Cement & Concrete Composites 25 (2003) 839–846

Cement &
Concrete
Composites

www.elsevier.com/locate/cemconcomp

C, O and S isotopic signatures in concrete which have suffered thaumasite formation and limited thaumasite form of sulfate attack

I.K. Iden [a,*], P. Hagelia [b]

[a] Institute for Energy Technology, P.O. Box 40, N-2027 Kjeller, Norway
[b] Norwegian Public Roads Administration, P.O. Box 8142 Dep, N-0033 Oslo, Norway

Abstract

Thaumasite formation and limited thaumasite sulfate attack has recently been discovered in sprayed concretes in contact with pyrrhotite-, pyrite- and calcite bearing Alum Shale in Oslo. In concretes, several types of calcite occur, including internal Popcorn calcite formed by replacement of both thaumasite and calcium silicate hydrate. In an attempt to throw further light on the origin of carbonates and sulfates involved, we have used the laser ablation probe to characterise these secondary minerals with respect to stable isotopes (C, O and S). Mitigation as well as repair may in several cases depend much on correct characterisation and location of the fluids provenance, and stable isotopic characterisation may be an appropriate tool to do so.

The preliminary results of this study indicate a complex open system with influence of fluids from several sources. There is a general difference in signatures between ordinary surface carbonation and internal carbonation associated with thaumasite. Calcite deposits within the Alum Shale/concrete contact zone show highly variable isotopic signatures reflecting a composite origin, probably significantly influenced by atmospheric CO_2. The sulfur isotopes in thaumasite appear to be much lighter than the Alum Shale constituents. This might possibly be explained by a contribution from atmospheric SO_2, or alternatively by sulfide oxidation in Alum Shale assisted by bacterial activity. A certain internal contribution from gypsum in cement clinker cannot be excluded.

Keywords: Stable isotopes; Thaumasite; Calcite; Provenance

1. Introduction

The use of stable isotope geochemistry has recently obtained extensive application within many environmental fields, but up to now only in a restricted way within concrete deterioration research. Basically, stable isotopes have the potential of providing information of reaction mechanisms due to fractionation during the transformations, as well as to identify the sources of the deterioration agents. Earlier work by Rafai et al. [1,2], Letolle et al. [3] and Macleod et al. [4,5] have elucidated the carbonation processes in concrete structures by using carbon and oxygen isotopes. Torf and Van Grieken [6] applied sulfur isotopes to identify the sources of gypsum formation on the surfaces of limestone buildings. These workers analysed small bulk samples or separates. However, laser assisted sample extraction is a micro-analytical technique which allows for precise analysis of sub-milligram sample sizes. To our knowledge no such data have been reported for concretes. We here focus on the potential of using stable isotopes by the laser method for investigations into the mechanisms of concrete alterations by various processes, as well as a monitoring tool.

Sulfate attack in concrete represents a multitude of chemical reactions, and several paths of reaction may be observed, as dependent on concrete mix and environmental conditions. Recent work has shown that the thaumasite form of sulfate attack (TSA) might cause significant deterioration in concretes made with ordinary Portland cement and sulfate resisting Portland cement (SRPC) (Thaumasite Expert Group [7]; Crammond [8]). In its non-deleterious early stage, thaumasite formation (TF), the thaumasite is restricted to pre-existing voids and micro cracks. In deleterious TSA, however, the thaumasite forms by extensive replacement of the calcium silicate hydrates (CSH), ultimately involving total destruction of the cement paste. This process is critically dependent on: (1) availability of sulfate- and carbonate ions (from external or internal

---

* Corresponding author. Tel.: +47-63-806142; fax: +47-63-815553.
E-mail address: iki@ife.no (I.K. Iden).

0958-9465/$ - see front matter © 2003 Elsevier Ltd. All rights reserved.
doi:10.1016/S0958-9465(03)00110-0

sources); (2) a wet and cool environment (most frequently below 10–15 °C); (3) a pore fluid pH greater than 10.5 and (4) that a significant portion of the cement paste can be accessed by the carbonate- and sulfate enriched fluids and react with Ca and Si in CSH to form thaumasite.

Works by Hagelia et al. [9] and Sibbick and Crammond [10] suggests that, in certain environments, internal carbonation represents an important late stage in the overall TF–TSA. *Both* decalcification of CSH resulting in cement paste depletion with Popcorn calcite formation *and* associated thaumasite decomposition to calcite with or without subordinate gypsum beneath ordinary surface carbonation [9,10] have been observed to take place. Although this late stage may be sustained in several chemical environments, the unifying feature is a reduction in the pore fluid pH from about 13 towards neutral (cf. [11] and [9,10]).

The TF–TSA–carbonation process leads to strength loss, enhanced concrete permeability and reduced service life of concrete structures. It is hence of great interest to the construction engineer to be able to identify the sources of carbonate and sulfate ions. Usually chemical analysis of water, aggregates and soils are employed in conjunction with petrography. However, only isotopic characterisation may be capable of discriminating between sources with similar chemical compositions.

2. Background and objectives

The chemical composition of thaumasite can be written:

$$Ca_6[Si(OH)_6]_2(CO_3)_2(SO_4)_2 \cdot 24H_2O \qquad (1)$$

The mineral is hexagonal, and its crystal structure contains columns of $(Ca_6[Si(OH)_6]_2 \cdot 24H_2O)^{8+}$ parallel to the *c*-axis, with $((CO_3)_2(SO_4)_2)^{8-}$ occupying the channels between them. Si in thaumasite may be substituted by some Al, and CO_3^{2-} by sulfate ions [12]. The channel carbonate–sulfate complex is loosely bound, involving some hydrogen bonds between hydrogen in water and oxygen in carbonate [13]. We therefore expected to achieve laser ablation and extraction of channel components sufficient to be analysed for stable isotopic composition. However, CP/MAS NMR investigations have shown that especially ^{13}C occurs in close proximity of ^{1}H [13], which to the present authors may indicate that the weak hydrogen bonds favour the heavy carbon isotope. Thus, one cannot exclude the possibility that laser ablation in thaumasite may involve a fractionation towards erroneously high $\delta\ ^{13}C$-values.

The present study focuses on two sprayed concretes in Oslo from (a) the first reported occurrence of TSA in Norway (e.g. [14]) in a road cut at Åkebergveien (13 years old spray), and (b) the Svartdal high way tunnel (2 years old). These concretes have suffered TF and limited TSA attack with contemporaneous and secondary formation of several textural types of calcite within the concrete interior. Ordinary surface carbonation was also present (cf. [9]). At both sites steel fibre reinforced concrete, made with SRPC (C_3A = about 1%) and ≈5–10% silica fume, had been sprayed directly on Alum Shale. This sulfide- and calcite bearing shale contains minor monoclinic pyrrhotite, which leads to catalytic oxidation of more abundant pyrite, and historically caused extensive deterioration with formation of soft mush of cement pastes [15]. We now believe that this in fact was a severe case of TSA [9]. Although the sulfate source in this case may be considered well constrained, several possible carbonate sources, such as atmosphere, calcite fines, complex ground water and anthropogenic material can in general be expected. Thus the objectives of this study were to

(a) characterise CSH, calcite, thaumasite as well as local Alum Shale constituents in terms of O, C and S isotopes;
(b) in view of these constraints, investigate the possibility that sources of carbonate and sulfate ions can be identified.

3. Methods and samples

Samples were first investigated under the petrographic microscope, and the mineralogical composition of characteristic micro-domains were studied in more detail by scanning electron microscopy (SEM). Sample chips for laser microprobe analysis were then selected from four concrete cores (some of which contain a bit of Alum Shale behind), and one spalled outer layer (≈2 cm thick) immediately adjacent to a 1–2 cm wide soft thaumasite + calcite mush zone. SEM was again performed in order to confirm the phase composition in each chip. Samples from Alum Shales and a few thaumasite rich deposits within chips were also selected for bulk S isotope analysis.

Laser microprobe analyses for carbon and oxygen isotopes were performed with a high-power Nd-doped YAl garnet (Nd:YAG) Quantronix laser, producing a beam wavelength of 1064 nm. A He–Ne aiming laser producing a visible red light is incorporated into the system for focusing the beam and positioning of the beam onto a target. The laser was operated at 30–32 A DC in a pulsed mode. The diameter of the beam will vary according to the material, but was commonly about 15 μm, and the analyses were followed through an optical microscope. The laser-ablation technique can be used for spot analyses if a sufficient amount of CO_2 gas is released. Alternatively, as in the present case, the sample is moved slowly along an X–Y table. The concrete minerals are generally very fine grained and thus individual mineral grains were too small to be analysed. Analyses of carbon and oxygen isotopes were performed along lines parallel to the sample surface and an integrated value for a specific depth was obtained in each case. Our sample chips widths were about 10×20 mm and 2–3 mm thick. The gas released was carried by He to a water absorbed $MgClO_4$ trap, and the CO_2 is separated in a poropackQ column, followed by analysis in a Optima IRMS (Micromass, England). A minimum of 2 μmol CO_2 is required. A reproducibility of ±0.2‰ (one sigma) for both O and C is based on repeated injections of reference gas. However, the precision vary with the quality of the sample, and the precision of thaumasite and CSH analyses will generally be somewhat lower (about ±0.5‰). Isotope values (C and O) are given relative to the PDB standard (cf. [16]).

The procedure for laser analysis of sulfur isotopes on sulfates and sulfides is yet not fully developed at IFE, so the few $\delta^{34}S$ data presented here represent small bulk samples. Sulfur isotopic composition was analysed on liberated SO_3 in sulfides and sulfates. Isotopic values are given relative to standard Canyon Diablo triolite. The precision in $\delta^{34}S$ is ±0.2‰ for both sulfides and sulfates.

For the fundamentals of the stable isotope technique is referred to the basic books of Faure [16] and Krouse and Grinenko [19].

4. Results

4.1. Petrography of analysed micro-domains

4.1.1. Åkebergveien road cut

Core 2 (18 cm) with near by spalled outer layer. Two sample chips were selected from this core: (a) inner parts close to concrete/Alum Shale interface (Bet4) and (b) outer surface exposed to air (Bet6), respectively). Bet5, representing the spalled outer layer, comprised two zones: (1) calcite dominated near the outer surface (mostly ordinary carbonation) and (2) thaumasite dominated in entrapment voids (Fig. 1: close to the TSA + calcite mush zone). A small bulk sample from the void material was analysed for S isotopes. Bet6 was characterised by ordinary surface carbonation and internal carbonation, with only small amounts of ettringite/thaumasite present. Bet4 contains variable amounts of thaumasite and ettringite.

Core 4 (12 cm) from the same locality was analysed by tracks from surface to about 4 cm inwards. This core displays a distinct porous internal reaction zone with a soft mush of calcite + thaumasite 2–2.5 cm from the surface, as seen in Bet11. A bulk sample of this zone, representing the thaumasite phase, was analysed for S isotopes. Bet11 was influenced by ordinary surface carbonation (1–2 mm) and internal CSH with or without calcite was also analysed about 4 cm farther inside the core.

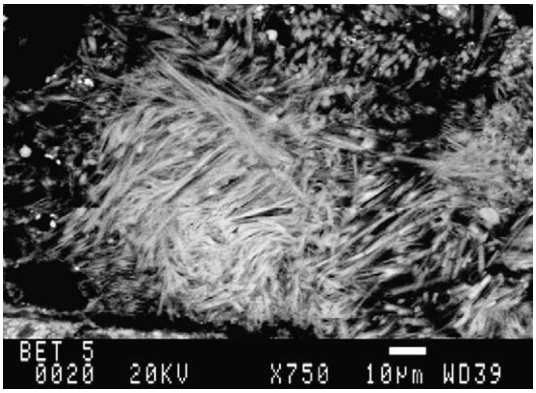

Fig. 1. Thaumasite within the thaumasite + calcite domain, Bet5 (Åkebergveien) BS image.

4.1.2. Svartdal tunnel

Core 370A (wet, 6 cm long) is represented by Bet7 and Bet10. In this core there was a porous reaction zone with thaumasite + calcite 1–3 cm away from the interface with the Alum Shale. A bulk sample of the reaction zone was collected for S isotope analysis.

Bet10 represents surface carbonation; depth 1–3 mm. Analyses of this sample also included internal CSH with or without calcite about 1.5 cm beneath the surface.

Bet7 is located close to the interface with the Alum Shale (0–3 cm). At the interface thaumasite was absent. However, coarse calcite deposits (ccd) were abundant within this fairly porous zone (Fig. 2). About 1 cm away from the interface there was a complex mixed zone consisting of very fine grained CSH, and thaumasite/ettringite with or without calcite. Thaumasite was also located in thin veins (Fig. 3). A bulk sample of such a vein was sampled for S isotope analysis. The outer part

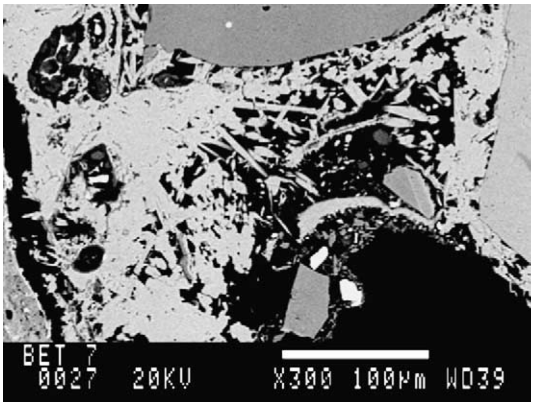

Fig. 2. Coarse calcite deposits (ccd) at the Alum Shale interface in Bet7, Svartdal tunnel. BS image.

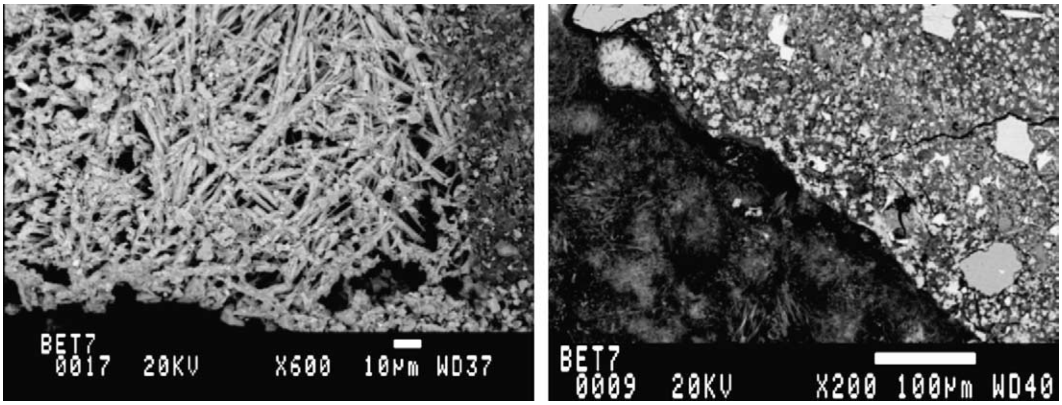

Fig. 3. Thaumasite veins of different morphology in Bet7, Svartdal tunnel: Coarse-grained crystals to the left, very fine grained to the right. BS images.

of the Bet7 sample chip was characterised by coarser calcites (ccd) + thaumasite.

Core 320B (dry, 5 cm long). Bet9 from this core was located at the Alum Shale interface. Thaumasite was only detected close to the shale. Laser tracks up to 6 mm from this interface represent CSH + some calcite.

4.1.3. Alum shale

The petrography of the Alum Shale was not investigated in detail. At the Svartdal locality, numerous thin calcite veins at the interface with concrete have intersected the shale. The amount of carbon rich organic material was high, and small sulfide grains were scattered all over. Two bulk sulfide separates from each locality, determined by XRD to be predominated by pyrite, were analysed for S isotopic composition. One bulk analysis of shale organics from Svartdal was also included.

4.2. Stable isotopes

The stable isotope data for C and O are reported for individual laser tracks in terms of the mineral assemblages established in Table 1, and are also plotted in Figs. 4 and 5. Bulk S isotopes are referred to in text.

Table 1
Summary of investigated samples and the mineralogy of analysed domains

Locality	Sample	Sample no	Laser analysis	Description	Bulk analysis
Svartdalstunnelen	Core 320B (dry)	Bet9	CSH + Th + cc	Interface Alum Shale	S in Alum Shale sulfides
			CSH + cc	Interface/Internal	Organic S in Alum Shale
	Core 370A (wet)	Bet7	ccd > CSH + cc	Interface Alum Shale	
			cc + CSH	Interface Alum Shale	
			complex CSH mix	Internal	
			Th veinlets	Internal	S in thaumasite
			Th + ccd	Internal/towards reaction zone (1–3cm from interface Alum Shale)	
		Bet10	cc > CSH(+ Th)	Surface carbonation	
			CSH > cc	Internal	S in CSH
Åkebergveien	Core 2	Bet6	CSH > cc(+ Th)	Outer surface/internal	
		Bet4	Th + cc + CSH	Interface Alum Shale	
			cc > CSH + Th	Interface Alum Shale	
					S in thaumasite
	Spall near Core 2	Bet5	cc + Th + CSH	Inner surface near TSA mush	S in thaumasite
			cc + CSH > Th	Outer surface	
	Core 4	Bet11	cc > CSH	Surface carbonation	S in Alum Shale sulfides
			cc + CSH	Surface/internal	
			cc + Th + CSH	Reaction zone, 19 mm from surface	
			CSH > cc	Internal	S in CSH

Predominating phases: CSH = somewhat depleted calcium-silicate hydrate; Th = thaumasite; cc = calcite, ccd = coarser grained calcite deposits.

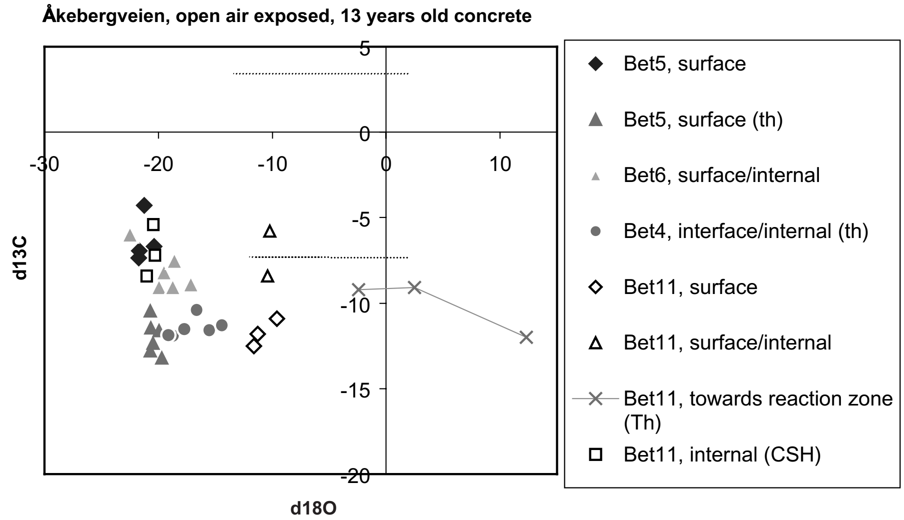

Fig. 4. Carbon and oxygen isotopic variation in calcite and thaumasite from sprayed concrete at Åkebergveien in Oslo. All values are normalised to PDB. Inserted horizontal lines indicate $\delta^{13}C$ of atmospheric CO_2 (lower) and equilibrium fractionation $\delta^{13}C$ for calcite precipitated from CO_2 dissolved in water (upper). See Table 1 and text for further details.

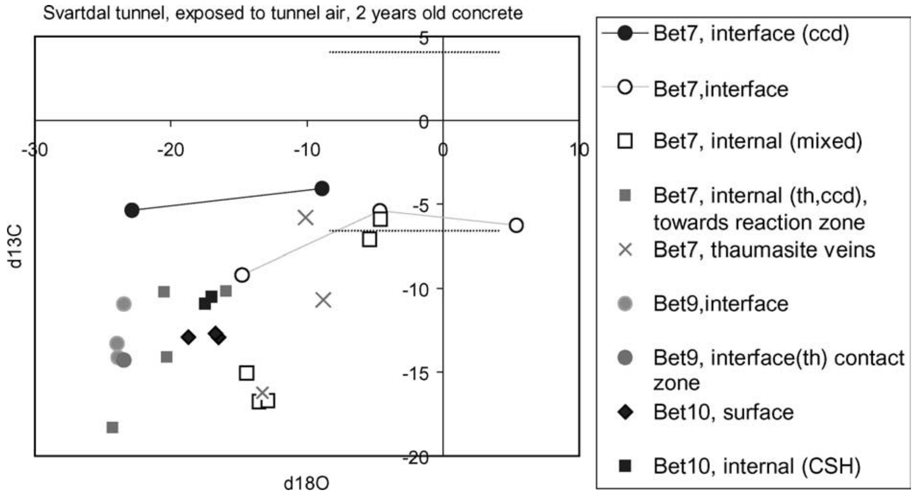

Fig. 5. Carbon and oxygen isotopic variation in calcite and thaumasite from sprayed concretes in the Svartdal tunnel in Oslo. All values are normalised to PDB. Inserted horizontal lines indicate $\delta^{13}C$ of atmospheric CO_2 (lower) and equilibrium fractionation $\delta^{13}C$ for calcite precipitated from CO_2 dissolved in water (upper). See Table 1 and text for further details.

4.2.1. Åkebergveien

At Åkebergveien $\delta^{13}C$ values range from −13.2‰ to −4.3‰, yet with a significant difference between petrographic types. Thaumasite + calcite assemblages in Bet5 (pH in pore fluid probably transient from >10.5 towards 8–9) have values lower than about −10‰. The surface carbonated zone in Bet5 has somewhat elevated carbon, with $\delta^{13}C$ values from −7.4‰ to −4.3‰. Pore fluid pH may be around 8–9 as judged from the assemblages. Bet6, which represents analysis from outer surface to internal carbonation is scattered between the domains mentioned above.

Bet11, which represents Core 4 is different. Surface carbonates are ^{13}C depleted compared to Bet5, with $\delta^{13}C$ values from −10.9‰ to −12.5‰. The values rise to −5.8‰ to −8.4‰ inwards, but decrease again to −9.1‰ to −12‰ towards the internal porous thaumasite + calcite mush zone. Where CSH dominates over calcite (Bet11 internal) values fall within −5‰ to −8‰.

The oxygen isotope values are also different in the two cores. The range in $\delta^{18}O$ values in Bet5, Bet6 and Bet4 is from −14.4‰ to −22.5‰ (lowest values in Bet4). The outer part of Bet11 has been enriched in ^{18}O, with $\delta^{18}O$ values from −9.6‰ to −11.3‰. However, the internal part of this sample chip has values similar to the samples from the first core (Fig. 4). The thaumasite/calcite internal reaction zone has distinctly different oxygen values, varying from −2.4‰ to +12.3‰.

The small bulk sample of the thaumasite + calcite reaction zone in Bet5 was analysed for sulfur stable isotopes. The δ^{34}S values range from 3.9‰ to 6.9‰. A void filled with thaumasite has a value of 4.0‰. CSH-gel was analysed in a small bulk sample, giving a δ^{34}S value of 10.6‰. This probably represents the composition of sulfur in gypsum added to the cement clinker.

4.2.2. Svartdal tunnel

The isotopic scatter is more pronounced here (Fig. 5). The δ^{13}C values range in total from −4.1‰ to −18.3‰. The surface carbonation (Bet10 in Core 370) has a narrow range in δ^{13}C from −12.7‰ to −12.9‰, which is only slightly lower than the range in internal CSH with or without calcite of −10.5‰ to −10.9‰.

The mineralogical complexity of Bet7, also Core 370, extends to the isotope signatures. At the porous interface with the Alum Shale, the δ^{13}C values of the coarse calcite are fairly heavy, from −4.1‰ to −5.4‰, decreasing to −9.2‰ towards the complex CSH matrix. This matrix has lower δ^{13}C values of −15.1‰ to −16.7‰. Two analyses of small areas assumed to represent pure CSH matrix have values −5.9‰ to −7.1‰ (same symbol in Fig. 4).

Thaumasite veinlets show highly variable values of δ^{13}C from −5.8‰ to −16.2‰. The outer part of Bet7 with thaumasite + coarse calcite (towards the reaction zone) ranges in δ^{13}C values from −10.2‰ to −18.3‰.

At the Alum Shale interface in Bet9 from the Core 320, the δ^{13}C value range is −10.9‰ to −14.3‰.

δ^{18}O values of the surface carbonates (Bet10) varies from −16.5‰ to −18.7‰. Internal δ^{18}O values are within the same range (about −17‰).

The coarse calcites (ccd) at the The Alum Shale interface in Bet7 have extremely variable oxygen isotope values, δ^{18}O ranging from −8.9‰ to −22.8‰ at the contact. Coarse calcite (ccd) at the immediate vicinity range from −14.8‰ to +5.4‰, in total this gives a range of −22.8‰ to +5.4‰! The CSH mixed zone has δ^{18}O values from −12.2 ‰ to −14.4‰, the "pure" CSH range from −4.6‰ to −5.4‰. Thaumasite veins vary in δ^{18}O values from −8.8‰ to −13.3‰, and the range in the thaumasite + coarse calcite (towards the reaction zone) is −20.3‰ to −24.3‰.

The carbonate phase of the Bet9 core (Alum Shale interface) has a δ^{18}O value of about −24‰.

A bulk separate of sufides in Alum Shale, dominated by pyrite, from right behind the concrete in samples. Bet9 contains very ^{34}S–enriched sulfur, with a δ^{34}S value of +27.3‰. Shale organics has a ^{34}S value of +21.2‰. A similar sulfide separate from the shale behind Bet7 is less enriched in ^{34}S. δ^{34}S values range from +15.8‰ to +22.1‰, averaging +18.7‰. The isotopic signature of the reaction zone in Bet10 (thaumasite + calcite) is very different, with a δ^{34}S value of +1.8‰. A small bulk sample of CSH-gel has the value of 11.8‰, which probably represents gypsum added to clinker. It is also possible that there is an influence from Al–sulfate admixture used as setting accelerator in this particular core [17].

5. Discussion

In a discussion of the isotopic signatures it is important to bear in mind the complexity of the systems investigated, which were characterised by very limited evidence of equilibrium reactions. Firstly, we assume that the isotopic signatures in concrete phases are reflecting the compositions of calcite, thaumasite and variably depleted CSH. Influence from portlandite and other subordinate phases should not be very great. Thus isotopic characteristics along a laser probe trail in a microscopic sub-domain are expected to represent the average composition of an unequilibrated assemblage. Schematically, the evidence suggests the following chemical reactions (cf. [9,17]):

(1) CSH + water with quite low pH → calcite + depleted CSH
(2) $CSH + CO_3^{2-} + SO_4^{2-} \rightarrow$ thaumasite
(3) Thaumasite + water with quite low pH → calcite + gypsum + Ca–Si–water complex (approximately)
(4) $CO_3^{2-} + H_2O + Ca^{2+} \rightarrow$ Calcite deposits
(5) Thaumasite + calcite + acidic water → dissolution

In addition to their age difference, the two localities have been exposed to somewhat different environments. The Åkebergveien sprayed concrete has been exposed to open air along a busy road, whereas the younger concrete at Svartdal has been influenced by tunnel air. In order to trace the sources and paths of deterioration using natural isotope systems, the sources need to be well characterised. In the case of the oxygen isotopes, the investigated systems are very complex, with many unknown participating phases (atmosphere, anthropogenic sources, meteoric water, groundwater, and oxygen bearing soluble minerals). In the following we therefore focus on the carbon and sulfur isotopes with only brief comments to oxygen.

5.1. Carbon isotopes

The ultimate carbon source for surface carbonation in concretes is atmospheric CO_2, which is dissolved into infiltrating water as meteoric rainwater or groundwater, or both. Precipitation of calcite in isotopic and chemical equilibrium with CO_2 gas should result in enrichment of ^{13}C of about 10–11‰ at 10 °C [16]. For atmospheric CO_2 the δ^{13}C value is about −7‰, thus the expected δ^{13}C value for precipitated calcite should be +3–4‰, which is certainly not the case in our samples. If the CO_2 gas transfer is diffusion dominated, a certain depletion of ^{13}C will occur in the reaction product. However, interactions between water molecules and dissolved substances will reduce this effect [18]. Kinetic fractionation will also result in product ^{13}C depletion, but values in the literature are highly variable. For example for the reaction $CO_2 + OH^- \rightarrow HCO^-$, which is dominant at high pH values (pH > 10), $\delta^{13}C$ values for kinetic fractionation varies from 11‰ to 39‰. Dissolution and reprecipitation of calcites should not include large fractionation effects [18].

Other carbon sources that can be present are added carbonate fillers, and also calcites within the Alum Shale. Calcite fillers are generally of marine origin, with $\delta^{13}C$ values about 0‰. We estimate the contribution to the carbon isotope signatures from such fillers to be very small in our samples. Unfortunately, we do not have data from carbonate phases within the Alum Shale, but rather low $\delta^{13}C$ values are presumed due to biogenic origin. Black shales usually have $\delta^{13}C$ values about −25‰ [16].

Little work has been published on isotopic characterisation of concrete phases, but cement pastes with normal initial pH are reported with $\delta^{13}C$ values generally below about −18‰ [1–3,5]. Modern concretes have $\delta^{13}C$ values ranging from about −10‰ to −30‰ [1]. Dietzel [20] describes two major ways of calcite sinter formation in concretes; by absorption of CO_2 in alkaline calcium hydroxide solutions within the concrete, or by deposition from ground water with dissolved $CaCO_3$. The first reaction will result in $\delta^{13}C$ values of about −25‰, and the second in values about −13‰. Intermediate values indicate overlap of the two processes.

Although highly variable, our $\delta^{13}C$ values are generally more elevated than literature data, and range from −4.3‰ to −13.2‰ in Åkebergveien, and from −4.1‰ to −18.3‰ in the younger Svartdal samples. The lowest values are seen in some thaumasite domains, although the scatter is obvious (Fig. 4). Analytical enrichment in ^{13}C cannot be excluded for the thaumasites, as mentioned earlier.

Surface carbonation at Åkebergveien differ in the two cores, with $\delta^{13}C$ values averaging −6.3‰ and −10.8‰ respectively. At the Svartdal tunnel values at the surface are slightly lower, about −12.5‰. This is possibly due to higher concentration of exhaust within the tunnel. The $\delta^{13}C$ value in petroleum range from −18‰ to −34‰, and values for CO_2 from exhaust should be slightly lower, probably about −25‰. A certain contribution from this source might be expected.

Carbon isotope signatures from "internal" domains are highly variable, in agreement with the presence of mixed stages of mineral reactions with various pore waters (reactions (1),(2),(3),(4),(5)). The range in ^{13}C values is more pronounced in the younger Svartdal concrete. However, it appears that domains where CSH dominates over calcite have $\delta^{13}C$ values as elevated as −5‰ to −8‰, in contrast to domains with CSH + calcite + thaumasite/ettringite. If surface carbonation results in $\delta^{13}C$ values down to about −12‰, as indicated above, the lower values seen in internal domains may be ascribed to a certain supply from additional carbon sources, such as the Alum Shale. However the biogenic signatures in this shale is as yet unknown.

The porous domain of Bet7 (Svartdal) near the interface with Alum Shale has somewhat elevated $\delta^{13}C$ values comparable to atmospheric CO_2. This may indicate an influx of different waters. The largest variation however is seen in the $\delta^{18}O$ values, also indicating atmospheric influence ($\delta^{18}O$ in CO_2 is about 10‰ PDB).

Highly variable $\delta^{18}O$ values are also specific for the porous reaction zone of Bet11 at Åkebergveien, extending to above atmospheric values. It is obvious that these porous zones have been available for influxes of diverse origins.

5.2. Sulfur isotopes

Isotopic geochemistry of sulfur compounds in water depends strongly on existing redox regimes. When oxidising conditions prevail the oxygen and sulfur isotopic composition of sulfate in waters are diagnostic of the origin of the sulfate [19]. Two possible external sulfur sources are actual in our samples: (1) antropogenic SO_2 from ambient atmosphere, oxidised to sulfates in meteoric water in contact with the surface of the concrete, or (2) circulating internal waters supplied with sulfate ions from oxidised sulfides and/or organics in the Alum Shale (or both). In addition one has to consider internal sources, such as gypsum additives.

The $\delta^{34}S$ values from the reaction zone closer to the surface in the Åkebergveien core (Bet5) vary from 3.9‰ to 6.9‰, while the values from the similar zone closer to the Alum Shale interface in the Svartdal core (Bet10) vary from 2‰ to 1.7‰. These values are rather different from $\delta^{34}S$ values of the Alum Shale phases (15.8–27.7‰). If the Alum Shale is providing the sulfate ions to the TS/TSA formation, a rather large fractionation of −12‰ to −25‰ has occurred during the sulfide/organics oxidation process. S isotope fractionation is expected to be very small during oxidation of sulfides. However, aerobic bacterial oxidation may result in significant fractionation effects [19].

SO_2 of urban air oil–gas varies in $\delta^{34}S$ from −8‰ to +30‰, but the majority lies in the range of 0–10‰ [19]. Fractionation during oxidation of antropogenic SO_2 to sulfate is assumed to be relative low [19]. Large variations in $\delta^{34}S$ over short distances are observed at other urban localities [6], thus lack of data of local ambient atmosphere makes conclusions at this stage somewhat speculative. From the above data it is not obvious however, that the Alum Shale is the only source of the TF in these concretes. Atmospheric SO_2 is a probable additional source. Furthermore, the $\delta^{34}S$ values of the

CSH-gel of about 10–12‰ are considered to represent internal primary sulfur sources. Thus a certain contribution from primary source cannot be excluded either.

6. Conclusions

Our data are indicative of various stages of reaction, precipitation and dissolution processes with supply from different sources in an open system. We feel that this preliminary work has demonstrated the potential of applying isotopic methods in delineating the complex concrete deterioration reactions, although we are not able to pinpoint the sources of the carbonate and sulfate ions of the various calcites and thaumasites with certainty at this stage. The idea of using laser ablation for micro-scale sampling was based on the fine-grained nature of the mineral phases. In future work, however, it is recommended to supplement this micro-analytic technique by isotope analysis of small bulk samples, in order to avoid some of the very fine-scale variability. Laser analysis is suitable for local, specific problems in a petrographically well-documented sample. More systematic work is needed to trace the sources of deterioration, and all relevant sources have to be characterised in terms of their isotopic composition. In doing this, however, our understanding of the mechanisms involved in concrete deterioration will increase, and allow for the appropriate remediation actions to be taken.

Acknowledgement

The authors are indebted to Ingar Johansen and Lars Kirksæther (IFE), and Per Geir Sigursen (NPRA) for technical assistance.

References

[1] Rafai N, Letolle R, Blanc P, Person A, Gegout P. Isotope geochemistry (^{13}C, ^{18}O) of carbonation processes in concrete. Cem Concr Res 1991;21:368–77.

[2] Rafai N, Letolle R, Blanc P, Gegout P, Revertegat E. Carbonation–decarbonation of concretes studied by the way of carbon and oxygen stable isotopes. Cem Concr Res 1992;22:882–90.

[3] Letolle R, Gegout P, Rafai N, Revertegat E. Stable isotopes of carbon and oxygen for the study of carbonation/decarbonation processes in concrete. Cem Concr Res 1992;22:235–40.

[4] Macleod G, Hall AJ, Fallick AE. An applied mineralogical investigation of concrete degradation in a major concrete road bridge. Min Mag 1990;54:637–44.

[5] Macleod G, Fallick AE, Hall AJ. The mechanism of carbonate growth on concrete structures, as elucidated by carbon and oxygen isotope analyses. Chem Geol 1991;86:335–43.

[6] Torfs KM, Van Grieken RE. Use of stable isotope measurements to evaluate the origin of sulfur in gypsum layers on limestone buildings. Environ Sci Technol 1997;31:2650–5.

[7] 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. London: DETR; 1999. p. 180.

[8] Crammond NJ. The occurrence of thaumasite in modern construction—A review. Cem Concr Compos 2002;24:393–402.

[9] 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, 2001. p. 131–8.

[10] Sibbick RG, Crammond NJ. Microscopical investigation into recent field examples of the thaumasite form of sulfate attack (TSA). In: 8th Euroseminar on Microscopy Applied to Building Materials, Athens, Greece, 2001. p. 261–9.

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

[12] Barnett SJ, Macpee DE, Lachowski EE, Crammond NJ. XRD, EDX and IR analysis of solid solution between thaumasite and ettringite. Cem Concr Res 2000;32:1–12.

[13] Skibstedt J, Hjorth L, Jacobsen HJ. Quantification of thaumasite in cementitious material by 29Si(^{1}H) cross-polarization magic angle spinning NMR spectroscopy. Adv Cem Res 1995;7(26): 69–83.

[14] Hagelia P, Grønhaug A. Thaumasite—infection causing concrete deterioration. Våre Veger 2000;9:54–5 [in Norwegian].

[15] Moum J, Rosenqvist ITh. Sulphate attack on concrete in the Oslo Region. J Am Concr Inst 1959;56:8, Proceedings, Title 56-18.

[16] Faure G. Principles of Isotope Geology. 2nd ed. New York: John Wiley & Sons; 1989.

[17] Hagelia P, Sibbick RG, Crammond NJ, Larsen CK. Thaumasite and secondary calcite formation in some Norwegian concretes. In: 1st International Conference on Thaumasite in Cementitious Materials, Garston, Watford, UK, 2002, this volume.

[18] Zeebe RE, Wolf-Gladrow D. CO_2 in seawater: Equilibrium, kinetics, isotopes. In: Elsevier Oceanography Series, vol. 65. 2001. 346pp.

[19] Krouse HR, Grinenko VA. Stable isotopes: Natural and anthropogenic sulphur in the environment. Scope 1991;43:440.

[20] Dietzel M. Measurements of stable carbon isotopes in calcite sinters on concrete. ZKG Int 2000;9:544–8.