

## SULPHATE CORROSION OF CEMENT PASTES WITH A HIGH CONTENT OF WASTE MARBLE POWDER

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**ABSTRACT.** The article focuses on sulphate corrosion of cement pastes with a high content of waste micronized marble powder. Micronized marble powder is used as a substitute for Portland cement CEM I 42.5R. The amount of micronized marble powder used is from 5 to 50 wt. %. The research also tested a reference mixture composed only of Portland cement. The used accelerated sulphate corrosion consists of cyclic saturation and drying with 10% Na<sub>2</sub>SO<sub>4</sub> solution for 56 days. During sulphate corrosion, samples are placed in a controlled environment at 5 ± 1 °C and 85 % relative humidity to allow thaumasite to form. During cycling, samples were continuously visually monitored and documented. Subsequently, after 56 days, the samples were destructively tested for compressive strength. The research revealed a negative effect of micronized marble powder on the resistance to sulphate corrosion, where in contrast to the reference mixture the decrease in compressive strength is up to twofold.

**KEYWORDS:** Sulphate corrosion, thaumasite, cement pastes, visual inspection, compressive strength.

### 1. INTRODUCTION

Currently, the most common way to use recycled marble waste is to apply it to cement-based composite materials. Cement-based composite materials (in the form of monolithic reinforced concrete, prefabricated parts, etc.) are currently probably the most widespread and most used building material in world. From the point of view of sustainable development, three basic components (cement, sand and water) are needed for the production of cement composite. However, their extraction, treatment and processing have negative effect on nature and the environment [1]. Specifically, cement production accounts for 7 % of global CO<sub>2</sub> production and large amounts of NO<sub>x</sub>. The use of recycled marble in the form of admixtures will significantly reduce the cost of raw material for concrete [2]. For example, the use of waste marble powder in a cement composite reduces CO<sub>2</sub> emissions by 12 % and reduces the cost of the composite from 40 USD/m<sup>3</sup> on 33 USD/m<sup>3</sup> [3].

One of the most common applications of marble powder is in the form of admixtures, where it forms a substitute for a binder. When replacing up to 15 wt. % there is no significant decrease of mechanical properties [4–7] and when replacing 50 wt. % cement pastes have twice value the flexural strength [5].

According to the ČSN EN 206 standard, marble powder is considered as an inert admixture, which does not participate in the hydration of cement. In the case of white and beige marble, it is a mineral filler that contains more than 75 % CaCO<sub>3</sub> [8]. The chemical

composition is very similar to limestone, which does not behave completely inertly during the hydration of cement [9]. Fine limestone grains act in the cement as nucleation centers for CH crystals and accelerate the hydration of silicate and aluminate phases. As a result, it affects the initial increase in the strength of the cement composite and accelerates the setting and curing time. In addition, even finely ground limestone can participate in hydration processes. It is mainly the hydration of C<sub>3</sub>S from clinker to form calcium carbonate aluminate hydrate (3CaO · Al<sub>2</sub>O<sub>3</sub> · 3CaCO<sub>3</sub> · 32H<sub>2</sub>O) in cements with a higher content of C<sub>3</sub>A. Tricarbonate can transform into a more stable monocarbonate [10] in later stages. The biggest disadvantage of limestone, and thus of sediment formed from CaCO<sub>3</sub>, is its sulphate corrosion in combination with silicates in a C-S-H gel. During sulphate corrosion at lower temperatures, crystalline thaumasite is formed (CaSiO<sub>3</sub> · CaCO<sub>3</sub> · CaSO<sub>4</sub> · 15H<sub>2</sub>O), which by volume changes it disrupts the structure, thus deteriorating the mechanical properties and integrity of the cement composite [11].

This article investigates the sulphate corrosion resistance of a cement composite containing waste marble powder. Marble (crystalline CaCO<sub>3</sub>) has a similar chemical composition to limestone (sedimentary CaCO<sub>3</sub>) and thus thaumisite can form during sulphate corrosion, which negatively affects the durability of structures. The sulphate corrosion of a cement composite containing marble powder and limestone powder was deal in an experimental study by M. Uysal et al. [12]. The results of the experiments were the

Set	Percentage replacement [%]	CEM I 42,5R [kg]	Micronized marble powder [kg]	Water ratio w/b
M0	0	3.00	0.00	0.35
M5	5	2.85	0.15	0.32
M10	10	2.70	0.30	0.32
M15	15	2.55	0.45	0.32
M50	50	1.50	1.50	0.32

TABLE 1. Composition of tested sets.

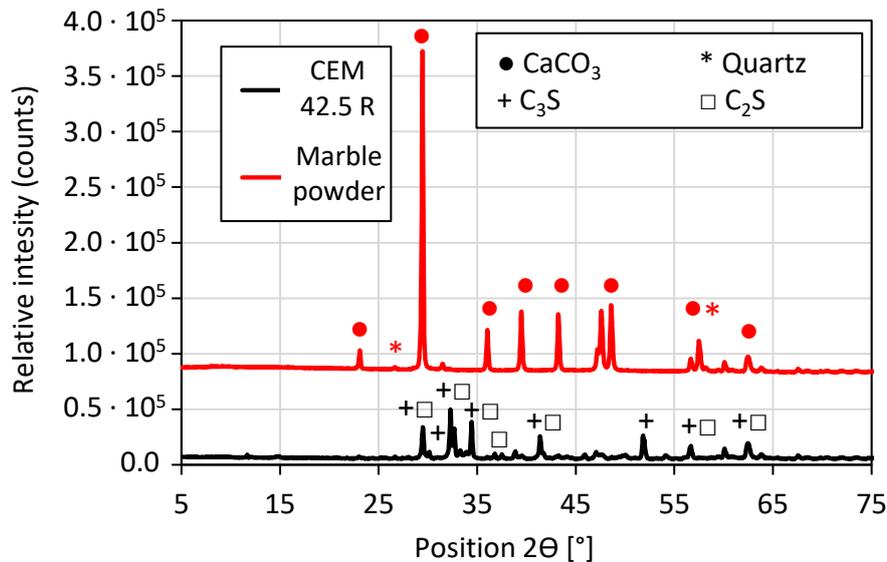


FIGURE 1. XRD patterns for portland cement CEM 42.5R and micronized marble powder.

percentage loss of compressive strength, where the samples with reference cement and samples with limestone and marble powder had the greatest loss of strength, namely 13 %. Samples with 30 wt. % marble powder as a substitute for cement, which had better mechanical properties than the reference samples. The loss of strength in this mixture was approximately 9 %. The authors attributed the improvement of the resistance to sulphate corrosion to the reduced porosity and especially to the permeability of the cement composite.

## 2. MATERIALS AND SAMPLES

The experiments were performed on cement pastes, where part of the cement was replaced by waste micronized marble powder. The Used portland cement was CEM 42.5R Radotín. It is a cement with a high  $C_3S$  content of 74.6 % and a lower  $C_3A$  content of 8.1 %,  $C_2S$  7.2 %,  $C_4AF$  8.5 % and  $MgO$  1.6 %. The micronized marble powder was created by recycling waste generated from the process of mining and processing of marble stone. The recycling of marble waste was performed using a high-speed mill, which guarantees the separation of individual clumps, reduces the grain size of the material (0–50 microns) and homogenizes the waste material. The research used a high-speed mill from Lavaris s.r.o. S1000. According

to XRF analysis, micronized marble powder has a high  $CaO$  content of 62.3 % together with a high loss of ignition of 33.7 %. This indicates a high content of  $CaCO_3$ , which can react to thaumasite during sulphate corrosion. XRD analysis was performed for confirmation. Figure 1 shows a diffractogram of portland cement and micronized marble powder. The results confirmed the previous assumption. Thus, the micronized marble powder is composed of 98 wt. %  $CaCO_3$  and the remaining 2 wt. % are other clay minerals contained in marble.

The composition of all tested mixtures is shown in Table 1. The first mixture was a reference and contained only portland cement. In other mixtures, part of the cement was replaced by micronized marble powder in various weight percentages, from 5 to 50 %. The ratio of water to the total weight of the dry mixture (water-to-binder ratio w/b) was designed to maintain the same workability of the fresh mixtures in flow table test. The flow varied for individual mixtures up to a maximum size of 5 mm. Specifically, the flow was determined to be 180 mm after 15 impacts.

All samples tested had nominal dimensions of  $40 \times 40 \times 40$  mm. The samples were produced in steel triple molds with dimensions of  $40 \times 40 \times 160$  mm according to ČSN EN 196-1 [13] and subsequently cut to final dimensions. 6 samples were taken from each set

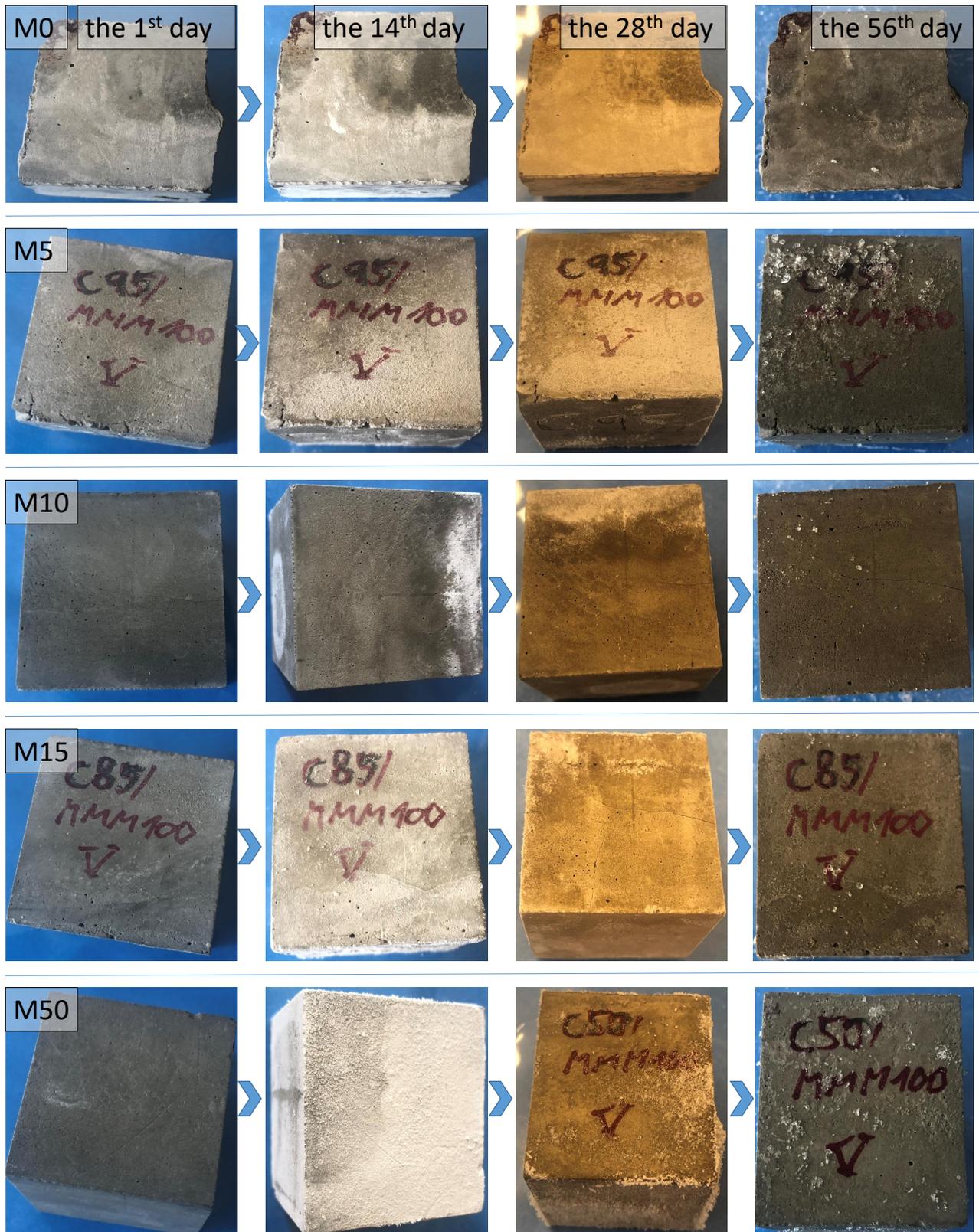


FIGURE 2. Visual determination of sulphate corrosion.

(mixture). On the second day after production, the test specimens were demolded and stored loose in a laboratory environment at a temperature of  $22 \pm 1$  °C and a relative humidity of  $50 \pm 2$  %. After 28 days, the samples were cut and subjected to sulfate corrosion

resistance testing.

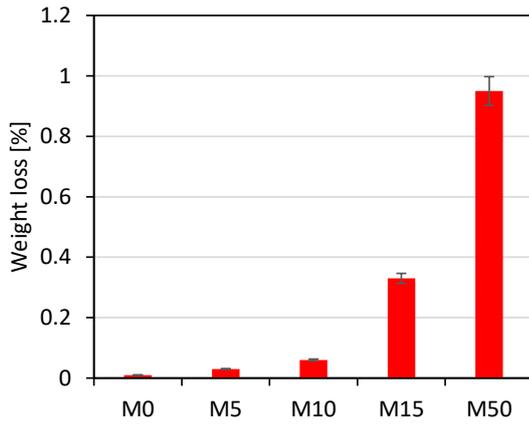


FIGURE 3. Percentage weight loss due to sulphate corrosion for 56 days, with standard deviations.

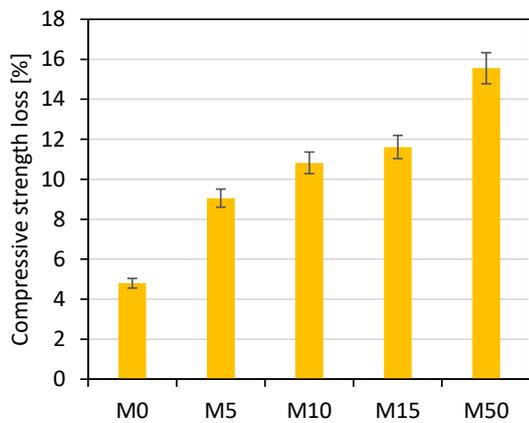


FIGURE 4. Percentage decrease in compressive strength due to sulphate corrosion for 56 days, with standard deviations.

### 3. EXPERIMENTAL METHODS

Depending on the composition of the recycled material, the resistance to sulphate corrosion was solved. ASTM C1012-04 [14] has been modified for this purpose. The test samples were stored in a 10%  $\text{Na}_2\text{SO}_4$  solution. Due to possible thaumasite formation, the ambient temperature was set to  $5 \pm 1$  °C and the relative humidity was  $85 \pm 5$  %. The whole process for accelerated sulfate corrosion was taken from Nielsen et al. [15]. The process uses a cycle of alternating saturation and drying of the samples, where one cycle consists of seven days of saturation of the sample with the solution and then another seven days of its natural drying. The samples were visually inspected during cycling and assessed after each completed cycle. Subsequently, the samples were weighed and destructively tested for determining compressive strength.

The compressive strength was determined using a Heckert (FP100 model) hydraulic press. The compressive strength was determined by a uniaxial pressure test. Testing was controlled by displacement at a constant rate of 3 mm/min. The test was performed on 6 samples with dimensions of  $40 \times 40 \times 40$  mm. The

compressive strength was determined according to ČSN EN 196-1 [13]. The compressive strength of a material is the amount of stress achieved at the point of failure when the integrity of the material is lost. The compressive strength was calculated from the maximum force achieved during the test  $F_{c,\max}$  as:

$$f_c = \frac{F_{c,\max}}{ab}, \quad (1)$$

where:

$f_c$  is the compressive strength in Pa,  
 $F_{c,\max}$  is the maximum force in N,  
 $a$  is the width of the sample in m,  
 $b$  is the height of the sample in m.

Corrosion resistance coefficients were calculated from the obtained compressive strengths of samples in a corrosive environment and samples stored in water, as:

$$k_{ko} = \frac{f_c}{f_{ref}}, \quad (2)$$

where:

$k_{ko}$  is corrosion resistance coefficients,  
 $f_c$  is the compressive strength in 10%  $\text{Na}_2\text{SO}_4$  solution [Pa],  
 $f_{ref}$  is the compressive strength in water [Pa].

### 4. RESULTS AND DISCUSSION

The process of visual examination of the tested mixtures can be observed in Figure 2. The monitored samples M50, M15 and M10 showed visible formation of white crystals on their surface after 14 days of accelerated sulphate corrosion in 10%  $\text{Na}_2\text{SO}_4$ . Reaction of sodium sulfate with the cement matrix at low temperatures produced thaumasite crystals with a larger volume. The first cracks formed in all examined samples, except for the reference mixture, after 28 days of sulfate corrosion. These were mainly capillary cracks caused by the crystallization of thaumasite. There was no further expansion of cracks after another 28 days (day 56), but leaching of calcium, which subsequently crystallized on the surface of the tested materials.

After 56 days, the cement pastes were tested for weight loss due to calcium leaching (Figure 3) and compressive strength (Figure 4), which are used to determine the corrosion resistance coefficient.

All mixtures with marble powder lost weight. The largest weight loss was in the sample M50, namely 0.95 wt. %. This decrease indicates deteriorated sulfate corrosion resistance. The assumption was subsequently confirmed by the compressive strength test, where the sample M50 achieved a 15.5 % lower compressive strength after 56 days in a 10% solution of  $\text{Na}_2\text{SO}_4$ . The corrosion resistance coefficient was

0.845. The remaining materials with micronized marble powder achieved a corrosion resistance coefficient of 0.9. The results are in agreement with other authors who have dealt with sulphate corrosion in their research [16]. In contrast to accelerated sulphate corrosion, they used the traditional method, which lasted one (whole) year. After a year, samples composed of 20 wt. % CaCO<sub>3</sub> had lower compressive strength by 20 %.

## 5. CONCLUSIONS

This work is focused on the effect of waste micronized marble powder on the sulphate corrosion resistance of cement pastes. Accelerated sulfate corrosion at lower temperatures was used. Cement pastes are composed of mixed cement, where micronized marble powder replaces Portland clinker. The micronized marble powder was used in 4 different concentrations, namely: 5 wt. %, 10 wt. %, 15 wt. % and 50 wt. %. Based on the results, it can be concluded that:

- Accelerated sulphate corrosion was used, where the results of the reference mixture were comparable to the commonly used sulphate corrosion test.
- Samples with micronized marble powder showed visible formation of white crystals on their surface after 14 days and the first cracks appear after 28 days.
- All samples with micronized marble powder indicate deteriorated sulfate corrosion resistance by losing your weight.
- Samples with micronized marble powder had lower values of compressive strength from 9 to 15 % after sulphate corrosion. The reference mixture had a compressive strength value only lower about 5 %.

Future research will build on the results in this article. In the next work, concrete mixtures will be tested. In addition, future research will use an electron microscope to describe the phase changes in the structure of the cement composite.

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