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# Efficiency of Composite Binders with Antifreezing Agents

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# Efficiency of Composite Binders with Antifreezing Agents

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**Abstract.** One of the non-heating methods of cold-weather concreting is using concretes hardening at negative temperatures. This method consists in using chemical additives which reduce the freezing temperature of the liquid phase and provide for concrete hardening at negative temperatures. The non-heating cold-weather concreting, due to 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 °C and combination with a plasticizer contained in the composite binder were 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 a structure of composite characteristic for cement stone in the conditions of below zero temperatures at using different binders; the hydration of such composite proceeded naturally. Low-water-demand binders (LWDB) based composites are characterized by a higher density and homogeneity due to a high dispersity of a binder and its complicated surface providing for a lot of crystallization centers. LWDB contains small pores keeping water in a liquid form and promoting a more complete hydration process.

## 1. Introduction

The contemporary global construction industry is generally based on the production of monolithic and industrialized buildings. A strong base for these technologies is provided by a sustainable domestic production of high-quality binders and concrete mixes. A wide application of monolithic concrete technologies is connected with some significant advantages of construction objects vs. industrialized technologies. Among them are the following: architectural expression reduced material consumption, high design reliability, low cost enhanced performance characteristics.

Over the past few decades the monolithic construction in Russia has experienced an extreme growth. At the same time, monolithic construction is more effective due to a high rate of construction (2–5 stages per a month), an opportunity of year-round construction meeting normative requirements in terms of strength, durability and convenience [1]. It induces the necessity to apply intensive concreting methods at below zero temperatures providing preferable curing conditions until the achievement of taking-off strength as well as a partial or full loading of construction elements. In many cases, providing certain values of freeze-thaw resistance, water resistance etc. in time should be taken into account when choosing concreting methods 10 at below zero temperatures [2-5].



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

Chemical admixture application is reasonable due to the improvement of some technological parameters and performance properties of concrete even albeit a cost increase. High-quality concretes are generally characterized by high frost-thaw resistance super-high strength and low water permeability. The joint use of antifreezing agents and concrete heating provides a complex effect: accelerates a concrete hardening period and reduces an electric heating period and energy consumption [6-9].

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

The effect of antifreezing agents is oriented towards providing a liquid phase in a concrete system at below zero temperatures promoting a positive temperature keeping in a hardened concrete until the achievement of required strength characteristics or the reduction of a liquid phase frost point. Besides direct reduction of the liquid phase frost point, 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 is salt concentration in water, the less the water content transforms to ice. Also, in modified concretes ice is formed gradually with the temperature reducing. A weaker and looser ice and salt solutions freeze with less growth in volume comparing to water [10].

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

One of the effective methods to enhance the performance characteristics of final materials is the use of composite binders [11-15]. Ordinary Portland cement replacement allows for the improvement of physical and mechanical properties of concretes on its base as well as the reduction of raw materials cost. Composite binders consist of cement and a filler of natural and technogenic genesis. To reduce the transportation costs, the application of local raw material is preferable.

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

## **2. Materials and equipment**

The determination of nano-sized pores distribution in materials was measured with the equipment SoftSorbi-II ver.1.0. Cement paste X-ray analysis was performed by WorkStation ARL 9900 with Co-anode radiation. The qualitative X-ray analysis of mineral crystal phases was accomplished with the database PDF-2. A full profile quantitative X-ray analysis allowed determination of 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 the requirements of the Russian Standard 31108–2003; quartz sands from Makhnevsk and Essk deposits meeting the requirements of the Russian Standard 8736–93, superplasticizer "Poliplast SP-1",

antifreezing agent for concrete and masonry MC Rapid 025, complex plasticizing and accelerating antifreezing agent MC Rapid 015 meeting the requirements of the Russian Standard 24211–2008, water meeting requirements of the Russian Standard 23732–79 (1993).

### 3. Experimental part

In the previous studies the opportunity of LWDB production on the base of feldspar sands from the north of Russia as well as a melamine-formaldehyde based plasticizer was confirmed [16]. LWDB production is accomplished by joint grinding of all components in a ball mill up to 500–550 m<sup>2</sup>/kg. The influence of the silica component composition on LWDB granulometry is determined. The presence of feldspars in the composition of polymineral sand with good cleavage and lower hardness vs. quartz results in following characteristics: enhancement of the binder grinding capacity and reduction of energy consumption at the grinding process; polymodal particle size distribution and formation of more compact particle packing in LWDB; reduction of cement stone microporosity in the 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 the cement content in a composite binder).

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

These admixtures have antifreezing effect and significantly accelerate setting and hardening processes in concrete. They also influence the solubility of silica components in cement and form double and basic salts at 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 crystallizes and water is introduced in cement hydration as well as crystalhydrate is formed, the admixture concentration increases. Upon stabilization of the salt formation process the water required for cement hydration is formed from melting ice. Optimal concentrations of admixtures were determined according to the Russian Standard 30459–2008.

The tests of workability and resistance to corrosion attack were conducted for concrete containing chemical admixtures. The concrete mix workability varies within 15 % during 15 min. The corrosion attack resistance test (50 frost cycles at -15 °C and 50 cycles of heat curing at 15 °C) shows the absence of the samples distraction. So, this agent can be used in a concrete system with an optimal concentration. The efflorescence test for concrete demonstrates an opportunity to apply the antifreezing admixture containing concrete on the base of LWDB in any building.

The results of the compressive strength test for concrete samples cured under refrigeration (at -20 °C) vs. reference compositions cured in ambient conditions (Table 1) allow making the following conclusion: at 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 binders. The strength properties of the LWDB-based samples with an optimum concentration of an antifreezing agent is 89 % of a reference value; for cement binder – 43 % of a reference one.

The data obtained (Table 1) are confirmed by the results of a quantitative Full Profile X-ray analysis (Fig. 1) where the concentration of portlandite and new-formed hydrosilicates in cement stone after 14 days of hardening grow in the following sequence: LWDB-70 free of the admixture at -20 °C; LWDB-70 containing the antifreezing agent at -20 °C; LWDB-70 free of the admixture at 20 °C.

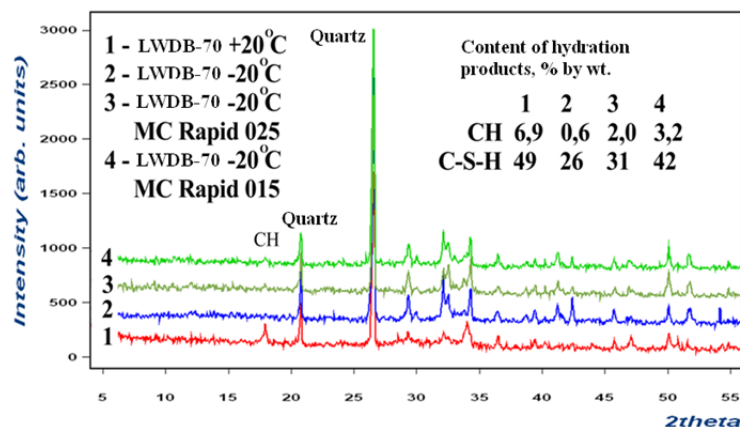
LWDB accelerated strength development at below zero temperatures and enhanced strength characteristics vs. cement (Figure 2) are determined by some factors. An effective pore radius for LWDB based cement stone is shifted to the zone of a smaller pore size up to 0.01 μm (Table 2) where

water freezes at lower temperatures allowing the concrete hardening at below zero temperatures. Also, the application of plastisizers promotes a formation of homogenous distribution of closed pores-spheroidites as formations defusing inner tension during ice formation in pores. Partially connected capillaries and pores-spheroidites are “reserve buffers” for water at ice formation.

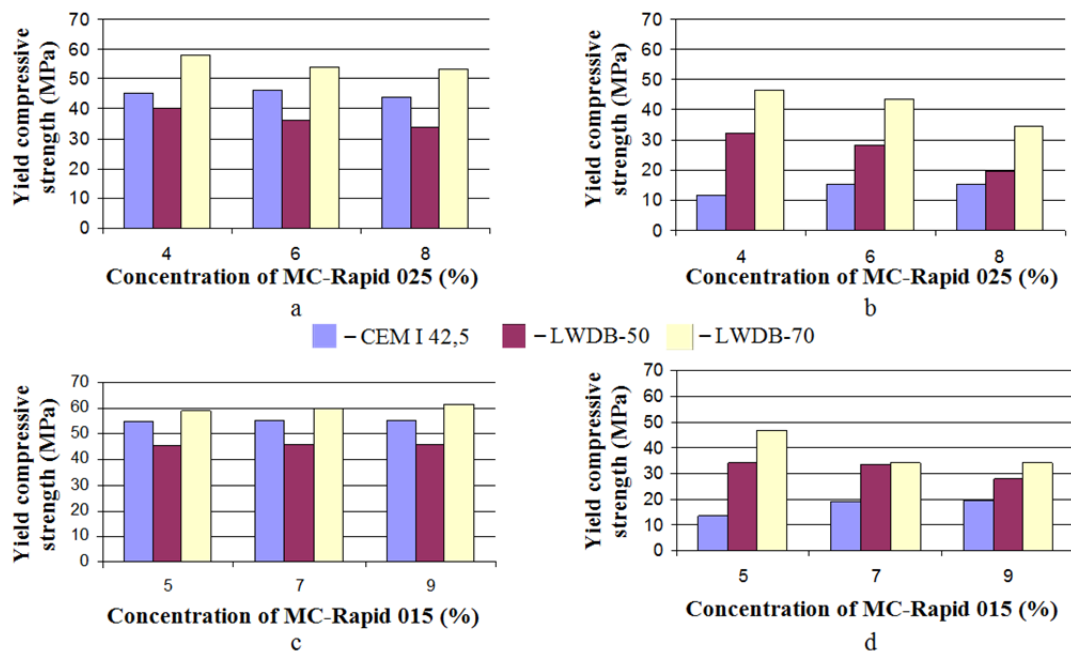
A lower cement content, reduced water demand and high specific surface area initiate enhanced heat evolution at the initial hardening stage.

**Table 1.** Concrete strength depending on the admixture type and concentration.

Binder type	Admixture type	Concentration (%)	Compressive strength after 28 days of hardening (Mpa)		Strength variation (%)
			in ambient conditions	in freezing chamber at -20 °C	
CEM I 42,5 N	–	0	43.04	8.61	20
	MC Rapid 025	4	45.20	11.75	26
		6	46.30	15.28	33
		8	44.20	15.03	34
	MC Rapid 015	5	54.60	13.65	25
		7	55.20	18.77	34
9		55.50	19.42	35	
LWDB–50	–	0	38.24	9.94	26
	MC Rapid 025	4	40.20	32.16	80
		6	36.20	28.24	78
		8	34.10	19.78	58
	MC Rapid 015	5	45.40	34.05	75
		7	46.20	33.73	73
9		46.10	27.66	60	
LWDB–70	–	0	55.31	16.59	30
	MC Rapid 025	4	58.10	46.48	80
		6	54.10	43.28	80
		8	53.10	34.51	65
	MC Rapid 015	5	59.10	46.69	79
		7	60.20	34.31	57
9		61.40	34.38	56	



**Figure 1.** Phase composition of cement stone based on LWDB depending on the type of antifreezing component and curing conditions.



**Figure 2.** Yield compressive strength depending on the binder type as well as the type and concentration of antifreezing agent: a, b – in ambient conditions; c, d – at -20 °C.

**Table 2.** Pore distribution vs. total volume (%).

D, nm Binder	3.5	4.4	5.9	8.4	15.0	29.3	43.5	71.8	118.8	142.3
CEM I 42,5N	27.7	0	0	1.0	14.0	21.2	16.7	0	19.4	0
LWDB-70	70.6	19.7	0	9.7	0	0	0	0	0	0

Thus, the application of the composite binder LWDB on the basis of field spar and quartz sands, which influenced the structure formation in concrete containing antifreezing admixtures in an integrated way, reduced the effect of below zero temperatures on the resulting hydration processes and strength development. LWDB use in concrete hardened at below zero temperatures allows reducing a concentration of antifreezing agent vs. cement based concrete as well as accelerated the construction process.

**4. Conclusion**

The technical results of the study demonstrate the introduction of antifreezing and complex admixtures at below zero temperatures and the use of different binders allowing for production of the composite structure typical to cement stone hardened in ambient conditions. It explains high values of physical and mechanical characteristics of fine-aggregate concrete on the basis of developed compositions of LWDB [16]. LWDB based composites are characterized by a higher density and homogeneity due to the binder high dispersity and its complicate surface providing a lot of crystallization centers. LWDB contains small pores keeping water in a liquid form and promoting a more complete hydration process.

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