The Cement Type Effect on Freeze – Thaw and Deicing Salt Resistance of Concrete

Gintautas Skripkiūnas, Džigita Nagrockienė, Giedrius Girskas, Marija Vaičienė, Erika Baranauskaitė

Abstract
This paper analyzes the effect of the four types of cement (Portland cement, blast-furnace Portland cement, limestone Portland cement and blast-furnace cement) on freeze-thaw and deicing salt resistance of concrete. Eight compositions of concrete with different cements were tested. Four compositions contained hydration retarder added at 0.3 wt% and 0.5 wt% by mass of cement and four compositions were without the retarder. All compositions contained 0.6 wt% of superplasticizer. 3% NaCl solutions was used as a freezing agent in freeze-thaw tests. The mass loss (the weight of scaled material), ultrasonic pulse velocity and residual deformations were measured every seven freeze-thaw cycle. The test results showed that the highest freeze-thaw and deicing salt resistance is observed in concrete made of blast-furnace cement (CEM III/B 32.5 N - LH) and the lowest freeze-thaw resistance is observed in concrete made of Portland cement (CEM I 42.5 R) and Portland blast – furnace cement (CEM II/A-S 42.2 N). Cement hydration retarder was found to have a negative effect on freeze-thaw and deicing salt resistance of concrete.

1. Introduction
Durability of concrete structures has been receiving much attention. Degradation of concrete exposed to freezing and thawing is the most common cause of destruction of concrete structures. It is a very acute problem not only in Lithuania but in other European states too as there are significant temperature fluctuations in Northern part of Europe.

Concrete degradation in aggressive mediums most commonly occurs in the binding hardened cement paste, whereas aggregate usually have higher density and chemical resistance. Concrete is rich in alkali and therefore it reacts actively with acidic gasses and liquids. For this reason the freeze-thaw resistance of concrete depends on the freeze-thaw resistance of hardened cement paste.

According to Kumara [1], freeze-thaw resistance of cement structures depends on the structure of the material, namely its porosity, the size of pores and capillaries, their distribution and type (open or closed pores). Freeze-thaw resistance is one of the indicators that can be used to describe the durability of concrete.

The results of tests conducted to forecast the freeze-thaw resistance of concrete according to porosity parameters showed that closed porosity had the most significant effect on freeze-thaw resistance of concrete. The authors claim that closed porosity depends on the concentration of coarse aggregate in concrete. Closed porosity and freeze-thaw resistance of

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concrete increases with lower concentration of coarse aggregate. Concretes with lower coarse aggregate content have smaller pores and such concretes have better freeze-thaw resistance [2].

According to Özbay et al. [3], cement containing 55 and 81 wt% of slag is freeze-thaw resistant. Freeze-thaw cycles in water or sodium sulphate solution showed that the ductility of specimens made of cementitious composites decreased remarkably, irrespective of slag content and applied freeze-thaw process. Reduction in mass loss was at the lowest level and no significant behaviour change was observed between the specimens subjected to freeze-thaw cycles in water and in aggressive sodium sulphate solution. Moreover, the decrease in flexural stiffness was more evident than the reduction of flexural strength for all mixtures of cementitious composites.

The chemical substances for pavement deicing are mainly used salts of NaCl and CaCl₂ in Lithuania [4]. The usage the salt for road maintenance has great influence on the durability of transport structures concrete.

Usage NaCl solution instead the water greatly accelerate the concrete degradation caused by cyclic freezing and thawing. NaCl solution accelerates concrete degradation by 4–5 times. Therefore, in this case the concrete freeze-thaw resistance should be 4–5 times higher than the concrete unexposed to salt solution [5].

J. J. Valenza II and G. W. Scherer [6, 7] investigations emphasizes the increase of concentration of solution has negative influence on the durability of hardened cement paste.

Individual salts solution doesn’t have a great negative influence on durability, but during cyclic freezing and thawing damages in concrete surfaces causes a more rapid penetration of salts into the inner structure of concrete, which have influence on the decrease of concrete strength [8, 9].

Skripkiūnas et al. [10] researched into hardened cement paste made of CEM I 42.5 R cement modified with synthetic zeolite admixture. The research results showed that mass loss and deformations after 28 freezing and thawing cycles were much lower in concrete modified with 10 wt% of synthetic zeolite compared to specimens without zeolite admixture. Ultrasonic pulse velocity after 28 freeze-thaw cycles increases. The obtained results indicate that synthetic zeolite admixture modifies the morphology of hardened cement paste: there is a drop in Ca(OH)₂ and ettringite content and the volume of C-S-H phase is bigger. These changes increase the paste’s density, strength and freeze-thaw as well as deicing salt scaling resistance.

The test results proved that cyclic freezing of concrete specimens previously soaked in Na₂SO₄ solution and subsequent thawing in the solution causes two or three-time faster destruction of the specimens. A faster method for determining the durability of cement products was developed. The recommended dimensions of specimens for the test are 40×40×160 mm. The paste shall be made of cement and conventional sand with C/S ratio = 1:4 and W/C ratio = 0.6. The freezing is done for 7±1 h at –18±2 °C and afterwards the specimen is kept in 5% Na₂SO₄ solution at room temperature for 15±1 h. One cycle lasts 24 h [11].

Skripkiūnas [12] and other authors conducted tests with concrete specimens made of CEM I 42.5 R cement modified with sodium silicate solution. 5% solutions of the following deicing salts were used in the tests: sodium chloride, calcium chloride and magnesium chloride. The deterioration of hardened cement paste was assessed by the changes in compressive strength, ultrasonic pulse velocity, specimen deformations and the amount of scaled material during cyclic freezing and thawing. Test results showed that destruction after 56 freeze-thaw cycles and exposure to deicing salt solutions is smaller in hardened cement paste modified with sodium silicate solution. Therefore, sodium silicate solution may be used to improve the durability of hardened cement paste and concrete used in road building.

According to many researches for the improving concrete durability in the deicing salt environment the cement modified with blast-furnace slag can be used in the concrete structures [13-15].

The effect of pre-saturation and three curing methods (standard 14-day, 3-day curing, and with curing compound) on salt scaling resistance was studied in three concrete types including plain, 25% fly ash and 35% slag. The concrete made with slag showed the highest salt scaling resistance. The addition of 35 wt% slag to the concrete gave good salt scaling resistance in accordance with both methods with 14 day curing in comparison with other two concrete types while it decreased the resistance according to the method using the curing compound significantly and the 3-day curing method slightly [16].

Deja [17] presents the results of investigations made into the concrete containing cement rich in granulated blast furnace slag (57 %). The test results showed that air entraining the concrete mix up to the level of 5–6 % guarantees high salt scaling resistance even at relatively high values of water/cement ratio.

Šelih and Wang [18, 19] obtained that a CaCl₂ solution, compared to NaCl and MgCl₂ solutions, had the most destructive effect on concrete performance, regardless of the type of concrete. Concrete with air entraining admixture and lower water content (rigid consistency) experienced a much lower (10 times) mass loss caused by deicing salts during cyclic freezing and thawing. NaCl, compared to CaCl₂, has a greater destructive impact on such concrete.

After 50 freezing and thawing cycles, the highest mass loss is 1.13 kg/m² for engineered cementitious composites with different fly ash content pre-loaded to 2 mm flexural deformation. Fly ash admixture (55 and 69 wt%) significantly reduces mass loss in concrete exposed to freezing and thawing in the presence of deicing salts [20].
Freeze-thaw resistance of concrete depends on water-cement ratio, air content and curing time. There are two mechanisms of concrete destruction (under freeze-thaw conditions): surface damage and internal damage. The test results showed that internal damage determines the need for air-entrainment in high-strength concretes while in normal or low-strength concretes, surface scaling determines the need for higher air content compared to the internal damage freeze-thaw mechanism [21].

Researchers [22] made extensive studies into the effect of sodium chloride solution, freeze-thaw cycling and externally applied load on the performance of concrete. The results show that the concrete specimens subjected to freeze-thaw cycling scaled more severely in chloride salt solution than those in water, and weight losses of the specimens tested in chloride salt solution were twice as much as those tested in water.

Researchers [23] studied the effect of diluted deicers on the durability of a Portland cement concrete. The CMA (hydrated calcium magnesium acetate) solid deicer and the MgCl₂ liquid deicer were benign to the concrete durability, whereas K-formate and the Sodium acetate/Na-formate blend deicer caused a moderate amount of weight loss and noticeable deterioration of the concrete. NaCl, the NaCl-based deicer, and the K-acetate-based deicer were the most deleterious to the concrete.

The goal of the tests was to determine the influence of the type of cement and hydration retarder on freeze-thaw and salt resistance of concrete. The paper analyses both the surface and the internal destruction of concrete.

2. Composition of tested mixtures, raw materials and research methods

Portland cements produced by AB Akmenės cementas and complying with LST EN 197-1:2001 requirements were used for the tests. Cements CEM II/A-S and CEM II/A-LL contained 6–20% of blast furnace and limestone, and cement CEM III/B contained 66–80% of slag. Compared to conventional CEM I type Portland cement, hydration heat in composite cement CEM II/A-S 42.5 N (MA) was 20% lower, 16 % in CEM II/A-LL 42.5 R (MA) and 26 % in CEM III/B 32.5 N-LH (SR). Specifications of different types of cements are presented in Table 1.

The fine aggregate used was 0/4 fraction sand with specifications presented in Table 2. The coarse aggregate used was 5/11 and 11/16 fraction crushed gravel stone. Crushed gravel specifications are presented in Table 3.

Table 1. Mechanical and physical properties of cements

<table>
<thead>
<tr>
<th>Cement properties</th>
<th>CEM I 42.5 R</th>
<th>CEM II/A-S 42.5 N (MA)</th>
<th>CEM II/A-LL 42.5 R (MA)</th>
<th>CEM III/B 32.5 N-LH (SR)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Compressive strength, MPa</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>after 2 days</td>
<td>28±2</td>
<td>22±3</td>
<td>29±2</td>
<td>–</td>
</tr>
<tr>
<td>after 7 days</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>21±3</td>
</tr>
<tr>
<td>after 28 days</td>
<td>54±3</td>
<td>51±3</td>
<td>52±3</td>
<td>41±3</td>
</tr>
<tr>
<td>Initial setting time, min</td>
<td>160</td>
<td>160</td>
<td>200</td>
<td>195</td>
</tr>
<tr>
<td>Amount of water for normal consistency, %</td>
<td>25.3</td>
<td>25.3</td>
<td>26.3</td>
<td>28.0</td>
</tr>
<tr>
<td>Specific surface area, cm²/g</td>
<td>3700</td>
<td>3800</td>
<td>4400</td>
<td>4800</td>
</tr>
</tbody>
</table>

The fine aggregate used was 0/4 fraction sand with specifications presented in Table 2. The coarse aggregate used was 5/11 and 11/16 fraction crushed gravel stone. Crushed gravel specifications are presented in Table 3.

Table 2. Fine aggregate specifications

<table>
<thead>
<tr>
<th>Particle density, kg/m³</th>
<th>Water absorption, %</th>
<th>Bulk density, kg/m³</th>
</tr>
</thead>
<tbody>
<tr>
<td>2650</td>
<td>0.59</td>
<td>1582</td>
</tr>
</tbody>
</table>

Table 3. Coarse aggregate specifications

<table>
<thead>
<tr>
<th>Particle density, kg/m³</th>
<th>Water absorption, %</th>
<th>Bulk density, kg/m³</th>
</tr>
</thead>
<tbody>
<tr>
<td>2650</td>
<td>1.30</td>
<td>1546</td>
</tr>
</tbody>
</table>

Superplasticizer Muraplast 63.30 based on synthetic polycarboxylic ether polymers and hydration retarder Centrament Retard 310 containing surface activation agents was used for the tests.

Eight cement mixtures were made for the tests. 0.6 wt% of superplasticizer and 0.3 wt% and 0.5 wt% of retarder were added to concrete mixtures. Compositions of concrete mixtures are presented in Table 4.
Concrete mixtures were mixed in forced action mixer. Cement and dry aggregates were dosed by weight, water and chemical agents were dosed by volume. Chemical agents were mixed in together with water used to prepare the paste.

Concrete specimens were made in the form of 100×100×100 mm cubes in metal moulds and compacted on laboratory vibrating table. For the first 24 hours the specimens were left in the moulds and covered with a plastic film to prevent excessive drying. After 24 hours the specimens were removed from the moulds and placed into a bath filled with tap water and maintaining 20±2 °C temperature. The specimens were left in water for 28 days.

Freeze-thaw testing of specimen surface was done in accordance with LST EN 1338:2003+AC:2006. Concrete paving blocks – Requirements and test methods (Annex D): Determination of freeze/thaw resistance with de-icing salt. All surfaces of the specimen, except for the test surface, were covered with a rubber sheet for the entire testing time. The edge of the rubber sheet reached (20±2) mm above the test surface.

At the beginning potable water with a temperature of (20±2) °C was poured on the test surface to a depth of (5±2) mm. Water was maintained for (72±2) h at (20±2) °C and was used to assess the effectiveness of the seal between the specimen and the rubber sheet. 15 min to 30 min before the specimens were placed in the freezing chamber, the water on the test surface was replaced with a (5±2) mm layer, measured from the top surface of the specimen, of 3% NaCl solution. To prevent the evaporation of solution it was covered with a polyethylene sheet. The specimens were subjected to repeated freezing and thawing in 28 cycles, one cycle lasting 24 h. The material that had scaled off was collected every 7 freeze/thaw cycle, weighed and the result expressed in kilograms per square metre.

According to ultrasonic pulse velocity evaluation method, freeze-thaw resistance of concrete is determined according to certain limit changes of the relative velocity of ultrasonic pulse in specimens subjected to freezing and thawing. The moment of freeze-thaw destruction of concrete is usually indicated by an abrupt drop in ultrasonic pulse velocity in the specimen. Ultrasonic pulse velocity was measured every 7 freeze-thaw cycle. The specimens were carefully dried before measuring. To ensure the proper contact between ultrasonic pulse sensors and the test surface (reference points in the centre of the specimen), a layer of jelly was applied in the place of contact. The equipment measures the time of ultrasonic pulse propagation. This value is recorded and ultrasonic pulse velocity is calculated from the formula.

Deformations of concrete specimens were measured by a micrometer in the centre of the specimen. Residual deformations in concrete specimens were measured through glass tubes every 7 freeze-thaw cycle. The test involved 28 freeze-thaw cycles.

3. Test results

Concrete mixtures differed by adding hydration retarded Centrament Retard 310 in compositions 1–4.

Specimens made of 8 different compositions were frozen on one side in 28 freeze-thaw cycles. Fig. 1 illustrates the change in mass loss every 7 cycles throughout the entire test.

The mass loss diagram (Fig. 1) illustrates that the biggest mass loss was in specimens of compositions 2 and 4 where 0.5% of retarder by mass of cement was added. The total mass loss in composition 2 specimen after 28 freeze-thaw cycles was 5.5 kg/m² and the total mass loss of composition 4 specimen was 4.6 kg/m². The retarder was also used in compositions 1 and 3 but at lower amount, i.e. 0.3 wt%. The lowest mass loss was observed in composition 8 specimen where CEM III/B 32.5 N-LH (SR) was used without retarding admixture.

Mass loss in this specimen was 0.1 kg/m² after 28 freeze-thaw cycles. A relatively big mass loss of 1.1 kg/m² was also observed in composition 5 specimen where cement CEM I 42.5 R was used.
The test results showed that cement CEM III/B 32.5 N-LH significantly increases freeze-thaw resistance of concrete. The analysis of mass loss results showed that the retarder and its amount have a negative effect of freeze-thaw resistance of concrete.

![Fig. 1. Mass loss due to surface scaling](image1)

Ultrasonic pulse velocity (Fig. 2) and residual deformations (Fig. 3) were also measured every 7 freeze-thaw cycle. Fig. 2 illustrates the average change of ultrasonic pulse velocity in compositions of concrete.

![Fig. 2. The change in ultrasonic pulse velocity in concrete specimens](image2)

The test results show that the retarder and its content have a significant effect on ultrasonic pulse velocity. The curves of specimens of compositions 1–4 (Table 4) show a significant drop in ultrasonic pulse velocity after 14 freeze-thaw cycles. It can be explained by the use of retarder that reduces freeze-thaw resistance of concrete. Cyclic freezing and thawing affects only the surface layer of the specimen. Deeper layers where ultrasonic pulse velocity was measured (middle of the specimen 50 mm from the surface) were not affected or less affected by salt solutions and cyclic freezing and thawing. From the
research data it is difficult to explain great increase of compositions 2 and 4 ultrasonic pulse velocity after 14 freeze-thaw cycles. The type of the change in deformation curves presented in Fig. 3 remains similar throughout the entire test time (28 freeze-thaw cycles).

After 7 freeze-thaw cycles the specimens experience negative deformations, i.e. shrink. After 14 cycles deformations tend to increase and remain negative. After 21 cycles deformations increase and deformations in specimens of compositions 6 and 8 become positive. Deformations become positive in all 8 compositions only after 28 freeze-thaw cycles.

Such type of deformation change might be because residual deformations are measured in the centre of the specimen (50 mm from the specimen surface) that is not affected by freezing and thawing as a result of good thermal insulation of the specimen. Bigger deformations in the second half of the test time indicate that destruction occurs in the middle of the specimen. The test results indicate that the biggest deformations of concrete occurred on the test surface that was covered by NaCl solution speeding up the deterioration of concrete structure.

4. Conclusions

1. Concrete containing slag cement CEM III/B 32.5 N-LH without hydration retarder was found to have the biggest freeze-thaw and deicing salt scaling resistance. Mass loss in the specimen made of this concrete was 0.1 kg/m² after 28 freeze-thaw cycles. Concrete containing Portland cement CEM I 42.5 R with 1.80% content of retarder have the lowest freeze-thaw and deicing salt scaling resistance with mass loss of 5.5 kg/m².

2. When hydration retarder is added at 0.3% by mass of cement, the mass loss increases up to 2.6 times and ultrasonic pulse velocity drops up to 25%. When hydration retarder is added at 0.5% by mass of cement, the mass loss increases up to 5 times and ultrasonic pulse velocity drops up to 34.0%. Cement hydration retarder was found to have a negative effect on freeze-thaw and deicing salt scaling resistance of concrete.

3. Cyclic freezing and thawing has a significant effect only on the surface layer. The effect of salt solution and cyclic freezing and thawing was less significant in deeper layers where residual deformations were measured.

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References