Extended research on the efficiency of internal crystallization chemical admixtures for cement concrete - mechanical and structural characteristics

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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.*
The new extended research on such several new types of those admixtures were reported and discussed. The complex mechanical and structural tests are conducted and respective results are compared to predict the admixture's efficiency 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].

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.

Since 2017 and at the moment, a part of the author's scientific interests are directed towards conducting specialized research for the comprehensive characterization of many such admixtures, more or less known on the Bulgarian market.

The admixtures, previously tested and compared are KRYSTALINE Add1, KRYSTALINE Plus 2.5, PENETRON Admix, XYPEX C1000 NF and BETOCRETE-CP-360-WP [2,3].

The present research is devoted to full-range testing and comparing of couple of different crystallization admixtures - KRYSTALINE Add1, Krystol Internal Membrane (KIM®), SIKA WT-200P, MAPEI Indrocrete KR1000 and ADING Hydrofob Crystal.

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 tests method used and all comparative characteristics are equal to previous already published ones [2,3]. 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 has the advantage of being dosed in all cases in constant quantities (1,0 kg/m^3) regardless of the concrete formulation of the concrete. The only requirement is cement content above 300 kg/m^3.

Krystol Internal Membrane (KIM®), SIKA WT-200P, MAPEI Indrocrete KR1000 and ADING Hydrofob Crystal 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 (accordance 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)
Krystol Internal Membrane (KIM®)	Krystol Internal Membrane (KIM®) is a chemical admixture in dry powdered form, effective in creating waterproof concrete. It enhances the hydration process by intensifying and prolonging the hydration of the cementitious materials in concrete. The admixture delays the setting time of concrete. Self-healing cracks up to 0,5 mm wide.	6,60 kg/m^3 (2% by weight of cement, max 8 kg/m^3 concrete)
SIKA WT-200P, SIKA Limited, U.K.	SIKA WT-200P consists of mixture of cements, amino alcohols and fillers to increase the water resistance and concrete durability. Some specific conditions can affect the setting time. Self-healing cracks enhancement.	3,50 kg/m^3 (for concrete with min cement content 350 kg/m^3 and max water-cement ratio 0,45)
MAPEI Indrocrete KR1000, Italy	Indrocrete KR1000 is a mixture of active components which, in presence of water, transform the by-products of cement hydration into crystals reducing concrete porosity and micro-cracks. Self-healing cracks up to 0,4 mm wide.	6,6 kg/m^3 (1-3 kg/100 kg cementitious materials)
ADING Hydrofob Crystal, North Macedonia	Crystallizing waterproofing admixture with hydrophobic effect. Self-healing – no data available.	3,50 kg/m^3 (3-4 kg/m^3 concrete, min compressive class C25/30)

4. Results and discussion

The focus of this paper is to emphasize the significant differences in respective mechanical and micro-structural characteristics at 28-days of age. The first range of testing are performed in accordance of all respective Bulgarian and EN standards. The second one - 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. Mechanical tests

All results are presented in Table 4. The characteristics of the hardened concrete with equal workability of the fresh concrete show significant advantages of crystallization admixtures KRYSTALINE Add1 over Krystol Internal Membrane (KIM®), SIKA WT-200P, Indrocrete KR1000 and Hydrofob Crystal - compressive, tensile splitting strength and modulus of elastic deformation increasing, a reduced depth of water penetration under pressure and significantly higher frost resistance.

***Table 4** Mechanical characteristics*

CHARAC-TERISTICS	**COMPOSITIONS TESTED (at equal workability)**					
	Ref. concrete without admixture	**KRYS-TALINE Add1 1,0 kg/m^3**	**KIM®, Kryton 6,6 kg/m^3**	**SIKA WT–200 P 3,5 kg/m^3**	**Indrocrete 6,6 kg/m^3**	**Hydro-fob Crystal 3,5kg/m^3**
Volume density (mean), kg/m^3	2330	2320	2330	2320	2330	2310
Compressive strength, (mean), MPa compared to reference concrete, %	27,30 0	38,10 +39,56	32,00 +17,21	32,30 +18,32	32,70 +9,78	30,80 +12,82
Tensile splitting strength, (mean), MPa Compared to reference concrete, **%**	2,28 0	2,78 +21,93	2,69 +17,98	2,61 +14,47	2,71 +18,96	2,58 +13,16
Static elastic modulus,GPa compared to reference concrete, %	27,6 0	30,1 +9,1	29,0 +4,7	29,1 +5,4	29,4 +6,1	28,3 +2,2
Depth of water penetration under pressure, mm compared to reference concrete, %	36 0	10 -360	20 -180	21 -171	16 -225	17 -212
Freeze-thaw resistance, weight lost up to 2%: - %, after 2 cycles, (C_{frost} 75); - %, after 3 cycles (C_{frost}100); - %, after 4 cycles (C_{frost}150); - %, after 5 cycles (C_{frost}200)	1,82 (passed) 2,5	0,42 (passed) 0,92 (passed) 1,79 (passed) 2,03	1,03 (passed) 1,60 (passed) 2,13	1,08 (passed) 1,56 (passed) 2,19	0,77 (passed) 1,13 (passed) 2,04	1,03 (passed) 1,94 (passed) 2,46

4.2. 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. 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 5 and Figures 1-6.

Table 5 *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	61	0,13	8,8
KRYSTALINE Add1	35	0,07	7,5
Krystol Internal Membrane (KIM®)	44	0,09	8,3
SIKA WT-200P	50	0,11	9,1
MAPEI Indrocrete KR1000	55	0,09	6,3
ADING Hydrofob Crystal	54	0,10	7,4

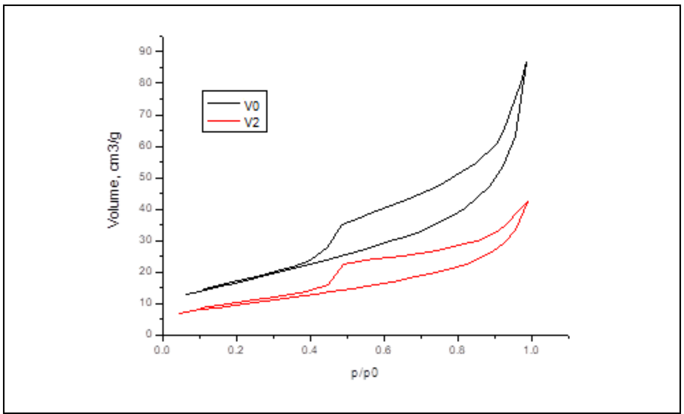

Fig. 1 *Total pore volume -*
Reference concrete (V0) vs. KRYSTALINE Add1 (V2)

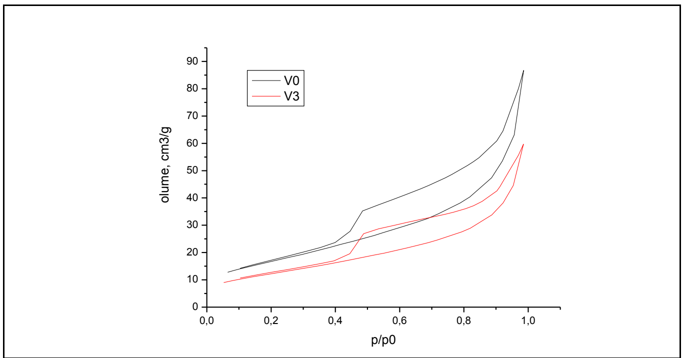

Fig. 2 *Total pore volume -*
Reference concrete (V0) vs. Krystol Internal Membrane (KIM®) *(V3)*

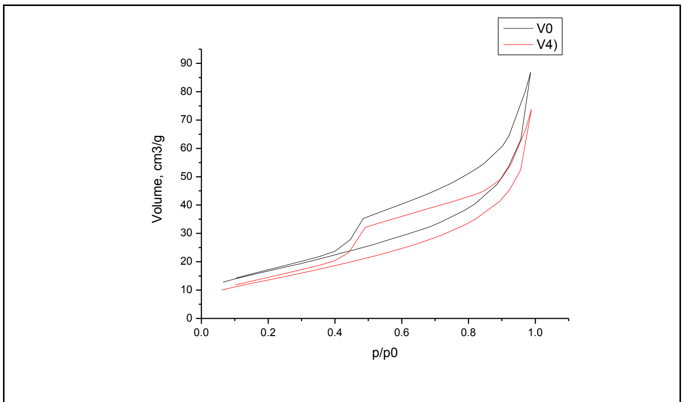

Fig. 3 *Total pore volume -*
Reference concrete (V0) vs. SIKA WT – 200P (V4)

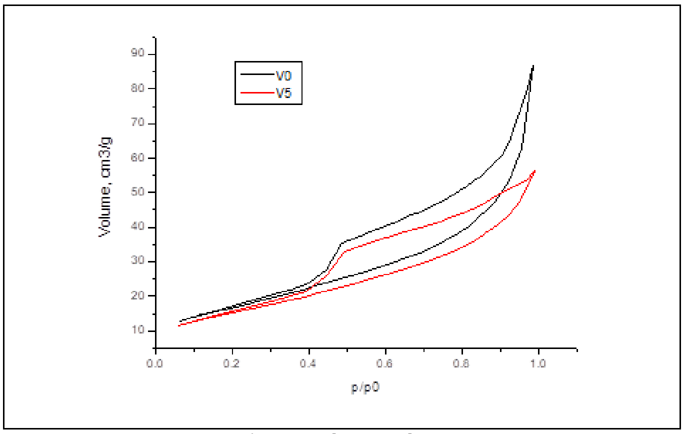

Fig. 4 *Total pore volume -*
Reference concrete (V0) vs. MAPEI Indrocrete (V5)

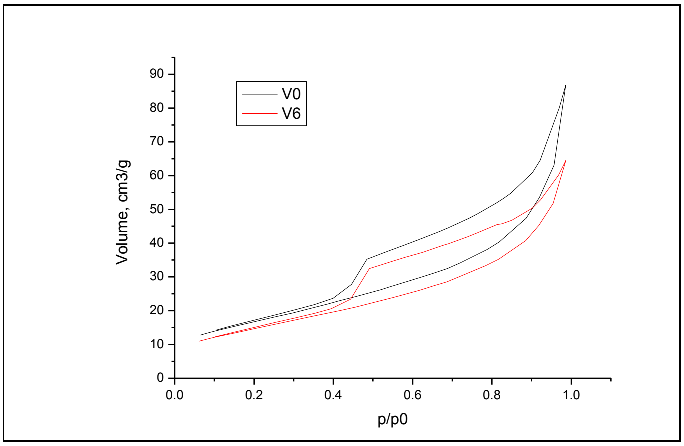

Fig. 5 *Total pore volume -*
Reference concrete (V0) vs Hydrofob Crystal (V6)

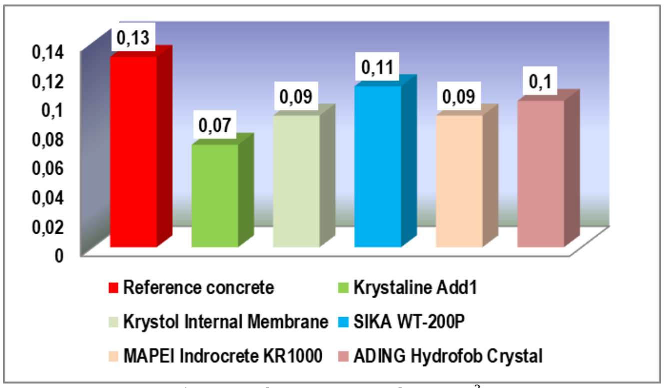

Fig. 6 *Total micro-pore volume, cm^3/g*

With the same workability of the fresh concrete, the crystallization admixture 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 Krystol Internal Membrane (KIM®), SIKA WT-200P, Indrocrete KR1000 and Hydrofob Crystal.

4.2. Differential-thermal analysis (DTA)

The results are presented in Table 6 and Figures 7-12.

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 6 *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	2,311	9,108
KRYSTALINE Add1	1,600	11,089
Krystol Internal Membrane (KIM®)	1,939	9,866
SIKA WT-200P	2,183	9,391
MAPEI Indrocrete KR1000	2,016	10,953
ADING Hydrofob Crystal	2,238	9,403

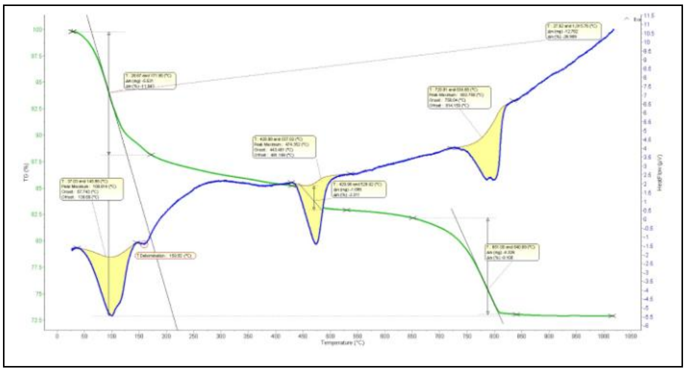

Fig. *7 DTA - Reference concrete*

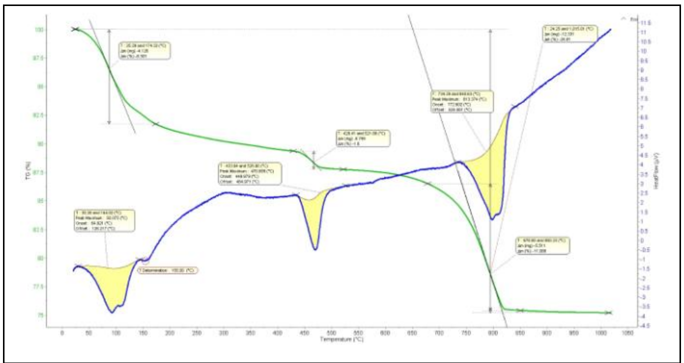

Fig. 8 *DTA - KRYSTALINE Add1*

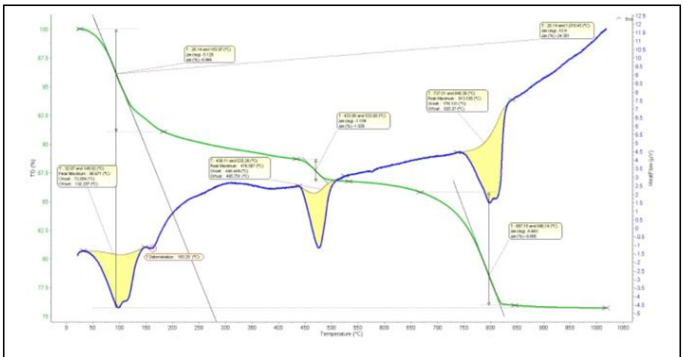

Fig. 9 *DTA- Krystol Internal Membrane (KIM®)*

With the same workability of the fresh concrete, the crystallization admixtures 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 Krystol Internal Membrane (KIM®), SIKA WT-200P, Indrocrete KR1000 and Hydrofob Crystal.

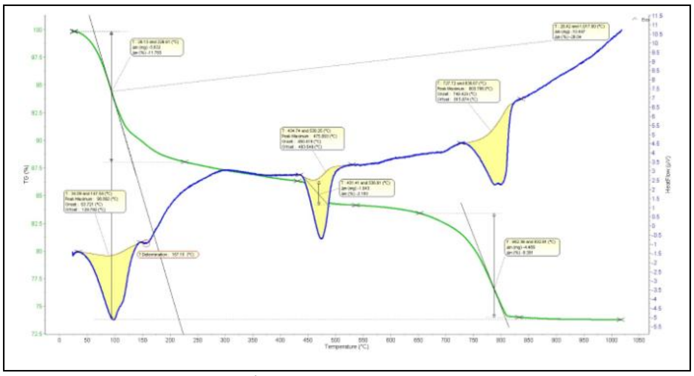

Fig. 10 *DTA - SIKA WT-200P*

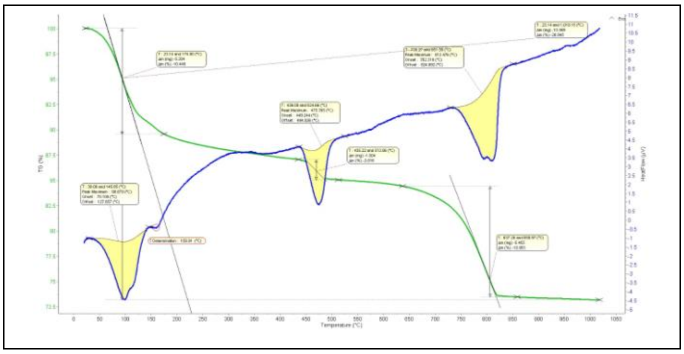

Fig.11 *DTA - MAPEI Indrocrete KR1000*

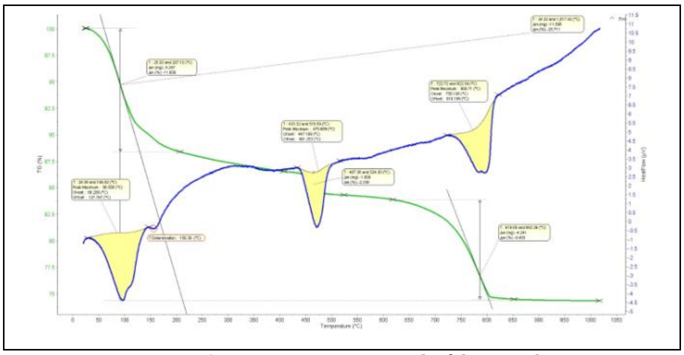

Fig. 12 *DTA - ADING Hydrofob Crystal*

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 additive KRYSTALINE Add1 over Krystol Internal Membrane (KIM®), SIKA WT-200P, Indrocrete KR1000 and Hydrofob Crystal, are the results obtained by using modern direct physics-chemical methods. They show that the concrete with 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.

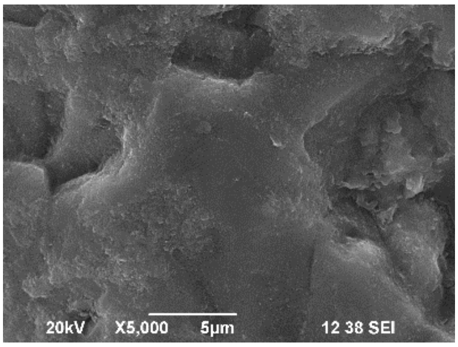

Photo 1 *Reference concrete*

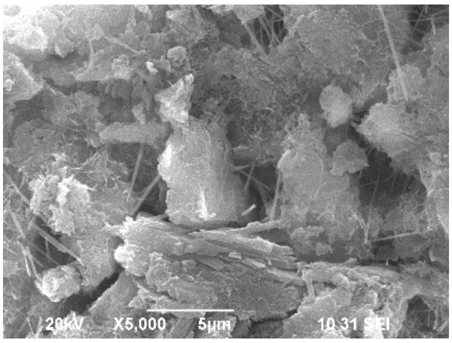

Photo 2 *KRYSTALINE Add1*

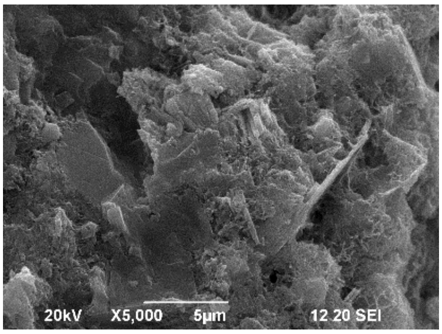

Photo 3 *Krystol Internal Membrane (KIM®)*

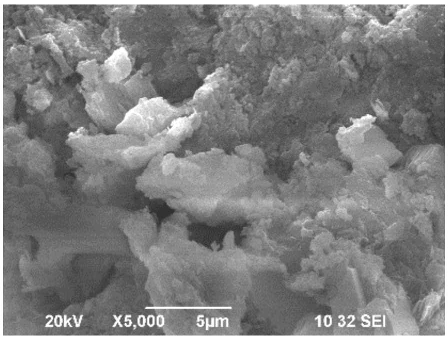

Photo 4 *SIKA WT-200P*

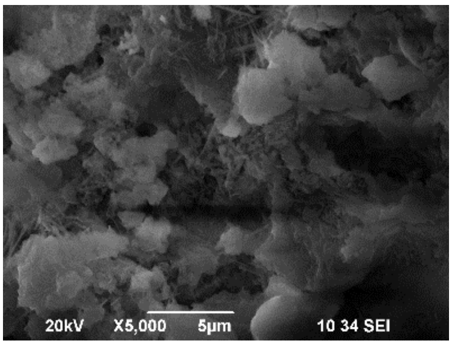

Photo 5 *MAPEI Indrocrete KR1000*

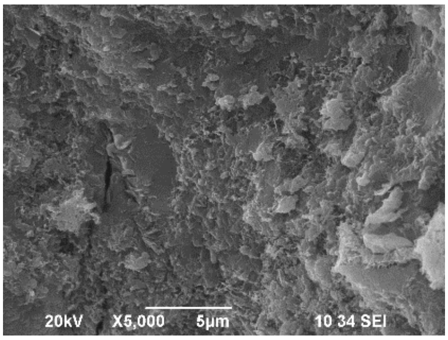

Photo 6 *ADING Hydrofob Crystal*

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 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 Add1 vs. Krystol Internal Membrane (KIM®), SIKA WT-200P, Indrocrete KR1000 and Hydrofob Crystal.

Concretes with the participation of KRYSTALINE Add1 (with a constant dosage rate of 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 has increased frost-resistance and durability without the need for accompanying repair and restoration work.

By all tested parameters, concrete with KRYSTALINE Add1 outperformed with Krystol Internal Membrane (KIM®), SIKA WT-200P, Indrocrete KR1000 and Hydrofob Crystal.

6. References

1. Maher Al-Jabari, Integral waterproofing of concrete structures – Advanced protection technologies of concrete by pore blocking and lining, Elsevier Ltd., 2022, ISBN: 978-0-12-824355-8, USA.

2. 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, ISSN 1314-7269, Volume 14, (25-31).*

3. V. Naidenov., M. Mironova, Investigation on the efficiency of internal crystallization chemical admixtures for cement concrete – structural characteristics, International Scientific Journal “MACHINES. TECHNOLOGIES. MATERIALS”, Issue 3/2020, Year XIV, ISSN print 1313-30226, ISSN web 1314-507X (114-128).