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Prevention of thaumasite formation in concrete exposed to sulphate attack

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Abstract

Thermodynamic calculations were performed to investigate at which sulphate ion concentration hardened concrete can be damaged by the formation of thaumasite. It is indicated that thaumasite can be formed from C–S–H phases and portlandite at very low sulphate concentrations in an aggressive solution. Higher sulphate ion concentrations are required in the absence of portlandite. Still higher sulphate ion concentrations are needed if C–S–H phases with a low calcium/silicon ratio are consumed. Therefore, it is suggested that the formation of thaumasite at low and moderate sulphate concentrations in the attacking solution can be avoided by lowering the calcium/silicon ratio in the C–S–H phases. This can be achieved by the addition of pozzolanic and latently hydraulic admixtures. During the reaction of these materials, portlandite is consumed and the calcium/silicon ratio of the C–S–H phases is lowered. The aforementioned concept was confirmed by studies published in the literature and also by experimental investigations reported in this paper.

Keywords: B-Thermodynamic calculations; C-Sulphate attack; Thaumasite

1. Introduction

The phenomenon that concrete can be damaged by sulphate attack has been known for some time. Early investigations in the 19th century were reported by Vicat and Candlot [1]. Traditionally, the destruction was attributed to the formation of ettringite ($C_3A{\cdot}3CaSO_4{\cdot}32H_2O$). Systematic studies by Thorvaldson demonstrated that a high content of the clinker phase aluminate (C_3A) can lead to the formation of ettringite and thus to expansion during sulphate attack on hardened cement paste [2]. The presence of the ferrite phase (C_4AF) in the unhydrated cement was found to be less detrimental due to lower reactivity. These observations led to the introduction of sulphate-resisting Portland cement (SRPC) with a low C_3A content by Ferrari [3]. At present, the use of sulphate-resisting Portland cement is adopted in most guidelines for the production of concrete that is exposed to sulphate attack. However, as it was already outlined by Candlot (1890), the formation of ettringite is an important factor in the destruction of concrete which is attacked by sulphates, but it is not the only one [1].

Beside ettringite, also the formation of gypsum ($CaSO_4{\cdot}2H_2O$) was observed during the exposure of hardened cement pastes to concentrated sulphate solutions. The presence of gypsum veins was reported after investigations using Scanning Electron Microscopy (SEM) [4,5]. It was demonstrated by Tian and Cohen that the formation of gypsum contributes to expansion during exposure to sodium sulphate solutions [6]. The higher the alite (C_3S) content in sulphate-resisting Portland cement, the more portlandite ($Ca(OH)_2$) is formed during hydration and the more are these cements vulnerable to the formation of gypsum [7,8]. The mineral forms preferentially in the highly concentrated sulphate solutions which are employed in laboratory investigations. In contrast to this, it is rarely observed under most field conditions where moderate sulphate concentrations dominate [9]. The formation of gypsum can be avoided by the addition of pozzolanic and latently hydraulic admixtures. During the reaction of these materials, calcium hydroxide is consumed. This phase is required for the formation of gypsum. The less the portlandite content in a hardened cement paste, the higher is its resistance against the formation of gypsum [6,7].

The formation of a third mineral during sulphate attack has been observed. Thaumasite ($CaSiO_3{\cdot}CaSO_4{\cdot}CaCO_3{\cdot}15H_2O$) was detected as early as 1965 by Erlin and Stark in damaged

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concrete [10]. Systematic investigations started more than 30 years later with the report of the Thaumasite Expert Group [11]. It was noticed that the formation of this mineral had led to severe damage on foundations of bridges on a motorway in the UK. Since 1999, many more cases of damage involving the formation of thaumasite have been reported [12]. It is agreed upon that C–S–H phases, present in hardened concrete can be converted into thaumasite if the concrete is exposed to sulphate attack at low temperatures. Mobile water and a source of calcium carbonate ($CaCO_3$) are required for the reaction to proceed. In contrast to the situation for ettringite (lowering the C_3A content of the cement) and gypsum (reducing the amount of portlandite present in hardened cement paste), no simple chemical concept has been introduced to ensure a protection of hardened cement paste against the formation of thaumasite. Such a simple chemical concept to prevent the formation of thaumasite would provide major benefits, because the use of SRPC has no protecting effect in this instance. It has been suggested that concrete with no internal source of calcium carbonate would be immune against a formation of thaumasite. However, an investigation by Collett et al. showed that thaumasite can also form when no internal source for calcium carbonate is available [13]. In this investigation, carbon dioxide required for the formation of thaumasite originated from the atmosphere. For this reason, chemical concepts other than the exclusion of calcium carbonate from concrete need to be considered. Such a reflection can be supported by thermodynamic calculations. A Gibbs free energy for the formation of thaumasite from its constituting elements at 8 °C was reported [14]. Based on this value, possible reaction paths that might be relevant for the formation of thaumasite in hardened concrete at risk of sulphate attack were calculated [15]. Solid phases such as gypsum and ettringite and also the ingress of dissolved sulphate ions were considered as sources for sulphate. If gypsum is present, the calculations indicated that thaumasite can be formed from virtually every phase assemblage that can occur in hardened cement paste. If ettringite is assumed as a source for sulphate, the formation of thaumasite is not likely in the presence of C–S–H phases and calcite. The sulphate ion concentration in the aggressive environment which is required for the formation of thaumasite was calculated to be low (<300 mg/l in the presence of portlandite). In the computations, only the carbonated surface layer that contains calcium carbonate and silicon dioxide instead of C–S–H phases and portlandite was indicated to be immune against a formation of thaumasite. This result is in agreement with field observations where a formation of thaumasite was often detected behind the carbonated surface layer [11]. Despite it being possible to obtain results on reaction paths which are relevant for the formation of thaumasite, no simple chemical concept to avoid the formation of this mineral has been derived from these calculations.

For this reason, other ideas need to be considered. In the present study, the investigation is to find out if C–S–H phases with a low calcium/silicon ratio have a higher resistance against the formation of thaumasite than C–S–H phases with a calcium/silicon ratio of approximately 1.7. The results of the thermodynamic calculations are compared to the outcome of laboratory investigations that have been reported in the literature. In the experimental program of this study, mortar bars were produced and exposed to sodium sulphate solution with a sulphate ion concentration of 1500 mg/l.

1.1. Thermodynamic calculations

This investigation looked at whether silicon-rich C–S–H phases have a higher resistance to sulphate solutions than calcium-rich C–S–H phases. The latter are formed during the hydration of Ordinary Portland Cement (OPC) and have a calcium/silicon ratio of about 1.7. C–S–H phases which are relatively rich in silicon are encountered during the hydration of blended cements containing a sufficient amount of pozzolanic or latently hydraulic material to convert virtually all of the portlandite into C–S–H and other phases. After the consumption of portlandite, the calcium ion concentration in solution is lowered and the calcium/silicon ratio of the C–S–H phases drops to about 1.1 during the further reaction of the pozzolanic and latently hydraulic materials [16]. Therefore, three different situations shall be discussed:

- C–S–H phases with Ca/Si = 1.7, portlandite present
- C–S–H phases with Ca/Si = 1.7, portlandite absent
- C–S–H phases with Ca/Si = 1.1, portlandite absent

The minimum sulphate ion concentration which is required to convert C–S–H into thaumasite can be calculated for these three situations. This is done by first calculating the difference in Gibbs free energy between the final and starting states for each situation. The calculations are based on Eqs. (1)–(3) which consider the three different situations in which thaumasite can be formed. The calculations refer to a temperature of 8 °C because this is the median temperature prevailing in underground conditions in Central Europe. For most species, thermophysical data given by Babuskin et al. [17] were used. The value for the Gibbs free energy for the formation of C–S–H phases from their constituting elements at 8 °C was calculated from data given by Fujii and Kondo [18] considering Ca/Si = 1.7 and Ca/Si = 1.1, respectively. The value of Gibbs free energy for the formation of thaumasite from its constituting elements was taken from [14]. With these data, which are given in Table 1, the change in Gibbs free energy during the reactions considered in Eqs. (1)–(3) was

Table 1
Gibbs free energy for the formation of selected compounds from the constituting elements at 8 °C

Compound	$\Delta_f G^{o,281}$
SO_4^{2-} (aq.)	−753.1
OH^- (aq.)	−161.3
$CaCO_3$-calcite (cr.)	−1133.2
$CaSiO_3 \cdot CaSO_4 \cdot CaCO_3 \cdot 15H_2O$ (cr.)	−7638.0
SiO_2 (am.)	−851.8
H_2O (l.)	−239.96
$Ca(OH)_2$ (cr.)	−902.0
$1.7CaO \cdot SiO_2 \cdot 2.617H_2O$ (cr.)	−2647.5
$1.1CaO \cdot SiO_2 \cdot 2.017H_2O$ (cr.)	−2101.8

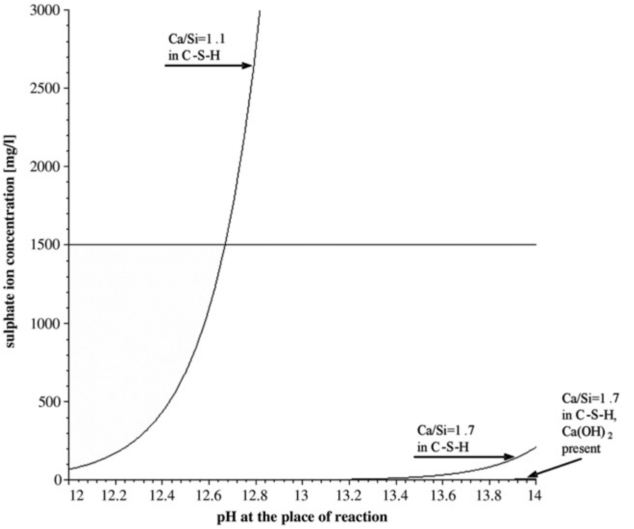

Fig. 1. Minimum sulphate ion concentration required for the transformation of C–S–H phases into thaumasite as obtained by thermodynamic calculation.

calculated. However, these values refer to the thermodynamic standard states of the involved compounds. For ions such as sulphate ions and hydroxide ions which appear in Eqs. (1)–(3), the standard state in the data compilation used refers to a concentration of 1 mol/kg and ideal behaviour. Therefore, equilibrium constants need to be calculated for Eqs. (1)–(3) by using Eq. (4). The calculated changes in Gibbs free energy serve as an input for these computations. The obtained results are presented in Eqs. (5)–(7) which refer to the reactions considered in Eqs. (1)–(3), respectively.

$$\begin{aligned}&1.7\mathrm{CaO}\cdot\mathrm{SiO_2}\cdot 2.617\mathrm{H_2O}+\mathrm{CaCO_3}+\mathrm{SO_4^{2-}}\\&\quad+0.3\mathrm{Ca(OH)_2}\\&\quad+13.083\mathrm{H_2O}\rightarrow\mathrm{CaSiO_3}\cdot\mathrm{CaSO_4}\cdot\mathrm{CaCO_3}\cdot 15\mathrm{H_2O}\\&\quad+2\mathrm{OH^-}\end{aligned}\tag{1}$$

$$\begin{aligned}&1.17647(1.7\mathrm{CaO}\cdot\mathrm{SiO_2}\cdot 2.617\mathrm{H_2O})+\mathrm{CaCO_3}+\mathrm{SO_4^{2-}}\\&\quad+12.9212\mathrm{H_2O}\rightarrow\mathrm{CaSiO_3}\cdot\mathrm{CaSO_4}\cdot\mathrm{CaCO_3}\cdot 15\mathrm{H_2O}\\&\quad+0.17647\mathrm{SiO_2}+2\mathrm{OH^-}\end{aligned}\tag{2}$$

$$\begin{aligned}&1.8182(1.1\mathrm{CaO}\cdot\mathrm{SiO_2}\cdot 2.017\mathrm{H_2O})+\mathrm{CaCO_3}+\mathrm{SO_4^{2-}}\\&\quad+12.3327\mathrm{H_2O}\rightarrow\mathrm{CaSiO_3}\cdot\mathrm{CaSO_4}\cdot\mathrm{CaCO_3}\cdot 15\mathrm{H_2O}\\&\quad+0.8182\mathrm{SiO_2}+2\mathrm{OH^-}\end{aligned}\tag{3}$$

$$\Delta_r G_f^{\circ} = -R\cdot T\cdot\ln 10\cdot\log K_{\mathrm{SP}}\tag{4}$$

$$\{\mathrm{SO_4^{2-}}\} = 7.5\cdot 10^{-4}\cdot\{\mathrm{OH^-}\}^2\tag{5}$$

$$\{\mathrm{SO_4^{2-}}\} = 0.019\cdot\{\mathrm{OH^-}\}^2\tag{6}$$

$$\{\mathrm{SO_4^{2-}}\} = 61.0\cdot\{\mathrm{OH^-}\}^2\tag{7}$$

It is evident from Eqs. (5)–(7), that the minimum sulphate ion concentration which is required for the transformation of C–S–H phases into thaumasite depends on the hydroxide concentration. The higher the hydroxide concentration (or pH value), the higher is the sulphate ion concentration up to which C–S–H phases are immune to a formation of thaumasite. A comparison of the different factors appearing in Eqs. (5)–(7) shows that at a given pH, a higher sulphate ion concentration is required for the transformation of silicon-rich C–S–H phases than for calcium-rich C–S–H phases. The derivation of exact values for the concentrations is complicated by the fact that activities appear in Eqs. (5)–(7) instead of concentrations. Activity coefficients for the conversion of ionic concentrations in activities and vice versa are only exactly calculated if the concentrations of all species in solution are known. This is not valid in the calculations reported here, because there is a wide range of types and concentrations of accompanying ions. Therefore, activity coefficients had to be estimated to allow a graphical visualization of Eqs. (5)–(7), which is given in Fig. 1. Beside the representation of Eqs. (5)–(7), the sulphate ion concentration of 1500 mg/l is indicated, which can be considered as moderate attack [19]. The curves in Fig. 1 refer to the three different situations discussed before. If the sulphate concentration at a given pH is above the curve under consideration, the formation of thaumasite should proceed according to the chemical reaction referring to this curve (Eqs. (1)–(3)).

From an inspection of Fig. 1 it is evident that the minimum sulphate ion concentration that is required for a transformation of C–S–H phases with Ca/Si = 1.7 into thaumasite is generally low. Only for very high pH values, an increase of the minimum sulphate ion concentration is calculated. The situation is worse in the presence of portlandite. In this case, the minimum sulphate ion concentration which can damage calcium-rich C–S–H phases (Ca/Si = 1.7) is even lower and there is virtually no protecting effect of high pH values. In contrast to this, silicon-rich C–S–H phases with Ca/Si = 1.1 are much more resistant against a formation of thaumasite. It is indicated that a formation of thaumasite is not possible if the pH values which are commonly found in the pore solution (13.0–14.0) can be maintained during sulphate attack. However, the exact position of the curves in Fig. 1 is very sensitive to the underlying data

Table 2
Chemical composition of the raw materials

	CEM I 42.5 R	CEM II/A-L 32.5 R	CEM III/B 32.5 N-NW/HS/NA	PFA
SiO_2 (M.%)	20.8	17.9	29.5	50.0
Al_2O_3 (M.%)	6.2	5.3	9.1	26.4
Fe_2O_3 (M.%)	2.5	2.5	1.5	8.8
CaO (M.%)	63.1	60.6	47.4	4.3
CaO_{free} (M.%)	1.1	1.1	0.5	0.0
MgO (M.%)	1.1	2.1	6.0	2.7
K_2O (M.%)	1.03	0.99	0.90	4.57
Na_2O (M.%)	0.20	0.08	0.29	0.65
SO_3 (M.%)	3.2	2.7	3.6	0.6
Loss on ignition (M.%)	1.1	7.3	0.9	1.4
Specific surface (Blaine) (cm^2/g)	3920	4620	3750	3220
Mean particle size (μm)	15.4	18.4	20.1	32.4

Table 3
Composition of the binders, estimated molar Ca/Si ratio in the C–S–H phases and total porosity of water stored companion samples

Sample	CEM I (M.%)	CEM II/A-L (M.%)	CEM III/B (M.%)	PFA (M.%)	Silica fume (M.%)	$CaCO_3$ (M.%)	estimated molar Ca/Si	Porosity (Vol.%)
CEM I	100	–	–	–	–	–	2.5	13.6
CEM I + 15% $CaCO_3$	85	–	–	–	–	15	2.5	15.2
CEM II/A-L	–	100	–	–	–	–	2.4	17.4
CEM II/A-L + 20% PFA	–	80	–	20	–	–	1.2	14.7
CEM II/A-L + 40% PFA	–	60	–	40	–	–	0.3	12.3
CEM II/A-L + 5% silica fume	–	95	–	–	5	–	1.9	19.2
CEM III/B	–	–	100	–	–	–	1.0	11.6
CEM III/B + 15% $CaCO_3$	–	–	85	–	–	15	1.0	15.7

and errors will have a strong effect on the results of the calculations. The reactions taking place may differ from the ones considered in Eqs. (1)–(3), e.g. it was assumed that amorphous SiO_2 can form but this phase can be consumed in other reactions which may change the position of the curves in Fig. 1. Therefore, the results of the calculations need to be confirmed by the outcome of experimental investigations. In the following section, data from the literature will be used to evaluate the results of the calculations. Further data are obtained by experimental investigations in which mortar bars were exposed to sodium sulphate solution at $SO_4^{2-} = 1500$ mg/l and 8 °C. The results of these investigations will be presented in subsequent sections of this report.

Köhler et al. investigated the formation of thaumasite in mixtures of synthetic clinker minerals by XRD-Rietveld [20]. Samples containing alite, aluminate, ferrite and gypsum were pre-hydrated for 28 days and then exposed to sulphate attack at 5 °C and 10 °C. Sodium sulphate solution having a SO_4^{2-} concentration of 3000 mg/l was employed. Thaumasite was detected in all samples except for those made from pure C_3S. Companion samples were prepared with a low calcium/silicon ratio by the addition of silica fume. The amount of silica fume was calculated to give calcium/silicon ratios of 1.0, 1.7 and 3.0, respectively. The results after 365 days showed that the formation of thaumasite did not take place in samples with $Ca/Si = 1.0$. Despite the fact that the calcium/silicon ratio of the C–S–H phases can only be estimated, this study supports the view that silicon-rich C–S–H phases are more resistant than calcium-rich C–S–H phases when exposed to sodium sulphate solutions.

In an investigation reported by Malolepszy and Mroz [21], C–S–H phases with different calcium/silicon ratios were produced by a reaction of calcium hydroxide with reactive silicon dioxide. Samples with molar calcium/silicon ratios of 0.8, 1.5, 2.0 and 2.5 were prepared and hydrated for 14 days at a temperature of 20 °C. Similar samples were produced under hydrothermal conditions at 180 °C. After drying, the C–S–H phases were mixed with $CaCO_3$, $Ca(OH)_2$ and Na_2SO_4 in a ratio of 7.5:1:0.5:1 and stored at 5 °C to investigate the influence of the calcium/silicon ratio on the resistance to the formation of thaumasite. Only samples with a calcium/silicon ratio of 0.8 were found to be resistant against the formation of thaumasite within 2 years. The mineral was detected in samples with calcium/silicon ratios between 1.5 and 2.5. The higher the calcium/silicon ratio in the samples and the longer the period of exposure, the higher was the amount of thaumasite that was detected.

The aforementioned studies confirm that C–S–H phases with a low calcium/silicon ratio are more resistant against the formation of thaumasite than C–S–H phases with a Ca/Si ratio of 1.7 which are formed in the presence of portlandite. More studies on the performance of blended cements containing blast furnace slag, silica fume and coal fly ash are available [22–26]. The results of these investigations can be compared to the outcome of the thermodynamic calculations that silicon-rich C–S–H phases are more resistant than calcium-rich C–S–H phases. Further

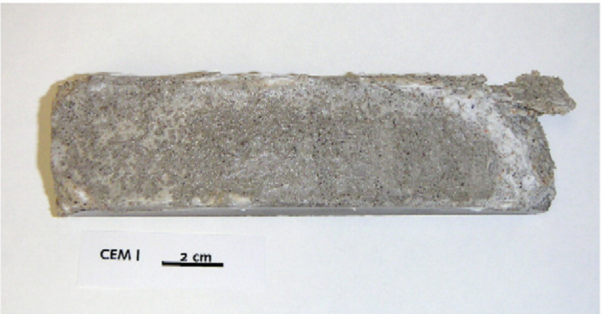

Fig. 2. Mortar bar made from Portland cement after 3 years of exposure ($SO_4^{2-} =$ 1500 mg/l and 8 °C).

Fig. 3. Mortar bar made from Portland limestone cement under addition of 5% silica fume after 3 years of exposure ($SO_4^{2-} = 1500$ mg/l and 8 °C).

information on the influence of mineral admixtures on the formation of thaumasite at moderate sulphate concentrations was obtained in the investigations reported below.

2. Materials and methods

The formation of thaumasite was investigated by exposing mortar bars to sulphate attack. Plain Portland cement, blended cements and mineral admixtures were used. The chemical composition of these materials is given in Table 2. In Table 3, the composition of the binders and the estimated Ca/Si ratios of the C–S–H phases are available. The latter were obtained in the following way from the chemical composition of the starting materials. The calcium oxide content of the cement was corrected for the amount of calcium oxide that is present as $CaCO_3$ using the loss on ignition data. The degrees of hydration of pulverised coal fly ash (PFA) and silica fume were assumed to be 75%, the degree of hydration of the cements to be 100%, respectively. It was further assumed that aluminium oxide reacts to a phase with a Ca/Al ratio as in AFm. The remaining calcium was used for the estimation of the calcium/silicon ratio of the C–S–H phases. Computed Ca/Si values higher than 1.7 can be read as an indication that C–S–H phases with Ca/Si = 1.7 are formed. The excess of calcium is present as portlandite in this instance. Such calculations can only be seen as a rather rough estimation because the results are highly dependent on the degrees of hydration that are assumed for the starting materials and to a minor extent on the nature of the phases that are formed (AFt/AFm, etc.).

Mortar was prepared from the binders with quartz aggregate at an aggregate/cement ratio of 3.0 and a water/binder ratio of 0.6. The mortar bars with dimensions of 4 cm × 4 cm × 16 cm were pre-hydrated in water at 20 °C for 14 days when they were exposed to sulphate attack. The sodium sulphate solution had a SO_4^{2-} concentration of 1500 mg/l and a temperature of 8 °C. The aggressive solution was replaced every 4 weeks.

After 3 years of exposure, the samples were investigated by XRD and SEM. Material was taken from the surface (0–2 mm) and from the core (>2 mm) of unaffected parts of the specimens for XRD analysis. The degree of damage was assessed by optical examination after 3 and 4.5 years. Polished sections of resin impregnated parts of the samples were examined by SEM using a Hitachi 2700-LB operating at 15 kV. To access the sulphate penetration profile, the SO_3-concentration was measured by EDX. Areas with a size of 70 μm × 200 μm were scanned for this purpose. The pore size distribution was measured by mercury intrusion porosimetry in companion samples that were stored for a period of 3 years in water (Micromeritics Autopore II 9220).

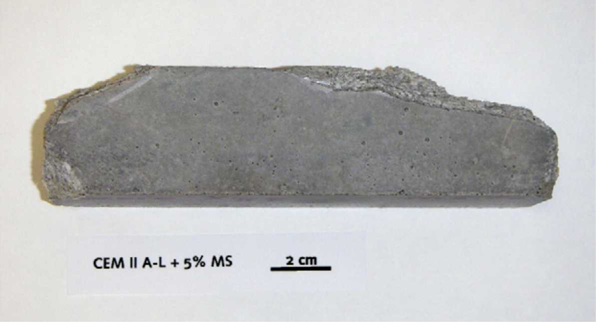

Fig. 4. Mortar bar made from Portland limestone cement after 4.5 years of exposure (SO_4^{2-} = 1500 mg/l and 8 °C).

Fig. 5. Mortar bar made from blast furnace slag cement after 4.5 years of exposure (SO_4^{2-} = 1500 mg/l and 8 °C).

Other methods such as surface hardness and ultrasonic pulse velocity were applied. The results obtained by these methods were found to be irrelevant and are not included in this paper. It was also attempted to measure the calcium/silicon ratio of the C–S–H phases by EDX. This was not possible because these phases are much smaller than the sample volume that is excited by the electron beam during analysis.

3. Results

A sulphate ion concentration of 1500 mg/l can be considered as moderate attack that can readily occur under field conditions. Already after 3 years of exposure, some of the mortar bars were badly corroded. The damage was evident on more samples after 4.5 years. Examples of damaged and undamaged mortar bars are presented in Figs. 2–5). Table 4 gives information on the phases that were identified by XRD analysis and the optical appearance of the samples. The pore size distribution of water stored companion samples is available in Fig. 6; total porosity is included in Table 3. Selected results for the sulphate penetration profiles are presented in Fig. 7. Only the results for three samples are given here for illustration, because different sulphate penetration profiles were measured on the same sample at different places. This was due to the fact that the microstructure is very heterogeneous, which leads to different rates of attack at different parts of the samples. Some samples were badly corroded in some parts while other parts had remained unaffected. For this reason it is difficult to compare the sulphate penetration profiles among the samples.

4. Discussion

The thermodynamic calculations presented in this paper suggest that C–S–H phases with a low calcium/silicon ratio can

Table 4
Results of XRD analyses (minerals which may additionally be present are printed in parentheses), optical appearance and estimated molar Ca/Si ratio in C–S–H phases after 3 years exposure (SO_4^{2-} = 1500 mg/l and 8°C)

Sample	Surface region	Core region	Physical appearance after 3 years	Physical appearance after 4.5 years	Estimated molar Ca/Si
CEM I	Calcite, quartz, portlandite, ettringite, monosulphate, (monocarbonate, vaterite), substantial amounts of thaumasite in damaged parts	Calcite, quartz, portlandite, ettringite, monosulphate, (monocarbonate, vaterite)	Serious signs of damage, loss of material (depth of erosion up to 1 cm)	These samples were removed before complete disintegration	2.5
CEM I + 15% $CaCO_3$	Calcite, quartz, portlandite, ettringite, monocarbonate, substantial amounts of thaumasite in damaged parts	Calcite, quartz, portlandite, ettringite, monocarbonate	Small signs of erosion on edges and corners	Signs of damage, loss of material (depth of erosion up to 0.5 cm)	2.5
CEM II/A-L	Calcite, quartz, portlandite, ettringite, thaumasite, (monocarbonate), substantial amounts of thaumasite in damaged parts	Calcite, quartz, portlandite, ettringite, monocarbonate, (thaumasite)	Small signs of erosion on edges and corners	Signs of damage, loss of material (depth of erosion up to 0.5 cm)	2.4
CEM II/A-L + 20% PFA	Calcite, quartz, portlandite, ettringite, monocarbonate, (thaumasite)	Calcite, quartz, portlandite, ettringite, monocarbonate	No sign of attack	No sign of attack	1.2
CEM II/A-L + 40% PFA	Calcite, quartz, ettringite, monocarbonate, (vaterite, mullite)	Calcite, quartz, ettringite, portlandite, (monocarbonate, vaterite, mullite)	No sign of attack	No sign of attack	0.3
CEM II/A-L + 5% silica fume	Calcite, quartz, portlandite, ettringite, monocarbonate, (thaumasite), substantial amounts of thaumasite in damaged parts	Calcite, quartz, portlandite, ettringite, monocarbonate, (thaumasite, vaterite)	Serious signs of damage, loss of material (depth of erosion up to 2 cm)	These samples were removed before complete disintegration	1.9
CEM III/B	Calcite, quartz, portlandite, ettringite, (thaumasite, vaterite)	Calcite, quartz, portlandite, ettringite, (monocarbonate, thaumasite, vaterite)	No sign of attack	No sign of attack	1.0
CEM III/B + 15% $CaCO_3$	Calcite, quartz, ettringite, vaterite, (monocarbonate)	Calcite, quartz, ettringite, portlandite, vaterite, (monocarbonate)	Very small signs of erosion on edges and corners	Very small signs of erosion on edges and corners	1.0

resist a moderate sulphate attack at low temperatures without being transformed into thaumasite. Such C–S–H phases with a low calcium/silicon ratio are formed when mineral admixtures such as blast furnace slag, silica fume, fly ash and others are used to convert calcium hydroxide from the hydration of the Portland cement clinker into C–S–H and other phases. After depletion of portlandite, the further reaction of the pozzolanic or latently hydraulic admixtures leads to a decrease of the calcium/silicon ratio in the C–S–H phases from approximately 1.7 to about 1.1. Silicon-rich C–S–H phases were calculated to be more resistant against a formation of thaumasite. The chemical resistance is also affected by the pH in the pore solution at the place of reaction. With increasing pH values, higher sulphate ion concentrations are required to form thaumasite. Due to leaching, the pH at the place of reaction will be higher than in the aggressive solution and lower than in the unaffected core of the concrete. This process can potentially destabilize a system that would otherwise be chemically immune against the formation of thaumasite. It can be counteracted by carbonation of the leaching zone.

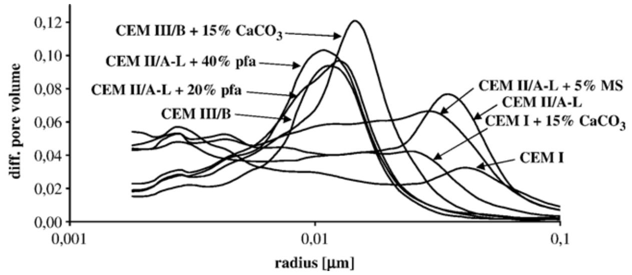

Fig. 6. Pore size distribution in companion samples that were stored in water at 8 °C.

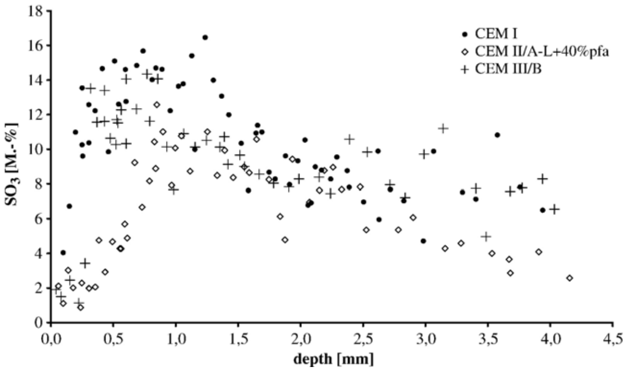

Fig. 7. SO_3-concentration in the samples after 3 years measured by EDX.

However, thermodynamic calculations cannot be seen as a direct proof. They are only indicators that a reaction can proceed. Other issues need to be considered additionally. The minimum sulphate concentration, up to which a given C–S–H is calculated to be resistant against a formation of thaumasite, depends on the pH value in the solution at the place of reaction. Since the aggressive solution has in most cases a pH value that is much lower than the one in the pore solution, the pH at the place of reaction can be significantly lower than assumed in Fig. 1. Furthermore, the outcome of the calculations is very sensitive to the thermodynamic data which are employed in the computations. For these reasons, a confirmation of the results of the thermodynamic calculations by experimental investigations is required. Data reported in the literature showed that lowering the calcium/silicon ratio in hydrated pastes by the addition of silica fume is able to increase the resistance during an exposure to sulphate solutions with $SO_4^{2-}=3000$ mg/l at 5 °C and 10 °C [20]. Also artificially prepared C–S–H phases with a low calcium/silicon ratio were found to be more resistant to the formation of thaumasite than C–S–H phases with high calcium/silicon ratios when exposed to sodium sulphate [21]. These data tend to confirm the conclusion of the thermodynamic calculations that C–S–H phases with a low calcium/silicon ratio can resist a moderate sulphate attack without being transformed into thaumasite.

Further confirmation of this result was obtained in the experimental investigations carried out in this study. Mortar bars were produced and exposed for almost 5 years to a moderate sulphate attack. The samples were stored in a sodium sulphate solution with $SO_4^{2-}=1500$ mg/l at a temperature of 8 °C. Within this period of storage, some of the specimens showed significant signs of attack. These mortar bars exhibited loss of material to a depth of almost 2 cm after only 3 years. Serious damage was found on specimens which had a high content in portlandite (CEM I, CEM I+15% $CaCO_3$, CEM II/A-L, CEM II/A-L+5% silica fume). Other mortar bars were found to be more resistant. These were samples that contained a sufficient amount of blast-furnace slag or coal fly ash to remove virtually all of the portlandite (CEM II/A-L+20% fly ash, CEM II/A-L+40% fly ash, CEM III/B, CEM III/B+15% $CaCO_3$). For the more resistant samples, a low calcium/silicon ratio of the C–S–H phases was estimated. In contrast, a high Ca/Si ratio was computed for less resistant samples. The resistance against sulphate attack at low temperatures is therefore at least to some extent attributable to lowering the Ca/Si ratio in the C–S–H phases. The calculation of the Ca/Si ratio in the C–S–H phases showed that portlandite should be absent from the microstructure in the resistant samples and the median calcium/silicon ratio should be about 1.0. Nevertheless, portlandite was detected in a small amount by XRD in most of the resistant samples. This is due to the fact that the microstructure of hardened cement paste is very heterogeneous. In some parts, where agglomerates of clinker minerals were still present after mixing of the cement with water, some portlandite can remain for many years. In contrast, most of the C–S–H phases in these samples have a very low calcium/silicon ratio because the reactions of fly ash and blast furnace slag consume calcium. Therefore, C–S–H phases with a low calcium/silicon ratio can be readily found in the vicinity of hydrated particles of blast furnace slag and coal fly ash. The more of these mineral admixtures are contained in the cement, the more C–S–H phases with a low calcium/silicon ratio are formed. In the present investigation, four binders contained enough mineral admixtures with pozzolanic and latently hydraulic properties to convert most of the portlandite and most of the calcium-rich C–S–H phases into silicon-rich C–S–H phases. In these samples, almost no sign of degradation was evident according to visual inspection. Thaumasite was not detected by XRD.

It can be argued that the good performance of four out of eight binders is not due to a low calcium/silicon ratio in the C–S–H phases, but to a high physical resistance. Samples with a high physical resistance have very narrow pores and are thus able to prevent the diffusion of the sulphate ions into the microstructure. The analysis of the pore size distribution (Fig. 6) supports this idea. However, there are serious arguments that the physical resistance can slow down the migration of sulphate ions but is not able to exclude the uptake of these ions from the solution. It was shown by SEM and EDX that all samples had a high SO_3 content in the first 2–3 mm (Fig. 7). This feature was present in all specimens, regardless whether or not they showed signs of damage. It can be concluded from this accumulation of sulphate in the specimens that sulphate ions have penetrated resistant and also non-resistant samples. Therefore, the improved physical resistance is not responsible for the prevention of the deterioration in some of the mortar bars.

The better performance of resistant samples can only be explained by a higher chemical resistance. Such a high resistance was achieved by lowering the calcium/silicon ratio in the C–S–H phases. If the silicon-rich C–S–H phases would not have been resistant to the formation of thaumasite, they would also have been transformed into this mineral. In damaged mortar bars, the high SO_3-level below the surface was due to the formation of thaumasite and ettringite according to spot analyses by EDX. In undamaged specimens, the high SO_3-concentration was solely due to the presence of ettringite. Only calcium-rich C–S–H phases were transformed into thaumasite, whereas silicon-rich C–S–H phases were able to resist a sulphate ion concentration of 1500 mg/l.

According to SEM investigations, thaumasite was only detected in damaged samples which had a high calcium/silicon ratio (Table 3). However, also resistant samples with a low calcium/silicon ratio contained traces of portlandite due to heterogeneities within the microstructure. These few, isolated portlandite crystals can coexist with a very minor amount of calcium-rich C–S–H phases which are prone to the formation of thaumasite. However, since these were only impurities, no deterioration of samples made with a high amount of pozzolanic or latently hydraulic admixtures was encountered.

5. Conclusions

Thermodynamic calculations have indicated that C–S–H phases with a calcium/silicon ratio of 1.7 which are usually formed in the presence of portlandite can be transformed into thaumasite at very low sulphate concentrations. If the calcium/silicon ratio in the C–S–H phases is reduced to about 1.1 by the addition of pozzolanic or latently hydraulic admixtures, these phases can resist much higher sulphate concentrations without giving way to thaumasite. This result of thermodynamic calculations was confirmed by studies reported in the literature and also by experimental investigations presented in this paper. In these investigations, mortar bars were produced using different cements and mineral admixtures. After pre-hydration, the samples were exposed to a moderate sulphate attack at SO_4^{2-} = 1500 mg/l and 8 °C. Within a few years, some of the samples were found to be badly corroded. This was the case for samples without a sufficient amount of mineral admixtures to convert portlandite into additional C–S–H phases and to lower the calcium–silicon ratio of the C–S–H phases. If a high amount of blast furnace slag and coal fly ash was added to lower the calcium/silicon ratio of the C–S–H phases to about 1.0, almost no signs of deterioration were detected within 4.5 years of exposure.

The higher resistance of C–S–H phases with a low calcium/silicon ratio against the formation of thaumasite can be used to derive a concept to avoid the formation of thaumasite in hardened concrete which is exposed to sulphate attack. The formation of thaumasite can be avoided, if a sufficient amount of pozzolanic or latently hydraulic admixtures is added to ensure that portlandite is consumed and the calcium/silicon ratio in the C–S–H phases is reduced. It is therefore suggested by the present authors to lower the calcium/silicon ratio in the binder to prevent the formation of thaumasite during exposure to sodium sulphate attack at low temperatures.

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