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Influence of sulfate solution concentration on the formation of gypsum in sulfate resistance test specimen

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Abstract

The sulfate concentration, which is required to form gypsum from portlandite, was derived from thermodynamical calculations and experimental measurements. The obtained results were compared to the sulfate concentrations in laboratory solutions that are commonly used to test the performance of concrete exposed to sulfate attack and also to sulfate concentrations that can be expected under field conditions. It was derived that the formation of gypsum can strongly affect the performance of binders in the tests, but has a less marked impact under most field conditions. An SEM investigation of mortar bars that were exposed to different sulfate concentrations supports the suggestion made.

Keywords: Sulfate attack; Gypsum; Thermodynamic calculations; SEM

1. Introduction

Concrete is a material somewhat susceptible to the ingress of sulfate ions from the environment. In most cases, the deterioration caused by sulfate attack is due to the formation of ettringite, thaumasite or gypsum. The precipitation of these minerals is accompanied by spalling, cracking, softening, expansion and various other forms of damage. Several concepts have been suggested to increase the resistance of concrete against sulfate attack. The most recognized ideas among these concepts are the decrease of the porosity (high cement content, low water–cement ratio) and the use of more resistant types of binders (sulfate-resisting Portland cement, addition of pozzolanas and blast furnace slag).

The performance of the aforementioned types of binders under sulfate attack can be investigated by field trials or by exposing test specimens to an aggressive sulfate solution in the laboratory. Since field studies have the disadvantage that many uncontrollable factors (e.g., temperature, humidity) have an impact on the test results, laboratory-scaled investigations are widely used. Usually, the sulfate concentration in the test solutions is much higher than the concentrations that concrete is exposed to under field conditions. These increased sulfate concentrations are chosen in the sulfate resistance tests to accelerate the damaging processes. Otherwise, the investigations would last for an unrealistic period of time.

However, that the advantage of obtaining a test result in a relatively short period of time (when compared to the service life of a structure) is accompanied by changes in the process of deterioration has to be brought into question [1]. The present study contributes to this discussion by investigating the influence of the sulfate concentration in the test solutions on the formation of gypsum in the exposed specimens.

The impact of the formation of gypsum on the performance of cement pastes, mortars and concrete under laboratory-scaled sulfate attack was previously studied. Information about the microstructure of damaged specimens after exposure to a sodium sulfate solution (24,000 mg SO_4^{2-}/l) was provided by Gallop and Taylor [2,3]. Using a scanning electron microscope (SEM), they showed the formation of gypsum layers parallel to the

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surface of the specimens. Cracks were found to be running from this gypsum layers through the microstructure. The authors were unable to find a correlation between the formation of the cracks and the presence of ettringite. Despite some differences in the degree of damage that had occurred, the same feature was present in all binder types used in that study. Cement paste specimens prepared from sulfate-resisting Portland cement were also damaged by the formation of cracks and gypsum layers, as were the ones made from Portland cement.

Tian and Cohen [4] investigated whether the formation of gypsum can cause an expansion. They prepared mortar bars from C_3S with aggregate and also from pure alite. After exposure to a 5% Na_2SO_4 solution, the tested specimens showed a serious expansion. This expansion was attributed to the formation of gypsum that had taken place in the microstructure according to XRD data. The expansion was avoided by the addition of silica fume, as the silica fume consumed the portlandite that had formed from the C_3S/alite hydration. With the depletion of portlandite, the formation of gypsum was suppressed. Tian and Cohen showed that the expansion due to the formation of gypsum can develop very slowly and can be delayed. In the case of the paste made from pure alite (without aggregate), expansion did not start for 12 months.

Apart from gypsum, expansion and microcracking can also be due to the formation of ettringite. This can occur during sulfate attack or by a delayed formation of ettringite (e.g., after heat curing). Since there are many studies on the formation of ettringite, the conditions for the formation of this mineral and the expansion resulting from it are not repeated here. The present study intends to concentrate on the formation of gypsum.

The underlying thermodynamic principles for the expansion resulting from the formation of gypsum and ettringite were demonstrated by Xie Ping and Beaudoin [5]. They calculated under what conditions the growth of crystals of gypsum or ettringite can apply a pressure to the pore walls.

Mehta and Monteiro stated that cements potentially containing little or no calcium hydroxide (precursor of gypsum) perform much better when exposed to sulfate attack than cements high in alite [6]. González and Irassar provided experimental data that supported this [7].

The above-mentioned studies clearly show that the formation of gypsum strongly proceeds during the sulfate resistance experiments performed in the laboratory. They also demonstrate that the formation of gypsum can lead to expansion and cracking. But all studies refer to high sulfate concentrations, which are used to accelerate the tests. The formation of gypsum under field conditions is not fully addressed, because the sulfate concentration from the environment in most cases is much below that used in the laboratories to accelerate the tests. Therefore, the present study was set up to investigate if the sulfate concentration has an impact on the formation of gypsum. This is important, because only a precise knowledge of the factors controlling the formation of gypsum allows the prediction under what field conditions a concrete can be damaged by the formation of this mineral.

2. Experimental

The precipitation of calcium ions (from portlandite) with sulfate ions (from the aggressive environment) as gypsum was investigated by thermodynamic calculations. Also, the influence of the pH on the formation of gypsum was simulated. The results of the calculations were compared to experimental observations. Additionally, mortar bars were exposed to different sulfate concentrations. After 12 months exposure, they were examined by SEM.

For the simulation, activities had to be calculated from ionic concentrations and vice versa. An activity is that part of a measured ionic concentration, which contributes to the formation of minerals, that is in an "active state." The calculation of activity coefficients was performed by using the mathematical framework of the Pitzer equations for solutions high in ionic strength and the appropriate interaction values [8]. Thus, it was possible to calculate the activities of the ionic species from the composition of the solution.

The calculations started at a chosen pH value by computing the corresponding activity of the hydroxide ions from the solubility constant of water ($K_{\text{water}} = 1.00 \times 10^{-14}$ at 25 °C). From the hydroxide activity, the activity of the calcium ions in the pore solution was calculated by using the portlandite equilibrium as stated in Eqs. (1) and (2). The solubility product $K_{\text{portlandite}} = 6.26 \times 10^{-6}$ was derived from thermophysical data [9] for a temperature of 25 °C. The obtained activity of the calcium ions was used to calculate the sulfate activity that is needed to precipitate gypsum according to Eqs. (3) and (4). For gypsum, the solubility product was taken from Møller [10] ($K_{\text{gypsum}} = 3.02 \times 10^{-5}$). Finally, the activity of the sulfate ions was converted to a concentration by using the appropriate activity coefficient. Potassium ions were assumed to maintain the charge balance in the solution. At high potassium concentrations, the formation of syngenite ($K_2SO_4 \cdot CaSO_4 \cdot H_2O$) had to be taken into account (Eqs. (5) and (6)). The solubility product of this mineral ($K_{\text{syngenite}} = 2.72 \times 10^{-8}$) was calculated from the chemical potential cited by Reardon [11]. Absence of magnesium ions was assumed in the calculations.

$$\mathrm{Ca(OH)_2} \rightarrow \mathrm{Ca^{2+}} + 2\ \mathrm{OH^-} \tag{1}$$

$$K_{\text{portlandite}} = \{\mathrm{Ca^{2+}}\} \cdot \{\mathrm{OH^-}\}^2 \tag{2}$$

$$\mathrm{CaSO_4 \cdot 2H_2O} \rightarrow \mathrm{Ca^{2+}} + \mathrm{SO_4^{2-}} + 2\ \mathrm{H_2O} \tag{3}$$

$$K_{\mathrm{gypsum}} = \{\mathrm{Ca}^{2+}\}\cdot\{\mathrm{SO}_4^{2-}\} \quad (4)$$

$$\mathrm{K_2SO_4 \cdot CaSO_4 \cdot H_2O} \rightarrow 2\ \mathrm{K}^+ + \mathrm{Ca}^{2+} + 2\ \mathrm{SO}_4^{2-} + \mathrm{H_2O} \quad (5)$$

$$K_{\mathrm{syngenite}} = \{\mathrm{K}^+\}^2\cdot\{\mathrm{Ca}^{2+}\}\cdot\{\mathrm{SO}_4^{2-}\}^2 \quad (6)$$

After obtaining the sulfate concentration that is required to precipitate gypsum from portlandite at a specific pH, the calculation was repeated for other pH values. In this way, it was possible to model the influence of the pH on the formation of gypsum during sulfate attack.

The results obtained by calculation were corroborated by experimental investigations. For this purpose, 3 g of portlandite and differing amounts of arcanite (K_2SO_4) were dissolved in 40 g water each. The solutions were prepared in a glove box under a nitrogen atmosphere and stored there in sealed plastic tubes. After 11–17 days, the solid phase was separated from the solution by filtration. The residue was dried and analyzed by X-ray diffraction (XRD) in a Siemens D 5000, the solution by inductively coupled plasma–optical emission spectroscopy (ICP-OES) using a Perkin-Elmer Optima 3000. The pH in the solutions was measured by a glass electrode.

The amounts of arcanite that were used in the test series are given in Table 1. With increasing arcanite content, more gypsum (or syngenite) is formed from portlandite as more sulfate is in solution. Following Eq. (7), the sulfate ions in solution are replaced by hydroxide ions, thus increasing the pH of the solution.

$$2\ \mathrm{K}^+ + \mathrm{SO}_4^{2-} + \mathrm{Ca(OH)_2} + 2\ \mathrm{H_2O} \rightarrow 2\ \mathrm{K}^+ + 2\ \mathrm{OH}^- + \mathrm{CaSO_4 \cdot 2H_2O}. \quad (7)$$

Additionally, the equilibrium concentrations in a mixture of portlandite and gypsum were measured.

The impact of the sulfate concentration on the formation of gypsum was further investigated by an SEM examination of mortar bars that were stored in Na_2SO_4 solutions of different concentrations. Since these samples were supplied from a research program on the formation of thaumasite, they had been stored at a temperature different from the temperature used in the thermodynamic calculations.

Table 1
Amounts of arcanite that were mixed with portlandite and water; results of the chemical analysis of the solution after equilibration; sulfate-bearing phase formed during reaction as determined by XRD

Arcanite (g)	Chemical analysis of the solution (mg/l)				XRD
	pH	SO_4^{2-}	K^+	Ca^{2+}	
0.31	12.59	3510	3240	862	Gypsum
0.50	12.64	4580	5120	661	Gypsum
1.01	12.74	9380	10,300	577	Gypsum
1.56	12.79	13,270	14,000	541	Syngenite
2.01	12.87	15,040	16,800	413	Syngenite
2.47	12.98	18,300	21,100	272	Syngenite

The mortar bars for this experimental procedure were made from a Portland cement with the following chemical composition: 63.1% CaO, 20.8% SiO_2, 6.2% Al_2O_3, 2.5% Fe_2O_3, 3.2% SO_3, 0.2% Na_2O, 1.03% K_2O and 1.1% free lime. From this composition, a potential phase distribution was estimated by a modified Bogue calculation [12], yielding 44% alite, 28% belite, 12% aluminate and 6% ferrite. Mortar was prepared from the cement with aggregate (1:3) and water ($w/c = 0.6$). The test specimens ($1 \times 4 \times 16$ cm) were cast and cured after demoulding in water at 20 °C. 14 days after production, they were exposed at 8 °C to Na_2SO_4 solutions containing SO_4^{2-} concentrations of 1500, 3000 and 30,000 mg/l, respectively. To assure a constant sulfate concentration, the aggressive solutions were renewed every 7 days. After 12 months, the mortar bars were investigated by SEM. For the examinations, polished sections and fracture surfaces of the specimens were used. The microscope (Hitachi S 2700-LB) was equipped with an EDX system (Thermo Noran). An acceleration voltage of 15 kV was applied.

3. Results

The results of the calculations and experimental investigations on the impact of the pH on the sulfate concentration, which is needed to convert portlandite to gypsum, are given in Fig. 1. The solid curve was obtained by calculation and the data points refer to the measurements. More detailed information on the latter is given in Table 1. In addition to the obtained results, horizontal lines are drawn in Fig. 1, which indicate the sulfate concentration in common laboratory sulfate resistance tests [13–15]. It can inferred from the data presented in Fig. 1 and Table 1 that portlandite will react to gypsum at a minimal sulfate concentration of approximately 1400 mg/l (pH = 12.45). This is confirmed by the measured equilibrium concentrations in the mixture of gypsum with portlandite and water ($SO_4^{2-} = 1354$ mg/l).

With rising pH, higher concentrations of sulfate ions are needed for the reaction to proceed. Therefore, alkaline pore solutions would prevent the formation of gypsum, if there is no leaching of sodium and potassium ions.

Between pH values of 12.45 and 12.7, the sulfate concentration slowly increases, whereas it rises dramatically from that level on. In solutions where the high pH is due to the presence of potassium ions, the precipitation of syngenite is expected to precede that of gypsum, starting at pH values of approximately 12.8. In solutions in which sodium ions are the counterpart of the hydroxide ions, the precipitation of gypsum can take place until pH values of approximately 12.9. Beyond that mark, a further increase of the sulfate concentration is unable to lead to the formation of gypsum.

An SEM investigation of test specimens that were exposed to different sulfate concentrations showed that there was no gypsum formed at a sulfate concentration of

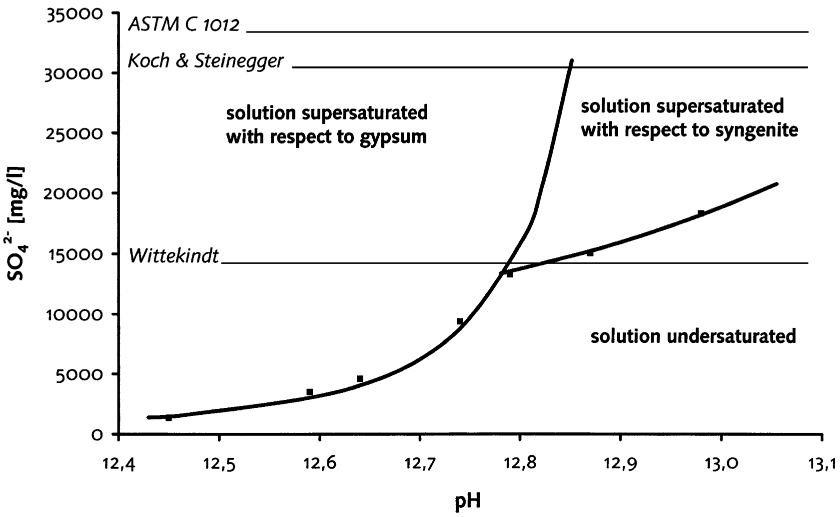

Fig. 1. Sulfate concentration that is required for a reaction of portlandite to gypsum or syngenite, calculations (line) and experimental measurements (dots). Potassium ions were assumed to maintain the charge balance in the solution.

1500 mg/l in the aggressive solution. Instead, ettringite and thaumasite were detected near the surface of the specimens.

Gypsum was also not detected in the microstructure of the mortar bars that were exposed to the higher sulfate concentration of 3000 mg/l.

The specimen treated with a conventional test solution (30,000 mg/l) suffered from microcracking, due to the formation of gypsum and ettringite. The gypsum had formed veins and layers in the first 2 mm beneath the surface of the mortar bars as described by Gallop and Taylor [2,3] for sodium sulfate and magnesium sulfate and also by Bonen and Cohen [18,19] for magnesium sulfate. Fig. 2 shows light appearing gypsum veins, which indicate a strong alteration of the microstructure. In Fig. 3, some portlandite is still present, but has already to some extent been converted to gypsum. The reaction of portlandite to gypsum can lead to an increase in volume and, therefore, to expansion and microcracking [4,5]. Gypsum crystals can grow very large, thus being much larger in size than all other phases present in the paste. Such huge crystals indicate a high supersaturation. Their formation can be a source of damage for the microstructure.

4. Discussion

The sulfate concentration in laboratory test solutions is indicated by horizontal lines in Fig. 1. For a wide range of pH values, the sulfate concentration in the test solutions is much higher than the concentration which is required to precipitate gypsum. For this reason, the formation of gypsum is very likely to proceed in the test specimens.

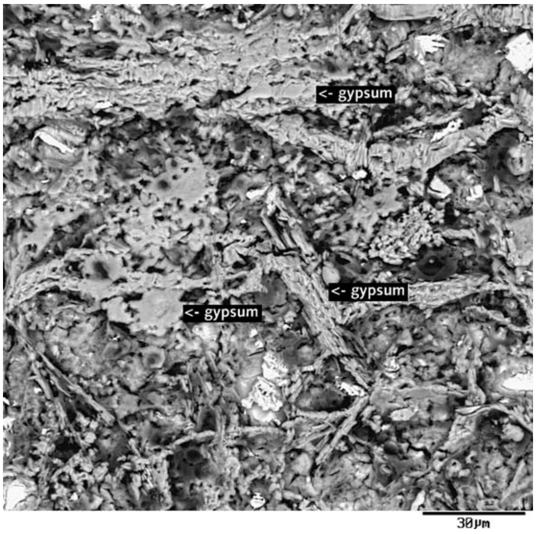

Fig. 2. Gypsum veins in a mortar bar after storage in an aggressive test solution (Na_2SO_4 = 30,000 mg/l).

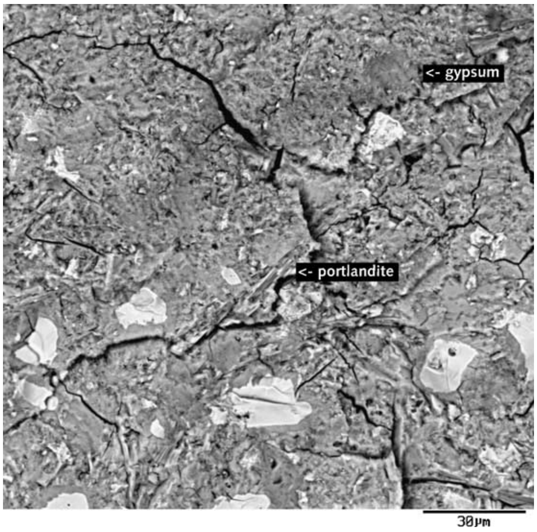

Fig. 3. Microcracks running from a massive deposit of portlandite which has partially been converted to gypsum (Na_2SO_4 = 30,000 mg/l).

Because the commonly applied test solutions are very concentrated, there is a very high supersaturation with respect to gypsum. The resulting high swelling pressure [5] during the growth of the minerals can damage the microstructure and lead to expansion [4].

In contrast to the high sulfate concentrations that the test specimens are exposed to, the sulfate concentrations under field conditions are usually much lower. They even can be restricted to a certain level as some building codes suggest [16] or require [17] the physical protection of a concrete that is exposed to sulfate concentrations higher than 6000 mg/l or 3000 mg/l, respectively.

The results of the present study suggest that at the common moderate concentrations up to 1500–3000 mg/l, the formation of gypsum is either not possible or cannot lead to damage, because supersaturation and swelling pressure are very low. At low sulfate concentrations, already minor amounts of alkali ions in the pore solution can protect the microstructure from the destructive process of the formation of gypsum. This conclusion is supported by the experimental investigation of mortar bars that were exposed to sulfate concentrations of 1500 and 3000 mg/l, because no gypsum was detected in these samples. Instead of gypsum, ettringite and thaumasite had formed. Therefore, a destruction of the mortar bars can only be due to the formation of these two minerals. An increase in the sulfate concentration of the test solution changes the process of damaging, because the expansion of the mortar bars and the formation of cracks therein is not caused by the formation of ettringite alone [2,3].

At higher sulfate concentrations, the formation of gypsum is possible (Fig. 1). The hardened cement paste contains a large amount of portlandite that is usually present in local agglomerates. A transformation of this portlandite into gypsum is accompanied by an increase in volume, as the molar volume of gypsum is higher than that of portlandite. This excess volume is unable to fill capillary pores, because the growing gypsum crystals are much larger than the pores. Thus, the conversion of portlandite to gypsum at high sulfate concentrations can lead to expansion and microcracking.

The formation of ettringite can proceed under field conditions with moderate sulfate attack and also in the highly concentrated test solutions. But AFm, the precursor of ettringite, does not form local agglomerates as large and dense as portlandite does. Also, AFm is present only in a minor amount when compared to portlandite.

With regard to ettringite, the commonly applied laboratory tests appear to represent the damage occurring under field conditions, but this seems not to be the case for gypsum. The conversion of portlandite to gypsum leads to expansion and microcracking of the mortar bars in the test solutions. Since the formation of gypsum is rare under most field conditions, the performance of concrete under field conditions is not accurately assessed in the laboratory tests.

Laboratory experiments have established that the addition of pulverized fly ash (pfa) increases the sulfate resistance of concrete. During the pozzolanic reaction of the pfa, C–S–H phases are formed from portlandite with the silicon dioxide from the pfa glass. This makes the concrete more dense and it is more difficult for the sulfate ions to penetrate the structure. Furthermore, the consumption of portlandite by the pozzolanic reaction prevents the formation of gypsum, because no calcium hydroxide is available for a formation of gypsum during the sulfate resistance tests.

This behavior might not have such a strong impact on the sulfate resistance of concrete under field conditions. It is commonly agreed upon that the addition of pfa makes the concrete more dense and, therefore, hinders penetration by sulfate ions. However, the chemical resistance might not be that much improved, as the laboratory investigations have suggested. This is because the prevention of the formation of gypsum does not play as strong of a role under field conditions and the sulfate concentration from the environment is in most cases too low to allow the damaging formation of gypsum. Furthermore, it should not be overlooked that pfa contains a large amount of reactive aluminum and that binders with an increased Al_2O_3 content can be more susceptible to the formation of ettringite. Therefore, it seems to be reasonable to the present authors to discuss if the improved resistance of pfa concrete under field conditions is in the first line due to an enhancement of their physical rather than their chemical properties.

5. Conclusions

The performance of concrete subjected to sulfate attack is affected by the formation of ettringite, gypsum and thaumasite.

The present study shows that test specimens are damaged in laboratory-scaled experiments by the formation of gypsum, whereas the mineral only rarely forms under field conditions. A precipitation of gypsum under field conditions requires a very strong, almost complete loss of the alkali ions from the pore solution by diffusing out of the concrete. The microcracking in the investigated test samples, which leads to an enhanced ingress of sulfate ions and thus accelerates the disintegration, can at least partly be attributed to the formation of gypsum. Therefore, the performance of concrete under field conditions might be significantly different from that suggested by laboratory tests. The kind of destructive process in the highly concentrated sulfate solutions can be different from that under field conditions because it is governed by the precipitation of gypsum and ettringite and far more aggressive than the mere formation of ettringite. Results obtained in the laboratories refer rather to the rarely occurring “very severe conditions” [6] in alkali soils [20] than to the very common "moderate/severe" conditions.

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