International Balkans Conference on Challenges of Civil Engineering, BCCCE,
19-21 May 2011, EPOKA University, Tirana, ALBANIA.

The Influence Of Calcium Nitrate On The Compressive Strength Of Concrete Exposed To Freezing Weather

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ABSTRACT

Based on ACI 306R-88, the minimum temperature necessary for maintaining concrete hydration and strength gaining is 5^0C. If the atmosphere weather becomes lower than 5^0C some preserve measurements 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 tried to carry out 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 and real Erzurum winter conditions. For this reason, calcium nitrate is used at level of 6% by weight of cement dosage in the mixes. After casting, one group of concrete samples were cured in the different deepfreezes at -5,-10,-15,-20^0C for 7, and then that same samples were cured in water for 28 days. With usage of calcium nitrate in the mixes, compressive strength of concrete increased between 96-297% at -5^0C, -10^0C, -15^0C and -20^0C, when compared to mixes without antifreeze admixtures that 7 days only freezer cured and 28 days water cured after 7 days freezer cured, respectively. The results showed that it is possible to use calcium nitrate as an antifreeze admixture in concrete placing process in cold weather concreting.

Keywords: *calcium nitrate, concrete compressive strength, cold weather concreting, antifreeze admixture*

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 when placing, finishing and curing. As temperatures drop, concrete sets more slowly, takes longer to finish and gains strength less rapidly. If plastic concrete freezes, its potential strength can be reduced by more than 50% and its durability will be adversely affected [1]. Concrete should be protected from freezing until it attains a minimum compressive strength of 3.5 MPa according to ACI 306R. Today many admixtures is used in concrete, for protect it from freezing. These admixtures allow concrete to gain strength and setting when the air temperature is below freezing [2]. They protect concrete by accelerating cement hydration. Consequently the weather temperature is decreased special precautions are necessary.

Chemical admixtures that can extend the temperature range at which concrete can be placed [3]. 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 cure properly [4]. The calcium nitrate is used for this aim commonly. This antifreeze admixture speeds up the normal process of hydration. Its advantage in the cold weather is the concrete becomes immune to frost damage [5].

The main purpose for cold weather concreting with Portland cement are developing an adequate temperature for curing the concrete and protecting the concrete from freezing without the thermal protection for example 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 many. Thus, the use of accelerators in concrete provides a shortening of setting time and/or an increase in early strength development [6]. These benefits listed as follows [7].

The benefits of a reduced setting time may include;

- Earlier finishing of surfaces
- Reduction 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
- Earlier placement in service of a structure or a repair
- Partial or complete compensation for the effects of low temperatures on strength development [8]

Besides, in Europe calcium nitrate has replaced calcium chloride as a setting accelerator. In spite of calcium chloride is the best acceleration but not an option due to severe corrosion hazards in steel reinforced concrete. Ramachandran found that Ca (NO3)2 acted as an accelerator of setting in cement paste at low concentrations [9]. Accordingly, calcium nitrate is a multifunctional admixture for concrete [6]. Today, most suppliers of concrete admixtures offer calcium nitrate based accelerators [10].

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

Consequently were cast two different mixtures. The first is control mixture without admixture. The other is calcium nitrate antifreeze admixture as 6 percentage of cement weight. The temperatures of ambient are -5, -10, -15, -20°C. The specimens taking from deep freezes were placed in water curing at predetermined curing time and made compressive strength tests. This tests results showed result and discussion section.

2. Materials and Methods

The cement used in this investigation was ordinary Portland cement (CEM I 42.5) and provided from "Ankara Set Cement", Ankara, Turkey. The calcium nitrate from (Tekkim Kimya San. ve Tic.Lt.Şti.) in Turkey and super plasticizer agent from SİKA was used. Super plasticizing agent "Sikament F 05 W" was used in all mixtures. Physical and Chemical properties of cement was listed in Tables 1 and 2. Chemical properties of the calcium nitrate were listed in Table 3. Ordinary Portland cement with a specific surface of 3285cm^2/g and specific gravity of 3,17 was used for all mixtures. The cement dosage was 400kg/m^3 for all mixtures.

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/gr)	3285	-	-
Specific gravity	3.17		

Table 2 Chemical Properties of Portland Cement

	Results	TS EN 197/1 Standard data
		(max)
Heating loss (%)	2,03	5,00
Insoluble matter (%)	0,25	5,00
Cl_2 (%)	0,0102	0,10
SiO_2 (%)	20,54	-
Al_2O_3 (%)	5,12	-
Fe_2O_3 (%)	3,69	-
CaO (%)	62,98	-
MgO (%)	1,70	-
SO_3 (%)	2,88	-
Main constituent (%)		
C_3S	53,2	
C_2S	16,7	
C_3A	7,6	
C_4AF	10,7	

Table 3 Chemical Properties of Calcium Nitrate ($Ca(NO_3)_2 . 4H_2O$ %98 pure)

Chemical Properties	Approx Values
Chloride (Cl)	<= 0.05 %
Sulphate (SO_4)	<= 0.5 %
Heavy metal (Pb)	<= 0.005 %
Ferrite (Fe)	<= 0.05 %
pH	5-7
Solubility in water	1470 g/l
Melting Point	45°C

The aggregates were natural sand from Erzurum/Aşkale region. Maximum aggregate size was 16 mm. The coarse and fine aggregates were separated four different sizes fractions. Aggregates sizes 0-2, 2-4, 4-8, 8-16 mm have the specific gravity of 2.40, 2.47, 2.54 and 2.63 respectively. Super plasticizer agent was used 0.5% of cement weight at all mixtures. All materials, i.e., cement, aggregate, water, chemicals were met applicable standards for concrete making materials [11].

54 specimens were tested: 27 calcium nitrate specimens and 27 control specimens in the 2010 October program. The counter mixes were prepared in a laboratory counter-current mixer for a total of 5 min. Hand compaction was used. All specimens were casted in 100 mm diameter and 200 mm height of cylinder PVC molds. 48 specimens remained in deep freezes for 7 days with temperatures of -5, -10, -15 and -20°C. The following these times, half of the specimens for all groups were immediately were moved water curing (23±1°C). They were hold in water curing for 28 days. 3 specimens for calcium nitrate contained mix and without calcium nitrate mix were exposed only water cure for 28 days. All of the specimens were tested for compressive strength in accordance with Turkish Standard TSE 800. All mixtures were mixed according to TSE (Turkish Standard Institute). The mixture proportions for $1m^3$ concrete were listed Table 5.

Table 5 The Mixture Proportions for $1m^3$ Concrete

Materials		Control mixture	Antifreeze mixture
Ratio of admixture (%)		0	%6
w/c ratio		0.40	0.40
Cement (kg)		400	400
Calcium nitrate (kg)		_	24
Water (kg)		160	160
Super plasticizing agent (%)		0.5	0.5
Air		0.02	_
Natural Aggregate (kg)	0-2 mm	498	487
	2-4 mm	256	251
	4-8 mm	352	344
	8-16 mm	638	625

Results were compared to the control samples that stayed in lime-saturated water until 28 days. The averages of the three samples were used for each experimental result.

3. Results and discussion

The results are given in Table 6. They are evaluated and discussed below.

3.1. Workability

Workability contains ease of placing, handling, and finishing. Concrete should be workable, finishable, strong, durable, watertight, and water-resistant. These qualities can be obtained by proper design of the mix using suitable materials.

The properties of freshly mixed concrete were determined in respect of slump. The average slump of control mixes was 4 cm. The average slump flow of the calcium nitrate mixes was 6 cm, which showed reasonably good flowability. Calcium nitrate sample's slump was higher than that of control sample. The main reason of this rising is that calcium nitrate behaved as a super plasticizer and increased the workability of the concrete mix.

3.2. Compressive strength

Antifreeze admixtures force the water within the concrete to remain at least partially liquid until the temperature falls below the 'eutectic point', the temperature at which no matter how much antifreeze is added, the solution will completely freeze. The temperature of the eutectic point varies depending on which compound is used. Because some ice crystals form at temperatures above the eutectic point, the operating range for each mix is usually limited to temperatures a few degrees higher than the eutectic point [4]. The eutectic point of calcium nitrate is -16°C for 35% percent solution.

Cold weather places serious constraints on concrete construction. As temperatures drop, concrete sets more slowly, takes longer to finish, and gains strength less rapidly. What's needed is a concrete that can be placed and cured in subfreezing weather without thermal protection. The goal in proportioning mixtures for cold weather is to achieve a concrete that cures rapidly. That is, one that sets more quickly and gains strength more rapidly than it ordinarily would [12].

Table 6 shows the effect of calcium nitrate as an antifreeze admixture on the compressive strength of concrete. The mixes tested at four temperature levels and plus water curing to investigate compressive strength. Three samples for each group were casted and these samples were immediately placed to the deep freezers. S2 and C2 mixes cured at various temperatures (-5, -10, -15 and -20°C) for 7 days in deep freezers and then at water curing (23±1°C) for 28 days. Furthermore S3 and C3 mixes were casted and cured only water cured for 28 days.

Table 6 Compressive Strength Test Results

Temperature (°C)	7 days freezer cure		7 days freezer cure + 28 days water cure		Only 28 days water cure	
	S1*	C1*	S2*	C2*	S3*	C3*
-5	31.45	7.92	38.69	26.18	46.57	51.40
-10	18.23	7.81	36.71	17.85		
-15	17.33	6.57	40.56	27.03		
-20	15.53	7.92	37.27	27.30		

S1*: denotes samples contain 6% calcium nitrate and 7 days stored in deepfreeze, C1*: denotes control samples 7 days stored in deepfreeze, S2*: denotes samples contain 6% calcium nitrate and 7 days stored in deepfreeze+28 days in water curing, C2*: denotes control samples 7 days stored in deepfreeze +28 days in water curing, S3*: denotes samples contain 6% calcium nitrate 28 days in water curing, C3*: denotes control samples 28 days in water curing.

3.2.a. Compressive strength after 7 days freezer cure

Compressive strength of various concrete mixtures is given in Table 6. The compressive strengths of S1 samples were in the range of 15.53–31.45 MPa, for -5, -10, -15, -20°C freezer temperatures. Compressive strengths of control samples' were between 6.57-7.92 MPa for the same temperature range.

Use of calcium nitrate increased compressive strength of samples for all temperatures. Adding 6% calcium nitrate caused an increment in the compressive strength of about 297, 133, 163, 96% for -5, -10, -15, -20°C freezer temperatures, respectively.

According to only 28 days water cured samples, the best compressive strength gained as 31.45 MPa at -5°C. This strength was 68 and 61% of S3 sample and C3 sample, respectively. C1 sample at -5°C was gained 15% of the 28 days compressive strength of C3 sample at 7 days. This result is very low, according to calcium nitrate sample for the same temperature. The calcium nitrate sample's compressive strength was 61% of those 28 days only water cured sample.

C1 samples were showed approximately the same compressive strength at all range of the freezing temperatures. These compressive strengths were changed between 6.57 and 7.92 MPa. The maximum compressive strength was observed at -15°C for calcium nitrate contained samples and was 31.45 MPa. The main factor to design the strength of concrete is commonly the 28 days compressive strength [11]. With this guidance; calcium nitrate showed very good performance at all level of below freezing temperatures they exposed. However, calcium nitrate contained samples at temperatures below -5°C without water curing is not enough for cold weather concreting. For example; calcium nitrate samples obtained 31.45, 18.23, 17.33 and 15.53 MPa compressive strength for -5, -10, -15, -20°C, respectively.

Table 6 shows effects of temperature and curing time on the strength gaining of antifreeze concrete. At these range of temperatures and times, antifreeze concrete was gained resistant to freezing for winter concreting.

3.2.b. Compressive strength after 7 days freezer cure and 28 days water cure

After 7 days freezer cure, the relative strength increment by 28 days water curing for S3 samples were 23, 101, 134 and 140% for -5, -10, -15, -20°C according to 7 days only freezer cured S1 samples, respectively.

S2 samples' compressive strengths were between 36.71–40.56 MPa, for -5, -10, -15, -20°C freezer temperatures. For the same temperatures range compressive strengths of control samples' were between 17.85-27.30 MPa.

The highest compressive strength was 40.56 MPa at -15°C for S2 samples according to all groups, except S3 and C3 samples.

C2 samples without calcium nitrate gained between 35-53% of compressive strength of 28 days when compared to the C3 sample. For the same C3 sample group, S2 samples' values are between 71-79%.

The compressive strengths of S2 samples were 79 and 87% of compressive strengths of S3 samples. The difference of compressive strength results between 7 days only freezer cured and plus 28 days water cured samples can be seen on Table 6.

It was clear that only freezer curing is not enough for strength development of concrete. To gain high level of compressive strength results, water curing is necessary.

4. Conclusions

Calcium nitrate was improved the workability of concrete. Compressive strengths of 7 days only freezer cured and plus 28 days water cured concrete samples were increased with calcium nitrate usage. The maximum result for 7 days only freezer cured samples was observed for calcium nitrate contained sample at -5°C. This result was 68 and 61% of S3 sample and C3 samples, respectively. The best result according to 28 days only water cured samples was gained at -5°C for 7 days freezer cured plus 28 days water cured calcium nitrate sample as 40.56 MPa. Both 28 days water curing and calcium nitrate usage increased compressive strength of 7 days freezer cured samples. It can be said that calcium nitrate can be used as an antifreeze admixture in concrete, according to test results.

5. Acknowledgments

This research was supported by the research project "The effect of antifreeze admixtures on the properties of concrete casted in cold weather" (BAP Code: 2009/271) from the Atatürk University, Scientific Research Projects (BAP) Program in Erzurum, Turkey.

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