

# Influence of the sulfate concentration on the results of laboratory investigations of sulfate resistance

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## Abstract

The sulfate resistance of cement, mortar and concrete is usually assessed by the exposure of samples of these materials to a sulfate attack under laboratory conditions. Highly concentrated sulfate solutions are used to accelerate the tests. The influence of the sulfate concentration on the formation of gypsum is investigated in this study. At high sulfate concentrations, as occurring in the sulfate resistance tests, the exposed samples are damaged by the formation of ettringite, gypsum and thaumasite. Gypsum forms by a reaction of calcium hydroxide with sulfate ions from the aggressive solution. The formation of gypsum can lead to expansion and microcracking. In contrast to the situation in the laboratories, gypsum can not form at the low sulfate concentrations that are commonly encountered in the field. The mineral was not detected in mortar bars exposed to sulfate concentrations up to 3000 mg/l. Therefore, the damage of test samples in laboratory investigations is due to processes that are different from those occurring under field conditions.

## 1. Introduction

Concrete is a material that is susceptible to the ingress of sulfate ions from the environment. Phases contained in the hardened cement paste can react with sulfate ions. During these reactions, ettringite ( $C_3A \cdot 3CaSO_4 \cdot 32H_2O$ ), thaumasite ( $CaSiO_3 \cdot CaSO_4 \cdot CaCO_3 \cdot 15H_2O$ ) and gypsum ( $CaSO_4 \cdot 2H_2O$ ) may be formed. To avoid deterioration, concrete exposed to sulfate attack is produced in a way that it has a high physical and chemical resistance against sulfate attack. The physical resistance depends on the permeability of the hardened cement paste. The lower the permeability, the less sulfate ions can penetrate the concrete and the higher is the physical resistance against sulfate attack. Alternatively, the durability in the presence of sulfate ions can be increased by using binders with high chemical resistance. A high chemical resistance is achieved if the hardened cement paste consists of phases that cannot interact with sulfate ions. Unfortunately, the formation of the three aforementioned minerals can not be excluded simultaneously by using one single binder. The resistance against the formation of ettringite can be increased by

using sulfate resisting Portland cement (SRPC). This cement has a low amount of the clinker phases aluminate ( $C_3A$ ) and ferrite ( $C_4AF$ ). Therefore, not much  $Al_2O_3$  (which is required for the formation of ettringite) is available in the hardened cement paste produced from these cements and the formation of ettringite can be restricted. In contrast to this, SRPC can be prone to the formation of gypsum or thaumasite. The formation of gypsum can be avoided by the use of high amounts of pozzolanic or latently hydraulic admixtures. During the reaction of these materials, portlandite ( $Ca(OH)_2$ ) is consumed. This substance is required for the formation of gypsum. Subsequently, gypsum can not be formed in the absence of portlandite.

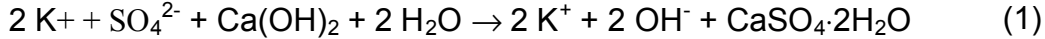
Despite the resistance against sulfate attack can be discussed qualitatively, the relative performance of different binders has to be assessed quantitatively. Such an assessment is possible by laboratory investigations of sulfate resistance which can be carried out by using specific test methods. In these tests, samples of hydrated cement paste, mortar or concrete are exposed to sulfate solutions and the expansion or other properties of the samples are measured in regular time intervals [1-4]. In these tests, sulfate ion concentrations between 14,000 and 34,000 mg/l are applied. Such high sulfate concentrations are rarely met under field conditions. In most situations, low and moderate concentrations up to 3000 mg/l prevail. Only in alkaline soils [5], the sulfate ion concentration can be as high as in the laboratory test solutions. High sulfate ion concentrations are used in the laboratories to accelerate the process of deterioration and to provide information on the relative performance of different binders when exposed to sulfate attack. However, it needs to be investigated if the process of damage is artificially changed in a way that it leads to erroneous predictions. For this reason, the influence of the sulfate ion concentration on the formation of gypsum is assessed in this study by thermodynamic calculations and laboratory investigations.

## **2. Materials and Methods**

In the thermodynamic calculations, the solubility of gypsum at high pH-values was investigated. A reaction of portlandite with sulfate ions to gypsum according to equation 1 was assumed. In the first step, the calcium ion activity was calculated from the pH-value and the solubility of portlandite at 25°C following equations 2-5. The activity of an ionic species is a corrected concentration because specific interactions among the ions themselves and with the solvent are responsible for the fact that there is no ideal behavior of the ions.

The equilibrium constant for portlandite appearing in equation 5 was calculated from thermophysical data [6]. The calcium ion activity that was obtained from the portlandite equilibrium was used to calculate the sulfate

ion activity that is required for the formation of gypsum at 25°C and the pH of interest (equations 6 and 7). The equilibrium constant for gypsum was

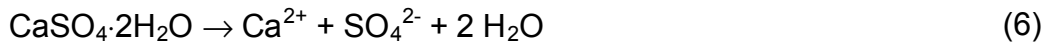


$$\text{pH} = -\log \{\text{H}^+\} \quad (2)$$

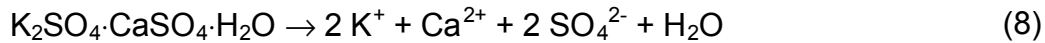
$$K_{\text{Water}} = 1.00 \cdot 10^{-14} = \{\text{H}^+\} \cdot \{\text{OH}^-\} \quad (3)$$



$$K_{\text{Portlandite}} = 6.26 \cdot 10^{-6} = \{\text{Ca}^{2+}\} \cdot \{\text{OH}^-\}^2 \quad (5)$$



$$K_{\text{Gypsum}} = 3.02 \cdot 10^{-5} = \{\text{Ca}^{2+}\} \cdot \{\text{SO}_4^{2-}\} \quad (7)$$



$$K_{\text{Syngenite}} = 2.72 \cdot 10^{-8} = \{\text{K}^+\}^2 \cdot \{\text{Ca}^{2+}\} \cdot \{\text{SO}_4^{2-}\}^2 \quad (9)$$

taken from [7]. The obtained sulfate ion activity was converted into a sulfate ion concentration by incorporating activity coefficients which were calculated using the Pitzer- model [8]. In these computations, it was assumed that charge balance is due to the presence of potassium ions. At high potassium ion concentration, the formation of syngenite was enclosed in the calculations (equation 8 and 9). The solubility product of this mineral was calculated from the chemical potential quoted in [9].

In the second part of the investigations, it was tested if the results obtained by thermodynamic calculation can be used to discuss the performance of concrete samples exposed to sulfate attack under laboratory conditions. For this purpose, test samples exposed to different sulfate solutions were examined by Scanning Electron Microscopy (SEM). The mortar bars were produced from an Ordinary Portland Cement (OPC) with the following chemical composition: 63.1% CaO, 20.8% SiO<sub>2</sub>, 6.2% Al<sub>2</sub>O<sub>3</sub>, 2.5% Fe<sub>2</sub>O<sub>3</sub>, 3.2% SO<sub>3</sub>, 0.20% Na<sub>2</sub>O and 1.03% K<sub>2</sub>O. The aggregate/cement ratio was 3.0, the water/cement ratio 0.6. The mortar bars had dimensions of 1 cm x 4 cm x 16 cm and were pre-hydrated in water at 20°C for a period of 14 days. At this age, the samples were exposed to sodium sulfate solution at a temperature of 8°C. This temperature is different from the one in the thermodynamic calculations because the samples were supplied from a program in which the formation of thaumasite was investigated. The latter is facilitated by low temperatures. The aggressive solutions had sulfate ion concentrations of 1500, 3000 and 30,000 mg/l and were renewed every 7 days. After one year of exposure, carbon coated polished sections and fracture surfaces of the samples were investigated by SEM to find out what kind of sulfate-bearing phases had formed during attack. The microscope was a Hitachi S-2700-LB equipped with an EDX system. An acceleration voltage of 15 kV was used in all examinations.

It was also investigated if the formation of gypsum in laboratory test solutions can be suppressed. For this purpose, mortar bars were stored in sodium sulfate solutions with different pH values. The addition of NaOH

was used to raise the pH in one of the solutions above 13.0 to avoid the formation of gypsum even at very high sulfate concentrations. The cement that was used in this investigation was a sulfate resisting Portland cement with the following chemical composition: 63.9% CaO, 21.0% SiO<sub>2</sub>, 4.2% Al<sub>2</sub>O<sub>3</sub>, 4.5% Fe<sub>2</sub>O<sub>3</sub>, 2.5% SO<sub>3</sub>, 0.16% Na<sub>2</sub>O and 0.90% K<sub>2</sub>O. Mortar bars were produced as described above. The samples were pre-hydrated for 14 days in water and then exposed to the aggressive solutions. Plain sodium sulfate solution with a sulfate ion concentration of 14,400 mg/l was used and also a solution with the same sulfate ion concentration to which furthermore 6,600 mg/l NaOH were added. The pH in the freshly prepared solutions was 8.1 and 13.1, respectively. Companion samples were stored in water. The length change of the mortar bars was recorded for a period of 34 months. At this age, the phase composition in the mortar bars was controlled by SEM and XRD.

### 3. Results

The sulfate ion concentration that is required to transform portlandite into gypsum was calculated for a range of pH-values. The results are plotted in Figure 1. Also a graph referring to the reaction of portlandite with potassium sulfate solution to syngenite is shown. The results presented in Figure 1 were corroborated by experimental investigations. In these experiments, the equilibrium concentrations of samples containing portlandite and gypsum (or syngenite) at different pH-values were measured. Details of the experimental procedures can be found in [10]. The results are presented as dots in Figure 1, whereas the results of the thermodynamic calculations are plotted as solid lines.

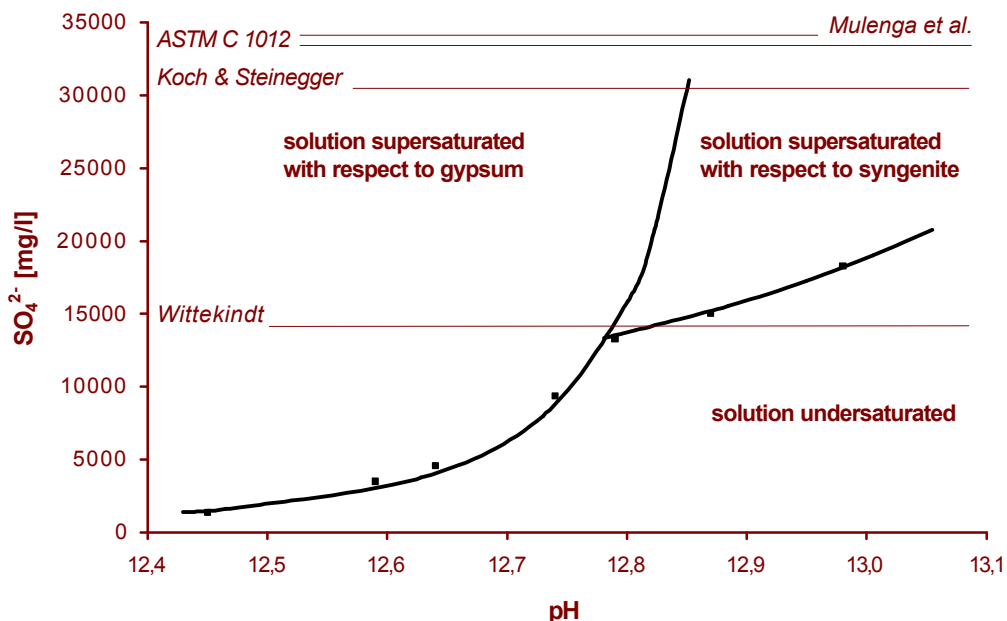


Figure 1: Sulfate ion concentration required for a conversion of portlandite into gypsum

Further confirmation was obtained by SEM investigations of mortar bars that were exposed to sodium sulfate solutions with sulfate ion concentrations of 1500, 3000 and 30,000 mg/l, respectively. In the samples stored at 1500 and 3000 mg/l, ettringite and thaumasite had formed during sulfate attack, whereas no formation of gypsum was detected. However, in the samples treated with a highly concentrated sodium sulfate solution, serious amounts of gypsum were present in the form of veins and layers below the surface. The first 2-3 mm of the samples were strongly altered by sulfate attack exhibiting expansion and microcracking in combination with a formation of gypsum and ettringite. The observed features are in agreement with other investigations by SEM [11-12]. Figure 2 shows gypsum crystals that have been formed below the surface of the mortar bar that was stored in highly concentrated sodium sulfate solution.

The expansion of mortar bars exposed to highly concentrated sulfate solutions is given in Figure 4. Sodium sulfate solution is compared to water and a solution containing simultaneously sodium sulfate and sodium hydroxide. The investigations by SEM and XRD revealed that gypsum was present in the mortar bars stored in sodium sulfate solution whereas this mineral was not detected in samples which were exposed to a solution that contained sodium hydroxide beside sodium sulfate. A micrograph showing the presence of gypsum in a pore is given in Figure 3.

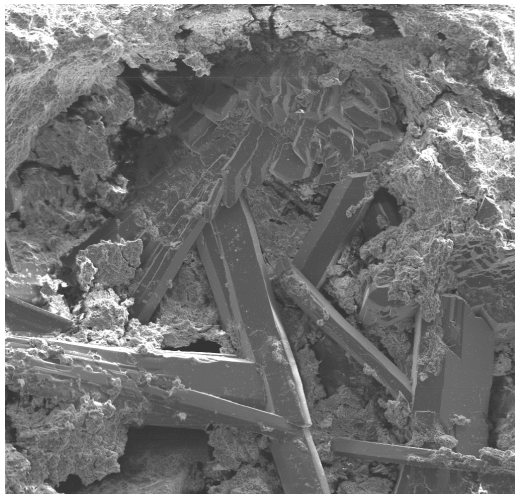


Figure 2: Formation of very large gypsum crystals in a mortar bar made from OPC after storage for one year at  $\text{SO}_4^{2-}=30,000$  mg/l and  $8^\circ\text{C}$

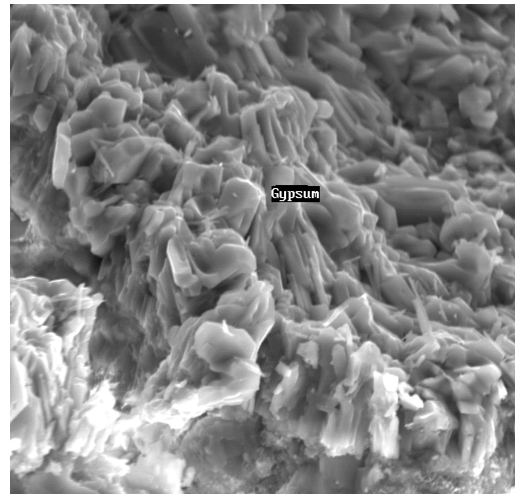


Figure 3: Formation of gypsum in a mortar bar made from SRPC after storage for 34 months at  $\text{SO}_4^{2-}=30,000$  mg/l and  $20^\circ\text{C}$

#### 4. Discussion

Thermodynamic calculations were performed to derive the sulfate ion concentration that is required for the formation of gypsum in mortar bars exposed to sulfate solutions. The results of these calculations are summarized in Figure 1. Inspection of this figure shows that the minimum sulfate ion concentration needed to transform portlandite into gypsum is close to 1500 mg/l. This value refers to a pH value of 12.45 that can be expected when portlandite is dissolved in water. At higher pH values, higher sulfate ion concentrations are required for a reaction of portlandite with sulfate ions to gypsum. Up to a pH value of 12.7, the minimum sulfate ion concentration increases rather slowly to about 6000 mg/l. Beyond that value, it rises very strongly. Figure 1 indicates that a reaction of portlandite with sulfate ions to gypsum is not possible in solutions with pH values higher than approximately 12.8. If potassium ions are present in solution, the formation of syngenite may proceed at pH-values higher than 12.8.

The pore solution of hardened cement paste usually has a very high pH-value. Due to the presence of portlandite, it can not be lower than 12.45 at 25°C. Alkali and hydroxide ions are responsible for a further rise of the pH value. In hardened cement paste, the pH value is about 13.0-14.0. Therefore, the formation of gypsum should be prevented by the high alkalinity of the pore solution (Figure 1). This situation is changed when the concrete is exposed to sulfate attack. In most cases, the attacking

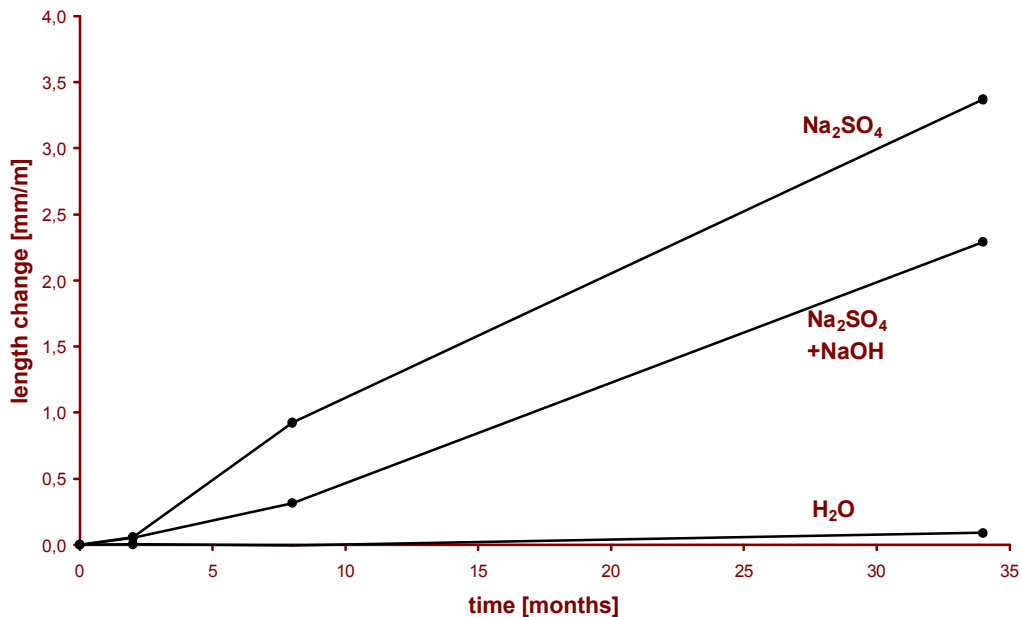


Figure 4: Expansion of mortar bars exposed to different aggressive

solutions (each point is an average obtained on three samples)

solution is neutral. Due to transport processes between the hardened cement paste and the attacking solution, sulfate ions will penetrate the concrete, whereas alkali ions and hydroxide ions will diffuse out of the hardened cement paste into the attacking solution. Thus, the pH in the first millimeters of the exposed surfaces will decrease due to the loss of alkali and hydroxide ions. It can become as low as 12.45. A further decrease is not possible as long as portlandite is present. For this reason, the pH can be found in a region between 12.45 and the original value.

A formation of gypsum can only proceed if there is a supersaturation in the pore solution with respect to this mineral. At moderate sulfate attack involving sulfate ion concentrations up to 1500 mg/l, a formation of gypsum is hardly possible. The sulfate ion concentration is too low to achieve a substantial supersaturation with respect to gypsum. Minor amounts of alkali and hydroxide ions can shift the pH to higher regions and may thus prevent the formation of gypsum. For these reasons, a formation of gypsum is not likely in most field situations where sulfate ion concentrations lower than 3000 mg/l dominate. Only at severe or very severe conditions [13] which can be met in some alkaline soils [5], much higher sulfate ion concentrations are possible. In these rare situations, the formation of gypsum may take place if there is no protection of the concrete by additional measures. In some national guidelines for the production of concrete, such a protection of the material by surface layers or other measures is suggested [14] or even required [15] if the sulfate ion concentration in the aggressive solution is higher than 6000 mg/l or 3000 mg/l, respectively. In conclusion, the formation of gypsum is expected to be rare under most field conditions where moderate sulfate ion concentrations prevail. This has been confirmed by experimental investigations. At sulfate concentrations of 1500 and 3000 mg/l, no formation of gypsum was detected within one year of exposure at 8°C.

However, the situation is different at the high sulfate ion concentrations that are used to accelerate the laboratory investigations of the relative performance of binders during sulfate attack. In these testing procedures [1-4], the sulfate ion concentration is much higher than under most field conditions. The concentrations that are applied are shown in Figure 1 as horizontal lines. It is evident from Figure 1 that there is a high supersaturation with respect to gypsum at a broad range of pH values in mortar bars exposed to conventional test solutions. Therefore, a substantial formation of gypsum can be expected in the sulfate resistance tests. Examinations by SEM have confirmed that gypsum forms at high sulfate ion concentrations. In the present investigation, the sulfate ion concentration was 30,000 mg/l. Other investigations reported in the literature confirm that the formation of gypsum can take place at the high sulfate ion concentrations used in the laboratory test procedures [11-12]. The

formation of gypsum can lead to expansion [16], especially if a high supersaturation with respect to this mineral exists in the pore solution [17].

The formation of gypsum has a significant influence on expansion. In Figure 4, the expansion is recorded for samples undergoing the formation of gypsum in relation to samples in which gypsum cannot be formed because the pH level is too high. A similar observation was reported in [18]. However, it has to be noted that the pH in alkaline solutions is not constant. Hydroxide ions can be replaced by carbonate ions due to ingress of atmospheric carbon dioxide. Therefore, the samples and solutions should be stored in a way to minimize the uptake of carbon dioxide.

## **5. Conclusions**

The here reported investigations have shown that the formation of gypsum can take place during the laboratory tests used to predict the performance of concrete exposed to sulfate attack. In contrast to this, a formation of this mineral is hardly possible under most field conditions where moderate conditions dominate. The sulfate ion concentration is usually much lower than in the sulfate resistance tests and a supersaturation with respect to gypsum is prevented by minor amounts of alkali and hydroxide ions in the pore solution.

The formation of gypsum is an artifact that has an influence on the expansion recorded during the sulfate resistance tests. It can be suppressed by the maintenance of a high pH value in the test solutions.



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