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The occurrence of thaumasite as a product of seawater attack

Ted Sibbick [a,*], Derek Fenn [b,1], Norah Crammond [a]

[a] *Centre for Concrete Construction, Building Research Establishment (BRE), Garston WD25 9XX, UK*

[b] *WS Atkins Consultants Limited, West Glamorgan House, 12 Orchard Street, Swansea SA1 5AD, UK*

Abstract

This paper describes the mechanism of the rapid deterioration caused by seawater attack on the bedding mortar of recently constructed harbour wall steps in South Wales. Within 2 years, the mortar had suffered severe cracking and spalling. The degraded mortars were examined under optical and electron microscopes and also using X-ray diffraction analysis. The reaction products formed included thaumasite, ettringite, brucite and hydrated magnesium silicate. A further end product of deterioration was the precipitation of large, non-interlocking crystals of calcite (termed popcorn calcite) in the areas of the mortar previously occupied by cement paste. Investigation of degradation of associated structural concrete from this site also showed the early stages of the thaumasite form of sulfate attack.

Keywords: Thaumasite form of sulfate attack (TSA); Popcorn calcite deposition (PCD); Seawater attack; Magnesium ions; Brucite

1. Introduction

Solva is a coastal village situated in Pembrokeshire, West Wales. The village huddles around a small tidal inlet where there has been a small harbour for hundreds of years. Solva has a 7 m tidal range and like so many South Wales harbours, the quay dries out completely at low water. In the summer of 1995, Queen Elizabeth II landed at Solva en route to make the cathedral town of St David's a City. There was no suitable landing point for the queen; so new access steps were quickly created for the occasion. The steps were designed by National Park officers and built by a local contractor. Unfortunately, the steps have been plagued with problems. The main worry has been the deterioration of a number of different cementitious mortars. The defects comprising typically: cracking of the mortar, expansion of mortar and complete loss of the cement binder from the mortar matrix. This paper describes the background to the construction of the steps, the various phases of remedial repairs and the laboratory investigation of the seawater attack by BRE.

2. Background history and structural design

The steps were constructed during the spring of 1995. The step construction consisted of a concrete foundation with a reinforced concrete rear wall. Local stonework was then used to face the structure. The stones were bedded and pointed using a 1:1:4, ordinary Portland cement (OPC):lime:sand mix. No records are available of the water/cement ratio. The Queen's visit went well and the steps have since proved to be a useful addition to the facilities of the local boat club. However, during April 1996 (only 1 year after the steps had been built), WS Atkins was contacted by the National Park to inspect some cracking in the masonry after concern had been expressed over the structural condition of the steps and the safety of the public.

Our initial observation was that the majority of the mortar within the inter-tidal zone had suffered from cracking. On closer inspection, the mortar was found to have a hard crust, which hid a sandy mortar without any cement binder remaining. Once dry, the mortar just crumbled into sand. Believing that the cement had been washed out by the tide, we recommended that the masonry was re-pointed using a pre-bagged cementitious mortar. These defective joints were repaired during May 1996.

By January 1997, we were called out to investigate new damage to the structure. The steps had suffered

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[*] Corresponding author. Tel.: +44-1923-664363; fax: +44-1923-664786.

E-mail addresses: sibbickt@bre.co.uk (T. Sibbick), dfenn@wsatkins.co.uk (D. Fenn).

[1] Tel.: +44-1792-641172; fax: +44-1792-472019.

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from differential movement and some of the repair mortar in the inter-tidal zone had cracked. Removal of a small inspection panel of masonry showed that facing stones had debonded from the structural wall. The decision was taken to remove all the facing stones and relay the masonry incorporating stainless steel wall ties at 450 mm centres and pointing using a 1:0.25:1, SRPC:lime:sand mix with an accelerator added on a rising tide. The cement lime sand mixes were used in preference to cement sand mixes to allow more movement potential during the early age. The cement sand mix would be hard and easily cracked by the movement, which was evident even at an early age. By April 1997, the works had been completed and the finished mortar appeared to be strong. In August 2000 we were once again called out to investigate further differential movement of the steps. There were continued signs of differential settlement and expansion of the mortar. Despite careful supervision of the works, the mortar had once again deteriorated rapidly into a soft sandy mortar with virtually no binder.

The BRE visited the site during June 2001 and took more samples from other areas of the harbour. Their inspection also identified attack of mass concrete foundations, which had been cast back in 1995. The analysis and findings of the laboratory investigation is discussed in detail in the following text.

3. Laboratory investigations

Following the identification of thaumasite in a sample of the soft crumbly degraded SRPC mortar from the harbour wall steps, the BRE visited the site during March 2001. During this visit the authors collected a series of material samples including those listed below in Table 1, as representative of the condition of the various types and ages of materials present.

The initial XRD findings showed that samples taken from the steps within the inter-tidal zone contained the presence of thaumasite, ettringite and brucite. Additional samples of the mortar taken from above the inter-tidal zone showed no evidence of degradation. Samples of the high tide seawater, low water channel water and water percolating through the structure were also collected. On return to BRE the samples shown in Table 1 were made up into petrographical polished and thin sections and were examined under the optical and scanning electron microscopes.

4. Results of petrographical examination

The petrographical examination of these cement based materials observed the thaumasite form of sulfate attack (TSA) in characteristics reminiscent of the four stage approach previously described in 'The Thaumasite Expert Group Report, 1999' [1]. This four-stage approach is summarised below in Table 2. The petrographical observations also refer to popcorn calcite deposition (PCD), previously termed cornflake calcite [2] which can simply be described as large (up to 60 μm) tightly packed rosette-like clusters of calcite crystals surrounded by calcium-depleted highly porous and an otherwise friable cement paste matrix (Fig. 1).

Sample 1: Degraded sulfate-resisting Portland cement (SRPC) mortar sample collected from the harbour steps in September 2000, reportedly 3 years old and composed of a standard mortar mix. This mortar contained an angular quartz sand fine aggregate with a small additional component of shell fragments, slate, limestone, chert, and other igneous lithologies. The surrounding cement paste was extremely porous and highly degraded. The little remaining sound matrix was completely devoid of portlandite and the remnant clinker grains were now only represented by colourless to orange well crystallised particles (50–100 μm), of very low birefringence (1st order grey). Some of the cement paste matrix had been completely replaced by thaumasite (Zone 4 TSA). In addition popcorn calcite deposition (PCD) was observed at various locations in this sample. Entrapped void and microcrack edges were also often

Table 1
Samples investigated by XRD, optical and electron microscopy

Sample no. Description and comments	Initial results from XRD analysis
1. Degraded sulfate resisting Portland cement (SRPC) mortar sample collected from the harbour steps in September 2000, reportedly 3 years old and composed of a standard mortar mix	Thin section produced T, Q, Cc, ISH
2. Reportedly degraded Portland cement (PC) mortar sample from the original historic harbour wall to the right of steps	Thin section produced T, E, Cc, Q, HC
3. Reportedly sound PC mortar sample from the original historic wall to the left of steps	Thin section produced Q, T, Cc, HC
10. Concrete sample from foundation to steps built in 1995 (degraded outer surface)	Thin section produced
11. Concrete material from the original historic harbour structure	Thin section produced
12. Render sample on original mass concrete harbour structure	Thin section produced
13. Degraded mortar sample from harbour steps. Unable to deduce whether original 1995 mortar or subsequent repairs	Thin section produced

Key to XRD results: Thaumasite = T, Ettringite = E, Brucite = B, Calcite = Cc, Quartz = Q, Hydrocalumite = HC, Iron sulfate hydroxide = ISH.

Table 2
The simple four-stage degradation sequence for TSA development

Zone 1: No visual evidence of attack; petrographic examination can reveal occasional voids and adhesion cracks around aggregate particles lined with thaumasite or ettringite
Zone 2: Thin cracks lined with white thaumasite begin to appear running sub-parallel to the concrete surface. Calcium carbonate is sometimes precipitated into these cracks. Little portlandite is observed within the cement paste matrix. There is no evidence of other sulfate-bearing minerals
Zone 3: An abundance of sub parallel cracks filled with thaumasite become wider and the amount of unattacked cement paste matrix is greatly reduced. Haloes of white thaumasite can be seen around coarse and fine aggregate particles. Calcium carbonate is sometimes precipitated into the cracks. Little portlandite is observed in the still unattacked cement paste. There is no evidence of other sulfate-bearing minerals
Zone 4: Complete transformation of the cement paste matrix to thaumasite. All that remains are occasional aggregate particles embedded in extremely soft white mush (thaumasite) and a few remnant 'islands' of heavily depleted cement paste

Fig. 1. General view of harbour wall steps. The SRPC bedding mortar is being severely eroded from the area under the limestone facing.

coated in secondary calcite some of it needle-like in nature, (possibly aragonite). The original outer surfaces were always heavily carbonated especially along the associated microcracks. The thaumasite form of sulfate attack (TSA) stages 2 and 3 and thaumasite formation (TF) were also apparent in many locations, but were not continuous throughout the sample. The development of TSA appears preferentially associated with carbonate fine aggregate particles, Fig. 2.

Sample 2: Reportedly degraded Portland cement (PC) mortar sample from the original historic harbour wall to the right of steps. This mortar was reportedly the older historic mortar from the original historic harbour wall. The aggregate was composed of more rounded sand with an abundance of carbonate shell fragments, quartz and other exotic lithologies. The aggregate size ranged between 2 mm and 50 μm, and the aggregate carbonate to silica ratio was around 80:20. The mortar contained a more typical PC-type matrix with more 'normal' looking remnant clinker grains occurring than observed in sample 1 within an apparently sound matrix. The material was however, still of modestly high capillary porosity and was also highly isotropic under crossed polarised light, containing no significant fine portlandite crystals. Abundant thaumasite and ettringite were found within voids as fill deposits, with no apparent associated cement matrix degradation. The inclusion of well formed fine calcite crystals (20–80 μm) was noted within the thaumasite fill material, (almost suggesting a conversion to calcite in a form similar to that observed within the popcorn calcite affected cement paste matrix). Heavy secondary precipitation of carbonate on void and microcrack edges was noted, the voids and cracks often also being partially filled with organic and clay–debris, presumably derived from the sea. Development of popcorn calcite deposition (PCD) within the matrix was also observed on the outer edges of the sample.

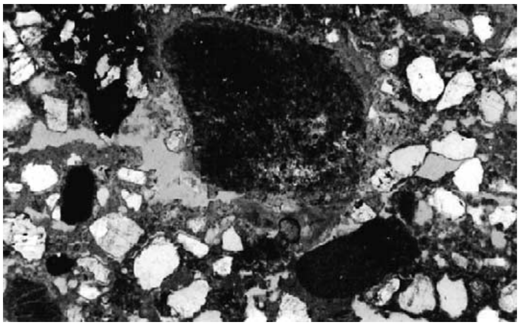

Fig. 2. Sample 1. Thaumasite halo developing around a carbonate fine aggregate particle as is often assigned to zone 3 TSA. Magnification ×60 taken in plane polarised light.

Sample 3: Reportedly 'sound' PC mortar sample from the original historic wall to the left of steps. The aggregate composition of this mortar was broadly similar to that of sample 2. The cement paste matrix was likewise highly porous and isotropic. However, the now 'depleted' clinker grains were more typical of the type observed in sample 1.

Thaumasite deposits were observed primarily as air void and microcrack fill deposits within the surrounding highly depleted cement paste matrix (TF). No halos or microcrack degradation were associated with its presence. However, some evidence of zone 4 TSA was apparent, especially within the centre of the sample Fig. 3. Locally there was slight evidence to suggest that TSA had occurred (zones 1 to 2) which was closely associated with the presence of 'Popcorn calcite deposition' within the nearby cement matrix. The cement paste matrix observed here was either highly depleted and porous, degraded showing popcorn calcite deposition, or fully carbonated into relatively coarse calcite crystal material.

Fig. 3. Sample 3 showing patchy complete degradation of cement paste matrix to thaumasite. Magnification ×32 taken in plane polarised light.

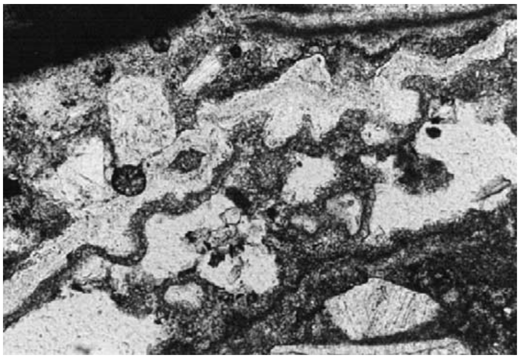

Fig. 4. Sample 10 showing calcite and brucite deposits within a microcrack. Magnification ×172 taken in plane polarised light.

There was little remnant unaffected cement paste matrix left. Occasional clay/debris deposits within the entrapped air voids suggested deposition by seawater as they also demonstrate 'way up' depositional features. Little ettringite was observed beyond the fine secondary gossamer-thin deposits within air voids.

Sample 10: Concrete sample from foundation to steps built in 1995 (degraded outer surface). The small sample of concrete taken from the foundation block below the steps was typical PC-based concrete. The coarse aggregate consisted of a 10 mm down, sub-rounded gravel comprising mainly chert and arkose sandstone with lesser amounts of metaquartzite and quartz arenite. The fine aggregate consisted of sub-angular quartz sand with lesser amounts of calcite metaquartzite, hornblende, acid igneous rock, sericitic siltstone and greywacke. The cement paste matrix was composed of a typical hydrated PC with a medium to high capillary porosity and medium to high remnant clinker content. This matrix also contained an even spread of small portlandite crystals. A few carbonate fines were also observed within the matrix. Finally a narrow depleted zone, 50 μm wide was observed below the carbonated outer surface, which was itself approximately 100–200 μm thick. The air voidage within the mix was high and often edged with ettringite deposits with no obvious associated deleterious cracking of the surrounding matrix.

This younger concrete had abundant outer surface carbonate deposits and a large amount of heavy internal microcracking was filled or edged with calcite. Modest deposits of brucite were also found on the outer surface and within these microcracks and voids associated with the carbonate deposits, Fig. 4. Popcorn calcite deposition within the cement paste matrix was usually found associated with the more microcracked areas. Thaumasite was found primarily as edge deposits to entrapped voids near the outer surfaces (TF) to a maximum depth of 5 mm. Additionally some air voids were observed to be edged with fine deposits of what were probably ettringite and carbonate, neither of which was considered deleterious. TSA zones 1 and 2 were developed in a patchy manner up to 3 mm from the outer surface. In this area underlying the carbonated zone, small deposits of brucite were again observed associated with the secondary calcite deposits.

Sample 11: Concrete material from the original historic harbour structure, Fig. 5. This older mass concrete making up the harbour structure consisted of a typical PC-based material, containing a sub-rounded to sub-angular gravel composed of limestone, siltstone, coarse crystalline acid igneous rocks, chert, quartz, metaquartzite, arkose sandstone, quartz arenite, fine grained basic igneous rocks, greywacke and schistose quartzite. The fine aggregate was composed primarily of quartz sand with shell fragments, metaquartzite, quartz arenite, limestone and calcite crystals. The cement paste matrix was highly depleted in portlandite as it was largely isotropic in many places. In other areas of the cement matrix clear evidence was found of the phenomenon described as Popcorn calcite deposition. The cement clinker grains had altered in a similar manner to the mortar samples 1 to 3 previously described. No deleterious TSA was observed within this sample. Thaumasite only occurred in the form of TF. Air voids were usually edged with non-deleterious ettringite and carbonate deposits. Modest microcracking was present especially close to the surface heavily filled with carbonate, and in

Fig. 5. Mass concrete from harbour structure from which sample 11 was collected within the inter-tidal zone.

parts brucite (colourless low relief mineral, low birefringence 1st order grey to white). Some of this microcracking passed through aggregate particles, apparently breaking them open.

Sample 12: Render sample on original mass concrete harbour structure (sample 11). This mortar-like material contained an angular to sub-angular crushed rock aggregate (5 mm down) consisting of carbonate sandstone, granitic material, arkose sandstone, rhyolite and andesite. The finer fraction consisted of angular quartz sand with small amounts of andesite, rhyolite and granite fragments. The cement paste was a modest dark PC-based material with abundant pseudomorph cement clinker grains now fully hydrated. Remnant clinker grains were relatively rare. There was a fine even spread of portlandite crystals throughout the modestly porous cement paste matrix, but, larger secondary portlandite crystals were rare.

Heavy carbonation was noted on the outer surface of the render. The mortar was heavily and randomly microcracked throughout with the microcracks being largely filled with calcite. A few air voids within the central part of the sample were filled with ettringite, which often appeared to be more like thaumasite. Below the outer carbonated area the mortar appeared to be relatively sound and typical of a 'normal mortar' with only a modest deposition of ettringite within voids. No evidence of TF or TSA was observed.

Sample 13: Degraded mortar sample from harbour steps. Unable to deduce whether original 1995 mortar or subsequent repairs, Fig. 6. This mortar consisted of quartz sand fine aggregate with larger (2.36–1 mm) particles of metaquartzite and siltstone particles also included. The bulk of the PC cement matrix was either largely depleted or converted to thaumasite. Outer surface carbonation was observed up to a depth of 1 mm with other forms of carbonation occurring in the region below this including needle-like carbonation within the entrapped voids and secondary calcite deposition within the surface parallel microcracks. Brucite was again found abundantly within the carbonate deposits within these cracks.

Fig. 6. Degraded friable mortar sample on site equivalent to sample 13 described here.

The fully degraded cement paste (Zone 4 TSA) was found in a patchy manner close to both these microcracks and the depleted areas of the cement paste matrix. Thaumasite deposits were also found within the microcracks associated with the carbonate deposits, and as halos around the fine aggregate particles, although not necessarily the carbonate particles.

5. Scanning electron microscopical examination

Following the petrographical examination a selection of samples were also examined under the SEM. A summary of these findings is described below.

Sample 1: The depleted cement paste areas within this sample were composed of primarily magnesium silicate hydrate. Semi-quantitative compositional ratios of $MgO:SiO_2$ were found to be in the ratio of 1:1 with additional amounts of aluminium, chlorine, and sodium. Calcium was just a trace and may represent the calcite fines element only. The secondary calcite filling the air voids also contained small traces of magnesium. The thaumasite deposits were compositionally more silica in composition, with some areas migrating towards more ettringite-like alumina-rich compositions. The thaumasite was similarly contaminated with small amounts of magnesium.

Sample 2: The unaffected (non-depleted) cement paste was compositionally more like normal OPC mixes being composed of calcium silicate hydrate. Semi-quantitative ratios of $CaO:SiO_2$ were found to be in the ratio of 1:1 with small amounts of sodium, and sulfur. Aluminium and chlorine were present at trace levels. The depleted cement paste areas were again primarily composed of magnesium silicate hydrate. Remnant cement clinker grains within these areas contained two phases:

(i) $CaO:Fe_2O_3:SiO_2 = 3:1.3:1.2$, plus trace amounts of magnesium, sulphur, chlorine and aluminium.
(ii) Complex combination and may represent a now partially decalcified calcium-silicate. $MgO:SiO_2:CaO = 3:1.3:1.25$, with trace amounts of aluminium, sulphur, chlorine and iron.

Ettringite was detected filling air voids and also as accumulations within the cement matrix. The compositions of some of these deposits were tending towards that of thaumasite. Analysis of the matrix indicated lower voidage than was detected in sample 1.

Sample 3: The depleted cement paste areas were composed of primarily magnesium silicate hydrate. Semi-quantitative ratios of $MgO:SiO_2$ were found in the ratio of 3:2 with small amounts of aluminium, sulfur, iron and sodium. Calcium was present in trace amounts and may represent the calcite fines component. The remnant clinkers also showed complex compositions.

(i) Fe_2O_3:SiO_2 = 3:1, plus trace calcium and small amounts of magnesium, sodium, and aluminium.
(ii) More complex combination and may represent a leached calcium alumino-silicate. MgO:SiO_2:Al_2O_3 found in the ratios 8:3:2, with trace amounts of sulfur, chlorine and iron. Entrapped air voids within the matrix frequently contained thaumasite or mixed crystals with compositions between thaumasite and ettringite.

6. Discussion

An overview of the various samples examined showed that the most degraded mortar samples were all located within the inter-tidal splash zone. This is well documented as the area where the affects of seawater attack are most severe [3–5]. This is normally considered to be due to the combined affects of wetting and drying and salt crystallisation within the material. It also appears that in structures like the seawall examined here, where more porous cementitious materials such as mortars and renders are situated in locations where the physical action of the sea can also work on them, can be particularly prone to seawater-induced degradation. The more porous the material the more severe the attack observed.

Revisions of the recommendations for new concrete mix designs for concrete structures placed in environments such as this are given in the recently published BRE Special Digest 1[6]. The seawater sample from this site, see Table 3, which contained high levels of sulfate and magnesium, corresponds to the new Design Sulfate Class DS-4, if the seawater is taken to represent very mobile ground water. This corresponds to a high level of sulfates. In this case the advice given states that new concrete placed within such an environment requires a number of design requirements in terms of aggregate type, cement content, water/cement ratio and additional protective measures to be undertaken in order to resist potential chemical attack in the future.

The complexities of seawater attack on cementitious material are well reported and even though the action of sulfate ions can lead to the formation of deterioration products like gypsum, thaumasite and ettringite, the principle component in seawater responsible for chemical deterioration is reportedly the magnesium ion [4,6]. In the first instance, the Mg^{2+} ion replaces calcium in $Ca(OH)_2$ to form $Mg(OH)_2$ (brucite). Brucite is very insoluble and its formation gradually removes the hydroxide ions present in the cement paste pore fluids. Eventually, as the pH drops from 13 towards neutral, all the Ca-bearing cement paste hydrates (can include any gypsum, thaumasite or ettringite formed as a result of sulfate attack) are at risk of Mg^{2+} ion attack. Decalcification of the calcium silicate hydrate binder (CSH) to form magnesium silicate hydrate (MSH) results in the complete breakdown of the cement paste matrix. In the literature, all the calcium, which is released during these reactions is reportedly removed in solution.

However, in the present study, at least some of the calcium appears to have precipitated in the form of large, non-interlocking calcite crystals, dispersed throughout areas of the degraded mortar previously occupied by cement paste. This type of calcite crystallisation under wet conditions has previously been termed 'cornflake calcite deposition' because of its granular appearance under the petrological microscope [2]. The term has since been changed to 'popcorn calcite' as suggested by Thaulow [7] as the habit of the secondary calcite crystals is more similar to irregular spheres than two-dimensional flakes. Further evidence of secondary calcite precipitation was found in the laboratory experiments of Gaze and Crammond [8]. They found that the action of an alkali sulfate solution on a crushed mortar exposed to the atmosphere reduced the pH of the solution to values of around 7. This process, which they termed 'alkali carbonation', resulted in the breakdown of calcium-bearing phases including thaumasite, ettringite and gypsum to produce $CaCO_3$ as the only remaining solid crystalline material. A simplified explanation of the mechanisms which are proceeding together and have been observed here are shown below in Table 4. A summary of the main observation made within the various samples is shown in Table 5.

Table 3
Chemical analysis of water samples

Sample number	SO_4^{2-}	NO_3^-	Cl^-	CO_3^{2+}	Na^+	K^+	Ca^{2+}	Mg^{2+}
	Mg/l							
Ground water seeping from wall	99	35	610	85	367	14	54	54
Low water channel water in harbour	117	24	316	79	170	10	37	28
Solva sea water sample taken at high tide	4008	7.4	13,496	N/D	4086	N/D	82	149
Standard sea water	2740	<0.7	19,700	152	1900	N/D	410	1310

Table 4
Combined seawater attack encountered within all these cement based materials

SO_4^{2-} from the seawater	Reacts with cement paste hydrates to form thaumasite, ettringite and gypsum, (T, E, G)
Mg^{2+} from the seawater	Ca in cement paste hydrates replaced by Mg PH gradually decreases from 13 towards 7 $Mg^{2+} + Ca(OH)_2$ [Portlandite] = $Mg(OH)_2$ [Brucite] + Ca^{2+} Mg^{2+} + CSH = MSH [Magnesium silica gel] + Ca^{2+} Mg^{2+} + T, E, G = Mg phase + Ca^{2+}

At lower pH, the Ca^{2+} was either washed away, deposited on crack and void walls as secondary calcite, or deposited within the body of the cement paste as popcorn calcite.

Table 5
Summary of observed degradation processes noted in each sample

Sample no.	Material type	Presence of TSA	Brucite	Depleted cement paste matrix	Popcorn calcite deposits (PCD)	Other secondary deposits
1	New SRPC mortar	TSA zones 1–4	No	Yes	Yes	Calcite (C) in cracks and voids
2	Older PC mortar	TSA zone 1 (TF)	No	Yes	Yes	Ettringite (E) + C cracks and voids
3	Historic mortar	TF + trace TSA zones 1,2 and 4	No	Yes	Yes	E + C deposits
10	New concrete	TSA zones 1–2	Yes	Yes close to carbonated zone	Yes	E + C deposits
11	Older concrete	TSA zone 1 (TF) only	Yes	Yes	Yes	+
12	Old cement render	None	No	No	No	E + C
13	Older mortar	TSA zones 1–4	No	Yes	No	E + C

7. Conclusions

1. Within the sea wall bedding mortar samples examined, extensive TSA and TF were observed to be associated with other deleterious processes relating to the 'normal' seawater attack of cementitious materials, which primarily involved the decalcification of the cement paste hydrates.
2. An additional interesting observation regarding this structure was the relative speed of attack. Some of the newly replaced bedding mortar was less than 2 years old when further evidence of severe degradation was observed. This could be the result of the relatively poor, very porous quality of the material, and the additional presence of magnesium ion attack associated with the seawater, which must be considered when assessing potential rates of TSA.
3. It was noted that the older concrete and new foundation concrete were also showing some evidence of at least modest development of TSA and decalcification. This would indicate that although these concretes are presently sound, largely as a result of their high quality, they may develop more serious TSA in the future. Heavy deposition of surface carbonates may prevent this development but it is debatable as to whether the heavy mechanical action of the seawater would allow this protective coating to build up.
4. The source of the sulfates clearly appeared to be the seawater, which was replenished by 'fresh' open seawater with each tide. There was no obvious potential method by which the sulfates could be concentrated within this location, but this does not, however, appear to be required. Bearing this in mind it has still to be fully established why this particular location or the materials used were so prone to TSA, Mg ion attack and popcorn calcite deposition.
5. As already discussed, popcorn calcite deposition was found in some of the degraded mortars examined. Popcorn calcite appears to be the last-stage reaction product formed as the pH of cement pore fluids drops, for whatever reason, from 13 towards neutral. The expelled calcium was either removed in solution or deposited within the degraded mortar as secondary crystals of 'popcorn' calcite. This distinctive form of calcite is therefore only the end product, forming after all the damage had been done, Sibbick and Crammond 2001[2].

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References

[1] Department of Environment, Transport and the Regions, The thaumasite form of sulfate attack: risks, diagnosis remedial works and guidance on new construction. Report of the Expert Group, DETR, 1999.

[2] Sibbick, Crammond. Microscopical investigations into recent field examples of the thaumasite form of sulfate attack (TSA). In: Proc. of the 8th Euroseminar on Microscopy Applied to Building Materials, Athens, Greece 2001. pp. 261–269.

[3] Lea FM. The chemistry of cement and concrete. 3rd ed. London: Edward Arnold Publishers Limited; 1988.

[4] St John DA, Poole AW, Sims I. Concrete petrography: a handbook of investigative techniques. London: Arnold; 1998.

[5] Mehta PK. In: Marchard J, Skalny JP, editors. Sulfate attack in a marine environment within materials science of concrete: sulfate attack mechanisms. 2000. p. 295–300.

[6] BRE Special Digest 1, Concrete in aggressive ground, Parts 1–4, Building Research Establishment Limited, 2001.

[7] Thaulow N, Lee RJ, Wagner K, Sahu S. The form, extent and significance of carbonation. In: Calcium hydroxide in concrete. The Materials Science of Concrete; 2000. p. 191–202.

[8] Gaze ME, Crammond NJ. The formation of thaumasite in a cement:lime:sand mortar exposed to cold magnesium and potassium sulfate solutions. Cement Concr Compos 2000;22:209–22.