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The Use of Secondary Crystallization in Cement-Based Composites

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***Abstract*—**The paper focuses on the study of the properties of cement-based composites produced using secondary crystallization (crystalline additive). In this study, cement mortar made with secondary crystallization was exposed to an aggressive environment and the influence of secondary crystallization on the degradation of the cementitious composite was investigated. The results indicate that the crystalline additive contributed to increasing the resistance of the cement-based composite to the attack of the selected environments (sodium sulphate solution and ammonium chloride solution).

***Keywords*—**Secondary crystallization, cement-based composites, durability.

I. Introduction

CONCRETE is a building material with a dominant position over other materials in modern civil engineering, which is why there is an effort to constantly improve it [1]. It is, relatively speaking, a very stable material with a long lifetime, but if a concrete structure is not properly protected, the surface layer of concrete will degrade over time [2].

In general, water permeability of exposed concrete structures such as pavements and bridge decks affect the durability and corrosion of the reinforcing steel in the structure. Water-related problems such as freezing and thawing also cause serious degradation in reinforced concrete [3]. To avoid water-related problems can be used so called “secondary crystallization” or “crystalline additives” or “crystalline technology” [2].

The possibility of self-healing processes in cement-based materials has been investigated for decades. The majority of authors agrees on opinion that the self-healing process includes two main mechanisms. It has been known that the internal crack healing process depends on further hydration or swelling of unreacted particles. Besides the further hydration, another mechanism affects the precipitation of calcium carbonate. The formation of calcium carbonate is the fundamental process needed for self-sealing of surface cracks in hardened cement-based composite [4]-[6]. Crystalline additives (CA) contribute to the increased resistance against the penetration of different liquids and against the attack of environmental conditions as well [7].

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Fig. 1 Image of a specimen with an addition of CA – 26 days after the application of CA (at a depth of 50 mm into the concrete sample) [7]

II. Materials and Properties

In order to observe the effect of secondary crystallization on the properties of cement composites, batches of specimens were made, including the reference (no CA) and mixtures containing a CA. Specimens with the dimensions of 40×40×160 mm were aged in the following environments: water, sodium sulphate solution (concentration of 36 000 mg of SO_4^{2}-) and ammonium chloride solution (concentration of 3 000 mg of NH_4^{+}). The specimens were stored in these and tested at the age of 90 and 180 days.

The cement used as a binder was Portland cement CEM I 42.5 R (Českomoravský cement A.S., factory in Mokrá, Czech Republic), sand was used as aggregate (ZEPIKO spol. s r.o., Czech Republic) and XYPEX Admix (XYPEX CHEMICAL CORPORATION, Richmond B.C. Canada) was used as the CA.

Table I shows mixture composition.

TABLE I
Composition of the Mixture

Cement CEM I 42.5 R	250 g
Sand (0–4 mm)	750 g
CA	2.5 g
Water/Cement ratio	0.5

III. Selected Results and Discussion

Figs. 2–4 show the results of compressive and bending tensile strength tests of specimens made of the reference mixture and mixtures containing a CA at the age of 28 days, 90 days and 180 days.

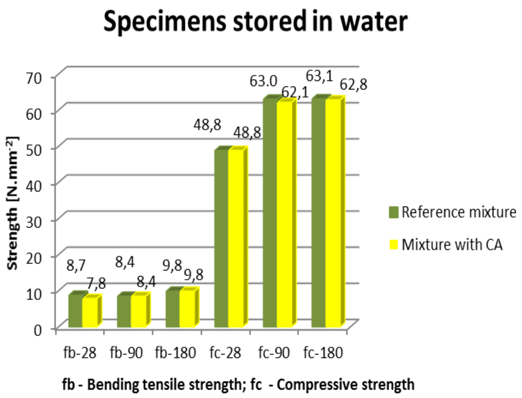

Fig. 2 Determination of strength of specimens stored in water

Fig. 3 and 4 show the positive influence of the addition of CA, which can be observed in compressive strength determined at the age of 90 and 180 days.

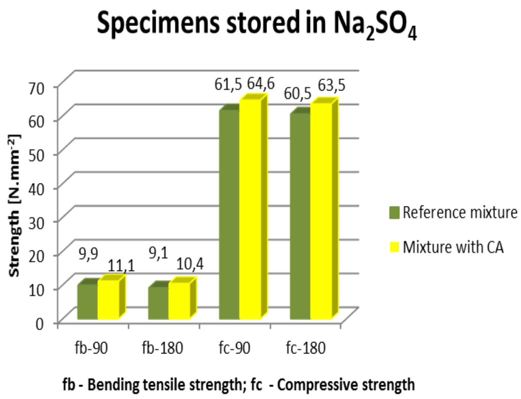

Fig. 3 Determination of strength of specimens stored in Na_2SO_4

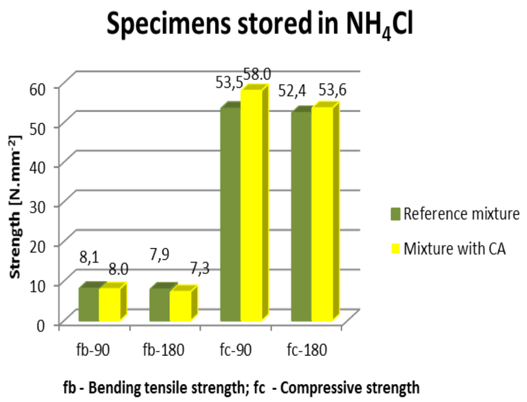

Fig. 4 Determination of strength of specimens stored in NH_4Cl

The following step was the examination of microstructure by means of a scanning electron microscope (SEM). The microscopic imaging confirmed the presence of new crystalline formations typical for CA. The images are in Figs. 5–10.

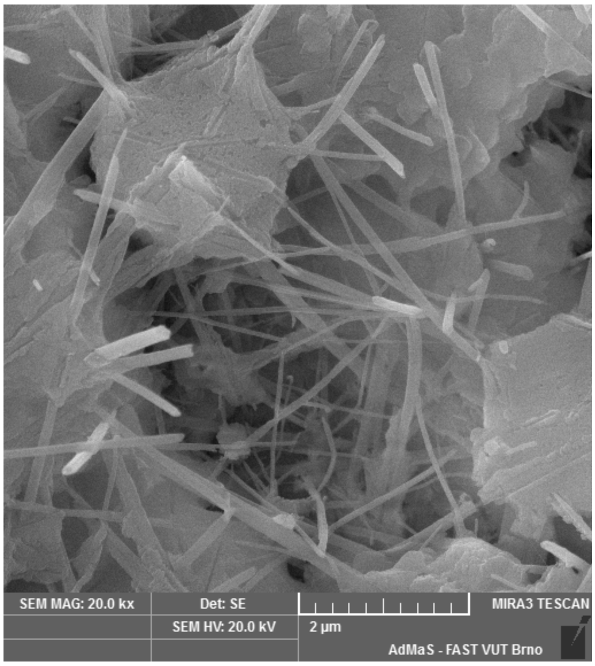

Fig. 5 Image of a specimen with an addition of CA stored in water at 20 000× (age 90 days)

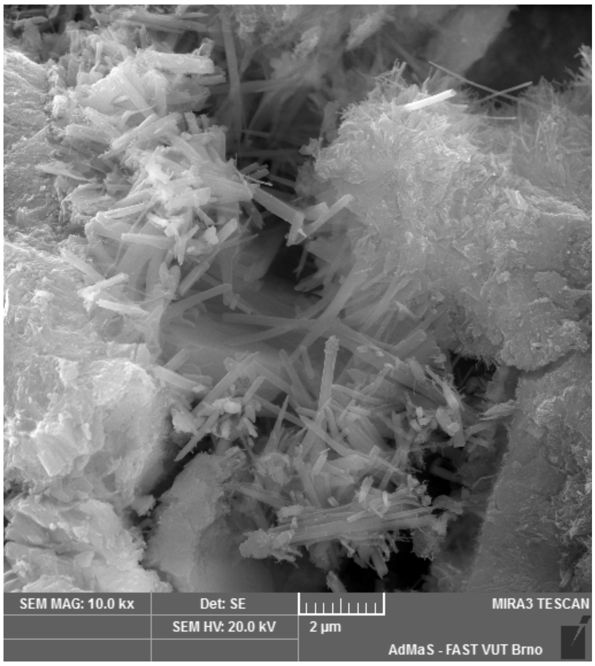

Fig. 6 Image of a specimen with an addition of CA stored in water at 20 000× (age 180 days)

The SEM analysis proved the growth of crystalline structure in pore system of tested cement-based composites with an addition of CA. In Figs. 5-10, it is possible to see the needle shaped crystals, which confirmed an ongoing crystallization process.

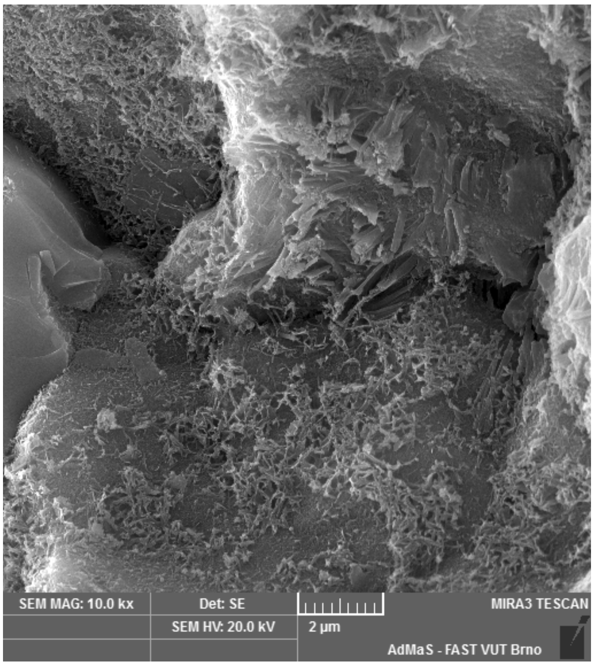

Fig. 7 Image of a specimen with an addition of CA stored in Na_2SO_4 at 10 000× (age 90 days)

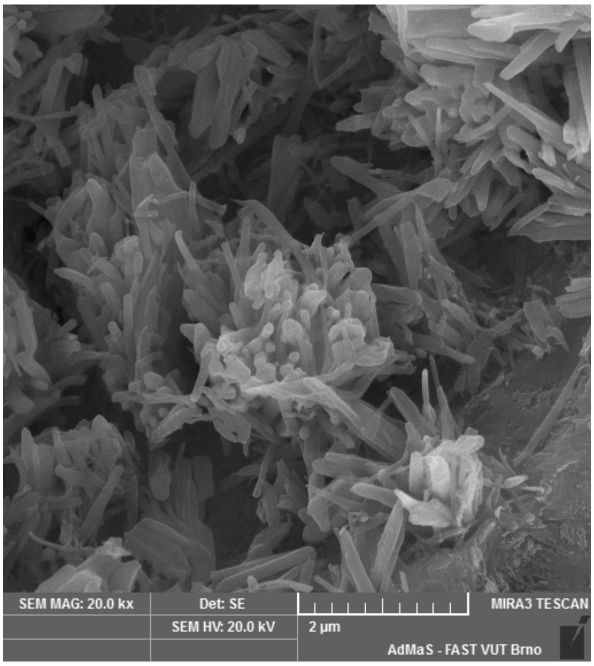

Fig. 8 Image of a specimen with an addition of CA stored in Na_2SO_4 at 20 000× (age 180 days)

Future experiments will focus on the observation of absorption, resistance to penetration of water under pressure and performing high-pressure mercury intrusion porosimetry with the purpose of determining the porosity of the mortars being studied.

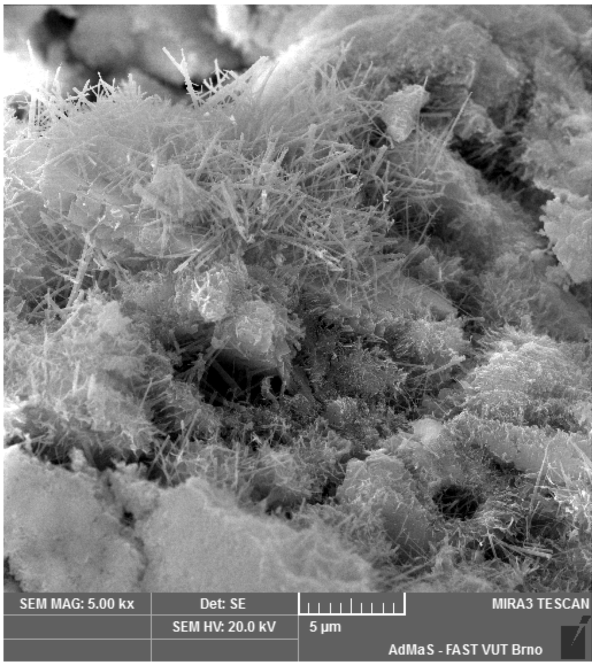

Fig. 9 Image of a specimen with an addition of CA stored in NH_4Cl at 5 000× (age 90 days)

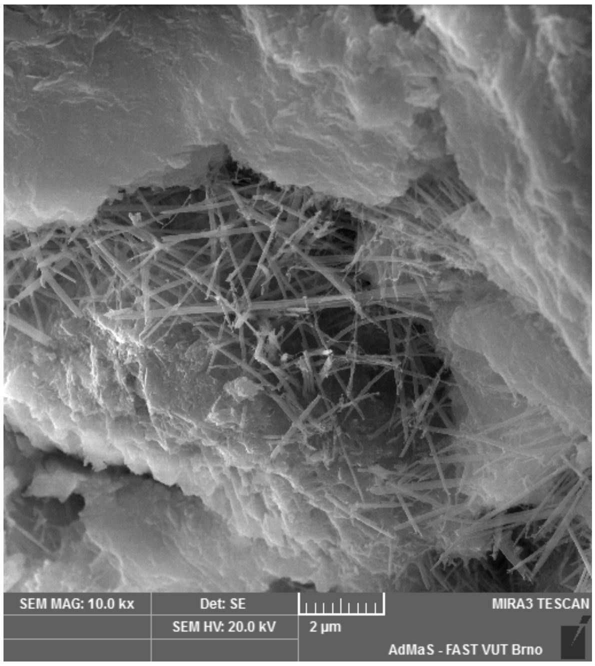

Fig. 10 Image of a specimen with an addition of CA stored in NH_4Cl at 10 000× (age 180 days)

IV. Summary

The experiment results confirm that the use of a CA can improve the resistance of cement composites exposed to the selected aggressive environments.

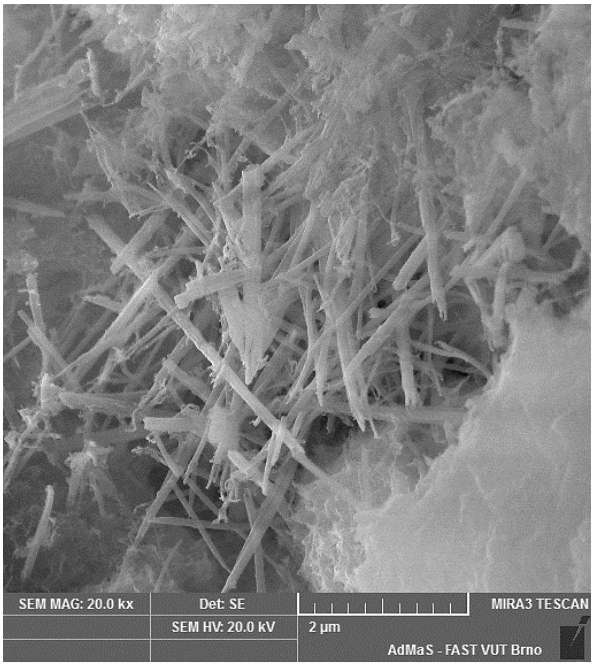

Fig. 11 Image of a specimen with an addition of CA stored in NH_4Cl at 20 000× (age 180 days)

Ascertaining the effectiveness of the selected type of secondary crystallization will require more follow-up experiments, since it is necessary to examine in greater detail the formation process of cement matrices containing this additive.

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