Specifics of Concrete Solidification with Anti-frost Admixture at Subzero Temperature

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Abstract. The objective of this research is to determine the characteristics of the "cold" concrete solidification process with anti-frost admixtures at various subzero temperatures. The obtained results reflect these characteristics. The effect of various subzero temperatures and anti-frost admixtures on the phase composition of the cement stone and the formation of concrete physical and mechanical characteristics have been studied. It has been established that at any subzero temperatures "cold" concrete does not solidify, but in the process of thawing the properties of concrete depend on the temperature the concrete is being kept at. The phase composition of the cement stone depends on the temperature because these characteristics are affected by the solubility of the minerals the cement contain and also by their interaction under certain conditions.

1. Introduction
Nowadays the construction industry rapidly develops. Concrete and reinforced concrete are still the main structural materials if we are considering the level of technical and economic indicators. Because of this the concrete is used in construction throughout a year. Today many admixtures manufacturers offer products which allow to pour concrete at subzero temperatures without using heat treatment. The impact of early freezing and antifreeze admixtures on the hydration of cement and the structure formation of concrete is a complex physicochemical process that requires in-depth study in order to produce a general impression of their effects to obtain high-quality materials.

In previous studies [1] we established that concrete solidification does not occur at -25 °C temperature, and the structure and phase composition of the cement stone with anti-frost admixtures and under the influence of subzero temperature in the early periods of solidification changes. Since the abovementioned conditions are critical for concrete pouring, it is necessary to study the effect of anti-frost admixtures and concrete solidification characteristics when being affected by other subzero temperatures.

The objective of this research is to study the influence of various subzero temperatures on the properties of concrete solidification with anti-frost admixtures.

To achieve this goal we have to:

1. Learn the characteristics of cement hydration and concrete solidification with anti-frost admixtures when being affected by various subzero temperatures.
2. Evaluate the influence of various subzero temperatures on the formation of the structure of concrete with anti-frost admixtures.
3. Evaluate the dynamics of the concrete strength development after defrosting during hardening under normal conditions.

4. Determine the effect of various subzero temperatures on the specifics of the phase composition of cement stone formation. These guidelines, written in the style of a submission to J. Phys.: Conf. Ser., show the best layout for your paper using Microsoft Word. If you don’t wish to use the Word template provided, please use the following page setup measurements.

2. Research materials and methods

The materials used to carry out the research were CEM I 42,5H cement produced by Dyckerhoff Korkino Cement LLC, quartz sand from Kalachyovskoye field in accordance with Russian National State Standard (GOST) 8736-93, and crushed granodiorite sized 5 to 20, according to the requirements of GOST 8269.0-97. The applied anti-frost admixtures were products of BASF company and superplasticizer СІІ (SP)-1 and ВІІ (VP) by Polyplast-Uralsib.

The influence of the admixtures and frost effect on the concrete properties were studied according to the technique of GOST 30459-2008 "Admixtures for concretes and cement mortars. Determination and efficiency assessment". The influence of preliminary freezing on phase composition of cement stone of concretes in question with various admixtures was studied using derivative thermal analysis (DTA), using LuxxSTA 409 model derivatograph manufactured by Netzsch company.

Several series of concrete samples of the same composition with manufacturer's recommended dosage of anti-frost admixtures were produced in order to determine the properties of concretes solidification with anti-frost admixtures at various subzero temperatures, and also several series of samples of the control composition without anti-frost admixtures were produced for a comparative analysis. Plasticizer SP-1VP was used to increase the fluidity value of the concrete mix. Using this admixture, concrete mixtures with fluidity value P3 (workability 10 to 15 cm) were produced. After careful condensation, the sample-cubes with a side of 100 mm were molded, and then the forms with the concrete mix were placed in a freezer, where they were kept for 28 days. After being kept at subzero temperatures (-5 °C; -10 °C; -15 °C), the samples were removed from the freezer and placed in a normal hardening chamber with relative air humidity of 95...100% and a temperature of 18...22 °C). Compositions of concretes (Table 1) for the research were taken in accordance with regulatory documents [2,3].

| Material consumption, kg/m³ | Control | Main |
|----------------------------|---------|------|
| Concrete                   | 350     | 350  |
| Sand                       | 850     | 850  |
| Gravel                     | 1080    | 1080 |
| SP-1                       | 7       | 7    |
| AFA                        | -       | 14   |
| Water                      | 157     | 143  |

3. Research results

The first batch of samples after being kept in a freezing chamber and thawing in a normal hardening chamber for 24 hours was tested for compressive strength. Strength rates are compared with the strength of control samples that has been solidifying under normal conditions for 28 days. The compressive strength testing results of the samples are detailed in Figure 1.

Time, which is needed for removal of formwork and loading of the construction of conduct of work, is an important parameter in the process of the construction of buildings and structures, so it is necessary that concrete obtains a certain minimum strength, according to the work project.

However, as was described above, during pouring concrete in winter, the dynamics of concrete strength development can significantly differ from pouring concrete in warm weather. Thus, it is
important to know how the strength varies in different conditions, including when being kept under normal conditions after an early freeze.

![Figure 1. Compressive strength of samples.](image)

In order to study the dynamics and rates of concrete strength development of concrete kept at different subzero temperatures, the samples were hardened under normal conditions (NC) and tested for compressive strength on 1, 2, 3, 7, 28th days of normal hardening. Samples of the control composition were tested at the same time. The results are detailed in Figure 2.

Based on the obtained results, we can determine that the early freezing greatly affects the rate of the concrete strength development during the early period after thawing. On the first day of normal hardening, the strength parameters of the samples held at -10 °C and -15 °C turned out to be lower than those hardened at -5 °C by approximately 33 ... 40%. However, even after 28 days of freezing at -5 °C and after hardening one day under normal conditions, the samples did not gain even 70% of the strength of the 1 day old control concrete sample.

![Figure 2. Compressive strength of samples.](image)

Thus, we can assume that the process of hydration at subzero temperatures happens insignificantly or does not happen at all. The higher strength in the early periods of samples kept at a low subzero temperature (-5 °C) is due to the fact that the cooling time of the samples in the freezer with the corresponding temperature was longer, and the defrosting which happens after happened faster than defrosting of the samples kept at lower temperatures.

After analyzing the dynamics of concrete strength development of the samples we can determine the following relations: during the initial period after thawing the samples kept at not low subzero
temperatures are characterized by slower rate of concrete strength development. A faster rate of concrete strength development at -10 °C and -15 °C is due to the fact that after defrosting, more unprocessed minerals remain in such samples. By the third day the rates are equalized and becoming comparable with samples kept at lower temperatures.

By the 28th day all the samples that had been frozen have approximately the same strength of 60 ... 65% of the strength of the control compositions.

Within the framework of the research, we also determined density and porosity of the control and main samples on different days. The porosity was determined using the water absorption, the results are detailed in Figure 3.

There is an obvious relation. The lower the subzero temperature when samples are being kept the higher the sample's porosity after thawing. However after solidification under normal conditions this property becomes almost equal for all the studied samples.

![Figure 3. Porosity and density of concrete under different conditions of hardening.](image)

On the first day of normal solidification there is a relation in terms of density properties, which proves dependence of porosity. Taking into account the data on the early strength, we can determine the explicit destructive effect of the freezing water. Crystals of ice do not allow to create a strong structure at the places where they are formed, therefore after thawing there are large pores where the ice formations were, which create an initial low-strength structure. It's important to know that water when being morphed into a solid state and increasing in volume causes a tension in the emerging pore space and destroys bonds of hydrosilicates which are still weak. Such formations create enabling cramped conditions, however the influence of the cramped conditions cause a positive effect only when there is a process of hydration in progress. Since the activity of the hydration process at temperatures close to 0 °C is very small, very few hydrosilicates are formed, so the consequences of this effect are insignificant. Since the density of the concrete mix when the samples are being molded is the same, the density of the concrete when being kept in the freezer is characterized by the amount
of moisture removed. At subzero temperature, sublimation of water occurs. This effect is stronger at lower temperatures, therefore, after keeping the samples in a chamber, the density of concrete is lower for those that were frozen at -15 °C. The density levels become equal during the process of solidification under normal conditions.

A derivative thermal analysis and X-ray phase analysis (DTA and XRPA) of the material were carried out in order to assess the phase composition of the cement stone.

As shown in the Figure 4 at an early age the largest amount of calcium hydroxide can be found in the samples kept at -5°C. This indicates the saturation of the system with calcium ions during the gyration of cement minerals. The solubility of calcium obtained during the dissociation of calcium salts by ions proves to be higher than that of silicon. It means that an environment with a high amount of alkaline is created, which promotes the formation of highly basic calcium hydrosilicates.

X-ray phase analysis data confirms the formation of highly basic hydrosilicates in samples kept at -5°C. After a cycle of freezing and subsequent solidification under normal conditions for 28 days there is an increase in free calcium hydroxide on radiographs compared to the control samples and samples defrosted after 1 day. This phenomenon may indicate the slowing down of cement hydration at low temperatures and the dynamic dissociation of C3S with the segregation of Ca2+ ions due to the high solubility of CaO at low temperatures, even during thawing and solidification under normal conditions, which confirms the strength characteristics which were obtained. So there is an accumulation of silica gel due to a decrease in its activity at low temperatures. The special interaction of calcium hydroxide and silica indicates a change in the mechanism of the hydration process, both during freezing and during solidification under normal conditions.

After analyzing data on the hydration of alite and the strength of the samples, it can be determined that the reduced strength of frozen samples is connected to the destruction of the crystalline hydrates for med in the early period and not to the slowing down of the solidification process.

![Figure 4. Amount of calcium hydroxide.](image)

4. Conclusion
The data that we have gathered allows us to make the following conclusions:

1. Early freezing of concrete affects its strength characteristics in a negative way, greatly reduces the rate of strength development in the initial period after thawing, thereby reducing the potential of using the material in the future.

2. The structure of the main samples in the initial period after defrosting is more porous, and the lower the temperature at which the concrete had been held, the higher this index. This indicates that there is a bigger amount of ice created under colder conditions. However after some time the concrete "heals" it's pores and on the 28th day it's porosity is compared to the characteristics of the control sample.
3. Samples that solidify under not very cold subzero temperatures (-5°C) have a different dynamics of rate of strength development in the early period compared to the samples which were affected by colder temperatures. They have a smaller increase in strength during the initial storage time under normal conditions, due to the intensive hydrolysis of the C₃S.

4. The temperature conditions affect the phase composition of the resulting material. Samples that are maintained at -5 °C form C-S-H (II) crystalline hydrates more than the control sample and the samples which are maintained at -10 °C and -15 °C. This is most likely due to the result of supersaturation of the system by calcium ions at a low concentration of silicate groups, which is characterized by low solubility of silicon compounds, while at the same time the solubility of CaO occurs more intensively at lower temperatures.

5. The degree of C₃S frozen samples hydration is proportional to their strength, therefore the strength characteristics of all the samples in the long-term future will be at the same level. The control composition concrete has a great potential according to this criteria.

6. The samples that have not been exposed to subzero temperatures are distinguished by a more crystallized structure represented by both high-basic and low-basic hydrosilicates, while the frozen samples have a more amorphous structure.

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