Effect of sulphate corrosion on the durability of air-entrained cement mortars

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Abstract. Sulphate corrosion is a complex sequence of chemical and physical processes that, when the aqueous sulphate solutions are exposed for a sufficiently long time, irreversibly destroys the microstructure of cement paste. In order to determine the durability of Portland cement mortars, mortar resistance tests were carried out on a 5% solution of sodium sulphate by measuring linear deformations. The tests included 1 series of non air-entrained mortars and 3 series of air-entrained mortars with air content: 7%, 10% and 13%. The biggest deformations were observed for non air-entrained samples, the smallest for mortar with an air content of 13%. Compressive strength tests of mortars after 28 days and 80 weeks of residence in a solution of sodium sulphate were also carried out. For all mortars, the strength measured after 80 weeks immersion in Na_2SO_4 increased in relation to the strength after 28 days of maturation. Observations of the cement mortar microstructure using a scanning electron microscope (SEM-EDS) showed that ettringite was present in both the C-S-H structure and the air pores. By means of XRD analysis, the occurrence of crystalline materials was detected. Based on the research, it was found that air-entrained cement mortars showed greater durability in the context of sulphate corrosion.

1 Introduction

The durability of the building material, including cement composites (concrete, mortar, paste), is most often referred to as the ability to preserve the original properties of the material throughout the assumed lifetime, without significantly reducing the usefulness and without the need for excessive maintenance [1]. Cement composites are exposed to many destructive factors, which may be chemical, physical or mechanical. Corrosion is thus defined as the destructive impact of various environments on the material. There are two types of concrete corrosion: internal, the cause of which are the components of the concrete itself and the external one, at which concrete is exposed to adverse external factors [2]. The term sulphate corrosion is understood as destroying cement composites, which is caused by the physicochemical interaction of aqueous sulphate solutions with cement hydration products [3]. Sulphate corrosion is associated with the emergence of new minerals (gypsum, ettringite) through chemical reactions. They can increase in volume and cause the expansion of cement paste. The dissolution of portlandite and the decalcification of the

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basic phase of hydrated calcium silicates also take place in the corrosion process [4]. The mechanism of sulphate corrosion has been studied for many years and is the subject of many hypotheses. Concepts of recent decades assume that expansion is caused by the additional volume generated by ettringite. However, the lack of research determining the relationship between the amount of ettringite formed and the size of the expansion and the origin of the necessary stress expansion, led to the assumption that the formation of ettringite, although necessary, is insufficient to create expansion. Ping and others [5] found that the reason for the expansion is the crystallization pressure, which is caused by the formation of ettringite from a supersaturated solution in small pores. This theory was also the subject of the Scrivener study [6], which is of the opinion that expansion is not dependent on the amount of ettringite formed, but on where it is created. The expansion involves the conversion of monosulphate, which in the form of crystals is incorporated into the C-S-H phase, in ettringite. At the beginning, the sulfate reacts with the hydrated aluminates in large pores. The result of this reaction is ettringite, but without expansion. If the freely available aluminate reacts, the concentration of SO_4^{2-} ions in the pore solution increases and the solution may be supersaturated in relation to ettringite. Then, if the monosulphate and gypsum are locally in the same place, the formation of ettringite inside the small pores of the structure can induce expansive forces due to the crystallization pressure generated [7].

Air entrainment consists in creating air bubbles with dimensions of about 0.01 - 0.20 mm, their uniform distribution (from 0.15 to 0.20 mm from each other) in the volume of grout and, what is very important, obtaining adequate stabilization (shape and place). Many positive of air entrainment effects are known. First of all, the frost resistance of cementitious composites is improved. In addition, air entrainment improves the viscosity and workability of the mix, reduces sedimentation and plastic shrinkage of the concrete [8]. In the context of chemical aggression, attention should be paid to changes in the microstructure of cement paste resulting from air entrainment, e.g. on the phase composition of the pore shells, the bladder-leaven transition layer and on the slurry occurring around the air gap. Changes around air voids are due to the presence of a paste containing a much smaller amount of cement, and a larger amount of water. It seems that there is a transition zone between the air layer and cement paste. [9]. The average width of this transition zone is 10-15 μm and has a significantly higher porosity than the surrounding cement paste. The air bubble has a coating on the surface of 1-5 μm , which consists of small mineral particles [10]. Air void shell consists of C-S-H with a different morphology than cement paste. In addition, there is also a small amount of ettringite needles on the surface of the air void. Air void shell itself has a higher density than the leaven around the air void. The ratio of calcium to silicon in air void is about 1.1, while in cement paste it is shaped at 1.5 [11]. Air entrainment can increase diffusivity and gas permeability even 2-3 times. This is due to the greater porosity in the vicinity of the air void shell [12]. However, this may suggest greater permeability and easy access of aqueous solutions in air entrained cement composites. Air voids may be a place for the precipitation of sulphate corrosion products, resulting in less damage to the cement paste [13]. Therefore, the significant influence of air entrainment on the sulphate expansion of cement mortars is likely.

2 Materials and methods

All tests were carried out on mortars made of Portland cement CEM I 42.5, natural aggregate (sand), tap water and air entrained admixture. The weight ratio of cement constituents: sand: water was constant and was 1: 3: 0.6. Water to cement ratio for standard mortars is 0.5. A higher water to cement ratio was adopted for the tests, because such

mortars are subject to faster destruction and deformation can be observed earlier. The research was aimed at preliminary identification of the topic. Subsequent tests will be carried out on the water to cement ratio according to the standard. The amount of air entrained admixture was determined on the basis of own tests and manufacturer's recommendations. The tests included 1 series of non-air entrained mortars (nAE) and 3 series of air entrained mortars (AE) with assumed air contents in the following ranges: 6-9%, 9-12% and over 13%. Finally, the amount of air in the air entrained series of mortars was: 7%, 10% and 13%. All series of mortars were made according to a unified procedure of dosing, mixing and forming of samples.

Studies of fresh mortars included determination of density of cement mortar, consistency according to PN-EN 1015-3: 2000 [14], as well as air content by pressure method according to PN-EN 12350-7: 2011 [15]. Immediately after the preparation of the mortar, the bars were formed, which were disassembled after 24 hours. Then they were placed in water at a temperature of 20 ± 1 ° C, on the grates, which ensured free access of water to the entire surface of the samples.

The research plan assumed a study of linear deformation of air entrained and non-air entrained mortar samples treated with 5% sodium sulfate solution based on the PN-B-19707: 2010 [16]. After 28 days of cure in water, the bars were transferred to the solution. The measurements of strains of cement mortars with dimensions of 20x20x160 mm and 40x40x160 mm were carried out by using the Graff-Kaufman's extensometer. Measurements were made every 4 weeks.

The compressive strength assessment was carried out on 40x40x160 mm rectangular specimens of cement mortars based on the PN-EN 196-1: 2006 [17] after 28 days of cure and 80 weeks of residence in a solution of sodium sulphate.

The research methodology also included SEM analyses, thanks to which the microstructure of cement mortars together with sulphate corrosion products and identification of chemical elements included in their composition were observed. In addition, identification of crystalline phases was performed using XRD analyses.

3 Test results

3.1 Research of fresh mortars

Table 1 presents selected properties of fresh air entrained and non-air entrained mortars: determination of density, consistency and air content of cement mortar. The air content of all mortars is within the assumed ranges. For mortar without air entraining admixture it is 5%. In the case of air entrained mortars (AE), the air content increases by 3% and amounts to 7%, 10% and 13%, respectively. With the increase of air, the density of mortars decreased. An increase in the air content by 1% caused an average density drop of approximately 34 kg/m³.

Table 1. Results of selected tests of fresh cement mortars.

Designation	Air content [%]		Density [kg/m ³]	Consistency [mm]
	established	real		
nAE	5-6	5	2190	115
7%	6-9	7	2120	117
10%	9-12	10	2030	120
13%	>12	13	1918	180

The greater amount of air also caused the consistency to change to become more and more fluid. The slump diameter for mortar with 5%, 7% and 10% air was 2 and 3 mm higher, respectively. The greatest change in consistency was observed for a mortar containing 13%.

3.2 Compressive strength

The results of the compressive strength test after 28 days of curing, shown in figure 1, show a decrease in strength with increasing air content. The highest strength was therefore recorded for non-air entrained mortar (nAE) of 40.03 MPa, the lowest for mortars in which the air content was 13%. The average drop in strength of all mortars was about 9.38%, which in the ratio of 1% of the air percentage is a decrease of about 3.85% strength.

Fig. 1. Average compressive strength of cement mortars after 28 days of curing and 80 weeks of residence in a solution of sodium sulphate.

Figure 1 also shows the compressive strength of samples immersed for 80 weeks in a 5% solution of sodium sulphate. For all mortars, the strength measured after 80 weeks immersion in Na₂SO₄ increased in relation to strength after 28 days of curing. However, there is still a tendency to decrease in strength with increasing air content in mortars, but the differences between individual mortars are not as great as in the case of 28-day strength. The highest increase in strength, which amounted to 10.19 MPa, was recorded for mortar with an air content equal to 13%. The smallest increase (4.23 MPa) was observed for non-air entrained mortar (nAE).

3.3 Expansion

Expansion of 20x20x160 mm samples immersed in a 5% sodium sulfate solution is shown in Figure 2. The letter D denotes the complete destruction of the samples. The fastest-destructed samples without air entraining admixture, for which a rapid increase in strains was observed at week 24. At the moment of destruction (at the 28th week of immersion in the solution), the deformations were 10.81 %. Mortar with the air content of 13% turned out to be the most resistant.

Fig. 2. Expansion of samples 20x20x160 mm immersed in a 5% solution of sodium sulphate.

Fig. 3. Expansion of samples 40x40x160 mm immersed in a 5% solution of sodium sulphate.

For samples with a size of 40x40x160 mm immersed in a 5% solution of sodium sulphate (figure 3), similar trends were observed. The largest deformations were observed for nAE mortars (18.26 ‰) and these expansions grew gradually from the beginning of immersion in the solution. In the case of air entrained samples (AE), strains were observed from about 32 weeks. Here, too, mortar with 13% of air turned out to be the most resistant.

3.4 Microstructure of cement mortars

Selected results of scanning microscopic analysis are presented in the following figures (Figure 4-6). SEM observations were performed on all series of mortars after 80 weeks immersion in a solution of sodium sulphate. In non-air entrained mortars there was a large number of ettringite needles in the C-S-H structure and air pores, which was confirmed by EDS analysis, which clearly shows a high concentration of calcium and a relatively high concentration of sulfur and aluminum.

Fig. 4. Microstructure of non-air entrained mortar (nAE) immersed in a solution of sodium sulphate with analysis of chemical composition at point A.

Fig. 5. Microstructure of mortars with different content of air immersed in a solution of sodium sulphate: a) 7% of air content, b) 10% of air content, c) 13% of air content.

In non-air entrained mortars (nAE) there was a large number of ettringite needles in the C-S-H structure and air voids, which was confirmed by EDS analysis, which clearly shows a high concentration of calcium and a relatively high concentration of sulfur and aluminum.

Fig. 6. The diffractogram of non-air entrained mortar (nAE) immersed in a solution of sodium sulphate.

Fig. 7. The diffractogram of air entrained mortar (13%) immersed in a solution of sodium sulphate.

Analysis of diffractograms (Fig.6-7) carried out also after 80 weeks of immersion in Na_2SO_4 solution showed that the basic products of sulphate corrosion are ettringite and gypsum. Apart from these phases, the presence of portlandite and quartz was also found, the high content of which results from the fact that mortar samples, not leavens, were used for the study.

4 Analysis and discussion of results

Based on the tests of fresh mortars, a typical air entrainment effect can be observed, ie a decrease in density. An improvement in workability was also observed. It results from the spherical shape of the introduced air bubbles, thanks to which it is possible to reduce the internal friction in the mixture.

The compressive strength test after 28 days of curing showed a decrease in strength with increasing air content. This is one of the undesirable effects of air entrainment. However, it should be noted that for all mortars, the compressive strength measured after 80 weeks immersion in a solution of sodium sulphate increased in relation to strength after 28 days of curing. The reason for the increase in strength are the changes in the microstructure caused by sulphate corrosion. Corrosion products, mainly ettringite, fill the voids, initially reducing porosity, and thus increasing strength [4]. The observed increase in strength is a proof of the significant progress of corrosion.

In turn, the measurement of expansion of cement mortar samples showed that air entrained (AE) mortars are more resistant to sulphate corrosion. For both samples 20x20x160mm and samples 40x40x160mm, the greatest expansions were noted for the mortar without air entraining admixture, and the smallest for the mortar, which contained 13% air. It should also be noted that the highest compressive strength increase was recorded for this series of mortars. As mentioned above, this means a significant progress in corrosion, but it did not adversely affect the expansion. The positive effect of air entrainment on changes in strain results from the fact that the products of sulphate corrosion (mainly ettringite) precipitate in the air pores [13]. As a result, less damage is caused by the cement paste and, consequently, less expansion. Observation of mortar microstructure also confirms this statement. In the air entrained samples (AE), ettringite crystallized both in the C-S-H structure, but also in the air voids. In the non-air entrained (nAE) mortar ettringite was mainly in the C-S-H phase and only partially filled the air voids. The recognition of crystalline phases using X-ray diffractometry confirmed that ettringite was the main product of sulphate corrosion.

5 Conclusions

Based on the research, the following conclusions were drawn:

1. Air entrained cement composites, although they exhibited lower compressive strength and show greater resistance to sulfate corrosion than non-air entrained cement composites.
2. In the case of samples immersed in a solution of sodium sulphate, high air content (13%) turned out to be the best in terms of their stability in the sulphate environment.
3. For all mortars, the compressive strength measured after 80 weeks immersion in a sulphate solution increased in relation to strength after 28 days of curing.
4. Microscopic observations of air entrained (AE) and non-air entrained (nAE) mortars showed that a large number of ettringite needles occurred both in the C-S-H structure and in the air voids.

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