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The influence of calcium nitrate as antifreeze admixture on the compressive strength of concrete exposed to low temperatures

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ABSTRACT

Based on ACI 306R-10, the minimum temperature necessary for maintaining concrete hydration and strength gaining is 5 °C. If the weather becomes lower than 5 °C, some special measures should be taken in order to prevent decrease in the rate of hydration and to prevent fresh concrete from freezing. Most of the cold weather living countries spend annually plenty of money in order to facilitate concrete placing in the cold weather and to extend the construction season. It has been investigated that the behavior of fresh and hardened concrete contained calcium nitrate at different curing temperatures below freezing temperature of water and compare the results with the both control samples. For this reason, calcium nitrate is used at level of 6% by weight of cement dosage in mixes. After casting, one group of samples was cured in the different deepfreezes at −5 °C, −10 °C, −15 °C, and −20 °C for 7, 14 and 28 days, and then the same samples were cured in water at (23 ± 1.7)°C for 7, 14, and 28 days. Calcium nitrate increased the compressive strength of concrete between 48–964, 50–721, 29–393 and 24–183%, for −5 °C, −10 °C, −15 °C and −20 °C, respectively, when compared to mixes without antifreeze admixtures. The results showed that it is possible to use calcium nitrate as an antifreeze admixture in concrete technology in cold weather concreting without additional precautions.

1. Introduction

Concrete is the backbone of modern construction. Cold weather is defined as a period when the average daily temperature falls below 4 °C for more than three successive days. These conditions require special precautions during placing, finishing and curing. As the temperature decreases, concrete sets more slowly, takes longer time to finish and gains strength less rapidly. If plastic concrete freezes, its potential strength will be reduced by more than 50% and its durability will be adversely affected (Concrete in Practice NRMCA (National Ready Mix Concrete Association), 1998). Concrete exposed to temperature cycles, where water freezes to ice and ice melts to water in winter, is deteriorated due to freezing and thawing (Polat et al., 2010).

Concrete should be protected from freezing until it attains a minimum compressive strength of 3.5 MPa according to ACI 306R-10 (ACI Committee 306 and ACI 306R-10, 2010). Today many admixtures are used in concrete, to protect it from freezing. These admixtures allow concrete to gain strength and setting when the air temperature is below freezing (Korhonen, 2002a). They protect concrete by accelerating cement hydration. Consequently, when the weather temperature decreases, special precautions should be taken and using of antifreeze admixtures is an important method. Antifreeze admixtures are chemicals which are added to the mixing water of concrete in order to lower the freezing point of the aqueous solution. They have been used even at temperatures as low as −30 °C. 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 these result in an intensification of the processes of crystallization of hydrate (Ramachandran, 1995).

During the hydration of C_3S, calcium hydroxide is formed which is capable of reacting with most of the antifreezing admixtures with the formation of hydroxysalts. The hydrolyzing salts not only change the ionic strength of the solution but also change the pH. Thus salts promote densification of cement phase and change its microstructure and physical characteristics of concrete. The calcium hydroxynitrate was composed of calcium nitrate, water and calcium hydroxide. This calcium hydroxynitrate was a double and basic salt form as well as shape needle crystals. The double and basic salts are able to form the initial structural skeleton and function as a micro reinforcement for the hydrosilicate matrix of the cement phase. The main cause for the higher strength development in specimens with antifreeze admixtures is the formation of an initial structural skeleton which

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becomes enveloped by calcium hydrosilicates. Observations show that a considerable amount of hydration occurs in forming the initial skeleton structure and, thereafter, even small amounts of the hydrates forming on the skeleton give comparatively larger strengths (Ramachandran, 1995).

Chemical admixtures can extend the temperature range at which concrete can be placed (U.S., 2003). These chemicals prevent the water in the mix from becoming solid ice and expanding in the spaces between aggregate particles before the critical hardness is reached. With their addition the concrete can be cured (Anon., 2002). The calcium nitrate is commonly used for this aim. This antifreeze admixture speeds up the normal process of hydration. Its advantage in the cold weather is the concrete immune to frost damage (Korhonen and Orchino, 2001). Furthermore Victor B Ratinove et al. reported that calcium nitrate has been used and classified as an antifreeze admixture and RILEM also recommended calcium nitrate as an antifreeze admixture (Korhonen, 2003; Ramachandran, 1995).

Two main purposes for cold weather concreting with portland cement are intended. One is an adequate temperature to cure the concrete and the other is protecting the concrete from freezing without the thermal protection such as foam sheets, mineral wool or cellulose fibers, insulating, housing, covering or heating newly placed concrete.

The purposes of using calcium nitrate and the advantages resulting from the use of this admixture are decreasing time setting and/or an increasing early strength development (Myrdal, 2007).

The benefits of a reduced setting time may include; earlier finishing of surfaces and reducing of hydraulic pressure on forms. The benefits of an increase in the early strength may include; earlier removal of forms, reduction of the required period of curing and protection, and earlier placement in service of a structure or a repair (Rixom and Mailvaganam, 1999). Partial or complete compensation for the effects of low temperatures on strength development may be prevented (Popovics, 1992).

Besides, in Europe, calcium nitrate has replaced calcium chloride as a setting accelerator. Although calcium chloride is the best accelerator, it is not a good option to severe corrosion hazards in steel reinforced concrete. Ramachandran found that $Ca(NO_3)_2$ acted as an accelerator of setting in cement paste at low concentrations (Ramachandran, 1972). Accordingly, calcium nitrate is a multifunctional admixture for concrete (Popovics, 1992). Today, most suppliers of concrete admixtures offer calcium nitrate based accelerators (Justnes, 2007).

The effectiveness of an admixture depends upon such factors such as the type and amount of cement, water content, aggregate shape, gradation and proportions, mixing time, slump, and the temperature of the concrete.

Based on ACI 306R-10, the minimum temperature necessary for maintaining concrete hydration and strength gaining is 5 °C. If the weather becomes lower than 5 °C, some special measures should be taken in order to prevent a decrease in the rate of hydration and to prevent fresh concrete from freezing. Most of the cold weather living countries spend annually plenty of money in order to facilitate concrete placing in the cold weather and to extend the construction season. Besides above precautions, using antifreeze admixture is an alternative without additional protection measures. However, the effects of calcium nitrate on the different freezing period of concrete are not well known. The influence of calcium nitrate on the different periods of the freezing and subsequently different water curing periods should be studied. In addition, a little attention was also taken in previous studies that (below 0 °C) without any additional protection method, calcium nitrate is able to prevent the reduction of the compressive strength of concrete, when compared to the control sample.

For these reasons, in the study, fresh and hardened concretes contained calcium nitrate at different curing temperatures below freezing temperature (−5, −10, −15 and −20 °C) and durations (7, 14 and 28 days) of water compare to the results of control samples. Higher dosage of calcium nitrate could accelerate the setting of the concrete to prevent consolidation and increase the cost. Then the moderate ratio of calcium nitrate is 6% by weight of cement dosage of concrete that has been chosen. After casting, each group of concrete samples was cured in the different deepfreezes at −5, −10, −15, and −20 °C for 7, 14 and 28 days, and then the same samples were cured in water for 7, 14, 28 days and tested in accordance with ASTM C 39.

2. Materials and methods

ASTM Type I portland cement (CEM I 42.5 R) and tap water were used for all mixtures throughout the study. Physical properties and chemical composition of portland cement are shown in Tables 1 and 2, respectively. Calcium nitrate antifreeze originated from Tekkim Kimya San. ve Tic. Ltd. Şti was used. The chemical properties of the calcium nitrate are given in Table 3.

Aggregate with a maximum nominal size of 16.0 mm was used as the coarse aggregates. The fine aggregate was natural sand from Erzurum/Aşkale region. The coarse and fine aggregates were separated into different size fractions (0–2, 2–4, 4–8, 8–16 mm) and recombined (30%, 15%, 20%, 35% by volume of total aggregate for 0–2, 2–4, 4–8, 8–16 mm size, respectively) to a specified grading as shown in Fig. 1. The specific gravity of 0–2, 2–4, 4–8, 8–16 mm was 2.40, 2.47, 2.54 and 2.63, respectively. Super plasticizer agent was used 0.5% of cement weight for all mixtures (Korhonen, 2002b) because the purpose of this study was to investigate the effects of the calcium nitrate alone. So the concrete mixture was not air entrained. The region where the study has been done is very cold and during night the temperature is below −20 °C for long period (approximately 40–60 days). Then the study temperature was very low such as −20 °C.

The concrete mix proportions are given in Table 4. The same water-to-cement ratio for the control mixtures and calcium nitrate mixtures was selected to be 0.40. 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 we preferred 400 kg/m^3 which are higher than that of normal concrete. The admixture calcium nitrate was dissolved in the mix water. At first the dry mixture of cement, fine and coarse aggregate was added in a laboratory counter-current mixer for 1.5–2 min. Then the calcium nitrate solution for concrete mixtures with calcium nitrate and mixed water for concrete mixtures without calcium nitrate were added into the mixer. The fresh concrete mixtures with and without calcium nitrate admixture were mixed in a laboratory counter-current mixer for a total of 5 min and were cast into 100 × 200-mm cylinder plastic molds from each mixture. The cylinders were consolidated with needle vibrator until homogenous specimen was achieved. After casting, the concrete mixtures in plastic state together with molds were immediately transferred to the automatic temperature control deepfreezes at −5 °C, −10 °C, −15 °C and −20 °C for 7, 14, and 28 days. The temperatures of deepfreezes were calibrated

Table 1
Physical properties of portland cement.

CEM I 42.5 (Ordinary portland cement)	Results	TS EN 197/1	Standard data
		(min)	(max)
2 days compressive strength, (N/mm^2)	27.9	20.0	–
7 days compressive strength, (N/mm^2)	44.9		
28 days compressive strength, (N/mm^2)	55.9	42.5	62.5
Initial set time, (minute)	170	60	–
Final set time (minute)	230		
Volume expansion, (mm)	1	–	10
Specific surface, (cm^2/g)	3285	–	–
Specific gravity	3.17		