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Thaumasite and secondary calcite in some Norwegian concretes

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Abstract

Thaumasite formation (TF) and limited thaumasite form of sulfate attack (TSA) has recently been detected in several Norwegian sprayed concretes. TF and TSA is frequently associated with contemporaneous and late stage internal calcite formation by: (a) decalcification of calcium silicate hydrate (CSH): (b) decomposition of thaumasite associated with secondary liberation of SO_4^{2-} and occasional formation of subordinate gypsum; (c) supersaturation of fluids in voids. Popcorn calcite and other textural forms were characteristic for these reactions. Also co-precipitation of popcorn calcite + thaumasite, as well as later stage dissolution of both minerals occurred. The entire process was represented by a drop in pore fluid pH from about 13 towards 5–7.

In this paper we study the *TF–TSA–carbonation* process in several environments: (1) three examples of 2–13 years old steel fibre reinforced sprayed concrete made with Sulfate Resisting Portland Cement (SRPC) and silica fume in contact with carbon-, calcite- and sulfide bearing Alum Shale: (2) two examples of ≈30 years old, and severely damaged, SRPC based sprayed concrete within the Alum Shale: (3) one 16 years old sprayed concrete made with Portland Cement (PC) and possibly fly ash in presence of sulfate bearing ground water and (4) one 10 years old steel fibre reinforced sprayed concrete in a sub-sea tunnel with inflow of somewhat modified seawater. This PC based concrete with silica fume had suffered localised crumbling and mush formation after less than 5 years. The critical factors for thaumasite formation are discussed together with consequences for further deterioration and timing of repair.

Keywords: Sprayed concrete; Thaumasite; Calcite; Durability; Norway

1. Introduction

During the last decade it has become increasingly apparent that formation of thaumasite represents an important degradation mechanism in concrete. The early non-deleterious stage called thaumasite formation (TF) is characterised by thaumasite growth restricted to pre-existing voids and microcracks. In deleterious thaumasite sulfate attack (TSA) thaumasite forms at the expense of calcium silicate hydrate (CSH), ultimately involving total disintegration of the cement paste matrix. Until very recently, neither TF nor TSA had been detected in Norway. Yet, during past decades a severe form of cement paste deterioration occurred in concretes associated with sulfide bearing Alum Shale in the Oslo region. This was previously attributed to ettringite and was compared to similar extensive forms of sulfate attack in the London district (cf. [1]). However, in 2000 the Geology and Tunnel Division at the Norwegian Public Roads Administration (NPRA) detected TF and local spalling caused by TSA mush formation in a deteriorated 13 years old steel fibre reinforced sprayed concrete in contact with Alum Shale [2]. This particular concrete was made with Sulfate Resisting Portland Cement (SRPC) and 5–10% silica fume, which is typical for mixes used in contact with the Alum Shale. We now believe that the old and more extensive sulfate attack observed within the Oslo area was in fact severe cases of TSA [3].

During the last 15 years the use of steel fibre reinforced sprayed concrete in Norway has increased dramatically. The largest volume is used as tunnel support in conjunction with rock bolts. In order to maintain stability of the rock mass around the tunnel space, it is important that the spray thickness (usually about 5–25 cm, depending on local conditions) does not become significantly reduced with time. Thus, extensive deterioration should certainly not be allowed to take place. Yet, sprayed concretes made with SRPC are employed in direct contact with the harmful Alum Shale, and Ordinary Portland Cement (OPC) may also be used in

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contact with other sulfide bearing rock types. TSA has now been encountered in a wide range of structures made with such cements around the world. The environmental loads, which favour TSA, are of various kinds, including structures affected by seawater. In most cases studied, TSA had occurred in a wet and cool environment [4,5]. It is therefore not unlikely that this form of sulfate attack may occur in sprayed concrete in sub-sea tunnels as well as in bridge pillars. Although TSA has not yet been detected in Norwegian bridges, this may well be due to current characterisation strategy, which seldom involves petrography, SEM and X-ray diffraction analysis.

2. Recent research in Norway and objectives of this work

A collaborative investigation programme was set up by the Building Research Establishment (BRE), UK and the Norwegian Public Roads Administration (NPRA), Norway in 2000. Our work involves field investigations, sampling, core extraction, petrography, X-ray diffraction, Scanning electron microscopy, electron microprobe analysis and water chemistry analysis by ion chromatography. We have found TF and TSA within high quality sprayed concretes in Oslo, even in concretes of less than 2 years age. TF and TSA were frequently associated with contemporaneous and late stage *decalcification* of both CSH and thaumasite, which in both cases leads to the formation of unusual forms of internal secondary calcite (e.g. popcorn calcite and several other textural forms). This suggests the existence of a *TF–TSA–carbonation process*. The thaumasite breakdown seldomly involved gypsum formation, leading to secondary liberation of sulfate ions with a potential for further attack. Secondary calcite deposits were also abundant in air- and entrapment voids and notably at the concrete–Alum Shale interface where initial permeability frequently was elevated (cf. [3]). The aim of the present contribution is to

(1) Summarise results from the BRE-NPRA collaboration, including structures subjected to a variety of environmental loads.
(2) Discuss the conditions which have led to the TF–TSA–internal carbonation process.
(3) Put constraints on the possibility for further reactions and durability.

3. Case studies

Table 1 gives a summary of the investigated concrete structures and their environment. All samples were collected in 2000. Sprayed concretes were made by the wet method unless otherwise stated. In general the concrete aggregates did not contain chemical components, which could have contributed significantly to TF and TSA. Hence the TF–TSA–carbonation process here seems to have been triggered mainly by the action of aggressive ground water. Although all four zones of TSA development (e.g. [4]) were encountered, it should be noted that the most advanced stage (i.e. “Zone 4”) in most cases was limited to a few rather small domains/zones less than 1–2 mm across. All samples have been carbonated by ordinary surface carbonation to normal depths of about 1–3 mm. The internal TSA-related carbonation was frequently much more extensively developed than surface carbonation, and resulted in a quite friable, permeable and brittle concrete. This internal carbonation was characterised by relatively coarse-grained largely non-interlocking calcite, comprising a great variety of textural forms. Popcorn calcite is preferred herein instead of “cornflake calcite”, previously used by some authors because the calcite crystals formed have three-dimensional shapes similar to popcorn.

3.1. Sprayed concrete on Alum Shale in Oslo

The Upper Cambrian–Lower Ordovician Alum Shale in Oslo is a black shale, which consists of nearly anthracitic carbon, quartz, feldspar, clay minerals and chlorite. Calcite as well as sulfides, e.g. pyrite and subordinate amounts of very reactive monoclinic pyrrhotite, occurs as abundant laminae and veins. Pyrrhotite is held responsible for the sulfate attack, since it oxidises very easily and causes catalytic oxidation of adjacent

Table 1
Summary of investigated sprayed concretes

Locality	Type of structure	Age of concrete	Ground conditions	TSA development (see Ref. [4])
Åkeberg, Oslo	Road cut	13 and 30 years	Alum Shale	Zones 1–4 mush
Ekeberg, Oslo	Highway tunnel	8 years	Alum Shale/clay stone	Zones 1–4
Svartdal, Oslo	Highway tunnel	2 years	Alum Shale	Zones 1–4
Oslo	Civil defence shelter	≈25–35 years	Alum Shale (swelling)	Zones 1–3
East Norway	Access tunnel to hydropower plant	16 years	Metasediments with black gneiss	Locally Zones 1–3
Freifjord	Sub-sea road tunnel	10 years	Modified sea water	Zones 3–4 mush

See text for further details.

pyrite with release of sulfate ions and associated production of sulfuric acid. Alum Shale is also known for its swelling properties in contact with air, and gypsum growth may be part of the swelling mechanism [1]. Natural weathering products involve significant jarosite and some gypsum, whereas other sulfates such as hexahydrite were probably subordinate (cf. [6]). The first three cases from Oslo have been reported in a previous paper [3], and a brief summary with additional comments is given herein.

Åkebergveien road cut. This first documented occurrence of thaumasite in Norwegian concrete [2] consists of 2–3 layers of steel fibre reinforced sprayed concrete made in 1987. The concrete was made with SRPC and 5–10% silica fume (not well dispersed with some lumps exceeding 100 μm in size), and water glass as setting accelerator. The *w*/*c*-ratio was about 0.45–0.5. TF and limited TSA occurs (a) quite near the open outer surface immediately beneath ordinary surface carbonation, (b) in vicinity of the concrete–Alum Shale interface, as well as (c) internally in entrapment voids between layers and in their surroundings. Thaumasite of Type 1 and 2 (as classified under the optical microscope in [4]) and all four stages of TSA development (i.e. Zones 1–4) were encountered [3]. At present this concrete has become deteriorated with extensive rusty surface deposits (from oxidation of sulfides) as well as calcite efflorescence being apparent. The aggregate did not contain any sulfate and carbonate source materials, except from minor amounts of calcite fines. The concrete was consistently moist with scattered tiny leakages throughout the spray. Spalling had started to develop in association with a 10–20 mm wide layer of *thaumasite* + *calcite* (*mush zone*). Other deformations in the sprayed concrete suggest that its initial shear strength had been significantly reduced since 1987. Destructive steel fibre corrosion was restricted to within the carbonated TSA mush zone, whilst fibres were intact or of limited degradation in the more sound, yet still friable zones with TF–TSA–carbonation.

Secondary internal calcite formation frequently involved the decalcification of CSH. This was closely associated with calcite ± subordinate gypsum formation at the expense of thaumasite. This breakdown reaction occurred both within the intact sprayed concrete as well as at an internal surface against the thaumasite + calcite mush zone, which was in contact with air. Presence of gypsum tends to be more common near the zone of ordinary surface carbonation. Calcite deposits with no obvious relationship to thaumasite or CSH were also frequently encountered in air- and entrapment voids. In general the calcite varied in form from blocky, branched/dendritic, popcorn- and cornflake like forms to acicular crystals.

One water sample taken as it leaked from a crack through the sprayed concrete had a pH of 7.6 (cf. Table 2 for water chemistry and Sulfate Class). This water composition is probably not very different from unaffected ground water behind. However non-oxidised ground waters in Alum Shale may be slightly acidic due to predomination of ferrous iron. As regards oxidised water in the vadose zone, pH may be 3–4 or slightly less, due to oxidation of ferrous iron and hydrolysis of ferric iron (cf. [1]).

TF–TSA and carbonation had also attacked remnants of a previous sprayed concrete layer from 1970. This concrete was made with SRPC but without silica fume. Further details from this severely degraded spray were reported in [3].

Ekeberg highway tunnel. The steel fibre reinforced sprayed concrete in this tunnel was placed in 1992, and the concrete mix was essentially the same as at Åkebergveien. *w*/*c*-ratio was about 0.45. Due to previous experience sprayed concrete was not applied on wet Alum Shale, but instead the rock surface was dried (as much as possible) using compressed air just before the spraying operation in order to achieve bonding [7]. Silica fume (≈8% by cement weight) was in this case well dispersed throughout the matrix. Yet TF, and limited

Table 2
Summary of water analyses

Locality	pH	Cl^-, mg/l	NO_3^-, mg/l	SO_4^{2-}, mg/l	CO_3^{2-}, mg/l	Na^+, mg/l	K^+, mg/l	Mg^{2+}, mg/l	Ca^{2+}, mg/l	Sulfate Class (Ref. [4])
Åkeberg 1	7.6	29	25	1841	274	26	22	110	615	3
Ekeberg 1	7.0	10	18	592	100	25	16	20	106	2
Ekeberg 2	7.0	10	14	2031	56	43	22	74	574	3
East-N 4	5.70	16.9	nd	111	na	3.2	7.8	2.3	59.9	1
East-N 5	5.67	13.2	nd	106	na	3.5	4.4	2.8	38.5	1
East-N 6-1	5.66	15.8	nd	102	na	11.0	5.0	1.5	58.5	1
East N 6-2	6.06	12.8	nd	105	na	3.4	nd	3.9	38.9	1
Freifjord 1	7.0	5600	na	460	na	na	na	158	1425	2
Freifjord 2	7.3	18,200	na	2400	na	na	na	1100	2200	3
Freifjord 3	7.3	17,400	na	2200	na	na	na	1095	2290	3
Sea water	7.8	18,980	0.7	2652	140	10,561	380	1272	400	3

Freifjord samples analysed by ICP, with all totals allocated to ionic species [8]. Otherwise by ion chromatography (na = not analysed: nd = below detection limit).

TSA were found. Calcite stalactites and rust deposits were commonly observed in presence of water leakages throughout the concrete. This was usually also associated with steel fibre corrosion in several places, although apparently not usually very severe. The overall TF–TSA internal carbonation process was somewhat less well developed than at Åkebergveien, but all features were broadly similar. Type 1–2 thaumasite and Zones 1–4 were all encountered. The pH range within the ground water was about 4–5 within this Alum Shale sequence just after blasting [7]. Water samples collected in 2000 from leaks associated with calcite stalactites as well as rusty brown deposits along a crack through the concrete had a pH of about 7. The water compositions may have been slightly modified by the concrete (cf. Table 2 for water chemistry and Sulfate Class).

Svartdal highway tunnel. The spraying method and concrete mix were essentially similar to the Ekeberg tunnel, although it also contains a small amount of limestone aggregate. The reported w/c ratio was slightly above 0.4 [7], and we have found that silica fume was very well dispersed. In fact all cores were extracted the day before the tunnel was officially opened for traffic in August 2000, when the sprayed concrete was already about 2 years old. Surprisingly the TF-limited TSA–carbonation process was also found in this younger concrete (Zones 1–4, predominated by thaumasite Type 1–2). The steel fibres were occasionally slightly corroded, when in contact with the secondary calcite. TSA within most samples was restricted to rather thin zones (<1.5 mm) in the vicinity of the concrete Alum Shale interface and elsewhere [3]. Although secondary calcite frequently had formed at the expense of CSH and thaumasite, additional euhedral calcite coexisted with thaumasite in some large entrapment voids. Some of them were multiple crystals resembling popcorn calcite (Fig. 1). This paragenesis represents simultaneous deposition of thaumasite and calcite, and not partial thaumasite decomposition. We have also found occasional evidence of a *later stage partial dissolution* of this assemblage (Fig. 3 in [3]), most likely due to the action of somewhat acidic water.

An Al-sulfate suspension (5–8% by cement weight [7]) was used as a rapid setting accelerator where the tunnel cuts through Alum Shale, but locally water glass also had been used. Comparison of samples of both types indicated a quite similar development of the TF–TSA–carbonation process. However, the long term effect of the Al-sulfate accelerator, as a contributor to TSA is as yet not clear: (1) in contrast to water glass, this accelerator allows for a rapid build-up of a much thicker spray in a single spraying round. Hence, the amount of entrapment voids and other discontinuities may be rather small, thereby reducing the number of nucleation sites for TF and TSA (cf. [4]). (2) The chemical stability of this added sulfate is to our knowledge not documented for the ambient environmental loads, thus representing a potential internal sulfate- and aluminium source.

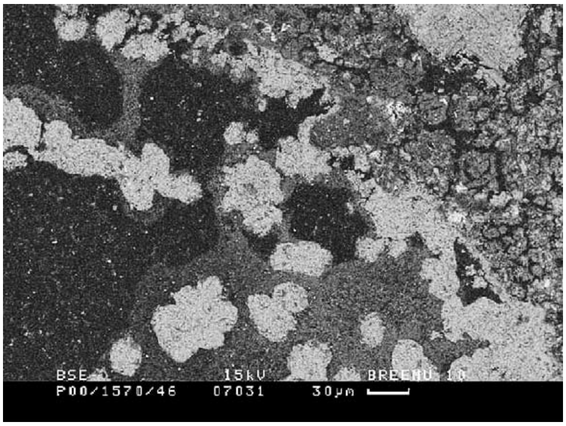

Fig. 1. Co-precipitation of popcorn calcite (bright) and surrounding Type 1–2 thaumasite (grey) in a partly filled entrapment void within 2 years old sprayed concrete in the Svartdal tunnel (BS-image). This TF–PCD process requires elevated concentrations of calcium and carbonate ions relative to sulfate ions. Notice the presence of very porous cement hydrates (granular/grey) next to aggregate (upper right), which may represent loss of calcium and silicon. See text for details. Scale bar = 30 μm.

Water samples were not analysed chemically during construction. The investigated concrete was locally moist or wet in 2000; however, no uncontaminated water sample could be collected. During construction the reactivity of Alum Shale was, however, determined by chemical analysis of milled samples according to a standard method [7]. The Alum Shale immediately behind one of our samples suggested virtual absence of reactive sulfur (= 0.00%). Total- and soluble sulfur were estimated to 7.87% and 0.03%, respectively. However, in view of the high reactivity of the Alum Shale sulfides this was of no surprise. The reactive component was very probably oxidised and lost before analysis. The ground water here most likely belongs to Sulfate Classes 2–3 and pH $\leqslant$ 7 similar to the Ekeberg Alum Shale (Table 2). In fact the Svartdal- and Ekeberg tunnels have been excavated in exactly the same Alum Shale sequence in close vicinity of each other.

Abandoned civil defence shelter in Oslo. Sprayed concrete (dry method, fibre free) was applied directly on Alum Shale in the late sixties or early seventies. Due to the earlier focus on sulfate attack in the Oslo region it was expected that all concrete constructions here were made with SRPC. This was however not easy to confirm due to severe deterioration. In 2000 about 1–5 m^2 areas of very friable sprayed concrete had spalled and fallen down in several places. Jarosite and gypsum were frequently observed at the now exposed Alum Shale, and internal swelling within the outer surface of the shale had obviously contributed a lot to this extreme spalling. Rust deposits occurred on the surface. In the sprayed concrete TF and TSA (Zones 1–3, thaumasite Type 1–2) were clearly present as a major cause of the observed degradation, at least within a 5 mm thick layer in contact with the Alum Shale.

The concrete adjacent to the shale was usually represented by microcracks now heavily filled with secondary carbonate, some of which had apparently been derived from thaumasite. Also abundant gypsum crystals as void filling, plus ettringite were observed to be contributing to degradation. The main degradation was still in the form of abundant surface parallel microcracks variously filled with thaumasite, gypsum, ettringite and calcite, which were co-habiting within relatively small domains. These sulfate deposits were often closely associated with abundant calcite deposits probably secondary, which were filling pre-existing surface parallel microcracks within the cement paste and aggregates particles. These aggregate particles and the surrounding cement paste matrix have clearly been degraded by a 'sulfate type' degradation at an earlier time. The sulfate minerals causing this degradation have since been either washed out and the microcrack subsequently filled with secondary calcite precipitate, or the thaumasite/gypsum and ettringite have become unstable and converted to calcite. Mottled and popcorn-like carbonation was also observed within the cement paste in several places, and must have contributed to the overall loss of strength.

3.2. Sprayed concrete in sulfate bearing ground in East Central Southern Norway

An access tunnel leading down to an underground hydro power station was also investigated. The ground conditions here were characterised by somewhat elevated sulfate and calcium contents in ground water, as evidenced with historically known surface precipitation of bitter salt (gypsum with some epsomite), due to the rather dry climate in this part of Norway [6]. The bedrock was characterised by various quartz–feldspar–mica gneisses and black gneiss ("shale"), which is equivalent to Alum Shale having additionally suffered higher temperature deformation during the Caledonian Orogeny. Locally within the tunnel jarosite and some gypsum had formed by weathering of the black gneiss. The present 1984 fibre free sprayed concrete was made with Portland Cement with about 8% C^3A and most likely with Fly ash (i.e. Norcem MP30 with 20%, Class F). Water glass was used as setting accelerator [7].

Locals tell that the tunnel was initially characterised by abundant water leakages, this being the main motivation for a sprayed concrete lining. In fact extensive white surface efflorescence was present, thus confirming the presence of significant water action at an earlier time. Several rusty brown deposits also occur, both on the concrete surface and as heavy rust-coloured sludge at the base. Sampling and petrography by the NPRA in 1997 indicated presence of a few Fly ash like fragments. White efflorescence consisted of abundant calcite (including stalactites) as well as "powder" and "cotton wool" deposits of thenardite. Thenardite might have formed from sulfate ions present in the ground water and sodium from water glass. It was not obvious that this sodium sulfate had caused any significant degradation of the concrete. Non-deleterious secondary ettringite and occasional minor non-deleterious ASR-gel was identified in air voids in the thin sections, but no thaumasite was found in the 1997 material. This may not necessarily imply absence of TF or TSA at that time, since sampling was restricted to a rather small section of the tunnel.

In 2000 BRE and NPRA extracted more cores as well as water samples. One core contained a 5–10 mm friable TSA + calcite layer (Zones 1–3, thaumasite Type 1–2) at the concrete black gneiss interface. Some thaumasite was locally observed in association with deleterious ettringite deposits within surface parallel microcracks. Popcorn calcite deposition (PCD) within thaumasite deposits was also noted. Apparently the formation of thaumasite and thenardite was associated with black gneiss. The patterns of surface efflorescence with calcite and thenardite had not changed since 1997 and the sprayed concrete tunnel lining presently appeared to be quite dry and sound. Thin sections generally indicated an overall quite dense and sound cement paste matrix. It seems possible at the present time that the secondary reactions have reached a stage where sprayed concrete permeability is at a minimum, or perhaps more likely the ground water level has been significantly lowered. The water samples from cracks through concrete have different composition than the ones in Oslo Alum Shale; pH ranges from about 5.7 to 6.1. Calcium and sulfate contents were low (e.g. Sulfate Class 1 see Table 2), which probably explains the limited development of the TF–TSA–carbonation process here.

3.3. Sprayed concrete in contact with seawater

The 5000 m long *Freifjord sub-sea tunnel*, located near Kristiansund, was opened for traffic in 1992, and steel fibre reinforced sprayed concrete was made with about 6–8% silica fume and Norcem RP 38: a rapidly setting Portland Cement that contains about 8% C_3A. Water glass was used as a setting accelerator and the reported w/c ratio was in the order of 0.37–0.47 [7,8]. Systematic investigations including tunnel mapping and laboratory analysis were undertaken in 1996 as part of a major project on durability of sprayed concrete. It was concluded [8] that there was no evidence of "chemical attack" on the local concrete lining. However, by 1996 calcite stalactites were abundant and in several restricted areas the concrete had been partially to completely transformed into a mush. These deteriorated concretes were located within a sequence of banded gneiss with layers of marble, and were typically associated with water leakages. The mush occurred as loose layers on the surface of more sound sprayed concrete and had usually also been accumulated as a sludge at the base. This phenomenon was thought by some authorities to have been caused by rebound during the spraying operation, while others claim this was not so.

Investigations based on about 20–100 mm size samples of less deteriorated white and friable remnants of sprayed concrete, within the now washed away mush, clearly shows that deterioration was caused by TSA and magnesium attack. Both thaumasite and brucite had partly replaced CSH. Even in fairly solid remnants of an initially 50–100 mm thick spray [8], full scale TSA (Zones 3–4) was observed (Fig. 2). TF had occasionally formed along microcracks that post dated the paste matrix, which had already been transformed into a friable TSA—depleted CSH assemblage (i.e. some TF was locally secondary to TSA). Thaumasites of Types 1–2 were found. Secondary carbonation was very extensive in all forms described above, and some gypsum and ettringite were also detected. The steel fibre reinforcement was frequently completely transformed into a rusty Fe-hydroxide most notably in presence of abundant popcorn calcite and other forms of calcite. From sound concrete samples elsewhere in the Freifjord sub-sea tunnel it was apparent that the silica fume was not well dispersed (i.e. globules <50–100 μm). However, there was no sign of silica fume globules within the TF–TSA affected areas, suggesting that this amorphous phase might have been incorporated into the thaumasite by chemical reaction.

Published water analyses [8] from the TSA affected tunnel sections, probably collected from cracks in vicinity of degraded concrete, had pH from 7.0 to 7.3, high contents of SO_4^{2-}, Mg^{2+}, Cl^- and very high Ca^{2+}, suggesting modified seawater (Table 2). Carbonate ion concentrations are as yet not available. Calcite in the marble layers may represent a potential carbonate source for thaumasite and secondary internal calcite. However, calcite is very slightly soluble at pH about 7 and calls upon another carbonate source. Hence a contribution from atmospheric CO_2 should not be excluded.

3.4. Steel fibre corrosion and role of silica fume in the TF–TSA–carbonation process

All observations indicate that it was the presence of internal carbonation that was most crucial to fibre corrosion. Steel fibres in presence of single thaumasite deposits in air voids were occasionally marginally corroded [3]. In contrast, corrosion was completely destructive in thaumasite–calcite mush. Within domains of well-developed Zones 3–4 with extensive carbonation, marginal steel fibre corrosion was usually observed. It is significant that the most severely corroded fibres were always in direct contact with calcite, and frequently in the form of popcorn calcite deposition (PCD). It should be noted that this form of internal carbonation invariably results in a quite porous, permeable and more or less friable cement paste matrix, which hence stands in marked contrast to the effects caused by ordinary surface carbonation. Silica fume appears to delay the development of TSA in concretes on Oslo Alum Shale (cf. [3]), but yet this does not appear to inhibit deleterious reactions, even when well dispersed.

4. Discussion

4.1. TF–TSA–carbonation and formation conditions

The TF–TSA–carbonation process requires a steady drop in pore fluid pH from about 13 towards neutral, and which takes place in presence of sulfate- and carbonate sources in a wet and cool environment (cf. [3]). These conditions were prevailing in all cases studied herein. The sprayed concrete layers sitting on rock sur-

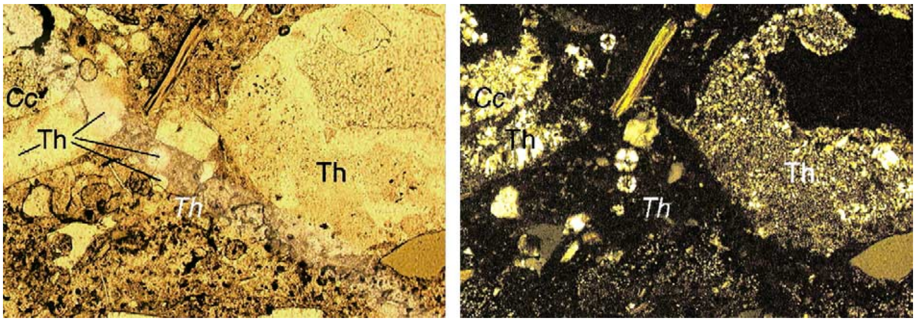

Fig. 2. TF and TSA (Zone 3) in a small remnant of sprayed concrete from within a TSA-mush in the Freifjord sub-sea tunnel. Thaumasite of Type 2 (Th) occurs: (a) in two large entrapment voids with subsequent calcite deposition (Cc in left void); (b) in smaller air voids and (c) as thaumasite of Type 1 and 2 scattered about in depleted cement paste (area around and below *Th*). Plane polarised light and crossed polars, respectively. Horizontal fields of view 1 mm.

faces were subjected to *hydraulic gradients*, and the TF–TSA–carbonation process was typically more advanced in presence of water leakages. There was substantial evidence to suggest that ground water seepage through concrete was not only restricted to minor cracks, but in fact frequently affected the bulk cement paste matrix. Our data show that ground waters with neutral to somewhat acidic pH have mixed with pristine alkaline pore fluids in these concretes. The petrographic observations suggest the following schematic chemical reactions:

$$\mathrm{CSH} + \mathrm{H_2O} \pm \mathrm{CO_3^{2-}} \rightarrow \text{Ca-depleted CSH (or silica gel)} \pm \text{calcite (PCD)} \qquad (1)$$

$$\mathrm{CSH} + \mathrm{H_2O} + \mathrm{CO_3^{2-}} + \mathrm{SO_4^{2-}} \pm \mathrm{Ca^{2+}} \rightarrow \text{thaumasite} \pm \text{calcite (PCD)} \qquad (2)$$

$$\text{Ca-depleted CSH} + \mathrm{H_2O} + \mathrm{Ca^{2+}} + \mathrm{CO_3^{2-}} + \mathrm{SO_4^{2-}} \rightarrow \text{thaumasite} \pm \text{calcite (PCD)} \qquad (3)$$

$$\text{Thaumasite} + \mathrm{H_2O} \rightarrow \text{calcite} \pm \text{gypsum (free } \mathrm{SO_4^{2-}}) + \mathrm{Ca^{2+}} + \text{Si-water complex (or Ca-silicate)} \qquad (4)$$

$$\mathrm{CO_3^{2-}} + \mathrm{H_2O} + \mathrm{Ca^{2+}} \rightarrow \text{Calcite deposits} \qquad (5)$$

$$\text{Thaumasite} + \text{calcite} + \text{acidic water} \rightarrow \text{dissolution (free } \mathrm{SO_4^{2-}}) \qquad (6)$$

The breakdown of CSH according to reaction (1) takes place when pore fluid pH drops below about 12.5. Carbonation in the form of PCD involved breakdown of portlandite as well as CSH [3]. Recent work by Sahu et al. [10] (and references therein) suggests that carbonation of CSH is governed by bi-carbonation, a process which takes place below $\mathrm{pH} = 11$. Thaumasite appears to be stable at pH ranging from about 11 to 6 [9]. The various calcite assemblages are probably stable within the pH interval 10–7. Ground water in contact with sulfide oxidation processes should in general have pH less than 7. Yet, calcite veins in Alum Shale most likely acted as a buffer, and probably sustained a pH near 7. Reaction (6) involving acidic water appeared to be uncommon.

Calcium carbonate efflorescence and stalactites were surface expressions of the decalcification of CSH-gel (e.g. Ca depletion of CSH). The internal calcite deposits associated with depleted cement paste represent the "root zone" of this process. If sulfate and carbonate ions are present, thaumasite forms by replacement (e.g. TSA) after some degree of cement paste decalcification (reaction (3)), rather than by direct decomposition of un-depleted CSH (reaction (2)). Early stage TF, with or without PCD (Fig. 1) in voids and cracks, seemingly precipitated from a fluid (similar to reaction (3), except silicon from Si-water complexes instead of depleted solid state CSH). Thaumasite later breaks down to form calcite and minor gypsum as pH drops further towards neutral. The essential scarcity of gypsum and thus apparent liberation of $\mathrm{SO_4^{2-}}$ (reaction (4)) needs to be explained, since the stoichiometric proportions of the components $\mathrm{CaCO_3}$ and $\mathrm{CaSO_4}$ in thaumasite are 1:1. This most likely reflects the solubility product of gypsum, which is two orders of magnitude higher than calcite. It seems significant that the assemblage gypsum + calcite usually occurred near the surface in contact with ordinary carbonation. Gypsum most probably precipitated here due to surface drying of the concrete. Thus, internally in a concrete where thaumasite breaks down to calcite, *sulfate ions are available for further attack*. The secondary availability of this aggressive anion is a function of the TF–TSA–Cc reaction progress. Gaze and Crammond [9] have demonstrated experimentally that "carbonation of thaumasite" is very efficient at 5 °C in specimens in contact with atmospheric $\mathrm{CO_2}$. Stable isotopic signatures (C and O) in Oslo sprayed concretes indeed suggest partial influence from atmospheric $\mathrm{CO_2}$ in the overall TF–TSA–carbonation process [11].

A significant result [3] was that secondary ettringite was not very common in the Oslo sprayed concretes and did not appear to have predated formation of thaumasite. Preliminary analysis suggests that the compositions of Oslo thaumasite vary from almost pure end-member to 1–2 wt.% $\mathrm{Al_2O_3}$ [3,7]. As a system component Al was apparently not important here; (1) Norwegian SRPC's have had quite uniform and low $\mathrm{C_3A}$ contents around 1% for perhaps three decades (cf. [3]); (2) The ground water associated with Alum Shale in Oslo typically contains trace amounts of Al when pH is 5–7 [1]. This offers a plausible explanation to the apparent scarcity of ettringite. But further analysis and more detailed SEM work is required to elucidate the ettringite problem in the TF–TSA–carbonation process, notably in view of associated pore fluid pH, which when dropping below 10.7 does not sustain ettringite stability.

Recent experimental synthesis of very Al-poor thaumasite made from an CaO–sucrose slurry mixed with sodium silicate, sodium sulfate, sodium carbonate, and with little or no sodium aluminate, show very interesting results [12]. Precipitation of end-member- and Al-poor thaumasite under a nitrogen blanket was accompanied with significant amounts of calcite and an as yet unidentified amorphous phase ($\mathrm{Th} < \mathrm{Cc} < \text{amorphous}$). The co-precipitation of quite poorly formed thaumasite and popcorn calcite depicted in Fig. 1 may therefore well represent a similar process. The possibility that an amorphous phase is present interstitially between thaumasite needles cannot be excluded, and the identification and quantification of this may in case have a direct bearing on the TF–TSA–carbonation reaction progress. One might speculate that the unidentified amorphous phase has a composition similar to thaumasite, and that this may be part of the explanation for the nearly isotropic Type 1 thaumasite. These experimental results also highlight a warning, in that the petrographer should take great care when attempting to discriminate between thaumasite–calcite deposits and calcite formed from thaumasite decomposition.

Comparison of Tables 1 and 2 suggests a good agreement between degree of TSA development and established Sulfate Classes as defined in [4]. It is noteworthy that the TF–TSA–carbonation reaction mechanism does not seem to be very sensitive to the C_3A contents in the cements, since the investigated cases represent a variation from ≈1% to 8% of this clinker phase. The role of Ca^{2+}, CO_3^{2-} and other ionic species should be investigated further, together with the influence from atmospheric carbon dioxide. These important constituents in thaumasite were not investigated to any great extent within the present study.

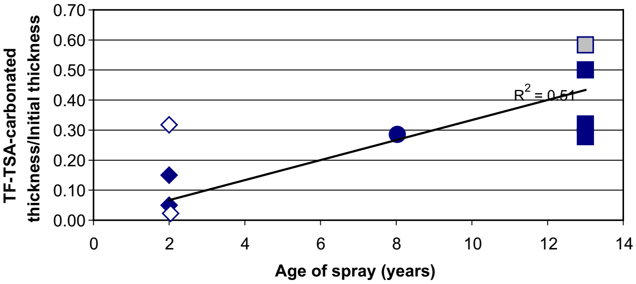

Fig. 3. Development of the TF–TSA–carbonation with time in modern steel fibre reinforced sprayed concretes made with SRPC and silica fume in contact with Oslo Alum Shale. w/c about 0.4–0.5. Squares = Åkebergveien cut (grey filled symbol contains some 1970 spray); Filled circle = Ekeberg tunnel; Diamonds = Svartdal tunnel: Open diamonds made with Al-sulfate accelerator: Filled symbols, with water glass accelerator. The TF–TSA–carbonated thickness in each core represents the sum of bleached-surface parallel zones within which this reaction was developed.

4.2. Deterioration and service life of sprayed concrete

Although the present day SRPC based mixes with silica fume appear to have eliminated the most severe forms of TSA in the Oslo region [1], a systematic durability study is still required. Based on preliminary data, Hagelia et al. [3] suggested that the “lifetime” of such sprayed concrete on Alum Shale probably is 15–20 years. Service life is a matter of definition that varies from one site to the next. In our context service life of sprayed concrete is a function of

(1) The chemical reaction rates involved in deterioration (depending on material properties and environmental loads).
(2) The relationship between chemical reaction stages and bearing capacity of sprayed concrete (i.e. when it becomes weaker and thinner than specifications for the local rock mass conditions).
(3) The local traffic and safety conditions (traffic prognosis, alternative routes when a tunnel tube must be closed, public safety, etc.).

Thus, a more precise and site-specific knowledge of these relations should provide a good basis for forecasting the optimal (i.e. most cost-effective) timing of repair.

We have investigated the available cores from modern sprayed concrete in Oslo and estimated the fraction of the initial sprayed thickness (assuming no loss of material), which was influenced by the TF–TSA–carbonation process. These sprayed concretes were typically attacked from both sides of the sprayed slab, yet with variably developed internal degradation [3]. The TF–TSA–carbonated thickness/initial thickness-ratio has increased roughly, from 0 to 13 years (Fig. 3). The most reacted concrete in the Åkebergveien road cut had started to develop localised TSA–calcite mush with associated extensive steel fibre corrosion, spalling and other evidence of strength loss. This suggests that, for these SRPC based mixes sitting on Alum Shale; the *initiation time* is somewhat less than 13 years. In fact structural deterioration by TF–TSA–carbonation had already started to propagate. It is expected that the trend hereafter will establish TSA at an even faster rate. A quite “critical stage” has been reached, and timing of repair depends mostly on traffic- and safety considerations.

The sprayed concretes in tunnel linings (i.e. Svartdal and Ekeberg) should perhaps have a shorter initiation time than sprayed concrete in the Åkebergveien road cut, due to the higher hydraulic gradients involved in tunnels. Indeed, the flow rate of aggressive waters through concrete should have a bearing on the TF–TSA–Cc reaction progress. This should be investigated further.

In the Freifjord sub-sea tunnel Portland Cement based sprayed concrete with silica fume was attacked by modified seawater. Evidently the initiation time for this brucite assisted TF–TSA–carbonation process was in this case <5 years in presence of several focused water leakages. Elsewhere in this tunnel, where influence from seawater is smaller, the sprayed concrete was a lot more durable [7,8].

There was also a significant influence on deterioration rate from the initial thickness of the spray, as well as presence- or absence of water: Fig. 4 shows the development of the TF–TSA–carbonation process as a function of initial spray thickness at Åkebergveien. All cores here were extracted from consistently moist concrete and there is a good negative correlation between initial thickness and state of reaction. An equivalent diagram for the Svartdal cores is shown in Fig. 5, representing concrete with more variable initial character-

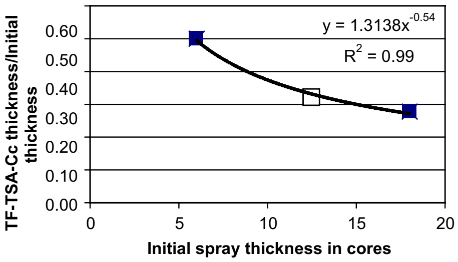

Fig. 4. TF–TSA–carbonation development in 13 years old sprayed concrete cores at Åkebergveien as function of initial spray thickness. The open square symbol represents a core with some internal reaction plus a soft TSA–calcite mush layer (2 cm) and a reaction zone (1 cm) within a spall just outside the mush. The remaining cores (filled squares) contained TSA mostly at microscale. The equation is empirical. A core with a remnant of 30 years old spray was excluded. All cores were extracted from consistently moist concrete.

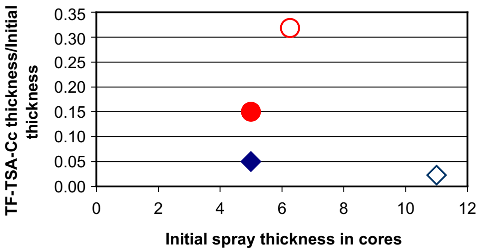

Fig. 5. TF–TSA–carbonation development in 2 years old sprayed concrete in the Svartdal highway tunnel as function of initial spray thickness. Open symbols = with Al-sulfate; Filled symbols = with water glass. Notice that the most reacted cores were extracted from surface wet concrete (circular symbols), whilst the least reacted were from surface dry concrete (diamonds).

istics. Also in this younger sprayed concrete the degree of reaction was perhaps essentially influenced by water. The most reacted cores were extracted from moist concrete, in contrast to the least reacted cores being surface dry. Yet, different influences from the two different setting accelerators here cannot be excluded; an Al-sulfate admixture bearing surface wet core was much more influenced by the TF–TSA–carbonation process than an approximately equivalent surface wet core made with water glass. A comparison of the pore structure and microchemistry in these cores is required in order to test this hypothesis.

5. Conclusions

(1) The TF–TSA–carbonation process in sprayed concrete was triggered by admixture of sulfate- and carbonate-bearing ground waters with mildly acidic to neutral pH.
(2) The process requires fluid flow trough the bulk cement paste matrix, and was found in concretes associated with sulfide oxidation as well as in seawater environment.
(3) The reaction progress is sensitive to spray thickness.
(4) TF–TSA–carbonation does not seem to be very sensitive *either* to the C3A contents within the 1–8% interval, *or* to the degree of dispersion of silica fume.
(5) Steel fibre corrosion begins in presence of popcorn calcite depositions (PCD) and other relative coarse and porous calcites. Destructive fibre corrosion was commonly associated with soft thaumasite + calcite mush formation.
(6) The lifetime of TSA affected SRPC- and PC based steel fibre reinforced sprayed concretes, made with 5–10% silica fume, is much shorter than the designed lifetime (= 50 years) for Norwegian tunnel concrete.

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References

[1] Moum J, Rosenqvist IT. Sulphate attack on concrete in the Oslo region. J. Am. Concrete Inst. 1959, Proceedings, Paper 56–18, 8 pp.
[2] Hagelia P, Grønhaug A. Thaumasite—infection causing concrete deterioration. Våre Veger 2000;(9):54–5 [in Norwegian].
[3] Hagelia P, Sibbick RG, Crammond NJ, Grønhaug A, Larsen CK. Thaumasite and subsequent secondary calcite deposition in sprayed concretes in contact with sulfide bearing Alum Shale, Oslo, Norway. In: 8th Euroseminar on Microscopy Applied to Building Materials, Athens, Greece, September 2001, p. 131–8.
[4] 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 London, 1999, 180 pp.
[5] Crammond NJ. The occurrence of thaumasite in modern construction—a review. In: Brown P, editor. Special edition. Cement Concrete Compos 2002:393–402.
[6] Neumann H. The minerals of Norway. Norges geologiske undersøkelse, 1985, Skrifter 68, 278 pp [in Norwegian].
[7] Norwegian Public Roads Administration (internal documents).
[8] Davik KI. Proper use of sprayed concrete in tunnels: Part B subsea tunnels. Norwegian Public Roads Administration 1997, 66 pp [in Norwegian].

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

[10] Sahu S, Badger S, Thaulow N. Mechanism of thaumasite formation in concrete. Cement Concrete Compos 2003;25(8).

[11] Iden IK, Hagelia P. C, O and S isotopic signatures in concretes which have suffered thaumasite formation and limited thaumasite form of sulfate attack. Cement Concrete Compos 2003;25(8).

[12] Barnett SJ, Macphee DE, Lachowski EE, Crammond NJ. XRD, EDX and IR analysis of solid solution between thaumasite and ettringite. Cement Concrete Res 2002;32:1–12.