Construction Science

ISSN 2255-8551 (online)
ISSN 1407-7329 (print)
October 2016, vol. 18, pp. 10–16
doi: 10.1515/cons-2016-0002
https://www.degruyter.com/view/j/cons

Influence of Mineral Additives on Environmental Resistance of Concrete

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Abstract – **Hydraulic concrete is a composite material that consists of coarse and fine aggregates and a binder, which transforms from liquid to solid state while curing and is exposed to destructive impacts during exploitation. The research was carried out with various cements – Portland cement, slag Portland cement, slag cement and limestone. The results of research showed that quantity of slag in hardened Portland cement paste influences freezing-thawing of concrete for hydraulic structures. Hydraulic concrete under impact of the Baltic Sea is influenced by sea water and freezing and thawing cycles. Under the mentioned impacts exerted simultaneously, experiment results enable assessment of durability of hydraulic concrete. The objective of the work is to assess the impact of the environment of the Baltic Sea on changes in properties of hydraulic concrete after cyclic freezing and thawing.**

Keywords – **Concrete, freezing-thawing, hydraulic concrete, scaling of specimens, various cement.**

I. Introduction

A lot of concrete structures are in contact with marine environment either directly or indirectly during their service life. Concrete structures are exposed to cyclic environment processes and chemical action. These detrimental processes on concrete can be divided in two groups: physical and chemical processes. Erosion, wetting-drying and freezing – thawing belong to physical processes while sulphate, chloride, magnesium and carbonic acid attacks are chemical effects [1].

Fig. 1. Damages in concrete surface of a hydraulic structure.

Seawater action on concrete structures can cause concrete deterioration in humid and aggressive environments. In this case corrosion and destruction of concrete structures can take place [2], [3]. Typical damages of concrete surfaces in Klaipeda Sea Port structures are displayed in Fig. 1. The main defects include hardened cement paste scaling up to the coarse aggregates particles and reinforcement.

Seeking the compliance of hydraulic structures operated in aggressive environments with durability requirements, it is required to determine technical parameters for concrete in order to ensure that hydraulic structures operate properly during the foreseen service life under aggressive conditions and meet the requirements of suitability for operation and use by STR 2.05.05:2005. Damages of the surface of hydraulic concrete are caused by freezing – thawing action and in some cases an entire protective layer of concrete is damaged, which is 50 mm on the docks of the Klaipėda Port (STR 2.05.14:2005).

Klaipėda City and the territory of Klaipėda County is attributed to the western climatic region of Lithuania with characteristic western winds and moist sea air where winter temperature is higher than in other climatic zones of Lithuania due to the ice-free sea [2], [4]. Scientists [5], [6] have measured air temperature variations per day within the climatic zone of Lithuania, air temperature around 0 °C may fluctuate in Klaipėda from 3.6 °C to 11.8 °C for several consecutive days.

Studies on variation in water temperature and salinity of the Baltic Sea from 1960 to 2009 showed that various parameters in the Baltic Sea vary constantly: water temperature, salinity, sea level, ice volume, run off of rivers which gets into the sea, etc. [7]. The performed study showed that within 50 years water surface temperature of the Baltic Sea in the central part increased by 0.14 °C and 1.20 °C, decreasing trends in salinity were established at other measuring stations, the biggest change was –0.32 ‰, however, at other stations opposing trends were established – insignificant increase in salinity by correspondingly 0.10 ‰ and 0.04 ‰.

Within the period from year 1861 to 2000, positive trend of ambient air temperature of the Baltic Sea in the region of the Baltic Sea was 0.08 °C per decade, while the global trend was 0.05 °C per decade [8]. Westerly air-mass transport dominates in the environment of the Baltic Sea, and the Atlantic Ocean and the Baltic Sea form humid climate [9], during the process of climatic warming droughts and heats have become increasingly frequent, e.g. in 1992, 1994, 2002, 2006 [6], [10], [11].

Scientists have established that contemporary studies on climate change and resolution of the issues related to climatic warming are related to the analysis of variation in geophysical phenomena and hydrological regime [12]. In such a case particular attention should be paid to the rise in water level which issues of wearing way of coasts is directly related to. The water level of the Klaipėda Strait (1898 to 2001) on the Lithuanian coast rose by 13.5 cm over a century, and from 1960 average water level rises by app. 3.0 mm per annum [12].

Scientists examined quantities of salts contained in water which came into contact with hydraulic concrete [2], the values were as follows: $SO4^{2-}$ (187 mg/l to 270 mg/l), Cl^{-} (145 mg/l to 214 mg/l), K^+ (217 mg/l to 400 mg/l), Na^+ (147 mg/l to 160 mg/l). Climatic conditions were examined and measured: water temperature (9 °C to 15 °C), air temperature (5 °C to −5 °C), water salinity (0.3 % to 2.7 %), hydrogen ion concentration pH (8.3 to 9.05), wind (4 m/s to 32 m/s), waves (0.25 m to 3.0 m).

Researchers T. C. Powers and R. A. Helmuth during their analysis of the structural degradation of concrete due to cyclic freezing and thawing processes in the water-saturated state have established that movements of unfrozen water in concrete pores towards frozen areas under pressure in capillary pores are one of the most important concrete-degrading effects during freezing and thawing, because pressure force depends on the state of water in pores. Hydraulic pressure can cause cracking of concrete [13].

The authors state that while concrete is frozen and thawed in salt solutions, degradation of concrete due to cyclic freezing and thawing speeds up, because osmotic forces are caused by differences in salt concentrations in liquid phase, which promote osmotic pressure in pores and capillaries of cement stone. In this case concrete degradation process may accelerate up to 4 to 5 times. According to "Osmotic Pressure Mechanism" [13], [14], first water in the coarser pores freezes during cooling and different salt concentrations take place in the close and in the distance region of the pore wall.

Analysing concrete surface using various substances it has been found that the exterior liquid concentration is more important than the liquid concentration in concrete voids [15]. When the surface is exposed to 3 % salt solution, surface scaling is 1–2 orders of magnitude higher than when exposed to water [16], [17]. Subsequent studies have supported these findings that there is the most-damaging (pessimum) solute concentration [18].

The microstructure and behaviour of any concrete against aggressive agents significantly depend on the kind of cement used [19]. It is well known that pozzolanic materials improve the sulphate and sea water resistance of concrete [20]. Dongxue et al. found that the strength of pure Portland cement (PC) decreased to various extents in sea water, while the strength of steel slag cement (SC) maintained or even increased to different extents; especially the flexural strength increased considerably [21].

The objective of the present paper is to examine how freezing-thawing resistance of hydraulic concrete is influenced by the type of cement and contend of blast furnace granulated slag and limestone in cement, as well as comparison of physical and mechanical properties.

II. Materials and Methods

Several distinct batches of concrete were formed for the purpose of the present research.

The following cements were used for research (produced at JSC Akmenės cementas): Portland cement CEM I 42.5 N, blast furnace slag Portland cement CEM II/ A-S 42.5 N, lime Portland cement CEM II/A-LL 42.5 N and blast furnace slag cement CEM III/B 32.5 N (Table I, II).

TABLE I

Mechanical Properties of the Cement

Cement type	Compressive strength after 28 days, MPa	Compressive strength after 2 days, MPa	Type of additive	Content of additive, %
CEM I 42.5 N(MA)	50	22	slag	0
CEM II A/S 42.5 N	51	22	slag	~17
CEM III/B 32.5 N-LH(SR)	41	21*	slag	~70
CEM II A/LL 42.5 N	47	21	limestone	~17

*Compressive strength after 7 days.

TABLE II

Chemical Composition of the Cement

Chemical properties	Cement type			
	CEM I 42.5 N(MA)	CEM II A/S 42.5 N	CEM III/B 32.5 N-LH(SR)	CEM II A/LL 42.5 N
Total loss of ignition, %	1.4	1.4	1.9	6.3
Insoluble residue, %	0.4	0.4	0.4	0.7
SO_3 content, %	2.8	2.7	2.6	2.6
Chloride content (Cl^-), %	0.003	0.007	0.010	0.004
Total alkali content, expressed as Na_2O equivalent, %	<0.8	<0.8	<1.2	<0.8
Heat of hydration, J/g	342	302	<270	288

Sand of 0/4 mm was used for research. Physical properties of fine-grained aggregates were measured following standard LST EN 12620:2003+A1:2008. Sand testing results are presented in Table III.

Crushed granite with fraction of 2/8 and 11/16 was used as coarse-grained aggregate during research. Physical characteristics of rubble are provided in Table IV.

A superplasticizer based on modified polycarboxylate of new generation and synthetic air entraining agent admixture were also used for research.

TABLE III

Physical Properties of Sand

Properties	Values
Granulometric composition (category)	G_F85
Bulk density, kg/m^3	1700
Particle density, kg/m^3	2700
Fine particles content, mass %	0.6

TABLE IV

PHYSICAL PROPERTIES OF CRUSHED GRANITE

Properties	Values	
	Fraction 2/8	Fraction 11/16
Granulometric composition (category)	$G_C90/15$	$G_C90/15$
Bulk density, kg/m^3	1331	1394
Particle density, kg/m^3	2750	2750

Three concrete mixtures were used for testing different types of cement (different content of slag in cement). Compositions of concrete used for this research are presented in Table V. Water and cement ratio in these concretes remained constant and varied from 0.28 to 0.30.

TABLE V

CONCRETE COMPOSITION WITH DIFFERENT TYPE OF CEMENT, 1 M^3

Composition	CEM I	CEM II	CEM III
Cement, kg	433	433	515
Crushed granite 2/8 fr., kg	411	411	411
Crushed granite 11/16 fr., kg	615	615	533
Sand 0/4 fr., kg	754	754	754
Water, kg	120	130	147
Superplasticizer, kg	3.5	3.5	3.5
Air entraining admixture, kg	0.09	0.13	0.13
W/C	0.28	0.30	0.29

Concrete mixture with composition specified in table VI was used to determine the influence of slag additive on concrete durability in marine environment. The quantity of slag in the cement varied from 0 % to 70 %. The mean quantities of slag in the cement were obtained by mixing different quantities of cements CEM I and CEM III. The water/cement ratio in that concrete was constant and equalled 0.33.

Two types of cements were used preserving the same water and cement ratio amounting to 0.52 to test concretes using different testing methods (Table VII). CEM I 42.5 N was used in V1, J1, N1 batches. CEM II A/S 42.5 N was used in V2, J2, N2 batches.

TABLE VI

CONCRETE COMPOSITION WITH DIFFERENT SLAG CONTENT IN CEMENT, 1 M^3

Composition	
Cement, kg	433
Crushed granite 2/8 fr., kg	411
Crushed granite 11/16 fr., kg	615
Sand 0/4 fr., kg	754
Water, l	142
Superplasticizer, kg	3.5
Air entraining admixture, kg	0.26
W/C	0.33

TABLE VII

CONCRETE COMPOSITION WITH TWO TYPES OF CEMENT, 1 M^3

Composition	
Cement, kg	320
Crushed granite 2/8 fr., kg	311
Crushed granite 11/16 fr., kg	715
Sand 0/4 fr., kg	889
Water, l	165
Superplasticizer, kg	3.5
W/C	0.52

Concrete mixtures were prepared using a forced mixing machine, duration of mixing – 120 seconds. Cement and concrete mixtures with various compositions were prepared. Slump of concrete mixture was determined following the requirements of standard LST EN 12350-2, air content was determined following the requirements of standard LST EN 12350-7, and the density of the concrete mixture – following standard LST EN 12350-6. Compressive strength of concrete was determined following the requirements of standard LST EN 12390-3.

Concrete specimens were produced using non-moisture absorbent and water tight demountable moulds 100 mm × 100 mm × 100 mm. The specimens were compacted under vibration on a vibrating table for (30 ± 2) s. Produced specimens were stored in moulds for one day, later they were moulded and cured in water at (20 ± 2) °C following the requirements of standard LST EN 12390-2. Resistance of concrete specimens to cyclic freezing and thawing was determined following CEN/TS 12390-9 CF and CDF test, using water, sea water and a 3 % NaCl solution as freezing liquids. The chemical composition of the Baltic Sea water used in the research: NaCl – 15.5 g (1.52 %); K_2SO_4 – 0.07 g (0.069 %); $MgSO_4 \cdot 7H_2O$ – 2 g (0.196 %) 1000 g of water.

During freezing and thawing cycles specimens were stored in plastic containers. A 5 mm high spacer was put on the bottom of the container, it holds the specimen and secures the set layer of liquid between the tested surfaces.

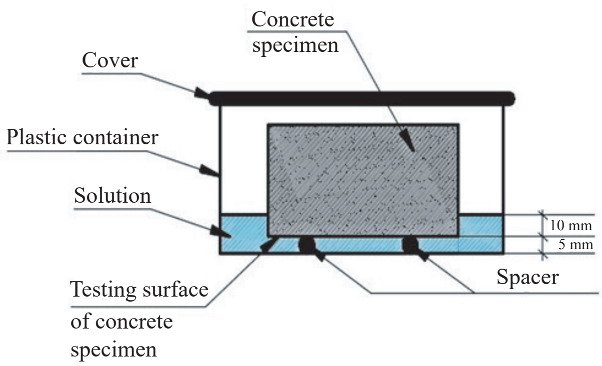


Fig. 2. The scheme of concrete durability testing method.

The freezing-thawing test was conducted after 28 days of curing with repeated saturation/adsorption of specimens. The freezing and thawing cycle takes 24 hours. Duration of one freezing and thawing cycle is 24 h + 0.5 h. Temperature in the freezing chamber does not drop below –22 °C, and does not rise above +22 °C. After 7, 28 and 56 cycles a test of the testing surface was performed, when temperature is equal to (20 ± 2) °C. The broken specimen material is filtered, dried and weighed.

III. Results

Concrete mixtures with different types of cement (Table V) and with different content of fly ash (Table VI) have similar technological properties. Slump of concrete mixtures with 0 %, 17 % and 35 % slag in the cements varies from 180 mm to 135 mm. The consistency of mixtures following the obtained experiment data are classified as slump class 3. Slump of concrete mixtures with 49 % and 70 % in the cements varies from 75 mm to 80 mm. In this case, experiment data are classified as slump class 2 (Fig. 3). But the amount of water for equal consistency is different for different cements – the slag cement requires higher water content in the concrete mixture, about 8.3 % and 22.5 % for CEM II and CEM III cements respectively (Table V).

The reduction of concrete consistency (viscosity) with increasing of slag content in cement was observed in the latest investigations [22] and irregular shape of slag particles is the reason why this phenomenon occurs. The slump of two mixtures for testing in different durability testing conditions (concrete saturation in water, water solution with chemical composition characteristic of the Baltic Sea and sodium chloride solution) was 70 mm and was classified as slump class S2.

Average air quantity in concrete mixtures with different cements (Table V) was 4.8 %. Air quantities in concrete mixtures with different content of slag are presented in Fig. 4. Lower air content was recorded in specimens from the third group of specimens for testing in different durability testing conditions – 2.77 %, because these concretes did not contain air entraining admixture. Researchers state that cement stone is a porous material, which may absorb high quantities of water. Therefore, the quantity of capillary pores in cement stone depends on the amount of water and the water/cement ratio in concrete.

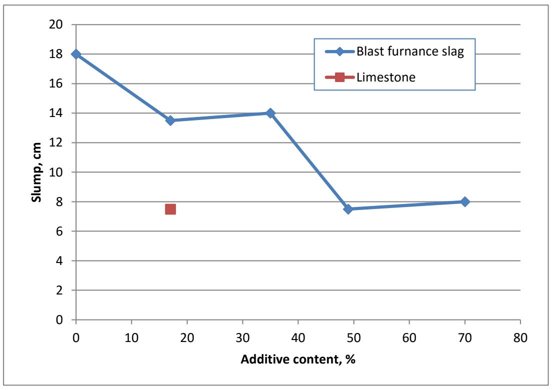


Fig. 3. Slump of concrete with different slag in the cements.

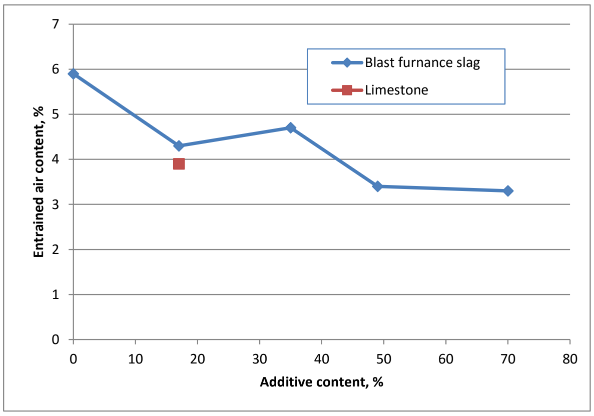


Fig. 4. Entrained air content of concrete with different slag in the cements.

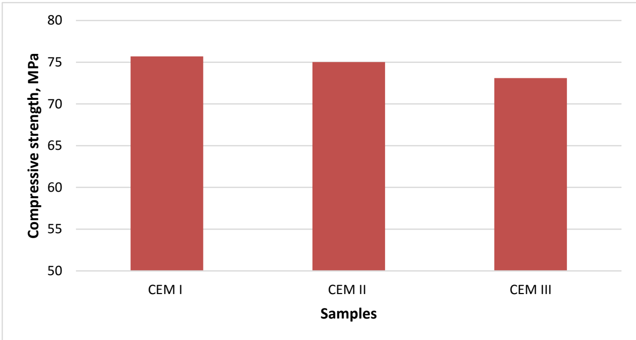


Fig. 5. Compressive strength of concrete with different cements.

Concrete strength is one of the main properties of materials for hydraulic structures. Compressive strength of concrete is a defined property which is directly related to cement stone and concrete structure and it significantly influences other properties and durability of concrete. Strength of concrete depends on the water/concrete ratio and air quantity in the concrete or its compaction (Fig. 5–7). The strength of concrete with the cement with high content of slag (70 % in CEM III type) has no influence on the strength of concrete with the same W/C ratio (Fig. 6). The compressive strength class of this cement is lower (32.5) than that of Portland cement without slag additive (42.5) (Fig. 5).

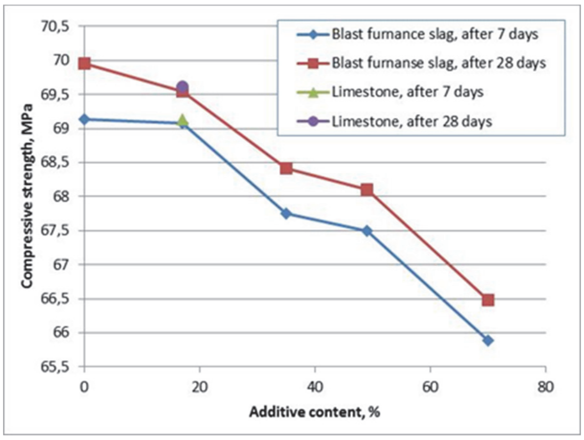


Fig. 6. Compressive strength of concrete with different slag in the cements.

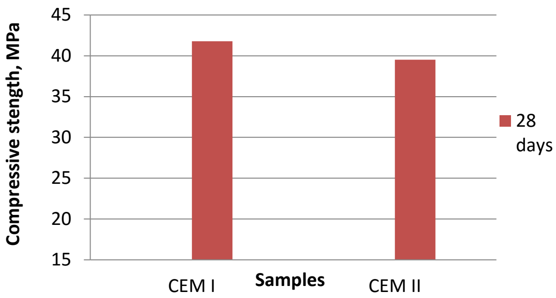


Fig. 7. Compressive strength of concrete with two cements.

Referring to the obtained results the highest compressive strength was in case of concrete specimens containing cement CEM I 42.5 N, and the lowest compressive strength was observed in case of CEM III/B 32.5 N cement. In addition, composition of concretes of the presented experiments, their density and water/concrete ratio, which also influence the changes in compressive strength, should be taken into account.

Freezing-thawing of concrete is greatly influenced by capillary porosity of concrete and decreases by increasing of open pores and capillaries, which were formed when loose water evaporated from the concrete. The quantity of such pores and capillaries depends on the water/cement ratio in concrete. The more water was poured into a concrete mixture, the more unbound water remained, and when it evaporated, open pores were formed. Therefore, water quantity in concrete influences freezing-thawing resistance and durability of the concrete.

The influence of cement type, slag content in the cement and durability testing conditions are discussed in the following part of this research paper.

Fig. 8 shows that in the beginning mass loss of specimens of all three batches of concrete with various cements after 7 freezing and thawing cycles is similar. Research was performed using the water composition, which is characteristic of the Baltic Sea. Differences of scaling from surface of concrete specimens become evident after 14 cycles. Trends in disruption of specimens with slag addition (CEM II and CEM III) are similar. Scaling from concrete surface is lower in case of specimen without slag (CEM I) only. Disrupted surfaces of specimens after 21 cycles are presented in Fig. 9.

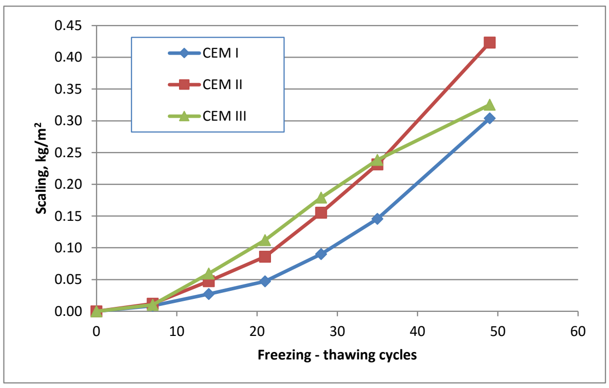


Fig. 8. Scaling of concrete with different cements.

Fig. 9. Destruction surface of samples with different cements after 21 cycles of freezing and thawing.

The figure shows that more intensive effects are present in specimens of batch with slag Portland cement (CEM II type). The surface of specimen belonging to batch with slag cement (CEM III type) was disrupted the least. From 35 freezing and thawing cycles the trends in scaling from concrete surface change. Growth of surface scaling of concrete specimens with slag cement (CEM III type) slows down. After 56 cycles in case of slag cement (CEM III type) surface scaling is the lowest and it amounts to 0.42 kg/m^2. Meanwhile, in other batches it amounts to 0.69 kg/m^2 and 0.49 kg/m^2. In case of concrete specimens with slag cement ongoing processes may be explained by the pozzolanic reaction of slag in the cement. Small scaling quantities for all concretes were obtained because very low W/C ratio in concretes was used (0.30).

Further research was performed with various compositions of concrete where the quantity of slag in the cement was altered (Fig. 10). In such case the composition of cement and Portland cement was simulated. In this case no slag was detected in concrete with CEM I 42.5 N and CEM II A/LL 42.5 N. In other concretes the quantity of slag increased from 17 % to 70 %. Freezing and thawing testing of concrete was performed up to 119 cycles. Trends in specimens with CEM I 42.5 N and specimens with CEM II A/S are similar, and after 119 cycles the surface scaling values are 0.13 kg/m^2 and 0.14 kg/m^2. When 35 % of slag was used in the cement, the outcomes were the best. In such case surface scaling is the lowest and amounts to 0.10 kg/m^2. When 49 % and 70 % of slag was used in cement scaling values were 0.224 kg/m^2 and 0.282 kg/m^2. Concrete specimens L1 were disrupted the most, where limestone Portland cement was used as a binding material. After 119 cycles the surface scaling of this concrete amounted to 0.40 kg/m^2.

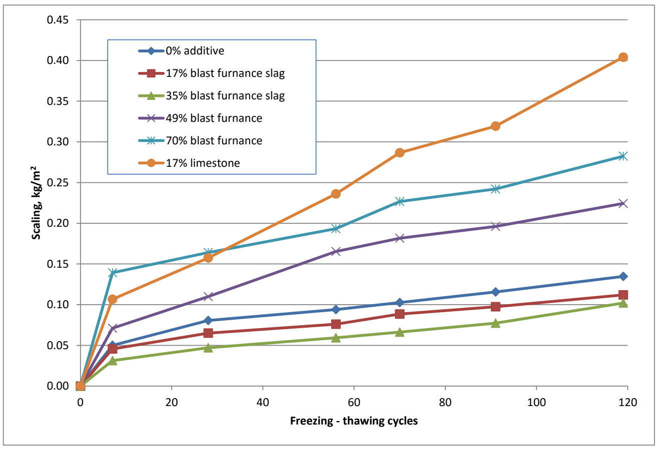


Fig. 10. Surface scaling of concrete with different slag in the cements.

Low values of surface scaling of all concretes were obtained because low W/C ratio and air entraining admixture were used.

The third experiment was aimed at determining the influence of saturation media of concrete specimens on surface scaling of concrete: distilled water, solution reproducing chemical composition of the water of the Baltic Sea and NaCl solution (3 %). Fig. 11 shows that concrete specimens were formed with high W/C ratio – 0.52, composition of concretes was formed with various cements: CEM I 42.5 N and slag Portland cement CEM II A/S 42.5. Concrete specimens were tested in various saturation media. The performed test with various freezing and thawing cycles showed that results of surface scaling were the lowest for the concrete specimens tested after saturation in the distilled water, however, concrete specimens affected by the solution reproducing chemical composition of the water of the Baltic Sea featured quite high surface saturation, and it varied from 1.1 kg/m^2 to 3.08 kg/m^2 (Fig. 11). The results of surface scaling of concrete saturated in NaCl solution show the destruction of concrete samples. Results of surface scaling after 39 cycles varied from 10.75 kg/m^2 to 10.92 kg/m^2.

In all cases, specimens were significantly damage when Portland cement without slag additive (CEM I type) was used (Fig. 12, 13 and 14). Therefore, the performed experiment showed that chemical composition of the water of the Baltic Sea should be assessed by evaluating durability parameters of concretes.

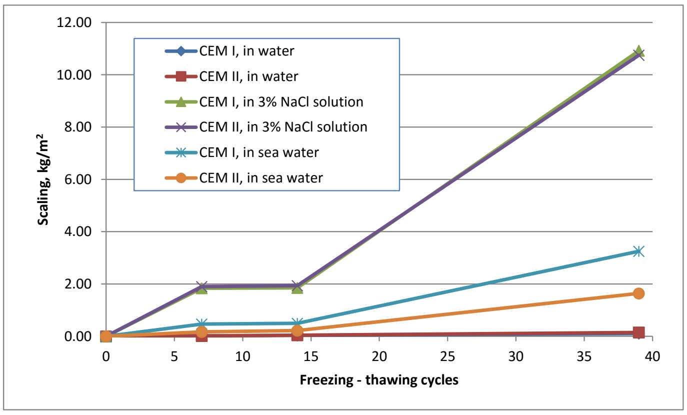
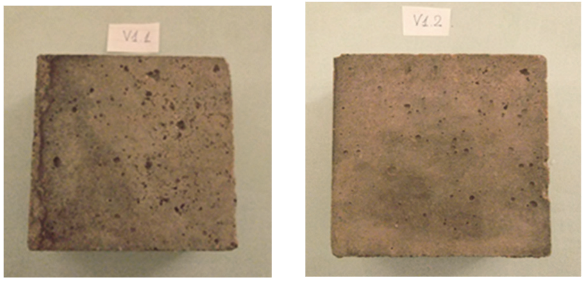
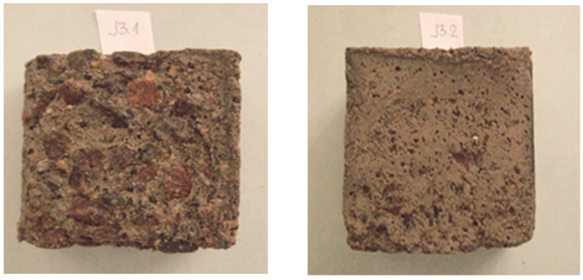


Fig. 11. Surface scaling of concrete tested in different media.



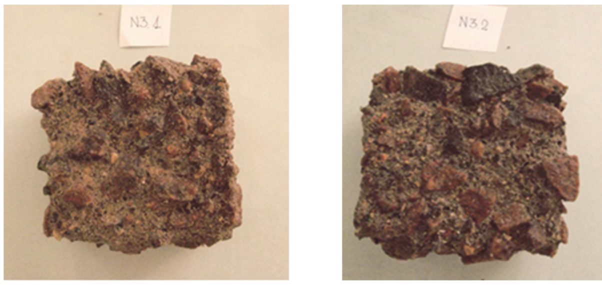
a) b)

Fig. 12. Destruction concrete samples after 39 cycles (water): a – with CEM I 42.5 N cement, b – with CEM II A/S 42.5 cement.



a) b)

Fig. 13. Destruction concrete samples after 39 cycles (water of the Baltic Sea) %): a – with CEM I 42.5 N cement, b – with CEM II A/S 42.5 cement.



a) b)

Fig. 14. Destruction concrete samples after 39 cycles (NaCl (3 %)): a – with CEM I 42.5 N cement, b – with CEM II A/S 42.5 cement.

IV. Conclusion

The analysis of results of the performed experiments showed that the compressive strength of concrete is not influenced by slag content in cement. The strength of concrete is highly affected by W/C ratio and air content in the concrete.

The investigation of freezing and thawing cycles showed that surface scaling of concrete specimens is the least in case slag content in cement equals 49 %. Quantity of slag up to 50 % in cement positively influences freezing-thawing of hydraulic concrete, higher content of slag has a negative influence on freezing-thawing resistance of concrete. Limestone additive is not suitable for the concretes intended for exposure to severe marine environment.

Durability of concrete operated in the marine environment may be assessed according to surface scaling of concrete specimens soaked in sea water under cyclic freezing and thawing.

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