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Thaumasite formation in concrete and mortars containing fly ash

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Abstract

Due to recent reports on deterioration of concrete structures, the thaumasite form of sulfate attack has become a subject of study and close investigation. This paper investigates the formation of thaumasite in concrete and mortars containing fly ash. The results show that thaumasite formation can occur within 84 days of exposure to sulfate solutions. High volumes of fly ash can limit or promote thaumasite formation depending on the type of cement used. Thaumasite and ettringite were found among the deterioration products. However, the thaumasite formation in the specimen prepared from sulfate resisting Portland cement was not accompanied by deterioration, except by 50% fly ash addition. The mixtures of Portland limestone cement with 40% fly ash exhibited a very limited thaumasite formation while the mixtures with 50% had no thaumasite at all. It is concluded that thaumasite can also be formed in mixtures incorporating fly ash.
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Keywords: Concrete; Mortars; Thaumasite; Sulfate attack; Fly ash

1. Introduction

One of the factors which adversely influences the durability of concrete is its ability to deteriorate due to sulfate attack. Whereas properly constituted, placed and cured concrete enjoys a long service life under most natural and industrial environments, premature failures of concrete structures world wide have attracted special attention to performance of concrete in sulfate bearing waters and soils.

Damage to concrete pavements, retaining walls, swimming pools, bridge decks, offshore structures and foundations has been reported and attributed to the thaumasite and ettringite formation. The thaumasite form of sulfate attack on concrete has been reported from different parts of the world, where most structures suffered from undesirably high degree of deterioration within a short period of service [1–3]. Despite the use of sulfate resisting cements such as Portland cement with less than 3% tricalcium aluminate (C_3A) and 5% Al_2O_3, slag cement containing a minimum 70% of granulated slag and cement with pozzolan additions formulated to produce durable concretes with high sulfate resistance [4], thaumasite formation can still occur and affect the durability of such concretes.

In view of thaumasite form of sulfate attack, the performance of concrete and mortars containing fly ash is of a particular interest. The present study was taken to investigate the formation of thaumasite in concrete and mortars containing fly ash. The specimens were exposed to sulfate solutions at 8 and 20 °C. The effect of temperature and period of exposure was also investigated. This paper focuses on the performance of binders containing a sulfate resisting Portland cement (SRPC) CEM I 42.5 R-HS, a Portland limestone cement (PLC) CEM II/A-L 32.5R and binders containing 20–50% fly ash.

Many natural pozzolans have demonstrated a satisfactory performance in blended cements exposed to sulfate environment [5,6]. Low calcium fly ash has been reported to decrease sulfate attack especially in high water–cement ratio and low unitary cement content concrete [7]. However most of the investigations have been carried out at 20 °C and hence not considering thaumasite formation. Low temperatures, generally below 15 °C (60 F), are needed for vigorous formation of thaumasite in concrete and mortars exposed to sulfate attack. The chemical processes leading to thaumasite formation are described in [10,12]. The formation of thaumasite is generally attributed to a consequence of the evolution of ettringite when it incorporates Si^{4+} (in octahedral coordination) in its structure, substituting for

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Al^{3+} ions in the presence of CO_3^{2-}. Another hypothesis on thaumasite is associated with the interaction between sulfates and carbonates present in the aqueous phase of the cement and C–S–H gel. This involves the destruction of the resistant structure of hydrated cement without volume alteration or without ettringite participation. A break up of the material may occur due to C–S–H gel destruction [2,10,12].

Considering the conventional sulfate attack, it is commonly believed that chemical reactions between ions and certain constituents (especially monosulfate hydrate (C_4ASH_{12}), calcium aluminate hydrates (C–A–H) and calcium hydroxide (CH)) in the hydrated cement paste, that result in the formation of ettringite and gypsum can cause excessive expansion, cracking and strength loss. Concrete deterioration due to conventional sulfate attack is often associated with the expansion of ettringite; however, the mechanisms by which ettringite formation causes expansion still remains unexplained [2]. Exertion of pressure by growing ettringite crystals, and swelling due to adsorption of water in alkaline environment by poorly crystalline ettringite, are two of the hypotheses that are supported by most researchers.

The role of pozzolans in improving the sulfate resistance of concrete as indicated by several investigators involves the removal of CH produced by calcium silicate hydration through the pozzolanic reaction [5,6], decrease of porosity by C–S–H (II) formation and protection of unstable cement compounds in sulfate environment, reduction of CH in paste–aggregate zone [7], ettringite formation in pore solution without expansion and relative decrease of C_3A content in blended cement [6,7]. Taking into account that the rate of ettringite expansion increases with falling temperature [4,5] and that by low temperatures the performance of concrete containing fly ash can even be more affected than ordinary Portland cement [5,8], the use of fly ash in concrete needs adequate verification.

The significance of this investigation is to help clarify the performance of concretes and mortars containing fly ash when subjected to both conventional and thaumasite form of sulfate attack.

2. Experimental

The binder types have been examined by immersing concrete specimens (40×40×160 mm normal prisms; max grain size 8 mm) and mortar specimens (10×40×160 mm flat prisms; sand/binder ratio = 3.0), in sodium sulfate solutions at 8 and 20 °C. The specimens were cast containing 0, 20, 30, 40, 50% of fly ash by mass of cement. The assessment of damage and deterioration of the specimens due to sulfate attack was conducted using the newly developed MNS-test method [11] (employing direct tension test on concrete prisms and cores) and the Wittekindt-test method [9] by measuring the linear expansion of flat prisms immersed in 4.4% sodium sulfate solution. Direct tensile strength and length changes have been recorded over a period of 120 days.

According to the MNS-test method [11] small concrete prism specimens analogous to ISO Rilem mortar prisms were adopted (40×40×160 mm, max grain size = 8 mm; $w/(z+f) = 0.60$) to accelerate the rate of sulfate attack. Freshly cast prisms were preliminary cured for 2 days in a fog room at 20 °C, then demoulded, marked and stored under distilled water for 5 days and then stored in an air conditioned room at 20 °C and 65% relative humidity for 7 days. The German siliceous sand and coarse aggregate were used. A 5% sodium sulfate solution (Na_2SO_4) was employed as the aggressive medium. Control specimens are stored in distilled water. To prepare for the performance of the direct tension test the top and bottom square surfaces of the concrete prisms were coated with a high strength expoxy adhesive. This prevents damage of these surfaces after exposure to sulfate attack and provides a suitable surface to glue the specimen to the metal end plates using another high strength expoxy adhesive.

The Wittekindt-test method [9] was used to assess the sulfate attack by linear expansion measurements on 10×40×160 mm mortar prisms ($w/(z+f) = 0.6$; sand/cement ratio = 3.0, prepared according to Germany Standard DIN EN 196 and compacted by jolting table). The siliceous sand employed was German Normensand according to the specifications of 1958 Germany Standard DIN 1164. Six flat prisms were cast for each fly ash binder combination. Stainless steel inserts were cast into the ends of specimens intended for length change measurements to enable more precise data to be obtained. The specimens were cured using the same curing conditions and period as stated by MNS-test method.

A maximum curing period of 14 days was chosen taking into account that most concretes are directly cast in sulfate bearing soils and water without considering adequate curing periods and the pozzolanic reaction of the fly ash which normally comes into effect after 28 days of concrete age [13]. The curing period was followed by immersion of both concrete and mortar specimens in separate baths of either sodium sulfate solutions (half the number of specimens) or distilled water at the same temperature (8 or 20 °C). The bath liquids were changed every 4 weeks. The volume ratio of bath fluid to submerged specimens was 3:1.

2.1. Materials

To allow detailed examination the type of cement was first restricted to only one German SRPC CEM I 42.5 R-HS and a PLC with 15% carboniferous limestone filler. The amount of fly ash was varied at 0%, 20%,

Table 1
Chemical and mineralogical composition of cement and fly ash used

	CEM I 42.5R-HS	CEM II/A-L 32.5R	EFA-Füller® S-B/E
Drying loss [%]	0	0.30	0.2
Ignition loss [%]	2.40	7.40	3.1
CaO [%]	63.0	60.40	4.0
CaO_{free} [%]	0.60	0.40	–
SiO_2 [%]	20.40	17.70	49.20
Al_2O_3 [%]	4.40	5.20	27.20
Fe_2O_3 [%]	5.0	2.30	8.10
SO_3 [%]	2.30	3.30	0.89
Na_2O_3 [%]	0.17	0.12	0.88
K_2O [%]	1.13	1.07	3.94
TiO_2 [%]	0.16	0.31	0.89
MnO [%]	0	0.03	0.07
MgO [%]	1.20	1.20	2.00
Cl^- [%]	0.015	0.021	–
C_3S [%]	55.7		
C_2S [%]	16.5		
C_3A [%]	3.2		
C_4AF [%]	15.2		
Density ρ_R [g/cm^3]	3.194	3.064	2.17
Specific surface Area A_0 [cm^2/g]	4350	4050	3200

30%, 40% and 50% replacement levels during the casting of prisms. A German fly ash EFA-Filler was used. The result of the chemical and mineralogical analysis giving their composition is shown in Table 1.

3. Results and discussion

3.1. Direct tensile strength tests

Direct tensile strength test were carried out on ISO-RILEM concrete prisms. For each strength measurement, three prisms were usually tested giving 3 tensile strength values for specimens exposed to sulfate attack which were then averaged. The flexural strengths of prisms stored in sulfate solution have been divided by the strengths of similar prisms stored in distilled water at the same temperature, to give the relative transverse tensile strength after a given time of storage in sulfate solution. According to the MNS-Test Method the relative transverse tensile strength of at least 0.80 after 84 days and not less than 0.70 after 120 days of exposure to sulfate attack is required for a given concrete to be considered sulfate resistant. Fig. 1 presents a summary of the tensile strength results for concretes with 0, 30 and 50% fly ash contents.

The results show that concrete employing the sulfate resisting cement CEM I 42.5R-HS performed very well and showed a high sulfate resistance despite the addition of fly ash and early exposure to sulfate attack. At both temperatures, the concrete mixtures with 50% fly ash recorded the lowest tensile strength but yet fulfilled the criteria for a sulfate resisting concrete. This strength loss can be attributed to the ettringite (at 20 °C) and

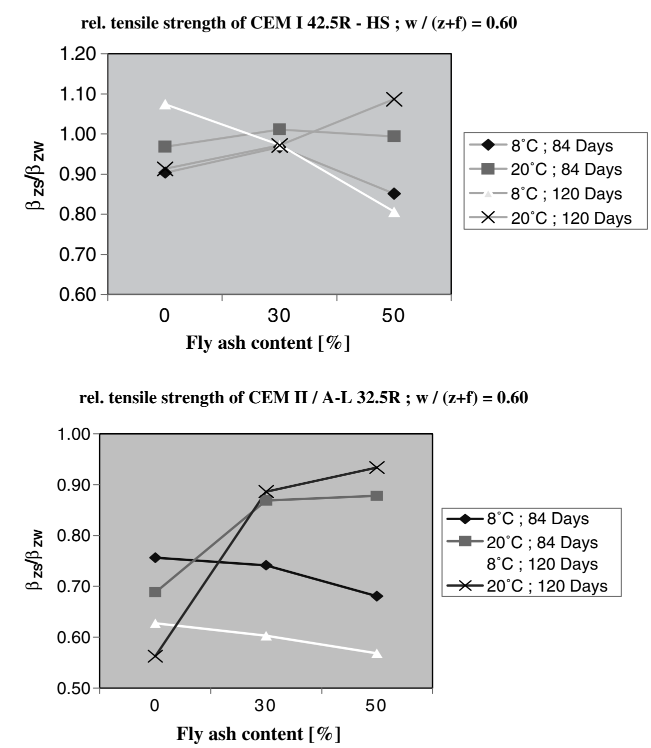

Fig. 1. Relative direct tensile of SRPC and PLC concrete prisms after immersion in 5% Sodium sulfate solutions (MNS-Test Method) for 84 and 120 days.

thaumasite formation (mainly at 8 °C exposure) which was detected in these mixtures within 84 days of sulfate attack. All specimens of concretes employing PLC exhibited lower tensile strength values in the sulfate solutions than in distilled water and severe loss of strength after 120 days of sulfate attack at 8 °C. The strength loss was accompanied by pronounced thaumasite formation (Fig. 5). However, the addition of fly ash seemed to improve the sulfate resistance of these concretes when they are exposed to sulfates at 20 °C. This can be attributed to the effects of the pozzolanic reaction taking place at a higher rate at 20 °C as compared to its retardation at 8 °C. In terms of tensile strength the performances of the plain SRPC as well as PLC specimens examined were considerably poorer than those of the PC/fly ash specimens. At 20 °C all binders except those with 0% fly ash showed higher strength retention than at 8 °C.

3.2. Specimen appearance

Considering the visual appearance of the concrete specimens, the sulfate resisting specimens did not show any visible signs of deterioration even after 120 days exposure to 5% Na_2SO_4 solutions. However, most of the specimens incorporating the PLCs showed signs of deterioration within 84 days of exposure to 5% Na_2SO_4 solutions. Some exfoliation of the corners and edges as well as cracks occurred on these specimens after 84 and 120 days respectively. At 8 °C, signs of attack on fly ash specimens were somewhat more pronounced with edge and corner corrosion appearing than at 20 °C. On the contrary, the specimens containing 30% and 50% fly ash were still in sound condition at 20 °C. The plain PC specimens showed a greater rate of corrosion at 20 °C than at 8 °C.

3.3. Linear expansion tests

Length measurements were made, using a small steel vertical frame which incorporated a dial gauge. In this case the test method adopted to study sulfate resistance of mortar specimens was the Wittekindt method [9]. This test measures the variation of length being recorded as expansion. Expansion data are presented as differences between the length changes observed in sulfate solutions and those in distilled water. As criterion, the sulfate resistance of the binder is satisfactory when the average expansion of the prisms is less than 0.5 mm/m after 56 days exposure to sulfate solutions.

All SRPC mortar specimens did not show any significant expansion and proved to be sulfate resistant. However, thaumasite formation was evident in fly ash mixtures. On the other hand, the PLC specimens, including those stored in distilled water, gradually expanded throughout the period of experiment. However, after approximately 90 days all specimens in distilled water did not show any further expansion. Generally, all PLC/fly ash binder combinations tested as flat mortar prisms at 20 °C exhibited lower expansions compared to the plain PLC specimens. According to the Wittekindt method they all proved not to be sulfate resistant as the average expansions of prisms exceeded 0.5 mm/m after 56 days. The sulfate attack at 8 °C was stronger and caused more deterioration than at 20 °C.

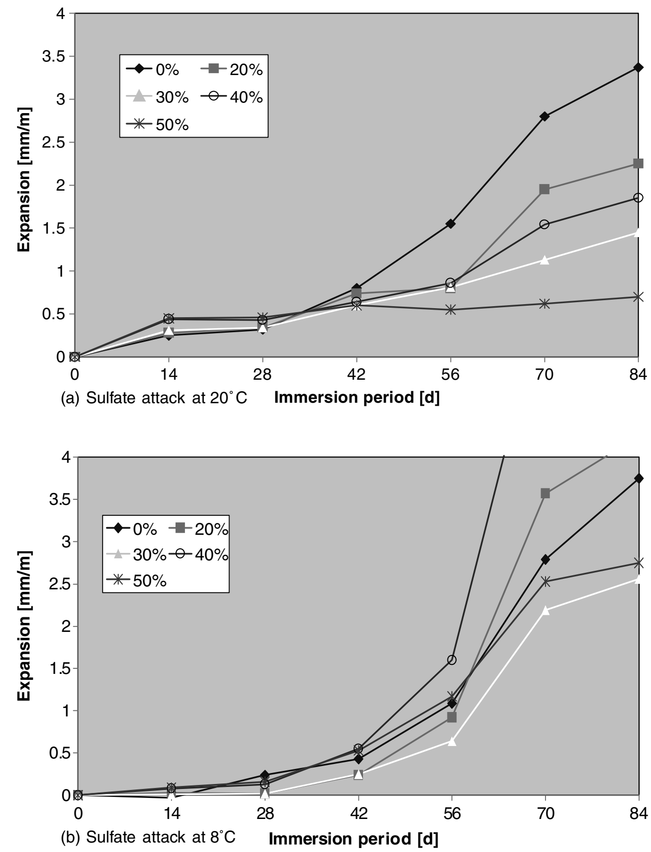

Fig. 2. Expansions of PLC mortar prisms containing fly ash after immersion in 4.4% Sodium sulfate solution (Wittekindt-TEST Method). $w/(z+5.f)=0.6$.

The expansion results of mortar prisms corresponded to the Visual assessment made by observing the physical appearance of specimens. All mortar prisms exhibited deterioration just after 56 days of immersion in sodium sulfate solution by developing cracks, softening and popouts. While this process continued at 20 °C for even more than 120 days without causing total destruction of the specimens, the mortar prisms at 8 °C were totally transformed into a mushy and incohesive mass within 120 days of sulfate attack. In this case the thaumasite formation appeared to have played a major role in the deterioration of the specimens as compared to that of 20 °C where mainly ettringite was formed (see Section 3.4). The expansion results are illustrated in Fig. 2.

3.4. XRD, REM observations

Mortar specimens of the expansion tests were examined by X-ray diffraction (XRD) and raster scanning electron microscopy (REM) after 84 as well as 120 days sulfate exposure in order to localize various SO_3 bearing phases and to identify possible variations in morphology. Ettringite, monosulfate and gypsum were well distinguished by their energy dispersive spectrum. At 20 °C ettringite needles in spherical pores were detected in most sulfate stored and many water stored specimens as well. A number specimens under sulfate attack additionally show portlandite and gypsum. However no signs of thaumasite were observed at 20 °C. The thaumasite formation took place in specimens at 8 °C accompanied by severe loss of strength by concrete prisms as well as by mortar prisms. Examples of these phases are illustrated in Figs. 3–5. While the PLC concrete with 0 and 30% fly ash exhibited a higher tendency to thaumasite formation after 84 and 120 days exposure to sodium sulfate solutions at 8 °C the concrete with 50% fly ash showed no signs of thaumasite at all. The investigations on SRPC however proved that thaumasite formation occurred even by concrete with 50% fly ash. These concretes also exhibited the highest strength loss in this series. XRD and REM investigations clearly show thaumasite and ettringite formation within some pores and areas of the matrix structure being filled with only thaumasite as illustrated in Figs. 3 and 5. Moreover, the specimens in which thaumasite was evident exhibited more structural damage than the specimens at 20 °C where mainly ettringite and no thaumasite was formed. The tendency to thaumasite formation seems to reduce with increasing amounts of fly ash in PLC concretes and to increase with increasing amounts of fly ash in SRPC concretes.

4. Conclusions

(1) The results confirm a strong effect of temperature on the performance of plain PLC and PLC/fly ash binders. At 20 °C PC/fly ash binders behaved significantly better than the plain PLC binder indicating that a partial replacement of Portland cement with fly ash can improve the sulfate resistance of mortars and concrete. According to the Wittekindt-test method all PLC mortars containing fly ash are not sulfate resistant. However, the concrete prisms with 30% and 50% fly ash performed much better and fulfilled the criteria according to the MNS-test method.
(2) Concrete and mortars containing fly ash appeared to be more vulnerable to sulfate attack at low temperatures. Therefore the use of fly ash in concrete to be used in sulfate bearing waters and soils at low temperatures requires adequate verification. The curing

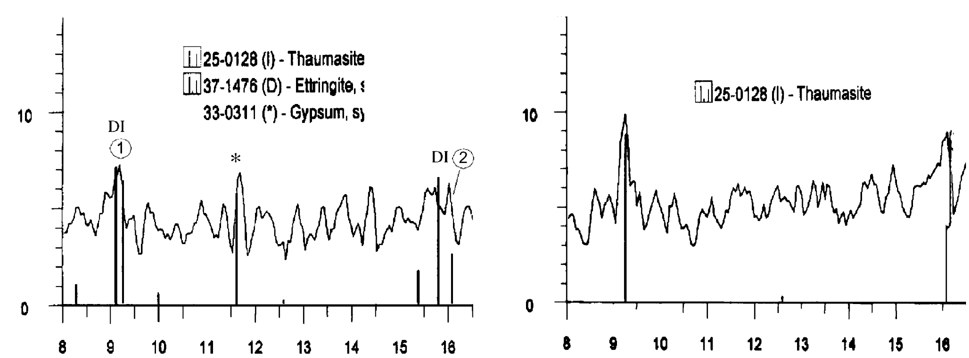

Fig. 3. Thaumasite formation in a plain SRPC concrete specimens (left) and with 50% fly ash (right).

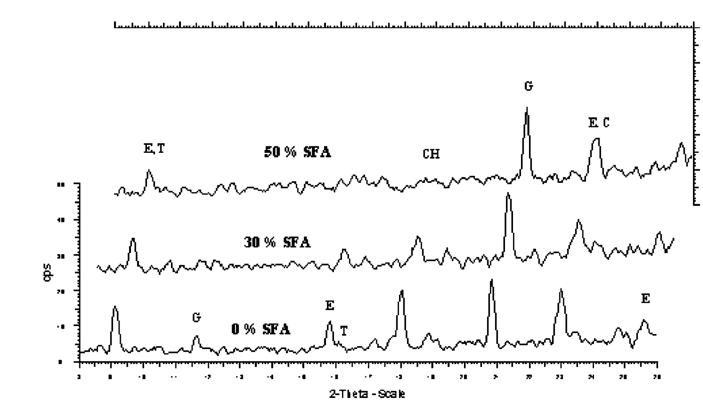

Fig. 4. Thaumasite formation in PLC concrete specimens decreasing with increasing amounts of fly ash (SFA) (diagram in 3D view).

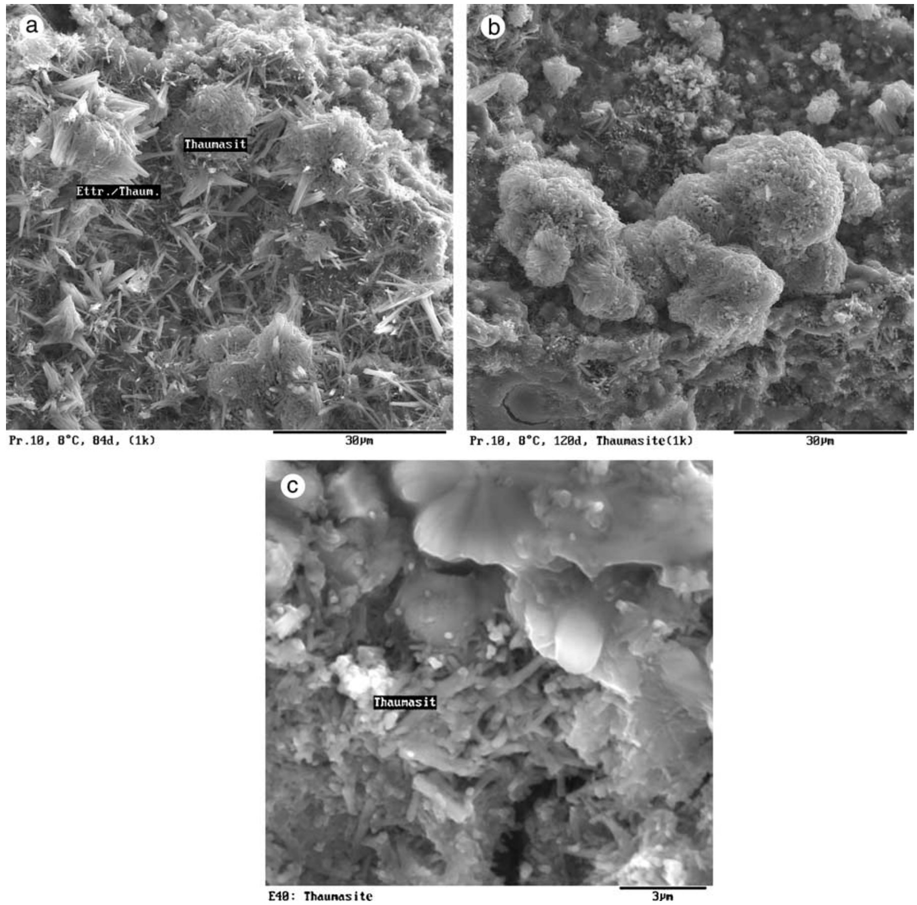

Fig. 5. Thaumasite formation in PLC specimens (a) plain after 84 days, (b) plain after 120 days (c) with 40% fly ash after 84 days of sulfate attack.

period before sulfate attack may have a strong effect as pertaining to the effects of the pozzolanic reaction.

(3) Thaumasite formation can occur within 84 days of exposure to sulfate solutions. High volumes of fly ash can limit or promote thaumasite formation depending on the type of cement used. Thaumasite and ettringite were found among the deterioration products. However, the thaumasite formation in the specimen prepared from SRPC was not accompanied by deterioration, except by 50% fly ash addition. The mixtures of PLC with 40% fly ash exhibited a very limited thaumasite formation while the mixtures with 50% fly ash had no thaumasite at all. It is concluded that thaumasite can also be formed in mixtures incorporating fly ash.

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