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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