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EXPERTISE ON THE IMPACT OF CEMENT ADDITIVE MCI-2006 NS ON THE PROPERTIES OF CEMENT AND CONCRETE

Report number: 150-01/22

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Content

1 INTRODUCTION

Based on the request of the Client Cortec Corporation, an expertise on the influence of the chemical additive MCI-2006 NS (hereinafter: inhibitor) on the properties of cement and concrete was carried out. The client delivered the chemical admixture for concrete MCl-2006 to the Laboratory for Materials, Faculty of Civil Engineering, University of Zagreb, while all other materials for sample preparation were provided by the Faculty of Civil Engineering, University of Zagreb. The aim of the expertise was to systematically prove the influence of a chemical additive added directly to cement on the relevant properties of cement and concrete, necessary for the application of such cement in the construction industry. For the purposes of expertise, tests were conducted at two levels (Table 1):

1) cement level - comparison of cement with the addition of MCI-2006 NS with ordinary cements according to the standard HRN EN 197-:1 2012 Cement -- Part 1: Composition, specifications and conformity criteria of general purpose cement [1],
2) concrete level – comparison of concrete prepared with cement with the addition of MCI-2006 NS with the reference concrete exposed to the environmental class (salts from the sea - XS) according to the standard HRN EN 206.

Table 1. Overview of the experimental plan on cement and concrete level

CEMENT LEVEL				CONCRETE LEVEL			
Materials	**Inhibitor**	**Testing**	**Standard**	**Materials**	**Inhibitor**	**Testing**	**Standard**
CEM II/B-LL 42,5 N CEM II/A-LL 42,5 R CEM II/A-M (S-V) 42,5 N CEM III/A 42,5 N LH	0,5 % weight of cem.	Chemical analysis	HRN EN 196-2:2013	CEM II/B-LL 42,5 N	0,1 % / 0,25 % / 0,5 % weight of cem.	Temperature	HRN EN 12350-1:2019
		Free lime	HRN EN 451-1:2017			Consistency - slump	HRN EN 12350-2:2019
		Fineness	HRN EN 196-6:2019			Density	HRN EN 12350-6:2019
		Density	ASTM C 188			Air content	HRN EN 12350-7:2019
		Heat of hydration	HRN EN 196-11:2019			Compressive strength	HRN EN 12390-3:2019
		Standard consistency	HRN EN 196-3:2016			Water permeability	HRN EN 12390-8:2019
		Setting time	HRN EN 196-3:2016			Chloride migration	HRN EN 12390-18:2021
		Volume stability	HRN EN 196-3:2016			Carbonation	HRN EN 12390-12:2020
		Compressive strength	HRN EN 196-1:2006			Gas permeability	RILEM TC116-PCD
						Freezing and thawing	HRN CEN/TS 12390-9:2006
						Accelerated corrosion	ASTM G109 – 07
						Accelerated corrosion with impressed voltage	HRN EN 480-14

2 INFLUENCE OF INHIBITOR ON CEMENT

For the purposes of testing the impact of the powder material MCI-2006 NS as an additive to cement, four different types of cement CEM II and CEM III from different manufacturers in the Republic of Croatia were used:

- Portland cement with the addition of limestone CEM II/B-LL 42.5 N manufactured by Holcim,
- Portland cement with mixed addition of slag and siliceous fly ash CEM II/A-M (S-V) 42.5 N manufactured by Nexe,
- Portland cement with mixed addition of limestone CEM II/A-LL 42.5 R manufactured by Holcim,
- Mixed cement with slag CEM III/A 42.5 N LH produced by Cemex,

whose denomination is given in Table 2. In consultation with the Client, CEM I 42.5 R produced by Holcim was replaced by cement CEM II/B-LL 42.5 N produced by Holcim due to its wide availability on the market.

According to the technical sheet, MCl-2006 is a powder additive to concrete, which acts as a corrosion inhibitor to protect metal reinforcement in concrete structures. According to the technical sheet, the recommended dose of inhibitor is 0.6 kg/m^3 of concrete. Since the idea of the project is to use the inhibitor as a mineral additive in the cement, the percentage of the recommended dose of the inhibitor is expressed as a percentage of the cement mass. For classic concrete with 300 - 350 kg of cement per m^3 of concrete, the recommended dose of inhibitor would be about 0.2% by mass of cement. In order to determine the influence of MCI-2006 NS powder material as an additive to cement on cement properties, tests were conducted on the mentioned cements with and without the addition of the inhibitor MCI-2006 NS, added in a significant dose of 0.5% of the additive by mass of cement.

Table 2. Cements used in the study

Nb	Designation	Type	Producer	Inhibitor	Description
1	CEM II/B-LL 42,5 N	CEM II/B-LL 42,5 N	HOLCIM	-	Portland cement with the addition of limestone with normal strength gain
2	CEM II/A-LL 42,5 R	CEM II/A-LL 42,5 R	HOLCIM	-	Portland cement with the addition of limestone with rapid strength gain
3	CEM II/A-M(S-V) 42,5 N	CEM II/A-M(S-V) 42,5 N	NEXE	-	Portland cement with mixed addition of slag and siliceous fly ash with normal strength gain
4	CEM III/A 42,5 N LH	CEM III/A 42,5 N LH	CEMEX	-	Mixed cement with slag, normal strength gain, low heat of hydration
5	CEM II/B-LL 42,5 N + 0,5 %	CEM II/B-LL 42,5 N + 0,5 % MCI-2006 NS	HOLCIM	0,5 % w_{cement}	Portland cement with the addition of limestone with normal strength gain with inhibitor 0,5% weight of cement
6	CEM II/A-LL 42,5 R + 0,5 %	CEM II/A-LL 42,5 R + 0,5 % MCI-2006 NS	HOLCIM	0,5 % w_{cement}	Portland cement with the addition of limestone with rapid strength gain with inhibitor 0,5% weight of cement
7	CEM II/A-M(S-V) 42,5 N+ 0,5 %	CEM II/A-M(S-V) 42,5 N+ 0,5 % MCI-2006 NS	NEXE	0,5 % w_{cement}	Portland cement with mixed addition of slag and siliceous fly ash with normal strength gain with inhibitor 0,5% weight of cement
8	CEM III/A 42,5 N LH + 0,5 %	CEM III/A 42,5 N LH + 0,5 % MCI-2006 NS	CEMEX	0,5 % w_{cement}	Mixed cement with slag, normal strength gain, low heat of hydration with inhibitor 0,5% weight of cement

2.1 Testing methods and sample preparation

For the purposes of testing the impact of the powder chemical additive MCI-2006 NS in cement, tests were carried out at the level of cement, cement paste and at the level of mortar. Powder material MCI-2006 NS was added to cement as 0.5% by weight of cement, where homogenization of the added material and cement was done by grinding for 60 seconds in a laboratory mill for processing fine powder samples Matest A091-02.

The determination of the chemical composition of cements is based on analyzing the mass fractions (wt. %) of individual oxides in the powder material. The chemical composition of cement and the loss on ignition were tested according to the HRN EN 196-2:2013 Cement test methods -- Part 2: Chemical analysis of cement [2]. The free lime content was determined according to the HRN EN 451-1:2017 Fly ash test method -- Part 1: Determination of the free calcium oxide content [3], while the cement density was determined using a Le Chatelier flask in accordance with the standard for determining the density of cement ASTM C 188 [4].

Grinding fineness is determined according to HRN EN 196-6:2019 Cement test methods -- Part 6: Determination of fineness [5] by sieving with air flow on a 63 µm sieve. The heat of hydration of cement pastes was determined using the TAM calorimeter device according to HRN EN 196-11:2019 Cement test methods -- Part 11: Heat of hydration -- Isothermal conduction calorimetry procedure [6]. The mixture was made in such a way that 50 g of cement was mixed with 20 g of deionized water for 2 minutes, where the ratio of water and binder is 0.4 for each type of cement. For testing purposes, it is necessary to use two samples for each type of binder: a test sample and a reference sample. The mass of the test sample of cement paste is 10 g. Before the start of the test, all materials were conditioned at a temperature of 20 ± 0.05 °C.

Standardized consistency, setting time and volume stability are determined in accordance with the standard HRN EN 196-3:2016 Cement test methods -- Part 3: Determination of setting time and volume stability [7]. For the purposes of preparing the paste samples, the cements given in Table 2 and tap water at a temperature of 20 ± 2 °C were used. The mixtures were made using 500 g of cement and 125 g of water in accordance with HRN EN 196 – 3 [7]. The standard consistency test was carried out using a Vicat apparatus with a standard roller (diameter 10 mm, standard weight). Setting time was determined using a ToniSET one/two model 7302/0063 automatic setting time test device, while control of volume stability was tested using Le Chatelier rings. The compressive strength of cement was tested on mortar mixes prepared according to HRN EN 196-1:2006, Cement test methods -- Part 1: Determination of strength [8]. The composition of the mortar and the storage of the material before use is in accordance with the specified norm, which determines that the mass ratio of the components of CEN standard sand, cement and water should be 3:1:0.5. Each batch of mortar contained 1350 ± 5 g of sand, 450 ± 2 g of cement and 225 ± 1 g of water. The properties tested and the standards according to which the tests were carried out are shown in Table 3.

Table 3. List of tests on cement/cement paste/mortar level

Testing	Purpose of test	Standard
Chemical analysis	Oxide composition, loss on ignition (LOI) - compliance with cement requirements	HRN EN 196-2:2013 Methods of testing cement-Part 2: Chemical analysis of the cement
Free lime	Influence of powder additive on the risk of volume expansion during curing	HRN EN 451-1:2017 Methods for testing fly ash-Part 1: determination of free calcium oxide content
Fineness	Influence of the additive on the particle size distribution of cement	HRN EN 196-6:2019 Methods for testing cement - Part 6: Determination of fineness
Density	Influence of the additive on density, which is taken into account when calculating the composition of concrete	ASTM C 188 Density test of hydraulic cement
Heat of hydration	Influence of the additive on the cement hydration development and on the total heat of hydration	HRN EN 196-11:2019 Methods of testing cement- part 11: Heat of hydration - Isothermal Conduction Calorimetry method
Standard consistency	Influence of the additive on the total water consumption	HRN EN 196-3:2016 Methods of testing cement-Part 3: Determination of setting times and soundness
Setting time	Influence of the additive on the setting time depending on the amount of additive added	HRN EN 196-3:2016 Methods of testing cement-Part 3: Determination of setting times and soundness

Volume stability	Elimination of the possible increased risk of volume instability of addition containing cement	HRN EN 196-3:2016 Methods of testing cement-Part 3: Determination of setting times and soundness
Compressive strength	Influence of different amount of admixture on mechanical properties of cement	HRN EN 196-1:2016 Methods for testing cement - Part 1: Determination of strength

2.2 Results

2.2.1 Tests on cement level

Table 4 shows the results of the physical and chemical properties of different cements compared to CEM II/B-LL 42.5 N cement with 0.5% MCI-2006 NS by weight of cement. It can be seen that with the addition of MCl-2005 to the mass of CEM II/B-LL 42.5 N cement, there are no deviations in the chemical and physical properties of the cement, and that there are no changes in the composition that would cause non-acceptance according to the HRN EN 197-1 standard.

Table 4. Chemical and physical properties of cement

mass %	CEM II/B-LL 42,5 N	CEM II/A-LL 42,5 R	CEM II/A-M(S-V) 42,5 N	CEM III/A 42,5 N LH	CEM II/B-LL 42,5 N + 0,5%	Requirements according to HRN EN 197-1
LOI, 950°C	10,6	7,9	2,77	2,83	10,7	≤5,0 % for CEM I and CEM III
SO_3	3,05	3,08	3,35	2,67	3,04	≤3,5 % for 42,5 N; ≤4,0 % for 42,5 R
Cl^{--}	/	/	0,033	0,067	/	≤0,1 %
CaO	63,63	62,32	55,64	55,22	63,59	
MgO	1,34	1,43	3,06	3,42	1,31	
Fe_2O_3	2,63	2,74	2,89	1,97	2,63	
Al_2O_3	4,5	4,7	6,47	6,95	4,55	
SiO_2	23,26	24,16	23,08	24,56	23,3	
Pozzolanic oxides	30,39	31,6	32,44	33,48	30,48	
MnO	0,03	0,79	0,28	0,236	0,03	
Na_2O	0,65	0,56	0,24	0,28	0,65	
K_2O	0,87	0,95	0,83	0,7	0,87	
Alkalis	1,22	1,19	0,79	0,74	1,22	
P_2O_5	0,08	0,07	/	/	0,08	
TiO_2	<0,01	<0,01	/	/	<0,01	
Density, g/cm^3	3,21	3,12	2,67	2,95	3,04	
Fineness, %	1,74	0,52±0,07	1,98±0,8	2,89±0,05	1,96	

2.2.2 Tests of cement paste in fresh state

Table 5 shows the results of testing the standard consistency, setting time and volume stability of the tested pastes in order to determine the possibility of using MCI-2006 NS as an additive to cement. In addition to the cement CEM II/B-LL 42.5 N manufactured by Holcim, tests of standard consistency and setting time were also carried out on the cements CEM II/A-LL 42.5 R manufactured by Holcim, CEM II/A-M(S-V) 42, 5 N produced by NEXE d.d. and CEM III/A 42.5 N LH manufactured by CEMEX to determine the inhibitor effect on different cements with different additives (slag, limestone and fly ash), Figure 1 and Figure 2. Slag, limestone and coal fly ash are the most common additives used in the production of mixed cements.

Table 5. Results of tests on cement paste

<table>
<tr><th colspan="2">Mixes</th><th>Standard consistency (%)</th><th>Initial setting time (min.)</th><th>Final setting time (min.)</th><th>Volume stability (mm)</th></tr>
<tr><td colspan="2">CEM II/B-LL 42,5 N</td><td>29,0</td><td>190,5</td><td>231,5</td><td>0,80</td></tr>
<tr><td colspan="2">CEM II/A-LL 42,5 R</td><td>29,7</td><td>135,0</td><td>210,0</td><td>0,41</td></tr>
<tr><td colspan="2">CEM II/A-M(S-V) 42,5 N</td><td>28,0</td><td>210,0</td><td>325,0</td><td>0,93</td></tr>
<tr><td colspan="2">CEM III/A 42,5 N LH</td><td>27,9</td><td>180,0</td><td>270,0</td><td>0,09</td></tr>
<tr><td colspan="2">CEM II/B-LL 42,5 N + 0,5%</td><td>27,0</td><td>504,5</td><td>556,0</td><td>0,41</td></tr>
<tr><td colspan="2">CEM II/A-LL 42,5 R + 0,5%</td><td>24,6</td><td>421,0</td><td>473,0</td><td>/</td></tr>
<tr><td colspan="2">CEM II/A-M(S-V) 42,5 N + 0,5%</td><td>25,5</td><td>848,5</td><td>1002,0</td><td>/</td></tr>
<tr><td colspan="2">CEM III/A 42,5 N LH + 0,5%</td><td>25,1</td><td>1032,0</td><td>1084,0</td><td>/</td></tr>
<tr><td colspan="6">Requirements according to HRN EN 197-1</td></tr>
<tr><td rowspan="3">Strength class</td><td>42,5 L</td><td rowspan="3">/</td><td rowspan="3">≥ 60</td><td rowspan="3">/</td><td rowspan="3">≤ 10</td></tr>
<tr><td>42,5 N</td></tr>
<tr><td>42,5 R</td></tr>
</table>

According to the obtained results, there are no significant deviations from the results of the standard consistency of the examined cements. All mixtures with the addition of inhibitors have a reduced need for water and greater workability, Figure 1. This is most noticeable when using cement with the addition of limestone and high early strength (cement CEM II/A-LL 42.5 R manufactured by Holcim), whose water requirement is reduced by 17% with the addition of inhibitors compared to the mixture without inhibitors.

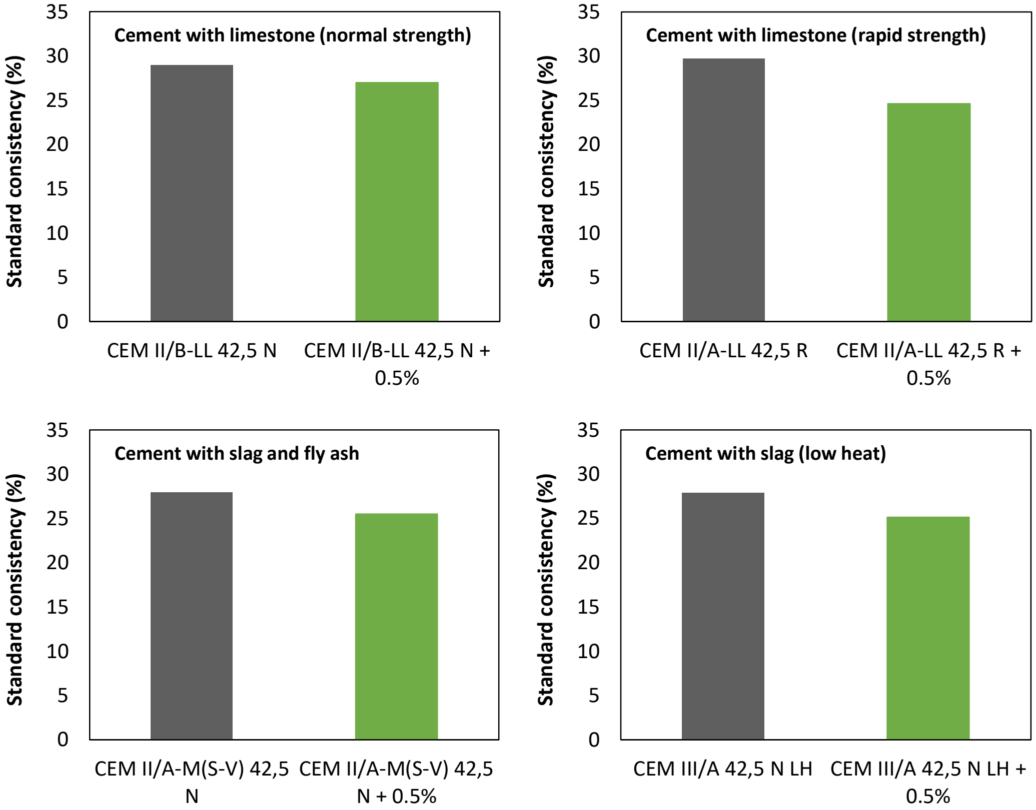

Figure 1 Standard consistency for: a) CEM II/B-LL 42,5 N without and with the addition of inhibitor; b) CEM II/A-LL 42,5 R without and with the addition of inhibitor; c) CEM II/A-M(S-V) 42,5 without and with the addition of inhibitor; d) CEM III/A 42,5 N without and with the addition of inhibitor

The requirement according to the HRN EN 197-1 standard [1] for a minimum initial setting time of 60 minutes is met by all tested mixtures, Figure 2. It can be seen that the initial setting time is prolonged in the case of the addition of inhibitors in all cements. The least significant increase in the initial and final setting time is in the case of cements with limestone, while the most significant increase in setting time was observed in cements with slag.

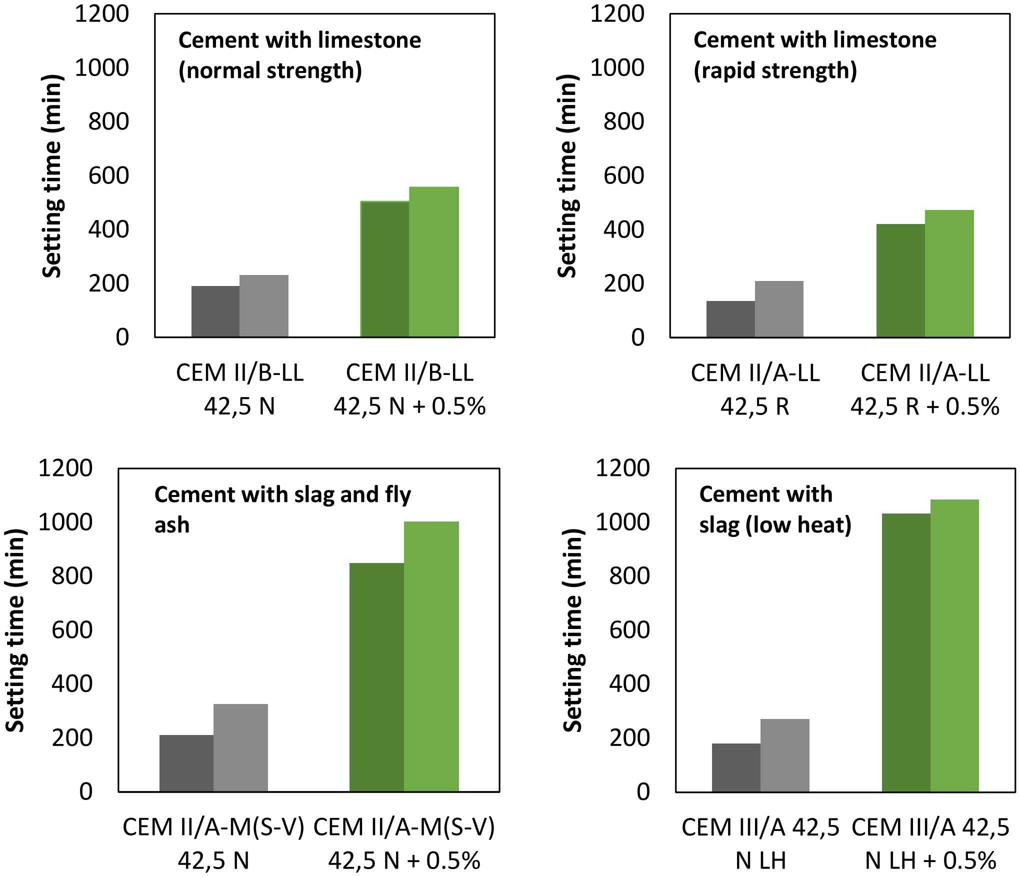

Figure 2. Initial and final setting time for: a) CEM II/B-LL 42,5 N without and with the addition of inhibitor; b) CEM II/A-LL 42,5 R without and with the addition of inhibitor; c) CEM II/A-M(S-V) 42,5 N without and with the addition of inhibitor; d) CEM III/A 42,5 N without and with the addition of inhibitor

Dimensional stability is one of the most important properties that contribute to the durability of concrete elements. The appearance of cracks enables the penetration of aggressive substances from the environment and, consequently, the reduction of the durability of structures [9]. Based on the results of the volume stability test, all tested cement paste mixtures meet the criterion of a distance between the ends of the needles of Le Chatelier rings of a maximum of 10 mm according to the HRN EN 197-1 standard [1]. Likewise, the mixture with the addition of inhibitors in the reference cement CEM II/B-LL 42.5 N did not show a significant change in dimensional stability.

2.2.3 Heat of hydration

Figure 3 shows the results of heat of hydration development and heat flow development for cements with and without the addition of inhibitors using the isothermal calorimetry method. Cement hydration is an exothermic reaction that takes place in several stages: (1) rapid initial processes; (2) induction period; (3) acceleration period; (4) retardation period and (5) long-term reactions [10].

Table 6 provides an overview of the heat of hydration in certain time intervals, the time in hours until the appearance of the maximum heat flow, as well as the value of the maximum (highest) peak of the heat flow curve.

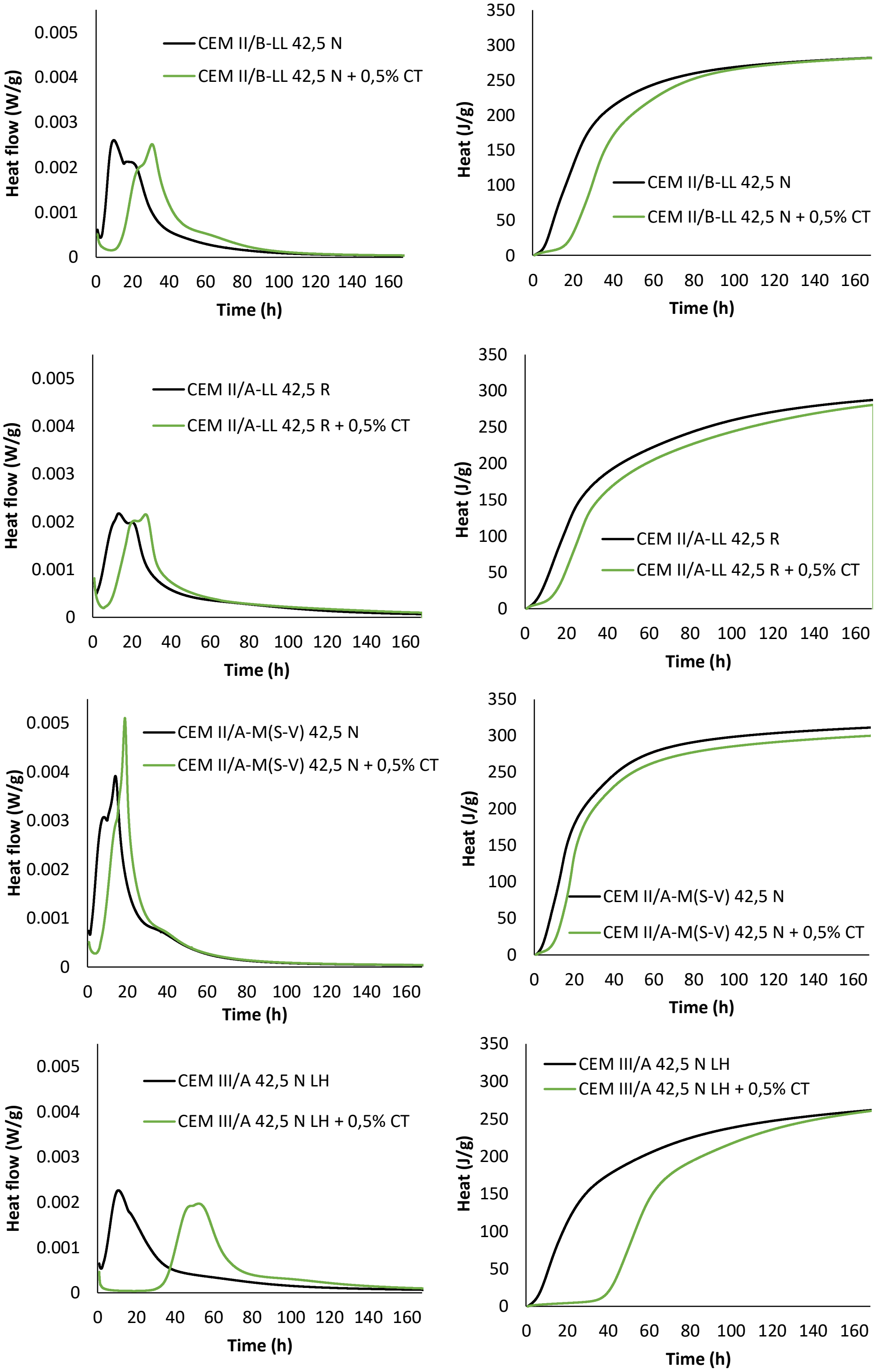

Figure 3. Development of heat flow over time of cements with (green line) and without inhibitors (black line) - images on the left; Development of the heat of hydration in time of cements with (green line) and without inhibitors (black line) - images on the right, for different cements

According to the diagrams, it can be seen that with the addition of inhibitors to all types of cement, there is a delay in the onset of the period of acceleration of hydration, which is correlated with the setting time values. This phenomenon is most pronounced in the mixture based on cement CEM III/A 42.5 N LH (Figure 3), where the beginning of setting is 1032 minutes, i.e. 473% delayed setting compared to the mixture without inhibitors. In addition, a reduced initial heat of hydration was observed for all mixtures with an inhibitor compared to those without an inhibitor. The retardation period is associated with the reaction of the aluminate phase (C_3A) and represents the additional formation of ettringite [11], which appears as an additional peak on the heat flow curve. It is noticeable that in the case of mixing inhibitors with cements containing fly ash from coal and slag (CEMII/A-M(S-V) 42.5 N) a significantly pronounced peak of the aluminate phase (C_3A). Regardless of the delay in the period of acceleration of hydration, after 7 days the same heat of hydration was released in cement with an inhibitor and the same type of cement without an inhibitor.

According to HRN EN 197-1 [1], for cements lower heat of hydration (label: LH), the criterion of 270 J/g must be met after 7 days of measurement, which is met for mixtures based on cement CEM III/ A 42.5 N LH without (263.50 J/g) and with added inhibitor (260.60 J/g).

Table 6. Values of heat of hydration measurements by isothermal calorimetry

Mix	CEM II/B-LL 42,5 N		CEM II/A-LL 42,5 R		CEM II/A-M(S-V) 42,5 N		CEM III/A 42,5 N LH	
	No inhibitor	0,5%	No inhibitor	0,5%	No inhibitor	0,5%	No inhibitor	0,5%
Heat after 1 hour (J/g)	0,543	0,493	0,618	0,722	0,691	0,466	0,587	0,369
Heat after 1 day (J/g)	158,62	99,50	145,67	83,02	191,57	172,01	136,63	5,10
Heat after 3 days (J/g)	248,52	247,87	237,20	217,25	268,05	272,93	221,71	179,43
Heat after 7 days (J/g)	277,73	282,39	285,37	280,64	290,96	299,87	263,50	260,60
Time at 1st peak (h)	8,67	25,43	12,98	27,05	14,17	18,78	10,34	52,34
Highest peak (mW/g)	2,440	3,217	2,306	2,153	3,802	5,111	2,355	1,968

2.2.4 Mechanical properties

The compressive strength of cements without and with the addition of inhibitors after 2 days and after 28 days is in the table (Table 7) and in the figures (Figure 4 and Figure 5). According to the criteria given in the HRN EN 197-1 standard [1], the early compressive strength must be greater than or equal to 10 MPa after 2 days for cements class N (normal strength gain) or R (high strength gain). All cements with or without inhibitors meet the specified criteria for compressive strength after 2 days for cements marked N (≥10.0 MPa) and cements marked R (≥20.0 MPa). By comparing the values of mixtures with and without inhibitors, it is evident that with the addition of inhibitors to cements containing limestone, there is a slight increase in early compressive strength by 8% (CEM II/B-LL 42.5 N + 0.5%)

and 3% (CEM II/ A-LL 42.5 R + 0.5%) compared to CEM II/B-LL 42.5 N and CEM II/A-LL 42.5 R mixtures. In cement mixtures with the addition of slag and fly ash or only slag with an inhibitor there is a slight reduction of early compressive strength 16 % (CEM II/A-M(S-V) 42.5 N + 0.5%) and 30 % (CEM III/A 42.5 N LH + 0.5%) compared to mixtures without inhibitors (CEM II/A-M(S-V) 42.5 N and CEM III/A 42.5 N LH).

After 28 days, the compressive strength must be greater than or equal to 42.5 MPa, or less than or equal to 62.5 MPa according to the criteria given in the HRN EN 197-1 standard [1]. Taking into account the standard deviation, all mixtures except for the mixture in which the inhibitor was added to the cement CEM III/A 42.5 N LH, meet the given criteria. As in the case of early compressive strength in cement mixtures with the addition of slag and fly ash or only slag with an inhibitor, there is a slight reduction of compressive strength after 28 days by 5% (CEM II/A-M(S-V) 42.5 N + 0.5%) and 14 % (CEM III/A 42.5 N LH + 0.5%) compared to mixtures without inhibitors (CEM II/A-M(S-V) 42.5 N and CEM III/A 42.5 N LH). The mixture CEM II/A-LL 42.5 R + 0.5% has a 14% lower compressive strength after 28 days compared to the mixture CEM II/A-LL 42.5 R, while only the mixture CEM II/B-LL 42 .5 N + 0.5% shows a slight increase in compressive strength by 5% compared to the CEM II/B-LL 42.5 N mixture.

Table 7. Results of compressive and tensile strength on mortar

Mix	**Compressive strength (MPa)**		**Standard deviation of compressive strength (MPa)**		**Tensile strength (MPa)**		**Standard deviation of tensile strength (MPa)**	
	2 days	**28 days**	**2 days**	**28 days**	**2 days**	**28 days**	**2 days**	**28 days**
CEM II/B-LL 42,5 N	26,74	41,88	0,16	1,22	3,31	8,15	0,07	0,20
CEM II/A-LL 42,5 R	32,38	54,18	0,75	0,93	4,76	5,99	0,11	0,51
CEM II/A-M(S-V) 42,5 N	23,49	46,99	0,33	3,46	5,44	6,95	0,38	0,29
CEM III/A 42,5 N LH	20,16	48,23	0,14	1,15	4,10	6,61	0,14	0,33
CEM II/B-LL 42,5 N + 0,5%	28,89	44,11	0,10	0,16	3,30	8,28	0,04	0,33
CEM II/A-LL 42,5 R + 0,5%	33,27	46,51	1,52	3,13	3,66	7,56	0,07	0,65
CEM II/A-M(S-V) 42,5 N + 0,5%	19,66	44,58	0,28	1,47	3,15	5,91	0,45	0,68
CEM III/A 42,5 N LH + 0,5%	14,21	41,40	0,29	2,62	1,56	8,56	0,27	0,48
Requirements according to HRN EN 197-1								
42,5 N	**≥10,0**	**≥42,5; ≤62,5**	/	/	/	/	/	/
42,5 R	**≥20,0**	**≥42,5; ≤62,5**	/	/	/	/	/	/

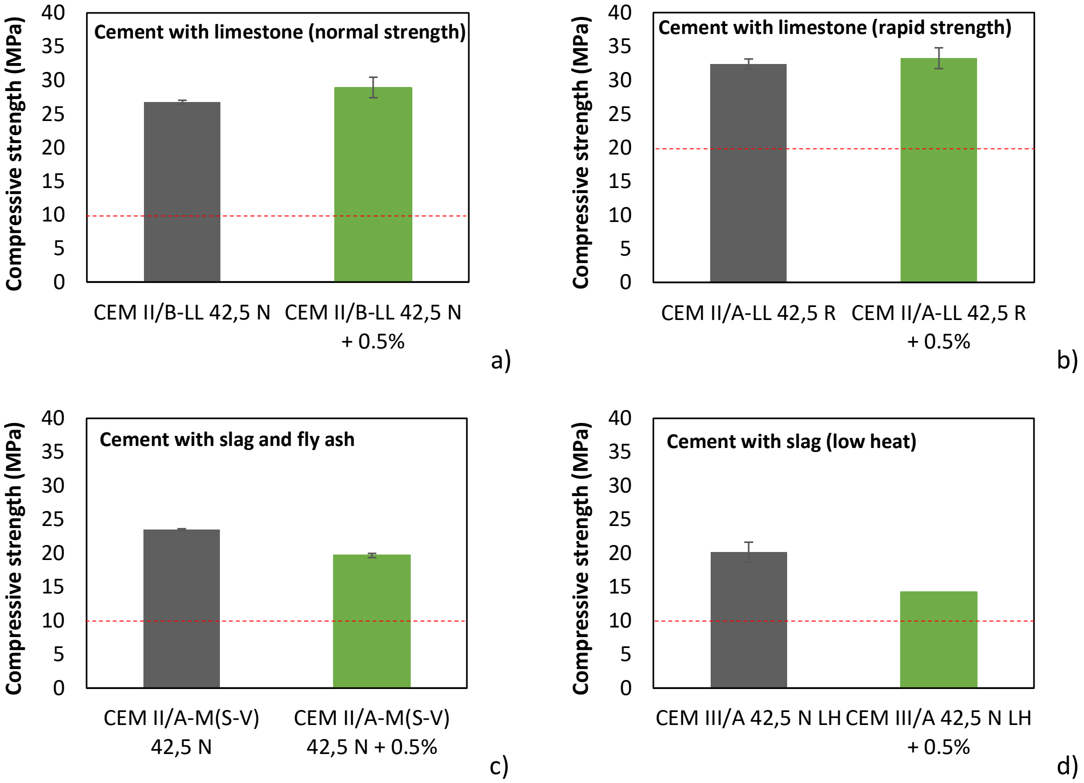

Figure 4 Compressive strength after 2 days for: a) CEM II/B-LL 42,5 N without and with the addition of inhibitor; b) CEM II/A-LL 42,5 R without and with the addition of inhibitor; c) CEM II/A-M(S-V) 42,5 N without and with the addition of inhibitor; d) CEM III/A 42,5 N without and with the addition of inhibitor

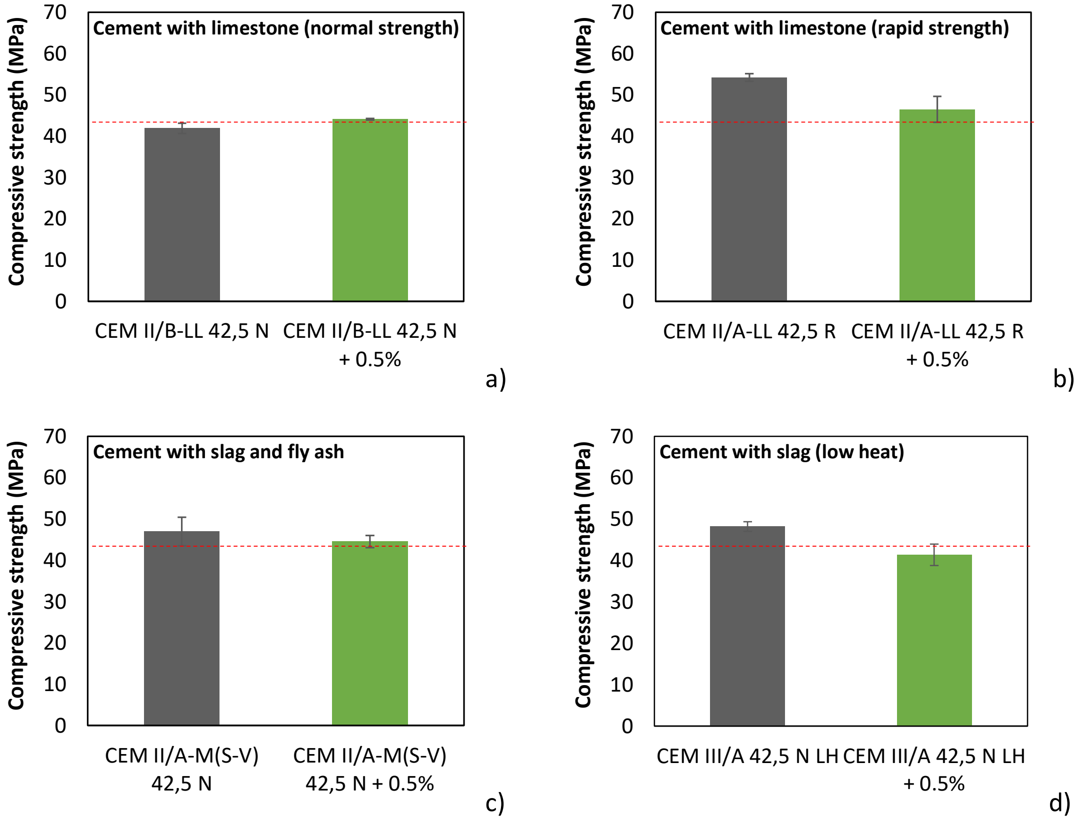

Figure 5 Compressive strength after 28 days for: a) CEM II/B-LL 42,5 N without and with the addition of inhibitor; b) CEM II/A-LL 42,5 R without and with the addition of inhibitor; c) CEM II/A-M(S-V) 42,5 N without and with the addition of inhibitor; d) CEM III/A 42,5 N without and with the addition of inhibitor

2.3 Conclusion on the effect of inhibitor on cement

Tests at the level of cement were carried out on the most represented cements on the market of the Republic of Croatia - cements with the addition of limestone, slag and fly ash. A significant amount of MCI-2006 NS inhibitor (0.5% by mass of cement) was chosen for the test, so that any influence of the inhibitor on the properties of the cement would be noticeable. The conducted tests are in accordance with a series of standards for the testing of cements according to European standards, and represent the tests that cements must pass before being placed on the European market.

From the results of the tests, it is evident that **the addition of an inhibitor in a significant proportion of 0.5% by mass of cement does not cause deviations in the chemical and physical properties of the cement compared to the cements available on the market, and that there are no changes in the composition that would cause cement with the addition of an inhibitor to be rejected according to HRN EN 197-1 standard**.

The addition of a significant amount of inhibitor does not cause significant deviations in the results of the standard consistency of the tested cements. The addition of inhibitors in the amount of 0.5% by weight of cement results in a reduced need for water and greater workability compared to the same cement without inhibitors in all four types of cement. The most pronounced reduction in the need for water was observed for cement with the addition of limestone. From the results of standard consistency, it can be concluded that **the inhibitor has a slight property of reducing the need for water in all tested cements, that is, it acts as a mild plasticizer or superplasticizer**. The most significant reduction in the need for water was recorded for both cements with limestone.

The requirement according to the HRN EN 197-1 standard for a minimum initial setting time of 60 minutes is met by all cements with the addition of a significant amount of inhibitor. **The addition of a significant amount of inhibitor to cements (0.5% by weight of cement) causes a prolongation of the initial setting time of all tested cements**. The least significant increase in setting time is in the case of cements with limestone, while the most significant increase in setting time is observed in cements with slag, which are already slow setting and have a reduced heat of hydration.

All tested cement paste mixtures show volume stability according to the criteria according to HRN EN 197-1. **The addition of a significant amount of inhibitor to CEM II/B-LL 42.5 N cement does not cause a change in the dimensional stability of the cement.**

All cements with the addition of a significant amount of inhibitor meet the criterion for compressive strength after 2 days for the compressive strength class of cement 42.5 N (≥ 10.0 MPa) and 42.5 R (≥ 20.0 MPa). With the addition of inhibitors to cements containing limestone, a slight increase in early compressive strength was recorded, while in cements with the addition of slag and fly ash or only slag, a slight decrease in early compressive strength was recorded compared to cements without inhibitors. In the case of 28-day strength, **all cements with the addition of a significant amount of inhibitors, except CEM III/A 42.5 N LH, meet the criterion for compressive strength after 28 days for the compressive strength class of cement 42.5 (≥ 42.5 MPa)**.

Based on all tests carried out at the level of cement, it is suggested to use inhibitor in cements with the addition of limestone, such as CEM II/B-LL 42.5 N and CEM II/A-LL 42.5 R cements. In this type of cement, the addition of a significant amount of inhibitor has only positive impacts: a reduction in the need for water for the same workability, a slight slowing down of setting and a slight increase in compressive strength after 2 and 28 days, while all other physical and chemical properties of the cement remain unchanged with the addition of inhibitor. Continuation of the test at the concrete level is carried out only on CEM II/B-LL 42.5 N cement as a reference cement with the addition of 0.1%, 0.25% and 0.5% inhibitor.

3 INFLUENCE OF INHIBITOR ON THE PROPERTIES OF CONCRETE

In order to determine the influence of the MCI-2006 NS additive added to cement on the properties of concrete, tests were carried out on the mechanical and durability properties of concrete, as well as the corrosion properties of reinforcement in concrete prepared with Portland cement with the addition of limestone CEM II/B-LL 42.5 N from the manufacturer Holcim (hereinafter: CEM II) and with the same concrete with three different amounts of MCI-2006 NS addition: 0.1%, 0.25% and 0.5% by weight of cement. Given that the main reason for adding the MCI-2006 NS additive is to increase corrosion resistance, the reference concrete mix with which the impact of the additive is compared is a mixture according to the HRN EN 206 standard [12] for environmental class XS – action of chloride from the sea, without the addition of MCI-2006 NS. The target class of compressive strength of concrete is C30/37.

3.1 Testing methods and sample preparation

The composition of the concrete was designed according to the absolute volume method in such a way as to meet the minimum criteria of the given exposure class XS. Four concrete mixtures were prepared for the purposes of the test: the reference mixture (CEM II/B-LL 42.5 N) and three mixtures with the addition of MCI-2006 NS in amounts of 0.1%, 0.25% and 0.5% inhibitor by mass of cement. In all mixtures, a cement mass of 340 kg and a water-cement ratio of 0.5 were used, while the powder material MCI-2006 NS was mixed into the cement before mixing the concrete. Crushed limestone with the largest grain of 16 mm was used as aggregate. The cumulative granulometric composition was calculated according to the recommended limiting curve A (Eq. 1).

$$A = 50(\frac{d}{d_m} + \sqrt{\frac{d}{d_m}}) \qquad (1)$$

where:
d – sieve size (mm)
d_m – maximum grain size (mm).

Additionally, for the purposes of proving resistance to freezing and thawing, two more mixtures were made with the addition of the minimum recommended amount of air entraining admixture, a reference (CEM II/B-LL 42.5 N_Air) and a mixture with 0.1% MCI-2006 NS addition (CEM II /B-LL 42.5 N + 0.1%_Air) to which 0.2% air entraining admixture and 0.05% superplasticizer were added by mass of cement. Chemical additives used are: Sika Luftporenbildner LPS A-94 and Sika ViscoCrete - 5380 l.

Tests of concrete in the fresh and hardened state and the standards according to which the tests were conducted are listed in Table 8.

Table 8. Methods for testing concrete in fresh and hardened state.

Property	Purpose of testing	Standard
Temperature	Influence of the addition on the basic property of fresh concrete	HRN EN 12350-1:2019 Testing fresh concrete - Part 1: Sampling
Consistency	Influence of the addition on the basic property of workability of fresh concrete	HRN EN 12350-2:2019 Testing fresh concrete - Part 2: Slump tes
Density	Influence of the addition on the basic property of fresh concrete	HRN EN 12350-6:2019 Testing fresh concrete - Part 6: Density

Air content	Influence of the addition on the basic property of fresh concrete	HRN EN 12350-7:2019 Testing fresh concrete - Part 7: Air content
Compressive strength	Influence of different amounts of the additive on the basic property of hardened concrete	HRN EN 12390-3:2019 Testing hardened concrete -- Part 3: Compressive strength of test specimens
Water permeability	Influence of different amounts of the additive on the basic durability of concrete, prescribed in almost all environmental classes	HRN EN 12390-8:2019 Testing hardened concrete - Part 8: Depth of penetration of water under pressure
Chloride migration	Influence of different amounts of the additive on the chloride penetration in concrete containing cement for application in the XS environmental exposure conditions according to the HRN EN 206 standard	HRN EN 12390-18:2021 Testing hardened concrete - Part 18: Determination of the chloride migration coefficient
Carbonation	Influence of different amounts of the additive on the accelerated carbonation resistance of concrete containing cement for application in the XC environmental exposure conditions according to the HRN EN 206 standard - tested on the reference mixture and on the mixture with the highest amount of MCI-2006 NS added	HRN EN 12390-12:2020 Testing hardened concrete – Part 12: Determination of the carbonation resistance of concrete. Accelerated carbonation method
Gas permeability	Influence of different amounts of the additive on gas permeability of concrete containing cement for application in the XC environmental exposure conditions according to the HRN EN 206 standard - tested on the reference mixture and on the mixture with the highest amount of MCI-2006 NS added	RILEM TC116-PCD: permeability of concrete as a criterion of its durability. Materials and Structures/Matériaux et Constructions, Vol. 32, April 1999, pp 174-179
Freezing and thawing	Elimination of the possible risk of scaling during freezing and thawing of concrete containing cement for application in the XF2 environmental exposure conditions according to the HRN EN 206 standard - tested on the reference mixture and on the mixture with the highest amount of MCI-2006 NS added	HRN CEN/TS 12390-9:2016 Testing hardened concrete - Part 9: Freeze-thaw resistance with de-icing salts - Scaling (28 cycle)
Accelerated corrosion test drying and wetting cycles	Determination of the effectiveness of the additive in corrosion inhibition by exposure to a simulated marine environment - long-term study	Instead of the HRN EN ISO 9227, ASTM G109 – 07 Standard Test Method for Determining Effects of Chemical Admixtures on Corrosion of Embedded Steel Reinforcement in Concrete Exposed to Chloride Environments was used.
Accelerated corrosion test with the application of external current source	Determining the effectiveness of an additive in corrosion inhibition by an artificially accelerated corrosion process using potential	Adapted HRN EN 480-14 standard

3.2 Testing of concrete in fresh state

Consistency by slump is tested according to HRN EN 12350-2:2019 [13]. Concrete is placed in the cone mold up to one-third of its height, and it is compacted with a metal bar that falls freely 25 times. The same procedure is repeated for the second and third thirds. After compaction, the mold is removed and placed next to the sample. A ruler is placed on the mold to measure the total slump of the sample. The temperature of fresh concrete is determined according to HRN EN 12350-1:2019 [14]. The temperature is measured at a depth of no less than 5 cm. The density of fresh concrete is tested according to HRN EN 12350-6:2019 [15]. A container of known volume (V) is weighed and thus the mass (m_1) is determined. The sample is incorporated and compacted in the container. The container with embedded concrete is weighed and the mass (m_2) is determined. The density of fresh concrete is calculated according to the Eq. 2:

$$\rho_b = \frac{m_2 - m_1}{V} \ (kg/m^3) \quad (2)$$

where:

ρ_b – density of fresh concrete, (kg/m^3)
m_1 – container mass, (kg)
m_2 – mass of container and concrete within the container, (kg)
V – volume of container, (m^3)

Determination of the air content with a porometer is described in the HRN EN 12350-7:2019 standard [16]. The operation of the porometer is based on the Boyle-Mariotte law. The concrete sample is placed in the container until it is completely compacted. After installation, the vessel is closed, and the space between the concrete sample and the chamber on the lid is filled with water. Then, in the pressure chamber on the lid, the pressure in the vessel is increased using a pump. Opening the valve on the porometer equalizes the pressure in the chamber and in the container, in which the only compressible part is the air pores in the concrete. The air content is read on the manometer of the porometer.

3.3 Testing of concrete in hardened state

3.3.1 Compressive strength

The compressive strength is determined according to the standard HRN EN 12390-3:2019 Testing of hardened concrete -- Part 3: Compressive strength of test samples [17] on cubes with dimensions of 150 x 150 x 150 mm. The test is carried out when the concrete samples are 28 days old. A hydraulic press is used for testing, in which the samples are centered and loaded to pressure perpendicular to the installation direction. Compressive strength is calculated using the Eq. 3:

$$\mathbf{Q} = \frac{\mathbf{F}}{\mathbf{A}} \ \ (\boldsymbol{N/mm^2}) \quad (3)$$

Where *F* is force in N, *A* is area in mm^2.

3.3.2 Water permeability

The test of the penetration depth of water under pressure was carried out according to the HRN EN 12390-8:2019 standard. Water permeability is defined as the ability of liquids to flow under a certain pressure through the material. For high-density concrete, the fastest way to determine water permeability is the pressurized water penetration test method. Water under a certain pressure is released into the cell during a time period defined by the standard. At the end of the test, the samples are split to determine the depth of water penetration. The test is carried out on three samples. The test equipment includes a device for testing the depth of water penetration, which supplies water under a constant pressure of 5 bar, for a duration of 72 ± 2 h, to the upper or lower surface of the sample. The mean value of three samples is taken as the result of water penetration. The result is recorded in millimeters. Standard HRN 1128:2007 Guidelines for the application of the standard HRN EN 206-1 [18] prescribes water permeability classes (VDP 1, VDP 2, VDP 3) according to the allowed average penetration of water through the sample.

Water permability class	Maximum allowed penetration of water, mm
VDP1	50
VDP2	30
VDP3	15

Figure 6 Device for testing the depth of water penetration under pressure and the limit value of the maximum water penetration for different classes according to HRN 1128:2007

3.3.3 Chloride migration

Measurement of chloride migration is performed according to HRN EN 12390-18:2021 Testing of hardened concrete -- Part 18: Determination of chloride migration coefficient (adopted from the standard NT BUILD 492). This test method is used to determine the chloride migration coefficient based on a non-stationary test and is intended for testing on samples at least 28 days old. The samples are installed in molds in the shape of a cylinder with a diameter of 100 mm and a height of 200 mm, and after 24 hours they are unmolded and placed in a humidity chamber until the day of the test. Samples must be free of voids and visible cracks. On the day of the test, the samples were sawed on three samples with a diameter of 100 mm and a height of 50 mm. The samples are placed in a desiccator and vacuumed for 3 hours. After vacuuming, $Ca(OH)_2$ solution is added and conditioning is continued for another hour. The samples remain in the solution for a minimum of 18 hours. After the preconditioning, the samples are placed in cells where one side of the cell is filled with a 10% NaCl solution, and the other with 0.3 M NaOH (12g/l) so that the cell meshes are covered. Cells with samples are connected to the device shown in Figure 7, and the current source and temperature are controlled via a computer. A current of 30 V is enforced into the samples, and after 10 minutes the test is stopped and the voltage values are read, which will determine the duration of the test and the voltage at which it will be tested. Current is passed into the sample so that the chlorides migrate faster from one container to another. At the end of the test, the samples are broken into two equal parts and sprayed with a 0.1 M solution of silver nitrate. After 15 minutes, on the part where the chlorides have penetrated, the solution will react and the sample will turn white. Chloride penetration is measured with a sliding scale at a distance of 10 mm. The obtained chloride migration coefficient shows the resistance to chloride penetration of the tested sample. It is important to emphasize that the coefficient obtained by this method cannot be directly compared with the chloride diffusion coefficient obtained by other methods. This method of testing chloride represents the movement of ions under the influence of external electric fields, that is, the movement of ions or molecules from an area of higher concentration to an area of lower concentration. The diffusion coefficient is calculated according to the Eq. 4, while the criteria for assessing the resistance of concrete are given in Table 9:

$$D_{nssm} = \frac{0.0239(23+T)h}{(U-2)t} \left(x_d - 0.0239\sqrt{\frac{(273T)Lx_d}{U}} \right) \quad (4)$$

where:

D_{nssm} – chloride migration coefficient, × 10^{-12} [m^2/s]
U – voltage applied, [V]
T – temperature, [◦C]
L – sample thickness, [mm]
x_d – chloride ingress depth, [mm]
t – test duration, [h]

Figure 7 Instrument for testing chloride migration

Table 9 Criteria for chloride diffusion

Chloride diffusion (m^2/s)	**Resistance of concrete to chlorides**
< 2 × 10^{-12}	Very good
2 – 8 × 10^{-12}	Good
8 – 16 × 10^{-12}	Average
> 16 × 10^{-12}	Poor

3.3.4 Gas permeability

Gas permeability is defined as the ability of gases to flow through a material under a certain pressure. The gas flow through the sample depends on: the pressure level, the tested density, the density and amount of open pores, and the viscosity of the gas used to test the sample. The test is performed by measuring the gas flow at the exit from the sample, and the gas permeability coefficient is calculated based on the obtained results. The gas permeability test of concrete was carried out according to the recommendations of RILEM TC116-PCD. The samples for the gas permeability test are cylinders with dimensions d=100±5 mm and h=50±5 mm. The samples are taken out of the mold and cured for 28 days. Then they are placed in an oven at a temperature of 110±5°C until a constant mass. The test is carried out with a device for determining gas permeability SO 2000H. Pressurized gas is released through the sample and the passage time of the gas bubbles through the liquid manometer is measured. The specific coefficient of gas permeability (m^2) is calculated according to the Eq. 5, while the criteria for assessing the resistance of concrete are given in Table 10:

$$\mu = \eta \cdot \frac{h}{A} \cdot \frac{1}{\Delta \mathrm{p}} \cdot q_v \cdot k_v \ (m^2) \qquad (5)$$

where:

η –viscosity of gas (Pas)
h – sample thickness (m)
A – sample area (m^2)
Δp – differences between gases (Pa)
q_v – the amount of gas passing through the sample (m^3/s)
k_v – correction factor (for air temperature 16 °C value taken is 0,982, for 24 °C 0,971).

Table 10. Criteria for gas permeability according to literature [19]

Gas permeability coefficient ($x10^{-18}$ m^2)	Resistance of concrete
>1000	Very low
300 - 1000	Low
100 - 300	Average
30 - 100	High
< 30	Very high

3.3.5 Carbonation

The depth of carbonation is determined according to the standard HRN EN 12390-12:2020 Testing of hardened concrete -- Part 12: Determination of resistance of concrete to carbonation -- Accelerated carbonation method. The consequence of the reaction of concrete with CO_2 is a decrease in the alkalinity of the solution in the pores, that is, a decrease in the alkalinity of the concrete. The depth of carbonation can therefore be determined using an alkalinity indicator solution. A solution of 0.8 g of phenolphthalein powder dissolved in 70 ml of ethanol and 30 ml of distilled water is used for this test. Such a solution shows a color change in the range from pH 8 to pH 11, which colors the part of the sample that is not affected by carbonation, while the carbonated part is colorless. The resistance to carbonation is tested on prism, cube or cylinder samples that are covered for 24 hours after moulding in laboratory conditions. When removing from the mold, the samples are placed in a water bath until they are 28 days old, after which they are conditioned in a controlled climate chamber (relative humidity 65±5 %, 20±2 °C) for an additional 14 days. The samples are then placed in a carbonation chamber with an inflow of carbon dioxide so that the following conditions prescribed by the standard are maintained: the carbon dioxide concentration occupies 3.0 ± 0.5% of the air volume, the relative air humidity is 57 ± 3%, and the temperature is 20 ± 2 °C. For this test, 2 prism samples with dimensions of 100 x 100 x 300 mm per mixture were moulded and placed in the carbonation chamber, and the depth of carbonation was measured on each of the two samples after 7, 28 and 70 days in the chamber. After each exposure period, a 50 mm thick sample was broken off from each prism with a mechanical splitting device while the rest of the prism was returned to the chamber. The broken side of the sample is cleaned of dust and sprayed with indicator solution. Carbonation depth is measured at 3 to 5 points on each edge of the sample. The measurement result is the mean value of all measurements at a certain age of the sample, rounded to the nearest 0.1 mm.

Carbonation rate is calculated according to the Eq. 6:

$$d_K = a + K_{AC}\sqrt{t} \qquad (6)$$

where:

d_K – average value of carbonation depth [mm]
a – intersection of the regression line on the ordinate axis [mm]
K_{AC} – carbonation rate [mm/$\sqrt{day}$]
t – time of exposure, day

3.3.6 Freezing and thawing

The test of resistance to freezing and thawing is carried out according to the standard CEN/TS 12390-9:2006 Testing of hardened concrete -- Part 9: Resistance to freezing and thawing - Spalling. The test for each mixture is carried out on 4 samples, each taken from one of the four cubes with side dimensions of 150 mm. After moulding, the samples are kept covered for 24 hours at an air temperature of 20 ± 2 °C. until 7 days old, the samples are kept in water at a temperature of 20 ± 2 °C, after which they are transferred to a controlled climate chamber (relative humidity 65 ± 5 %, 20 ± 2 °C) until testing. At the age of 21 days, a (50 ± 2) mm thick specimen was cut from the cube perpendicular to the upper surface so that the test surface emerged from the central part of the cube (Figure 8). After sawing, the sample is measured and returned to the chamber so that the test surface is laid vertically and with a mutual distance of 50 mm. At the age of (25 ± 1) days, the samples are placed in rubber molds and the surface of the sample in contact with the mold is filled with silicone to ensure the impermeability of the exposed surface of the sample (Figure 8). At the age of 28 days, a layer of deionized water with a height of 3 mm, or 67 ml, is applied to the test surface of the sample. Such resaturation is carried out for 72 ± 2 hours at 20 ± 2 °C with constant maintenance of the water layer on the surface. Testing of samples begins at the age of 31 days. At least 15 minutes before placing the sample in the chest, deionized water is replaced with 67 ml of defrosting agent. Equipment for testing resistance to freezing and thawing complies with the HRN EN 12390-2:2010 standard. Samples are tested in cycles of 7±1, 14±1, 28±1 days in the thawing phase. One cycle lasts 24 hours, and the temperature range is - 22 to + 24°C. Peeled material is picked up from the surface using a brush and water and placed to dry. Then 67 ml of new defrosting agent is placed on the surface of the samples and returned to the chamber. After each cycle, the mass of the scaled and dried material is measured. Sn is calculated, the cumulative amount of scaled material per surface after n cycles according to the Eq. 7:

$$S_n = \frac{m_{s,n}}{A} \cdot 10^3 \ (kg/m^2) \quad (7)$$

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S_n – scaled material after nth cycle, kg/m^2,
$m_{s,n}$ – cumulative mass of scaled material after nth cycle, kg
A – surface area, m^2.

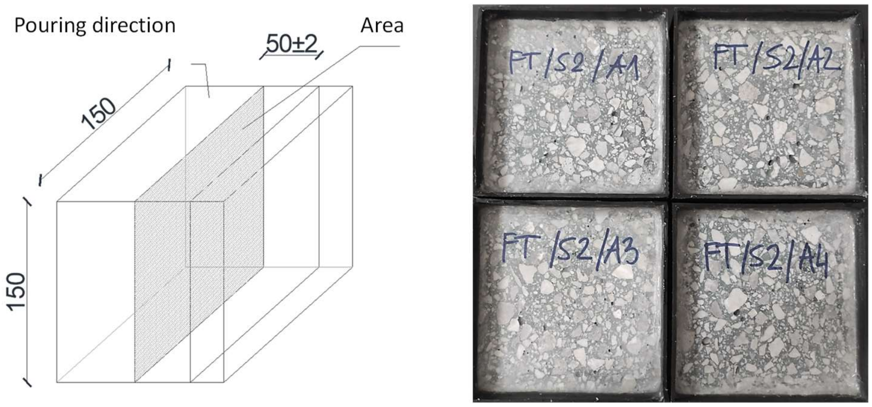


Figure 8 Sample preparation according to CEN/TS 12390-9:2006.

3.3.7 Corrosion testing

The determination of the effect of the MCI-2006 NS additive on the susceptibility of reinforcement to corrosion was carried out according to the HRN EN 480-14:2007 for the reference mixture (CEM II), and the mixture with 0.10. 0.25, 0.5% addition of MCI-2006 NS to the mass of cement. This standard serves to detect possible negative effects that certain additives may have on the risk of corrosion in concrete. Therefore, according to the standard, the sample is tested in a passive environment. But in order to prove the effectiveness of the inhibitor, it is necessary to conduct the test in an aggressive medium. For this reason, the effectiveness of the additive in inhibiting corrosion was determined using the adapted standard HRN EN 480-14:2007. Three samples were prepared from each mixture: the reference mixture (CEM II), and the mixture with 0.10. 0.25, 0.5% addition of MCI-2006 NS to the mass of cement. A schematic representation of the used three-electrode cell is visible in Figure 9. The samples are first immersed in a 3.5% NaCl solution for 24 hours, and then connected to a multi-channel potentiostat Bio-Logic SA as described in the EN 480-14:2007 standard. In order to accelerate the corrosion, the sample was potentiostatically polarized at 1 V vs SCE and the change in current was measured over time. Instead of a duration of 24 hours as specified in the standard, the steel reinforcement in the sample is polarized until a sudden increase in the amount of current is recorded, which indicates the beginning of the corrosion process. In addition to polarization at 1 V vs SCE, a set of samples was also made for testing with polarization at a weaker potential of 500 mV vs SCE, whereby the testing lasted significantly longer.

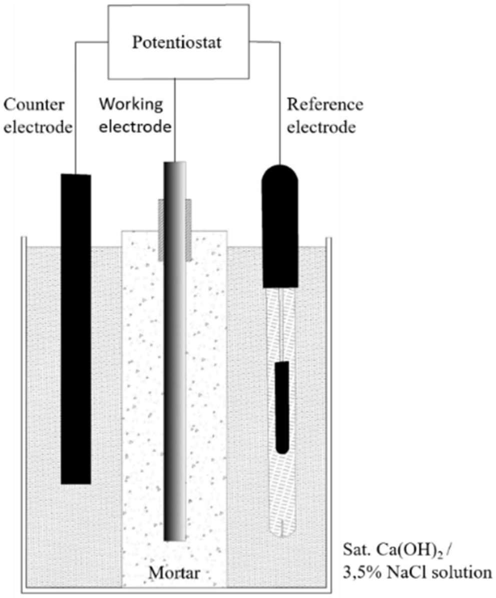


Figure 9 Three-electrode cell used in the testing.

In agreement with the client, the test of accelerated corrosion using drying and wetting cycles was not done according to the offered HRN EN ISO 9227 standard, but according to the American standard ASTM G109 - 07 Standard Test Method for Determining Effects of Chemical Admixtures on Corrosion of Embedded Steel Reinforcement in Concrete Exposed to Chloride Environments. The samples are prepared according to the specified standard, and are cyclically wetted and dried, with periodic measurement of the corrosion potential.

3.4 Results

3.4.1 Results of concrete properties in fresh state

The results of measuring the properties of concrete in fresh state (Figure 10) show that increasing the proportion of MCI-2006 NS admixture affects certain properties, but this influence is not unambiguous. The density of fresh concrete with and without additives is approximately the same, about 2500 kg/m^3. Temperature and air content are slightly lower in mixtures with the addition of MCI-2006 NS. The greatest influence of the additive is visible in the consistency by slump. By increasing the proportion of the MCI-2006 NS additive, the slump value of the fresh mixture also increases, which means that workability increases. These results of the effect of inhibitors on workability are in agreement with the results obtained at the level of cement. It can also be seen that the proportion of inhibitors of 0.1% by mass of cement does not significantly affect the consistency of concrete.

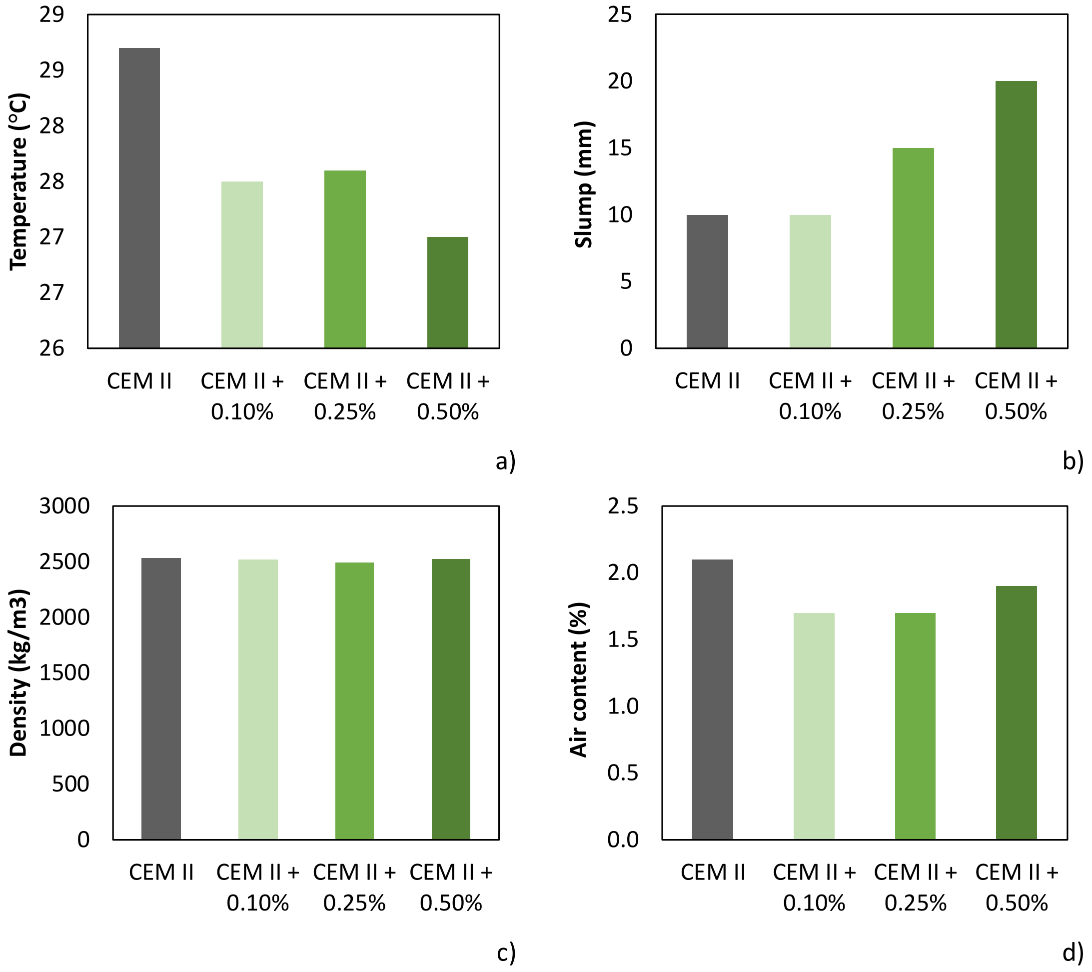


Figure 10 Results of concrete properties in fresh state a) temperature, b) consistency by slump, c) density and d) air content

3.4.2 Compressive strength

The results and standard deviations of tests of hardened concrete with and without MCI-2006 NS admixture are presented below. The test of the compressive strength indicates a favorable influence of the MCI-2006 NS additive, because increasing the proportion of the additive also increases the mean value of the compressive strength compared to the reference mix (CEM II). Figure 11 shows the results of the test of the compressive strength of the cubes after 28 days of curing. All samples meet the specified strength class, with a strength of 46.80 MPa, sample CEM II has the lowest value, CEM II + 0.1% additive and 0.25% additive give similar values, 47.57 and 47.06 MPa, while 0.50% addition gives the highest recorded value of 48.06 MPa.

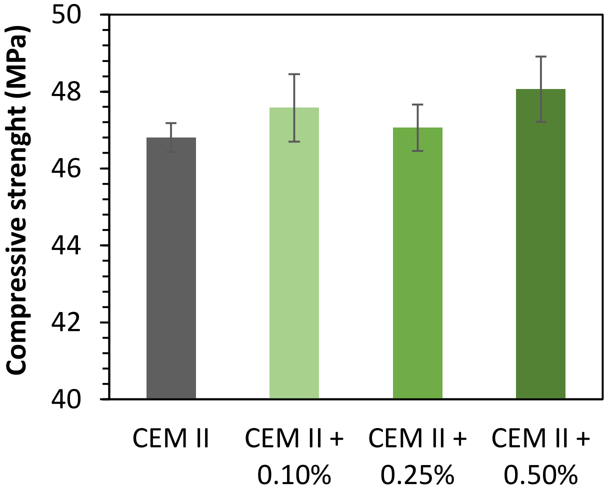


Figure 11 Compressive strength results

3.4.3 Water permeability

Figure 12 shows the results of the water penetration test under pressure. From the presented results, it is evident that the addition of MCI-2006 NS increases the water permeability of concrete, that is, it increases the penetration of water through the sample compared to the reference mixture. But according to the categorization prescribed in HRN 1128:2007, with an average water penetration between 15 and 30 mm, all mixtures would be placed in the same water permeability class - VDP 2. Although the highest average water penetration was obtained for the mixture with 0.10% additive, taking into account the deviation in the results, it can be concluded that different proportions of the MCI-2006 NS additive give approximately equal results of water penetration under pressure and that all concretes, regardless of the addition of inhibitors, fall into the same category of water permeability.

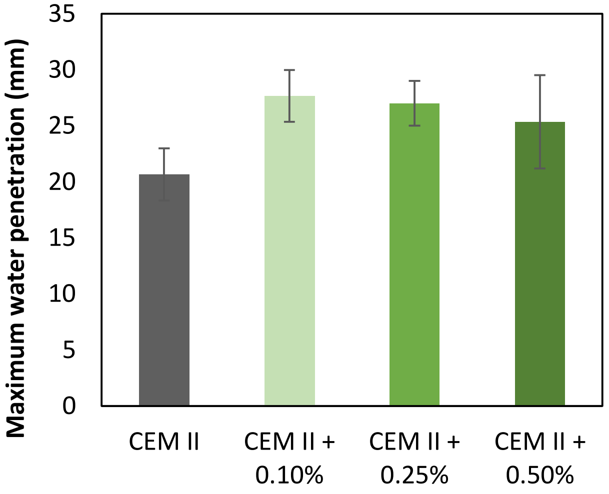
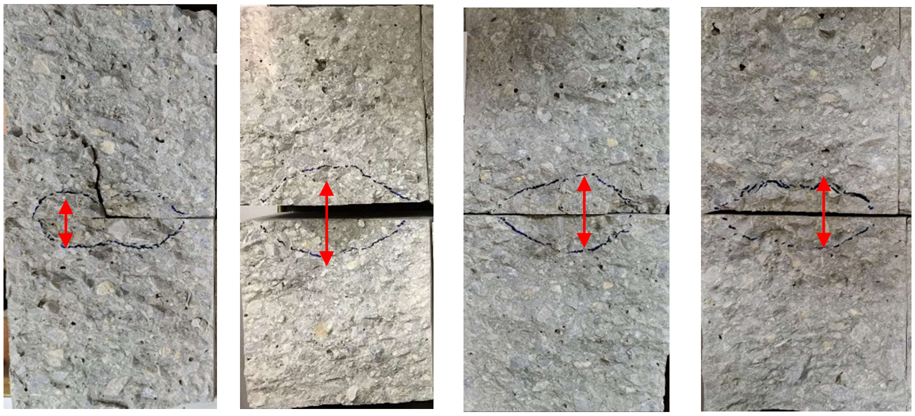


Figure 12 Results of water permeability of concrete



CEM II CEM II + 0.1% CEM II + 0.25% CEM II + 0.5%

Figure 13 Water penetration depth for different mixes of concrete

3.4.4 Chloride migration

By measuring chloride penetration on samples aged 28 days, the values of the migration coefficient D_{nsms} shown in Figure 14 were obtained. The mixture with 0.10% additive gives approximately the same results as the reference mixture. The positive influence of the MCI-2006 NS inhibitor is visible with the highest proportion of the additive, CEM II+0.50%, where the migration coefficient is the lowest. The deviation in the results is visible in the mixture with 0.25% additive, where the result of measuring chloride migration is slightly higher than the reference mixture.

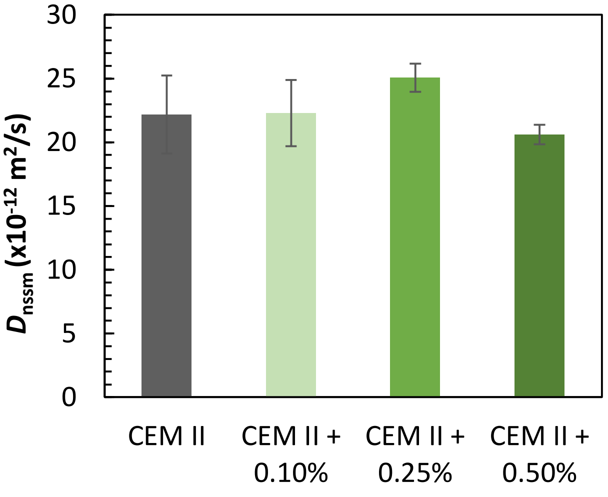


Figure 14 Results of chloride migration

3.4.5 Gas permeability

The results of the gas permeability measurement are shown in Figure 15. The average values of the gas permeability coefficient with the addition of inhibitors of 0.10 and 0.25% by mass of cement are lower than the reference mixture, while the mixture with 0.50% inhibitor gave slightly higher values.

Regardless of the differences in the results, all mixtures fall into the same category of resistance to gas penetration, and can be characterized as concretes with high resistance to gas penetration [19].

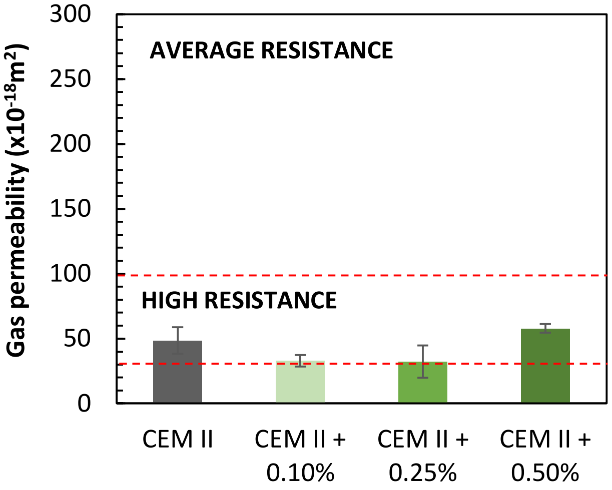


Figure 15 Results of gas permeability of concrete

3.4.6 Carbonation resistance

The carbonation depth is shown in Figure 16. Up to 28 days of exposure to accelerated carbonation, the sample with 0.25% inhibitor shows the greatest depth of carbonation penetration, while after 70 days the resistance to carbonation equalizes for all samples with the addition. The greatest drop in resistance to carbonation is visible after prolonged exposure to accelerated carbonation (70 days), when the difference between the results of the reference mixture and the mixture with the addition of inhibitors is the largest.

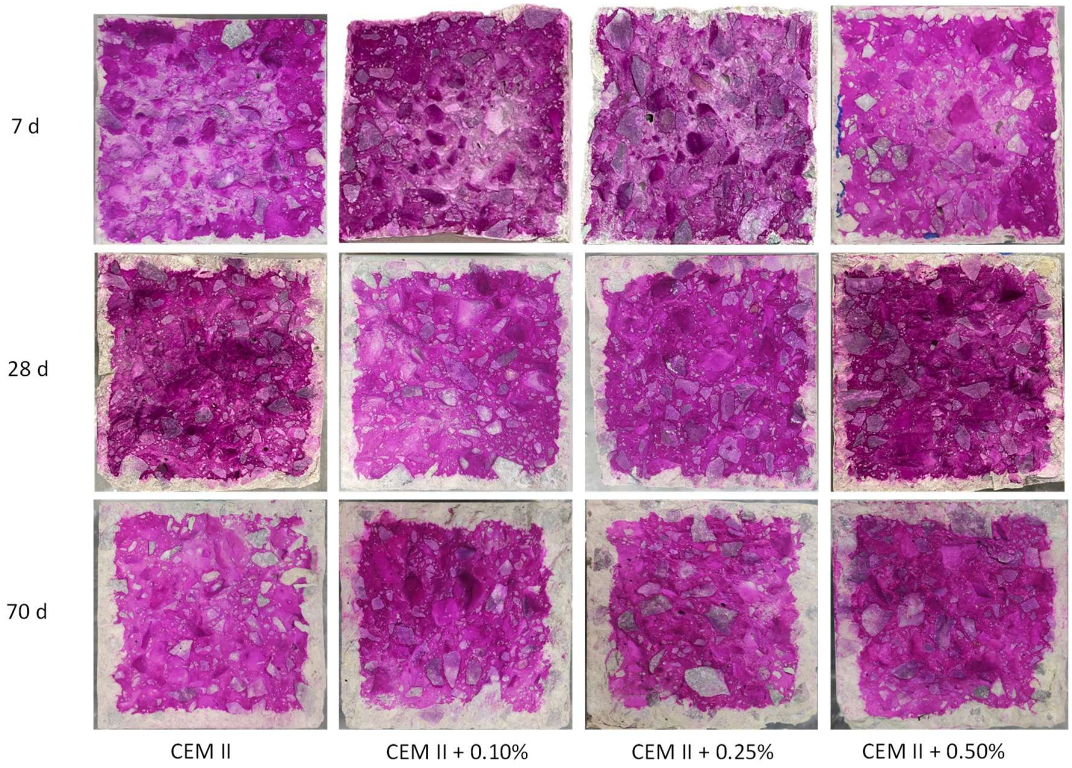


Figure 16 Carbonation depth after nakon 7, 28 and 70 days in carbonation chamber

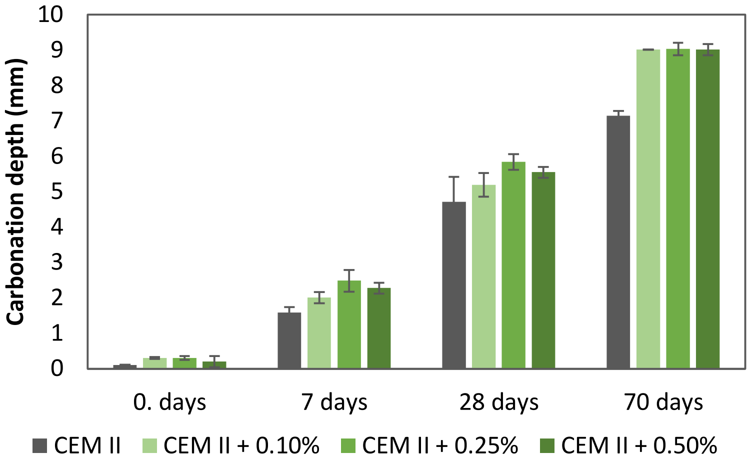


Figure 17 Results of carbonation depth

3.4.7 Resistance to freezing and thawing

The results of the test of resistance to freezing and thawing through 28 cycles are shown in Figure 18. It can be seen that the addition of MCI-2006 NS in the first 14 cycles has no significant effect on the behavior of the concrete. After the 14th cycle, there is a significant degradation of the concrete, where the scalling is a little more significant than in the case of concrete without the addition of inhibitors. According to the HRN CEN/TS 12390-9:2006 standard for environmental class XF2, the average value of the scaled material after 28 cycles must not exceed 0.5 kg/m^2. None of the mixtures met this criterion. Images of the samples during freezing and thawing cycles are shown in the Figure 19. It can be seen that all samples undergo a scalling process during freezing and thawing.

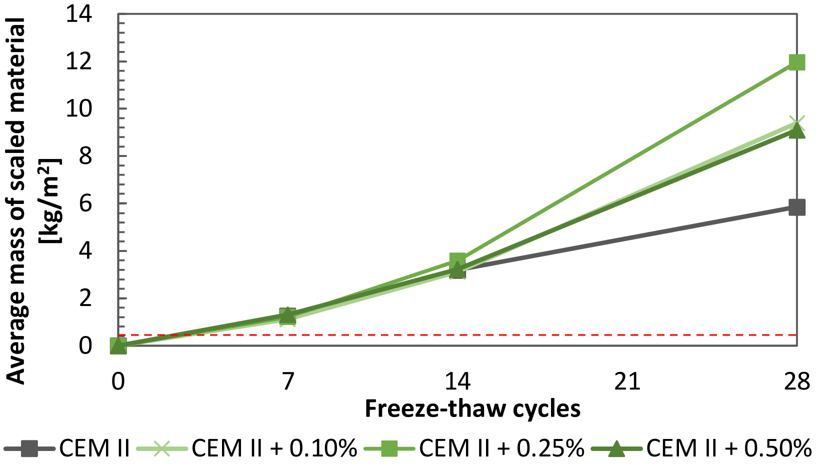


Figure 18 Results of resistance to freezing and thawing

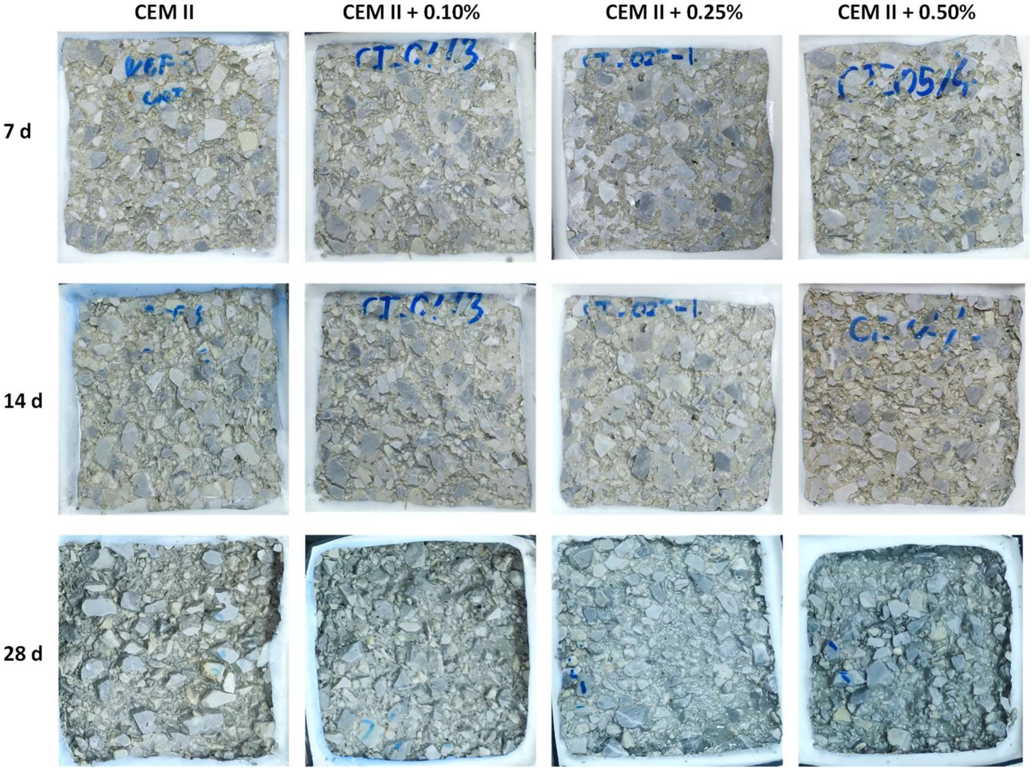


Figure 19 Samples degradation during freezing and thawing cycles

Considering that neither the reference nor the mixture with the inhibitor met the requirement for environmental class XF2, the test was repeated with the addition of air entrainer and superplasticizer. It should be noted that classic concrete generally has a weak resistance to freezing and thawing. If a concrete building is designed for environment with freezing and thawing during its service life, the concrete must contain a chemical additive air entrainer, which significantly improves the concrete's resistance to freezing and thawing. In order to evaluate the influence of inhibitor in concrete to which air entraining was added, an additional set of samples was made with the addition of air entrainer (CEM II_Air) and with the addition of an inhibitor in the amount of 0.1% by mass of cement and air entrainer (CEM II+0 ,1 %_Air).

The results of tests on freezing and thawing of aerated concrete mixtures of CEM II and CEM II + 0.10% inhibitor are shown in Figure 20. The dosage of the minimum recommended amount of air entrainer greatly affects the resistance to freezing and thawing of both mixtures. Although the criterion of a cumulative amount of flaked material of 0.5 kg/m^2 is still not met, it has been proven that the addition of MCI-2006 NS improves the effectiveness of air entrainers and, in aerated concretes, improves the concrete's resistance to freezing and thawing compared to the reference mixture without inhibitors.

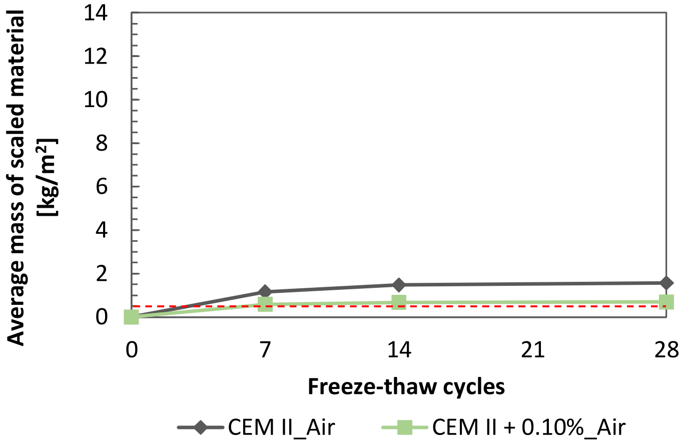
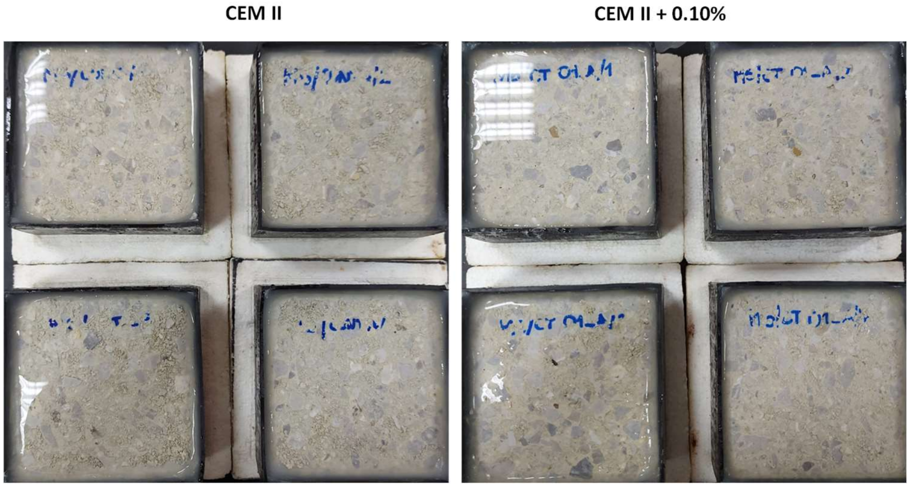


Figure 20 Results of testing freezing and thawing resistance of concretes with the addition of air entrainer



CEM II

CEM II + 0.10%

Figure 21 Samples during testing of freezing and thawing without and with inhibitor (only 0.1% addition of inhibitor was tested)

3.4.8 Corrosion testing

Figure 22 shows the results of the assessment of the sensitivity of reinforcement to corrosion with the addition of the MCI-20026 NS inhibitor in proportions of 0.1%, 0.25% and 0.5%. The tests were carried out in a passive solution of saturated calcium hydroxide according to HRN EN 480-14. It is evident from the test results that in the case of all mixtures the current is low, which indicates a low risk of corrosion. It is possible to notice that in the case of the addition of 0.1%, the current is slightly higher compared to the reference mixture without the addition of inhibitors. On the contrary, with additions of 0.25% and 0.5% of inhibitors, there is an additional reduction of the current during potentiostatic anodic polarization. The amounts of currents are expressed in the diagrams.

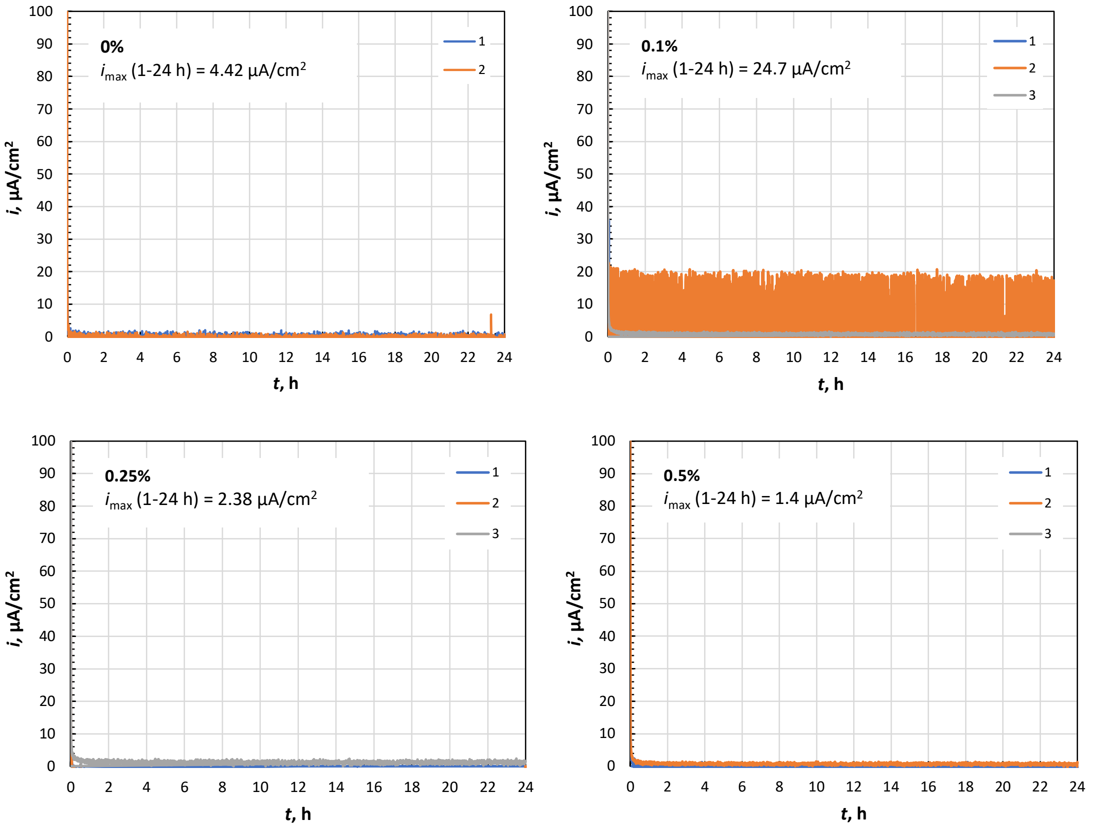


Figure 22 Measurement of current during potenciostatic anodic polarization according to HRN EN 480-14

The results of the accelerated corrosion test are presented below. Tests were performed with potentiostatic anode polarization, ensuring polarization of the working electrode at 1 V vs SCE, with continuous current monitoring. The procedure partially followed the norm HRN EN 480-14, but compared to the standard, a higher potential was used and a longer duration of the test.

The figures show sets of samples that were exposed to a 3.5% NaCl solution for the same period before testing. As it was impossible to test all samples simultaneously due to the limited number of channels on the potentiostat and the long duration of the test, the samples were tested in sets of one sample from each mixture. Each diagram below shows samples of each mixture that were under the same conditions throughout the test. After the first set of samples had corroded, the sets were replaced and a second set of samples was installed, consisting of one sample from each mixture. The samples shown in the first diagram were therefore exposed to the chloride solution for a shorter time before the test, compared to the samples of the third set, which were continuously exposed to the chloride solution until the testing of the first and second set of samples was finished.

It is evident from the results that the proportion of inhibitor of 0.1% by mass of cement has no significant effect on retardation of the corrosion process. In the case of the second set of samples, the samples with an inhibitor content of 0.1% by mass of cement have a certain effect on retarding corrosion (50 hours until corrosion occurs in the case of concrete without an inhibitor, compared to 80 hours in the case of concrete with 0.1% inhibitor to the mass of cement). But in the case of the first and third set of samples, the samples with a proportion of 0.1% inhibitor by mass of cement corroded even earlier than the reference mixture without inhibitor. In the case of the addition of 0.25% inhibitor, the retardation of the corrosion process is visible in the first set of samples (40 hours until the appearance of corrosion in the case of concrete without inhibitor, compared to 115 hours in the case of concrete with 0.25% inhibitor by mass of cement). However, in the case of the second and third set of samples, the positive influence of the additive in the amount of 0.25% on the mass of cement was absent. Finally, only the addition of an inhibitor in the amount of 0.5% by mass of cement in all sets of samples clearly showed a significant prolongation of the corrosion onset time. In the case of the first set of samples, the time until the appearance of corrosion for the sample with 0.5% inhibitor per mass of cement was extended 4.75 times, in the case of the second set of samples 2.55 times, and in the case of the third set of samples 2.4 times.

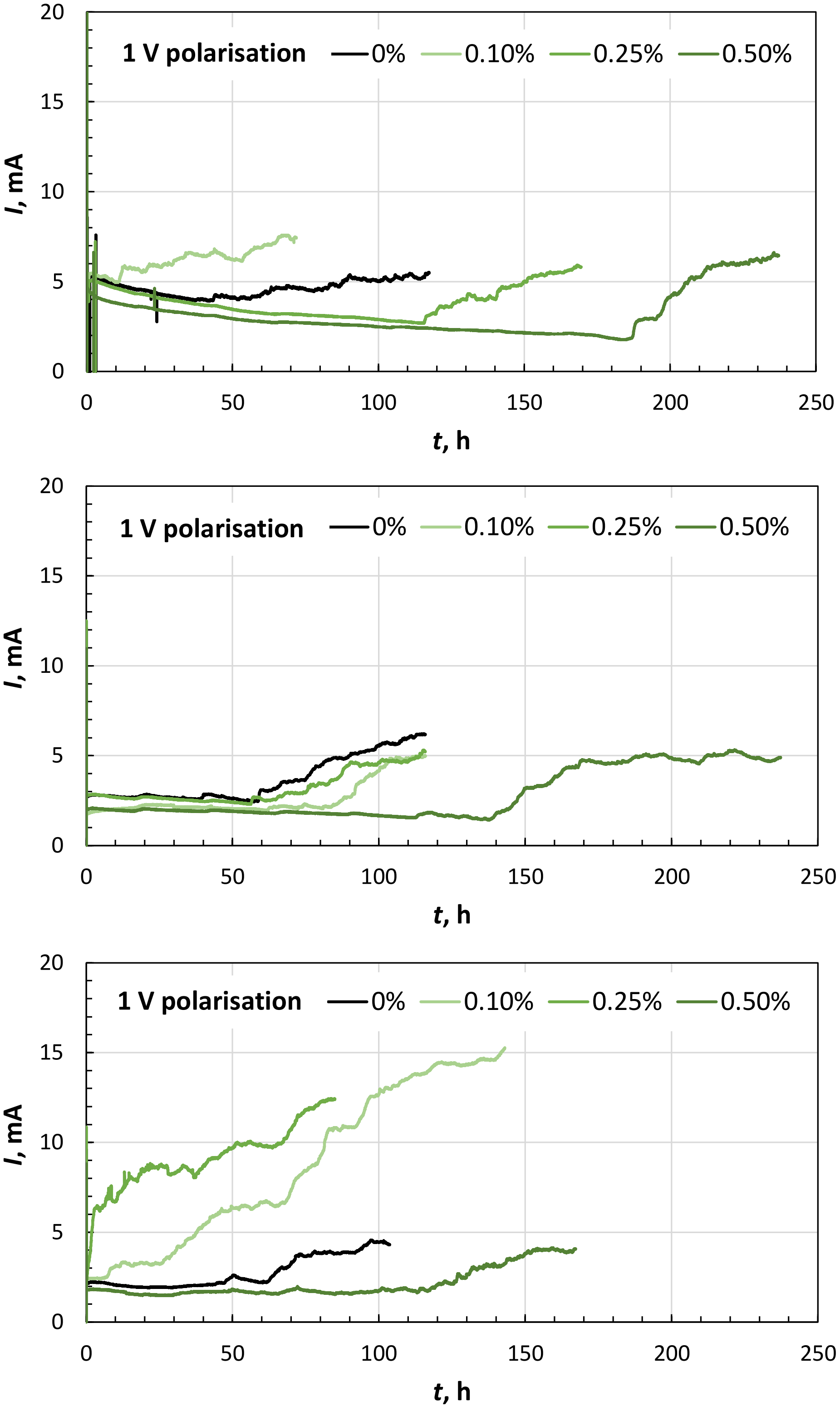


Figure 23 Potenciostatic anodic polarization of samples on 1000 mV vs SCE with continuous current measurement (rapid increase in current signaling corrosion onset).

In the previous tests, a polarization potential of 1 V was used, which resulted in the appearance of a significant corrosion current. To ensure that the test results are not influenced by significant acceleration of corrosion and unrealistically high amounts of corrosion current, the test was repeated on a set of three samples of each mixture, which were polarized at a potential of 500 mV vs SCE. This polarization caused corrosion currents below 200 μA/cm^2, which is defined in the literature as a current that can appear on real structures. However, such mild polarization significantly lengthens the test time, which for some samples lasted almost 3 months. The test results are shown in the Figure 24. It is evident from the results that in the case of the sample with the addition of an inhibitor of 0.1% by mass of cement, the corrosion time is the same as that of the sample without the inhibitor (500 hours in the case of both mixtures). In the case of the addition of an inhibitor of 0.25% to the mass of cement, the corrosion time was extended by 2 times compared to the sample without the inhibitor (500 hours for the mixture without the inhibitor and 1000 hours for the mixture with 0.25% inhibitor). Finally, in the case of the sample with the addition of 0.5% inhibitor to the mass of cement, the corrosion time was prolonged by 3.8 times compared to the mixture without the inhibitor.

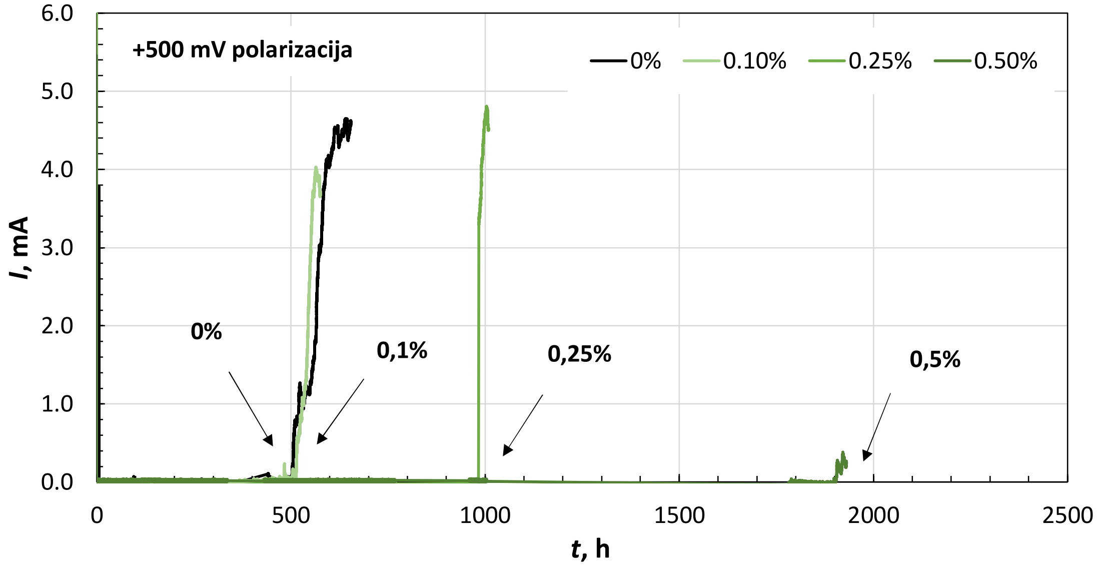


Figure 24 Potenciostatic anodic polarization of samples on 500 mV vs SCE with constant current monitoring (rapid increase in current signaling corrosion onset).

3.5 Conclusion on the influence of inhibitor in cement on concrete properties

The tests carried out at the level of concrete had the purpose of detecting possible effects of corrosion inhibitors on the properties of concrete, which are usually prescribed in the design phase of concrete structures and controlled during the construction. All tests were performed on concrete prepared with cement with the addition of limestone CEM II/B-LL 42.5 N manufactured by Holcim, and on the same concrete with three different amounts of MCI-2006 NS addition: 0.1%, 0.25% and 0. 5% by mass of cement. From the conducted tests, it is possible to conclude that the influence of inhibitors on concrete in its fresh state is significant only on the workability of concrete, and in amounts of inhibitor above 0.1%. With **the addition of inhibitor above 0.1%, the workability of concrete increases and the need for water decreases for the same workability**. These results of the effect of inhibitor on workability are in agreement with the results obtained at the level of cement.

The addition of inhibitor induces a slight increase in the compressive strength of concrete compared to the reference mixture without inhibitor. The increase in compressive strength with the addition of inhibitor is not significant and is only about 3%. In terms of durability properties, all properties of concrete without and with an inhibitor (regardless of the amount of added inhibitor) belong to the same resistance class - when tested for water permeability, all concretes fall into the VDP2 class, gas permeability into the class of high resistance to gas penetration, and chloride migration into the class of weak resistance to chlorides. Therefore, it can be concluded that **the inhibitor added in any of the three tested amounts has no significant effect on the durability properties of concrete**.

In terms of resistance to carbonation, **the addition of inhibitors has no significant effect on the resistance of concrete to carbonation**. All prepared concretes have poor resistance to freezing and thawing. When used in concretes that require resistance to freezing and thawing, the application of air entraining additive is necessary, and tests have **proven the compatibility of inhibitors with air entrainer. Certain improvement in the effectiveness of air entrainer in controlling scalling during freezing and thawing was obtained with the presence of corrosion inhibitors**.

From the conducted electrochemical tests of the sensitivity of steel reinforcement to corrosion by potentiostatic polarization, it can be concluded that the inhibitor does not affect the increase of the sensitivity of steel reinforcement to corrosion according to the HRN EN 480-14:2007 standard. From the test results using the modified HRN EN 480-14 method, in which the polarization potential was increased and the test time was extended, it is possible to conclude that at high acceleration of corrosion (1 V polarization), only concrete with the addition of 0.5% inhibitor by mass of cement showed significant retardation of the time of corrosion. At smaller accelerations of the corrosion process (500 mV polarization), concrete with an added 0.25% inhibitor per mass of cement shows the effectiveness of retardation the corrosion onset time, while concrete with an added 0.5% inhibitor per mass of cement shows the most significant effectiveness of retardation the onset of corrosion time. The addition of 0.1% inhibitor to the mass of cement did not show an effect on the time of corrosion.

4 CONCLUSION AND RECOMMENDATION

From all the tests carried out at the level of cement and at the level of concrete, it is possible to conclude that the addition of MCI-2006 NS added in a significant proportion of 0.5% by mass of cement causes an increase in the workability of cement paste and concrete, and slows down the setting. The retardation of setting is more significant with cements based on slag and fly ash, which by themselves already have a slower setting and a slower increase in strength. The retardation of setting is the least significant in the case of cement with the addition of limestone.

The addition of inhibitor to cements with limestone also has the effect of slightly increasing the compressive strength of cement and concrete, especially of cement early 2-day strength. The addition of inhibitor in none of the tested proportions did not significantly affect the durability properties of concrete (water permeability, gas permeability, chloride migration, carbonation). All concretes with the addition of inhibitor belong to the same class of resistance to environmental effects as concrete prepared with cement without inhibitor. In case of freezing and thawing, the compatibility of inhibitor and air entrainer (additive to increase the resistance of concrete to freezing and thawing) has been proven.

Electrochemical testing using the potentiostatic polarization method showed that when corrosion is greatly accelerated, only a proportion of 0.5% of the inhibitor per mass of cement retards the time of corrosion compared to concrete with cement without inhibitors. In the case of lower acceleration of corrosion, the proportions of 0.25% and 0.5% of the inhibitor per mass of cement are effective in retarding corrosion. The addition of 0.25% inhibitor to the mass of cement slows down corrosion by about 2 times, while the addition of 0.5% inhibitor to the mass of cement slows down corrosion by about 4 times.

Based on all the tests conducted and the conclusions reached, it is recommended that the inhibitor MCI-2006 NS is used in mixed cements with limestone, and that in an amount of 0.5% by mass of cement. In this way, the rate of corrosion is effectively slowed down, while the workability and mechanical properties of concrete are improved, and all other durability properties are kept within the same resistance category as with cement without inhibitors. In the case of cements with slag and fly ash, there is a retardation of setting, which can be of interest in hot climates and with transport concrete. For such applications, additional tests on the effect on corrosion are required.

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