Diamidoamine Salt as the Admixture for Concrete Increasing the Resistance to the Freeze-Thaw Cycle

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Abstract. Concrete freeze-thaw resistance, along with compressive strength, is one of its basic features, which have a significant impact on the durability of structures and engineering structures. Numerous studies presented in domestic and foreign literature showed that there is a relationship between the concrete mix’s composition and the extent of frost damage. The frost durability of concrete depends on many factors. Therefore, cyclic changes of air temperature in winter conditions (over 100 freeze-thaw event cycles per year are estimated in Poland) must be taken into consideration as soon as in the phase of designing a concrete mix and structural elements. Proper designing of the concrete mix, optimal selecting of proportions and kinds of components, applying of appropriate kinds of additives and admixtures as well as proper maintenance of concrete can protect the investor against serious financial consequences. The paper discussed the influence of sub-zero temperatures effect on cement concretes properties. The requirements that are imposed on designers in terms of concretes resistance to frosts cyclic effect by the currently applicable standards were presented. The paper also presents the results of an original research programme showing the effectiveness of diamidoamine salt as an admixture for concretes that increases their resistance to the freeze-thaw cycle. Within the preliminary tests, the influence of the diamidoamine salt on early and 28-day compressive strength was marked. The air content in fresh concrete, absorbability and water permeability were also specified. The freeze-thaw resistance of concretes with the addition of the diamidoamine salt after 50 freeze-thaw cycles was determined. The conducted preliminary laboratory tests showed that applying the diamidoamine salt causes the decrease in compressive strength. This decrease is proportional to the admixture content. The applied admixture significantly decreases the absorbability, improves waterproofness and freeze-thaw resistance of the concrete.

1. Introduction

The European harmonised standards “Eurocode” strongly emphasise the durability of designed and erected facilities. Providing structural elements with appropriate resistance to frost damage is one of durability and safe operation’s criteria. This issue is particularly relevant in temperate climate countries, where big changes in air temperature, especially cyclic freeze-thaw events, are reported within a year.

In construction, the term “low temperatures” means the period, when the average daily air temperature is below +5°C. After cement contacts with water, a lot of cement ingredients, mainly
alkalies decreasing the freezing point, dissolve. That is why water in the concrete mix freezes at c. -10°C. Freezing of the part of entire mixing water in curing concrete restricts the processes of cement’s setting and hardening almost completely. The phenomenon of frost corrosion occurs. It was shown that there is a relationship between the concrete mix composition and the extent of frost damage. The concrete durability depends on the water-cement ratio (its decrease is beneficial), the content of cement and mineral additives, concrete air entrainment and the freeze-thaw resistance of applied aggregates [1-4].

The paper presented the results of the preliminary tests of the influence of the diamidoamine salt on concrete’s selected properties. The aim of the paper was to show the effectiveness of admixture’s effect in terms of improving concretes’ resistance to frost’s cyclic effect.

2. Freeze-thaw cycles of concretes

Concrete deterioration caused by the cyclic effect of sub-zero temperature is related to its thermal deformations and physical phenomena that occur in it. The freezing water increases its volume by c. 9%. As a result of formed pressure, internal stresses are generated, whose values exceed concrete’s tensile strength. This causes the damage to the concrete structure manifested by cracking, surface scaling and splinters [1, 3, 5].

![Figure 1](image-url). Frost damages to concrete structures

Over the years, a lot of hypotheses describing the mechanism of low-temperature concretes destruction have been made. The simplest one – often compared to the “sealed container mechanism” – says that if a sealed container filled with water in 92% is cooled to -1°C, the pressure inside it will reach c. 10 MPa [6]. In 1945, Powers noticed that the main cause of concrete destruction is not the pressure caused by the increase in ice volume, but the hydraulic pressure that increases during ice formation, when water is removed from pores, in which freezing occurred [3, 7]. In 1953, Powers and Helmuth presented the so-called osmotic pressure hypothesis which says that freezing starts in bigger pores – capillaries – and the pressure increases in smaller pores as the temperature decreases. At a given temperature, in capillary pores, there is the balance between ice and water quantity. After some quantity of water transforms into ice, the concentration of the remaining solution increases and is so high that further transformation of water into ice does not occur without a decrease in temperature. The difference in the solution concentration in small pores, which causes osmotic pressure, arises [3, 8]. The third theory proposed by Litvan is based on the laws of thermodynamics. Water runs from capillaries towards air pores in order to level the differences in vapour pressure (there is higher vapour pressure over the supercooled water than over the ice). The pressure will increase also in line with the growth in the distance that the water must cover. As in the earlier hypotheses, the cooling speed heightens the water movement. All these factors fasten the concrete destruction [3, 5, 8, 9].

The modern theories and hypotheses on destructive effect of low temperature on concrete are based on the 3 above-mentioned hypotheses to a greater or lower extent. In concrete, water is in the interconnected pore system. These pores are of various shape and structure. The pore sizes in the
cement matrix change to a great extent and most pores are available for the water. The concrete permeability, and thus durability, depends on its porosity. The pores are partially or completely filled with water. It was adopted to determine the relationship between freeze-thaw resistance and the porosity structure of hardened cement paste with the air pores spacing coefficient [4, 6, 9]. According to the current state of knowledge, the shorter the distance between the air bubbles is, the greater the concrete’s frost resistance is. It is adopted that the air pores spacing factor L should be lower than 0.25mm if the air entrainment is to increase significantly the concrete’s resistance to the freeze-thaw cycle [4].

Figure 2. Diagram of pores of various diameters and spacing operating in concrete, when water freezes [6, 9]

Table 1. Exposure classes of concrete exposed to the aggressive effect of freezing/thawing [10]

| Class indicator | Description of the environment                                      | Examples of occurrence                                                                 |
|-----------------|--------------------------------------------------------------------|----------------------------------------------------------------------------------------|
| XF1             | Moderately saturated with water without de-icing agents            | Vertical concrete surfaces exposed to rain and freezing                                 |
|                 |                                                                    | Vertical concrete surfaces of road structures exposed to freezing and the effect of de-icing agents in the air |
| XF2             | Moderately saturated with water with de-icing agents               |                                                                                       |
| XF3             | Highly saturated with water without de-icing agents                | Vertical concrete surfaces exposed to rain and freezing                                 |
|                 |                                                                    | Roadways and bridge decks exposed to the effect of de-icing agents. Concrete surfaces exposed directly to the effect of aerosols containing de-icing agents and freezing Splatter zones in marine buildings exposed to freezing |
| XF4             | High saturation with water with de-icing agents or sea water       |                                                                                       |

The tests of porosity of hardened concrete and determining of distribution and size of pores in concrete are classified as indirect methods of assessing the concrete frost resistance [4]. The test method is described in EN 480-11 [11], but it concerns testing the effectiveness of admixtures for concrete. It does not refer to the concrete’s resistance to the harmful effect of frost in any way. The concrete standard EN 206 [10] expresses the freeze-thaw resistance in concrete exposure classes (table 1). Then, after specifying the exposure class, the standard imposes requirements on the minimum cement content, W/C ratio, strength class, and the minimum air content (table 2).
Table 2. Recommended cut-off values concerning the composition and properties of concrete [10]

| Exposure class | XF1  | XF2  | XF3  | XF4  |
|----------------|------|------|------|------|
| Max w/c        | 0.55 | 0.55 | 0.50 | 0.45 |
| Min strength class | C30/37 | C25/30 | C30/37 | C30/37 |
| Min cement content (kg/m³) | 300 | 300 | 320 | 340 |
| Min air content (%) | --- | 4.0 | 4.0 | 4.0 |
| Other requirements | Aggregate compliant with PN-EN 12620, with appropriate freeze-thaw resistance |

In the construction practice, direct methods of determining concretes’ freeze-thaw resistance are still applied in most cases. Two basic tests are determining of the air content in a concrete mix [12] and determining of the freeze-thaw resistance degree defined by the already inapplicable Polish standard PN-B-06250 [13]. In the test of concrete’s freeze-thaw resistance with an ordinary method [13], cubic-shaped samples after 28 days of curing are applied. The test begins with saturating the concrete samples with water. The reference samples intended to test the compressive strength are left in water at +18±2°C for the entire duration of marking the frost resistance. The samples to be frozen are placed in a freezer chamber so that there is 20-cm spacing between them. The freezer freezes them cyclically at -18±2°C for 4 hours and thaws them by drowning them completely in water at +18±2°C within 4 hours. After the last thawing, the strength test is conducted on the reference samples and the ones exposed to frost. Then, the average decrease in the samples’ strength is calculated. The freeze-thaw resistance degree is reached if, after the number of freeze-thaw cycles of concrete samples, which is indicated by its symbol (e.g. F50), the following requirements are met:

- the sample does not show cracks,
- the total mass of concrete holes in the form of destroyed corners and edges, splinters, etc. does not exceed 5% of the frozen samples’ mass,
- the decrease in the compressive strength in relation to the not frozen samples is not higher than 20%.

3. Materials and methods
The following were used in the tests:
- CEM I 42.5R cement;
- distilled water;
- the mixture of sand, fine gravel and granite chippings with grain size distributions shown on aggregate grading curves (fig. 3);
- diamidoamine salt (admixture).

Five concrete mixtures of mix designs presented in table 3 were made.
Figure 3. Aggregate grading curves.

Table 3. Mix designs of concrete mixes per 1 m³

| Item | Admixture content [% of cement mass] | Cement [kg] | Water [kg] | Sand [kg] | Fine gravel [kg] | Granite chippings [kg] | Diamidoamine salt [kg] |
|------|------------------------------------|-------------|------------|-----------|-----------------|------------------------|------------------------|
| 1    | Control sample                     | 320         | 145        | 620       | 800             | 500                    | -                      |
| 2    | 0.10%                              | 320         | 145        | 620       | 800             | 500                    | 0.32                   |
| 3    | 0.25%                              | 320         | 145        | 620       | 800             | 500                    | 0.80                   |
| 4    | 0.50%                              | 320         | 145        | 620       | 800             | 500                    | 1.60                   |
| 5    | 1.00%                              | 320         | 145        | 620       | 800             | 500                    | 3.20                   |

Diamidoamine salts are chemical substances formed as a result of aminolysis of natural fats, fatty acids and waste materials (used cooking oils, waste tallows, sludge acids). As the air entraining agent, amidoamine lactate with a formula: \([\text{RCONHCH}_2\text{CH}_2\text{NH}_2]+\text{[CH}_3\text{CH(OH)COO]}^-\), where \(\text{R=}(\text{CH}_2)_n\text{CH}_3\ n=16\) with one double bond was used.

![Molecular structure of diamidoamine lactate](image)

Figure 4. Molecular structure of diamidoamine lactate

The assessments of the admixture’s effectiveness were conducted on the basis of the following tests
- the determining of the air content in the concrete mix [12];
• the determining of compressive strength after 7 and 28 days of curing [14];
• the determining of the concrete’s water absorption by weight [13];
• the determining of the concrete’s water permeability [15];
• the determining of the freeze-thaw resistance degree [13].

4. Results and discussions

Table 4 presents the influence of diamidoamine salt on the change in the air content in fresh concrete (tested with the pressure method). The addition of diamidoamine salt causes a significant increase in the air content in fresh concrete. The air content is proportional to the quantity of the added admixture. In the case of 1.0% of admixture content in the cement mass, a 2.5-fold increase in air content is observed – from 2.2% to 5.6%.

Table 4. The air content in fresh concrete

| Item | Admixture content [% of cement mass] | Air content in fresh concrete [%] |
|------|-----------------------------------|---------------------------------|
| 1    | Control sample                    | 2.20                            |
| 2    | 0.10%                             | 3.20                            |
| 3    | 0.25%                             | 3.25                            |
| 4    | 0.50%                             | 5.20                            |
| 5    | 1.00%                             | 5.60                            |

Table 5 presents the results of tests of compressive strength after 7 and 28 days of concrete curing. On the basis of the obtained results, it can be said that the applied admixture causes decrease in compressive strength of concrete both after 7 and 28 days of curing. The decrease in compressive strength is proportional to the quantity of the applied admixture. The greatest decrease in compressive strength is observed for 0.5% of the admixture after 7 days of curing and is about 14% in relation to the reference concrete, as well as for 1.0% of the admixture after 28 days of curing and is about 17% in relation to the strength of the reference concrete.

Table 5. The compressive strength after 7 and 28 days of concrete curing

| Item | Admixture content [% of cement mass] | Compressive strength after 7 days of curing [MPa] | Decrease in compressive strength in relation to the control samples [%] | Compressive strength after 28 days of curing [MPa] | Decrease in compressive strength in relation to the control samples [%] |
|------|-----------------------------------|-----------------------------------------------|-------------------------------------------------|-----------------------------------------------|-------------------------------------------------|
| 1    | Control sample                    | 55.09 ± 2.94                                 | -                                               | 72.06 ± 3.46                                 | -                                               |
| 2    | 0.10%                             | 50.70 ± 1.70                                 | 7.97%                                          | 68.25 ± 3.41                                 | 5.29%                                          |
| 3    | 0.25%                             | 49.35 ± 1.75                                 | 10.42%                                         | 64.42 ± 1.83                                 | 10.60%                                         |
| 4    | 0.50%                             | 47.50 ± 4.35                                 | 13.78%                                         | 60.28 ± 1.32                                 | 16.35%                                         |
| 5    | 1.00%                             | 50.13 ± 2.68                                 | 9.00%                                          | 59.73 ± 2.77                                 | 17.11%                                         |

Table 6 presents the results of marking absorbability and water permeability of the hardened concretes. As a result of the admixture’s effect, the decrease in concretes’ absorbability from c. 4% to 2.3% in the case of concretes with 1% of salt content was observed. The admixture of diamidoamine salt caused the significant decrease in water permeability in relation to the reference concrete – the decrease in value by c. 50%. The obtained values of absorbability and water permeability are very similar. However, the proportional relationship between the admixture content and absorbability as well as water permeability of the tested concretes can be observed.
Table 6. The absorbability and water permeability of the hardened concretes

| Item | Admixture content [% of cement mass] | Absorbability [%] | Decrease in absorbability in relation to the control samples [%] | Water permeability [cm] | Decrease in water permeability in relation to the control samples [%] |
|------|------------------------------------|-------------------|-------------------------------------------------------------|------------------------|-------------------------------------------------------------|
| 1    | Control sample                     | 3.96              | -                                                           | 12.0                   | -                                                           |
| 2    | 0.10%                              | 3.65              | 7.8                                                         | 5.9                    | 50.8                                                        |
| 3    | 0.25%                              | 3.23              | 18.4                                                        | 5.6                    | 53.3                                                        |
| 4    | 0.50%                              | 2.74              | 30.8                                                        | 5.3                    | 55.8                                                        |
| 5    | 1.00%                              | 2.29              | 42.2                                                        | 5.1                    | 57.5                                                        |

Table 7 summarises the results of marking the freeze-thaw resistance degree after 50 free-thaw cycles for the hardened concretes. In the case of the control concrete samples, the decrease in strength by c. 40% was observed. The addition of diamidoamine salt causes significant improvement of concrete’s frost resistance. The decreases in strength after 50 days of freeze-thaw cycles are at the level of 1%-2% in the case of all samples with the addition of diamidoamine salt.

Table 7. The freeze-thaw resistance degree after 50 free-thaw cycles

| Item | Admixture content [% of cement mass] | Average compressive strength of not frozen samples [MPa] | Average compressive strength of samples after 50 freeze-thaw cycles [MPa] | Decrease in compressive strength in relation to the control samples [%] |
|------|------------------------------------|-------------------------------------------------------------|------------------------------------------------------------------------|-------------------------------------------------------------|
| 1    | Control sample                     | 74.06                                                        | 45.32                                                                  | 38.81                                                        |
| 2    | 0.10%                              | 69.04                                                        | 68.54                                                                  | 0.72                                                         |
| 3    | 0.25%                              | 65.02                                                        | 63.93                                                                  | 1.68                                                         |
| 4    | 0.50%                              | 62.44                                                        | 61.21                                                                  | 1.97                                                         |
| 5    | 1.00%                              | 65.54                                                        | 64.89                                                                  | 0.99                                                         |

The achieved results allow stating that the tested admixture causes the decrease in compressive strength of cement concretes that is proportional to its content. 1% of the admixture content causes the decrease in strength by 10% (after 7 days of curing) and 17% (after 28 days of curing). However, at the admixture content of 0.1% of the cement mass, the decrease in strength by 8% (after 7 days of curing) and 5% (after 28 days of curing) in relation to the reference concrete was reported. The decrease in compressive strength is caused by the increase in the air content. However, taking into account the fact of the beneficial effect of the admixture on the concrete’s waterproofness and freeze-thaw resistance, the obtained decreases in strength at the admixture content at 0.1%-0.25% of the cement mass are acceptable according to the authors.

At the same time, the observed positive effect of the diamidoamine salt admixture on the other physical properties of the cement concretes was observed. It was shown that the admixture caused significant improvement of concretes’ resistance to the adverse effect of the freeze-thaw cycle. The increased frost resistance is the result of the air entraining effect of the diamidoamine salt, the decrease in absorbability and the improvement of waterproofness of concretes.

5. Conclusions
The paper discussed the influence of sub-zero temperatures’ effect on cement concretes’ properties. The requirements imposed by the currently applicable standards on designers in terms of concrete’s resistance to frost’s cyclic effect were discussed. The original solution of applying diamidoamine salt...
as the admixture increasing the freeze-thaw resistance of cement concretes was proposed. The conducted preliminary laboratory tests showed that applying the diamidoamine salt causes the decrease in compressive strength. This decrease is proportional to the admixture content. The applied admixture significantly decreases the absorbability, improves waterproofness and freeze-thaw resistance of the concrete. The application of diamidoamine salt as the admixture improving the concretes’ freeze-thaw resistance seems to be an interesting issue that is worth conducting further research. The problem that the authors raise in the subsequent phase of the research project is the development of optimal dosing the admixture – obtaining high freeze-thaw resistance at a decrease in compressive strength as low as possible.

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