Improving the Resistance of Cement-Based Composites to Sulphur Dioxide

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Abstract. The paper describes an investigation into the influence of a crystalline additive on the sulphur dioxide resistance of cement-based composites. Cement mortars made with the assistance of secondary crystallization were exposed to an aggressive environment and tested for ways how the crystalline additive (CA) influences their degradation. The results indicate that the crystalline additive improved the resistance of the cement-based composites to sulphur dioxide attack.

1. Introduction
Cement-based composites, which are materials with an alkaline matrix, are vulnerable to corrosive attack. Corrosive gases of acidic character are a common corrosive medium for all types of concrete structures. Most of these corrosive gases are product of industrial pollution [1]. Industrial combustion of fuel with a high sulphur content in generates oxidized sulphur compounds (SOx) [2]. SO2, produced by fuel or gasoline combustion, appears to be one of the most corrosive atmospheric pollutants [3]. The deteriorative effect of sulphur dioxide on concrete is called sulphation [1]. The impact of sulphur dioxide (SO2) exposure on cement-based composites was described by Matousek and Drochytka [4] and is shown in Figure 1.

The reaction of SO2, water, sulphurous acid and sulphuric acid with free Ca(OH)2, CaO, dicalcium silicate (2CaO·SiO2) and tricalcium aluminate (3CaO·Al2O3) forms crystals or precipitates in the concrete matrix with a volume of 5 – 30 times greater than the initial volume of these crystals [2]. The increase in the volume of the crystals increases internal pressure and eventually causes the loss of strength and loss of compactness.

One of the progressive technologies for protecting cement-based composites against aggressive environments is the use of coatings, sprays or additives known as “secondary crystallization” or “crystalline technology” [5]. Laboratory studies [6] have shown that CA as additives contribute to crack healing.

The study [7] confirmed an improvement in the resistance of cement-based mortars containing CA against cyclic freezing as well as gaseous CO2. An important parameter that influences the effectiveness of the crystalline additive is the curing conditions during the first 28 days of ageing. The research [8] was focused on defining optimum curing conditions. The results showed that the best curing conditions for mortars containing CA are 95 % relative humidity and a temperature of 23 °C. The addition of
Polypropylene fibres can be harmful to the porosity of hardened mortars, while a higher CA content, i.e. 1.5%, can bring about a reduction in the porosity of mortars exposed to aggressive environments. The research [9] confirmed the positive influence of a crystalline additive on the porosity of mortars containing polypropylene fibres as well as on the values of compressive strength after exposure to aggressive environments: sulphate solution (concentration of 36 000 mg·L\(^{-1}\) of SO\(_4^{2-}\)), ammonium chloride solution (concentration of 3 000 mg·L\(^{-1}\) of NH\(_4^+\)) and gaseous CO\(_2\) at the concentration of φ 65% and 75% relative humidity.

![Chemical reactions diagram](image)

**Figure 1.** A simplified diagram: final products of concrete sulphation and carbonation [4].

2. **Experiment**

The goal of this experiment was to investigate the influence of a crystalline additive (CA) on the resistance of cementitious composites to gaseous SO\(_2\). Mortar specimens were made with the dimensions of 40×40×160 mm and were tested for physical-mechanical properties and examined to study their microstructure.

Table 1 shows the composition of the mixtures. Six sets of samples were prepared with Portland cement CEM I 42.5 R as binder, crystalline additive, quartz sand and polypropylene fibres. Crystalline additive was added in an amount of 0.5 and 1.5% of cement weight, see Table 1.

| Mixture ID | OPC [g] | Sand [g] | CA [g] | PP Fibres [g] | Water/Cement ratio |
|------------|---------|----------|--------|---------------|-------------------|
| S/I        | –       | –        | –      | –             | 0.5               |
| S/II       |         | 2.25     | –      | –             | 0.5               |
| S/III      | 450     | 1350     | 6.75   | –             | 0.5               |
| SF/I       | –       | –        | 0.9    | –             | 0.5               |
| SF/II      | 2.25    | 0.9      | 0.5    |               |                   |
| SF/III     | 6.75    | 0.9      | 0.5    |               |                   |
All the specimens were stored for 28 days at a temperature of 23 °C and relative humidity of 95 %, and subsequently exposed for 90 days to the following 18 cycles: 96 hours at a temperature of 40 °C in gaseous SO$_2$ at the concentration of $\varphi = 2.2$ % and saturated water vapour in a corrosion chamber and then for 24 hours at a temperature of 23 °C and relative humidity of 50 %.

XRD analysis was performed using a Panalytical EMPYREAN and SEM imaging using a TESCAN MIRA3 XMU.

3. Results and Discussion
The results of compressive and flexural strength tests performed at an age of 118 days (28 + 90) are shown in Figure 2 and 3. The compressive strength of mortars aged at a temperature of 23 °C and relative humidity of 95 % and tested after 18 SO$_2$ cycles does not show a marked difference, see Figure 2. Flexural strength increases mainly in mortars containing 1.5 % of CA.

![Figure 2. Determination of 118-day compressive strength.](image1)

![Figure 3. Determination of 118-day flexural strength.](image2)
Once the 18 SO₂ cycles were completed, samples of material located 1 cm beneath the specimen surface were taken and analysed by XRD, see Figure 4 and 5.

**Figure 4.** XRD record of mixture S/I (without CA) after 18 SO₂ cycles: SiO₂ (blue), Ca(OH)₂ (green), CaSO₄·½H₂O (violet), C₃S (yellow).

**Figure 5.** XRD record of mixture S/III (with 1.5 % of CA) after 18 SO₂ cycles: SiO₂ (blue), Ca(OH)₂ (green).

XRD analysis identified calcium sulphate hemihydrate (CaSO₄·½H₂O) in mixture S/I (without CA).

**Figure 6.** Surface detail of mixture S/I (without CA) after 18 SO₂ cycles.

**Figure 7.** Surface detail of mixture S/III (with CA) after 18 SO₂ cycles.

Figure 6–7 show a detail of the surface of samples subjected to 18 SO₂ cycles. While sample S/I (without CA) suffered corrosion to the depth of 3 mm, sample S/III (with 1.5 % of CA) corroded down to 0.3 mm. Sample S/I had its surface layer removed and analysed by XRD, which identified calcium sulphate hemihydrate (CaSO₄·½H₂O) and calcium sulphate (CaSO₄).

Figure 8–11 show differences in the microstructure of samples S/I and S/III exposed to 18 SO₂ cycles. Authors [10] demonstrated that SO₂ is rapidly absorbed into the concrete surface, forming sulphate and sulphite species. Our study has found that the surface of samples exposed to 18 SO₂ cycles shows two sulphate formations: calcium sulphate hemihydrate (CaSO₄·½H₂O) and calcium sulphate (CaSO₄). The chemical corrosion mechanism of SO₂ occurring in cementitious composites was described before [11]. This process begins first with the transformation of oxidized sulphur compounds in sulphurous acid (H₂SO₃) and sulphuric acid (H₂SO₄), as follows [11]:

\[
SO_2 (g) + H_2O (aq) \rightleftharpoons H_2SO_3 (aq) \\
H_2SO_3 + \frac{1}{2}O_2 \rightarrow H_2SO_4
\]
Figure 8. Picture of mixture S/I (without CA) after 18 SO₂ cycles.

Figure 9. Detail of newly formed (CaSO₄·½H₂O) crystals.

Figure 10. Picture of the surface of mixture S/I (without CA) after 18 SO₂ cycles.

Figure 11. Detail of newly formed (CaSO₄·½H₂O) crystals on the surface.

The reactions of SO₂, water, H₂SO₃ and H₂SO₄ with calcium hydroxide (Ca(OH)₂), calcium oxide (CaO), dicalcium silicate (2CaO·SiO₂), and tricalcium aluminate (3CaO·Al₂O₃) are forming crystals or precipitates [11]. Newly forming crystals such as corrosion products tend to have a large volume than the original compounds, which causes substantial crystalline pressure inside the cement matrix resulting in damage. One of these corrosion products is calcium sulphate dihydrate (CaSO₄·2H₂O), which is a calcium slat with a crystallization pressure of 28.2 MPa. The sample without a crystalline additive examined herein contained calcium sulphate hemihydrate (CaSO₄·½H₂O). Calcium sulphate hemihydrate (CaSO₄·½H₂O) reacts by the following reaction:

$$2(CaSO_4 \cdot \frac{1}{2}H_2O) + 3H_2O \rightarrow 2(CaSO_4 \cdot 2H_2O)$$

(3)
Another possible product is monosulphate (3CaO·Al₂O₃·3CaSO₄·12H₂O) and ettringite (3CaO·Al₂O₃·3CaSO₄·32H₂O). Monosulphate and ettringite, much like calcium sulphate dihydrate (CaSO₄·2H₂O) are corrosion products with a larger volume and thus present a risk of increased internal pressure within the cement matrix, which causes cracking, deformation and loss of strength.

Calcium sulphate hemihydrate (CaSO₄·½H₂O) was found on the surface of samples subjected to 18 SO₂ cycles. Samples containing CA suffered 90 % less severe corrosion than samples without CA. XRD analysis (of material located 1 cm beneath the specimen surface) identified calcium sulphate hemihydrate (CaSO₄·½H₂O) only in mixture S/I, which contained no CA.

4. Conclusion

The experiments confirmed that the SO₂ resistance of cementitious mortars can be improved by the addition of a crystalline additive. Concerning strength, the flexural strength of mortars containing the crystalline additive increased. No influence on compressive strength was confirmed. However, the study of microstructure showed an improvement in the SO₂ resistance of the mortar containing the crystalline additive.

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