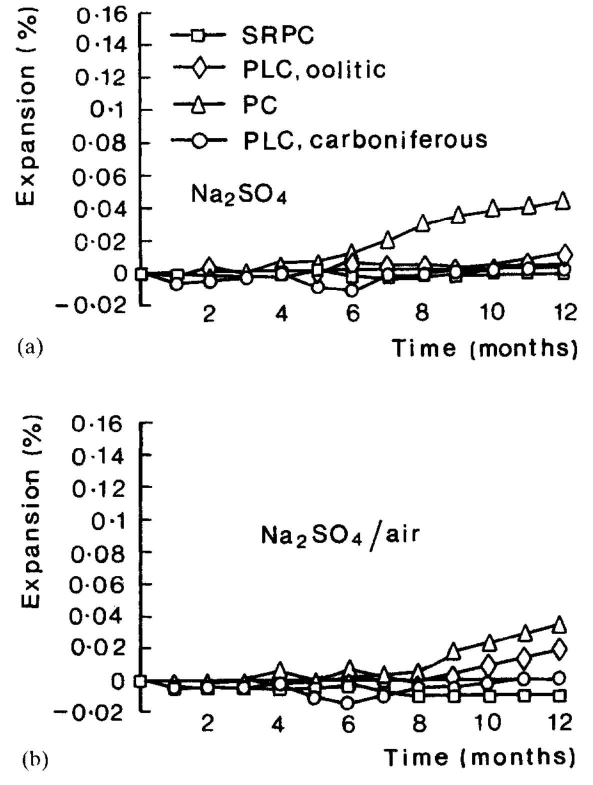

Fig. 4. Expansion data for 0.75 w/c mortars. Sodium sulfate solution.

4.3. *Flexural and compressive failure loads*

The flexural and compressive failure loads at 12 months are given in Tables 3 and 4. The percentage failure loads retained for PC and PLC mortars are shown plotted against w/c ratio and w/PC ratio in Figs 5 and 6, respectively.

The prisms prepared using SRPC had the highest failure loads and exposure to either water or sulfate solutions for periods of 12 months resulted in prisms of similar failure loads. The flexural failure loads for the PC and PLC prisms with a water–cement ratio of 0.5 were little influenced by exposure to sulfates. However, the flexural failure loads were reduced for the 0.75 w/c PLC prisms immersed in any of the sulfate solutions and for the 0.75 w/c PC prisms immersed in the magnesium sulfate solution.

The compressive failure loads of the 0.75 w/c PC and 0.50 and 0.75 w/c PLC prisms were reduced by exposure to sulfates (Table 4). The proportional reductions in strength were greater for the PLC prisms and were a function of w/PC ratio rather than w/c ratio (Fig. 6).

4.4. *Qualitative X-ray diffraction*

Qualitative X-ray diffraction data obtained on material removed from deteriorated PLC prisms with a w/c ratio of 0.75 showed the formation of ettringite and thaumasite for prisms exposed to both sulfate solutions with and without air (Fig. 7). The deteriorated PC prisms with a w/c ratio of 0.75 showed the formation of ettringite for prisms exposed to these solutions (Fig. 8).

5. Discussion

A significant point to emerge from the results is that the 0.75 w/c ratio PC prisms expanded more than 0.75 w/c PLC prisms and that the compressive failure loads for the 0.5 and 0.75 w/c PLC prisms and 0.75 w/c PC prisms were reduced significantly by exposure to sulfates. The compressive failure load retained was related to w/PC ratio rather than w/c ratio.

The above observations, together with the X-ray diffraction analysis, are consistent with the PC prisms having suffered sulfate attack through excess ettringite formation and with the PLC prisms having suffered sulfate attack through excess ettringite and thaumasite formation. Despite these differences, the work has shown that mortar prisms made using PLC, containing 15% limestone, were similarly susceptible to attack when exposed to a Class 4 sulfate exposure as mortar prisms made using PC although the mode of attack was modified.

Table 3
Flexural failure loads at 12 months

Cement type	w/c Ratio	Flexural failure load (kN)					
		H_2O	H_2O/air	$MgSO_4$	$MgSO_4$/air	Na_2SO_4	Na_2SO_4/air
SRPC	0.5	3.50	3.50	3.49	3.96	3.86	3.77
PC	0.5	3.07	3.24	3.25	3.29	3.73	3.45
PLC, carboniferous limestone	0.5	3.05	2.99	2.96	2.84	3.05	3.12
PLC, oolitic limestone	0.5	2.84	3.11	3.14	3.16	3.40	2.91
SRPC	0.75	2.57	2.57	2.85	2.84	2.71	2.71
PC	0.75	2.15	2.38	1.14*	0.25*	2.05	2.27
PLC, carboniferous limestone	0.75	2.21	2.44	1.27	1.34	1.74	1.11
PLC, oolitic limestone	0.75	2.25	2.12	1.17	1.33	1.57	1.57

*Two prisms broken.

Table 4
Compressive failure loads at 12 months

Cement type	w/c Ratio	Compressive failure load (kN)					
		H_2O	H_2O/air	$MgSO_4$	$MgSO_4$/air	Na_2SO_4	Na_2SO_4/air
SRPC	0.5	117	117	113	114	114	112
PC	0.5	102	106	94	96	97	104
PLC, carboniferous limestone	0.5	89	90	57.5	56	55	73.5
PLC, oolitic limestone	0.5	103	107	61.5	67	80	58.5
SRPC	0.75	61.5	61.5	60.5	60	58.5	58.5
PC	0.75	52	55	16.5	19	39	50.5
PLC, carboniferous limestone	0.75	45.5	47	13.3	15	22	10.4
PLC, oolitic limestone	0.75	47	47.5	9.8	9.5	11.3	12.5

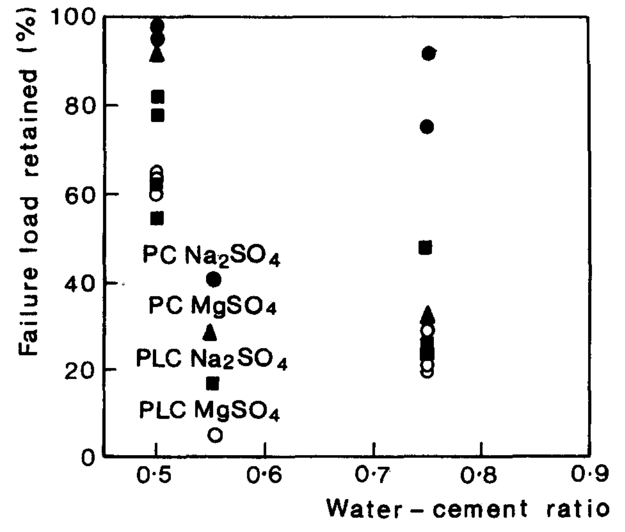

Fig. 5. Dependence of compressive failure load retained upon water–cement ratio.

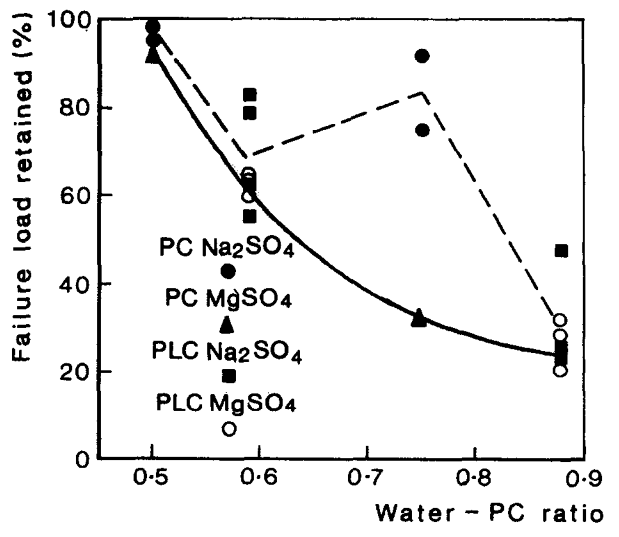

Fig. 6. Dependence of compressive failure load retained upon water–Portland cement ratio.

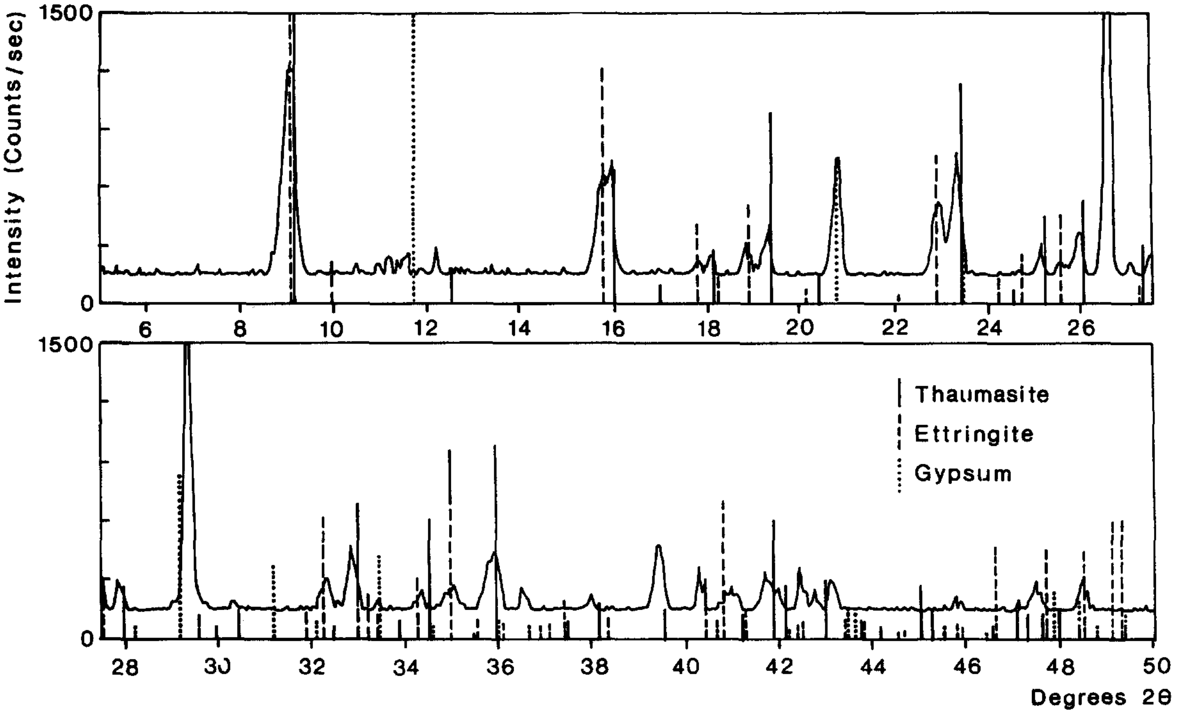

Fig. 7. X-ray diffraction traces showing the presence of thaumasite, ettringite and gypsum in oolitic limestone cement mortar stored in sodium sulfate solution. w/c 0.75.

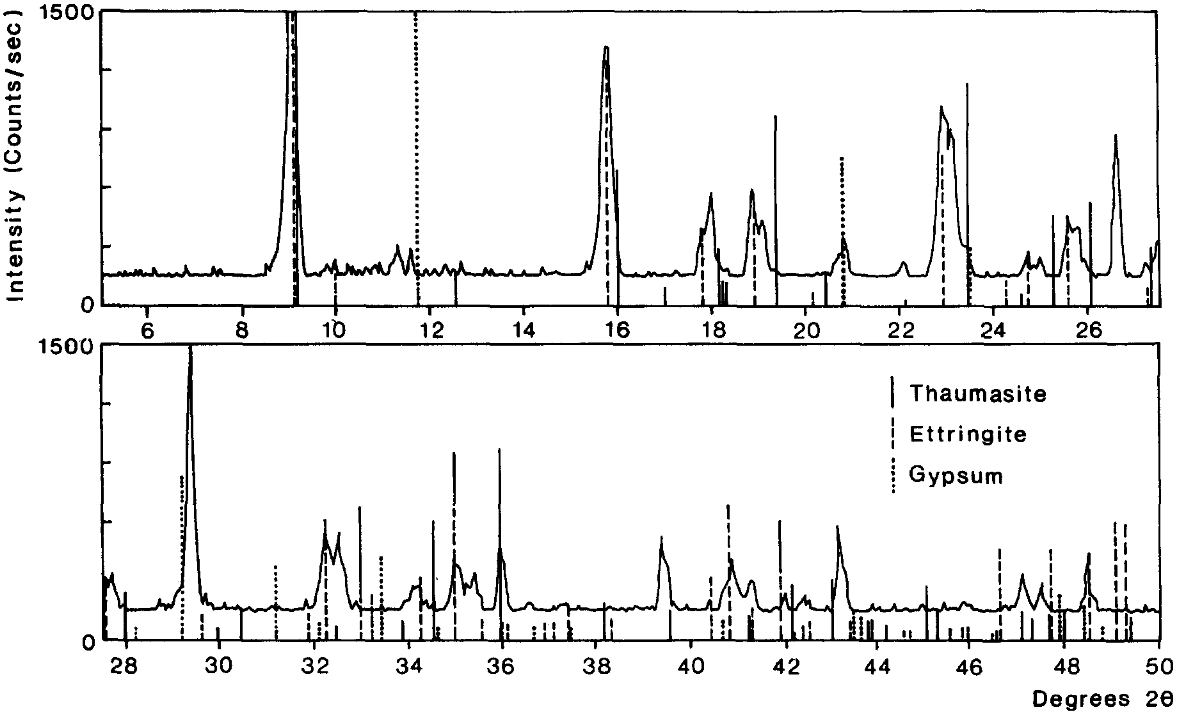

Fig. 8. X-ray diffraction traces showing the presence of ettringite and gypsum in PC mortar stored in sodium sulfate solution. w/c 0.75

6. Conclusions

Mortar prisms of w/c ratios 0.5 and 0.75 were immersed in sodium and magnesium sulfate solutions maintained at 5°C for periods up to 12 months. The mortars were prepared from four cements: a Portland cement; a sulfate-resisting Portland cement; and two Portland limestone cements containing 15% by mass of an oolitic limestone and a carboniferous limestone. The following conclusions are applicable to the particular Portland cement and Portland limestone cements, mortars and the Class 4 sulfate exposure conditions employed:

1. Portland limestone cement mortars are broadly similar in their susceptibility to sulfate attack to Portland cement mortars, although the mode of attack is modified;
2. the Portland cement mortars with a w/c ratio of 0.75 were more susceptible to sulfate induced expansion than the equivalent Portland limestone cement mortars;
3. the compressive failure loads of the 0.75 w/c PC and 0.50 and 0.75 w/c PLC prisms were reduced by exposure to sulfates, the PLC prisms being more susceptible to reductions in failure loads than the comparable PC prisms;
4. in deteriorating Portland cement mortars, ettringite was observed and in deteriorating Portland limestone cement mortars, ettringite and thaumasite were observed;
5. carbon dioxide from the air did not participate in thaumasite formation;
6. the Portland cement and Portland limestone cement mortars showed greater deterioration in a magnesium sulfate solution than in a sodium sulfate solution;
7. as would be expected, the sulfate-resisting Portland cement mortars exhibited little visual deterioration, no expansion and small increases in flexural strength;
8. overall, the PLC mortars containing oolitic limestone suffered slightly greater deterioration than those containing carboniferous limestone.

Acknowledgements

The authors thank Ms J. Hardcastle, Mr A. Gransby, Mr B. Adderson and Mr D. Richardson of the Building Research Establishment, and Dr C. D. Lawrence, previously of the British Cement Association, for their help with the experimental work.

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