On Deterioration Mechanism of Concrete Exposed to Freeze-Thaw Cycles

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Abstract. At present, concrete and reinforced concrete are gaining ground in all sectors of construction including construction in the extreme north, on shelves, etc. Under harsh service conditions, the durability of reinforced concrete structures is related to concrete frost resistance. Frost resistance tests are accompanied by the accumulation of residual dilation deformations affected by temperature-humidity stresses, ice formation and other factors. Porosity is an integral part of the concrete structure which is formed as a result of cement hydration. The prevailing hypothesis of a deterioration mechanism of concrete exposed to cyclic freezing, i.e. the hypothesis of hydraulic pressure of unfrozen water in microcapillaries, does not take into account a number of phenomena that affect concrete resistance to frost aggression. The main structural element of concrete, i.e. hardened cement paste, contains various hydration products, such as crystalline, semicrystalline and gel-like products, pores and non-hydrated residues of clinker nodules. These structural elements in service can gain thermodynamic stability which leads to the concrete structure coarsening, decrease in the relaxation capacity of concrete when exposed to cycling. Additional destructive factors are leaching of portlandite, the difference in thermal dilation coefficients of hydration products, non-hydrated relicts, aggregates and ice. The main way to increase concrete frost resistance is to reduce the macrocapillary porosity of hardened cement paste and to form stable gel-like hydration products.

1. Introduction

The main building material, which will remain so in the foreseeable future, has always been concrete, a composite material, characterized by the properties that depend both on the constantly changing properties of the matrix, i.e. hardened cement paste, and on the qualitative characteristics of aggregates, additives, technology, and also on the cohesion between the matrix and the aggregates. The liquid phase of concrete has various binding forms with the solid surface and participates both in the formation of hydrate compounds and structural bonds of the matrix, and in the formation of concrete porosity. Pores of various genesis, sizes and configurations, filled with liquid or gaseous phase, are an integral structural element of concrete, which has a significant effect on its strength and in-service properties.

Due to high physical and mechanical performance, manufacturability, fire resistance and durability, concrete has proved to be an effective material both for large-scale and unique building for various purposes. In order to identify new possibilities of increasing the efficiency and reliability of service
conditions of concrete and reinforced concrete structures, further extension of knowledge about concrete is required.

Physical and physical-chemical effects on concrete lead to changes in the hydrated phases and the structure of hardened cement paste, which causes a decrease in strength and durability of concrete. The most aggressive effects on concrete are produced by cyclic freezing of concrete saturated with deicing salts or water and the action of aqueous solutions of certain salts, especially sulphates. A large number of studies devoted to increasing the resistance of concrete to these effects do not deprive this subject of topicality, since neither the causes of destruction, nor the ways to prevent it have been established yet; and the structural changes in hardened cement paste caused by corrosion action have been hardly identified. Moreover, new types of binders, additives and aggregates obtained including from industrial by-products and technological treatment are still being widely introduced into construction practice. Construction in northern regions of a country with severe climatic conditions and development of shelves require materials of high durability, which provide reliable and durable service life for building structures.

An improvement in frost resistance of concrete, according to an expert assessment of the Technical Committee RILEM, is one of the main factors that determine the density, reliability and durability of concrete and reinforced concrete structures.

2. Main points

Theoretical and experimental studies of destructive processes in concrete caused by external aggressive effects and the corresponding methods of increasing its resistance are almost exclusively devoted to the effect of concrete porosity. Peculiarities of pore volume of concrete often have a major effect on its durability in service conditions, but do not take into account the whole variety of phenomena associated with the changing structure of hydrated phases of hardened cement paste that affects micro and macro cracking, when stresses and corresponding deformations reach the maximum values. Directing structure formation of hardened cement paste, improving the stability of hydrated phases of hardened cement paste in aggressive environmental conditions, increasing deformation and crack resistance, reducing permeability and creating reserve porosity are the main components of increasing frost resistance of concrete in severe climatic conditions.

There are various views on the mechanism of concrete deterioration under cyclic freezing:

1. Crystallization pressure of ice on the walls of concrete pores due to the growth of crystals in cavities and voids, which is affected by the moisture migrating from microcapillaries. These notions are adopted from soil science and can explain some features of deformation and deterioration of concrete with fully connected porosity under cyclic freezing.

2. Hydraulic pressure of the water expelled by the ice from the site of freezing (T.K. Powers’ hypothesis) [1]. Since water begins to cool from the surface, this leads first to ice formation in the mouths of capillaries, which get as if plugged with ice. When a concrete layer that is more remote from the surface is cooled, freezing of water is characterized by an increased volume of ice by 9.07%; it leads to excessive pressure in yet unfrozen water, which is then expelled into the concrete depth. Expulsion of water through the narrow spots of pores and microcapillaries is accompanied by an increase in pressure, which acts on the walls of pores and capillaries and brings them into a stressed state. As a result, hardened cement paste gets local deformations leading to microfractures, which accumulate when cyclic freezing repeats.

Basing on these representations, T.K. Powers made very important practical conclusions, first, about the critical degree of water saturation of concrete: it should not exceed about 91.0% of the pore volume in order to accommodate the formed ice crystals; and second, about entrained air that is required to provide reserve capacity for the water, expelled during ice formation. Nowadays, it is universally accepted to ensure frost resistance of concrete by air entrainment when preparing a concrete mix. This measure upgrades the frost resistance of concrete up to three times. Entrained air or gas in the form of bubbles with a diameter of 100...500 μm [2] in concrete reduces the hydraulic pressure the more the closer the air cavity is to the dangerous capillary. If air bubbles are located close
enough to the capillary, where water freezes (according to T.K. Powers this “distance factor” should not exceed 0.0254 cm), the hydraulic pressure will not exceed the tensile strength of concrete and it will not deteriorate.

According to G. Verbeck [3], concrete does not deteriorate under cyclic freezing if its cement-sand matrix contains uniformly distributed gas-filled bubbles that provide a distance factor of less than 0.02 cm in order to keep the concrete intact during frost aggression under severe service conditions. The American Concrete Institute Committee 201 recommends that air entrainment be between 4.0 and 7.5% of the concrete volume when maximum aggregate size is reduced from 150 to 9.5 mm [4]. According to GOST 31384 the volume of entrained air should not be less than 4% in service environments XF2 ... XF4, and GOST 26633 determines the volume of entrained air from 1 to 7% for pavements and hydraulic concrete and reinforced concrete structures.

G. Eremeev criticized [5,6] the hypothesis of T.K. Powers, who, using an idealized scheme of a concrete capillary, established that the hydraulic pressure of water for capillaries longer than 10 mm with a diameter of $1 \times 10^{-5}...1 \times 10^{-6}$ cm can exceed the tensile strength of concrete. These conditions, according to G. Eremeev, are unlikely, although it is known that concrete may contain even smaller pores. It is also believed that T.K. Powers did not take into account the increase in water viscosity, which is especially intense in thin capillaries and slits smaller than $1.5 \times 10^{-5}$ cm [7] with the pressure that is necessary to expel water through thin gel pores, which retain the liquid phase at a low negative temperature.

In later works, T.K. Powers showed that the hydraulic pressure hypothesis fails to explain some experimental data [8]. When concrete is frozen, the bulk of moisture moves towards the freezing front, according to the regularities of thermal-moisture diffusion [9], although a part of it is expelled by the formed ice. Dilation deformations during freezing of concrete decrease when cooling rate increases, which contradicts this hypothesis; that is why, in order to explain the reasons of concrete deterioration, the crystallization pressure hypothesis was also involved, and was supplemented [10,11] with statements on the pressure arising from the growth of ice crystals in capillary pores.

Water in macrocapillaries (more than 10 nm in size) [12] freezes at a temperature of minus 1...6 °C; gel pores and microcapillaries still retain water in liquid phase at this temperature. Migration, condensation and freezing of this water on the surface of the ice body leads to an increase in its volume and initiation of crystallization pressure. Especially large values of crystallization pressure should be expected when water-saturated concrete is cured for a long period at slightly low negative temperatures. Since the increase in volume of the ice body is under diffusion control, the rate of pressure increase will be small.

The most informative method to reveal dilation deformations in concrete samples during freezing and thawing is dilatometry; the sample decreases in volume during cooling, but this regular deformability fails when testing water-saturated samples. Figure 1 shows a typical dilatogram obtained in the process of freezing of a concrete sample in air and its thawing in water [13].

![Figure 1. Deformations of dry (1) and water-saturated (2) fine concrete samples during freezing and thawing, $+\varepsilon$ - relative dilation deformations, $-\varepsilon$ - relative shrinkage deformations.](image)
A dry sample shrunk when cooled to -60 °C, and dilated linearly according to the coefficient of thermal expansion, when heated. A water-saturated sample shrunk linearly to point B when frozen in air, i.e., before supercooling of water below 0 °C by 6°, after that, a sharp increase in dilation deformations up to the point C was observed as a result of ice formation in macrocapillaries; at that, latent crystallization heat was released and the temperature rose to -1 °C, then there was a rapid drop in dilation deformations (section CD on curve 2) with a further exit into the linear section (to point L). Starting from point L, further cooling is accompanied by a gradual increase in dilation deformations in the temperature range -30...-44 °C due to ice formation in microcapillaries of different sizes. At -50 °C at point E, a linear section of concrete deformation with the formed ice begins again, so the inclination of this line is $\alpha_2 > \alpha_1$. When heated from -60 to -33 °C, linear section MN represents ice thawing in microcapillaries, GH represents ice thawing in macrocapillaries and KA is the value of residual dilation deformations, that is, destruction of concrete in one cycle. Thus, dilation deformations are observed when ice forms in capillary pores (sections BC and LE) and during heating in section EMNG due to a higher coefficient of thermal expansion of concrete with ice than without it. It is explained by the fact that the coefficient of volumetric thermal expansion of ice (about $150 \cdot 10^{-6}$ mm / mm °C) is approximately 5 times greater than that of concrete.

Ice formation in macrocapillaries results in an elastic expansion of concrete, reaching its maximum at point C, then it sharply decreases due to the movement of microcapillary moisture in the concrete cavity. Such microcavities may be caused by several reasons:

- undercompaction of a concrete mixture during molding; Building regulations 3.09.01-85 allow up to 2% for mixtures of heavy concrete, and up to 4% for fine-grained and hard concrete mixtures;
- contraction of the “cement-water” system in the process of hydration due to chemical and adsorptive binding of water;
- adsorptive contraction, i.e. a decrease in the volume of adsorption moisture during cooling.

In the process of cyclic freezing, the compressive strength of concrete samples varies ambiguously: initially the strength of cyclically frozen samples exceeds the strength of control samples, and then, with an increase in the number of cyclic freezes, destructions of different intensities begin [14]. In addition, the samples of hardened cement paste, which fail to form ice during the first freezing, after a number of freezing and thawing cycles, show expansion deformations due to ice formation depending on w/c ratios (figure 2).

![Figure 2. Dilatometric curves taken during freezing of samples of hardened cement paste: 1 - at the first freezing; 2 - freezing after 42 cycles at -20 °C, 3 - thawing (43rd cycle).](image)
This behavior of concrete samples and hardened cement paste during cyclic freezing is probably associated with aging of cement gel. The shell of hydration products formed on cement clinker nodules creates an obstacle to the movement of water molecules, because the pores of cement gel have a size of no more than 2 nm, and the hydration process, as well as the increase in the strength of the samples practically ceases. During cyclic freezing, the basicity and crystallization of cement gel increase, its pore size grows by more than 6 nm (this is observed when the expansion deformation freezes due to ice formation in macrocapillaries), which disrupts the impermeability of hydrate shells, stimulates the process of hydration of clinker residues and the increase in strength of hardened cement paste. Then, as the number of cycles increases, the destruction of the samples prevails both as a result of the formation of a more crystallized structure of hardened cement paste with a smaller capacity for relaxation of stresses and as a result of ice formation.

Low-basic gel-like calcium hydrosilicates that are stable during cyclic freezing are formed by introducing an active mineral additive, like silica fume, into the binding. This additive is characterized by a high dispersity; it increases water demand of binding and concrete mixtures, therefore it should be used with a water-reducing component.

With cyclic changes in temperature, the solubility of portlandite varies: it increases when the temperature decreases, and decreases when the temperature increases. Therefore, at a cooling stage of the samples, the concentration of lime in pore liquid increases, and at a heating stage, it crystallizes and carbonizes.

Thus, cyclic freezing and thawing significantly activate the processes of dissolution of lime and its removal from hardened cement paste; and in order to increase its frost resistance, it is necessary to take measures to increase its resistance to corrosion of type 1 according to the classification of V.M. Moskvin. One of the measures to increase the resistance to corrosion of type 1 is to use active mineral additives.

During cyclic freezing, temperature stresses and deformations contribute to concrete deterioration in a certain way. To estimate the temperature stresses resulting from the difference in the coefficients of linear thermal expansion (CLTE) of a large concrete aggregate and its mortar part, the model of a spherical aggregate grain covered with cement-sand mortar [15,16] is usually considered. In accordance with the solution of the Lamé elastic problem, the radial and tangential stresses reach their maximum values in the area of contact between the filler grain and the shell and are proportional to the relative deformations of these components. With an increase in the degree of crystallization of cement hydration products, the modulus of elasticity and the stress rate in the contact zone increase.

3. Conclusions

1. During freezing and thawing of a water-saturated concrete sample in the air, expansion deformations are observed. They are caused by:
   - ice formation in macrocapillaries at a temperature of minus 4 ... 6 °C;
   - freezing of water in microcapillaries at a temperature of minus 30 ... 40 °C;
   - ice having a greater value of the coefficient of thermal expansion than concrete when it is heated with ice.

2. Air entrainment facilitates the reduction of water pressure in microcapillaries when ice forms in large capillaries, but fails to prevent destruction by means of other two reasons.

3. During cyclic freezing of hardened cement paste, the aging of hydrosilicate gel and the leaching of portlandite are observed, which is the reason for the subsequent destruction of hardened cement paste when there is no ice during the first freezing.

Pozzolanization facilitates the formation of low-basic hydrosilicates, reduces corrosion of leaching and slows down the aging processes of hydrate phases, which preserves the finely dispersed structure of hardened cement paste and increases its resistance to cyclic effects.

4. Another reason of concrete stresses and deformations during cyclic freezing may be disagreements of thermal deformations of its components.
5. In spite of the variety of possible causes of destruction, the concrete stress rate during cyclic freezing can be reduced through structuring of hardened cement paste and facilitating the formation of damping gel-like hydrate phases.

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References
[1] Kuntsevich O V 1985 Requirement to the parameters of conditionally closed pores for frost-resistant concrete (Ufa) 106
[2] Verbeck G J 1966 American Society for testing and materials 169 pp 211–9
[3] Reading T and MacInnis C 1977 JACI 74 pp 573–609
[4] Vlasov O 1963 Durability of enclosing and building structures (Gosstroizdat) 115
[5] Eremeev G G 1961 Concrete and reinforced concrete 5 pp 234–5
[6] Zhelezny B, Zorin Z and Sobolev V D 1972 Engineering-geological properties of clay rocks and processes in them 1 pp 94–101
[7] Powers T C 1956 Proc. RILEM Symp. Winter concrete 3 pp1–47
[8] Lykov A V and Mikhailov Yu A 1963 Theory of heat and mass transfer (Gosenergoizdat) 535
[9] Cordon W 1966 JACI 53 pp 613–8
[10] Pigeon M, Prevost J and Simard J 1985 JAC 82 pp 684–92
[11] Moshchansky N 1959 Frost resistance of concrete, NIIZhB 12 pp 5–18
[12] Trofimov B Ya and Kramar L Ya 2014 Building materials 8 pp 46–51
[13] Trofimov B Ya and Shuldyakov K V 2014 Sat. Scientific articles of the III All-Russian (II Int.) Conf. on Concrete and Reinforced Concrete 5 pp 124–138
[14] Gorchakov G I, Lifanov I I and Teryokhin L N 1968 Coefficients of temperature expansion and temperature deformation of building materials (Standards) 168
[15] Sychev V P 1976 Investigation of the frost resistance of concrete with respect to the climatic conditions of the Yakutia (Kharkov) 21