INVESTIGATION ON THE EFFICIENCY OF INTERNAL CRYSTALLIZATION CHEMICAL ADMIXTURES FOR CEMENT CONCRETE - MECHANICAL CHARACTERISTICS

Valeriy B. Naidenov[1], Mirona K. Mironova[1], Ivan A. Rostovsky[2]

[1]Institute of Mechanics, Bulgarian Academy of Sciences, Acad. G. Bonchev Street, Block 4, Sofia 1113, Bulgaria

[2]University of Architecture, Civil Engineering and Geodesy, Hr. Smirnensky Blvd. 1, 1046 Sofia, Bulgaria

Abstract

In recent years, the use of internal crystalline 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 insulations (membranes, rolls, brushed or sprayed coatings, etc.) by purposefully improving the physical-mechanical characteristics of structural concrete, rendering it 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 purpose of the investigations reported 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: *concrete, crystalline chemical admixtures, fresh concrete characteristics, hardened concrete mechanical characteristics*

1. INTRODUCTION

The crystalline waterproofing technology has been invented around for more than 50 years, but it is still considered as a "state-of-the-art" one. Nowadays it has been embraced by the construction industry as a superior replacement method for conventional insulating membranes. For the moment there are a lot of investigations, research and tests performed - virtually in every developed country in the world *(C. Edvardsen, 1996), (X. Shaozhu, 2001), (F. Klouda, 2010), (Y. Zhang, X. Du, Y. Li, F. Yang, and Z. Lip 2012),* (*P. Reiterman and V. Bäumelt, 2014), (S. Bohus and R. Drochytka, 2012), (Reiterman P., J. Pazderka, 2016).*

Shortly, most of crystalline waterproofing systems are based on a revolutionary crystalline technology that turns porous concrete into an impermeable barrier. The result is a innovative structure of concrete cross-section with modified structure with reduced cracking, self-healing and waterproofing abilities which provides a powerful defence against water damage and corrosion of reinforcing steel. In case of new construction, or repaired old one, it is out of doubts, this technology will help to build quality, reliability and cost-effectiveness into the concrete.

The mechanism of crystalline admixtures could be summarized as follow - when water is added to cement, each of the compounds undergoes hydration and contributes to the final concrete product. The tri-calcium silicate (which contributes to initial strength) and di-calcium silicate (which reacts more slowly than the tri-calcium silicate and contributes only to the strength at later times) begins a reaction when water is added to concrete eventually leading to the formation of calcium silicate hydrate crystals within the concrete. Crystalline admixture assists un-hydrated tri-calcium silicate and di-calcium silicate to form millions of thicker and longer calcium silicate hydrate crystals to fill the pores and capillaries.

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 - KRYSTALINE, XYPEX, PENETRON, SCHÖMBURG, etc. The purpose of the investigations reported 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.

The results reported are obtained by set of different tests performed in Bulgarian Academy of Sciences - Institute of Mechanics, Institute of General and Inorganic Chemistry and Institute of Physical Chemistry.

2. MATERIALS AND METHODS

2.1. Materials

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.**

№	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 1. Concrete mix design

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

Table 2. Mineral composition of the Portland cement used

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 **(Table 3).**

Product	Description	Dosage Rates (according producer's recommendations)
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.	**2,50 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)**

Table 3. Product description and dosage rates

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 a 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.

2.2. Methods

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.

In accordance of respective BDS EN 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.

3. RESULTS

*3.1. Fresh concrete **(Table 4)***

Characteristics	Composition tested (at equal workability)					
	Reference concrete without admixture	KRYSTA-LINE Add1 1,0 kg/m^3	KRYSTA-LINE Plus 2,5 2,5 kg/m^3	PENE-TRON Admix 3,0 kg/m^3	XYPEX C1000 NF 4,5 kg/m^3	SCHÖM-BURG BETO-CRETE-CP-360-WP 3,3 kg/m^3
Water-cement ratio for equal workability/	0,763	0,701	0,667	0,720	0,689	0,725
slump, cm	130	130	130	130	130	130
Water reduction compared to K "0", %	0	8,12	12,58	5,64	9,70	4,98
Slump, after 30 min, (cm)	90	110	110	80	80	90
Slump, after 60 min, (cm)	75	90	100	60	60	60
Slump, after 90 min, (cm)	50	70	70	50	50	30
Air entrainment, %	3,2	4,3	3,1	5,1	5,0	4,5
Change, compared to K "0", ±%	0	+34,38	-3,12	+59,38	+56,25	+40,62

Table 4. Fresh concrete comparative characteristics

The established performance of the fresh concrete with equal workability shows significant advantages of crystallization admixtures **KRYSTALINE PLUS 2,5 and KRYSTALINE Add1,** compared to **PENETRON Admix, XYPEX C1000 NF** and **SCHÖMBURG BETOCRETE-CP-360-WP.**

KRYSTALINE PLUS 2,5 and **KRYSTALINE Add1** have a predominantly plasticizing effect over the other admixtures tested - they reduce the water-cement ratio to achieve even workability, at the same time having a significant advantage in terms of fresh concrete retention time.

KRYSTALINE PLUS 2,5 provides a 3,12% reduction in air content over reference concrete. The air content of the concrete with the participation of **KRYSTALINE Add1** slightly exceeds that of the reference concrete, but this increase is less than that realized with the use of the other crystallization admixtures.

3.2. Hardened concrete

Characteristics	**Composition tested (at equal workability)**					
	Reference concrete without admixture	KRYSTA-LINE Add1 1,0 kg/m^3	KRYSTA-LINE Plus 2,5 2,5 kg/m^3	PENE-TRON Admix 3,0 kg/m^3	XYPEX C1000 NF 4,5 kg/m^3	SCHÖM-BURG BETOCRE-TE-CP-360-WP 3,3 kg/m^3
Compressive strength, MPa	27,90	38,40	37,90	31,70	35,60	28,20
Compressive strength increasing compared to K "0", %	0	37,63	35,84	13,62	27,60	1,07
Tensile splitting strength, MPa	2,31	2,84	3,10	2,82	2,63	2,84
Tensile splitting strength increasing compared to K"0", %	0	22,94	34,20	22,08	13,85	22,94
Static modulus of elasticity, GPa	28,0	30,4	30,2	28,8	29,6	28,1
Static modulus of elasticity increasing compared to K "0", %	0	8,5	7,9	2,9	5,7	0,4
Depth of water penetration under pressure, mm	42	15	20	19	23	20
Water penetration decreasing, compared to K "0", %	0	280	210	221	183	210
Freeze-thaw resistance - accelerated method (by mass lost - up to 2%):						
- mass lost (%) after 2 cycles (C_{frost} 75);	1,90 (passed)	1,65 (passed)	1,37 (passed)	1,78 (passed)	1,32 (passed)	1,40 (passed)
- mass lost (%) after 3 cycles (C_{frost} 100);	2,6	1,73 (passed)	1,48 (passed)	1, 96 (passed)	1,70 (passed)	1,89 (passed)
- mass lost (%) after 4 cycles (C_{frost} 150);	-	1,85 (passed)	1,85 (passed)	3,07	2,16	3,18
- mass lost (%) after 5 cycles (C_{frost} 200)	-	2,56	2,13	-	-	-

Freeze-thaw resistance - accelerated method (to reduce the speed of the ultrasonic pulse - up to 15%):						
- reduce the speed (%) after 2 cycles (C_{frost} 75);	13,30 (passed)	11,60 (passed)	10,80 (passed)	11,20 (passed)	10,70 (passed)	10,70 (passed)
- reduce the speed (%) after 3 cycles (C_{frost} 100);	15,00	12,30 (passed)	11,10 (passed)	14,90 (passed)	12,90 (passed)	14,40 (passed
- reduce the speed (%) after 4 cycles (C_{frost} 150);	-	14,50 (passed)	11,90 (passed)	16,30	15,10	17,40
- reduce the speed (%) after 5 cycles (C_{frost} 200)	-	15,00	12,20 (passed)	-	-	-
	-					

Table 5. Hardened concrete comparative characteristics

The so called "accelerated test method" (in accordance of BDS EN standard) was used to determinate the freeze-thaw resistance of the concrete tested. The relationship between the concrete frost resistant class and accelerated cycles passed is given in **Table 6.**

Numbers of accelerated cycles	**2**	**3**	**4**	**5**	**8**	**12**
Frost resistance class of the concrete C_{fr}	**75**	**100**	**150**	**200**	**300***	**400***
*NA. Remark: Frost resistance classes 300 and 400 according to NA.4.3.6 do not exist, but with some responsible equipment, such as airplane runways, extended cycles may be resorted to.						

Table 6. (Table NA.0.2.1. from Bulg. State Standard EN 206: 2013+A1:2016/National Annex A:2017 Relationship between the number of accelerated cycles and the frost resistance class)

4. DISCUSSION

The established performance of the fresh concrete with equal workability shows significant advantages of crystallization admixtures KRYSTALINE PLUS 2,5 and KRYSTALINE Add1, compared to PENETRON Admix, XYPEX C1000 NF and SCHÖMBURG BETOCRETE-CP-360-WP. KRYSTALINE PLUS 2,5 and KRYSTALINE Add1 have a predominantly plasticizing effect over the other admixtures tested - they reduce the water-cement ratio to achieve even workability, at the same time having a significant advantage in terms of fresh concrete retention time. KRYSTALINE PLUS 2,5 provides a 3,12% reduction in air content over reference concrete. The air content of the concrete with the participation of KRYSTALINE Add1 slightly exceeds that of the reference concrete, but this increase is less than that realized with the use of the other crystallization admixtures.

The characteristics of the hardened concrete with equal workability of the fresh concrete show significant advantages of crystallization admixtures KRYSTALINE PLUS 2,5 and KRYSTALINE Add1 over PENETRON Admix, XYPEX C1000 NF and SCHÖMBURG BETOCRETE-CP-360-WP - compressive, tensile splitting strength and modulus of elastic deformation increasing, a reduced depth of water penetration under pressure and significantly higher frost resistance.

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.

Concrete 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 ones.

ACKNOWLEDGMENTS

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

REFERENCES

1. C. Edvardsen, “Water penetrability and autogenously healing of separation cracks in concrete,” *Betonwerk und Fertigteil-Technik*, vol. 62, no. 11, pp. 77–85, 1996.
2. F. Klouda, “Concrete crystallization gives India's greenest airport wings,” *Concrete*, vol. 44, no. 3, pp. 33–34, 2010.
3. X. Shaozhu, “Research and development of cement-based permeable crystallization type waterproof materials abroad,” *China Building Waterproofing*, vol. 6, 2001.
4. Y. 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, pp. 286–290, 2012.
5. S. Bohus and R. Drochytka, “Cement based material with crystal-growth ability under long term aggressive medium impact,” *Applied Mechanics and Materials*, vol. 166–169, pp. 1773–1778, 2012.
6. P. Reiterman and V. Bäumelt, “Long-term sorption properties of mortars modified by crystallizing admixture,” *Advanced Materials Research*, vol. 1054, pp. 71–74, 2014.
7. Reiterman P., 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