Rational Design of Effective Antifreeze Additives for Mortars and Concretes

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Abstract. The principles of designing complex anti-frost organomineral additives for mortars and concretes have been developed. The nature of the influence of the components of additives on the composition of the products of hydration of cement stone is analyzed. The influence of polynirminer complex additives used in conjunction with hyperplasticizers on the kinetics of high-strength concrete hardening has been studied.

1. Introduction

Improving the efficiency of winter concreting is an extremely important task for climatic conditions in Russia, when the time period of low positive and negative temperatures is from 6 to 8 months. Under these conditions, there are serious restrictions when performing concrete work on an open construction site due to the need to prevent concrete mixes from freezing and provide appropriate care for the concrete.

Modern concrete is a multi-component material and to a greater extent it refers to the new generation of concrete, an integral part of which are chemical modifiers of various functional purposes, allowing to regulate the properties of concrete mixtures and concrete in a wide range. Anti-frost modifiers are no exception and are widely used in winter concreting technology. Moreover, today for the construction industry, an industry of chemical modifiers produced industrially on a huge scale has been created.

On the one hand, the appearance of a wide range of chemical additives is a positive factor, since it becomes possible to choose modifiers based on production conditions and requirements for ensuring the necessary properties of concrete mixes and concretes.

On the other hand, a huge number of additives, the composition of which in many cases is not specified, is quite difficult to understand without understanding the main mechanisms of their action. For multicomponent organomineral supplements, this issue becomes even more difficult to solve.

Let us briefly analyze some issues related to the use of antifreeze additives in winter concreting technology.

It is known that the hardening of cement mortars and concretes slows down at low positive and low negative temperatures and practically stops when the liquid phase of concrete freezes. However, it should be noted that hydration can only continue in thin capillaries, in which the water does not freeze
at a temperature of minus 30°C and below. In most cases, at temperatures of minus 5-10°C. With the
hardening of concrete almost stops.

Concretes subjected to freezing at an early age subsequently have lower physical and mechanical
characteristics than concretes that have achieved critical strength before freezing.

In this regard, one of the main tasks in winter concreting technology is to ensure hardening
conditions in the cold, under which the effect of negative temperatures becomes minimal.

Currently, one of the most common methods of winter concreting is the use of moderate anti-frost
additives while ensuring the necessary conditions for hardening concrete in the cold in various ways
(heating, surface protection, etc.). In most cases, anti-frost additives are complex, which include
plasticizers that reduce the water requirement of concrete mixtures, and anti-frost components.

Taking into account the possible sharp drops of negative temperatures at the construction site and
the possibility of technological irregularities in the process of concrete care, the above described
winter concreting method is subject to significant risks. A more reliable method is the use of pure anti-
frost components (in most cases, electrolytes), which reduce the freezing point of the liquid phase of
concrete [1, 2].

However, in this case, the dosage of additives increases dramatically, and individual modifiers, for
example, based on chloride salts, have significant restrictions on use due to the risk of corrosion of
concrete steel reinforcement. In this case, the most effective additives are sodium and calcium nitrates,
nitrites, acetates and formates. Potash in most cases leads to a loss of technological properties and
early setting of concrete.

It is known that the most effective additives that can lower the freezing point of the liquid phase of
concrete are inorganic substances, and the lower the value of their molecular weight, the more they are
able to lower the freezing point of the liquid phase of concrete.

An important factor in the appointment of the type and dosage of antifreeze additives that are part
of complex mixtures is the assessment of their influence on the formation of crystallization structures
of cement stone and the composition of hydration products, which largely determines the kinetics of
initial structure formation and subsequent hardening. It is known that substances such as chloride salts,
nitrates, acetates and formates of sodium and calcium are actively involved in the formation of cement
stone hydrates and contribute to increasing the density, reducing porosity, increasing the strength and
durability of cement materials.

It should be noted that the recommendations for the use of many antifreeze additives indicate low
dosages (2-4% of the weight of cement in terms of dry matter), which allow performing concrete work
at temperatures up to minus 25°C. However, with such dosages, it is impossible to prevent freezing of
the liquid medium of concrete, since the freezing temperature of the solution decreases in proportion
to the molar concentration.

If we talk about complex additives based on superplasticizers and hyperplasticizers (SP and GP)
and anti-frost components, it is not advisable to use such mixtures at high dosages due to the
possibility of slowing down the hydration and hardening of concrete with excess organic additives.
Thus, the meaning of using such complex mixtures at temperatures up to 20-25°C without reservation
to the need for special care for concrete is lost.

In accordance with Raul’s law, the change in the freezing temperature of the solution (ΔT₃)
depending on the molar concentration of the solute is described by the equation:

\[ \Delta T_3 = K_{lp} \cdot i \cdot c. \]  (1)

where \( K_{lp} \) - is the cryoscopic constant; \( i \) - is the coefficient that takes into account the degree of
dissociation of the additive; \( c \) - is the molar concentration of the solute.

However, real solutions in most cases do not obey the laws of ideal solutions, including Raul’s law,
due to positive and negative deviations due to physicochemical phenomena in solutions. Therefore,
Raul’s law can only be applied to dilute solutions and taking into account known isotonic coefficient
values for certain substances. However, in designing the anti-frost additive compositions for practical
use, equation (1) can be used to determine the value of the expected decrease in freezing temperature of the liquid phase of cement concretes.

Approximate calculations of the freezing temperatures of the liquid phase of cement concretes with some traditional additives in the dosage range of 3-10% by weight of cement (table 1) showed that the best anti-frost properties are possessed by additives NaCl, CaCl₂, NaNO₂ at increased dosages. However, even these electrolytes do not allow us to speak with confidence about the possibility of concreting at temperatures of minus 20-25°C.

Table 1. Expected decrease of freezing temperature of aqueous solutions of additives

| Additive | Molecular weight | Amount of additive, % by weight of cement |
|----------|------------------|------------------------------------------|
|          |                  | 3  | 5  | 7   | 10             |
| NaCl     | 58.44            | -3.816 | -6.365 | -8.909 | -12.729        |
| KCl      | 74.56            | -2.991 | -4.988 | -6.982 | -9.977         |
| CaCl₂    | 110.99           | -2.511 | -4.189 | -5.863 | -8.379         |
| MgCl₂    | 95.22            | -2.929 | -4.882 | -6.835 | -9.765         |
| NaNO₂    | 69               | -3.232 | -5.390 | -7.547 | -10.780        |
| Ca(NO₃)₂ | 164.09           | -1.697 | -2.832 | -3.966 | -5.668         |
| CH₃COOH (Na acetate) | 82 | -2.719 | -4.535 | -6.350 | -9.073         |

Of important importance is the nature of the influence of anti-frost additives on the composition of hydration products and the formation of the structure of cement materials.

Previous studies have shown [3] that the period of acceleration of hydration of cement mortars with additives containing calcium salts at negative temperatures occurs much earlier than with additives of alkali metal salts, and compositions with calcium chloride are characterized by the shortest activation time. In the presence of the additives containing NaCl, KCl, NaNO₂, the period of the accelerated hydration it is displaced to the area of lower temperatures, and more it is noted for structures with NaCl additives.

Studies carried out on ordinary cements have shown [3] that in the early stages of hardening of cement materials at negative temperatures (especially in harsh conditions at temperatures minus 20-22°C), the degree of participation of anti-frost additives in the formation of the early structure of cement stone, due to the formation of an aluminate framework, even at increased dosages, is very insignificant, and ice formation processes in most cases are predominant. It has been found that anti-frost additives based on calcium chloride, in general, contribute to the rapid loss of mobility of solutions. Anti-frost mixtures containing sodium chloride, in comparison with others, are more preferable, since they lower the freezing point of solutions to a greater extent than other additives, and, as x-ray phase studies have shown, the compositions of hydration products of aluminate and silicate minerals of cement with additives of chloride salts differ more in quantitative, rather than qualitative indicators. Therefore, additives based on sodium chloride do not fundamentally change the phase composition of hydrated cement stone.

However, it has been found [4] that the mechanism of activating action of electrolytes-based accelerating additives on the early structure of cement systems is mainly determined by their effect on the formation and stabilization of calcium hydroaluminates at an early stage of hydration and a change in the ratio between AFm-phase hydrates and C₃AH₆. With increasing dosages of additives, the stabilizing effect of electrolytes increases.

With regard to the nature of the influence of SP and GP on the cement hydration process, it should be noted that in the presence of almost all SP and GP, the hydration of cement silicate phases is retarded and calcium hydroaluminates of AFm phases are stabilized [3, 5].
In order to confirm the conclusions made earlier and study the nature of the influence of microsilica, a series of x-ray phase studies of the composition of hydration products of pure cement stone and cement stone and with additives of SP and GP and microsilica was performed.

The results of changes in the lime intensities and anhydrous cement silicate phases shown in Tables 2 and 3 showed that the GP-added cement had a decrease in lime reflection intensity compared to the control composition. While the high reflectance intensities of the anhydrous silicate phases of the GP-added cement also indicate a retardation of hydration. In the presence of additives of microsilica and GP, the intensity of lime reflections decreases even more compared to the control composition and the composition with the addition of GP. Obviously, this indicates that part of the hydrate lime is bound in the hydrosilicate structure, evidenced by reduced intensities of the anhydrous silicate phases in the sample with the additive of microsilica and the GP compared with the sample with the additive GP, although these values are higher than for the control composition and it also indicates a slowing of the hydration of cement systems with the addition of GP, even in the presence of microsilica (table 3).

### Table 2. Reflection intensity Ca(OH)₂.

| Composition                                           | Intensity I max at d [Å] |
|-------------------------------------------------------|--------------------------|
|                                                       | 4,93 | 3,11 | 2,63 | 1,93 | 1,79 | 1,69 | 1,485 |
| №1 control                                            | 350  | 75   | 175  | 90   | 63   | 40   | 40    |
| Cement+ hyperplasticizer (1% by weight of cement)     | 130  | 56   | 117  | 60   | 50   | 38   | 42    |
| Cement+ microsilicon (7% by weight of cement, hyperplasticizer 1% by weight of cement) | 67   | 40   | 68   | 40   | 39   | 38   | 40    |

### Table 3. Intensity of reflection of anhydrous silicate phases of cement.

| Composition                                           | The intensity at d [Å] |
|-------------------------------------------------------|------------------------|
| Cement without additives (control composition)        | 2,7761 2,744           |
| Cement+ hyperplasticizer (1% by weight of cement)     | 108 100                |
| Cement+ microsilicon (7% by weight of cement, hyperplasticizer 1% by weight of cement) | 90    72                |

In the technology of modern concretes, finely dispersed micro-fillers obtained by grinding rocks of various mineralogical composition are increasingly being used.

The use of micro-fillers in concretes is well known. However, if previously used to replace part of the cement (in an amount of 15-30% without loss of strength), then in new generation concretes, micro-fillers (in particular stone flour) are used to create (increase especially in small-cement concretes) a rheologically active fine-dispersed matrix.

It is known [6-11] that many mineral powders and, especially received by a grinding of dense and strong rocks more than cements are subject to the diluting action of the joint venture and GP. This results from the fact that from the very beginning of hydration in cement systems the hydrate phases...
connecting a large amount of water are formed (especially AFm- and AFt-phases). Particles of microfiller don't form hydrate phases and therefore are better diluted in the presence of the joint venture and GP. However, the nature of the plasticizing action in many respects is defined by a charging condition of particles. Thus, when using mineral powders in quantity up to 100% of the mass of cement, conditions for increase in a disperse matrix and increase in efficiency of use of the joint venture and GP in cement and mineral systems in comparison with purely cement are created. In turn it allows to achieve bigger decrease in water content and according to bigger increase in durability of concrete. This fact is extremely important in technology of winter concreting.

A positive factor is also the filling of voids and the convergence of the binder and filler particles to short distances, at which it is possible to form crystallization bridges and build up hydrates both on the surface of the cement particles and on the surface of the particles of the micro-filler.

For example, microcrystals of calcium hydroaluminates are more likely to form on the surface of mineral particles of microfillers that have the structure of an elementary crystal cell close to the structure of, for example, AFm phases. Such microfillers include powders obtained by grinding carbonate rocks. In order to reduce energy consumption when grinding strong and dense rocks (for example, granite), binary systems can be used as mineral fillers, for example, a mixture of granite powders and less durable rock – calcite, etc.

In addition, the use of binary systems makes it possible to increase not only the rheological activity of additives, but also their hydration activity, i.e. the possibility of forming hydrate structures with hydrate lime of cement.

In order to study the nature of the effect of complex polymineral additives on the kinetics of concrete hardening, a series of experiments was carried out on the non-addition CEM I 42,5.

**Table 4. Effect of polymineral additives on sand concrete strength.**

| Concrete composition                              | Number of components, [kg/m³] | Compressive strength, [MPa] (day) |
|--------------------------------------------------|-------------------------------|----------------------------------|
| CEM I 42,5 the city of Krasnoyarsk               | 678                           | 23,2                             |
| The sand is thin                                 | 1016                          | 66                               |
| Limestone                                        | 339                           | 96                               |
| Bio-silica                                       | 34                            | 140                              |
| With the addition of GP – 0,8%                   |                               |                                  |
| Water-solid ratio 0,115                          |                               |                                  |
| CEM I 42,5 the city of Krasnoyarsk               | 656                           | 38,8                             |
| Fine feldspar sand (the city of Krasnoyarsk)    | 984                           | 81,2                             |
| Limestone                                        | 164                           | 94                               |
| Olomite the city of Voronezh                     | 492                           | 126                              |
| Microsilica the city of Novokuzeznetsk           | 66                            |                                  |
| With the addition of GP – 0,8%                   |                               |                                  |
| Water-solid ratio 0,126                          |                               |                                  |
| CEM I 42,5 the city of Krasnoyarsk               | 653                           | 28,8                             |
| Fine feldspar sand (the city of Krasnoyarsk)    | 980                           | 72                               |
| Limestone                                        | 163                           | 83,6                             |
| Dolomite city of Voronezh                        | 489                           | 110                              |
| Silica white BS155                               | 33                            |                                  |
| With the addition of GP – 0,8%                   |                               |                                  |
| Water-solid ratio 0,143                          |                               |                                  |
Concrete composition | Number of components, [kg/m³] | Compressive strength, [MPa] (day) |
|---------------------|-----------------------------|-------------------------------|
| CEM I 42,5, the city of Krasnoyarsk | 685 | 685 |
| The sand is thin | 1028 | 1028 |
| Limestone | 171 | 171 |
| Dolomite city of Voronezh | 513 | 50 | 78 | 106,8 | 131 |
| Microsilica the city of Novokuznetsk | 69 | 69 |
| With the addition of GP – 0,8% | 50 | 78 | 106,8 | 131 |
| Water-solid ratio 0,110 | 669 | 669 |
| CEM I 42,5, the city of Krasnoyarsk | 1004 | 1004 |
| The sand is thin | 167 | 167 |
| Limestone | 501 | 501 |
| Dolomite city of Voronezh | 67 | 21,0 | 60 | 96 | 125 |
| Microsilica the city of Novokuznetsk | 67 | 67 |
| With the addition of GP – 0,8% | 21,0 | 60 | 96 | 125 |
| Water-solid ratio 0,110 | 67 | 67 |

The results presented in Table 4 showed that using 2-4 micro-fillers together with GP, it is possible to achieve stable high strength (85-100 MPa) of sandy concretes. At the age of 90 days, the strength increases to 110-140 MPa.

Thus, the use of mixed microfillers together with GP allows you to neutralize possible negative (from the point of view of rheology) phenomena and consistently obtain high-strength concretes.

2. Conclusion

The performed studies and analysis make it possible to define several basic principles of design of complex anti-frost additives:

1. Separate use of plasticizing and anti-frost components, since with increased dosages of SP and GP additives, their retarding effect on concrete hardening kinetics can be manifested, and an insufficient amount of the anti-frost component in the additive will not be able to provide the necessary conditions for hardening in the cold.

2. When designing complex anti-frost additives, it is necessary to take into account the nature of the influence of SP and GP on the composition of hydration products and the kinetics of initial structure formation and hardening of concrete. The retarding effects of SP and GP on the hydration of cement silicate phases and their stabilizing effect on AFm and AFt phase hydrates should be taken into account. For the anti-frost component, the nature of the effect of additives on earlier setting and the possibility of reducing the freezing temperature of the liquid phase of concrete should be evaluated. It should also be taken into account that the increased amount of inorganic salts also contributes to the stabilization of the formed AFm phases in cement systems and makes it difficult for them to transition to the most thermodynamically stable phases. Recrystallization of metastable calcium hydroaluminates during the hardening process can lead to loosening of the concrete structure and loss of strength.

3. When assigning anti-frost components, the nature of their influence on the processes of setting and hardening under various temperature conditions should be taken into account until concrete reaches critical strength. When using anti-frost components, especially in cases of possible early freezing, the accelerated formation of the crystallization structure of concrete with additives can negatively affect the final strength of concrete.

4. When developing concrete compositions and complex anti-frost additives, it is necessary to use mineral fine powders and their mixtures in order to increase the effectiveness of the plasticizing effect of SP and GP and, as a result, to achieve a greater reduction in the water demand of concrete mixtures and obtain high strength.
5. When prescribing the type of mineral additives, their rheological and hydration activity should be determined (tested).

3. References

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