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TECHNICAL CALCIUM NITRATE AS SET ACCELERATOR FOR CEMENT AT LOW TEMPERATURES

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ABSTRACT

The objective was to test the efficiency of technical calcium nitrate (CN) as a set accelerator for different cements at low temperatures (5-7°C). The applied dosages were 0.00, 1.55, 2.32, 3.10, 3.86 and 7.73 % CN of the cement weight, corresponding to 0.00, 1.00, 1.50, 2.00, 2.50 and 5.00 % NO_3^-, respectively. Five different portland cements were chosen covering a wide range in C_3A contents, since it was initially believed that the set regulating mechanism involved C_3A (i.e. the efficiency depend on the C_3A content). The setting characteristics of the cement pastes with w/c = 0.40 were determined by an automatic Vicat-needle apparatus in a room with an ambient temperature of 5-7°C. The results revealed that the set accelerating efficiency of CN depended very much on the cement type. However, no correlation with the C_3A content was found. On the other hand, the set accelerator efficiency of CN seems to increase with increasing belite content according to the Bogue analyses of the cements, or other cement characteristica promoting belite formation in the clinker process.

Introduction

The growing concern about chloride-induced corrosion of reinforcing bars embedded in portland cement concrete has led to the development of a number of chloride-free admixtures. Particular attention has been given to the formulation of chloride-free set accelerating admixtures to replace the widely used calcium chloride accelerator.

Dodson (1) has given a review of non-chloride, non-corrosive set accelerating salts; Dodson began research on such salts in 1962 and found calcium formate, $Ca(CHO_2)_2$, to meet all these requirements (2). The second salt to fulfill the requirements was calcium nitrite, $Ca(NO_2)_2$, which was introduced in 1968 and patented in 1969 (3). It was not until 1979, after 5 years of intensive research, that is was determined that calcium nitrite was also a very effective corrosion inhibitor for metals embedded in concrete. Calcium nitrate, $Ca(NO_3)_2$, was proposed as a basic component of a set accelerating admixture, in conjunction with triethanolamine, in 1981 (4). However, no claims were made by the developers that the admixture would inhibit corrosion. The most recent non-chloride, non-corrosive set accelerating salt to be introduced to the concrete market was thiocyanates (salts of SCN^-) (5). Like the nitrate, the thiocyanates should be accompanied by an alkanolamine in order to attain the desired end results. The combination of the thiocyanate salts with those of nitric acid and alkanolamine was patented in 1984 (6). Triethanolamine itself accelerates the reaction between C_3A and gypsum (7), and at dosages of 0.1 and 0.5 % of the cement weight, setting occurs rapidly within about 2-6 min.

Abdelrazig et al (8) compared the accelerators calcium chloride, calcium nitrate and sodium thiocyanate. Their laboratory results agreed with knowledge from site practice; calcium chloride being effective at all ages, calcium nitrate at early ages and sodium thiocyanate at later ages.

Rettvin and Masdal (9) showed that additions of 50 % technical calcium nitrate solution (ammonium free) to concrete gave a set acceleration proportional with the dosage up to 0.50 % of the cement weight. They also described the utilization of calcium nitrate to secure the slip forming rate during the construction of the shafts for the Troll Gravity Based Structure (369 m height) placed in the North Sea.

Less commonly applied salts like thiosulphates ($S_2O_3^{2-}$ salts) have been shown to accelerate the setting of cements. The calcium salt, CaS_2O_3 (10), increased the 1 day strength, while the sodium salt, $Na_2S_2O_3$ (11), decreased the strength slightly. The naturally occuring mineral Spodumene, $LiAlSiO_6$, was found (12) to be an excellent accelerator of set and an enhancer of early compressive strength. The same investigators found (13) that the use of lithium oxalate, $Li_2C_2O_4$, would perform in essential the same way.

The effects of the more common alkali carbonates (i.e. Li_2CO_3, Na_2CO_3 and K_2CO_3) on setting times and strength of cements were studied by Valenti and Sabatelli (14). Sodium and potassium carbonates retarded the setting at lower dosages, but accelerated the setting and increased the 28 days compressive strength at dosages higher than 0.1 %. Lithium carbonate, on the other hand, acted as a set accelerator at all concentrations studied (14).

In addition, alkali silicates and aluminates are well known "flash" setting accelerators used for shotcreting, but this is not the topic here. Furthermore, due to potential alkali aggregate reactions (AAR), the content of alkalies (except for lithium) in all concrete admixtures should be minimized. AAR was considered non-existing in Norway for many years, until a thorough study (15) showed slowly reacting aggregates. Thus, calcium based admixtures are preferred.

In 1992, a thorough study was initiated by the fact that technical CN, a complex nitrate salt based on calcium and ammonium with some crystal water, is used as an admixture for concrete in some countries. So far the results of CN additions on the setting characteristics of cement, on the compressive strength of concrete, on the chloride induced corrosion of steel and on the freezing and thawing resistance of concrete has been published as reports (16, 17, 18), with the exception of a few papers reporting on the influence of CN additions on the setting of cements at 20°C (19), the chloride initiated corrosion of steel embedded in mortars with and without CN additions

(20) and the effect CN additions have on the setting characteristics of different French portland cements at low (5°C) and normal (20°C) temperatures (21).

The present publication reports on the effect CN additions might have on the setting characteristics of different cements at low temperatures (5-7°C). The higher dosages tested may not be relevant for set acceleration, but was included since it was found (20) that CN is an effective anodic corrosion inhibitor.

Since some literature sources suggest that nitrates may form a complex salt with the aluminate phase in cement, it was initially assumed that the accelerating effect, if any, was dependent on the aluminate content of the cement. Thus, portland cements with different aluminate content were selected. However, during the study, it was shown by X-ray diffraction that ettringite was stable in sealed cured cement pastes with a high dosage of CN (5.6 % of the cement weight), and that it was not possible to detect any reflections arising from the calcium-aluminate-nitrate compound, $Ca_3Al_2O_6 \cdot Ca(NO_3)_2 \cdot 10H_2O$. The X-ray diffraction study is excluded from the present publication, but is discussed in detail elsewhere (16,19).

Experimental

Components

Technical calcium nitrate (CN) may in general be written as $xNH_4NO_3 \cdot yCa(NO_3)_2 \cdot zH_2O$. The CN used in the present work had x = 0.092, y = 0.500 and z = 0.826, or in other words 19.00 % Ca^{2+}, 1.57 % NH_4^+, 64.68 % NO_3^- and 14.10 % H_2O. In addition, the CN contained < 0.1 ppm Cd, about 2 ppm Mn, < 0.5 ppm Pb and < 0.5 ppm Zn (heavy metal salts may in small concentration retard the cement hydration significantly). The technical CN was delivered by Norsk Hydro A/S, Porsgrunn, Norway.

The technical calcium nitrate was added to cement pastes with w/c = 0.40 based on five different portland cements with decreasing calcium aluminate, C_3A, content; P30 (normal type produced until 1993), P30'93 (replacing P30 from 1993), P30-4A (high strength type produced until 1993), HS65 (replacing P30-4A from 1993), and SR (sulphate resistant type). The cement analyses are given in Table 1. The specific surfaces (Blaine) were 290, 358, 407, 418 and 290 m^2/kg for the P30, P30'93, P30-4A, HS65 and SR cements, respectively. The cements and their analyses were all obtained from Norcem A/S, Brevik, Norway.

Vicat needle method

The setting of the cement pastes was registrated by an automated Vicat apparatus of the type RMU (Resistenze Macchine Unificate), produced by L. Giazzi, Bergamo, Italy. This apparatus is capable of measuring the setting of 4 independent cement pastes simultaneously. The setting is registered by penetrating a needle of a fixed cross-section and with a constant force into the cement paste. The needle was pressed into the cement paste every 10 minutes, while the containers for the cement paste did rotate in a manner preventing the needle to hit the same hole twice. The initial setting time is determined to be when a full depth intrusion of the needle is not obtainable, while the final setting time is taken when the needle no longer penetrates the cement paste at all. The method comply with the code ASTM C 191-82, but the w/c was kept constant to 0.40 rather than to let it vary to obtain normal consistancy for the different cement pastes.

TABLE 1
Chemical Analyses of Oxides and Minerals (%) of Cements.

Cement types	P30	P30'93	P30-4A	HS65	SR
Oxides					
CaO (C)	63.56	63.44	64.60	64.32	64.62
SiO_2 (S)	20.31	20.92	22.27	22.13	21.98
Fe_2O_3 (F)	3.52	3.54	3.29	3.39	4.88
Al_2O_3 (A)	5.02	4.60	4.05	4.05	3.48
SO_3 (S)	2.88	3.06	2.52	3.07	2.18
MgO (M)	2.34	1.80	1.47	1.03	1.45
Na_2O (N)	0.39	0.36	0.20	0.23	0.20
K_2O (K)	1.18	0.88	0.60	0.42	0.56
Free lime	1.87	-	1.26	-	0.73
Minerals (Bogue)					
C_3S, alite	57	55	55	53	60
C_2S, belite	15	19	23	24	18
C_4AF, ferrite	10.7	10.8	10.0	10.3	14.9
C_3A, aluminate	7.4	6.2	5.2	5.0	1.0

Results and discussion

The object was to document the set accelerating effect CN might have on the hydration of cement at a typical winter temperature of +5 to +7°C.

The Vicat needle penetration profiles for the cement pastes (w/c = 0.40) based on P30, P30-4A and SR cements with CN dosages of 0.00, 1.55, 3.86 and 7.73 % of the cement weights (corresponding to 0.00, 1.00, 2.50 and 5.00 % NO_3^-, respectively) at 7°C are shown in Figures 1, 2 and 3, respectively. Analogouse profiles for the P30'93 and HS65 cement pastes (w/c = 0.40) with CN dosages of 0.00, 1.55, 2.32 and 3.10 % (corresponding to 0.00, 1.00, 1.50 and 2.00 % NO_3^-, respectively) at 5°C are depicted in Figures 4 and 5, respectively. The CN dosage range was reduced for the two latter cements in order to cover a more practical range.

Figures 1-5 reveal that the effect of CN on the setting time for cement paste is strongly dependent of the cement type at low temperatures and that there is no proportionality with the C_3A content of the cements (see Table 1), and thereby confirming the analogouse results obtained at 20°C (19).

CN has a moderately accelerating effect on the setting time of P30 cement at 7°C until a dosage of 3.86 %; 1 h 30 min (22 %) earlier initial set and 40 min (5 %) earlier final set when 1.55 % CN is added, and 2 h 30 min (37 %) earlier initial set and 2 h (15 %) earlier final set when 3.86% CN is added. A dosage of 7.73 % CN, on the other hand, retards the cement hydration; 1 h 20 min (20 %) later initial setting time and 50 min (6 %) later final setting time. Thus, the optimum accelerator dosage (among those tested) for P30 cement is 3.86 %. The initial setting

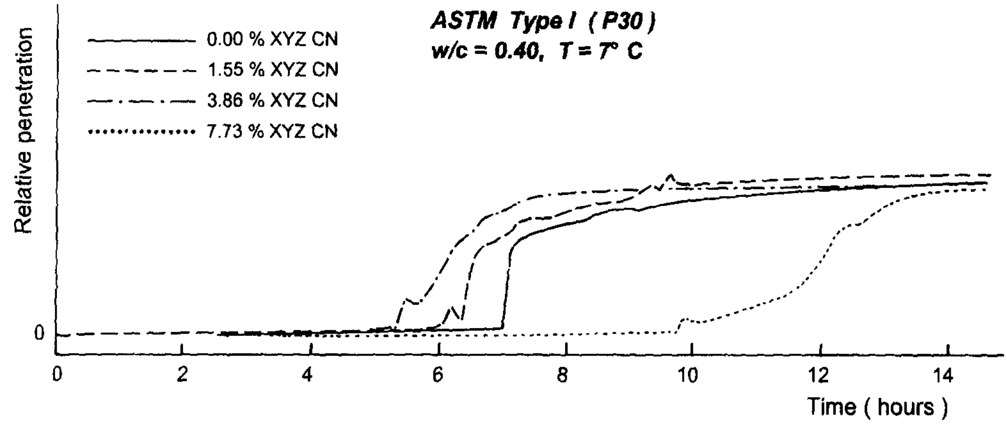

Figure 1. The penetration profiles for P30 cement with different dosages of CN at 7°C.

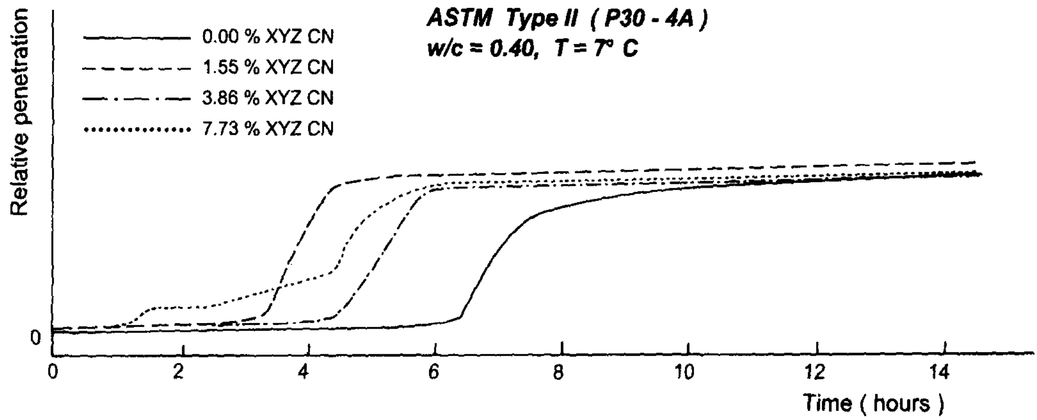

Figure 2. The penetration profiles for P30-4A cement with different dosages of CN at 7°C.

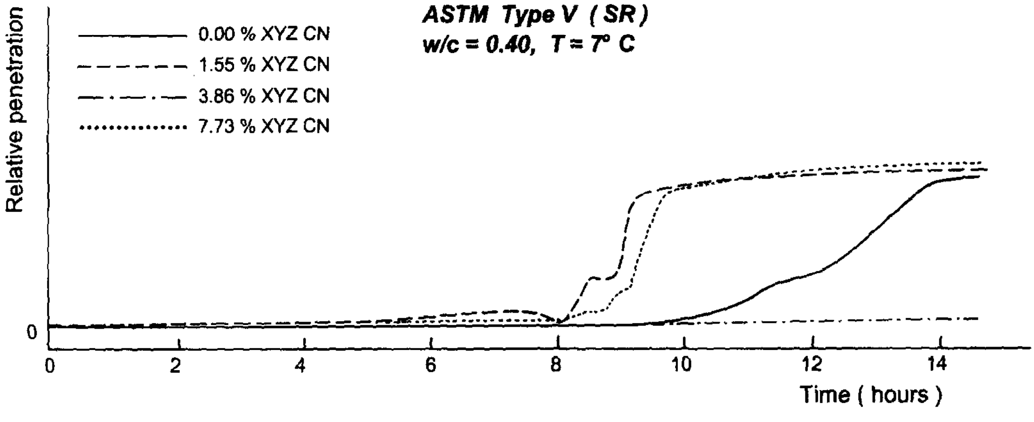

Figure 3. The penetration profiles for SR cement with different dosages of CN at 7°C.

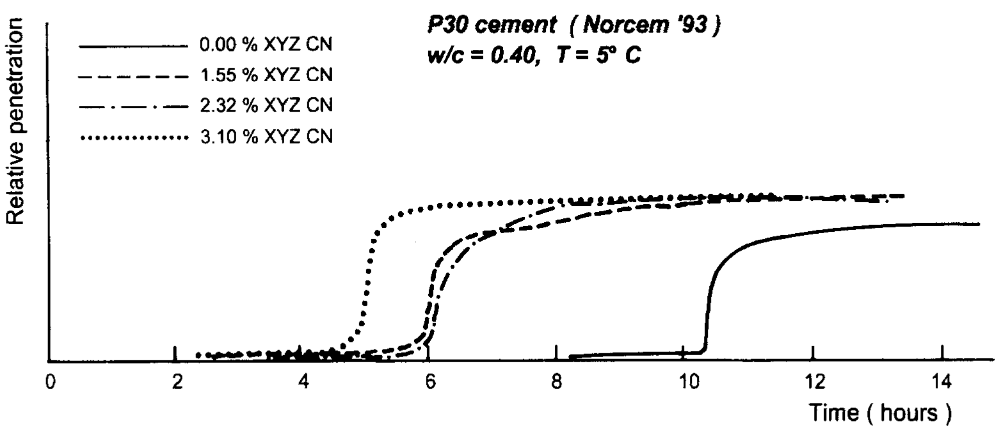

Figure 4. The penetration profiles for P30'93 cement with different dosages of CN at 5°C.

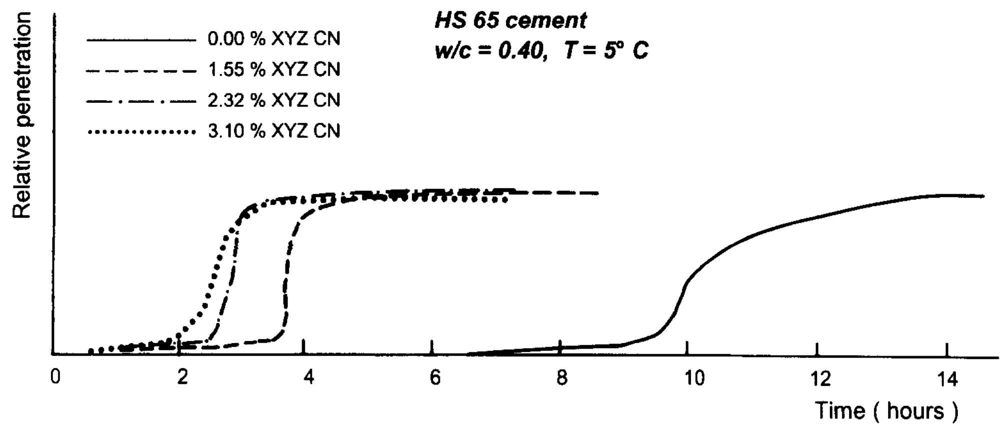

Figure 5. The penetration profiles for HS65 cement with different dosages of CN at 5°C.

seems slightly more accelerated at 7°C than 20°C (19), while the change in the final setting time is of the same order. Note that a dosage of 7.73 % CN had a slightly accelerating effect at 20°C (19), compared to the retarding effect at 7°C.

CN is a powerful setting accelerator for P30-4A cement at 7°C (and at 20°C (19)), but the change in setting time with CN dosage is somewhat complex; the initial & final setting times are reduced by 3 h 10 min (58 %) & 7 h 5 min (50 %), 2 h 20 min (42 %) & 4 h 5 min (29 %) and 5 h (91 %) & 4 h 45 min (33 %) for the dosages 1.55, 3.86 and 7.73 % of the cement weight, respectively. The optimum accelerating dosage for P30-4A cement at 7°C seems to be 1.55 % CN when the difference in time between initial and final set is considered. However, an even lower dosage may be more cost efficient. Note that the optimum accelerator dosage for P30-4A at 20°C was 3.86 % (19), which was the least effective dosage within the test serie at 7°C.

CN works as a setting accelerator for SR cement at 7°C when the dosage is 1.55 and 7.73 % of the cement weight, while a dosage of 3.86 % retards the cement hydration; the reductions of initial setting time for CN dosages of 1.55, 3.86 and 7.73 % are 4 h 10 min (45 %), > - 5h 20 min (> -57 %) and 1 h 40 min (18 %), respectively. Note that a negative sign for the 3.86 % dosage imply a retardation of the setting. Only changes in the initial setting time are discussed, since the final setting of the plain cement paste exceeded the recording time. An analogous behaviour for the three CN dosages was measured for the SR cement at 20°C as well (19).

An isothermal calorimetry study of the three preceding cements at 20°C with CN dosages 0.00, 0.39, 0.77, 1.55 and 2.32 % of the cement weight (16,19) revealed a linear correlation between the generated heat the first 5 h and the dosage of CN, proving that an exothermal reaction occur. Furthermore, the slope of the line from linear regression analyses was directly proportional with the efficiency of CN as a set accelerator for the different cements; P30 < SR < P30-4A. An analogous study was carried out for five French cements at 5°C with CN dosages 0.00, 1.55, 3.86 and 7.73 % of the cement weight (17,21). A linear correlation between the generated heat the first 5 h and CN dosage was found for these cements as well, with the exception of the highest dosage that had to be excluded from the linear regression analyses (i.e. more CN than what could take part in the exothermal reaction). Again it was proven that the energy evolved by the initial exothermal reaction pr % CN added (i.e. the slope) was directly proportional to the set accelerating efficiency for the different cements as determined by Vicat-measurements.

The results in Figures 4 and 5 reveal that a dosage of 1.55, 2.32 and 3.10 % CN reduces the initial set relative to control (final set out of scale) by 51, 46 and 59 %, respectively, for the P30'93 cement and reduces the initial & final set by 70 & 62, 76 & 69 and 83 & 72 %, respectively, for the HS65 cement.

The CN is more effective in set accelerating the HS65 cement than the P30'93 cement, and the effect increases with increasing dosage for both cements, with the exception of 2.32 and 1.55 % CN added to P30'93 cement paste where the initial set is slightly higher for the higher dosage. However, inspecting the penetration profile in Fig. 4 reveals that the steep slope indicating the rapid transition from plastic to rigid state occurs at about the same time and that the final set occurs earlier for the highest dosage. In fact, initial set may sometimes be difficult to define since a penetration depth very slightly different from base line may persist for some time before the large differences are registered. This might be due to separation of the cement slurry when the applied w/c of 0.40 is much higher than the w/c of normal consistency (about 0.27).

Comparing the setting times obtained for the P30, P30-4A and SR cements at 7°C with those for the same cements at 20°C (19), the optimum CN dosage seems to depend on the temperature as well as the cement type. Even though the mechanism of the accelerating process is not known yet (see (16) for a thorough discussion), the supersaturation and subsequent crystallization of calcium hydroxide, $Ca(OH)_2$, and/or depression of sulphate solubility due to the high calcium concentration (i.e. slower growth of ettringite on the surface of the cement grains) may be involved. Thus, it may be worthwhile noting that the solubility of calcium hydroxide decreases with increasing temperature (an anomali); 1.85, 1.15, 0.92, 0.80 and 0.59 g/l at 0, 21, 50, 70 and 90°C, respectively.

The dependency of accelerator efficiency on the Portland cement composition is well known. Calcium formate is for instance an efficient accelerator when the ratio C_3A to SO_3 is greater than 4 (22). Smith (23) compared the effect of the two non-chloride accelerators sodium thiocyanate and calcium nitrate on the setting characteristics of two different Portland cement mortars with the accelerator calcium chloride, and found that any one of the three accelerators may be more effective with one cement than with another cement having similar setting characteristics without accelerators. Smith (23) also drew the general conclusion that the three accelerators; calcium chloride, calcium nitrate and sodium thiocyanate, were more effective at 4°C than 21°C.

According to the mineral composition of the different cements in Table 1, the content of belite, C_2S, increases in the order P30 (15 %) < SR (18 %) < P30'93 (19 %) < P30-4A (23 %) < HS65 (24 %). This is the same order as the relative reduction in initial set with a constant (1.55 %) dosage of CN; P30 (22 %) < SR (45 %) < P30'93 (51 %) < P30-4A (58 %) < HS65 (70 %). The same correlation was confirmed in a similar investigation of five French cements (17,21). However, since belite is generally believed to be a slowly reacting mineral, it might be that the CN efficiency is governed by other cement characteristica promoting ß-C_2S formation in the clinker process.

Conclusions

CN does function as a set accelerator for cement at both 7 and 20°C.

The efficiency of the CN as a set accelerator is strongly dependent of the cement type.

The set accelerator efficiency of CN seems to increase with increasing belite content according to the Bogue analyses of the cements, or other cement characteristica promoting belite formation in the clinker process.

An initial hypothesis for the accelerating mechanism, based on the interaction between nitrates and the aluminate phase (C_3A), has been disproved.

The optimum dosage of accelerator may depend on the ambient temperature.

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