



Behavior of fresh and hardened concretes with antifreeze admixtures in deep-freeze low temperatures and exterior winter conditions



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HIGHLIGHTS

- Effects of antifreeze admixtures on the exterior winter condition were investigated.
- Workability of concrete was improved.
- Calcium nitrate protects concrete against freezing even in the plastic state.
- Urea provides protection up to $-10\text{ }^{\circ}\text{C}$ without any extra protection precaution.
- Best results have been obtained with the combination of calcium nitrate and urea.

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ABSTRACT

This research investigates properties of concrete prepared with urea and calcium nitrate anti-freeze admixtures and cured in different low deep-freeze temperatures and exterior winter conditions in Erzurum, Turkey. Four different mixtures were prepared and they are control, 9% calcium nitrate, 9% urea and combination of 4.5% urea + 4.5% calcium nitrate. Antifreeze admixtures were used by weight of cement dosage. After casting, one group of samples from each batch were immediately cured in four different low deep-freeze temperatures (-5 , -10 , -15 and $-20\text{ }^{\circ}\text{C}$) for 7, 28, 90 and 365 days (90 days deepfreeze curing + 275 days laboratory condition). Another group of samples was cured in water (23 ± 2) $^{\circ}\text{C}$ for 7, 28, 90 and 365 (90 days water curing + 275 days laboratory condition) days, according to ASTM C 192. The others were exposed to exterior winter conditions of Erzurum, Turkey, for 90 and 365 days. Ultrasonic pulse velocity (UPV) and compressive strength were evaluated for 7, 28, 90 and 365 days. Both compressive strength and UPV were very low for -15 and $-20\text{ }^{\circ}\text{C}$ at 7 and 28 days of curing durations, especially for control and samples containing 9% urea. However, with the increase of curing period, both compressive strength and UPV values of samples with the combination of 4.5% urea + 4.5% calcium nitrate increased. Adding 4.5% calcium nitrate and 4.5% urea caused an increment in the compressive strength of about 108% and 82% for 90 and 365 days in exterior winter conditions, respectively, when compared to the compressive strength of control sample that was exposed to the same conditions.

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1. Introduction

The service life of concrete structures is affected by the exposure to severe environmental conditions. Among the different types of attack of concrete structures, cold weather is the most widely exposing. ACI 306R-10 defines “cold-weather concreting” as the operations concerning the placing, finishing, curing and protection of concrete during cold weather. More specifically, it defines “cold weather” as a period of three or more successive days

during which the average daily outdoor temperature drops below $4\text{ }^{\circ}\text{C}$ and the air temperature is not greater than $10\text{ }^{\circ}\text{C}$ for more than one-half of any 24-h period. Concrete that gains initial compressive strength of 3.5 MPa without freezing can withstand a cycle of freezing and thawing [1].

At temperatures below $-5\text{ }^{\circ}\text{C}$, 92% of the water in fresh concrete turns into ice. Consequently, strength development essentially stops, but there is little water to react with the cement. Moreover, the 9% volume expansion of water turning into ice can halve the final strength of the concrete. Even though strength gain is reestablished when the concrete is thawed, the resulting concrete must usually be rejected [2].

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The temperature variation caused by the heat of hydration or the change of external environment has a large influence on the mechanical properties of early age concrete. Therefore, effects of temperature and aging on the mechanical properties must be studied and quantified. Although a higher temperature during placing and setting increases strength in the very early stages, it may adversely affect the strength from about 7 days onwards. Because, an increase in the early curing temperature makes the hydration rate and concrete strength increase rapidly, but due to the non-homogeneous diffusion of the hydration products and the difference in the thermal expansion coefficients of the concrete's constituents, the porosity of the cement paste increases and micro cracks develop, which finally leads to decreased strength at a later time [3]. Cold weather, on the other hand, can be beneficial when it comes to long term strength gain. But at early ages, cold weather slows down the pace of construction by causing strengths to develop slowly [4].

Cold weather is an ideal time to place concrete if the work is adequately controlled and protected. The ultimate strength of concrete placed during cold weather, not permitted to freeze, and allowed to gain strength slowly, exceeds that of the same concrete exposed at higher temperatures [5].

Antifreeze admixtures are capable of depressing the freezing point of water in concrete considerably and their use at temperatures as low as -30°C enables an extension of the period of construction activity. When fresh concrete freezes, the strength of such concrete is lowered by 20–40%, its resistance to freeze–thaw cycling as given by the durability factor is lower by 40–60% and the bond between reinforcement and concrete is lowered by 70% compared with normally cured concrete [6]. Thus, when concreting is done under cold weather conditions it is important to ensure that the concrete will not freeze while it is in the plastic state. The newly placed concrete should be adequately insulated to retain this heat and thereby maintain favorable curing temperatures.

Concrete accelerators increase the rate of hardening of cement and concrete mixes [7]. The major material used to obtain this effect, calcium chloride, has been used since 1885 and finds application mainly in cold weather, when it allows the early strength gain to approach that of concrete cured under normal curing temperatures and, probably more importantly, reduces the setting time so that finishing operations can proceed without undue delay. In this way the concrete is less liable to damage by early age freezing. It should be pointed out that calcium chloride is not antifreeze. The use of calcium chloride in concrete containing embedded metal is the cause of corrosion [6].

Today, 'chloride-free' accelerators are replaced of calcium chloride in reinforced concrete. For example both the calcium nitrate and urea antifreeze admixtures do not cause to corrosion.

Calcium nitrate is a concrete admixture that can function as (1) set accelerator, (2) counteraction of retardation by plasticizers while maintaining rheology, (3) long term strength enhancer, (4) anti-freeze admixture or winter concreting admixture and (5) inhibitor against chloride induced corrosion of steel. Thus, it is fair to denote it a multifunctional concrete admixture [8]. Successful cold weather concreting requires an understanding of various factors that affect concrete properties. Antifreeze admixtures are used in cold weather concreting to reduce the time that concrete needs to be kept warm [9].

A chemical reaction the cement and water forms a gel that binds the aggregate. As long as the cement is wet, the concrete continues to gain strength at a rate that is strongly influenced by temperature [10]. An antifreeze admixture that is both non-chloride and non-alkaline has been developed in Japan. This admixture contains polyglycol ester derivate and calcium nitrite–nitrate [11].

In the long term, concrete becomes stronger when cured at temperatures that are low but above freezing. Thus in the long

term, concrete becomes stronger in low temperatures. An antifreeze admixture should [12], produce freeze–thaw durable concrete, not react with silica aggregate, not corrode steel, not adversely alter hydration products, be cost effective, depress the freezing point of water, promote strength gain of concrete at low temperatures, not interfere with concrete strength gain at normal temperatures, maintain the workability of the concrete and achieve a reasonable concrete setting time.

Antifreeze admixtures are chemicals which are added to the mixing water of concrete in order to lower the freezing point of the aqueous solution. The mode of action of the antifreezing admixtures is (a) to lower the freezing point of water in concrete and act as either a weak accelerator or retarder of setting and hardening using sodium nitrite, sodium chloride, weak electrolytes and organic compounds such as high molecular weight alcohols and carbamide, or (b) to accelerate significantly the setting and hardening with good antifreezing action using chemical such as calcium chloride, sodium chloride, sodium nitrite, calcium nitrite–nitrate and urea. When the admixtures such as urea do not contain the same ions as in the cement phases (i.e., Ca, Si or Al ions), they accelerate the hydration process chiefly by increase in the solubility of C_3S and C_2S . Antifreezing admixtures (electrolytes) not only accelerate concrete hardening and reduce the electric heating period but also raise the electrical conductivity of the liquid phase, thus allowing electric heating at a temperature below 0°C [13]. The admixtures such as calcium chloride, calcium nitrite and calcium nitrate that contain the same cations as C_3S and C_2S accelerate hydration by nucleating action of such ions and this result in an intensification of the processes of crystallization of hydrate [13,14].

The ultrasonic pulse velocity (UPV) method is frequently adopted for evaluating the quality of in situ concrete structures [15]. The application of UPV to the nondestructive evaluation of concrete quality has been widely investigated for decades [16]. UPV method is based on measuring the velocity of compression stress waves. Higher the elastic modulus, density and integrity of the concrete is higher the pulse velocity. The UPV depends on the density, homogeneity, integrity and elastic properties of the material being tested. Age, mix proportions, water/cement ratio, cement type and aggregate type have an influence on the pulse velocity test results and their relationship to compressive strength [17]. The UPV method, also known as the transit time method, uses a detector to measure the time of flight it takes for an ultrasonic pulse to pass through a known thickness of solid material [16]. The measurement of the ultrasonic compressional wave velocity has been used for a long time to evaluate the setting and hardening of cementitious systems [18].

Objective of this research is to evaluate the low temperature strength performance of antifreeze concrete in both exterior winter condition of Erzurum, Turkey and different deep freezes low temperature, develop new cold weather admixture combinations, and use antifreeze admixtures to maintain the concrete strength development when exposed to exterior cold weather without insulation.

2. Materials and methods

The cement used in this investigation was ordinary ASTM Type I Portland cement (CEM I 42.5 R). The physical and chemical properties of cement were given in Tables 1 and 2. The chemical properties of the calcium nitrate and the urea were given in Tables 3 and 4, respectively. In cold weather concreting practices the dosage of the cement changes between 350 and 500 kg/m^3 . However higher dosages such as 450 and 500 kg/m^3 associate durability problems such as shrinkage. Thus the cement dosage was kept 400 kg/m^3 and the water cement ratio was 0.40 throughout the study. Super plasticizer agent (SPA) was used 0.5% by cement weight and it was constant throughout the study. All antifreeze and SPA were added into the mixing water. The region where the study has been done is very cold and during night the temperature drops below -20°C for long period (approximately 40–60 days). Then the study temperature was kept up to -20°C [14].

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