

CHEMICAL REAGENTS TO PREVENT THE THAUMASITE FORM OF SULFATE ATTACK

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ABSTRACT

Two reagents were used to prevent the thaumasite formation in Portland limestone cement mortar; disodium hydrogen phosphate chelating agent and barium hydroxide. 3 and 5% of each reagent were added to the cement mortar with 1:2 cement to sand and a w/c ratio of 0.46. The specimens were immersed in 5% magnesium sulfate solution at 7°C up for 90 days. The compressive strength of the cubic samples were measured at different time intervals. After 90 days exposure, the appearance of the cubic samples were inspected visually and the phases formed were monitored by means of X-ray diffraction.

The results revealed that barium hydroxide is capable to prevent the formation of thaumasite whilst the samples with chelating agent were significantly damaged. The discussion is based on previous work in this field.

1. INTRODUCTION

As early as the end of the nineties, and the beginning of the millennium, different mechanisms were reported for the thaumasite formation (1-9): The most important condition for its formation was reported to be the presence of lime (10). Pozzolanic admixtures were therefore used to reduce the concentration of lime and prevent the thaumasite form of sulfate attack (11-13). In order to understand the mechanism of the thaumasite formation more deeply, different routes were used to obtain this salt in pure systems and Portland limestone cement pastes and mortars (14-17). It was confirmed that the requirements for its existence are the availability of carbonate, reactive silica, sulfate and enough calcium.

In reference 14, studies were carried out on the addition of small concentrations of 0.3% from disodium hydrogen phosphate chelating agent as well as from barium hydroxide to prevent the thaumasite form of sulfate attack in Portland limestone cement pastes. With these additions, both reagents showed positive results. The present work is an extension of this work and deals with the effect of higher concentrations of 3 and 5%, from these reagents on the durability of Poland limestone cement mortars and its susceptibility to form the destructive thaumasite salt (17).

2. EXPERIMENTAL

Portland limestone cement was prepared by mixing 70% of CEM I 42.5 with 30% high purity commercial limestone. Commercial sand was used for mortars. Reagent grade sodium hydrogen phosphate (NaH_2PO_4) chelating agent and barium hydroxide ($\text{Ba}(\text{OH})_2$) were provided..

The effect of chelating agent and barium hydroxide on the pH-value of the cement was performed by measuring the pH-of a cement slurry made of 20 g cement in water (W/C ratio= 20) as well as in mixes of the cement with 3 and 5% from each reagent. The pH-values were recorded as soon as the water was added as well as after 30, 60, 90 and 120 minutes. The effects of the reagents on the water consistency and setting times of the cement was carried out according to EN196-3:2016(18).

The cement was mixed with sand at a ratio of 1:2, and water was added with a w/c ratio of 0.46. Mixing was performed in compliance to ASTM C 305-20(19). The mix was cast in 5x5x5 cm stainless steel molds, stored 24 h in humidity chamber, demolded then cured in 5% MgSO₄ at 7°C for 3 months .The effect of the reagents was performed by adding 3%, and 5% by weight chelating agent or barium hydroxide to Portland limestone cement then proceeding as described.

The appearance of the mortars cubes was examined after 3 months curing in sulfate solution and were recorded photographically. The compressive strength of the hardened mortar samples were measured during the 90 days curing according to B.S. EN 196-1:2016(21). The 90-day samples were analyzed by means of X-ray diffraction.

3. RESULTS

Table 1 (a, b) illustrates the oxide and phase composition of CEM I 42.5 N.

Table (1, a): Oxide composition of CEM I 42.5N (m. %)

	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	K ₂ O	Na ₂ O	SO ₃	Cl	LOI
%	18.98	4.81	3.72	62.49	1.75	0.27	0.50	3.13	0.081	3.2

Table (1, b): Phase composition of CEM I 42.5N (m. %)

	C ₃ S	C ₂ S	C ₃ A	C ₄ AF
%	59.5	16.48	6.47	11.31

The pH-values of the cement slurry was not affected by the addition of chelating agent and barium hydroxide and remained alkaline with a value of ~ 13.

Table 2 presents the effect of chelating agent and barium hydroxide on the water consistency and setting time of Portland limestone cement. The results indicate a clear increase in the water consistency and the retardation of the cement with the addition of the chelating agent, whilst the variation in the original values are changing only slightly in presence of barium hydroxide.

Table (2): Effect of chelating agent and barium hydroxide on the water consistency and setting time of Portland limestone cement paste

	Chelating agent			Barium hydroxide		
	Consistency	I.S.	F.S.	Consistency	I.S.	F.S.
0%	28	135	325	28	135	325
3%	29	188	510	28.5	155	324
5%	30	195	535	28.9	157	327

The effect of both reagents on the compressive strength of Portland limestone cement paste shown in Figure 1 (a, ab) indicate a clear drop of strength with the addition of 3 and 5% sodium hydrogen phosphate (NaH_2PO_4) cheating agent, the decrease in strength in presence of barium hydroxide is not significant.

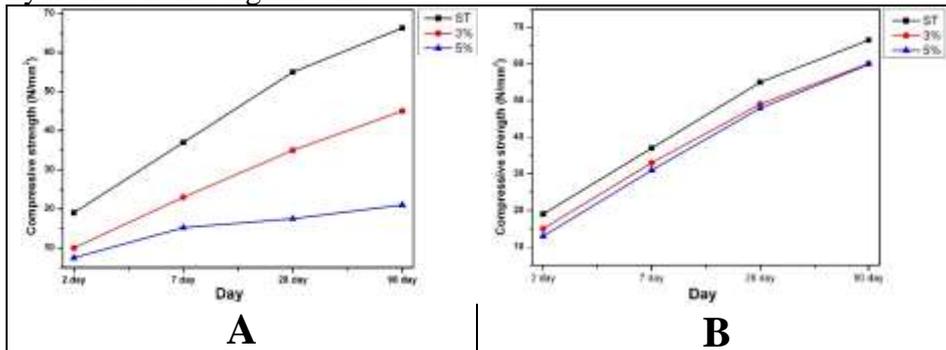
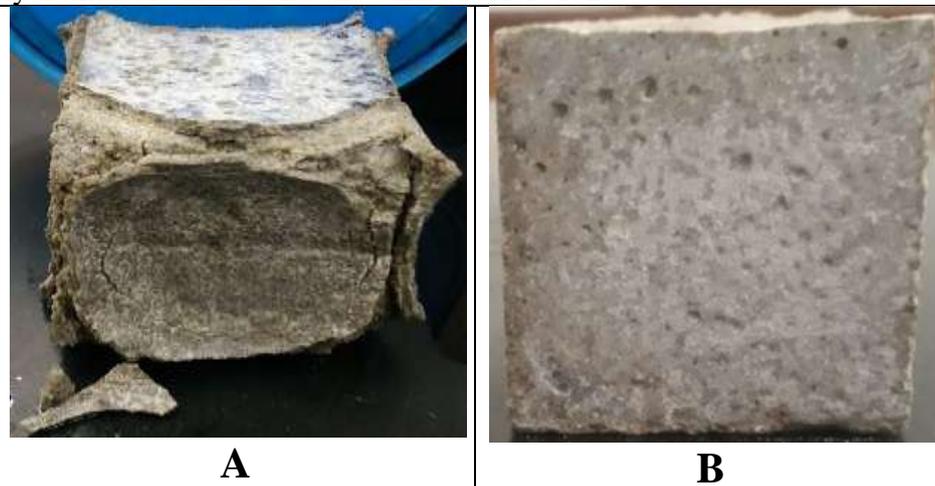


Figure 1: Effect of a) chelating agent, b) barium hydroxide on the compressive strength of Portland limestone cement mortar

Picture 1 (a, b) illustrates the visual appearance of Portland limestone cement mortar in presence of 3 and 5% disodium hydrogen phosphate chelating agent and barium hydroxide and cured 3 months in 5% MgSO_4 solution at 7°C . The appearance of the samples in the two concentrations was similar. The results show that, the cement cubes treated with disodium hydrogen phosphate are strongly deteriorated, that with barium hydroxide are sound and show no deterioration.



Picture 1: The visual appearance of Portland limestone cement mortar with a) 3 and 5% chelating agent b) 5% barium hydroxide cured in 5% magnesium sulfate solution for 3 months at 7°C

The X-ray diffraction patterns of Portland limestone mortars with a) 5% chelating agent b) 5% barium hydroxide cured in 5% magnesium sulfate solution for 3 months at 7°C are depicted in Figure 2 (a. b). The figures show the formation of thaumasite in the mortar sample with 5% chelating agent and that with barium hydroxide indicates the absence of thaumasite patterns, instead the gypsum phase forms.

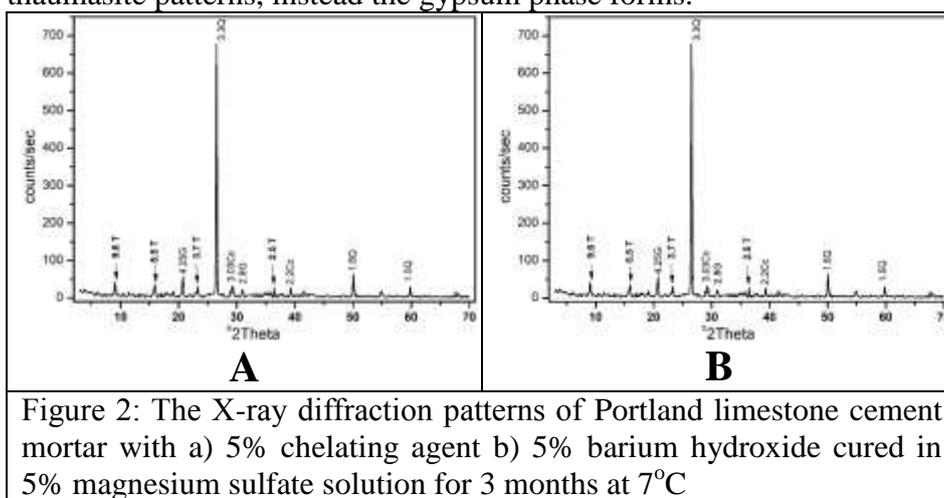


Figure 2: The X-ray diffraction patterns of Portland limestone cement mortar with a) 5% chelating agent b) 5% barium hydroxide cured in 5% magnesium sulfate solution for 3 months at 7°C

4. DISCUSSION

4.1 The thaumasite formation

The thaumasite form of sulfate attack known to damage the cement system, depends on the availability of carbonate, sulfate and calcium ions in presence of reactive silica. Recent work has shown that the mechanism of thaumasite formation follows a sequence expressed as stages which can be described as follows:

a. Stage 1: The carbonation process

In this stage the pH-value of the cement decreases and reduces its alkalinity from ~12-13 to ≤ 10 through carbonation. The carbonation process is initiated by intensive exposure of the cement system to atmospheric CO₂ and humidity, or by the presence of calcium carbonate as inorganic admixture. Under these conditions the calcium silicate hydrates decompose to calcium carbonate and silica gel, and the calcium sulfoaluminate and sulfoferrite to aluminum hydroxide, ferric hydroxide and gypsum. Calcium carbonate is a common decomposition product from portlandite as well as from the cement hydrates. Worth to note that the silica gel freshly precipitated exists in a reactive form.

b. Stage 2: The thaumasite formation

The carbonation process takes place at the surface of the cement system, the bulk of the cement remains unaffected because of the

thickness factor. The calcium hydroxide is a strong nucleophilic agent. It originates from the calcium silicate hydrate of the bulk or from newly hydrated residual calcium silicate. The splitted calcium hydroxide attacks the carbonated layer. The reactive silica precipitating from the carbonation of the CSH phase, dissolves as silicon hexa-coordinated with OH ions which then combines with the calcium ions to form a positively charged silicate column similar to the aluminate column of the ettringite. The column is neutralized by the negatively charged carbonate and sulfate of the surrounding or provided from the system internally. The next question is to determine the minimum concentration of sulfate needed to form the thaumasite.

4.2 Prevention of the thaumasite formation

To prevent the thaumasite formation the carbonation process of the must be avoided, and the calcium supply must be controlled.

The present work used a chelating agent to encapsulate the calcium ions and control its supply, and barium hydroxide to precipitate the carbonate and sulfate ions.

The use of 0.3% of disodium hydrogen phosphate chelating agent prevent the thaumasite formation successfully (14). But higher concentrations of 3 and 5% damage the cement system. This is due to the possible chelation of excess calcium ions beside the precipitation of calcium phosphate causing a lack of alkalinity upon long exposure.

On the other hand, the addition of 0.3 to 5% barium hydroxide to Portland limestone cement prevented the thaumasite formation. The insolubility of barium sulfate and barium carbonate has probably limited the supply of these ions and the respective concentrations needed for the thaumasite to be formed.

5. CONCLUSIONS

The prevention of thaumasite formation can be performed by using chemical reagents suitable for this process. 0.3% disodium hydrogen phosphate chelating agent can be safely added to Portland limestone cement but higher concentrations of 3 and 5% lead to the thaumasite damage of the cement system. On the other hand, a high concentration range of 0.3 to 5% can be used from barium hydroxide to prevent the thaumasite form of sulfate attack successfully.

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مواد كيميائية لمنع تكون ملح التومازيت الناتج من هجوم الكبريتات

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في هذه دراسة تم استخدام مادتين لمنع تكوين ملح التومازيت في اسمنت الحجر الجيري المادة الاولى ماده مخلبية (داي صوديوم هيدروجين فوسفات) والمادة الثانية باريوم هيدروكسيد، تم تحضير مونة من الاسمنت مكونة من ١ : ٢ اسمنت لرملة ونسبة ماء للاسمنت ٦ ، ٤ ، ٠ . تم حفظ العينات المحضرة في محلول كبريتات المغنسيوم تركيز ٥ % وتخزينها عند درجة حرارة ٧ لمدة ٩٠ يوم. اجريت اختبارات التكسير للعينات في ازمنا مختلفة ومعاينة العينات بالفحص البصري واجراء الاختبار عليها باستخدام الاشعة السينية.

اثبتت الدراسة نجاح الباريوم هيدروكسيد في منع تكوين ملح التومازيت بينما العينات

التي استخدم فيها المادة المخلبية تضررت تماما.