The efficiency of using antifreezing agents in monolithic construction

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Abstract:

The modern construction in the world is based mostly on making buildings and constructions of monolithic and monolithic-precast concrete. The wide application of monolithic technologies is conditioned by a number of serious advantages of the constructed objects in comparison with precast ones. Along with advantages of monolithic construction, which consist in reduction of costs and construction period, and improvement of reliability of buildings and constructions, it also has drawbacks: the influence of climatic factors on the operating cycle of concrete placing and maintaining it, the imperfection of building plot's conditions in comparison with the plant conditions. For solving these problems in the building practice the heating and non-heating methods of cold-weather concreting are used. One of the non-heating methods of cold-weather concreting is using concretes, hardening at negative temperatures. This method consists in using chemical additives, reducing the freezing temperature of the liquid phase and providing the concrete hardening at negative temperatures. The non-heating cold-weather concreting, due to using antifreezing agents allows saving heat and electric energy at the more flexible work performance technology. At selecting the antifreezing components the possibility of concreting at temperatures up to minus 20 ºC and combination with plasticizer, contained in the composite binder, was taken into account. The optimal proportions of antifreezing and complex agents produced by MC-Bauchemie Russia for fine-grained concretes were determined. So, the introduction of antifreezing and complex agents allows obtaining in conditions of below zero temperatures at using different binders a structure of composite, characteristic for cement stone, the hydration of which was going on in the natural conditions.

Key words: monolithic construction, composite binder, antifreezing agents, fine-grained concretes, cold-weather concreting.

1. Introduction

Current global construction industry is generally based on production of monolithic and industrialized buildings. Strong base for these technologies is sustainable domestic production of high-quality binders and concrete mixes. Important factor when choosing of construction technology is its energy efficiency in climate conditions of required construction zone. Wide application of monolithic concrete technologies is connected with some significant advantages of construction objects vs. industrialized technologies. Among them are followings: architectural expression reduced material consumption, high design reliability, low cost, enhanced performance characteristics. However, the energy efficiency of monolithic construction at below zero temperatures is reduced.

Over the past few decades the monolithic construction in Russia extremely grows. Now it dominates in civil construction due to some properties (Fig. 1). At the same time the monolithic construction is more effective due to high rate of construction (2–5 stages per a month), opportunity
of year round construction, meeting normative requirements in strength, durability and convenience [1]. It leads to necessity of application of intensive concreting methods at below zero temperatures providing preferable curing conditions until achievement of taking-off strength as well as partial or full loading of construction elements. In many cases the providing of certain values of freeze-thaw resistance, water resistance etc. in time should be taken account when choosing of concreting methods 10 at below zero temperatures [2]. Using of traditional heating methods for acceleration of concrete curing at below zero temperatures leads to significant increasing of energy consumption when construction process. Thereby, the investigation of new methods of reducing of energy consumption when monolithic construction at below zero temperatures is very actual.

Production of qualitative monolithic concrete using traditional raw materials is difficult. Hardening of Portland cement based concrete at below zero temperatures is characterized by extended period of concrete strength development. One of the solutions of this problem can be application of composite binders consisting of jointly grinded cement, silica component and chemical admixtures of different purpose. This composition allows significant enhancement the strength characteristics of binders and materials on its base with minimum of energy consumption. Thus, the goal of this study is production of composite binder and fine aggregate concrete, hardened at below zero temperatures using local raw materials taking into account its mineral composition.

In construction industry some traditional methods of concreting at below zero temperatures, providing achievement 30–50 % of design strength before its freezing are widely used (Fig. 1). It allows avoiding the negative influence of temperature below freezing point on the concrete physical and mechanical properties.

Technological modes are chosen depending on economical efficiency, concreting conditions, type of construction, concrete features as well as availability of cheap methods of concrete heating [3]. Experience of monolithic construction confirms its real necessity in North lands of the country when concreting, including concrete production on the base of heated raw materials providing a preferable temperature when casting process as well as freezing protection of concrete by additional heating.

Concrete heating process in monolithic construction is realized by controlled curing until achievement the required strength properties and provides with heating cable, heat generator or combination of both ones [4].
Concreting with heating methods in situ is prospective from the point of view of nearness to construction process taking into account stability of all designed properties of concrete. Technology of monolithic construction applied heating methods is energy saving [5] as it allows the following:

– reducing the construction period in 5–10 times at below zero temperatures;
– effective using a personnel and equipment including capital intensive casting;
– application of cheaper traditional (free of additional components) concrete mixes;
– avoiding a concrete freezing at early age providing a required quality of concrete and buildings.

To realize a high-rate construction in North lands of the country the methods of controlled temperature and concrete strength in buildings are applied. For this the control method of concrete curing conditions at early age when monolithic concreting is applied. The method is developed by the Technical Research Centre of energy-saving technologies, ecology and complex automatization and consists of providing of concrete curing conditions for all elements of buildings during 2–3 days after casting [6].

Disadvantage of heating methods is necessity of high taking-off strength leading to high energy consumption as well as reducing the construction quality due to long intensive heat treatment and extending a construction period.

Also in monolithic construction the "thermostat method" is widely used. It is based on casting in of heated to 20–80 °С concrete mix in heat insulating shuttering. Open concrete surface protects the construction from frost [7]. Transportation of heated concrete mix to concreting place is accompanied by significant heat loss, hardness growth of concrete mix and reducing of its workability. To avoid these effects the concrete is heated in situ.

It should be noted additional special equipment, certain electric and heat power as well as high skills of stuff is required to organize a heating process. But not always it is efficient. Therefore the chemical agents are used allowing reducing energy consumption of technological process [8]. Chemical admixture application is reasonable due to improving of some technological parameters and performance properties of concrete even albeit a cost increase. High-quality concretes generally are characterized by high frost-thaw resistance super high strength and low water permeability. Usage of antifreezing agents jointly a concrete heating provides a complex effect: accelerates a concrete hardening period and reduces an electric heating period and energy consumption as a result.

For solution of the above problems in monolithic construction there are update building systems based on complex application of methods allowing realization an intensive monolithic construction in North lands of the country [9].

Depending on action mechanism the antifreezing agents tentatively can be divided in three groups;

1) Antifreezes – substances reducing a freezing point of liquid phase in concrete and not effect on structure formation rate;
2) Agents with low antifreezing properties and with strong accelerating characteristics when concrete hardening;
3) Agents with good accelerating characteristics when concrete hardening and good antifreezing effect.

Depending on method of application, effect on concrete system as well as concentration in concrete, the used antifreezing agent over the last 50 years can be tentatively divided on followings three groups:

1) Electrolytes, introduced in concrete in concentration of 4–15 %.
2) Complex antifreezing modifiers consisting of electrolytes and effective plasticizers and superplasticizers. Introduction of water reducing component into the antifreezing complex allows...
reducing electrolytes demand by 1.5–2.5 times and significantly improving a quality of a "winter" concrete.

3) Update additives consisting news electrolytes such as formiates, acetates, thiosulfates, rhodanates etc. as well as water reduced components applied jointly a heating method.

At early stages of concrete hardening at below zero temperatures such negative processes as strength and workability reducing takes place. It is connected with decreasing of its reactivity when temperature reducing as well as crystallization of pore liquid (ice formation) leading to crystallization stress of ice on pore and capillary walls, hydraulic stress of pore liquid, osmotic pressure. In this case the character of pore structure of cement paste, for example, ratio of content of gel, capillary and contraction pores significantly influent on resistance to frost damage.

Effect of antifreezing agents is oriented to providing a liquid phase in concrete system at below zero temperatures promoting a positive temperature keeping in hardened concrete until required strength characteristics or reducing a frost point of liquid phase. Besides direct reduction of frost point of liquid phase, antifreezing agents initiate pore redistribution in cement stone with micro-pore structure formation. In this case a physically and chemically-bounded water freezes at below zero temperatures. The higher a concentration of salt in water the less water content transforms to ice. Also in modified concretes an ice forms gradually with the temperature reducing. A weaker and looser ice and salt solutions freeze with less growth in volume then water.

Widely applied salt based antifreezing admixtures lead to change of physical and chemical properties of water, change in solubility of cement minerals and hydration products, change of colloid and chemical properties of cement particles and change of hydration processes as a result. Physical and chemical interaction of the admixtures with cement minerals and hydration products takes place. It leads to change of kinetics of setting and hardening of cement minerals. News chemical formations – products of reaction between cement phases and antifreezing agents are formed. Micro- and macrostructure of cement stone is changed. Unreacted admixtures with cement particles are crystallized in form of individual salt phases.

Hardening rate of concrete with antifreezing agents generally depends on content and binding force of water molecules with ions and molecules of introduced components as well as participation of these components in hydration process. Using the above modifiers initiates an intensification of hydration processes. In reactivity they can be ranged by following: $K_2CO_3 \rightarrow NaCl+CaCl_2 \rightarrow NaNO_2$.

Winter concreting with antifreezing agents allows application another admixtures such as gas forming agents, air-entraining agents oriented to improving of frost-thaw resistance in concrete [10].

Thus, the full range of admixtures allows choosing the methods of regulation and structure formation of hydraulic binders in monolithic construction in North lands of the country as well as successful application in different content depending on required properties.

One of the most popular composite binder in Russia is low-water-demand binders (LWDB), consisting of clinker, silica components of different genesis and plasticizers. This composition allows reducing significantly cement content due to introduction of silica component saving the strength and others technological parameters.

2. Materials and equipment

Determination of nano-sized pores distribution in materials was measured with the equipment
SoftSorbi-II ver.1.0. X-ray analysis of cement paste was realized by WorkStation ARL 9900 with radiation of Co-anode. Qualitative X-ray analysis of mineral crystal phases was accomplished with database PDF-2. Full profile quantitative X-ray analysis allowed determination the quantitative ratio of crystal phases (by wt. %).

In the study the followings raw materials were used: Portland cement CEM I 42.5 N, meeting requirements Russian Standard 31108–2003; quartz sands from Makhnevsk and Essk deposits meeting requirements Russian Standard 8736–93, superplastosizer "Poliplast SP -1", antifreezing agent for concrete and masonry MC Rapid 025, complex plasticizing and accelerating antifreezing agent MC Rapid 015 meeting requirements Russian Standard 24211–2008, water meeting requirements Russian Standard 23732–79 (1993).

3. Experimental part

In earlier studies the opportunity of LWDB production on the base of feldspar sands from North of Russia as well as melamine-formaldehyde based plasticizer was confirmed [16]. LWDB production is accomplished by joint grinding of all components in ball mill up to 500–550 m²/kg. The influence of silica component composition on granulometry of LWDB is determined. Presence of feldspars in composition of polymineral sand with good cleavage and lower hardness vs. quartz leads to following characteristics: enhancement of the binder grinding capacity and reducing of energy consumption when grinding process as a result; polymodal particle size distribution and formation of more compact particle packing in LWDB; reducing of microporosity of cement stone in based fine-aggregate concrete. For further studies the samples of LWDB-50 and LWDB -70 were obtained (50 and 70 in LWDB-50 and LWDB -70 indicate on cement content in composite binder).

To provide good conditions for monolithic concreting at below zero temperatures in this work the antifreezing agents were introduced in concrete mix. Choice of antifreezing agents is based on possibility of concreting process at temperature up to 20 ºС and good compatibility with plasticizers in LWDB. As antifreezing admixtures in this study the MC Rapid 025 and MC Rapid 015 (MC -Bauchemie, Russia) were used. Opportunity of organization of construction process at below zero temperatures without heating of raw materials and further heating of concrete or masonry containing these admixtures is based on optimal content of the agents allowing a keeping a liquid phase in concrete system and providing a good condition for a cement hydration at below zero temperatures.

These admixtures have antifreezing effect and significantly accelerate setting and hardening processes in concrete. Also they influent on solubility of silica components in cement and form a double and basic salts when interaction with products of a cement hydration. The salts also form a structure of cement stone. Due to chemical binding the frost point of liquid phase grows. When the ice crystallization and introduction of water in cement hydration as well as formation of crystallohydrate, the concentration of admixture increase. When stabilization of salt formation process, water required for cement hydration is formed from melting ice.

For the experiment the compositions of fine aggregate concrete on the base of following types of binders: CEM I 42.5 N, LWDB-50, LWDB-70 containing antifreezing admixtures MC Rapid 025 and complex antifreezing admixtures MC Rapid 015 are prepared.

Optimal concentrations of admixtures were determined according to Russian Standard 30459–2008: «cement –sand» ratio is 1:3; water content in concrete mixture is determined experimentally to provide the slump of 15 cm. After moulding the samples of fine aggregate concrete are divided in two series: with curing in ambient condition (reference compositions) and curing in refrigerating chamber at -20 ºC (working compositions). After 28 days of curing foe the samples were determined following characteristics: compressive strength (Table 1, Fig. 2), mineral composition (Table 2, Fig. 2), nano-pore distribution (Table 3). Last column in Table 1 is value of percentage of working compositions strength of reference compositions (%).

Workability test and resistance to corrosion attack test for concrete containing chemical admixtures were carried out. Workability of concrete mix is varied within 15 % during 15 min. Resistance to
corrosion attack test (50 cycles of frost at -15 °C and 50 cycle of heat curing at 15 °C) shows the absence of the samples distraction. So, this agent can be used in concrete system with optimal concentration. Efflorescence test for concrete is demonstrates opportunity of application of the antifreezing admixture containing concrete on the base of LWDB can be applied in any building.

Results of compressive strength for concrete samples cured under refrigeration (at -20 °C) vs. reference compositions cured in ambient conditions (Table 1) allow concluding the following: Results of compressive strength for concrete samples cured under refrigeration (at -20 °C) vs. reference compositions cured in ambient conditions (Table 1) allow concluding the following: at below zero temperatures fine-concrete based on Portland cement CEM I 42.5 N has 20 % of compressive strength of reference composition; fine-concrete based on LWDB-50 – 26 %; fine-concrete based on LWDB-70 – 30 %. Introduction of antifreezing and complex antifreezing admixtures allows acceleration of strength development at below zero temperature.

When LWDB application the optimal concentrations of admixtures can be reduced from 6 to 4 % for antifreezing agents and from 7 to 5 % for complex admixtures vs. cement binder (Fig. 2). Strength properties for LWDB based samples with optimal concentration of antifreezing agent is 89 % of reference value; for cement binder – 43 % of reference one.

<table>
<thead>
<tr>
<th>Binder type</th>
<th>Admixture type</th>
<th>Concentration of admixture (%)</th>
<th>Compressive strength after 28 days of hardening (Mpa)</th>
<th>Strength variation (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>in ambient conditions</td>
<td>in freezing chamber at -20 °C</td>
</tr>
<tr>
<td>CEM I 42,5 N</td>
<td>–</td>
<td>0</td>
<td>43,04</td>
<td>8,608</td>
</tr>
<tr>
<td></td>
<td>MC Rapid 025</td>
<td>4</td>
<td>45,2</td>
<td>11,752</td>
</tr>
<tr>
<td></td>
<td></td>
<td>6</td>
<td>46,3</td>
<td>15,279</td>
</tr>
<tr>
<td></td>
<td></td>
<td>8</td>
<td>44,2</td>
<td>15,028</td>
</tr>
<tr>
<td></td>
<td>MC Rapid 015</td>
<td>5</td>
<td>54,6</td>
<td>13,65</td>
</tr>
<tr>
<td></td>
<td></td>
<td>7</td>
<td>55,2</td>
<td>18,768</td>
</tr>
<tr>
<td></td>
<td></td>
<td>9</td>
<td>55,5</td>
<td>19,425</td>
</tr>
<tr>
<td>LWDB–50</td>
<td>–</td>
<td>0</td>
<td>38,24</td>
<td>9,9424</td>
</tr>
<tr>
<td></td>
<td>MC Rapid 025</td>
<td>4</td>
<td>40,2</td>
<td>32,16</td>
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<td></td>
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<td>6</td>
<td>36,2</td>
<td>28,236</td>
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<td></td>
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<td>34,1</td>
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<td>MC Rapid 015</td>
<td>5</td>
<td>45,4</td>
<td>34,05</td>
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<tr>
<td></td>
<td></td>
<td>7</td>
<td>46,2</td>
<td>33,726</td>
</tr>
<tr>
<td></td>
<td></td>
<td>9</td>
<td>46,1</td>
<td>27,66</td>
</tr>
<tr>
<td>LWDB–70</td>
<td>–</td>
<td>0</td>
<td>55,31</td>
<td>16,593</td>
</tr>
<tr>
<td></td>
<td>MC Rapid 025</td>
<td>4</td>
<td>58,1</td>
<td>46,48</td>
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<tr>
<td></td>
<td></td>
<td>6</td>
<td>54,1</td>
<td>43,28</td>
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<td></td>
<td></td>
<td>8</td>
<td>53,1</td>
<td>34,515</td>
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<td></td>
<td>MC Rapid 015</td>
<td>5</td>
<td>59,1</td>
<td>46,689</td>
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<td></td>
<td></td>
<td>7</td>
<td>60,2</td>
<td>34,314</td>
</tr>
<tr>
<td></td>
<td></td>
<td>9</td>
<td>61,4</td>
<td>34,384</td>
</tr>
</tbody>
</table>

The data obtained (Table 1, Fig. 2) are confirmed by results of quantitative Full Profile X-ray analysis (Fig. 3), where the concentration of portlandite and new formed hydrosilicates in cement stone after 14 days of hardening grow in following sequence: free of admixture LWDB-70 at -20 °C; LWDB-70 containing antifreezing agent at -20 °C; free of admixture LWDB-70 at 20 °C.
Fig. 2. Yield compressive strength depending on type of binder as well as type and concentration of antifreezing agent: a, b – in ambient conditions; c, d – at -20 °C.

Fig. 3. Phase composition of cement stone based on LWDB-70 depending on type of antifreezing component and curing conditions.

Accelerated strength development of LWDB at below zero temperatures and enhanced strength characteristics vs. cement (Fig. 2) are determined by some factors. Effective pore radius for LWDB based cement stone is shifted to zone of smaller pore size up to 0.01 µm (Table 3), where water...
freezes at lower temperatures allowing the concrete hardening at below zero temperatures. Also, application of plastisizers promotes a formation of homogenous distribution of closed pores-spheroidites as formations defusing inner tension when ice formation in pores. Partially connected capillaries and pores-spheroidites are «reserve buffers» for water when ice formation.

Table 2. Content of hydration products of cement stone based on LWDB-70 depending on type of antifreezing component and curing conditions

<table>
<thead>
<tr>
<th>№</th>
<th>Type of antifreezing component</th>
<th>Curing conditions, °C</th>
<th>Content of hydration products, %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>CH</td>
</tr>
<tr>
<td>1</td>
<td>-</td>
<td>+20</td>
<td>6.9</td>
</tr>
<tr>
<td>2</td>
<td>-</td>
<td>-20</td>
<td>0.6</td>
</tr>
<tr>
<td>3</td>
<td>MC Rapid 025</td>
<td>-20</td>
<td>2.0</td>
</tr>
<tr>
<td>4</td>
<td>MC Rapid 015</td>
<td>-20</td>
<td>3.2</td>
</tr>
</tbody>
</table>

Lower cement content, reduced a water demand and high specific surface area initiate enhanced heat evolution at initial hardening stage.

Table 3. Pore distribution vs. total volume (%)

<table>
<thead>
<tr>
<th>D, nm</th>
<th>Binder</th>
<th>3,5</th>
<th>4,4</th>
<th>5,9</th>
<th>8,4</th>
<th>15,0</th>
<th>29,3</th>
<th>43,5</th>
<th>71,8</th>
<th>118,8</th>
<th>142,3</th>
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<tbody>
<tr>
<td></td>
<td>CEM I 42,5N</td>
<td>27,7</td>
<td>0</td>
<td>0</td>
<td>1,0</td>
<td>14,0</td>
<td>21,2</td>
<td>16,7</td>
<td>0</td>
<td>19,4</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>LWDB-70</td>
<td>70,6</td>
<td>19,7</td>
<td>0</td>
<td>9,7</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

Thus, application of composite binder LWDB on the base of field spar and quartz sands, complexly influenced on structure formation in concrete containing antifreezing admixtures allows reducing effect of below zero temperatures on hydration processes and strength development as a result. Usage of LWDB in concrete hardened at below zero temperatures allows reducing a concentration of antifreezing agent vs. cement based concrete as well as acceleration of construction process.

4. Conclusions

To reduce the energy consumption when monolithic construction at below zero temperatures the complex application of composite binder and antifreezing admixture is proposed. It allows avoiding usage of energy consuming heating methods in-situ or preliminary heating of components in concrete mixture.

Results of the study demonstrate the introduction of antifreezing and complex admixtures at below zero temperatures and using the different binders allows production the composite structure typical to cement stone hardened in ambient conditions. When curing at below zero temperatures the strength of fine-aggregate concrete on the base of LWDB-50, LWDB-70 with optimal content of antifreezing admixture MC Rapid 025(4 %) achieves 80 % of reference composition and with complex antifreezing admixture MC Rapid 015 (80%) achieves only 34 % of reference composition. Fine-pored structure of LWDB gives opportunity of requirement reducing antifreezing admixture for a good cement hydration at below zero temperatures.

It explains high values of physical and mechanical characteristics of fine-aggregate concrete on the base of developed compositions of LWDB [16]. LWDB based composites are characterized by a higher density and homogeneity due to high dispersity of binder and its complicate surface providing a lot of crystallization centers. Results of mineral composition of concrete samples cured at below zero temperatures demonstrate the concentration of portlandite and new formed hydrosilicates grows when using of antifreezing admixtures. LWDB contents small pores keeping water in liquid form promoting a more complete hydration process.
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