International Journal of Applied Engineering Research
ISSN 0973-4562 Volume 10, Number 10 (2015) pp. 25711-25719

http://www.ripublication.com

Density Of Structure And Extent Of Saturation By Water Of Composites As A Factor Of Change Of Their Durability When Freezing And Thawing

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Abstract

Results of pilot studies of frost resistance of polymeric concrete are given in article. It is shown that destruction of the concrete which is exposed to freezing and thawing begins with a peeling and emergence of microcracks on a surface. Dependence of frost resistance of polymeric concrete from extent of water saturation of a material is studied. The method of mathematical planning of experiment picked up the optimum quantitative maintenance of components and the fillers, providing the increased frost resistance of polymeric concrete.

Key words: Frost resistance, polymeric composite, saturation by water, structure, component, filler, durability.

During operation the building materials and structures may be exposed to external factors: moisture or corrosive environment, radiation, temperature fluctuations, etc. These factors whose effects largely depend on their intensity and combinations, may act individually, collectively, and in different sequences. At that, their effect may be accompanied not only by the deterioration of the material quality but also by their hardening.

The strength and durability of composite products may be increased during the operation of buildings, if the cyclic change of material temperature and humidity is provided under the influence of climatic conditions which improve its structural and mechanical properties [5, 6]. The temperature and humidity fluctuations in certain optimal ranges may promote the crystallization centre (of embryos) with their subsequent development into crystals.

However, in actual use of the material the listed environmental factors, moisture (water) and temperature, may influence on it with a dangerous combination of intensity and duration. The durability of composites in these conditions depends on their frost-resistance, which is estimated by accelerated methods under laboratory conditions.

The frost resistance of materials is characterized by their ability to withstand the impact of variable freezing and thawing in a water-saturated condition. The water penetrating into the material pores at low temperatures is freezed and develops tensile stresses in the structure due to the increased volume. They are summarized with the stresses arising from the difference of thermal expansion coefficients concerning the material components.

The destruction of concrete subjected to freezing and thawing starts from the peeling and the appearance of microcracks. Originally they develop mainly along the boundaries between a filler and a matrix in the places of maximum structural stresses gradually combining into more extended cracks running both along filler grain boundaries and through a matrix and a large filler, which leads to the concrete destruction.

The domestic and foreign researchers found that the frost resistance of composites is determined by their composition and structure. A large number of studies is devoted to cement composites. Besides different views concerning their destruction factors evaluation are presented. At the same time the frost resistance of nonporous composites, for example, polymer concretes is studied insufficiently. Moreover, the issue concerning the water saturation degree effect on the frost resistance of these materials remains unexplored. In particular, are the ways of cement composite frost resistance improvement suitable for polymer concretes?

All composites according to A.V. Lykov and S.P. Rudobashty classifications may be divided into three types by their structure: capillary-porous, capillary-porous with colloidal component and non-porous ones [9, 16]. Capillary-porous materials include the materials which bind the penetrant liquid mainly by capillary forces (e.g., water may penetrate in the form of liquid and vapor). These materials include ceramic and gypsum stones.

The substance (water) transfer in a non-porous material occurs like molecular diffusion, which is usually presented as a sequence of single diffusing molecules jumps into free intermolecular spaces of a body, resulting from the thermal molecule motion [16, 17].

Capillary-porous colloidal materials are presented mainly by the composites where a penetrating fluid has different forms of relations, inherent to capillary-porous and non-porous bodies. The example of such a material is cement concrete. The transfer of moisture in such a material is conditioned by the combined effect of mechanisms typical for capillary-porous and non-porous materials. Let's consider the Russian studies concerning cement composites frost resistance. The frost resistance of cement concrete depends not only on the water-cement ratio, the quality of fillers, cement [7, 8, 12] but also on the conditions of incubation to a large extent. Dry and slightly moistened concrete may resist freezing and thawing for a long period of time, while the water saturated concrete undergoes serious damages during these cycles [6].

According to the work [15], the formation of ice makes only a partial damage of cement concrete. The main source of destruction, according to its authors, is the process of water migration and the resulting hydraulic fluid pressure during the formation of ice. The process is equivalent to drying, the water will migrate from the fine pores to the location of the "mass" ice. The freezing of water in the fine pores of the cement concrete may occur only at the temperatures ranging from -25 to -36.5 °C.

According to A.V. Volzhensky opinion [2], the water filling the cement stone and containing a certain amount of $Ca(OH)_2$ and alkali compounds in a dissolved state starts to transfer into ice first of all in large pores and cavities at the temperature of 0 and -1 °C. At further lowering of the system temperature the ice begins to form in the capillaries of a decreasing diameter. The most delicate of these The water freezes at the temperature of t = -25 °C in the finest of them. Obviously, the freezing of water in non-porous materials may also occur at the temperatures lower than conventional cement concrete.

Since the rate of the cement composite destruction depends on the operating temperature and the degree of material hydration they strive to saturate it completely within the laboratory conditions in order to accelerate the destruction. However, it is not stated whether this condition is applicable to all types of concrete.

According to GOST at the determination of cement concretes frost resistance and mortars one cycle is carried out for 6 hours according to a usual manner: 4 hours of freezing at the temperature of -15 ... -20 °C and the thawing in a water bath at the temperature of 15-20 °C for 2 hours. At that, the saturation of cement concrete over the entire volume with water prior to frost resistance testing is achieved within a short period of time. These test conditions for cement concretes are close to the conditions of their operation.

Other operation conditions may contain low permeability construction materials, such as polymer concretes. Their full saturation with water is not possible or may happen only in a few years. In this regard, at alternate freezing and thawing the low temperature impact on polymer concrete depending on the degree of its saturation may be spread locally or throughout the entire depth. Initially, therefore, an outer layer undergoes a degradation, while the inner layers do not have any changes. The destructive effect of alternating temperatures is exacerbated by internal stresses arising in the polymer concrete as the result of the coefficient difference concerning the thermal and moisture expansion of layers. The periodic variation of temperatures and, consequently, stresses accelerates the fatigue processes and leads to the formation of cracks.

The study of polymer concretes frost resistance is conducted by different methods, which do not take into account the specific conditions of use. For example, the samples before testing were kept in water for 30 days and then underwent freezing (see. I.E. Putlyaev and N.A. Moshchansky works [11, 13]). According to I.M. Elshin data [3], 200 cycles of freezing and thawing are equivalent to 120 days of keeping samples in water, and the frost resistance of polymer concretes depends on their water resistance.

In this regard, the study of polymer cements frost resistance dependence on the degree of a material water saturation deserves a particular interest. These studies were carried out by us with the polymer concretes of the following composition (pts. wt.): epoxy resin ED-20 - 100; polyethylenepolyamine - 10; marshallit - 110; quartz sand with 1.4 - 290 fineness modulus. 2×2×7 cm prism samples were cured in a heat chamber for 6 hours at the temperature of 80 °C after a daily curing in normal temperature and humidity conditions. After weighing, the samples were placed in water for saturation. The degree of material saturation with water was regulated at various duration of samples curing. The maximum saturation with water was achieved by the curing of samples for 8 months. The reduction of mass content for water saturated samples was observed due to the leaching of polymer concrete components at more extensive curing of material. Thus, the batches of samples were obtained with the water content from 0.05 to 0.2% by weight.

The frost resistance tests were carried out according to accelerated procedure. One cycle of tests consisted of a four hour freeze at -50 °C and two hour thawing in water at the temperature of +18 - +20 °C. The frost resistance was evaluated by frost resistance ratio change according to the sample resistance ratio subjected to freezing and thawing, to the sample strength kept in normal conditions, as well as by the resistance coefficient according to stiffness. The latter is the latter was obtained as the ratio of the sample elastic modulus of samples subjected to testing, and control samples. Fig. 1 shows the graphic dependences of frost resistance ratio after 100 cycles of freezing and thawing.

Fig. 1 shows that the frost resistance ratio of epoxy polymer concrete greatly depends on the degree of samples saturation with water before testing.

Figure 1 gives the opportunity to trace three peculiar regions. The first one, dating back to the beginning of sample saturation of the samples has the decline of frost resistance. This apparently happens due to the appearance of stresses at the boundary of the soaked and dry material, which lead to the formation of microdefects [10, 14]. The greatest reduction of frost resistance for epoxy polymer is observed at water saturation of 0.05% by weight, which is achieved by the immersion in water for four months. The second region has the frost resistance increase that occurs, apparently, due the impregnated layer thickness increase and smoothing the stress distribution along the sample section. In the third area, located close to the area of the material chemical degradation beginning from the impact of water, the decrease of frost resistance is observed. The cyclically operating temperatures accelerate the degradation process.

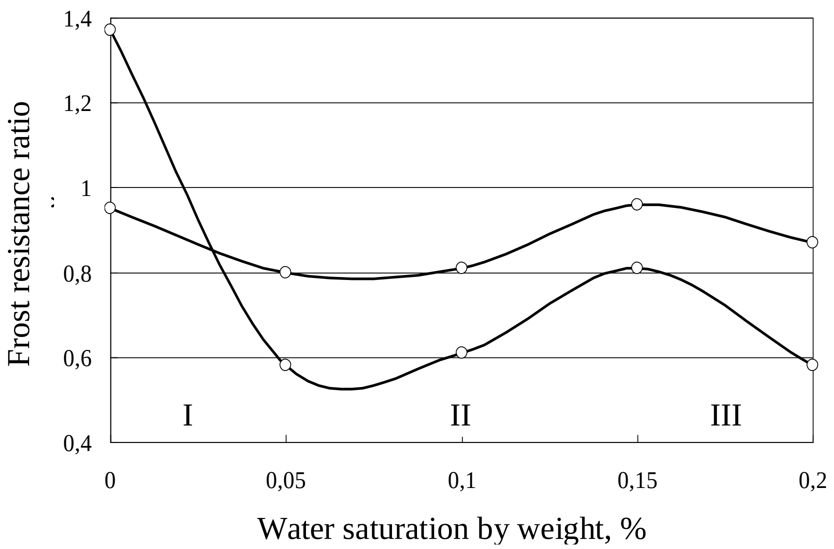

Fig. 1. Change of frost resistance ratio for polymer composites after 100 cycles of freezing and thawing according to the degree of samples preliminary saturation by strength and stiffness

The frost resistance indicator essentially depends on such structural parameters of polymer concrete as the degree of filling a filler size. The increased frost resistance corresponds to the compositions of optimal filling with fine fillers (Fig. 2). The figure shows that the introduction of a filler in a small amount leads to the compound delamination. Therefore the structural tensions are increased in such a polymer concrete. The filling of polymer concrete above the limit leads to the material decompaction [4].

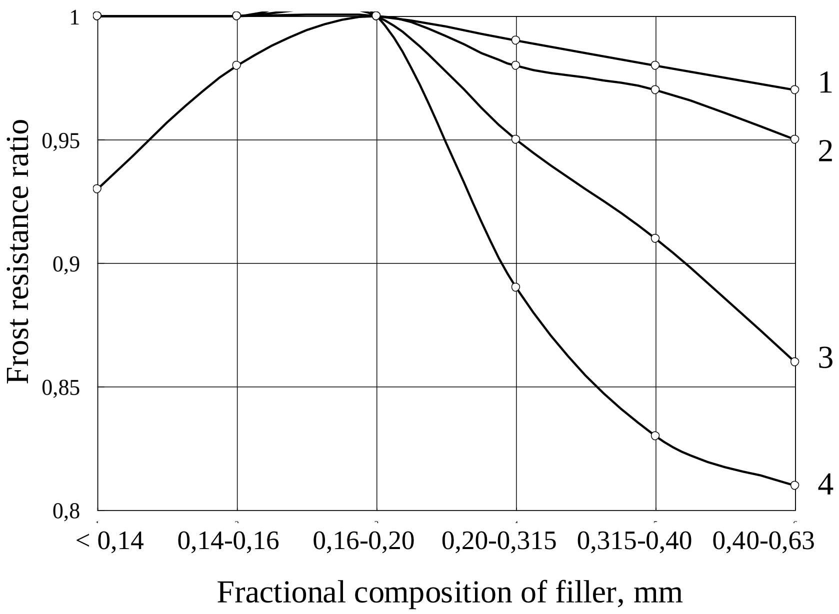

Fig. 2. The dependence of frost resistance coefficient change for epoxy composites on the fractional composition and filler content:

1 – п/н = 0,25; 2 – п/н = 0,3; 3 – п/н = 0,4; 4 – п/н = 0,5

It is clear that the prerequisite for the frost resistance provision for polymeric compositions is their high resistance to fractures and water.

The compositions with a high elongation limit have a high resistance to fractures. According to [1], the compositions based on polyester resins, filled with a mixture of cement and graphite have the high limit elongation and water resistance. In order to establish the frost resistance of compositions V.T. Yerofeyev performed the planning matrix studies in the laboratory of building materials at Mordvinian state university named after N.P. Ogarev. The coefficient of frost resistance among 25 polyester compositions was determined after 50 (K_{50}) and 200 (K_{200}) test cycles. After the processing the experiment results according to the central composite matrix the mathematical models are developed described quadratic equations:

$$K_{50} = 1{,}1 + 0{,}04x_1 + 0{,}028x_2 + 0{,}005x_3 + 0{,}016x_4 + 0{,}005x_1^2 +$$

$$+ 0{,}01x_2^2 - 0{,}106x_3^2 - 0{,}123x_4^2 - 0{,}009x_1x_2 + 0{,}038x_1x_3 +$$

$$+ 0{,}005x_1x_4 - 0{,}014x_2x_3 + 0{,}002x_2x_4 - 0{,}017x_3x_4; \quad (1)$$

$$K_{200} = 0{,}952 + 0{,}03x_1 - 0{,}005x_2 - 0{,}016x_3 + 0{,}033x_4 - 0{,}0122x_1^2 -$$

$$- 0{,}039x_2^2 - 0{,}117x_3^2 - 0{,}121x_4^2 - 0{,}007x_1x_2 + 0{,}05x_1x_3 +$$

$$+ 0{,}03x_1x_4 - 0{,}006x_2x_3 + 0{,}024x_2x_4 - 0{,}053x_3x_4; \quad (2)$$

The analysis of equations shows that at the alternate freezing and thawing various physical and chemical processes occur in the polymeric binders. The value of the absolute term of an equation (1) indicates a slight increase of sample strength at the initial testing phase. The positive role of portland cement as an active filler makes an influence here. Obviously a surface hardening of samples due to the partial hydration of cement happens during water impact. With the increase of test cycles number the frost resistance of materials decreases, the positive process starts to change into a destructive one.

The dependence of frost resistance ratio on the quantitative composition of components may be viewed on the graphs developed with respect to the equation (2). Two-dimensional sections were developed according to four factor model. At that two other factors were fixed at an optimum level, which is defined by differential equation system solution, composed according to the partial derivatives of the parameter K_{200}. Two-dimensional sections of responses depending on the content of fillers and a curing system are described by revolving ellipsoids (Fig. 3).

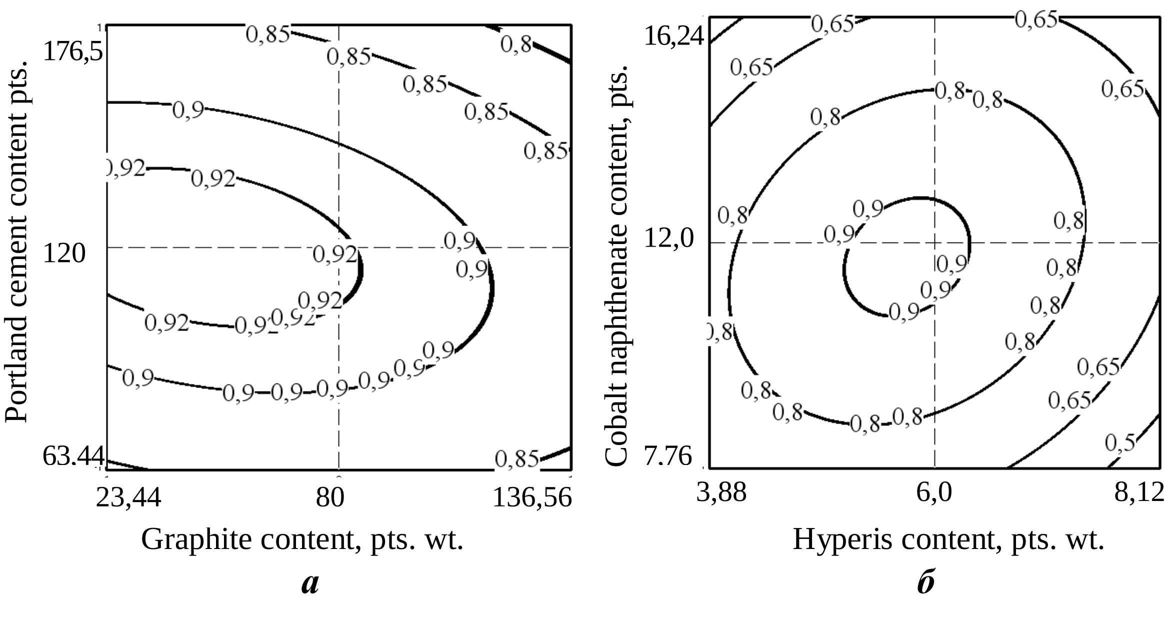

Fig. 3. The dependence of frost resistance ratio change for polyester composites on the quantity of graphite and Portland cement (a) and also cobalt naphthenate and hyperis (b)

The maximum values were obtained during the movement to the surface center. If you deviate from the optimum area the frost resistance of compositions decreases. Especially significant decrease is observed at the change of curing system content. At a low level of Portland cement its active role is reduced and humid environment to a greater extent breaks the binding element. At the increase of Portland cement content with a more definite limit the structure is loosened, the permeability of the material is increased and, consequently, the frost resistance is reduced.

The durability of polymer composites depends on the completeness of their curing. It is believed that the materials with a high degree of curing are more durable ones. However, Fig. 3б shows that at large and small content of the curing system the frost resistance of compositions decreases. This suggests the existence of an optimal polymer curing degree, used in conditions of freezing and thawing. The excessive density of polymer molecules stitching reduces the deformability, the overstrain of bonds, develops structural inhomogeneities in the polymer and at a section boundary.

Conclusion

Thus, the study of materials frost resistance, the non-porous structure (of polymer composites) revealed a significant discrepancy with the provisions adopted during the study of cement concrete frost resistance.

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