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CALCIUM NITRITE EFFECT ON SETTING OF CEMENT AT VARIOUS TEMPERATURES

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ABSTRACT

Calcium Nitrite, which is used as corrosion inhibitor, accelerates stiffening rates of cement. This paper deals with the effect of calcium nitrate on setting times of cement pastes at various curing temperatures. Four pastes were used to study the effect of two dosages of calcium nitrate as well as the effect of an additional set-retarding superplasticiser on rates of hardening at 25, 35 and 50°C. The results indicated significant acceleration in setting as a result of either calcium nitrite addition or higher curing temperatures. The combined effect of calcium nitrite and high curing temperatures was very significant. Setting times were reduced by over 80% when comparing paste containing calcium nitrite at 50°C to plain cement paste at 25°C.

INTRODUCTION

Corrosion of steel in concrete is one of the fastest growing problems facing concrete industry worldwide[1,2]. Billions of dollars are spent annually to repair concrete structures damaged by corrosion of the reinforcement. To minimize such problem, various systems and/or materials have been developed. Epoxy coated rebars [3], High durability concrete by aid of low w/c or pozzolans [4], and corrosion inhibiting materials [5-9] are only few methods of many others used to combat corrosion.

Corrosion Inhibitor is defined by ACI 116R-85 as "a chemical compound, either liquid or powder, that effectively decreases corrosion of steel reinforcement before being embedded in concrete, or in hardened concrete if introduced, usually in very small concentrations, as admixture". Calcium nitrite is one of those corrosion inhibitors. It is an inorganic material that reacts with ferrous ions from the rebar to strengthen the passive film on the surface of reinforcement [1].

Calcium nitrite (as a corrosion inhibitor) has been recommended for use in concrete in certain aggressive environments [10]. Although concrete itself provides good physical and chemical protection against corrosion, corrosion still takes place as a result of chlorides ingress, carbonation and moisture penetration. Berke and others [11] showed that corrosion was delayed significantly with the addition of Calcium nitrite. This effect was improved further as the dose of calcium nitrite increased [11].

The climate of the UAE is classified as hot. It is accustomed for maximum daily temperature to exceed 45°C for many months of the year. High temperatures accelerate setting of cement [12]. Various set-retarding materials are used to control such acceleration. The inclusion of calcium nitrite in such environment, should however, be dealt with caution since itself is an accelerator. According to Berke [13] calcium nitrite meets ASTM C494 specification as an accelerator. They showed that calcium nitrite accelerates setting, and the higher the dose the greater the accelerated effect [13].

Initial and final setting times are reduced significantly as curing temperatures increase [12]. This accelerated trend in setting times is also observed with mixes containing set-retarding admixtures. In fact the effectiveness of set-retarding admixtures was lowered as curing temperature increased.

The use of calcium nitrite in cold regions or in cold seasons may result in beneficial effects as far as setting rate is concerned. The use however of such material in regions of high ambient temperatures should be carefully evaluated. The current paper investigates the effect of calcium nitrite on setting time of cement paste at various temperatures similar to what can be found in hot-climate countries.

EXPERIMENTAL DETAILS

Materials

Normal Portland Cement (NPC) used was conforming to BS 12:1995. Calcium nitrite was obtained from WR Grace Ltd. and is given the symbol DCI-S as reported by the British Board of Agre'ment (BBA)[14]. BBA described it as being aqueous solution of calcium nitrite (30% ± 2%) with residual calcium nitrate (up to a maximum of 3%). DCI-S contained additionally calcium naphthalene sulphonate formaldehyde copolymer superplasticiser to offset the acceleration of set normal with calcium nitrate corrosion inhibitors. The specific gravity of the DCI-S at 20°C is 1.27-1.30.

In an attempt to offset the acceleration effect of temperature on setting, an additional set-retarding superplasticiser was used. It was naphthalene-based superplasticiser with mild retardation effect based on modified lignosulfonates and polyoxycarbon acids and conformed to ASTM C494-80 types A, B and D (chloride free).

Details of Mixes

Four cement pastes were prepared, for the purpose of measuring setting times using NPC, water, calcium nitrite, and superplasticiser as shown in Table.1.

Table 1. Mix Proportions

Mix	NPC	W	DCI	SP	Comments
1	400g	28%	-	-	control
2	400g	24.5%	10 ml	-	DCI equivalent to 2.5 liters/100 kg of NPC
3	400g	21.5%	20 ml	-	DCI equivalent to 5 liters/100 kg of NPC
4	400g	17.75%	10 ml	8 ml	DCI equivalent to 2.5 liters/100 kg of NPC, SP = 2 liters/100 kg

The first mix contained no DCI-S or SP , and was considered to be the control mix. Two doses of DCI-S were used; one equivalent to 7.5-10 liters/m^3 of concrete (300-400 kg of NPC per cubic meter of concrete) whereas the second dose was double this amount (15-20 liters/m^3). Such doses were inline with the recommendation outlined by the manufacturer. In the forth mix (DCI-S dosage similar to mix 2), an additional dose of superplasticiser was included which was equivalent to 6-8 liters/m^3 of concrete to combat the acceleration effect of temperature and DCI-S on setting.

Setting times was measured using Vicat apparatus following the procedure outlined in BS1881. Three curing temperatures were simulated as follows: 25°C+2°C, 35°C+1°C, and 50°C+ 1°C. The first one was normal laboratory environment whereas the other two were obtained using temperature-controlled chambers.

RESULTS AND DISCUSSIONS

Increasing curing temperature reduced setting times for all cement mixes, see Fig. 1a and b. This effect was maximum for plain NPC paste where setting times were reduced by about 60% as temperature increased from 25°C to 50°C. Setting times of pastes containing DCI-S and/or superplasticiser were also reduced significantly in a similar manner.

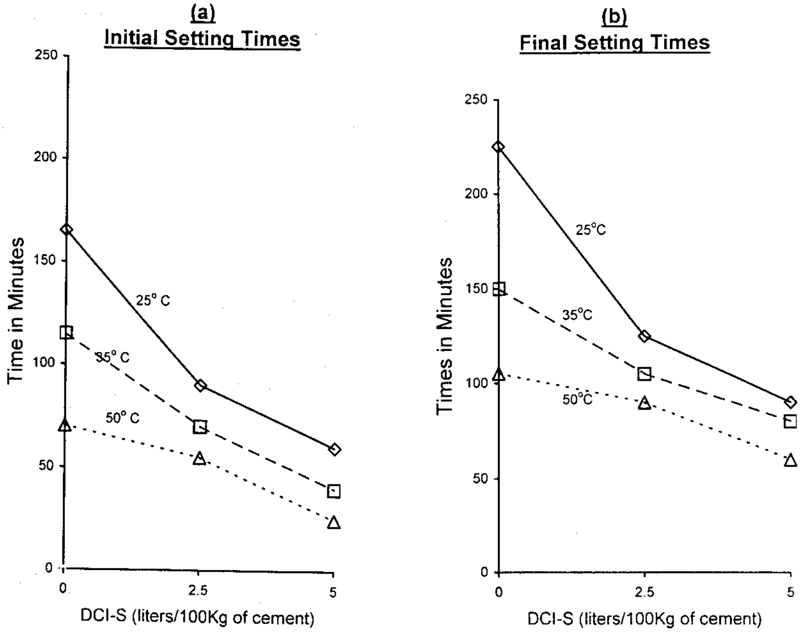
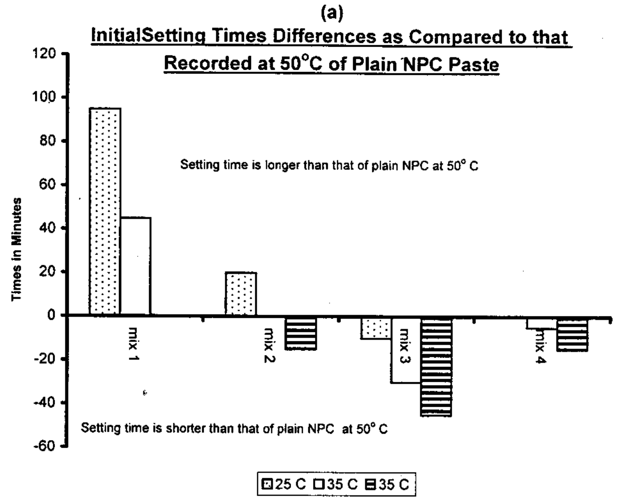


Fig. 1. Calcium nitrate influence on setting times of pastes at different curing temperatures.

Despite the fact that the Calcium nitrite used in the current study included superplasticiser (DCI-S), an acceleration effect was observed for both DCI-S doses at all curing temperatures. In the case of the addition of 2.5 liters/100 kg of cement (paste 1) initial and final setting times were reduced by about 40% at 25 ° C and 35 ° C, and by about 20% at 50° C, see Fig. 1. Doubling the dose of DCI-S to 5 liters/ 100 kg of cement increased the acceleration effect even further. Initial setting times for paste 3 were reduced by about 65% when compared to paste 1 at all curing temperatures. Final setting times were also reduced in a similar manner to that of initial setting time but to a lesser degree.

To minimize the acceleration effects observed using DCI-S at all curing temperatures, a set-retarding superplasticiser was added (paste 4 opposed to paste 2). The overall trend of the results indicates that such admixture was successful in retarding initial setting at all curing temperatures, see Fig. 2a. As far as final setting times is concerned (Fig 2b), the addition of the set-retarding superplasticiser resulted in delaying setting times at 25°C only. The effect on final setting times for samples stores at the other 2 curing temperatures was actually reversed.



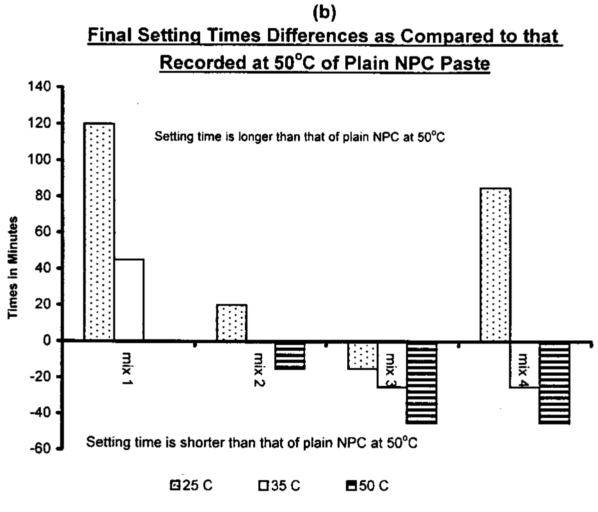


Fig. 2. Setting time differences as compared to results recorded for plain NPC at 50^{0}C

Furthermore, the results also show that the set-retarding superplasticiser was clearly effective at normal curing temperatures only. At higher temperatures, such effectiveness is significantly reduced. This phenomena was also recorded in earlier works [12].

Tables 2 and 3 illustrate the combined effect of DCI-S and temperatures on both setting times respectively. Significant reductions in setting times were found when comparing the results of pastes including DCI-S at 35° C and 50° C to those of plain NPC. For example, initial and final setting times for paste 2 were reduced by about 60% at 35°C and 50°C as opposed to NPC at 25°C. Increasing the dose of DCI-S (paste 3) resulted in further reductions; between 75% and 85%.

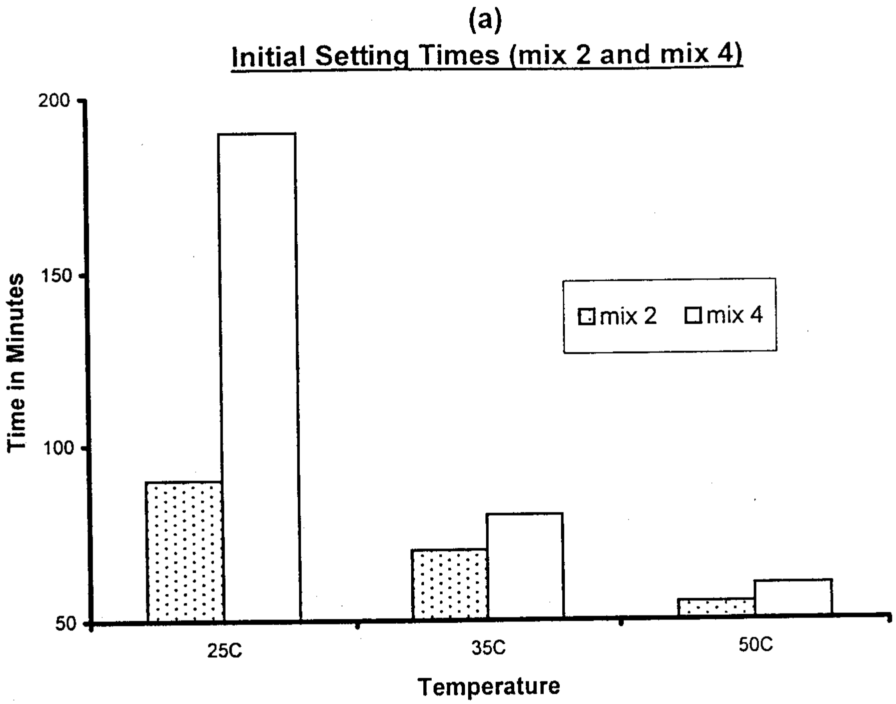
Table 2. Initial Setting Times(% of control, plain NPC at 25°C)

	25°C	35°C	50°C
Paste 1	100	69.7	42.42
Paste 2	54.5	42.42	33.33
Paste 3	36.4	24.24	15.15
Paste 4	42.42	39.39	33.33

Table 3: Final Setting Times(% of control, plain NPC at 25oC)

	25°C	35°C	50°C
Paste 1	100	66.67	46.67
Paste 2	55.6	46.67	40
Paste 3	40	35.56	26.67
Paste 4	84.4	35.56	26.67

In an attempt to simulate a practical environment condition at which concrete usually cast in UAE, 35° C is chosen to be the target. Fig 3a, illustrates that initial setting time at 25°C for plain NPC was never reach by the other mixes at all curing temperatures. This shows that the effect of 2.5 and 5 liters/100 kg of cement was greater than influences of increasing temperature from 25°C to 35°C for NPC. Final setting time (Fig 3b) shows similar trend with the exception of mix 4, which included a set-retarding superplasticiser at 25°C.



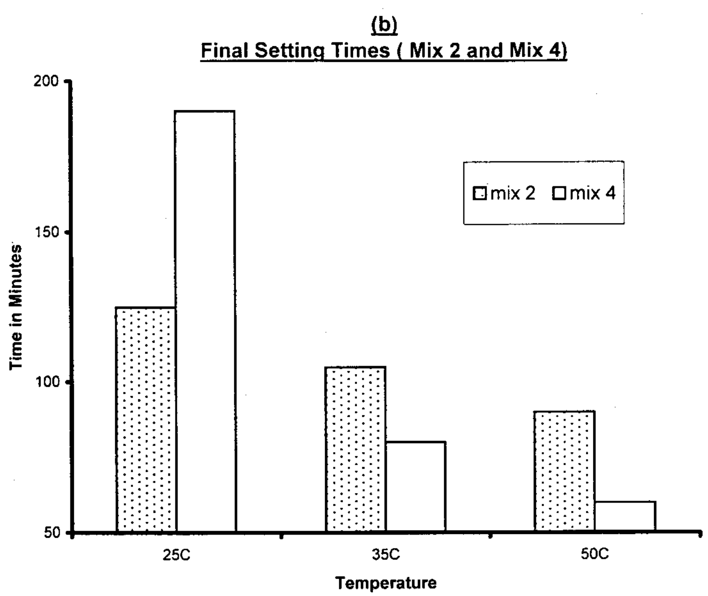


Fig. 3. Effects of set-retarding superplasticiser on setting times.

CONCLUSION

Based on the preceding results and discussion, the following remarks can be made:

Calcium Nitrate accelerates setting significantly despite the use of additional set-retarding admixtures. At high ambient curing temperatures, mixes containing calcium nitrate showed an extremely accelerated setting effects. These results emphasis the need for controlled concreting practices when dealing with DCI-S in hot climates.

The performance of the set-retarding superplasticiser was reduced at high curing temperatures.

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