



Investigation of the Precipitates on the Concrete Surface due to Sulphate Exposure

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Abstract

The aim of this study is to investigate the durability of cement-based materials subjected to the effects of sulphuric acid in terms of surface deterioration. Damaged concrete surfaces and the samples' mass changes were studied during 270-day simulation of both chemical and biological attacks. Chemical corrosion was simulated by sulphuric acid with pH of 3.0 and 4.0, respectively, while biological corrosion was simulated by activity of bacteria *Acidithiobacillus thiooxidans*. XRD and SEM analyses confirmed a massive sulphate precipitate formation on the concrete surface due to chemical and biological sulphate corrosion.

Key words: concrete, precipitates, deterioration

1 Introduction

Deleterious changes that occur in cementitious materials as a consequence of the chemical interactions between hydrated cement paste and sulphate ions are known as sulphate attack [1]. Sulphate attack can be external - due to penetration of sulphates in solution, in groundwater for example, into the concrete from outside or internal - due to a soluble source being incorporated into the concrete at the time of mixing, gypsum in the aggregate, for example. Sulphate attack can lead to formation of ettringite ($3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 3\text{CaSO}_4\cdot 31\text{H}_2\text{O}$), gypsum ($\text{CaSO}_4\cdot 2\text{H}_2\text{O}$), basanite ($\text{CaSO}_4\cdot 0.5\text{H}_2\text{O}$) which results in expansive degradation of the concrete.

The chemical reaction of this neutralization phenomenon with sulphuric acid is given by Zivica and Bajza [2] as in Equations (1) and (2) resulting in internal pressures, formation of cracks and eventually, the loss of strength [3]. Consequently, the concrete becomes more vulnerable to aggressive exposure [4].



Second type of sulphate attack is formation of thaumasite ($\text{CaSiO}_3 \cdot \text{CaCO}_3 \cdot \text{CaSO}_4 \cdot 15\text{H}_2\text{O}$), which is calcium-silicate-sulphate-carbonate hydrate that possesses no capacity for binding the aggregate particles together [5] and can be form in concrete by reaction of the calcium-silicate hydrates (C-S-H) with sulphates in the presence of carbonate ions [6]

2 Material and methods

This study analyzed mass and surface changes of cement-based materials exposed to sulphate environments.

2.1 Concrete composite samples

Mixture of concrete (A) using cement CEM I 42.5 N was used for the preparation of concrete samples. The composition of this mixture was proposed considering its utilization in a moderately aggressive chemical environment, exposure class XA2. The quality of concrete, particularly its strength and durability, strongly depend on the water content. Therefore, in EN 206-1 [7], recommendations in terms of water-cement ratio (w/c) and strength class are given for each environmental exposure. Mixture A was designed to meet the requirement of at least C30/37 concrete strength class and a maximum of 0.5 water-cement ratio (w/c) in accordance with EN 206-1. The proportions for concrete mixture are reported in Table 1.

Table 1: The proportions of concrete mixture for 1 m³ in (kg).

Components	A
Cement	360
Water	170
Aggregates, fraction 0/4 mm	825
Aggregates, fraction 4/8 mm	235
Aggregates, fraction 8/16 mm	740
Plasticizer	3.1

Standardized concrete prisms measuring 100 x 100 x 400 mm were cured for 28 days in a water environment prior to testing the required mechanical parameters. The concrete samples met the recommended criteria for exposure class XA2 with a w/c ratio of 0.47 and compressive strength of 41.18 MPa for concrete samples. The bulk density of concrete samples measured 2350 kg/m³. Subsequently, the concrete prisms were cut into small prisms measuring 50 x 50 x 10 mm for corrosion testing. The test specimens were slightly brushed in order to remove polluting particles, sterilized in 70% ethanol for 24 hours and dried at 80°C to a constant mass before use in the experiments, thus simulating chemical and biological corrosion.

2.2 Chemical corrosion simulation

The concrete samples were exposed to H₂SO₄ solutions in order to simulate an acidic and sulphate chemical corrosion:

- H₂SO₄ (0.005 wt. %) with a pH of 3.0 (sample A1),
- H₂SO₄ (0.0005 wt.%) with a pH of 4.0 (sample A2).

The concentration of liquid media was based on the standards for concrete corrosion resistance testing. The volume ratio of the concrete sample and liquid phase S/L was set at 1:10 at the beginning of the experiment. The exposition of the concrete sample proceeded over a period of 270 days at a temperature of 23°C. The pH value of H₂SO₄ solutions was kept at a constant level of 3.0 and 4.0, respectively.

2.3 Microbial corrosion simulation

The prepared concrete sample was exposed to:

- diluted medium of activated bacteria (sample A3).

The diluted medium was prepared by dilution of the concentrated medium consisted of bacteria *Acidithiobacillus thiooxidans* inoculum (20 vol. %) and a Waksman and Joffe nutrient medium with a pH 4.0 (80 vol. %) with deionized water (1:1). The volume ratio of solid sample to liquid phase S/L was set similarly to 1:10 as was done for the chemical corrosion experiments. Experiments were carried out in covered glass jars in an aerobic atmosphere at a controlled temperature of 23 °C using a liquid medium with bacteria *Acidithiobacillus thiooxidans*. The pH value of media was kept at an optimal level of 4.0. Bacterial culture was inoculated at 7-day intervals over a period of 270 days.

2.3.1 Microorganisms

The bacterial culture of sulphur-oxidizing bacteria – *Acidithiobacillus thiooxidans*, used in the experiments, was isolated from acid mine drainage (Pech shaft, in the locality of Smolnik, Eastern Slovakia). The composition of the selective nutrient medium by Waksman and Joffe (pH 4.0) used for the preparation of the active bacterial culture as well as for the isolation and cultivation of bacteria is described in Table 2 [8].

Table 2: The selective nutrient medium by Waksman and Joffe

Chemical compound	Amount
CaCl ₂ ·6H ₂ O	0.25 g/L
(NH ₄) ₂ SO ₄	0.2 g/L
K ₂ HPO ₄	3.0 g/L
MgSO ₄ ·7H ₂ O	0.5 g/L
FeSO ₄ ·7H ₂ O	Trace amount
S ^o	10.0 g/L
Deionized water	Up to 1000 mL

2.4 Analytical methods

The performance of the samples was monitored using the visual observations assessment of concrete samples made on a 90-day basis by removing the samples from the solutions and photographing them. Particular note was made of any spalling and precipitation of any materials. The change in concrete sample mass was measured as the difference between the original mass and the final mass after the experiment. The precipitates on the surface of concrete samples after the experiments were investigated with the aid of scanning electron microscopy (SEM/EDX), infrared spectroscopy (FTIR) and X-ray powder diffraction (XRD).

XRD experiments were performed using a D2 PHASER diffraction meter (Bruker, Germany) using Cu K α radiation generated at 10 mA and 30 kV. All scans were performed on powdered samples. Scan conditions were identical for all samples with a ramp rate of 0.04° over the range 2 θ from 10 to 90°.

The infrared spectroscopy analysis was performed using spectrometer Alpha FTIR with module ATR (Bruker Optics, Germany) alongside XRD, using the same powder samples. Measurement of surface precipitations in powder form was realized in transmittance mode in interval 400 – 4000 cm⁻¹ with 4 cm⁻¹ resolution.

Changes in microstructure of concrete samples provide evidence about the nature of reactions and deterioration mechanisms and any changes in composition reflect the chemical interactions between the aggressive ions in solution with cement paste. The SEM studies were performed using an SEM Tescan MIRA3 FE microscope equipped with an energy dispersive X-ray microanalysis system (EDX – Oxford Instruments). The sample was placed on an adhesive carbon slice and carbon coated.

3 Results

3.1 Changes in mass

The results of mass changes of analyzed concrete samples before and after the experiments are given in Table 3.

Table 3: Changes in mass after the 270-day experiment of chemical and biological corrosion

Liquid medium	Sample	Before the experiment [g]	After the 270-day experiment [g]	Mass change [%]
H ₂ SO ₄ pH 3	A1	69.61	68.1	-2.17
H ₂ SO ₄ pH 4	A2	69.81	69.28	-0.76
diluted medium of bacteria	A3	74.73	75.76	+1.378

A decrease in mass (-2.17 and -0.76 %) was noticed for concrete specimens A1 and A2 after 270 days of the chemical corrosion experiments. The increase in mass as a result of the formation of precipitations on the surfaces of the samples was detected for sample A3 after the bacterial exposure as can be seen in Table 3.

3.2 Visual observations assessment

The assessment was made in terms of surface changes (cracking, swelling, spalling, and precipitation). Surface changes of sample A1 and A2 are illustrated in Fig. 1 and Fig. 2.

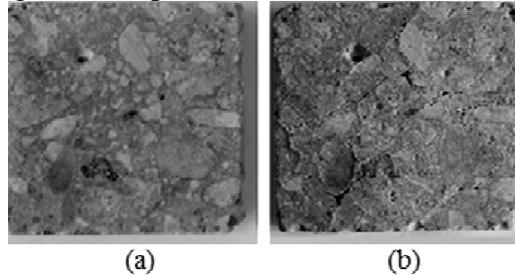


Figure 1: Concrete sample A1 in sulphuric acid with pH of 3.0: (a) before and (b) after the 270-day experiment

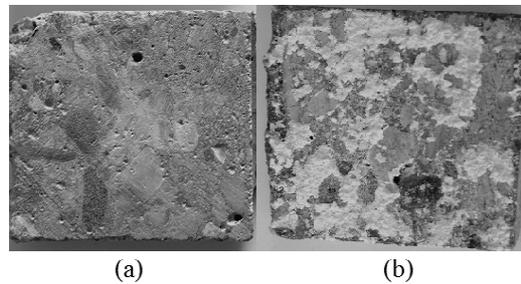


Figure 2: Concrete sample A2 in sulphuric acid with pH of 4.0: (a) before and (b) after the 270-day experiment

The first sign of damage of sample A1 was detected within 90 days of immersion in sulphuric acid with pH of 3.0 characterized by formation of microcracks of concrete sample, whereas sample A2 stored in sulphuric acid with pH of 4.0 suffered attack by surface precipitation (Fig. 2).

Surface changes of sample after biological corrosion are illustrated in Figure 3.

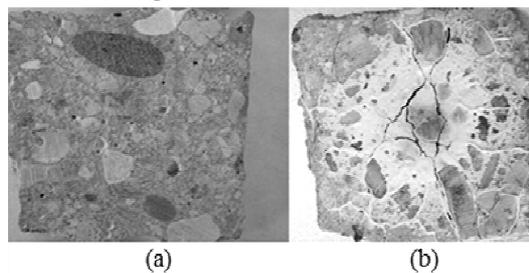


Figure 3: Concrete sample A3 in diluted medium of activated bacteria: (a) before and (b) after the 270-day experiment

The highest extent of damage characterized by forming extensive white crystalline compounds on the surface was observed for A3 sample under bacterial exposition (Fig. 3), therefore the surface compounds analysis was focused on A3 sample.

3.3 Surface compounds analysis

The precipitates of concrete sample A3 exposed to diluted bacterial medium with a pH of 4.0 were also analyzed using SEM and EDX. The SEM micrograph of surface precipitates is illustrated in Figure 4.

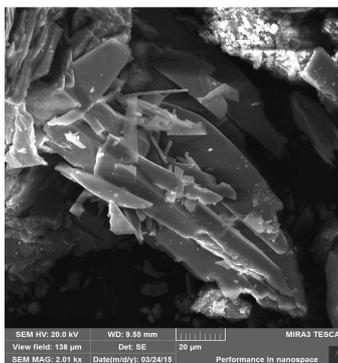


Figure 4: SEM micrograph of surface compounds of A3 sample in diluted medium of activated bacteria

The precipitates observed were analyzed by EDX in order to confirm the presence of calcium and silicon compounds. The presence of 18.9 wt. % of Ca, 15.9 wt. % of S, 60.7 wt. % of O and 4.0 wt. % of S in the surface compounds was confirmed. Based on the EDX analysis, the presence of thaumasite ($\text{CaSiO}_3 \cdot \text{CaCO}_3 \cdot \text{CaSO}_4 \cdot 15\text{H}_2\text{O}$), gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) or basanite ($\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$) can be assumed to be acting on the concrete surfaces.

The IR spectra of surface precipitates confirmed the presence of sulphates as shown in Fig. 5. Peaks at around 600 cm^{-1} , 670 cm^{-1} and 1100 cm^{-1} are indicative of SO_4^{2-} groups, which belong to sulfate phases such as thaumasite, ettringite and gypsum [9].

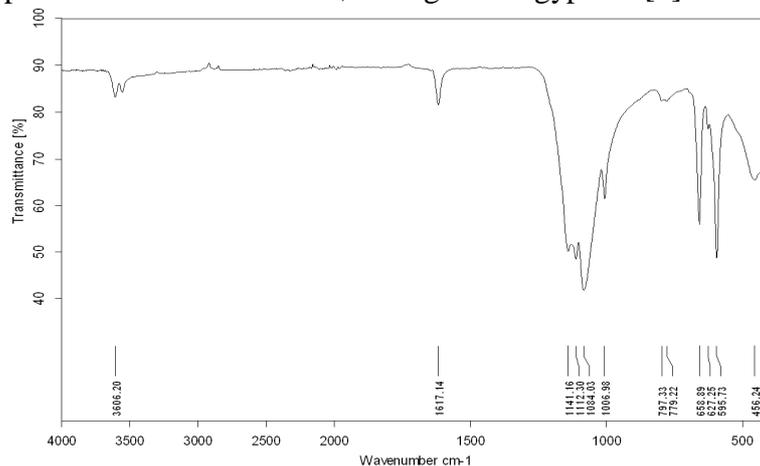


Figure 5: IR spectra of surface precipitates

The precipitation of newly formed compounds containing calcium and silicon on the concrete surfaces was observed also using XRD. The XRD diffractogram of new-formed material collected from surface of sample is shown in Fig. 6.

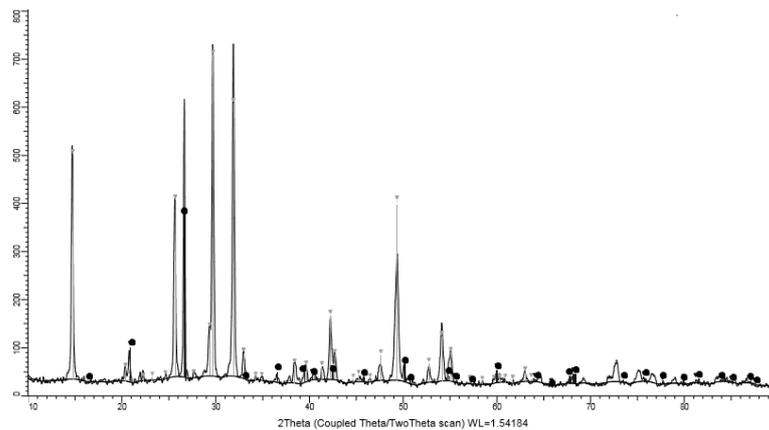


Figure 6: XRD diffraktogram of the surface precipitates

The peak position of the general reaction products according to published literature are as follow (Table 4) [9, 10]:

Table 4: The peak position of the general reaction products

Calcite	29.4° 2θ
Portlandite	18.0; 34.0° 2θ
Aragonite	26.3° 2θ
Quartz	26.5° 2θ
Gypsum	11.6° 2θ
Brucite	18.5; 38.0° 2θ
Ettringite	9.0; 15.8; 18.9° 2θ
Thaumasite	9.2; 16.0; 19.4° 2θ

Traces of gypsum and quartz on the surface of concrete samples were confirmed by XRD analysis (Fig. 6).

4 Conclusion

The results obtained from this study indicate the complexity of the chemical interactions of sulphates. The mass and surface changes were of interest. The major findings can be drawn from the obtained results:

- the decrease in mass was noticed for concrete samples A1 and A2 after the 270 days of chemical corrosion experiments,
- the increase in mass as a result of the formation of precipitations on the surfaces of the samples was detected for sample A3 after the bacterial exposure,
- a presence of sulphate-based compounds on the samples' surfaces was confirmed by XRD, SEM and FTIR,
- microbiological attack precipitated by *Acidithiobacillus thiooxidans* was more dangerous, in terms of the surface deterioration, than chemical sulphate attack.

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