

TECHNICAL NITRATE AS SET ACCELERATOR FOR CEMENT



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Abstract

The objective was to test the efficiency of technical nitrate (CN) as a set accelerator for different cements. Technical nitrate, $x\text{NH}_4\text{NO}_3 \cdot y\text{Ca}(\text{NO}_3)_2 \cdot z\text{H}_2\text{O}$ with $x = 0.092$, $y = 0.500$ and $z = 0.826$, was used as set accelerator. The applied dosages were 0.39, 0.77, 1.55, 2.32, 3.87 and 7.73 % of the cement weight, corresponding to 0.25, 0.50, 1.00, 1.50, 2.50 and 5.00 NO_3^- , respectively. Three different cements; ASTM type I (P30), ASTM type II (P30-4A) and ASTM type V (SR), were chosen since it was believed that the set regulating mechanism involved the C_3A (i.e. the efficiency depend on the C_3A content). The set accelerating efficiency of the technical nitrate was very dependent on the cement type. However, no correlation with the C_3A content was found.

Key words: Set, Accelerator, Cement, Nitrate

1. INTRODUCTION

The reason for this study was the fact that CN, a complex nitrate salt based on calcium and ammonium with some crystal water, is used as an admixture for concrete in some countries.

The objective was to document the accelerating (set or hardening) effect CN might have on the hydration of cement. The main methods chosen for cement pastes were Vicat-needle (standardized method for setting time) and isothermal heat flow calorimetry (setting time and hardening rate).

Since it is known from literature that nitrates may form a complex salt with the aluminate phase in cement, it was initially assumed that the accelerating effect, if any, is dependent on the aluminate content of the cement. Thus, three cements with different aluminate content were selected, fulfilling the criteria for ASTM type I (ordinary Portland cement), ASTM type II (moderately sulphate resistant) and ASTM type V (sulphate resistant). In order to further elucidate the mechanism of CN action on cement hydration, the experiments were supplied with X-ray diffraction (crystalline phases) and pore solution chemistry.

2. PRINCIPLE OF ADMIXTURES AFFECTING CEMENT HYDRATION

There are four basic types of admixtures affecting the cement hydration; set accelerator, set retarder, hardening accelerator and hardening retarder.

The best way of understanding the effect of admixtures on cement hydration is to consider the rate of heat evolution from isothermal calorimetry vs time, as revealed in Fig. 1 //.

The initial heat evolution within the first hour is partly due to the dissolution of calcium and hydroxide ions from C_3S leaving behind a silica rich surface, hydration of free lime, dissolution of free alkalis and sulphates, but perhaps more important due to the reactivity of C_3A .

If sulphates were not present, C_3A would have hydrated so fast that the cement paste would have set immediately ("flash set"). However, if too much calcium sulphate, CSH_x , is present in the form of anhydrite ($x = 0$) or hemihydrate ($x = \frac{1}{2}$), gypsum ($x = 2$) will be formed and cause a set ("false set") that unlike "flash set" may be counteracted by remixing.

Calcium sulphate is added to the clinker during the milling process in order to control the setting of the cement. Needle shaped ettringite crystals, $C_6AS_3H_{32}$, are generally the first stable hydration product when there is an ample supply of calcium sulphate available;



If the sulphate supply drops, ettringite becomes unstable and converts to platy monosulphoaluminate hydrate, C_4ASH_{12} ;

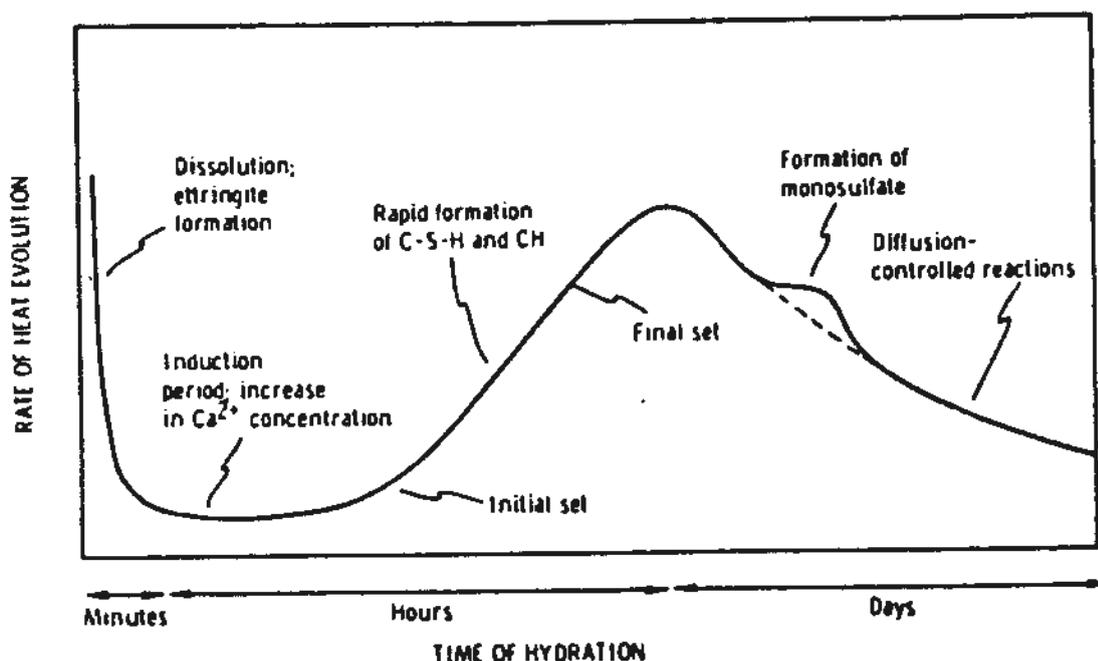


Fig. 1. The heat evolution profile of hydrating cement obtained by isothermal calorimetry //.

The period between the two heat peaks in Fig. 1 is called the induction period or a dormant period where the cement state still remains fluid. During this period, the C_3S is believed to dissolve incongruently forming a silica rich layer which creates an electrical double layer at the surface. The Ca^{2+} and OH^- concentration reaches a level of supersaturation before the period is terminated by the precipitation and growth of CH and CSH-gel. The growth of the former is rate controlling.

The second heat peak in Fig. 1 is dominated by the reaction of alite, C_3S ;



The binder is the CSH-gel with ideal stoichiometric composition $C_3S_2H_4$. However, since the composition may vary within wide limits, it is often simply denoted CSH. The reaction of belite, C_2S ;



does also form CSH gel and CH, but only one third of the CH from C_3S per mole. The CSH gel precipitates close to the surface of the cement grain, while the CH diffuse through and crystallize as large plates throughout the matrix. During the period of the second heat peak there is thus a gradual change from reaction kinetics controlled by the rate of dissolution of C_3S or the rate of crystal growth of CH to diffusion control by the CSH layer.

The setting of the cement paste is often registered by penetrating a needle of a fixed cross-section and with a constant force into the cement paste (Vicat-apparatus). The initial resistance registered is when a full depth intrusion of the needle is not obtainable, which is associated with the first bridging between cement particles by hydration products, and denoted initial set in Fig. 1. When the hydration proceed further and the particles become progressively interweaved by hydration products, the needle is not able to penetrate the paste at all at a given time, which is called the final set as indicated in Fig. 1.

The phenomena called hardening is associated by the strength build up, which is a secondary effect of the hydration products developing during the second heat peak and more slowly during days, weeks and months. The hardening rate is proportional with the rate of heat evolution from the isothermal calorimetry curve in Fig. 1. However, one should note that concrete in practice cures under non-isothermal conditions, and that the temperature build up due to the heat of hydration does accelerate the hardening considerably.

Pure set accelerators and set retarders shorten or prolong, respectively, the induction period, while the left hand slope of the second heat peak (initial hardening acceleration [rate/time]) remains the same, as indicated in Figure 2.

Pure hardening accelerators and hardening retarders do not change the induction period, but increase or reduce, respectively, the left hand slope of the second heat peak, as indicated in Figure 3.

However, many of the admixtures have a combined action on the cement hydration, affecting both set and hardening. A typical accelerator acting on both set and hardening is calcium chloride, $CaCl_2$, while sodium chloride, $NaCl$, only is a hardening accelerator [2].

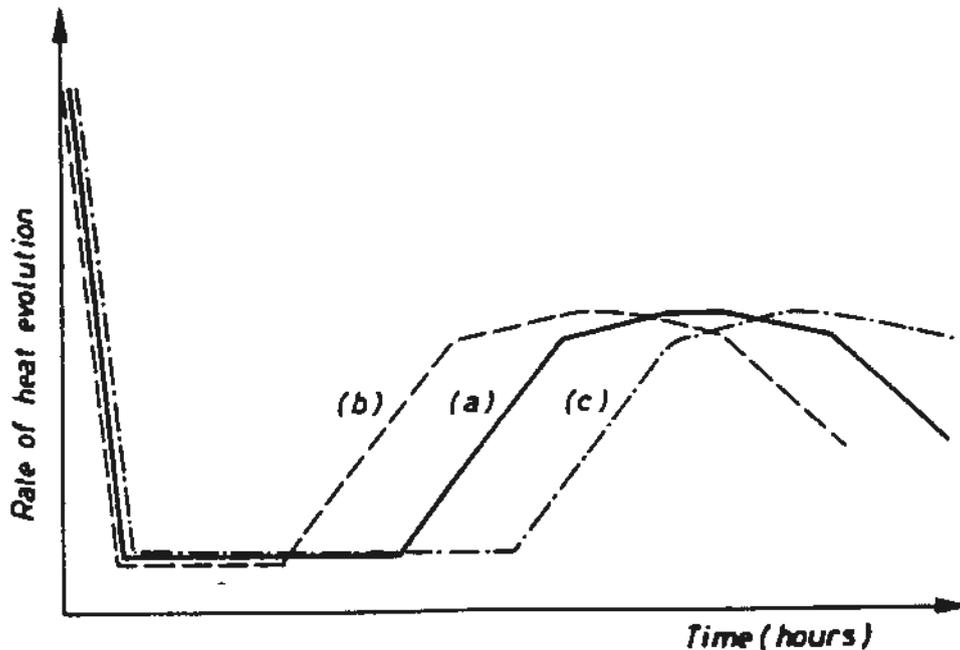


Fig. 2 The idealized effect of a set accelerator (b) and set retarder (c) on the rate of heat evolution from a non-modified (a) cement paste.

No pure set accelerator able to shorten the induction period proportional with the dosage exists today. However, sodium silicate ("water glass"), carbonates and aluminates are used at present in order to obtain a "flash set" utilized in shotcreting. If found, a pure set accelerator reducing the induction period may be used for the following reasons in practice;

- 1) Winter casting (to avoid cooling of fresh concrete prior to the onset of hardening).
- 2) Production of prefabricated elements (increased re-use of molds).
- 3) Shotcreting.
- 4) Decreased risk of cracks in a structure due to settlements.
- 5) Decreased risk of cracks due to plastic shrinkage.
- 6) Shortened time before concrete decks may be surface smoothed.

On the other hand, a number of set retarders of both inorganic (borates, phosphates, zinc salts and lead salts) and organic (lignosulphonates, sugars and carboxylic acids) nature are known.

The most common hardening accelerators are chloride containing (CaCl_2 and NaCl), but in the later years chloride free hardening accelerators like calcium formate, $\text{Ca}(\text{CHO})_2$, sodium thiocyanate, NaSCN , and calcium nitrate, $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, have become available (since chlorides increase the rate of corrosion of rebars in reinforced concrete structures). However, the chloride free accelerators are not as effective as those based on chlorides.

Hardening retarders do not exist today. If found, they might have been used in practice for any massive concrete structure in order to lower the maximum temperature in the concrete, and thus reduce the general negative influence on the hardened concrete properties (e.g. reduced thermal cracking).

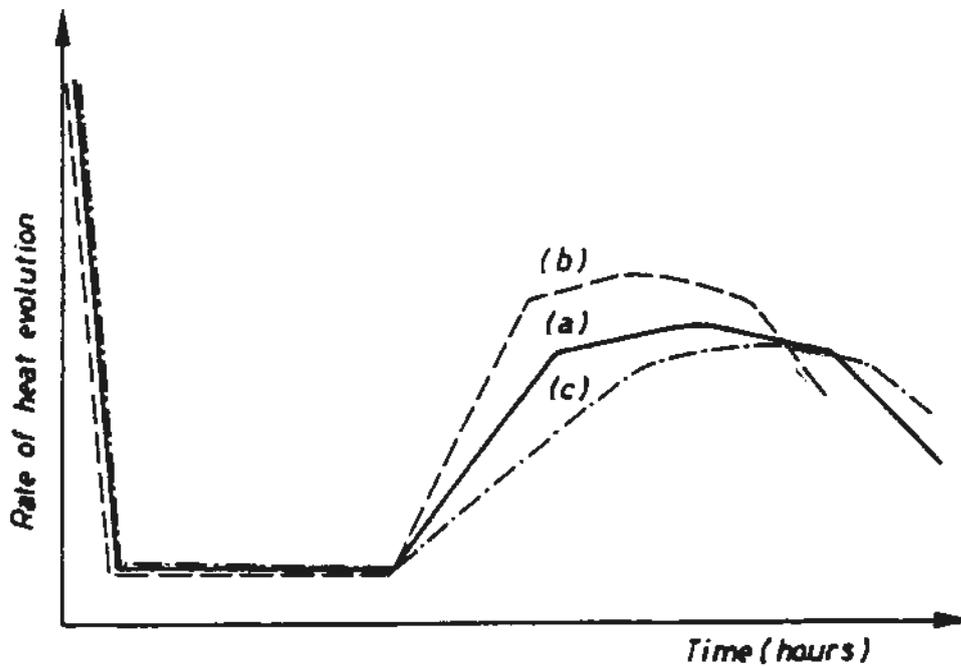


Fig. 3 The idealized effect of a hardening accelerator (b) and hardening retarder (c) on the rate of heat evolution from a non-modified (a) cement paste.

3. EXPERIMENTAL

3.1 Chemicals

Technical calcium nitrate (CN) may in general be written as $x\text{NH}_4\text{NO}_3 \cdot y\text{Ca}(\text{NO}_3)_2 \cdot z\text{H}_2\text{O}$, and named xyz according to short hand practice. In this manner, pure calcium nitrate with 4 crystal water, $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, is named 014. 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 based on three different cements; ASTM type I (ordinary Portland cement = P30), ASTM type II (moderate sulphate resistant = P30-4A) and ASTM type V (sulphate resistant = SR). The cement analyses are given in Table 1. The specific surfaces (Blaine) were 290, 407 and 290 m^2/kg for the P30, P30-4A and SR cements, respectively. The cements and their analyses were all obtained from Norcem A/S, Brevik, Norway.

Condensed silica fume, CSF, containing 96.6 % SiO_2 was used for one mix based on ASTM type I cement (P30). The CSF was of the type Microsilica from Elkem A/S, the Fiskaa plant, Kristiansand, Norway.

Table 1. Chemical composition of cements (% of cement weight).

Cement types	P30 ASTM I	P30-4A ASTM II	SR ASTM V
Oxides			
CaO (C)	63.56	64.60	64.62
SiO ₂ (S)	20.31	22.27	21.98
Fe ₂ O ₃ (F)	3.52	3.29	4.88
Al ₂ O ₃ (A)	5.02	4.05	3.48
SO ₃ (S)	2.88	2.52	2.18
MgO (M)	2.34	1.47	1.45
Na ₂ O (N)	0.39	0.20	0.20
K ₂ O (K)	1.18	0.60	0.56
Free lime	1.87	1.26	0.73
Minerals (Bogue)			
C ₃ S, alite	57	55	59.5
C ₂ S, belite	15	23	18.2
C ₄ AF, ferrite	10.7	10.0	14.9
C ₃ A, aluminate	7.4	5.2	1.0

3.2 Methods

The heat evolution vs time for the hydrating cement pastes was monitored by isothermal calorimetry. The calorimeter consists of a metal base plate on which six units are mounted, surrounded by insulation foam (every second unit for cement paste, the other three units for reference; sand and water). Every unit is built up in a heat flow meter on the base plate, a reaction chamber provided with a heating wire winding for calibration and a specimen chamber of teflon coated aluminum. The instrument was closed water-tight by means of an aluminum cover and a rubber O-ring. The cover was fastened to the base plate by turning the hand-wheel on the top of the cover clockwise, while adjustment was achieved by a metal pin. The whole apparatus was submersed in a water bath in order to obtain isothermal conditions at 20°C. The chambers were filled with dry cement and sand, respectively. After thermal equilibrium had been obtained, distilled water or water with dissolved CN was added to the samples through surfacing tubes connected to the chambers (reaction time = 0). W/C = 0.50 was used in order to ensure complete wetting of the cement grains. The instrument was developed and delivered by TNO, Delft, the Netherlands.

The setting of the cement pastes was registered 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 5 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 complies with the code ASTM C 191-82.

Water from crushed pastes sealed cured for 14 days was squeezed by a pore water press (< 375 MPa). The pH of the pore water was analyzed by titration with HCl and phenolphthalein as indicator. The calcium content of the pore water was determined by atomic absorption spectrometry (AAS), while the nitrate and sulphate contents were measured by ion chromatography.

The X-ray diffractograms of pastes sealed cured for 14 days were recorded by a diffractometer after an internal reference consisting of 10 % anatas (TiO_2) was interground. Cu K_α -radiation with wavelength $\lambda = 1.5418 \text{ \AA}$ and a Ni-filter were used.

4. RESULTS

4.1 Isothermal calorimetry

The rate of heat evolution (W/kg Cement) curves for the cement pastes (w/c = 0.50) based on ASTM type I (P30), II (P30-4A) and V (SR) cements with dosages of CN ranging from 0.00 to 2.32 %, are integrated to give the cumulative heat evolution (kJ/kg cement). The cumulative heat evolutions are listed in Table 2 for some time intervals. The 0-1 h interval is separated in order to omit the initial heat flow. Note that CN dosages of 0.39, 0.77, 1.55 and 2.32 % correspond to 0.25, 0.50, 1.00 and 1.50 % NO_3^- of the cement weight, respectively. Rate of heat evolution vs time profiles for P30-4A cement pastes with 0.00 and 1.55 % CN are plotted in Fig. 4 as an example.

4.2 Setting times

The initial and final setting times for the cement pastes (w/c = 0.40) based on ASTM type I (P30), II (P30-4A) and V (SR) cements with dosages of CN ranging from 0.00 to 7.73 % are given in Table 3, while the penetration profiles for the pastes based on the same cements are revealed in Figures 5, 6 and 7, respectively.

Since a water/cement-ratio of 0.40 for the cement pastes gives a mix far from the standardized consistency, paste mixes with w/c = 0.28 were made for the ASTM type I cement. The results from the Vicat test (setting characteristics) on this series are included in Table 3 as well, while the corresponding penetration profiles are given in Figure 8. In addition, the effect of replacing some of the ASTM type I cement (P30) with condensed silica fume (CSF) was investigated, since this will affect the alkalinity of the water phase. The results of the Vicat test for P30 cement paste with 5 % CSF replacement and w/(c+s) = 0.40 are also included in Table 3, while the corresponding penetration profiles are revealed in Figure 9.

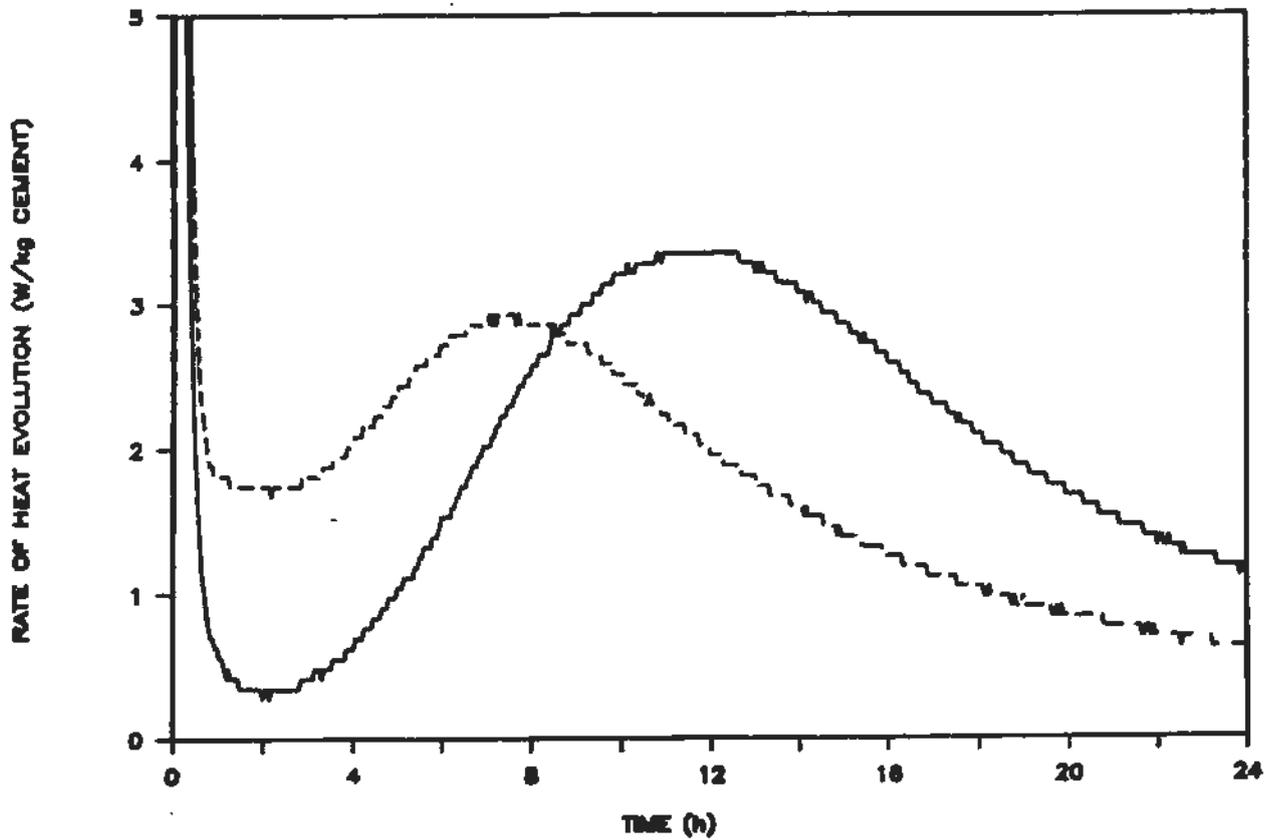


Fig. 4 Rate of heat evolution vs time profiles for P30-4A cement pastes ($w/c = 0.50$) with 0.00 (solid line) and 1.55 % (dashed line) technical calcium nitrate (CN).

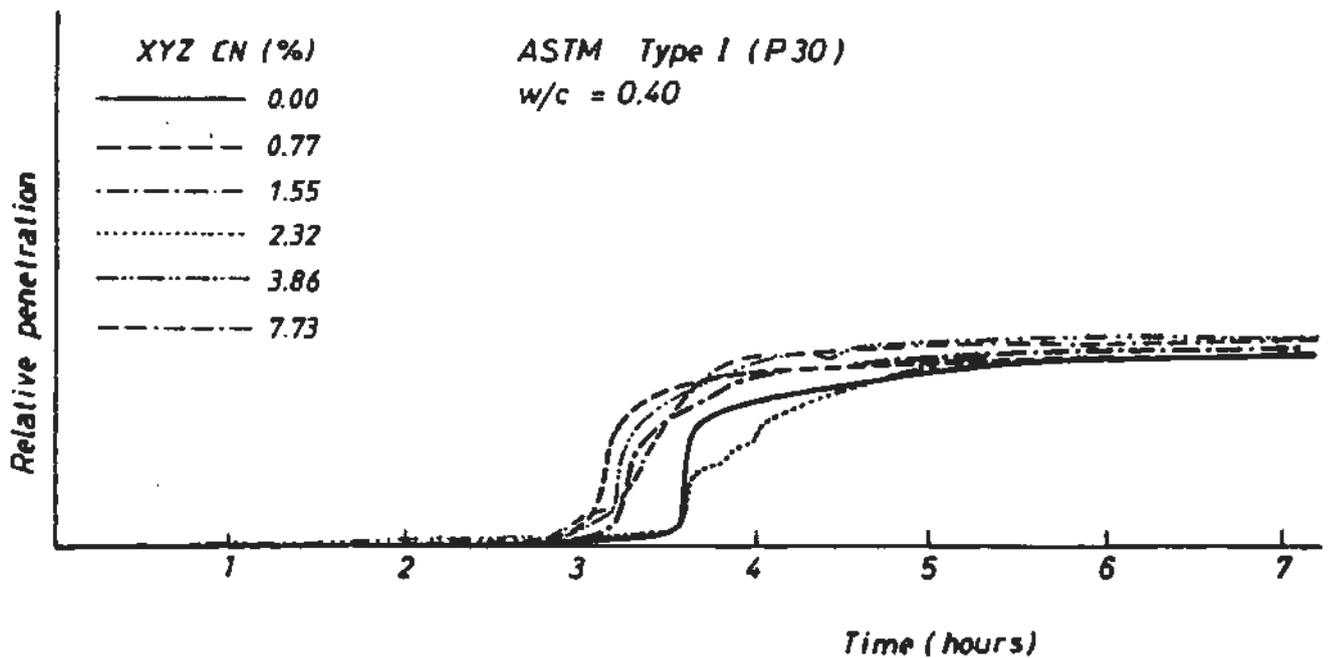


Fig. 5 The penetration profile for ASTM type I cement with different dosages of CN.

Table 2. Cumulative heat evolution (kJ/kg cement) for some time intervals (hours) for different cement pastes (w/c = 0.50) as a function of CN dosage.

ASTM type	CN-dose	0-1	1-2	1-3	1-4	1-5	1-6	1-24
I	0.00	4.8	1.2	2.3	4.1	7.2	11.8	157.3
I	0.39	6.0	1.4	2.9	5.1	8.5	13.5	155.4
I	0.77	12.4	2.4	5.4	9.7	15.7	23.4	153.2
I	1.55	9.9	2.5	5.3	9.1	14.3	21.2	155.2
I	2.32	11.9	3.8	7.7	12.4	18.5	25.9	148.5
II	0.00	12.9	1.4	2.7	4.6	7.7	12.2	165.6
II	0.39	13.6	2.4	4.9	8.1	12.7	18.9	158.8
II	0.77	18.7	4.5	9.5	15.2	22.3	31.1	146.2
II	1.55	17.9	6.3	12.6	19.5	27.5	36.7	141.1
II	2.32	21.3	9.3	17.8	26.1	35.0	44.4	142.8
V	0.00	5.5	0.8	1.8	3.6	6.4	10.3	124.4
V	0.39	6.8	1.8	3.8	6.8	10.9	16.3	121.0
V	0.77	9.5	2.9	5.9	9.8	14.8	20.9	114.3
V	1.55	10.8	4.2	8.4	13.3	19.3	26.2	108.1
V	2.32	14.0	6.3	12.0	17.8	24.3	31.0	102.4

4.3 Pore water analyses

Cement pastes based on both ASTM type I (P30) and V (SR) cements, w/c = 0.50 and with 0.00 and 5.26 % addition of CN were sealed cured for 14 days before the pore water was pressed out and analyzed with respect to Ca^{2+} , NO_3^- , SO_4^{2-} and OH^- . The ion concentrations for these mixes are presented in Table 4 together with the pH and the sum of charges from measured cation and anion concentrations. A dosage of 5.26 % CN is calculated for a stoichiometric reaction between the calcium nitrate and the aluminate phase in the P30 cement (containing more aluminate than SR cement).

4.4 X-ray diffraction

The analysis of interplanar spacings, d , and relative intensities, I , for reflections from X-ray diffractograms of cement pastes based on both ASTM type I (P30) and V (SR) cements, w/c = 0.50, with 0.00 and 5.26 % addition of CN and sealed cured for 14 days revealed that

Table 3. Time for initial and final set for different cement pastes as a function of CN dosage.

ASTM type / Cement	w/c- ratio	CN (%)	Initial set	Final set
I / P30	0.40	0.00	3 h 10 min	5 h 15 min
I / P30	0.40	0.77	2 h 40 min	4 h 15 min
I / P30	0.40	1.55	2 h 40 min	4 h 30 min
I / P30	0.40	2.32	2 h 45 min	4 h 50 min
I / P30	0.40	3.86	2 h 50 min	4 h 30 min
I / P30	0.40	7.73	2 h 55 min	4 h 15 min
II / P30-4A	0.40	0.00	4 h 10 min	6 h 15 min
II / P30-4A	0.40	0.77	1 h 30 min	2 h 35 min
II / P30-4A	0.40	1.55	1 h 40 min	2 h 50 min
II / P30-4A	0.40	2.32	1 h 20 min	2 h 30 min
II / P30-4A	0.40	3.86	1 h 5 min	2 h 25 min
II / P30-4A	0.40	7.73	3 h 30 min	5 h 0 min
V / SR	0.40	0.00	4 h 40 min	6 h 40 min
V / SR	0.40	0.77	3 h 50 min	6 h 10 min
V / SR	0.40	1.55	3 h 0 min	5 h 10 min
V / SR	0.40	2.32	2 h 20 min	5 h 0 min
V / SR	0.40	3.86	6 h 5 min	>7 h 15 min
V / SR	0.40	7.73	4 h 0 min	5 h 25 min
I / P30	0.28	0.00	1 h 45 min	2 h 55 min
I / P30	0.28	0.77	1 h 30 min	2 h 55 min
I / P30	0.28	1.55	1 h 55 min	3 h 5 min
I / P30	0.28	2.32	1 h 35 min	3 h 0 min
I / P30, 5% CSF	0.40	0.00	2 h 50 min	4 h 20 min
I / P30, 5% CSF	0.40	1.55	3 h 10 min	4 h 50 min
I / P30, 5% CSF	0.40	3.86	2 h 30 min	3 h 35 min
I / P30, 5% CSF	0.40	7.73	2 h 25 min	4 h 30 min

ettringite (Eq. 1) exists in all the samples. There was no evidence for the presence of neither the mineral $C_3A \cdot CN \cdot 10$ nor the mineral monosulpho-aluminate hydrate, $C_3A \cdot CS \cdot 12H$.

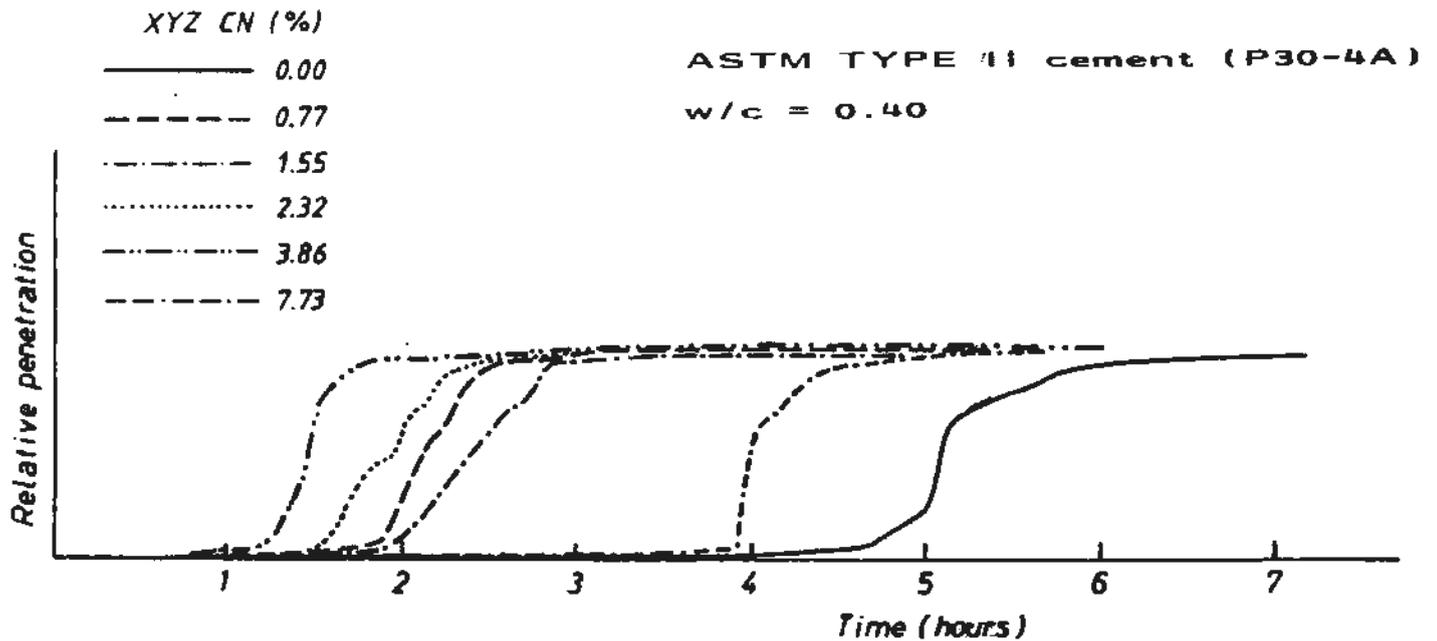


Fig. 6 The penetration profile for ASTM type II cement with different dosages of CN.

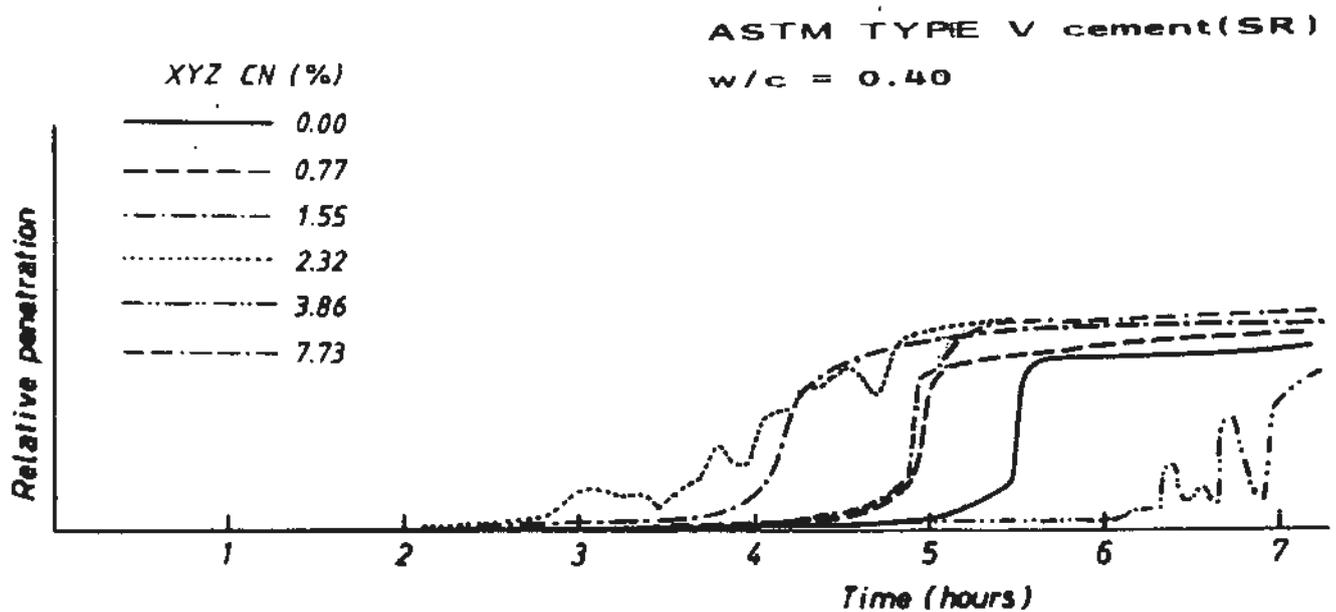


Fig. 7 The penetration profile for ASTM type V cement with different dosages of CN.

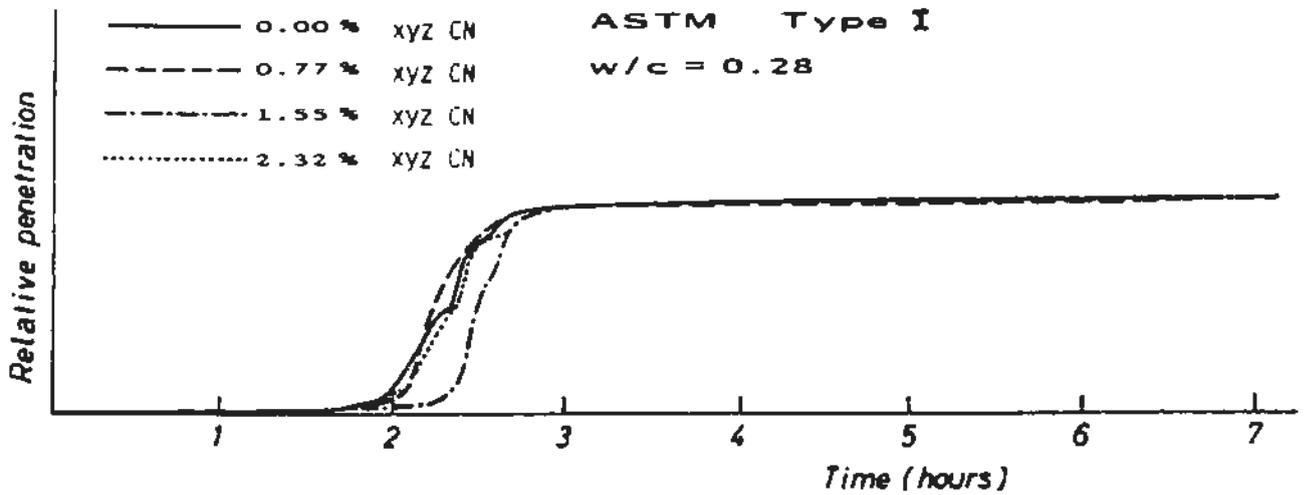


Fig. 8 The penetration profile for ASTM type I cement (w/c = 0.28) with different dosages of CN.

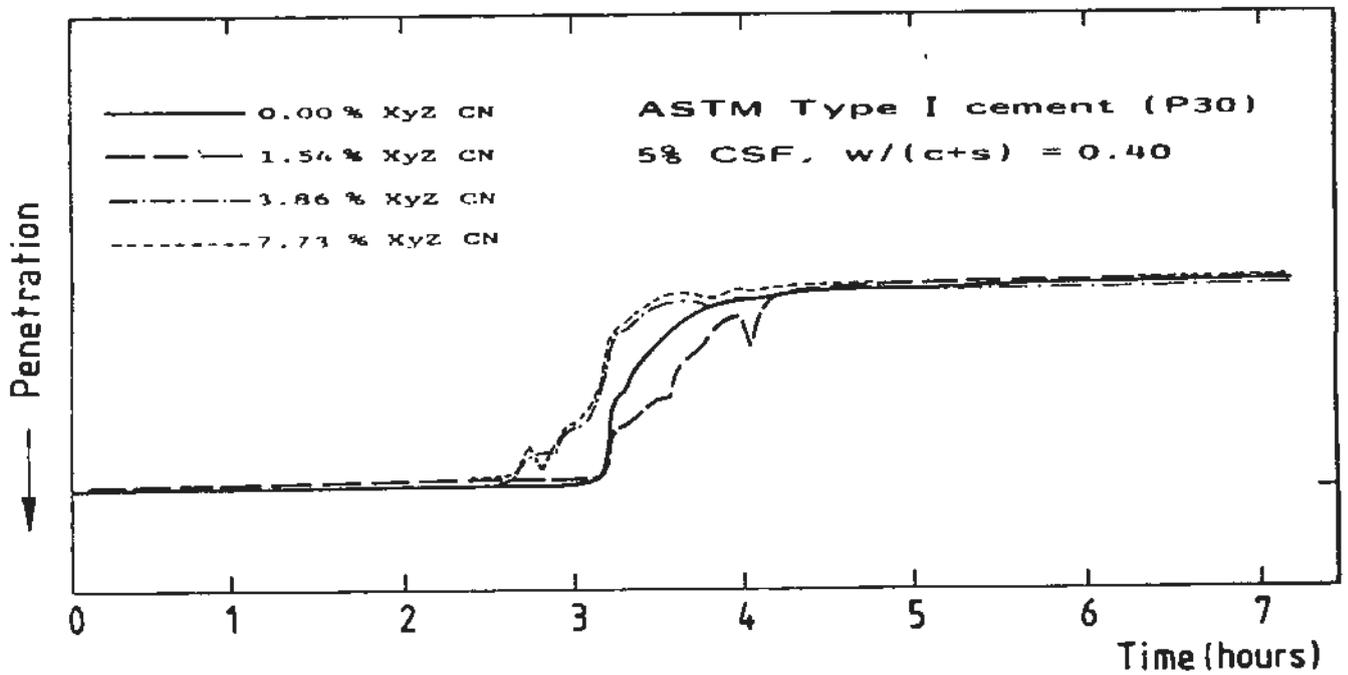


Fig. 9 The penetration profile for ASTM type I cement with 5 % CSF and w/(c+s) = 0.40, with different dosages of CN.

Table 4. Ion concentration (upper value = g/l and lower value = mole/l) in pore water from different cement pastes (w/c = 0.50) with and without CN, and the sum of cations and anions (mol/l), after 14 days sealed curing.

Cement	CN dose	Ca ²⁺	NO ₃	SO ₄ ²⁻	OH	pH	Σ ⁺	Σ ⁻
P30-cement	0.00 %	0.066	0.08	5.9	13.82	13.91	0.0032	0.9371
		0.0016	0.0013	0.0614	0.8130			
ASTM type I	5.26 %	0.061	326	2.4	10.98	13.81	0.0030	6.3960
		0.0015	5.2500	0.0250	0.6460			
SR-cement	0.00 %	0.034	0.05	1.1	5.90	13.54	0.0016	0.3706
		0.0008	0.0008	0.0114	0.3470			
ASTM type V	5.26 %	0.29	331	0.3	4.64	13.44	0.0145	5.6192
		0.0072	5.3400	0.0031	0.2730			

5. DISCUSSION

5.1 Isothermal calorimetry

By analysing the heat evolution profiles (see example in Fig. 4), it turns out that the profiles are parallel displaced towards a shorter time when CN is added, in addition to a pronounced increase in heat evolution in the range 1-5 h. The latter effect is elucidated in Table 2 (cumulative heat evolution). Remember (Figures 2 and 3) that a pure setting accelerator leads to a parallel displacement of the heat evolution profile only, while a pure hardening accelerator starts the second heat evolution peak at the same time as for the reference, but with a steeper increase (i.e. increased acceleration (rate/time) of hydration).

The heat evolution development for P30 cement without CN coincides with the curve for 0.387 % CN. For the other mixes (0.773, 1.543 and 2.319 %), the profiles have the same shape (except for the mix with the highest dosage, where the heat evolution between 1 and 5 h is slightly increased), but are parallel displaced towards a lower time. This parallel displacement (about 1 h) is only to a minor extent visible in the Vicat measurements; at w/c = 0.40 the initial and final set are reduced with 30 min and 60-25 min, respectively, while no effect is noticeable at w/c = 0.28. However, a w/c effect (concentration variations in the water phase) can not be excluded, since cement pastes for isothermal calorimetry have w/c = 0.50.

The addition of CN to the P30-4A cement paste has a strong effect on the heat evolution profile. A dosage of 0.387 % (a mix not included in the Vicat measurements) and 0.773 CN displace the curve ½ and 2 h, respectively, relative to the profile for the reference mix. Furthermore, the heat evolved between 1 and 4 h increases with increasing dosage of CN. In fact, at the highest dosages of CN (1.546 and 2.319 %), the heat generated between 1 and 5 h is so dominating that the hydration peak is difficult to resolve.

The effect of CN addition on the heat of hydration curves for SR cement is analogous to the effect on P30-4A cement, but to a smaller extent. The parallel displacements of the curves for 0.387, 0.773, 1.541 % CN are 20, 40 and 60 min, respectively, relative to the reference mix. For the paste with the highest dosage (2.319 %), the heat evolution in the 1-5 h range was so pronounced that the displacement of the second heat peak could not be quantified. Realizing that the accelerations in initial-final setting from the Vicat measurements were 50-30 min, 100-90 min and 140-100 min for dosages of 0.773, 1.541 and 2.319 % CN, respectively, the values are slightly higher than what to expect from the calorimetry curves. The difference may be due to different w/c-ratios (0.40 for Vicat and 0.50 for calorimetry measurements).

Since ammonium, NH_4^+ (a weak acid), will react immediately with the hydroxyl ions, OH^- (a strong base), to ammonia and water in a strongly exothermal reaction;



a few experiments were carried out in order to find the contribution to the cumulative heat the first hour. The conclusion was that the extra heat caused by Eq. 5 was negligible at these small ammonium nitrate dosages compared with the variations in heat generated by the cement-water reactions in the same period (e.g. Eq. 1).

The cumulative heat evolutions in the period 1-5 h are plotted as a function of CN dosage in Figure 10 for the three cements together with their fitted lines after a linear regression analysis. The factors **a** and **b** for the linear equation;

$$[\text{Cumulative heat}] = \mathbf{a}[\text{CN dosage}] + \mathbf{b} \quad (6)$$

are listed for the three cements in Table 5 together with the residuals about mean explained, r (%). Increasing value of factor **a** denotes increasing response per unit added CN. Thus, the cements may be ordered according to increasing CN efficiency; P30 < SR < P30-4A, which is the same order as revealed by the Vicat-method in the next section.

Note that the time required for the extra heat output may depend on cement type and CN dosage, indicating that the unknown exothermal reaction(s) are concentration and/or surface fraction (heterogenic reaction) dependent.

Table 5. Parametres from the linear regression analysis for the cumulative heat evolution in the period 1-5 h at 20°C vs CN dosage for 3 cements.

Cement type	Factor a	Factor b	r (%)
ASTM I (P30)	4.593	8.224	79
ASTM II (P30-4A)	11.757	9.407	96
ASTM V (SR)	7.359	7.666	98

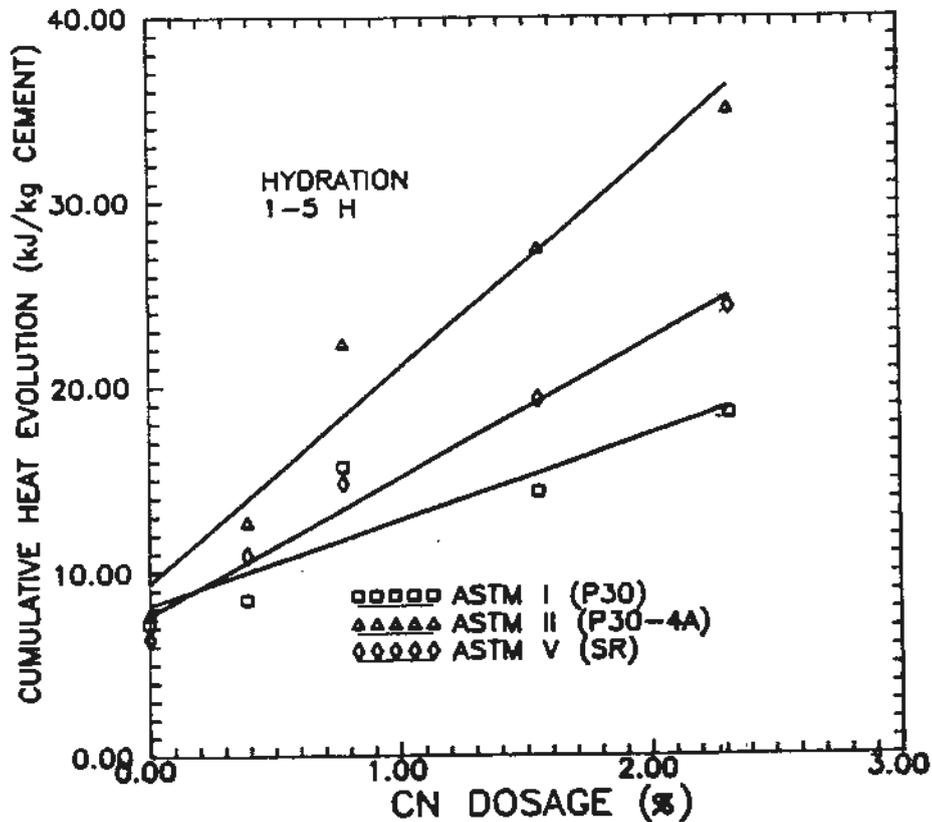


Fig. 10 Cumulative heat evolution for three different cements for the period 1-5 h at 20°C as a function of CN dosage.

5.2. Vicat measurements

The results in Table 3 and Figures 5 - 9 reveal that the effect of CN on the setting time for cement paste is strongly dependent of the cement type:

CN has no significant effect on the setting time of P30 cement (ASTM type I), neither at $w/c = 0.40$ nor at $w/c = 0.28$. Replacing 5 % of the P30 cement with condensed silica fume did not change the situation at $w/(c+s) = 0.40$, indicating that the reaction dominating the setting is not sensitive to the hydroxyl concentration in the pore water.

CN is a setting accelerator for P30-4A cement (ASTM type II); it works already at small dosages (≤ 0.77 %) and the effect do not increase with increasing dosage. However, the effect on P30-4A cement is very strong, since a small dosage of CN leads to less than half the setting time of the reference (from 4 to 1.5 h initial setting when 0.77 % CN is added).

CN works as a setting accelerator for SR cement (ASTM type V), and the effect increases with increasing dosage. However, the effect is not as strong for SR (initial setting time reduced with $\frac{1}{2}$ h when 0.77 % xyz CN is added) as for P30-4A cement.

The order of CN efficiency on cement setting is $P30 < SR < P30-4A$ (same as from isothermal calorimetry), which is not the same order as increasing aluminat (C_3A) content; $SR < P30-4A < P30$. However, it is the same order as the belite (C_2S) content; $P30 < SR < P30-4A$ (see

Table 1). The same tendency was confirmed in a similar investigation of five French cements /3/. However, since belite is generally believed to be a slowly reacting mineral and the simple Bogue calculation is a crude approximation, it might be more correct to state "cements with a decreasing Ca/Si ratio" rather than "increasing belite content".

Since this investigation started, Norcem has changed the P30 cement composition (lower Ca/Si ratio) and produces a new P30 from 1993 with a different mineralogy. The P30-4A cement has been subjected to only minor changes from 1993, but has been renamed HS65. CN does function as set accelerator for both of this new cements at 5°C /4/.

5.3 Pore solution chemistry

The results from the pore solution measurements; the concentration of Ca^{2+} , NO_3^- , SO_4^{2-} and OH^- , listed in Table 4, reveal for all mixes a deficit for the sum of positive charge from cations (Σ^+) compared with the sum of negative charge from anions (Σ^-). This is partly due to the alkali cations, Na^+ and K^+ , which were excluded from the analysis.

P30 without CN has for instance a cation deficit of 0.9339 mol/l. According to Table 1, P30 contain 0.39 % Na_2O and 1.18 % K_2O . If the degree of hydration after 14 days sealed curing is taken as 65 %, and it is assumed that the cement binds 40 % water relative to its own weight, the amount of free water in the cement paste is $0.50 - 0.65 \cdot 0.40 = 0.24$ parts by weight. Another assumption to be made is that 65 % of all alkalis (i.e. the alkalis are evenly distributed in the cement grains) then is present in the water phase (very soluble compounds). The concentration of Na_2O in the pore water becomes then $0.39 \% \cdot 0.65 / 0.24 = 1.06 \%$ or 10.56 g/l, while the concentration of K_2O is 31.96 g/l. Using the molar weights of 61.98 g/mol for Na_2O and 94.20 g/mol for K_2O , concentrations of 0.170 mol $\text{Na}_2\text{O}/\text{l}$ or 0.341 mol Na^+/l and 0.339 mol $\text{K}_2\text{O}/\text{l}$ or 0.679 mol K^+/l (the sum is 9.2 % more than the deficit) are obtained. Considering the crude assumptions made, and knowing that some K^+ will be bound in the calcium silicate hydrate, it is evident that the deficit of positive charge in the pore solution from P30 cement without CN can be subscribed to alkalis.

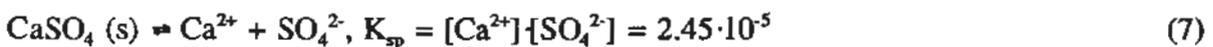
If an analogue calculation is performed for SR-cement without CN, which contain 0.57 % alkalis (Table 1), with a positive charge deficit from cations of 0.3690 mol/l, a Na^+/K^+ -concentration of 0.4968 mol/l (35 % more than the deficit) is found by employing the same assumptions.

The greater excess of cations calculated for SR- (35 %) than for P30-cement (9 %), is probably because it is not correct to assume the same degree of hydration for the two cements. SR contains less C_3A (rapid hydration) and more C_2S and C_4AF (slow hydration) than P30. Assuming 55 instead of 65 % hydration, results in a Na^+/K^+ -concentration of 0.3613 mol/l (2 % less than the deficit).

However, the alkali cations can not explain the great excess of anions in the pore solutions from cement pastes with CN. A theoretical degree of hydration of 100 % for the P30 cement would lead to a maximum alkali cation concentration of 3.7754 mol/l, which is still not sufficient to explain the deficit in positive charge of 6.3930 mol/l.

The cation deficit may on the other hand be explained by iron and/or aluminum, which can exist as free cations or bound in complex anions. However, iron will probably be precipitated as $\text{Fe}(\text{OH})_3$ in water with $\text{pH} > 13$, while aluminum may exist as the complex anion $\text{Al}(\text{OH})_4^-$. Note that during the titration for OH^- determination, a mole of the latter complex anion will be registered as four moles OH^- . Another possibility is that nitrates will increase the solubility of aluminum by forming complex anions of the type $\text{Al}(\text{NO}_3^-)_x^{3-x}$. Pore solution analyses in the future should include the ions Na^+ , K^+ and Al^{3+} as well.

Another effect that may be extracted from Table 4, is that both the concentration of sulphates and hydroxyl ions decrease when CN is added. This is due to the low solubility of both calcium sulphate and calcium hydroxide;



and



The product of the ion concentrations for calcium and sulphate (Table 4) is quite close to the solubility product for gypsum (Eq. 7), while the ion product of calcium and hydroxyl is way above the solubility product for lime (Eq. 8). The latter effect strongly suggest that a major part of the hydroxyl ions are bound in water soluble complex anions (e.g. $\text{Al}(\text{OH})_4^-$).

Another feature that might be seen from Table 4, and may point at why CN do work as a set accelerator for SR- but not for P30-cement, is that the calcium concentration increases when CN is added to SR cement, but not for P30-cement. An increased calcium concentration in the pore water at an early stage may promote setting in two ways (see chapter 2);

- 1) The supersaturation of calcium hydroxide will be reached earlier, with an early start of CH precipitation and growth of CH and CSH-gel.
- 2) The sulphate concentration will be lower due to Eq. 7, and consequently the ettringite formation on C_3A will be slower, leading to the formation of a thinner layer and earlier rupture.

A low calcium concentration in the pore water in the fresh mix (of interest for the setting time) and at a later stage, is connected to a high alkali content (as for P30). However, the setting times of P30 with 5 % CSF indicates that the assumed slight decrease of hydroxyl concentration when condensed silica fume is included, has no influence on the efficiency of technical calcium nitrate as a set accelerator.

Thus, the hypothesis for further work is that a high calcium concentration in the water phase of the fresh mix leads to an acceleration of the cement setting, which may be the case for low alkali cements. In the future work, water should be filtered from the fresh mix (no pore water press needed) and analysed with respect to Na^+ , K^+ , Ca^{2+} , Al^{3+} , NO_3^- , SO_4^{2-} og OH^- . This may also be performed as a function of time and with/without addition of CN, in order to obtain a better understanding of what is happening until the cement sets.

5.4 Crystalline phases

The presence of ettringite (Eq. 1) and the absence of the minerals $C_3A \cdot \bar{CN} \cdot 10$ ($\bar{N} = NO_3^-$) and monosulpho-aluminate hydrate, $C_3A \cdot CS \cdot 12H$ (Eq. 2) in all the samples, disprove the initial hypothesis suggesting that the calcium nitrate would react with the aluminate phase, C_3A , to the mineral $C_3A \cdot \bar{CN} \cdot 10H$ at the expenses of ettringite, $C_3A \cdot 3CS \cdot 31H$, or monosulpho-aluminate hydrate, $C_3A \cdot CS \cdot 12H$. It seems like ettringite is the most stable compound under the present conditions.

The intensities of the reflections from the remains of the crystalline clinker minerals, C_3S og C_2S , indicate that the degree of hydration is somewhat higher for cement pastes with CN than without, even after 14 days. For the P30 pastes the corresponding calcium hydroxide (CH) content (hydration product of Eqs. 3 and 4) is somewhat higher in the mix with CN, while the opposite is the case for SR cement.

6. CONCLUSIONS

CN does function as a set accelerator for cement.

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

The set accelerator efficiency of CN for different cements seems to increase with decreasing Ca/Si-ratio from the chemical analysis of the cement.

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

The energy per % CN added evolved from an exothermal reaction the first hours has been found to be proportional to the set accelerating efficiency for the different cements.

The pore water of hydrated cement with CN added has a considerably cation deficiency not explainable by calcium and alkalies, which may be due to complex ions of Si, Al and/or Fe.

7. REFERENCES

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