Kinetics of UHPC Strength Gain at Subfreezing Temperatures

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Synopsis: It is well-known that cooling of fresh concrete to a subfreezing temperature interrupts the structure formation and can lead to serious damages of constructions. Most of the existing antifreeze additives reduce this destructive effect, however it should be acknowledged that the processes of cement hydration is still interrupted to an extent that the strength gain in these conditions is simply negligible. When using these admixtures, it is merely expected that concrete will not lose its integrity during the phase of cooling and that strength will be gained after the ambient temperature will reach positive values. However, in our work we aim at proving the possibility of rapid strength gain of UHPC with reduced water-cement ratio even at subfreezing temperatures. The following article presents analysis of the influence of various in-house developed admixtures on kinetics of strength gain of UHPC at negative temperatures.

Keywords: ultra-high-performance concrete, water-cement ratio, antifreeze admixtures, subfreezing hydration, cold weather concreting, strength gain
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**INTRODUCTION**

A lot of research has been dedicated to the problem of cold weather concrete hardening. It is a common opinion that the freezing of mixing water in fresh concrete leads to irreversible disruption of hardening and inevitable destruction of concrete structure. The reason being the free mixing water, yet unbound, crystallizes and expands in volume by 9%, breaking the microstructure of concrete. In ordinary concrete where w/c ratio often lays between 0.4 and 0.6 the amount of free water sometimes reaches 2/3 of the total amount. The two classical methods of solving this problem are heating concrete by technical means and adding antifreeze admixtures to the mixing water. The first is typically realized with the use of heating equipment and insulation, a rather expensive and inconvenient method to use on a construction site. The second method is more practical since it doesn’t require additional equipment and is more cost-effective. As it was earlier estimated by Mironov and Lagouda [1], concrete advanced with such an admixture continues to harden in subfreezing environment, however this process is extremely slow and the strength gain was considered insignificant. While the use of such an admixture is still combined with heating of the fresh concrete prior to casting, it’s required that concrete would gain a minimal strength before its temperature would drop down to subfreezing levels. As it was described by Ramachandran [2], the minimal strength was considered to be 20% of the final strength of a given concrete grade, since after passing this mark the freezing of concrete doesn’t cause damages. In other words, it was restricted to cool fresh concrete even in presence of antifreeze admixtures. Therefore, it can be concluded that unstable weather preconditions inevitable risks for cold weather concreting. However, reduction of mixing water in ultralow w/c ratio concrete may reveal an alternative method of solving the problem, providing UHPC that is resistant to low temperatures from the very moment of mixing.

Therefore, in our approach we identify two aspects that may provide efficient cold weathering concreting that are:

1. Preservation of batching water in fluid phase at subfreezing temperatures
2. Chemical acceleration of cement hydration

In this work we intend to present results of experiments on concrete hardening at various levels of frost. The mix designs we’ve been testing had w/c ratio ranging from 0.18 to 0.25 with an addition of adjusted antifreeze admixtures composed of sodium chloride, sodium nitrite and calcium chloride in combination with a superplasticizer.

**ANALYTICAL INVESTIGATION**

Since water is the only component in a concrete blend that is reactive to temperature changes, it is crucial to clarify its physical properties and behavior in a fresh mix, since different types of interaction between water and solid particles condition alteration of water freezing point. A lot of studies have been made focusing on the states of water in mature concrete, and it has been substantially determined by work of authors such as Tamtsia and Beaudoin [3] and more recently by Prochoña and Piotrowska [4]; however, in a premature concrete the problem hasn’t been well assessed yet. Therefore, our research has commenced with introduction of a classification of water states in a fresh mix.

**Water States in Fresh Concrete**

Depending on a degree of interaction with solid particles of reactive cement and inert aggregate, the mixing water can be divided in two categories: unbound (e.g. free) and bound (Fig. 1(4)). Immediately after batching, a part of the mixing water starts a transition from free to physical-mechanical bound state, and develops a physical-chemical bound with cement.

Since we are interested in the process of this transition, we focus on the physical-mechanical bound. It is known that in this condition physical properties of water differ from such of regular fresh water. It has increased density (1200-2400 kg/m³ (75-150 pcf)) and lower freezing point (-100°C (-148°F)). Traditionally, this water divides in two classes – low-bound (film water) and hard-bound (hygroscopic water). The amount of this water and the thicknesses of formed film vary (from 3 to 20 molecules) and depend on granulometric and mineralogical properties of cement and aggregate. The power of this bound intensively increases as water molecule approaches
a solid particle, therefore it can be gradually removed in the temperature range from 90°C (194°F) to 300°C (572°F).

An additional class of water that should be identified in a concrete mix is related to the phenomenon of osmosis. When water diffuses colloid particles of cement minerals, its molecules act as solvents since the concentration of ions here is higher. This class signifies a part of bound water that will be the first to develop a chemical bond with the reactive particles of cement. However, at the very first stage of physical interaction it soaks into cement particles, producing the cement gel. Physical properties of this class of water are also altered – the freezing point is significantly reduced.

After mixing the water that remains in an unbound condition divides on gravitational and capillary classes. During the drying of concrete, this water produces directed porosity and therefore decreases the physical-mechanical performance of concrete. Additionally, it is exactly this water that causes damages to concrete during cold weather concreting, since its physical properties remain identical to such of fresh water, with freezing point remaining at 0°C (32°F). Therefore, our goal was to exclude presence of this class in the mix, while preserving good workability and mouldability of the mixture.

In light of above mentioned, our initial hypothesis was that in fresh mixes of UHPC with w/c ratio less than 0.25, practically all mixing water transits from free to bounded states prior to setting of concrete, and therefore it can be assumed that cooling it down to negative temperatures won’t damage the structure of the material. Results of our numerous experiments have proved this initial assumption. Of course, the transition of water from free to bound states in fresh concrete is a more complex process that can be examined further, however we claim that the method of reduction of water to the minimal amount necessary for hydration of cement will stay true in all cases.

**EXPERIMENTAL INVESTIGATION**

**Materials**

Our UHPC design is based on white portland cement M500 (CEM I 42.5), free of mineral additives (tab. 1). As an aggregate, we’ve used an ordinary construction sand with fineness modulus from 2.5 to 3.0. The dust presence in the sand did not exceed 1% of its mass. All the aggregate was dried prior to mixing at room temperature and normal humidity.

We have tested several compositions of antifreeze additive based on sodium chloride (SC), sodium nitrite (SN) and calcium chloride (CC). The different version included separate use of these salts, as well as compositions such as SC+CC and SN+CC. By dissolving a certain additive in mixing water the freezing point was decreasing down to -20°C (-4°F). We have also identified that the presence of these salts does not degrade the rheology of fresh concrete. We were concerned with the fact that presence of SC in concrete can lead to corrosion of steel reinforcement, and therefore it can be used only in unreinforced structures. On the other hand, SN is known to produce inhibiting effect on steel, and therefore can serve as an additional protection of the reinforcement. At last, even a very little amount of CC can significantly accelerate the hardening of concrete, but may also reduce workability of a mixture.

In our work we have also used a superplasticizer based on polycarboxylate produced in Russia.

**Specimens**

Due to the type of aggregate we have been using, it was possible to conduct all experiments and to identify compressive and tensile strengths using 40mm*40mm*160mm (1.57in.*1.57in.*6.30in.) concrete specimens.

**Methodology**

An important methodological aspect is that all raw materials have been cooled to a negative temperature specific to an experiment prior to mixing. After mixing and moulding (which took from 8 to 10 minutes to prevent significant increase in temperature) specimens were immediately placed in freezing chamber with a constant subfreezing temperature. After 24 hours samples were demolded, wrapped in plastic foil and placed back in the chamber until the very examination of strength. The testing of compressive and tensile strengths was conducted on specimens aged 1, 3, 7, 14, 28 and 56 days. Prior to testing samples were defrosted by submerging in water of 20°C (68°F) for one hour. To the best of our knowledge, this allowed to eliminate influence of heat on hydration of cement, and achieve pure and reliable results of cement hydration at negative temperatures.

**EXPERIMENTAL RESULTS AND DISCUSSION**

The results of these tests have revealed that concrete with w/c ratio from 0.2 to 0.25 and a specified composition of antifreeze additives is able to rapidly gain strength even at -10°C (14°F) temperature. In particular, the compressive and tensile strengths of concrete with SN+CC and w/c 0.22 on the 14th day were 82 MPa (11 892 psi) and 14 MPa (2 030 psi) correspondingly. The performance of SC+CC was 40% lower than SN+CC applied in an equal amount. It has to be mentioned that the addition of SN+CC has lesser effect on rheology and allows producing moldable mixes with lower w/c ratio than SC+CC. It can even be said that SN increases plasticity of the mixture with decrease of its temperature.
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In these circumstances we consider this method of preliminary cooled concrete mix is a promising solution for cases, where temperature of concrete while hardening should not exceed the temperature of melting point of water. Such cases can be found in permafrost regions as well as in tunnel constructions combined with ground freezing technologies.

**NOTATION**

\[ \text{w/c} = \text{water to cement ratio} \]

\[ \text{UHPC} = \text{ultra-high performance concrete} \]

\[ \text{SC} = \text{sodium chloride} \]

\[ \text{SN} = \text{sodium nitrite} \]

\[ \text{CC} = \text{calcium chloride} \]

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**TABLES AND FIGURES**

**Table 1 – Mineralogical composition of clinker**

| Signifier | Percentage by mass |
|-----------|-------------------|
| C3S       | 63.1              |
| C2S       | 12.8              |
| C3A       | 13.9              |
| C4AF      | 1.3               |
| CaO       | 2.5               |

**Table 2 – Fine aggregate grading**

| ACI 318M Units | ASTM E 11 | Percentage passing by mass |
|----------------|-----------|-----------------------------|
| 9.5 mm         | 3/8 in.   | 99                          |
| 4.75 mm        | No. 4     | 95 to 100                   |
| 600 µm         | No. 30    | 35 to 55                    |
| 150 µm         | No. 100   | 0 to 5                      |

**Table 3 – Mineralogical and petrological content of sand**

| Mineral    | Percentage by mass |
|------------|-------------------|
| Quartz     | 54.1 to 68.5      |
| Granite    | 10.3 to 13.8      |
| Feldspars  | 7.0 to 8.0        |
| Limestone  | 6.1 to 7.9        |
| Dolomite   | 0 to 2.9          |
| Silica     | 1.2 to 2.0        |
| Quartzite  | 0.2 to 0.4        |
| Mica       | 0 to 0.6          |
| Sandstone  | 0 to 1            |
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**Fig. 1** – Classification of water states in fresh concrete in regards to a degree of its bound with inert and reactive particles.

**Fig. 2** – Compressive strength gain of concrete at temperature of -10°C (14°F); after 14 days samples were removed from the freezing chamber to 20°C (68°F) and continued to harden.
- Blue - with SN+CC, w/c = 0.22;
- Red - with SC+CC, w/c = 0.24;
- Green – no additives, w/c = 0.19;

**Fig. 3** – Tensile strength gain of concrete at temperature of -10°C (14°F); after 14 days samples were removed from the freezing chamber to 20°C (68°F) and continued to harden.
- Blue - with SN+CC, w/c = 0.22;
- Red - with SC+CC, w/c = 0.24;
- Green – no additives, w/c = 0.19;
Fig. 4 – Compressive strength gain of concrete at temperature of -5°C (23°F)
Blue - with SN+CC, w/c = 0.22;
Red - with SC+CC, w/c = 0.24;
Green – no additives, w/c = 0.19.

Fig. 5 – Tensile strength gain of concrete at temperature of -5°C (23°F)
Blue - with SN+CC, w/c = 0.22;
Red - with SC+CC, w/c = 0.24;
Green – no additives, w/c = 0.19.

Fig. 6 – Reference test: compressive strength gain at 20°C (68°F)
Green – no additives, w/c = 0.17.
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Fig. 7 – Reference test: tensile strength gain at 20°C (68°F)
Green – no additives, w/c = 0.17.

Fig. 8 – Structure of concrete on the surface of cleavage;
concrete contains SN+CC antifreeze additive and has harden at -10°C (14°F).