

Effect of some admixtures on the setting time and strength evolution of cement pastes at early ages

S. Aggoun^{a,*}, M. Cheikh-Zouaoui^b, N. Chikh^b, R. Duval^a

^a *Laboratory of Mechanics and Materials of Civil Engineering, University of Cergy-Pontoise, 5, Mail Gay-Lussac, Neuville sur Oise, 95031 Cergy Pontoise Cedex, France*

^b *Laboratory of Material and Durability of Constructions, University of Constantine, Constantine 25000, Algeria*

Received 6 August 2004; received in revised form 19 April 2006; accepted 25 May 2006

Available online 9 November 2006

Abstract

The purpose of this work is to investigate the effect of using some admixtures such as calcium nitrate, triethanolamine and triisopropanolamine, on the setting and hardening process of cement pastes at 20 °C temperature. Tests were performed on specimens from various mixes considering two types of cements. The results obtained indicate that the calcium nitrate used alone acts as a setting accelerator and has relatively little beneficial effect on the long term development of mechanical resistances. Regardless of the cement type used, both alkanolamines used alone performed well as a hardening accelerator at all ages. The combined additions produced at very early age significant and promising results with respect to both setting and hardening acceleration, and to a continuous compressive strength increase with time.

© 2006 Published by Elsevier Ltd.

Keywords: Hardening accelerator; Setting accelerator; Early age; Cement paste; Compressive strength; Setting time; Temperature

1. Introduction

The present economic constraints require acceleration in the speed of work in the construction industry. The need for a concrete with sufficient strength at a very early age is in many situations very important. Such concrete is obtained through the use of some admixtures such as water-reducing superplasticiser, set accelerators and hardening accelerators. Standards about admixtures for concrete and mortar differentiate between set and hardening accelerators namely;

- Set accelerator is defined as an admixture that decreases the initial setting for the transition of the mix from the plastic to the rigid state.

- Hardening accelerator is defined as an admixture that increases the rate of development of early strength in the concrete with or without affecting the setting time.

Various admixtures have been used to get a concrete with sufficient strength at a very early age, the calcium chloride has been in the past the most widely used set accelerator in this field. However, the presence of chloride causes serious problems regarding corrosion of reinforcing bars embedded in concrete members. This has renewed interest to develop a number of chloride-free admixtures. Dodson [1] presented a review of non-chloride, non-corrosive set accelerating salts. His investigation started in 1962, it was found that the calcium formate, $\text{Ca}(\text{CHO}_2)_2$, can be used as a set accelerator [2]. The second salt to fulfill requirements was calcium nitrate, $\text{Ca}(\text{NO}_3)_2$, which was patented in 1969 [3]. After an intensive research, it was established that the calcium nitrate was also a very effective corrosion inhibitor for metal imbedded in concrete.

* Corresponding author. Tel.: +33 1 34 25 69 13; fax: +33 1 34 25 69 41.
E-mail address: salima.aggoun@iupc.u-cergy.fr (S. Aggoun).

The effect of calcium nitrate additions on the setting characteristics of cements and the steel corrosion has been studied by Justnes [4–6]. It was initially assumed that the accelerating effect was dependent on the aluminat content of the cement. This assumption was not verified for cements at low temperature (5 °C). The results obtained showed that calcium nitrate does function as a set accelerator for cement between 7 °C and 20 °C, but the set accelerating efficiency of calcium nitrate depended very much on the cement type used. It was also found that the set accelerating efficiency of calcium nitrate seems to increase with increasing belite content in cement or other cement characteristic promoting belite formation in the clinker process.

Triethanolamine (TEA), a low tertiary alkanolamines, is used as a grinding aid in cement manufacture and as a constituent in certain admixture formulations in concrete practice. Depending on the cement type and addition rate, TEA can produce either set acceleration or retardation. An addition rate of 0.02% to the type I Portland cement, TEA acts as a set accelerator, at 0.25% as a mild set retarder and at 0.5% a severe retarder and at 1% a very strong accelerator [7,8]. The effect on the strength development in cement pastes is also dependent on the added amount of TEA [9,10]. The addition of small amounts of higher tertiary alkanolamines such as triisopropanolamine (TIPA) resulted in interesting increases in the strength of cement pastes at different ages [11,12]. A recent study carried out on the strength enhancing mechanism of triisopropanolamine presented compressive strength data for 10 Portland cements tested as cement paste after 28 days of hydration [13]. The average strength improvement with 200 ppm TIPA added to the mix water was 10%.

The purpose of the present study is to find combinations of calcium nitrate with other compounds so as to fulfill the criteria for both a setting and a hardening accelerator. In this respect, the choice of alkanolamines presenting a developed spatial molecular structure like TEA and TIPA seems to be appropriate to verify previously indicated criteria.

2. Experimental study

The physical properties and the chemical analyses of the two cements (C1 and C2) used in this investigation are shown in Table 1. Both cements present similar specific surface and tricalcium silicate (C_3S) content but their tricalcium aluminate (C_3A) content are different, with C2 cement containing a lower amount in C_3A . Each of the cement type used is manufactured by separate cement plant situated in east Algeria.

The general formula of the calcium nitrate used in the present study is: $X \cdot NH_4NO_3 \cdot Y \cdot Ca(NO_3)_2 \cdot Z \cdot H_2O$. The coefficients X , Y and Z values are respectively $X = 0.092$, $Y = 0.500$ and $Z = 0.826$, which correspond to 19.00% Ca^{2+} , 1.57% NH_4^+ , 64.68% NO_3^- and 14.10% H_2O . The chemical formulae of the triethanolamine and the triisopropanolamine added was respectively $N(CH_2CH_2OH)_3$ and $(CH_2CH_2CH_2OH)_3$ [$C_9H_{21}O_3N$]. The latter additions were

Table 1
Physical properties and chemical analyses of the cements

Chemical composition	Cement 1 ^a (C1) (%)	Cement 2 (C2) (%)
CaO	64.36	63.91
SiO ₂	22.00	21.62
Al ₂ O ₃	5.02	4.49
Fe ₂ O ₃	2.94	315.37
SO ₃	1.94	1.92
MgO	2.07	1.66
K ₂ O	0.47	0.25
Na ₂ O	0.26	0.08
Mineralogical composition		
C ₃ S	51.28	52.48
C ₂ S	24.68	22.69
C ₃ A	8.33	2.82
C ₄ AF	8.94	16.32
Physical properties		
Ignition Loss, %	0.64	0.81
Blaine surface, m ² /kg	352.00	332.00

^a Addition used for C1 cement: either 18% of pozzolan or 10–12% of limestone.

used for the purpose of providing the hardening criteria to the blend admixture. The w/c ratio for the various mixes investigated is 0.3. The characteristics of these mixes are shown in Table 2.

The setting test on the cement pastes was performed using a Vicat apparatus and following EN196–3 procedure. The hardening criteria were determined through simple compressive strength tests on cubic specimen $50 \times 50 \times 50$ mm³. These latter were cast in metallic moulds and kept for 24 h at 20 ± 1 °C and at $55 \pm 5\%$ RH. They were then demoulded and conserved in water at 20 °C until required for testing. Using a hydraulic testing machine, compressive strength tests were carried out according to the code NF18–406. Each compressive strength value represents the average of the results from 3 specimens tested.

The study of the hydration process and the recording of temperature evolution during cement setting and initial hardening were performed through calorimetric tests in compliance with standard NF P15–356. These tests have been carried out at 20 °C temperature for a period of 4 days.

Table 2
Mixes investigated

Cement type	Mixes designation	% Nitrate	% TEA	% TIPA
C1	M10	0.00	0.00	0.00
	M11	1.00	0.00	0.00
	M12	0.00	0.05	0.00
	M13	0.00	0.00	0.05
	M14	1.00	0.05	0.00
	M15	1.00	0.00	0.05
C2	M20	0.00	0.00	0.00
	M21	1.00	0.00	0.00
	M22	0.00	0.05	0.00
	M23	0.00	0.00	0.05
	M24	1.00	0.05	0.00
	M25	1.00	0.00	0.05

3. Results and discussions

3.1. Setting Times and Compressive Strength

Tests were carried out on specimen at the age of 1, 3, 7 and 28 days. The various results obtained regarding setting times and compressive strength are given in Table 3 and Figs. 1 and 2. Both C1 and C2 cements present higher dicalcium silicate content but a different comparing content in aluminate and aluminate–ferrite.

3.1.1. Effect of calcium nitrate (M11, M21)

In regards to C1 cement, with normal tricalcium silicate content (8.33%), the calcium nitrate affected significantly the evolution in the early age compressive strengths, they increased by almost 50% at 1 and 3 days compared to control mix values. The improvements noticed on the setting times were very small. Considering C2 cement, which has a low tricalcium silicate content (2.82%), the obtained results show that calcium nitrate acts as a good setting

Table 3
Experimental setting times and compressive strengths results

Mixes investigated	Setting times (± 10 min)		Compressive strength (MPa)			
	Initial	Final	1 day	3 days	7 days	28 days
M10 (control)	137	205	18	25	38	60
M11 (Nitrate)	125	195	27	36	41	67
M12 (TEA)	150	235	28	36	45	70
M13 (TIPA)	140	210	32	48	80	96
M14 (Nitrate + TEA)	75	130	25	32	40	72
M15 (Nitrate + TIPA)	75	110	36	48	80	88
M20 (control)	188	330	11	17	35	50
M21 (Nitrate)	150	260	9	15	29	60
M22 (TEA)	190	240	17	25	40	62
M23 (TIPA)	175	210	32	48	80	100
M24 (Nitrate + TEA)	130	195	14	26	50	70
M25 (Nitrate + TIPA)	120	175	28	48	88	104

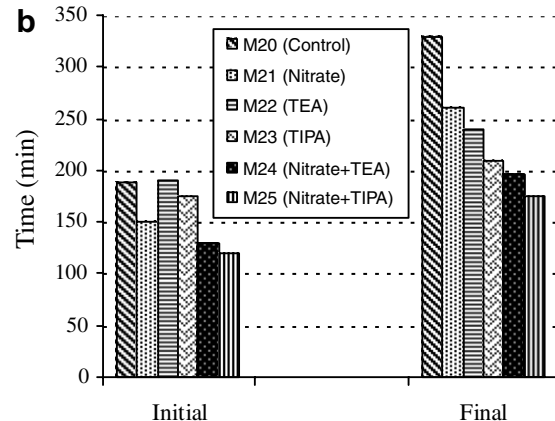
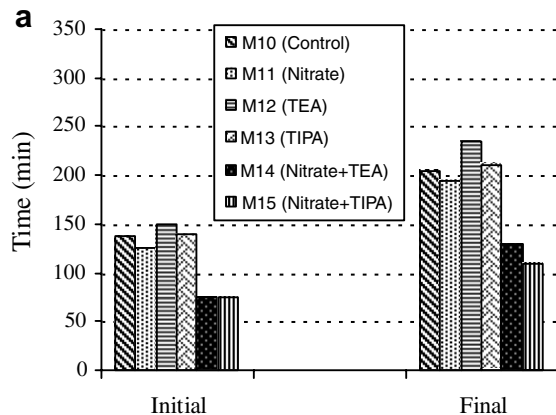


Fig. 1. (a) Setting times for C1 mixes. (b) Setting times for C2 mixes.

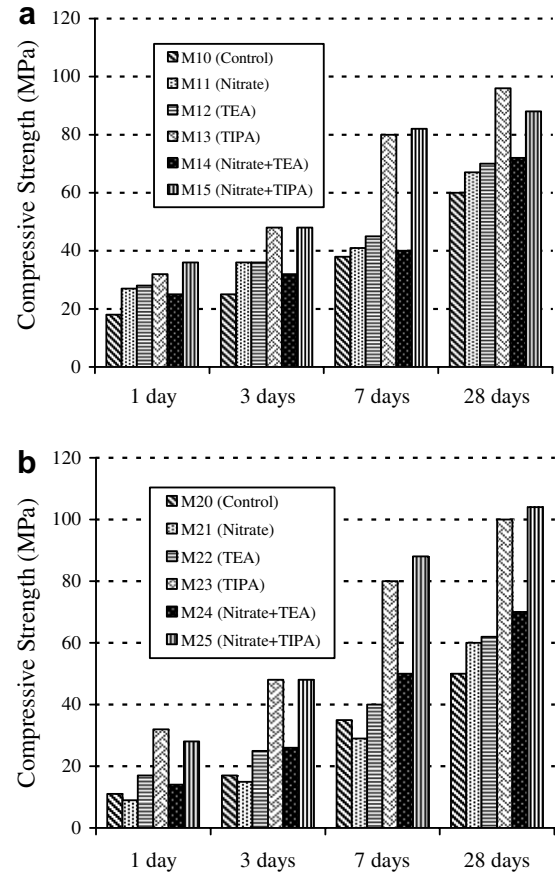


Fig. 2. (a) Compressive strength for C1 mixes. (b) Compressive strength for C2 mixes.

accelerator. Compared with control mix initial and final setting times, the presence of calcium nitrate reduces them by 20%. However, as the early age compressive strength was not improved, calcium nitrate can not be classified as a hardening accelerator though it improved the 28 days strength by 20%.

Thus the efficiency of the calcium nitrate as a set accelerator seems to be dependent on the cement chemical composition, confirming thereby the results obtained by Justnes [5].

3.1.2. Effect of triethanolamine (M12, M22)

The addition of 0.05% TEA with C1 cement produced little effect on M12 mix setting times. The increase was significant on its early age compressive strength, 50% at 1 and 3 days, but reasonable in the long term, about 20% at 28 days. Regarding C2 cement, this addition rate reduced the M22 final setting time to 75% control mix value. It also improved significantly the compressive strength at 1 and 3 days by about 50%, but moderately at 7 and 28 days by 15 ÷ 20%.

These results clearly show that the triethanolamine performed well as a hardening accelerator regardless of the cement type used.

3.1.3. Effect of triisopropanolamine (M13, M23)

The initial and final setting times were hardly affected by the use of 0.05% TIPA with C1 cement. However, it produced a major improvement on the compressive strength of M13 mix at all ages. Compared to control mix M10, the increase in strength was about 80% at 1 day, 90% at 3 days, 110% at 7 days and 60% at 28 days. In the case of C2 cement rich in C_4AF , the use of the same amount of TIPA reduced the final setting time by about 40%. It also improved considerably the compressive strength at all ages of M23 mix, about 185% at 1 and 3 days, 130% at 7 days and 100% at 28 days.

Regardless of the cement type used, the performance of triisopropanolamine as a hardening accelerator is greater than that of triethanolamine.

3.1.4. Effect of calcium nitrate combined with triethanolamine (M14, M24)

The use of calcium nitrate in combination with TEA resulted in their joining effects. The initial and final setting times were reduced respectively to 55% and 65% for C1 cement and to 70% and 60% for C2 cement of their respective control mix values. The mechanical resistances were also enhanced by 40% for M14 mix and 30% for M24 mix at early age, and at successive ages by respectively 5 ÷ 30% for M14 mix and 40 ÷ 50% for M24 mix.

Thus calcium nitrate combined to triethanolamine leads at the early ages to some interesting results in terms of accelerating both setting and hardening.

3.1.5. Effect of calcium nitrate combined with triisopropanolamine (M15, M25)

The joining effects were also illustrated with the use of calcium nitrate in combination with triisopropanolamine. The initial and final setting times compared with control mix values were reduced respectively by 45% for C1 cement and by 35% and 45% for C2 cement. Regarding M15 mix, the compressive strength increase for short and long term ages was respectively more than 90% and 45%. Such increase was further improved with M25 mix as it recorded

more than 150% and 110% respectively for short and long term ages. Thus better admixture reactivity took place with C2 cement which contains high aluminate–ferrite content.

The process of accelerating both setting and hardening at early ages was further explicit with the use calcium nitrate combined to triisopropanolamine.

3.2. Hydration temperature evolution

The heat released by the cement during its hydration is translated into an important temperature increase from which the heat quantity developed can be evaluated. The rate of hydration seems to depend on the permeability and cohesion of the C–S–H gel coatings around the cement grains such that its modification to a more open flocculated structure facilitates diffusion and accelerates hydration [14].

Calorimetric tests have been realised for some mixes elaborated with C2 cement only. The results may be presented graphically in terms of rate of heat evolution versus time [7], or maximum rate of heat evolution versus reciprocal to peak height [14] or temperature evolution versus time [11]. This latter presentation is adopted in the present work.

The general profile of all the curves displayed in Fig. 3 was similar but with different rates, in consistence with

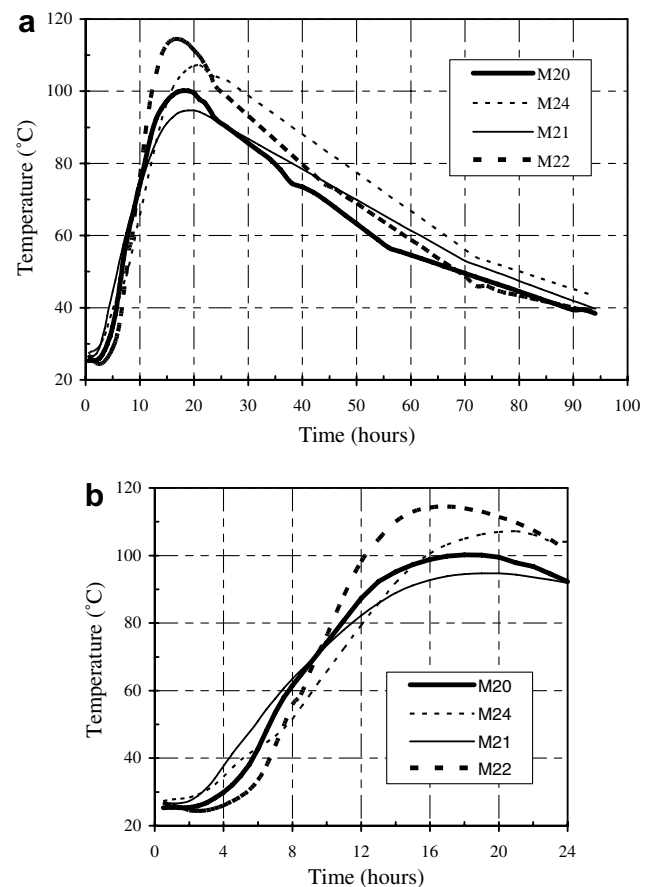


Fig. 3. (a) Temperature evolution with time (0–100 h). (b) Temperature evolution with time (0–24 h).

the times results shown in Table 3. The first hydration peak, indicating initial hydration reactions, appeared quickly (between 0–30 min) for M21, M22 and M24 mixes and was quite difficult to locate precisely. The main peak, corresponding to the maximum temperature, indicated the principal reactions taking place during the hardening phase.

With respect to control curve, M21 temperature slope has undergone an increase during the starting process indicating thereby the presence of a setting accelerator. The use of TEA alone, M22 curve, delayed during the first hours the hydration reaction. The highest temperature recorded by M22 mix illustrated clearly the potentiality of a hardening accelerator. The combination of calcium nitrate with TEA, M24 curve, performed better as the temperature slope increased during the initial setting (0–5 h) and a higher temperature value was achieved compared to control curve, which means an extra hardening effect. Hence, M24 mix included both aspects of setting and hardening accelerator.

Referring to Fig. 3(b), it may be interesting to examine the joining effects through the variation of M24 curve. Within the first hours, calcium nitrate acted as a setting accelerator by increasing the hydration rate, then follows a second phase where TEA slowed the hydration rate making M24 curve below control curve. After 16 h from the starting process, the hydration reaction was reactivated with a higher degree in the long term. Thus it may be inferred that calcium nitrate acted initially as a setting accelerator then triethanolamine took over by accelerating mainly the hardening phase.

According to Gartner [12], the triethanolamine seems to be mostly absorbed by cement prior to the development of a catalytic mechanism which facilitates the transport of ferric ions through the aqueous phase in the form of ferric-alkanolamine complexes.

4. Conclusions

Tests have been carried out on cement pastes specimens to investigate the effect of using some admixtures such as calcium nitrate, triethanolamine and triisopropanolamine, on the setting time and compressive strength evolution. In view of the admixture rates added, the main results show that:

- The calcium nitrate acted mainly as a setting accelerator with efficiency depending on the cement chemical composition. In the long term, the effect on the strength increase was insufficient for it to be considered as a hardening accelerator.
- Regardless of the cement type used, both triethanolamine and triisopropanolamine performed well as a hardening accelerator at all ages.
- The combination of calcium nitrate with either triethanolamine or triisopropanolamine resulted in their joining effects with time, translated by a reduction in the initial and final setting times and a strength enhancement at all ages of the cement pastes, particularly at early ages.
- Used with equal dosage, triisopropanolamine is far more efficient in terms of strength increase than triethanolamine.

References

- [1] Dodson VH. Concrete admixture. New York: VN Reinhold; 1990.
- [2] Dodson VH, Farkas E, Rosenberg AM. US Patent No. 3,210,207, October 5, 1965.
- [3] Angtadt RL, Hurley FR. US Patent No. 3,427,175, February 11, 1969.
- [4] Justnes H. Report STF F93013. SINTEF Structures and Concrete. Norway: Trondheim; 1993.
- [5] Justnes H, Nyguard EC. The influence of technical calcium nitrate additions on the chloride binding capacity of cement and the rate of chloride induced corrosion of steel embedded in mortars. In: Swamy RN, editor. Proceedings of international conference on corrosion and corrosion protection of steel in concrete. UK: Sheffield; 1994. p. 491–502.
- [6] Justnes H, Nyguard EC. Technical calcium nitrate as set accelerator for cement at low temperatures. *Cement Concr Res* 1995;25(8): 1766–74.
- [7] Ramachandran VS. Action of triethanolamine on the hydration characteristic of tricalcium silicate. *J Appl Chem Biotechnol* 1972;22: 1125–38.
- [8] Rixon R, Mailvaganam N. Chemical admixtures for concrete. London: E and FN Spon; 1999.
- [9] Heren Z, Ölmez H. The influence of ethanolamines on the hydration and mechanical properties of Portland cement. *Cement Concr Res* 1996;26(5):701–5.
- [10] Aiad I, Mohammed Abo-El-Enein SA. Rheological properties of cement pastes admixed with some alkanolamines. *Cement Concr Res* 2003;33:9–13.
- [11] Justnes H. Accelerator blends for Portland cement. In: Second international symposium on cement and concrete technology in the 2000s. Turkey: Istanbul, 2000. p. 433–42.
- [12] Gartner E, Myers D. Influence of tertiary alkanolamines on Portland cement hydration. *J Am Ceram Soc* 1993;76(6): 1521–30.
- [13] Sandberg PJ, Doncaster F. On the mechanism of strength enhancement of cement paste and mortar with triisopropanolamine. *Cement Concr Res* 2004;34:973–6.
- [14] Wilding CR, Walter A, Double DD. A classification of inorganic and organic admixtures by conduction calorimetry. *Cement Concr Res* 1984;14(2):185–94.