Investigation on the efficiency of internal crystallization chemical admixtures for cement concrete - structural characteristics

Valeriy Naidenov[1], Mirona Mironova[1]
Institute of Mechanics[1], Bulgarian Academy of Science, Sofia, Bulgaria
valna53@mail.bg

Abstract: *In recent years, the use of internal crystallization chemical admixtures for concrete and mortar to increase their water-tightness and other physical and mechanical characteristics has been of increasing importance in modern construction. These types of chemical modifiers allow for the effective replacement of conventionally performed waterproofing works (membranes, rolls, brushed or sprayed coatings, etc.) by purposefully improving the physical-mechanical characteristics of structural concretes, rendering them, to one degree or another, impermeable to water or/and aggressive agents from different origins. In the specialized world market for such products there are several leading competing companies - producers of internal-crystallization chemical admixtures, which have different activity in Bulgaria. Based on results of purposeful set of structural investigations (DTA, SEM, BET) conducted the purpose of the report is to assist participants in the construction investment process in understanding the nature, specific characteristics and differences in the performance (effectiveness) of different products in terms of their ability to limit the ingress of water into concrete and reinforced concrete sections, as well as their ability to increase the durability of concrete as the main structural material.*
Keywords*: PORTLAND CEMENT CONCRETE AND MORTAR, INTERNAL CRYSTALLIZATION CHEMICAL ADMIXTURES, CONCRETE WATERPROOFING, DTA, SEM, BET STRUCTURAL INVESTIGATIONS*

1. Introduction

In recent years, the use of internal crystallization chemical admixtures for concrete and mortar to increase their water-tightness and other physical and mechanical characteristics has been of increasing importance in modern construction. These types of chemical modifiers allow for the effective replacement of conventionally performed waterproofing works (membranes, rolls, brushed or sprayed coatings, etc.) by purposefully improving the physical-mechanical characteristics of structural concretes, rendering them, to one degree or another, impermeable to water or/and aggressive agents from different origins [1, 2 ,3, 4, 5].

In the specialized world market for such products there are several leading competing companies-producers of internal-crystallization chemical admixtures, which have different activity in Bulgaria.

The admixtures tested and compared are KRYSTALINE Add1, KRYSTALINE Plus 2.5, PENETRON Admix, XYPEX C1000 NF and BETOCRETE-CP-360-WP.

The purpose of the investigation is to assist all participants in the construction investment process in understanding the nature, specific characteristics and differences in the performance (effectiveness) of different products in terms of their ability to limit the ingress of water into concrete and reinforced concrete sections, as well as their ability to increase the durability of concrete as a main structural material.

2. Tests methods and comparative characteristics

The mix design of ordinary reference concrete (Table 1) was used to perform the studies, with the mineral composition of the cement being presented in Table 2.

For the purpose of comparative studies to the mix of reference concrete (Table 1), the appropriate crystallization chemical admixtures are incorporated in the dosage and according to the technology prescribed by their manufacturer.

The homogenization of the fresh concrete is accomplished by adding a metered amount of mixing water to obtain the same workability as assessed by the slump measure. The chosen method of comparison on the basis of **"equal workability"** of the concrete mixture is directly related to the actual production conditions at the construction site, where the **"workability"** factor is the key one to the quality of the concrete works performance.

The following physical-mechanical and structural characteristics have been selected to compare the same age of the fresh concrete and the hardened concrete:

- **fresh concrete** - water-cement ratio, consistency by slump test (cm), change of consistency in time after homogenization, air content (%);
- **hardened concrete** - compressive strength (MPa), splitting tensile strength (MPa), the static modulus of elasticity deformation (GPa), the depth of penetration of water under pressure (mm), frost resistance under an accelerated method (loss of mass change and the speed of ultrasound propagation) - cycles, structural studies (low-temperature gas absorption (BET method), differential thermal analysis (DTA), X-ray phase analysis (RFA) and scanning electron microscopy (SEM);
- **cement-sand mortar** - capillary absorption.

Table 1: *Concrete mix design.*

№	Materials	Quantity, kg/m^3
1.	Portland cement CEM II 42,5 A-LL, Devnya Cement Plant, Bulgaria	330
2.	River sand, fraction 0-4 mm, Quarry "Chepinzi"	810
3.	Crushed stone, fraction 4-11,2 mm, Quarry "Studena"	1060
4.	Mixing water for fresh concrete slump 13 cm (S3)	≈250 (for reference concrete)

Table 2 *Mineral composition of the Portland cement used*

Cement type	**Specific surface, cm^2/g**	**Mineral composition, % by mass**			
		C_3A	**C_3S**	**C_2S**	**C_4AF**
CEM II 42,5 / A-LL	3620	9,40	55,50	24,60	10,50

3. Description of crystallization admixtures tested

The description and basic peculiarities of the admixtures tested is given in Table 3. Their dosage rates are in accordance of the respective manufacturers.

KRYSTALINE Add1 and KRYSTALINE Plus 2,5 have the advantage of being dosed in all cases in constant quantities (1,0 kg/m^3, or 2,5 kg/m^3) regardless of the concrete formulation of the concrete. The only requirement is cement content above 300 kg/m^3.

PENETRON Admix, XYPEX C1000 NF and SCHOMBURG BETOCRETE-CP-360-WP are dosed depending on the type and amount of cement used in the concrete mix design, which determines the need for specific calculations and non-constant costs in different projects.

Table 3 *Product description and dosage rates*

Product	Description	Dosage rates (according producer's recommend-dations)
KRYSTALINE Add1 Krystaline Technologies SA, Spain	Crystallizing waterproofing admixture with catalytic action to increase the water resistance and durability of concrete. Slightly slows down the concrete setting and hardening times and decreases exothermic. Self-healing cracks up to 0.5 mm wide.	1,00 kg/m^3 (permanent, regardless of the cement content)
KRYSTALINE Plus 2,5 Krystaline Technologies SA, Spain	Crystallizing waterproofing admixture with catalytic action to increase the water resistance and durability of concrete. Slightly slows down the concrete setting and hardening times and decreases exothermic. Self-healing cracks up to 0.5 mm wide.	2,5 kg/m^3 (permanent, regardless of the cement content)
PENETRON Admix PENETRON HELLAS, Greece	Crystallizing waterproofing admixture with catalytic action to increase the water resistance and durability of concrete. Slightly slows down the concrete setting and hardening times and decreases exothermic. Self-healing cracks up to 0.4 mm wide.	3,00 kg/m^3 (1% from mass the cement)
XYPEX C1000 NF XYPEX CHEMICAL CORPORATION, Canada	Crystallizing waterproofing admixture with catalytic action to increase the water resistance and durability of concrete. Slightly slows down the concrete setting and hardening times and decreases exothermic. Self-healing cracks up to 0.4 mm wide.	4,5 kg/m^3 (3-6 kg/m^3, according producer's TDS)
BETOCRETE-CP-360-WP SCHOMBURG GmbH & Co. KG, Germany	Crystallizing waterproofing admixture with hydrophobic effect.	3,30 kg/m^3 (0,75-1,25% - in function of type and cement content)

4. Results and discussion

The respective physics and mechanical properties of hardened concrete are discussed in other publication of ours [5] (to be published).

The focus of this paper is to emphasize the significant differences in respective micro-structural characteristics obtained by using of advanced direct physics methods - low-temperature gas absorption (BET method), differential thermal analysis (DTA), X-ray phase analysis (RFA) and scanning electron microscopy (SEM).

4.1. Low temperature gas absorption (BET- method)

Gas adsorption is a modern method of characterizing porous materials. In the case of physical gas adsorption, inert gas (most commonly nitrogen) is adsorbed on the surface of a solid material. Physical absorption is the result of the electromagnetic attraction forces between the particles of the two phases, which have different charges. This occurs on the superficial outer layer of the bodies and on the surface of their pores (in the case of porous bodies). The reverse process is called desorption. The adsorption process is accompanied by an increase in the sample mass and a decrease in gas pressure. Based on the amount of adsorbed gas and the corresponding gas pressure, so-called an Arizona thermal adsorption curve from which basic parameters of the pore structure of materials can be determined.

The results are presented in Table 4 and Figures 1-5.

Table 4 *Micro-pore structure characteristics*

CONCRETE TESTED	STRUCTURE CHARACTERISTICS		
	Specific surface of pore structure, S_{BET}, m^2/g	Total pore volume, Vt, cm^3/g	Pore size distribution by diameter, D_{av}, nm
Reference concrete – without admixture	24	0,09	15
KRYSTALINE Add1 1,0 kg/m^3	19	0,05	10
KRYSTALINE Plus 2,5 2,5 kg/m^3	26	0,09	14
PENETRON Admix 3,0 kg/m^3	30	0,09	13
XYPEX C1000 NF 4,5 kg/m^3	17	0,07	17
SCHOMBURG BETOCRETE-CP-360-WP 3,3 kg/m^3	44	0,12	11

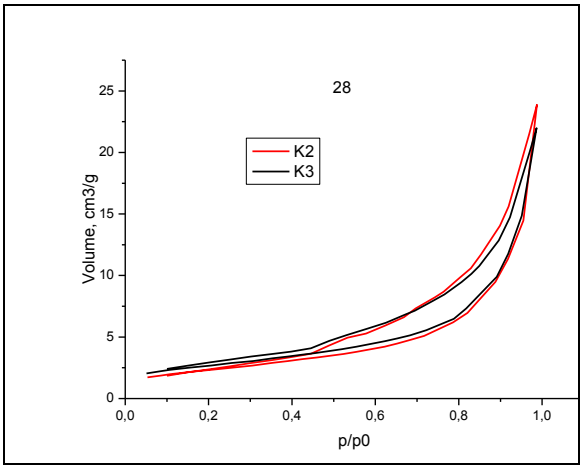

Fig. 1 *Total pore volume - KRYSTALINE Add1 (K2) and KRYSTALINE PLUS 2,5 (K3)*

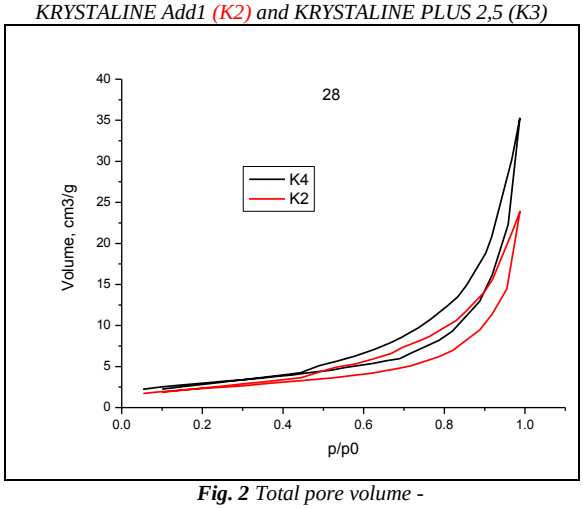

Fig. 2 *Total pore volume - KRYSTALINE Add1 (K2) and PENETRON Admix (K4)*

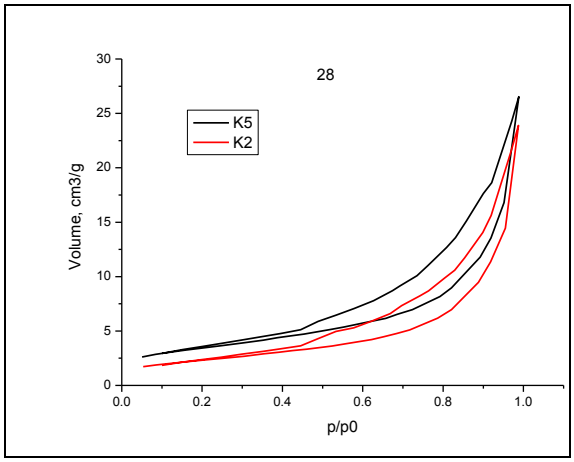

Fig. 3 *Total pore volume - KRYSTALINE Add1 (K2) and XYPEX C1000 NF (K5)*

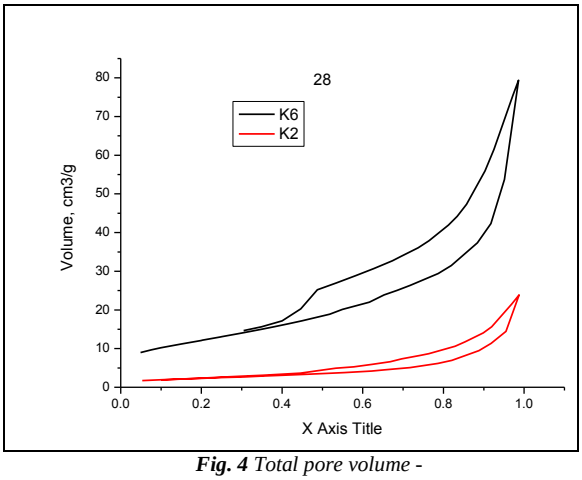

Fig. 4 *Total pore volume - KRYSTALINE Add1 (K2) and BETOCRETE -CP-360-WP (K6)*

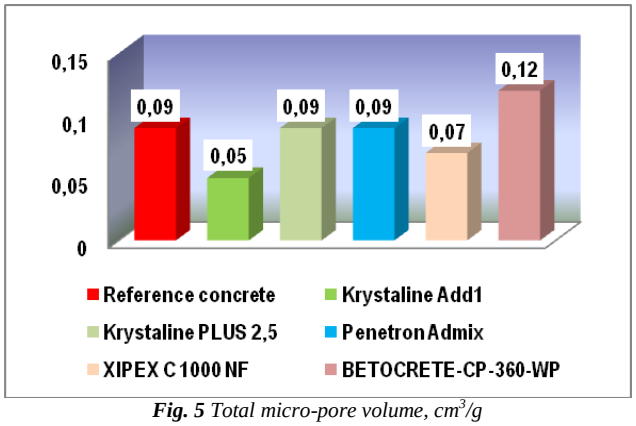

Fig. 5 *Total micro-pore volume, cm^3/g*

With the same workability of the fresh concrete, the crystallization admixture KRYSTALINE PLUS 2.5 and KRYSTALINE Add1 form a fine-dispersed cement stone structure in the concrete with a significantly reduced total micro pore volume, compared to the concrete with the participation of PENETRON Admix, XYPEX C1000 NG and SCHÖMBURG BETOCRETE -CP-360-WP.

4.2. Differential-thermal analysis (DTA)

The results are presented in Table 5 and Figures 6-10.

Differential thermal analysis (DTA) is a method that belongs to the set of direct physical methods for the study of crystalline structure in silicate composites. It is based on the characteristic feature of the hydrated formations in the cement stone to dehydrate in a precisely defined temperature range. The corresponding dehydration is accompanied by a characteristic thermal effect that alters the heat balance of the system. The monitoring of the respective endo- and exo-effects allows one to judge the phase transformations identified by the release of chemically bound water. Knowing the reference for the individual silicate formations and temperatures of the phase transition, one can directly judge the presence and the indicative amount of the corresponding compound.

Table 5 *Structure characteristics*

CONCRETE TESTED	BASIC STRUCTURE COMPOSITIONS	
	Portlandite $Ca(OH)_2$, rel.%	Crystals C-S-H, Calcite $CaCO_3$, rel.%
Reference concrete (K "0") without admixture	1,937	8,733
KRYSTALINE Add1 1,0 kg/m^3	1,491	10,685
KRYSTALINE Plus 2,5 2,5 kg/m^3	1,455	11,880
PENETRON Admix 3,0 kg/m^3	1,849	4,878
XYPEX C1000 NF 4,5 kg/m^3	2,999	11,051
SCHÖMBURG BETOCRETE-CP-360-WP 3,3 kg/m^3	1,669	8,232

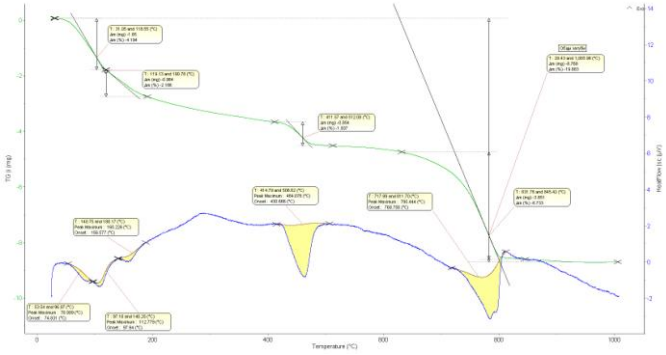

Fig. 5 *DTA - Reference concrete*

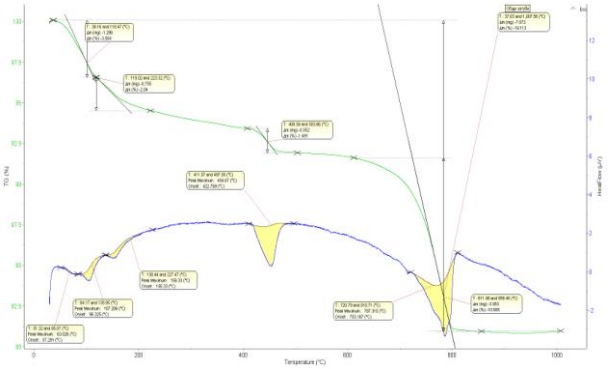

Fig. 6 *DTA - KRYSTALINE Add1*

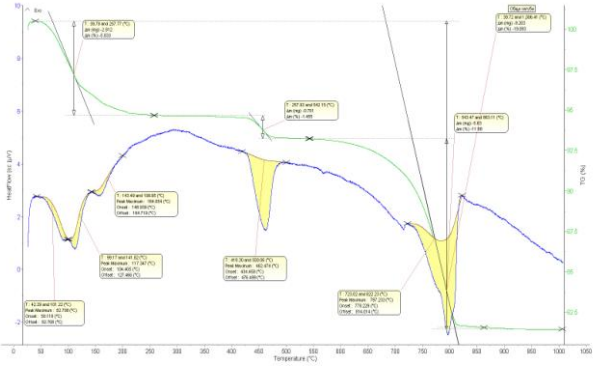

Fig. 7 *DTA - KRYSTALINE PLUS 2,5*

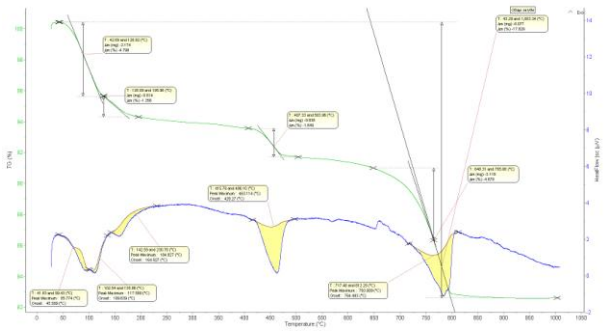

Fig. 8 *DTA - PENETRON Admix*

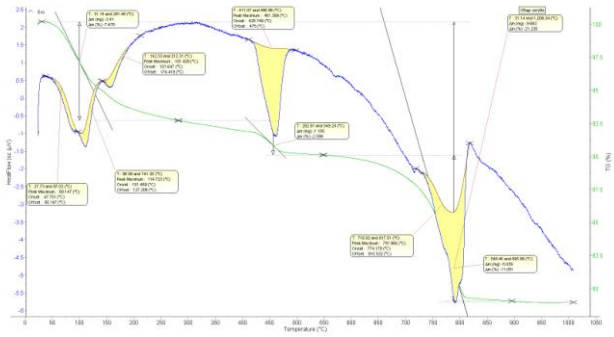

Fig. 9 *DTA - XYPEX C1000 NF*

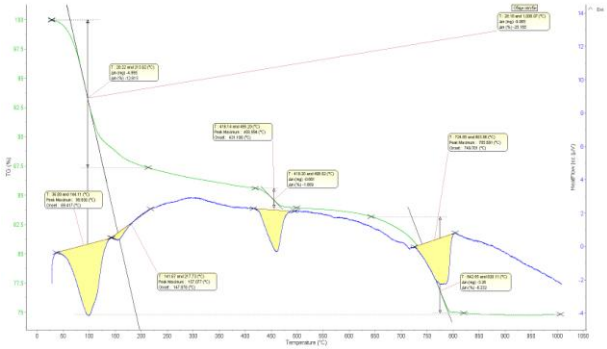

Fig. 10 *DTA - SCHÖMBURG BETOCRETE-CP-360-WP*

With the same workability of the fresh concrete, the crystallization admixtures KRYSTALINE PLUS 2.5 and KRYSTALINE Add1 form a waterproof crystalline structure with a predominant involvement of CSH-type high-alkalinity hydrate formations (main carriers of high mechanical properties of the composite), compared to concrete with PENETRON Admix, XYPEX C1000 NF and SCHÖMBURG BETOCRETE-CP-360-WP.

4.3. Scanning Electron Microscopy (SEM)

The results are presented in Photos 1-6.

Scanning electron microscopy (SEM) is performed using a high magnification electron microscope (up to 10,000 times), resulting in visual data on the shape and size of individual sub-microscopic crystals, their growth, decomposition and destruction processes, and this base passed is sued for past chemical interactions in solution and solid phase, incl. to seal the structure.

In support of the demonstrated significant advantages with respect to the basic physics-mechanical properties of the crystallization additives KRYSTALINE PLUS 2.5 and KRYSTALINE Add1 over PENETRON Admix, XYPEX C1000 NF and SCHÖMBURG BETOCRETE-CP-360-WP, are the results obtained by using modern direct physics-chemical methods. They show that the concrete with KRYSTALINE PLUS 2.5 and KRYSTALINE Add1 form a denser waterproof crystalline structure with a dominant participation of high-alkalinity C-S-H hydrate formations, bearing high mechanical performance of the composite.

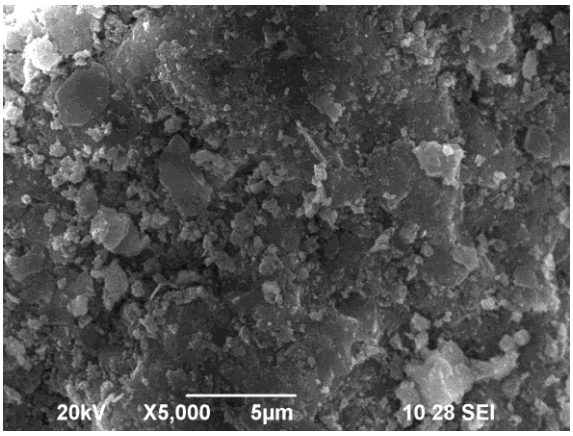

Photo 1 *Reference concrete*

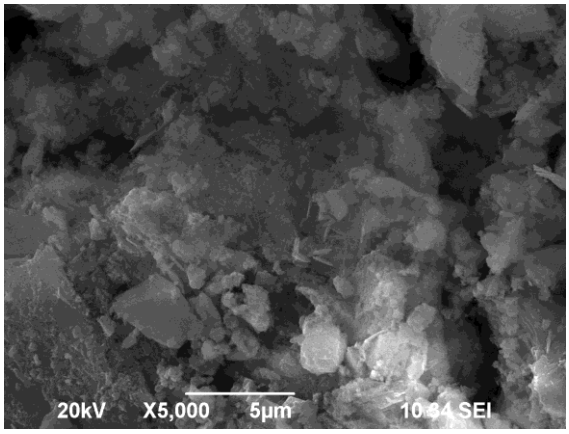

Photo 2 *KRYSTALINE Add1*

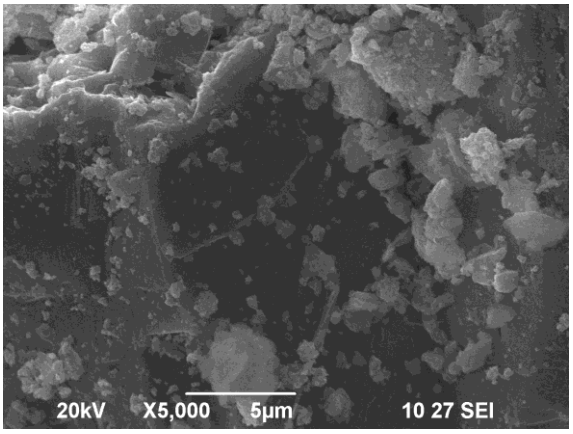

Photo 3 *KRYSTALINE PLUS 2,5*

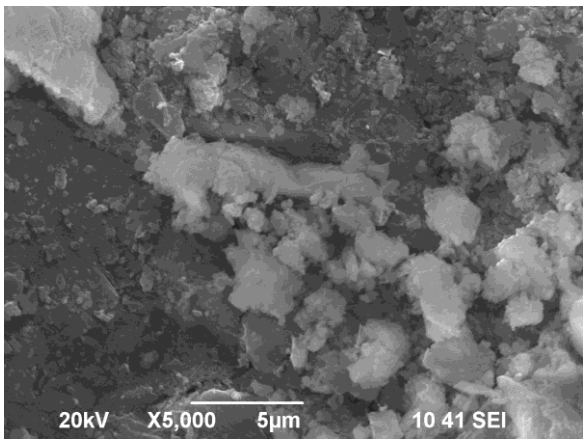

Photo 4 *PENETRON Admix*

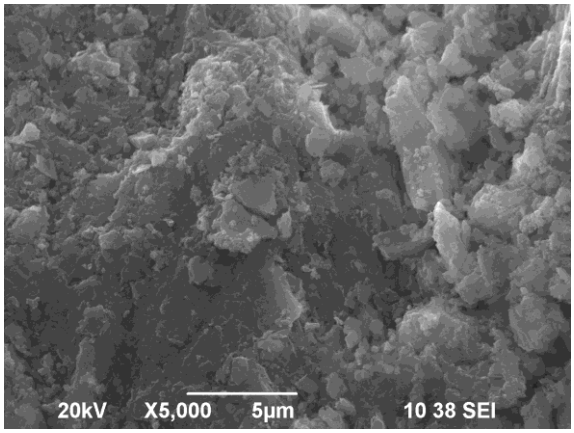

Photo 5 *XYPEX C1000 NF*

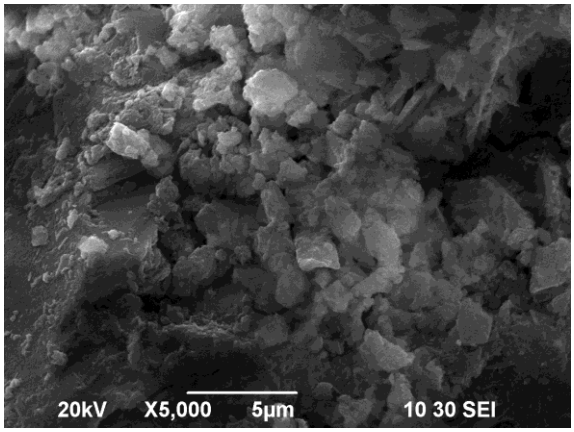

Photo 6 *SCHÖMBURG BETOCRETE-CP-360-WP*

5.Conclusions

The above comprehensive comparative analysis for the evaluation of the basic physical-mechanical and structural characteristics of the fresh and hardened concrete with 5 types of internal crystallization chemical admixtures entering the Bulgarian construction market, objectively presents the characteristics of the compared products.

In accordance with the stated goal, this **TECHNICAL REPORT** is able to assist the participants in the investment construction process (investors, designers, contractors, project managers and supervisors), in situation of an informed choice, to evaluate the complex advantages of KRYSTALINE PLUS 2,5 and KRYSTALINE Add1 to PENETRON Admix, XYPEX C1000 NF and SCHÖMBURG BETOCRETE-CP-360-WP.

Concretes with the participation of KRYSTALINE PLUS 2.5 and KRYSTALINE Add1 (with a constant dosage rate of 2.5, respectively 1.0 kg/m^3), ensure the impermeability and safe water-tightness of the concrete cross section, even under water pressure, without the need for additional waterproofing activities of various types - brushed and sprayed coatings, coiled and membrane conventional systems. At the same time, such concrete have increased frost-resistance and durability without the need for accompanying repair and restoration work.

By all tested parameters, concrete with KRYSTALINE PLUS 2.5 and KRYSTALINE Add1 outperformed with PENETRON Admix, XYPEX C1000 NF and SCHÖMBURG BETOCRETE-CP-360-WP one.

6. References

1. F. Klouda, F. Concrete crystallization gives India's greenest airport wings, *Concrete, vol. 44, no. 3, 2010*
2. X. Shaozhu X., Research and development of cement-based permeable crystallization type waterproof materials abroad, *China Building Waterproofing, vol. 6, 2001*.
3. Y. X. Zhang, X. Du, Y. Li, F. Yang, and Z. Li, Research on cementations capillary crystalline waterproofing coating for underground concrete works, *Advanced Materials Research, vol. 450-451, 2012.*
4. S. Bohus S, R. Drochytka, Cement based material with crystal-growth ability under long term aggressive medium impact, *Applied Mechanics and Materials, vol. 166–169, 2012*
5. P. Reiterman, J. Pazderka, Crystalline coating and its influence on the water transport in concrete, *Advances in Civil Engineering, Vol. 2016, ID 2513514, https://doi.org./10.1155/2016/2513514*
6. V. Naidenov, M. Mironova, I. Rostovsky, Investigation on the efficiency of internal crystallization chemical admixtures for cement concrete - mechanical characteristics, *International Conference Materials, Methods & Technologies, 22-26 June 2020 in Burgas, Bulgaria (to be published).*

Acknowledgments

The financial support of the National Science Fund of Ministry of Education and Science, Bulgaria, contract КП -06 - Н 27/7, 2018, is gratefully acknowledged