Chloride-Free Accelerators for Concrete Setting and Hardening

by H. Justnes

Synopsis: Calcium chloride is an excellent accelerator for concrete, improving both setting time and hardening rate. However, it can not be used for reinforced concrete in efficient dosages because of initiation of rebar corrosion. In the search for other bulk chemicals working as accelerators, calcium nitrate has proven to be a good candidate as set accelerator; however it is not a hardening accelerator (e.g. improving 1 day strength). Efforts have been made to combine calcium nitrate with other admixtures in order to make the mix work as a combined chloride-free setting and hardening accelerator. This paper sums up research over the last 10 years regarding this matter and also compares performance with other chemicals.

Keywords: accelerator; chloride-free; hardening; setting; strength

Dr. Harald Justnes is Chief Scientist at SINTEF Concrete, Trondheim, Norway. His field of interest covers the chemistry of cement, concrete, admixtures and additives (including polymers) from production, through reactivity, to durability. Justnes is also Adjunct Professor in "Cement and Concrete Chemistry" at Institute of Materials Technology, Norwegian University of Science and Technology (NTNU), Trondheim.

INTRODUCTION

In the past, a concrete accelerator was synonymous with an admixture increasing the 1 day compressive strength. It is only in the recent years, with the implementation of the European standards that the industry distinguishes between <u>setting</u> and <u>hardening</u> accelerators, realizing practical utilizations of both admixture effects independently.

According to the European admixture standard EN 934-2 of 2001¹, a <u>setting</u> accelerator must give at least 30 min initial setting time at 20°C, and maximum 60% of the initial setting time of the reference at 5°C measured on mortar with equal flow. A <u>hardening</u> accelerator should give minimum 120% compressive strength compared to the reference after 1 day at 20°C, and minimum 130% compressive strength compared to the reference after 2 days at 5°C, as measured on concrete of equal flow. Requirements are established for long term strength and air content also.

Note that the European standard¹ uses the practical approach of equal flow of mixes allowing variations in water-cementitious materials ratio (w/cm). However, variations in w/c may mask the chemical effects of admixtures, so more fundamental studies searching for active accelerators tend to use constant w/cm and cement content.

Concrete is a relatively low priced construction material, which means that any highpriced chemical admixture must enhance its performance at a relative small dosage, or alternatively a cheaper chemical can be allowed at moderate dosage. Hence, accelerators should be sought among industrial bulk chemicals.

Calcium chloride, CaCl₂, was an ideal accelerator being both a setting and hardening accelerator in one compound, in addition to being an industrial bulk product. However, in 1960's awareness of corrosiveness of chlorides on embedded reinforcement arose and today chloride containing admixtures is limited for steel reinforced concrete (< 0.4% Cl⁻ of cement mass for ordinary concrete, but < 0.1% Cl⁻ for reinforced concrete serving in chloride containing environment, based on SR cement or with pre-stressed steel²).

Dodson³ 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 requirements⁴. The second salt to fulfill the requirements was calcium nitrite, $Ca(NO_2)_2$, which was introduced in 1968 and patented in 1969⁵. Calcium nitrate, $Ca(NO_3)_2$, was proposed as a basic component of a set-accelerating admixture, in conjunction with

triethanolamine, by Tokar⁶. The most recent non-chloride, non-corrosive set accelerating salt to be introduced to the concrete market was thiocyanates (salts of SCN⁷). Like the nitrate, the thiocyanates should be accompanied by an alkanolamine in order to attain the desired end results. Gerber⁸ patented the combination of thiocyanate salts with those of nitric acid and alkanolamine. Abdelrazig et al.⁹ compared the accelerators calcium chloride, calcium nitrate and sodium thiocyanate. Their laboratory results agreed with the known effects from site practice; calcium chloride is effective at all ages, calcium nitrate at early ages and sodium thiocyanate at later ages.

In the search for a relatively cheap chloride-free accelerator, calcium nitrate, $Ca(NO_3)_2$, has arisen as an alternative setting accelerator, but it must be combined with other components to function as a hardening accelerator as shown in the proceeding sections. Unless otherwise stated the calcium nitrate referred to here is of granulated, technical quality with formula $xNH_4NO_3 \cdot yCa(NO_3)_2 \cdot zH_2O$ where x = 0.092, y = 0.500 and z = 0.826, or in other words composed of 19.00 % Ca²⁺, 1.57 % NH₄⁺, 64.68 % NO₃⁻ and 14.10 % H₂O.

SINGLE COMPOUND, CHLORIDE-FREE, SETTING ACCELERATORS

When testing accelerators, it is important to know that outcome may strongly depend on the composition of the portland cement used. Justnes and Nygaard¹⁰ published the set accelerating efficiency of calcium nitrate at 5-7°C on pastes (w/cm = 0.40) based on 5 different portland cements with a C_3A content ranging from 7.4 to 1.0 %. The accelerating efficiency ranged from very strong to slight and there was no correlation between set accelerating efficiency and C_3A as initially assumed, but rather surprisingly with the belite, C_2S , content as plotted in Fig. 1. The correlation between belie content and set accelerating efficiency of calcium nitrate was confirmed by Justnes and Nygaard¹¹ in a study of five other cement pastes at 5°C. According to Gebler¹², calcium formate, Ca(HCOO)₂, is an efficient accelerator when the ratio C_3A to SO_3 of the cement is > 4. Heikal¹³ recently confirmed the set accelerating effect of calcium formate at 20 °C with a 1 day compressive strength increase in the order of 120%. Smith¹⁴ 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.

Justnes and Nygaard¹⁵ found the reason for acceleration efficiency differences among portland cements through analyses of the liquid of cement pastes prior to setting. The mechanism for accelerated setting might be caused by calcium suppressing gypsum solubility and precipitating sulfate from soluble alkali sulfates. A lower sulfate concentration will lead to slower or reduced formation of ettringite, which will shorten the onset of aluminate, C_3A , hydration. Interaction of anions (e.g. nitrate) with C_3A hydration products can not be ruled out. It was noted that a cement with very low response to $Ca(NO_3)_2$ contained much more of the mineral Aphthitalite, $K_3Na(SO_4)_2$, which leads to a

high initial sulfate concentration in the fluid. When $Ca(NO_3)_2$ was added, much of the calcium precipitated as minimally soluble gypsum. The authors¹⁵ showed a linear correlation between the alkali content of the fluid of 9 cement pastes in the fresh state with the reduction in initial setting time when 1.55 % calcium nitrate was added, as reproduced in Fig. 2. The linear correlation between belie content and set accelerating efficiency in Fig. 1 is then understandable as an indirect effect since belite can incorporate a portion of the total alkalis in its structure and consequently prevent them from taking part in the early fluid chemistry since belite is a slow reacting mineral. Hence, for a series of cements with about equal total alkali content and increasing belite content, it is expected that the set accelerating efficiency of $Ca(NO_3)_2$ will increase.

In order to find out whether setting acceleration is dominated by the calcium cation or nitrate anion in $Ca(NO_3)_2$, Justnes (unpublished data) tested the efficiency of both calcium nitrate (65% NO₃⁻ due to some crystal water) and sodium nitrate (73 % NO₃⁻) as set accelerators for 4 different portland cements (see Table 1 for compositions) pastes at 5 °C by Vicat needle. The dosages were 0.00, 0.25, 0.50, 0.75 and 1.00 % calcium nitrate of cement mass, while sodium nitrate was dosed to give correspondingly equimolar nitrate content. The influence on setting time is listed in Table 2. From this limited study, calcium nitrate seems in general to be a substantially better set accelerator than sodium nitrate for portland cements. Specifically, Ca(NO₃)₂ gave shorter setting time relative to reference than NaNO3 in 10 out of 12 comparative tests and about twice or more reduction in setting time in 6 of the 12 cases. For portland cements with a rather high alkali content (≥ 1% Na₂O_{equiv}), calcium nitrate performs better than sodium nitrate for higher dosages only (about 1% of cement mass). This effect may be explained by alkali counter-ions (e.g. hydroxide or sulfate) precipitating calcium and forming alkali nitrate in situe. Thus, Ca²⁺ seems to dominate setting, while NO₃ may have an effect as well, depending on cement type.

Temperature evolution profiles in insulated concrete (i.e. semi-adiabatic) and early compressive strengths for concrete cubes cured at 20°C have been measured¹⁶ for different additions of Ca(NO₃)₂. The concrete composition corresponded to w/cm = 0.45 and 4 % silica fume replacement of both CEM I 52,5R-LA and CEM I 42,5R cements¹⁷ (compositions as in Table 1). The accelerating effect of $Ca(NO_3)_2$ was also compared to additions of calcium acetate, Ca(CH₃COO)₂, and formate, Ca(HCOO)₂, at equimolar concentrations of Ca²⁺ for 3.5 % Ca(NO₃)₂ added to the CEM I 42,5R concrete. Calcium acetate and formate gave about the same acceleration according to the temperature profiles in Fig. 3, while $Ca(NO_3)_2$ showed greater accelerating effect in spite of soluble calcium ions dominating the set accelerating effect. The reason for the lesser efficiency of calcium salts of organic acids (i.e. formate, acetate etc) may be due to partial complex formation with one of the anions (e.g. CaOOCCH₃⁺), meaning that the overall chemical equilibrium of the paste fluid does not experience the same effective concentration of Ca^{2+} ions as for $Ca(NO_3)_2$. In fact, the logarithm of the complex formation constant, log K1, is 0.60 and 0.28 for acetate and nitrate, respectively, which corresponds to 61 and 75 % "free" Ca2+ in 0.1 N solutions of these salts. The temperature profiles in Fig. 3 reveal that setting time is accelerated (criterion is 2°C above base line) and not the early strength development rate (i.e. temperature increase slope not steeper than reference).

Justnes et al.¹⁸ tested setting time of cement pastes (two different cements) where different calcium salts with equal amounts of Ca^{2+} ions were added. The order of effectiveness of anions as set accelerators was $CH_3COO^- \le NO_2^- < NO_3^- \le HCOO^- < Cl^-$ for CEM I 52,5R-LA cement¹⁷ (see Table 1) and as $CH_3COO^- < HCOO^- \le NO_2^- < NO_3^- < Cl^-$ for a similar Swedish portland cement.

A neat concrete with CEMI 52,5R-LA (composition as in Table 1) and w/cm = 0.62 exhibited compressive cube strengths after 8 h and 48 h moist curing of 2.5 ± 0.0 and 23.1 ± 0.3 MPa, respectively, while the corresponding strengths when 2 % Ca(NO₃)₂ was added were 4.0 ± 0.1 (due to earlier setting) and 27.7 ± 0.2 MPa. However, 1 day strength for concrete accelerated by only calcium nitrate, is usual equal or slightly lower than reference. Further examples of concrete strength data with calcium nitrate are given by Justnes and Nygaard¹⁹.

Another important parameter to control when testing accelerators is the temperature. Justnes et al.¹⁸ measured reductions in initial and final set at 5 °C, 13 °C and 23 °C for cement pastes with 1.55% calcium nitrate and equimolar Ca dosage of calcium chloride hexahydrate, and compared them with neat cement pastes (two different portland cements). The results revealed that the efficiency of calcium nitrate as set accelerator is higher at lower temperatures. Assuming that the same amount of hydration product is necessary to obtain initial setting at all temperatures, and knowing that reaction rate simply is amount of hydration product divided by time, it is possible to make linear Arrhenius plots; ln (1/t) = a·(1/T) + b, where t is initial setting time (s) and T is absolute temperature (K). The slope of such a plot, $a = E_a/R$, where R is the universal gas constant and E_a is the overall activation energy for the hydration. The concept functions very well for neat cement paste and for cement paste with calcium chloride as shown in Fig. 5, but not with calcium nitrate. The reason is that calcium nitrate is much more effective at 5 °C than predicted by the slope, indicating a different mechanism at this temperature.

Practical utilizations of set accelerators are often to start concrete hardening earlier to avoid cooling of concrete in winter concreting or to counteract the retarding effect of plasticizers. Rettvin and Masdal²⁰ 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 Base Structure (369 m height) in the North Sea, since calcium nitrate counteracted the retarding effect of the plasticizer and super-plasticizer used.

SINGLE COMPOUND, CHLORIDE-FREE, HARDENING ACCELERATORS

The perhaps most promising single compound, hardening accelerator is sodium thiocyanate. It can be seen from mortar strengths in Tables 3 and 4 that 0.25% NaSCN gives compressive strength increase of 121% after 1 day at 20 °C and 113% after 2 days

at 5 °C. Although fulfilling the 20 °C criterion of the EN 934-2 standard1, it fails on the 5 °C criterion (>130%). In fact, the present author is not aware of any single compound that fulfils these criteria, and blended accelerators seem to be required.

BLENDED, CHLORIDE-FREE, SETTING AND HARDENING ACCELERATORS

Justnes²¹ tested calcium nitrate in combination with inorganic salts like sodium thiocyanate, NaSCN, and thiosulfate, Na₂S₂O₃, and with amines like triethanolamine (TEA) and triisopropanolamine (TIPA) at equal w/cm in a search for combined setting and hardening accelerators. The amines did not affect setting or contributed to 1 day strength, but they lead to enhanced 28 days strength. According to Gartner and Myers²² small amount of amines may have a catalytic effect on C₄AF that may explain the long term strength increase. Calcium nitrate in combination with sodium thiocyanate was the most promising combination as shown by the results reproduced in Table 3 for 20°C curing and Table 4 for 5 °C curing. The 24 h compressive strength is $\geq 120\%$ of reference for all mixes with admixtures at 20°C, except 1 % Ca(NO₃)₂. The mixture 1.0 % Ca(NO₃)₂ with 0.25 % NaSCN seems to be a chloride free alternative to calcium chloride with an even better strength as early as 6 h. None of the admixtures fulfilled the compressive strength criterion of >130% compared with the reference after 2 days at 5 °C, not even 1 % calcium chloride hexahydrate (i.e. 0.32% Cl⁻ of cement mass). However, note that the comparisons in this study are done at constant w/cm, and not equal flow.

The objective of Justnes²³ was to compose a liquid accelerator blend from calcium nitrate and a plasticizer or super-plasticizer that fulfilled the criteria for both <u>set</u> and <u>hardening</u> accelerators according to the EN 934-2 standard¹ (i.e. equal flow). Earlier findings by Petersen and Justnes^{24, 25} showed that calcium nitrate was capable of at least partly counteracting the retardation of plasticizers while maintaining rheology.

Justnes²³ formulated a total of 5 accelerators before the preceding objective was reached. The composition of the 5 accelerator blends are listed in Table 5 as % active ingredient in components (i.e. water subtracted). The test results for 2 accelerators (no. 3 and 5) according to the EN 934-2¹ criteria for both set and hardening acceleration are given in Table 6. Accelerators 1 and 2 were skipped after failure in an initial cement paste test. Accelerator 1 was an effort to make an alkali-free blend, but it retarded too much at particular 5 °C. Accelerator 2 retarded also too much at 5 °C. Accelerator 3 nearly fulfilled the requirements (failed compressive strength after 2 days at 5°C only), while accelerator 5 passed the criteria with a good margin. Accelerator 4 was actually not tested since accelerator 5 had an excellent performance and a potential market advantage of being colorless and odorless compared to the dark brown smelly solution (due to SNF) of accelerator 4. Note that accelerator 5 consisting of about 30% calcium nitrate, 11% melamine based super-plasticizer and 6% sodium thiocyanate in water (53%) was not optimized in this limited study, but merely demonstrating a possibility. Furthermore, it was assumed that the strength improvement found for mortar will occur

in concrete as well, but this has to be documented prior to practical application. Combinations with the newer polyether grafted polyacrylate super-plasticizers were not tried out at this point.

CONCLUSIONS

Calcium nitrate is the most promising chloride-free set accelerator considering performance at low temperature, availability and industrial mass production. However, it is not a hardening accelerator with sufficient improvement in 1 day strength.

It has been demonstrated that ternary blends of calcium nitrate, sodium thiocyanate and sulphonated melamine-formaldehyde plasticizer have the potential of fulfilling the criteria of the European admixture standard EN 934-2 as both setting and hardening accelerator.

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CEMENT NAME	STANDARD	STANDARD FA	ANLEGG	SR
Cement type	CEM I	CEM II A-V	CEM I	CEM I
1	42,5R	42,5R	52,5R-LA	42,5R-LA
Composition (%):				
CaO	62.25	-	64.19	64.62
SiO ₂	19.69	<i>≌</i>	21.27	21.98
Fe ₂ O ₃	3.41	-	3.41	4.88
Al_2O_3	4.55		4.39	3.48
SO ₃	3.43	2.68	2.91	2.18
MgO	2.32		1.80	1.45
Na ₂ O	0.41		0.22	0.20
K ₂ O	1.15		0.47	0.56
Free lime	0.87	0.78	0.78	0.73
Carbon	0.55		0.56	
Fly ash		16.30		Dec.
Loss on ignition	2.93	1.82	2.42	
		PLI SUIR SOF		
Bogue Minerals (%):				
C ₃ S (Alite)	55.0	2	53.8	56.5
C ₂ S (Belite)	15.0	×	20.4	20.4
C ₄ AF (Ferrite)	10.4	2	10.4	14.8
C ₃ A (Aluminate)	6.3	2	5.9	1.0
CS (Anhydrite)	7.4	×	6.3	4.7
Properties :				
Blaine (m ² /kg)	360	467	369	290
Water demand (%)	26.8	29.4	26.4	
Le Chatelier (mm)	0.0	0.3	0.3	
Initial set (min)	140	125	135	
Final set (min)	165	150	160	
1 day σ_c (MPa)	19.7	22.5	16.9	12
2 day σ_{c} (MPa)	32.7	32.1	29.2	-
7 day o. (MPa)	43.5	43.8	44.0	
28 day σ_c (MPa)	51.2	57.1	56.2	

Table 1 Specifications of tested portland cements

 σ_c (MPa) = compressive strength, SR = sulfate resistant cement.

Table 2 Initial setting time for different cement pastes (w/cm = 0.40) at 5°C with different dosages of calcium nitrate, $Ca(NO_3)_{2}$, and sodium nitrate, NaNO₃. Setting times are listed in hours with relative setting time (%) to reference in brackets.

NAME	STANDARD	STANDARD FA	ANLEGG	SR
Cement type	CEM I	CEM II	CEMI	CEM I
	42,5R	A-V 42,5R	52,5R-LA	42,5R-LA
Ca(NO3)2 (%)				
0.00	8.10 (100)	6.75 (100)	7.40 (100)	12.25 (100)
0.25	5.50 (67.9)	5.41 (80.1)	5.80 (78.4)	4.7 (38.4)
0.50	5.25 (64.8)	4.41(65.3)	3.00 (40.5)	7.5 (61.2)
0.75	5.33 (65.8)	5.83 (86.4)	4.60 (62.2)	3.8 (31.0)
1.00	4.30 (53.1)	5.70 (84.4)	1.80 (24.3)	4.0 (32.7)
NaNO3 (%)				
0.25	5.60 (69.1)	5.15 (76.3)	6.10 (82.4)	8.33 (68.0)
0.50	5.55 (68.5)	6.55 (97.0)	5.40 (73.0)	6.33 (51.7)
1.00	6.00 (74.1)	7.52 (111.4)	4.80 (64.9)	5.00 (40.8)

Table 3 Estimated setting times (min) from heat evolution curves (Fig. 4) for paste (w/cm = 0.4) and flexural (lower value) and compressive (upper value) strengths (MPa) of mortar (w/cm = 0.5) cured at 20°C with admixtures based on calcium nitrate (Ca(NO₃)₂) and sodium thiocyanate (NaSCN) versus calcium chloride hexahydrate, CaCl₂·6H₂O.

Property	Ref. (0%)	1.0% CaCl ₂ ·6H ₂ O	1.0% Ca(NO ₃) ₂	0.25% NaSCN	1.0/0.25% Ca(NO ₃) ₂ /NaSCN
Setting	190 min	-	130 min	190 min	120 min
$6 h \sigma$	0.85±0.06	1.7±0.1	2.0±0.1	1.4±0.1	2.2±0.1
	0.4±0	0.6±0.1	0.7±0.1	0.6±0.1	0.7±0.1
$24 h \sigma$	19.3±0.2	23.6±1.1	20.3±0.2	23.4±0.9	23.3±0.9
	4.3±0.1	4.4±0.2	4.3±0.1	4.7±0.2	5.0±0.1
28 d o	61.3±1.4	71.9±1.6	66.2±1.0	65.7±1.2	68.9±2.8 (!)
	8.7±0.1	9.1±0.2	9.0±0.1	8.4±0	9.1±0.1

 $\begin{array}{l} \mbox{Table 4 Flexural } (\sigma_f) \mbox{ and compressive } (\sigma_c) \mbox{ strengths } (MPa) \mbox{ of mortar } (w/cm=0.50) \\ \mbox{ with different admixtures when mixed and cured at 5°C.} \end{array}$

Admixture	$2 d \sigma_c$	$2 d \sigma_f$	$28 d \sigma_c$	$28 d \sigma_f$
None, Ref.	13.6±0.3	2.9±0.2	54.0±1.0	8.0±0.5
1% CaCl ₂ ·6H ₂ O	15.3±0.5	3.17±0.03	58.5±2.3	8.8±0.3
1% Ca(NO ₃) ₂	12.1±0.2	3.0±0.1	56.3±0.6	8.1±0.4
1% CN/0.1% NaSCN	13.2±0.3	3.22±0.03	55.0±1.5	8.2±0.4
1% CN/0.2% NaSCN	14.6±0.3	3.3±0.2	56.5±0.7	9.3±0.9
1% CN/0.3% NaSCN	14.2±0.4	3.4±0.2	55.9±2.5!	7.8±0.3
0.2% NaSCN	15.3±0.3	3.4±0.2	56.5±1.6	7.8±0.2
0.3% NaSCN	15.5±0.5	3.2±0.1	60.4±2.2	8.1±0.8