SINTEF REPORT

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Accelerating admixtures for concrete

State of the art

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ABSTRACT

Accelerating admixtures affect the rates of reactions between cement and water to give an overall increase in the hydration rate. Thus, the use of accelerators in concrete provides a shortening of setting time and/or an increase in early strength development. This report gives a historical and technical overview of liquid accelerators used for concrete, their mode of actions and the characteristics of today’s commercial accelerators. Accelerators for both ‘normal’ and sprayed concrete are covered. Antifreeze admixtures for winter concreting are also discussed.
Calcium chloride, the beste accelerator ever, is no longer an option due to severe corrosion hazzards in steel reinforced concrete. Inorganic salts of nitrate (for setting) and thiocyanate (for hardening) are common alternatives, although they are less efficient than calcium chloride. Many commercial admixtures today are made of mixtures of nitrate and thiocyanate. Some also contain alkanolamines and carboxylic acids or their salts. Combinations of chemicals may give interesting synergistic effects.

Alkali-free shotcrete accelerators are based on aluminum sulphate as main ingredient, often combined with diethanolamine and organic acids (oxalic, formic) and/or inorganic acids (phosphorous, hydrofluoric).

The report gives recommendations for further research and development of accelerators for concrete.

KEYWORDS	ENGLISH	NORWEGIAN
GROUP 1	Materials technology	Materialteknologi
GROUP 2	Concrete	Betong
SELECTED BY AUTHOR	Accelerator	Akselerator
	Cement	Sement
	Hydration	Hydratisering

Foreword

COIN - Concrete Innovation Centre - is one of presently 14 Centres for Research based Innovation (CRI), which is an initiative by the Research Council of Norway. The main objective for the CRIs is to enhance the capability of the business sector to innovate by focusing on long-term research based on forging close alliances between research-intensive enterprises and prominent research groups.

The vision of COIN is creation of more attractive concrete buildings and constructions. Attractiveness implies aesthetics, functionality, sustainability, energy efficiency, indoor climate, industrialized construction, improved work environment, and cost efficiency during the whole service life. The primary goal is to fulfill this vision by bringing the development a major leap forward by more fundamental understanding of the mechanisms in order to develop advanced materials, efficient construction techniques and new design concepts combined with more environmentally friendly material production.

The corporate partners are leading multinational companies in the cement and building industry and the aim of COIN is to increase their value creation and strengthen their research activities in Norway. Our over-all ambition is to establish COIN as the display window for concrete innovation in Europe.

About 25 researchers from SINTEF (host), the Norwegian University of Science and Technology - NTNU (research partner) and industry partners, 15 - 20 PhD-students, 5 - 10 MSc-students every year and a number of international guest researchers, work on presently 5 projects:

- Advanced cementing materials and admixtures
- Improved construction techniques
- Innovative construction concepts
- Operational service life design
- Energy efficiency and comfort of concrete structures

COIN has presently a budget of NOK 200 mill over 8 years (from 2007), and is financed by the Research Council of Norway (approx. 40 %), industrial partners (approx 45 %) and by SINTEF Building and Infrastructure and NTNU (in all approx 15 %). The present industrial partners are:

Aker Kværner Engineering and Technology, Borregaard LignoTech, maxitGroup, Norcem A.S, Norwegian Public Roads Administration, Rescon Mapei AS, Spenncon AS, Unicon AS and Veidekke ASA.

For more information, see www.sintef.no/coin

TABLE OF CONTENTS

1 Introduction

The rates of chemical reactions between clinker materials in cements and water, often referred to as cement hydration reactions, may be altered by adding small amounts of chemical substances to the cement-water mix. Substances affecting these rates to give an overall increase in the hydration rate, i.e. an accelerating effect, are termed accelerating admixtures or simply accelerators. Hence, an accelerator is added to concrete for the purpose of shortening setting time and/or increasing early strength development. In the first case the main action of the accelerator occurs in the plastic state of the cement paste, while in the latter case the accelerator acts primarily in the hardened state. Some accelerators affect either setting or hardening, while several accelerate both setting and hardening.

The aim of this report is to provide an overview of chemical admixtures reported to accelerate setting and/or hardening of Ordinary Portland Cement (OPC) and OPC based concrete. Both accelerators for normal concrete and nozzle added accelerators for sprayed concrete (shotcrete) will be discussed. First, an outline of accelerators in general is given including an overview of accelerator consumption in Norway over the last years, followed by a description of specific accelerators and their mode of action during cement hydration. Also commercial accelerators are treated.

As almost 100 % of concrete accelerators on the market are in liquid form (a few are sold as readily soluble powders), and the fact that most operators at concrete mixing plants prefer to handle accelerators in liquid form, this report does not treat powder accelerators insoluble in water.

The effect of accelerating admixtures on high alumina cements or CAC (Calcium Aluminate Cement) is covered only briefly.

2 Background and accelerators in general

2.1 Classification of accelerators

Accelerators may be classified in numerous ways. For instance, the European norm EN 934-2:2001 [1] makes a distinction between setting and hardening properties when defining accelerators for concrete:

Set accelerating admixture
Admixture which decreases the time to commencement of transition of the mix from the plastic to the rigid state.

Hardening accelerating admixture
Admixture which increases the rate of development of early strength in the concrete, with or without affecting the setting time.

Setting is normally determined by measuring the time until a certain mechanical resistance is obtained when a penetration needle is forced into the cement paste (e.g. the Vicat apparatus). A distinction is even made between initial and final setting time. The level of hardening is normally determined by measuring the compressive strength of hardened cement paste, mortar and concrete prisms.

Setting and hardening may also be determined indirectly by measuring the heat evolution or temperature increase generated from the chemical reactions between cement and water. The hydration of cement, being an exothermic reaction, produces heat and if the hydration is accelerated, heat is either produced earlier (setting) and/or at a faster rate (hardening). This is illustrated in Figure 2.1.

It should, however, be realised that a lot of accelerators affect both setting and hardening, sometimes depending on the dosage of the accelerator.

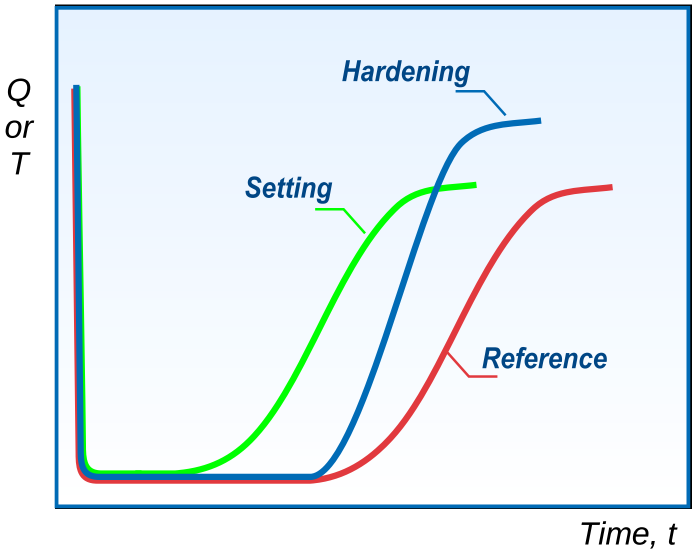


Figure 2.1 The effects of setting and hardening accelerators upon the rate of heat evolution Q (W/kg) or temperature T (^{o}C) during hydration of cement.
Reference: Cement paste without accelerator.
Setting: Cement paste with setting accelerator.
Hardening: Cement paste with hardening accelerator.
The setting accelerator produces heat earlier than the reference, but the slopes of the curves are parallel (equal dQ/dt).
The hardening accelerator starts the production of heat at the same time as the reference, but the slope is steeper (higher dQ/dt).

From a more practical point of view, accelerators are sometimes classified simply according to the type of concrete in which they are used:

Accelerator for normal concrete
Accelerator added during mixing of the concrete at the concrete plant

Shotcrete accelerator for sprayed concrete
Accelerator added in the nozzle of the equipment during spraying

Another way of making distinctions between different accelerators is to divide them into groups according to their physical form and chemical nature, for instance:

Liquid form:
Water soluble inorganic and organic salts and compounds

Slurry form:
Insoluble inorganic salts and compounds dispersed in water

Powder form:
Insoluble inorganic salts and compounds

A detailed overview based on the chemical nature of liquid accelerators is presented in Chapter 3.

2.2 Benefits provided by accelerators

The purposes of using accelerators and the advantages resulting from the use of accelerators are many. The benefits of a reduced setting time may include [2]:

- Earlier finishing of surfaces
- Reduction of hydraulic pressure on forms
- More effective plugging of leaks against hydraulic pressure

The benefits of an increase in the early strength may include [2]:

- Earlier removal of forms
- Reduction of the required period of curing and protection
- Earlier placement in service of a structure or a repair
- Partial or complete compensation for the effects of low temperatures on strength development

2.3 Consumption of accelerators in Norway

Accelerator consumption – normal concrete
Even though the benefits of using accelerators are obvious, helping the contractor to meet specified construction schedules, the total volume of accelerators used for normal concrete is surprisingly low. According to the European Federation of Concrete Admixture Associations accelerators for normal concrete make up about 4 % of all admixtures sold in Europe [3]. The same picture is seen in Norway. In 2006 accelerators (shotcrete accelerators excluded) stood for only 3.4 % of all admixtures for normal concrete sold in Norway [4]. Figure 2.2 shows the trend in consumption over the last 15 years. There was an increase in the use of accelerators since early 1990s. This is to some extent caused by the increase in cement consumption in the same period (see Figure 2.3). However, it is shown in Figure 2.4 that despite the increase in cement consumption, the average consumption of accelerators for normal concrete has increased to about 0.5 kg/ton cement or more the last years compared to less than 0.1 kg/ton cement in the early 1990s. The very high application of accelerators in 2002 (see Figure 2.4) must be linked to specific building projects that particular year.

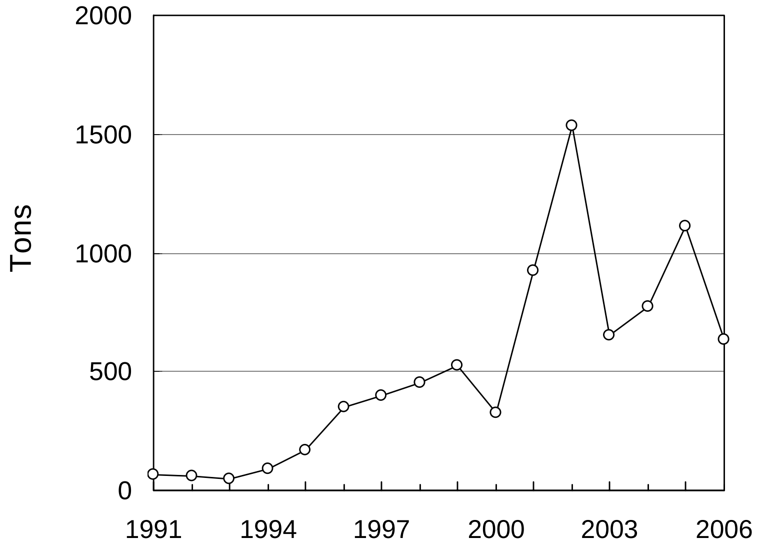


Figure 2.2 Total Norwegian consumption of accelerators for normal concrete in the period 1991–2006 (Data from NCCA [4]).

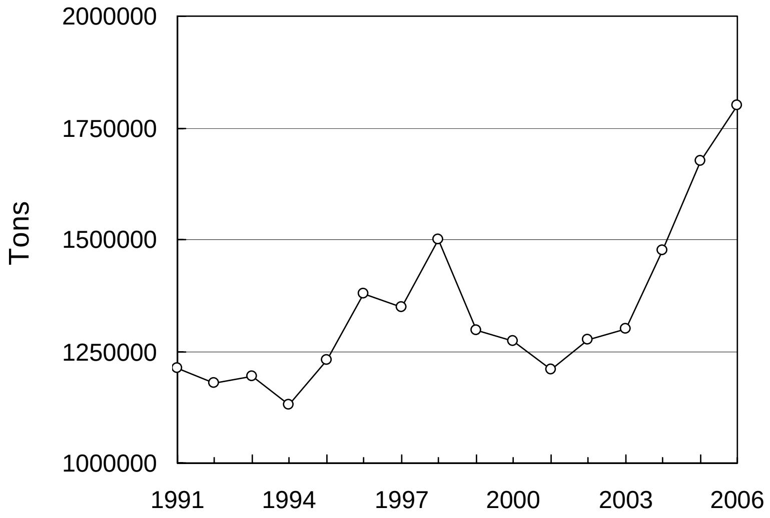


Figure 2.3 Total use of Portland cement in Norway in the period 1991–2006 (Data from NCCA [4]).

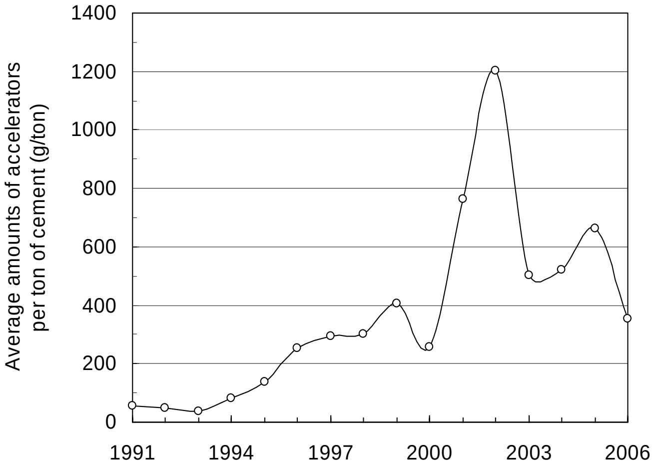


Figure 2.4 Ratio between total application of accelerators for normal concrete and the total use of Portland cements in Norway in the period 1991–2006 (Data from NCCA [4]).

Accelerator consumption – sprayed concrete

Due to the large volumes of shotcrete production and the high dosage of shotcrete accelerators (typically more than 5 % by cement weight), shotcrete accelerators is by far the most used class of accelerator in terms of volume. For instance, the volume of shotcrete accelerators sold in Norway in 2006 was approximately 10 times that of accelerators used for normal concrete in the same period (see Figures 2.2 and 2.5). Unlike the situation for normal concrete, there is no trend of increase in shotcrete accelerator consumption per ton cement used during the 1990s. On the other hand, a very clear increase in accelerator consumption relative to cement consumption has been observed since 2003 (see Figure 2.6). It seems to be a consensus among Norwegian shotcrete operators today, although not documented, that higher dosages of shotcrete accelerators are needed to compensate for slower strength development in the concrete nowadays compared to the late 1990s or early 2000s. The reason for this trend has not yet been clarified, but may be partly caused by the introduction of alkali-free shotcrete accelerators the very same period (see Chapter 13) and/or the increasing use of blended cements.

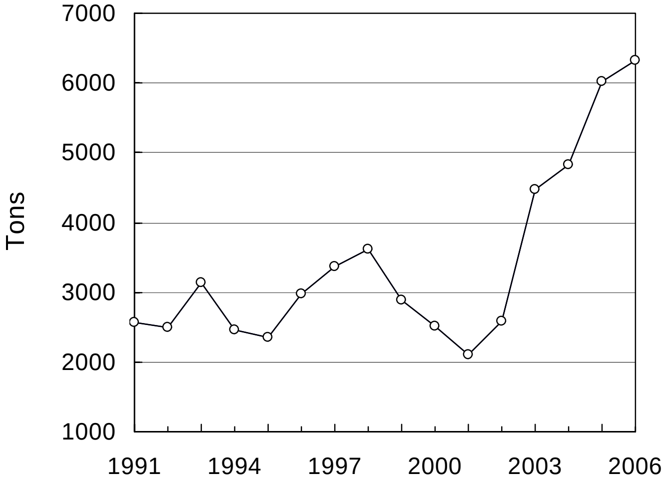


Figure 2.5 Total Norwegian application of accelerators for sprayed concrete (shotcrete) in the period 1991–2006 (Data from NCCA [4]).

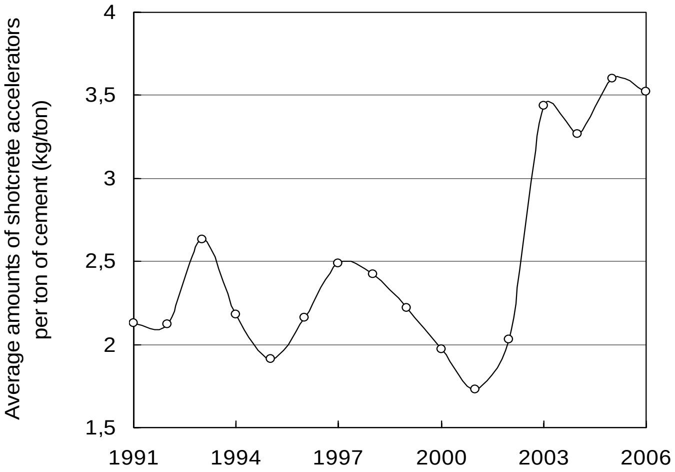


Figure 2.6 Ratio between total consumption of accelerators for sprayed concrete (shotcrete) and the total use of Portland cements in Norway in the period 1991–2006 (Data from NCCA [4]).

3 Chemical overview of accelerators

Many inorganic and organic compounds have been reported to accelerate hydration of Portland cements. For convenience, the compounds may be divided into *soluble inorganic salts* and *soluble organic salts and compounds*, the first category being the largest. Many commercial accelerators are blends of compounds taken from both groups (see Chapters 12 and 13). To a much lesser extent, *insoluble solid compounds* – for instance cementitious materials, silicate minerals and finely ground magnesium and calcium carbonates – have been used as accelerators [5]. Calcium sulphoaluminates are used as powder accelerators in Japanese shotcreting. Despite some use of powder accelerators today, the discussions below are restricted to *soluble* accelerators only.

Soluble inorganic salts of alkali and alkali earth metals

A variety of soluble inorganic salts accelerate setting and/or hardening of Portland cement, typically alkali and alkali earth salts of [2, 5]:

- Hydroxide
- Chloride, bromide and fluoride
- Nitrite and nitrate
- Carbonate
- Thiocyanate
- Sulphate
- Thiosulphate
- Perchlorate
- Silicate
- Aluminate

Both type of anion and type of accompanying alkali or alkali earth cation play a role. A screening of different combinations of some of the anions and cations within this group, based on high and equivalent molar concentrations, has given the following accelerating effects on tri-calcium silicate (C_3S) hydration in decreasing orders [6]:

Anions: $Br^- \approx Cl^- > SCN^- > I^- > NO_3^- > ClO_4^-$

Cations: $Ca^{2+} > Sr^{2+} > Ba^{2+} > Li^+ > K^+ > Na^+ \approx Cs^+ > Rb^+$

This ranging points out calcium chloride to be an effective accelerator. Indeed, it has been widely used for many decades. However, due to its tendency to promote corrosion of steel, it is no longer recommended for use in steel reinforced concrete. Today, most commercial accelerators for normal concrete (shotcrete excluded) contain sodium and calcium salts of nitrate (NO_3^-), nitrite (NO_2^-) and/or thiocyanate (SCN^-) (see Chapter 12).

Silicates and aluminates listed above show quick setting or flash setting properties and are used a lot in shotcreting. To some extent, potassium carbonate has also been used for this purpose [5]. Potassium carbonate has also been used in binary and ternary antifreeze admixtures [7].

Hydroxides are seldom used as such, but may be part of aluminate solutions to increase pH. High pH (high concentration of OH^-) reduces the risk of precipitation of insoluble aluminium hydroxide according to the equilibrium

$$Al(OH)_4^- = Al(OH)_3 + OH^- \quad (1)$$

Soluble organic salts and compounds

Soluble organic salts and compounds can be divided into two main groups:

- Carboxylic and hydroxycarboxylic acids and their salts
- Alkanolamines

Among the first group, calcium formate is a well known accelerator, while triethanolamine (TEA) is the most common among the alkanolamines. Alkanolamines are typically used as ingredients in accelerator blends, and rarely, if ever, as a sole ingredient. Probably, the most common use of TEA is to compensate for the retarding effect of some plasticizers.

4 Calcium chloride

Since use of chloride containing admixtures is no longer an option for steel reinforced concrete, only a short description of calcium chloride will be given. Calcium chloride ($CaCl_2$) is characterised by:

- $CaCl_2$ accelerates both setting and hardening of OPC [2].
- $CaCl_2$ is the oldest chemical admixture for OPC based concrete; reported as early as 1886 [8].
- $CaCl_2$ is the cheapest and the most effective accelerator to date [9].
- Although not fully understood , the mode of action of $CaCl_2$ in concrete and its effect on the hydration kinetics are well documented [2, 8].
- The effect of $CaCl_2$ on other cement paste properties is known; for instance freeze/thaw resistance, sulphate resistance and porosity [2, 10].
- $CaCl_2$ accelerates both the reaction between tricalcium aluminate (C_3A) and gypsum ($CaSO_4 \cdot 2H_2O$) and the hydration of tricalcium silicate (C_3S) [11].

$CaCl_2$ does not accelerate the hydration of high-alumina cements [2, 12], but has been reported to accelerate the pozzolanic reaction between $Ca(OH)_2$ and rice husk ash [13]. It is also reported that $CaCl_2$ activates the hydration of slag [14]. However, a comparison between $CaCl_2$ and Na_2SO_4 (sodium sulphate) as activators for the pozzolanic reaction of fly ash, showed that Na_2SO_4 increased both early and later strengths, while $CaCl_2$ mainly increased later strengths [15].

Despite the research on $CaCl_2$/cement paste interactions for several decades, it has been stated that the mechanisms responsible for the accelerating effect of $CaCl_2$ on the hydration of C_3S still are poorly understood [16]. The new chloride-free accelerators, replacing $CaCl_2$, are even less understood, and also less effective. The general situation today can be summarised like this [17]:

Chloride-based accelerators	*Chloride-free accelerators*
• Severe corrosion hazards	• No (or low) corrosion hazards
• Low cost/performance ratio	• High cost/performance ratio

The development of chloride-free accelerators with low cost/performance ratios has been a challenge for manufacturers of admixtures for many years, and still is.

5 Calcium nitrate and other nitrate/nitrite salts

Nitrates

According to the ranging of accelerating anions described above, nitrate (NO_3^-) is less effective than chloride (see Chapter 3). The isothermal conduction calorimeter curves shown in Figure 5.1, comparing the effects of different calcium salts on the rate of hydration of synthetic C_3S, clearly show that calcium nitrate ($Ca(NO_3)_2$) is less effective than $CaCl_2$ on both setting and hardening [8].

Ramachandran [18] found that $Ca(NO_3)_2$ acted as an accelerator of setting in cement paste at low concentrations, but showed no effect on early strength development. According to El-Didamony et al [19] $Ca(NO_3)_2$ is more effective than $CaCl_2$ as accelerator for the hydration of belite (β-C_2S). This has been confirmed by Justnes [20, 21] who has carried out a series of research studies on technical grade calcium nitrate (including a small amount of ammonium, NH_4^+) as concrete admixture since early 1990s. His findings regarding mode of action in OPC paste are as follows:

- Set acceleration is achieved by low dosages.
- Must be combined with other components to function as a hardening accelerator.
- No correlation between set accelerating efficiency and content of C_3A in the cement.
- Initial setting time decreases with increasing content of belite in the cement.
- Initial setting time decreases with decreasing alkali content in the cement.
- The mechanism for accelerating setting is two-fold:
  (1) An increased calcium concentration leads to a faster super-saturation of the water with respect to calcium hydroxide ($Ca(OH)_2$).
  (2) A decreased sulphate concentration leads to slower/less formation of ettringite which will shorten the onset of C_3A hydration.

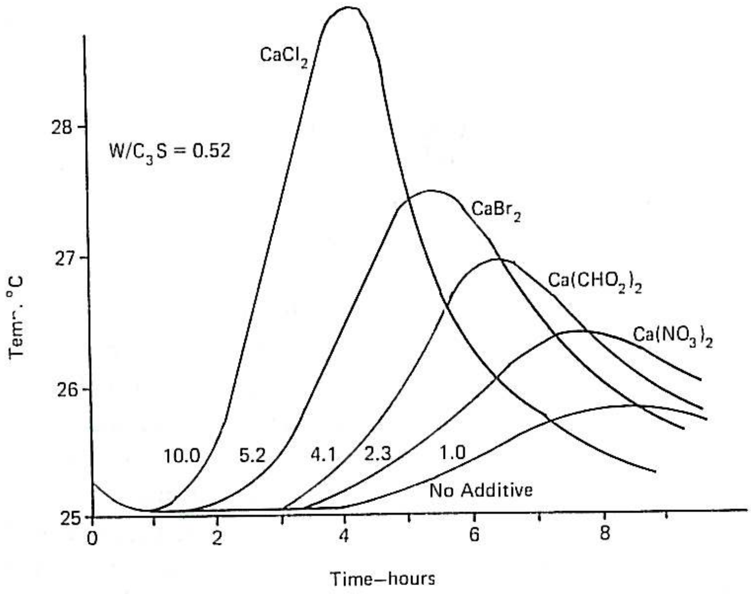


Figure 5.1 Isothermal conduction calorimeter curves for C_3S with various calcium salts. Dosage is 2 % anhydrous salt by weight of C_3S. The numbers indicate the slopes of the temperature-time curves from the end of the dormant period to the peak temperature relative to that of untreated C_3S, which assigned a value of 1.0 [8].

Rixom [22] investigated the relationship between temperature and setting and found that $CaCl_2$ can compensate for approximately 15°C drop in temperature, while $Ca(NO_3)_2$ can compensate for a 10°C drop.

Calcium nitrate at relatively high dosages has proven to be an effective inhibitor against chloride induced corrosion of steel reinforcement in concrete [20]. Accordingly, calcium nitrate is a multifunctional admixture for concrete.

Today, most suppliers of concrete admixtures offer calcium nitrate based accelerators (see Chapter 12).

The behaviour of alkali nitrates in concrete has also been investigated, but not as thoroughly as $Ca(NO_3)_2$. It seems that sodium nitrate ($NaNO_3$) has hardly any accelerating effect on setting behavior [20, 23], but is used to some extent in winter concreting admixtures, so-called antifreeze admixtures (see Chapters 10 and 12).

Nitrites

Nitrite (NO_2^-) differs chemically from nitrate (NO_3^-) only in the oxidation state of nitrogen: Nitrite (ox. state +5) versus nitrate (ox. state +7).

Calcium nitrite ($Ca(NO_2)_2$) has probably been the most popular non-chloride setting accelerator in the USA since late 1960s [8]. Many commercial accelerators today, and particularly antifreeze admixtures (see Chapters 10 and 12), contain calcium and/or sodium salts of nitrite. Even strength development effects produced in concrete are reported to be almost comparable to those obtained with $CaCl_2$ [9]. Despite this widespread use, reports describing the mode of action and mechanisms involved in cement paste setting are lacking.

$Ca(NO_2)_2$ has also proved to be an effective anodic corrosion inhibitor for metals embedded in concrete [24]. This is probably the main research area today regarding use of $Ca(NO_2)_2$ in concrete.

Nitrites suffer from one big commercial disadvantage compared to nitrates. Even though calcium nitrite seems to be “the best non-chloride admixture to date“ [9], nitrites are toxic and environmentally unfriendly. This means that nitrites, at least for future applications, will be discouraged due to health and environmental requirements and regulations.

6 Thiocyanates

Unlike nitrates and nitrites, alkali and calcium salts of thiocyanic acid, HSCN, i.e. thiocyanates (SCN^-), hardly affect setting of OPC, only hardening [25]. Justnes [20] found that a smaller amount of sodium thiocyanate (NaSCN) together with technical grade calcium nitrate can counteract the retarding effect of lignosulphonate based plasticizers and give 1 day strength values in the same range of what was found for samples accelerated by $CaCl_2$.

NaSCN are probably the most recent non-chloride hardening accelerating admixture introduced on the concrete market (since early 1980s) [8]. Although quite effective, NaSCN is expensive compared to technical grade calcium nitrate and $CaCl_2$ [26]. Nevertheless, roughly 10,000 tons of NaSCN are used wordwide every year to accelerate hardening of concrete [26]. Unfortunately, NaSCN shows some hazardous properties and has to be labelled *Xn Harmful* [26]. Another drawback for alkali-thiocyanate based admixtures is the high amount of alkalis introduced into the concrete and the corresponding potential for alkali-aggregate-reactions (AAR) [7].

Surprisingly little has been published regarding mode of action in cement paste and reaction mechanisms involved. Most of the information is available only in the patent literature, where it is seen that thiocyanate salts are often combined with other accelerating admixtures [27]. Some examples of commercial accelerators containing thiocyanate salts are shown in Chapter 12.

Wise et al [25], probably the first who published research on alkali-free thiocyanates, studied the effect of different thiocyanates on the hydration of OPC at low temperatures and found:

- Calcium thiocyanate ($Ca(SCN)_2$) is the most effective thiocyanate for promoting strength development. (In accordance with the ranging of ionic combinations in Chapter 3)
- The addition of 3 % $Ca(SCN)_2$ (by cement weight) to a paste hydrated at – 5°C resulted in 28-days compressive strength that was 74 % of the strength of the paste cured at room temperature.
- The least effective salt on compressive strength development was potassium thiocyanate (KSCN). The paste with KSCN, although producing the highest heat development after 3 days at room temperature, had strength values as low as 2/3 of the reference value.
- Ammonium thiocyanate (NH_4SCN) releases offensive ammonia vapour and therefore is not a viable chemical for practical applications.

A possible solution to this last point could be to try out amines with less offensive vapours than ammonium; for instance, alkanolamines like di- or triethanolamines which are also accelerators for cement hydration (see Chapter 9).

Unfortunately, Wise et al [25] used very high dosages in their study – between 1.5 and 3 % by weight of cement. This is probably far too high for many practical applications (high cost and high amount of alkalis if alkali thiocyanates are used). Furthermore, practical experiences recommend a maximum dosage below 1 % by cement weight. One supplier of a NaSCN based accelerator states that a dosage higher than 0.8 % of a 40 % solution (i.e. 0.32 % active material) does not give further increase in acceleration, but can in certain cases have a retarding effect [28].

Abdelrazig et al [29] estimated the degree of hydration of OPC pastes by differential scanning calorimetry and found that addition of NaSCN produced more calcium hydroxide than an equal molar amount of calcium chloride between 6 and 18 hours after mixing.

Since NaSCN is regarded a corrosive chemical [26], studies have been carried out in order to find out to what extent addition of this compound causes corrosion of steel reinforcement in concrete. Nmai and Corbo [30] found that NaSCN at maximum dosage levels recommended (0.75 to 1.0 %) either reduced or did not affect the corrosion rate of steel in concrete.

7 Alkali carbonates

Alkali carbonates are easily soluble powders, and have been used to some extent in antifreeze admixtures for concrete (see Chapter 10), in shotcrete accelerators (see Chapter 11) and in mortars. Potassium carbonate (K_2CO_3) is probably the most common. These carbonates are characterised by their quick-setting properties at moderate to high dosages, probably by promoting the flash-setting of tricalcium aluminate (C_3A) [5]. One study, comparing sodium, potassium and lithium carbonates in OPCs, showed [31]:

- At low dosages sodium and potassium carbonates retarded the setting times.
- At higher dosages (> 0.1 %) sodium and potassium accelerated the setting.
- Lithium carbonate acted as an accelerator at all concentrations studied.

The quick-setting properties of alkali carbonates can be eliminated by adding a retarder. In this way it is possible to formulate accelerators to be used in normal concrete [7]. However, controlling setting time with carbonate based accelerators is a difficult task.

Schwarz [32] found that high dosages of K_2CO_3 in combination with high dosages of potassium citrate are highly efficient accelerators for aluminate and ferrite hydration in OPCs. It is assumed that citrate promotes the dissolution of the ferrite phases by acting via surface complexation and ligand-promoted dissolution [32]. Citric acid and its salts are normally used as retarders for cement hydration, but may act as accelerators a high dosages [33].

8 Carboxylic acids and their salts

Accelerating properties are found among several types of carboxylic acids and their salts:

- *monocarboxylic*
- *dicarboxylic*
- *hydroxycarboxylic*

Popovics [2] claims that water soluble organic materials belonging to the carboxylic acid group are some of the most effective chloride-free accelerators for cement hydration. Without being specific regarding type of acid, he states that one acid with a short hydrocarbon chain is effective due to its ability to promote the dissolution of calcium ions from the cement compounds [2].

Monocarboxylic (formates and acetates)

Accelerating properties have been reported for the lower monocarboxylic acids (C1 to C4) and their salts (formic, acetic, propionic and butyric), while higher carboxylic acid homologes (>C4) are retarders [5]. It seems that those belonging to C1 are the most efficient ones, and that the calcium salt of formic acid, calcium formate ($Ca(HCOO)_2$), are the most common. Dodson [8] began research on $Ca(HCOO)_2$ in early 1960s and found that although $Ca(HCOO)_2$ was not as effective as $CaCl_2$, it does produce satisfactory increases in early strength as well as that of later ages. According to Dodson [8] $Ca(HCOO)_2$ also accelerates setting of OPC. Heikal [34] found that the initial and final setting times of both OPC and pozzolanic cement pastes are shortened with the addition of $Ca(HCOO)_2$.

Hewlett [35] has compared the calcium salts of chloride, nitrite and formate, and related their accelerating efficiencies to the mobility of the anions in order to penetrate into the silicate particles. Consequently, their size is of major importance. Taken this consideration into account, $Ca(HCOO)_2$ is less suitable with a relatively large anion size (0.45 nm compared to 0.34 nm for nitrite and 0.27 nm for chloride) [35]. Heikal [34] claims that the accelerating effect of $Ca(HCOO)_2$ on calcium silicate hydrate formation is mainly attributed to the fact that the diffusion rate of $HCOO^-$ ions is much higher than for the Ca^{2+} ions, and that the $HCOO^-$ ions can penetrate into the hydrated layers covering C_3S and β-C_2S grains. As a consequence, the precipitation of $Ca(OH)_2$ is accelerated as well as the decomposition of calcium silicates [34].

Justnes [20] found that $Ca(HCOO)_2$ and calcium acetate ($Ca(CH_3COO)_2$) was less effective accelerators than $Ca(NO_3)_2$ at equimolar concentrations of calcium ions, and suggests the reason to be possible complex formation of Ca^{2+} with the accompanying organic anion, leading to a lowering of the Ca^{2+} concentration in the paste fluid.

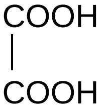
Ramachandran [36] reports that $Ca(HCOO)_2$ accelerates the hydration of C_3S, and one explanation is that $HCOO^-$ ions interfere with the protective layer normally formed on the surface of the cement particles. Furthermore, the effect of $Ca(HCOO)_2$ as an accelerator is influenced by the C_3A/SO_3 ratio in the cement. According to Gebler [37] cements that are "undersulfated" (C_3A/SO_3>4.0) provide the best potential for $Ca(HCOO)_2$ to accelerate the early age strength of concrete.

Rixom [9] claims that $Ca(HCOO)_2$ accelerates the setting and hydration of all types of cement, but at dosages beyond 2 % (by cement weight) – especially with respect to the first 24 hours – the effect is not significant.

The biggest problem in using $Ca(HCOO)_2$ as an accelerating admixture for concrete is its low solubility in water (approx. 16g/100g H_2O at room temperature). Therefore, it is not commercially available in liquid form, and must be added to concrete in solid powdered form [9]. This can create dispensing problems. Sodium formate (NaHCOO), which has also accelerating properties, is approximately 3 times more soluble in water, but the potential problem of the added alkali at relatively high dosages discourages its use [8].

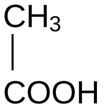
Dicarboxylic (oxalic acid)

Dicarboxylic acids are acids in which there are two carboxyl groups. The simplest of these acids, ethanedioic acid (IUPAC name) or oxalic acid (trivial name), consists simply of two carboxyl groups (–COOH) linked together. Although chemically related, the properties of oxalic acid are very different than for ethanoic acid (acetic acid):



$$\begin{array}{c} COOH \\ | \\ COOH \end{array}$$

Oxalic acid (ethanedioic)
pKa_1=1.27



$$\begin{array}{c} CH_3 \\ | \\ COOH \end{array}$$

Acetic acid (ethanoic)
pKa=4.76

From the pKa values it is seen that oxalic acid is a much stronger acid than acetic acid. The inductive effect of one carboxyl group in oxalic acid is expected to enhance the acidity of the other [38].

Oxalic acid is reported to decrease the setting time of OPC and increase early compressive strength [36]. Taylor [39] found that calcium oxalate is precipitated when oxalic acid is added to C_3S, and the concentration of Ca^{2+} ions close to the surface of the C_3S is thereby kept low until all the oxalic acid has been used up.

Ramachandran [18] compared hydrated cement with and without oxalic acid using the DTA technique and found the existence of calcium oxalate in the cement containing oxalic acid, and suggested that much of the strength development may be due to the formation of calcium oxalate during hydration.

In a fundamental study on the kinetics of C_3S hydration, Odler [40] found that when adding oxalic acid to the C_3S/water system the initial hydration progresses with a fast rate as long as the liberated calcium hydroxide is bound to oxalic acid and the liquid phase stays undersaturated with respect to $Ca(OH)_2$.

Singh et al [41] tested several dosages of oxalic acid in OPC and found that this acid acted as an accelerator at dosages from 0.5 % to 4 % (by cement weight), but acted as an retarder if present below 0.05 %. The accelerating effect is probably caused by the ability of carboxylate to form ionic bonds with free lime and calcites of cement and form calcium oxalate [41]. When present in small amounts in cement it seems that the retarding effect of oxalic acid is similar to that found for acetic acid at low dosages [41].

Hydroxycarboxylic (glycolic and lactic acids)

Although most hydroxycarboxylic acids and their salts *retard* the setting of OPC [35], there are examples of hydroxycarboxylic acids with accelerating properties in cement. This information is typically disclosed in the patent literature [42, 43]. As early as 1964 Zach et al [42] found that the two first members of the series of α-hydroxycarboxylic acids (with a hydroxyl group adjacent to the carboxyl group – see Table 8.1 below) caused a significant increase in the late (28 days) compressive strength of concrete when admixed at low dosages, typically from 0.01 % to 0.1 % by cement weight. Neither the mechanism of action in cement paste, nor the effect on early strength was discussed by Zach et al [42].

Table 8.1
Characteristics of two α-carboxylic acids [44] reported to accelerate cement hydration

Trivial name	Other name	IUPAC name	Chemical formula	pK_a
Glycolic acid	Hydroxyacetic acid	2-hydroxyathanoic acid	$CH_2(OH)COOH$	3.83
Lactic acid	Milk acid	2-hydroxypropanoic acid	$CH_3CH(OH)COOH$	3.85

Schutz [43] found that high dosages of sodium glycolate and sodium lactate (sodium salts of glycolic and lactic acid respectively) shortened setting time and speeded early strength development. Mechanisms causing the accelerating ability of α-hydroxycarboxylic acids are probably unknown, but may be linked to the ability of these acids to complex metals. For instance, glycolic acid is used as a component of household cleaners due to its dissolution capabilities for hard-water scale (calcium and magnesium) [45].

9 Alkanolamines

Alkanolamines are amines containing either one (primary amine NRH_2), two (secondary amine NR_2H) or three (tertiary amine NR_3) hydroxy alkyl groups (R). Showing accelerating effect on OPC hydration, these organic chemicals are sometimes used as ingredients in admixture blends. They are all weak bases.

Triethanolamine (TEA)

TEA, $N(CH_2CH_2OH)_3$, is both a tertiary amine and a tri-alcohol, and is probably the most common alkanolamine for concrete purposes. TEA was introduced as early as 1934, when it was interground as an addition with OPC in combination with calcium lignosulphonate [8]. This was done to increase the early compressive strength of the concrete made from the cement. Since 1958 TEA has become a common ingredient of some water reducing admixtures to off-set possible set retardation caused by the water reducer [8]. One of the most characteristic features of TEA is its ability to either accelerate or retard cement hydration depending on dosage. TEA tends to accelerate C_3A hydration kinetics, but act as a retarder on the hydration of C_3S [31, 35]. Rixom [46] has summarised some of the features of TEA in OPC:

- In the presence of TEA the reaction between C_3A and gypsum is accelerated.
- The subsequent conversion of the ettringite to monosulphate by reaction with C_3A is also accelerated by TEA.
- The formation of the hexagonal aluminate hydrate and conversion to the cubic form is accelerated by TEA.
- There may be a chelating effect whereby TEA reacts with the ferrite phase of OPC.
- There is some evidence for the formation of a surface complex between C_2S and C_3S initial hydrates and TEA.

Hewlett [35] screened potential accelerators and found flash-set of OPC admixed with 0.5 mole and 1.0 mole TEA per kg cement (i.e. approximately 0.75 % and 1.5 % by weight of cement respectively). At lower dosages the effect of TEA on C_3A and C_3S can be summarised like this [35]:

- At low dosages (0.1 – 0.5 % by weight of cement) TEA accelerates the hydration of C_3A in OPC.
- At dosages higher than 0.5 % TEA causes retardation of C_3S hydration.

Dodson [8] claimed that "the most popular addition rate of TEA is in the range of 0.010 % to 0.025 % on the weight of cement". Figure 9.1 shows the effect of dosage.

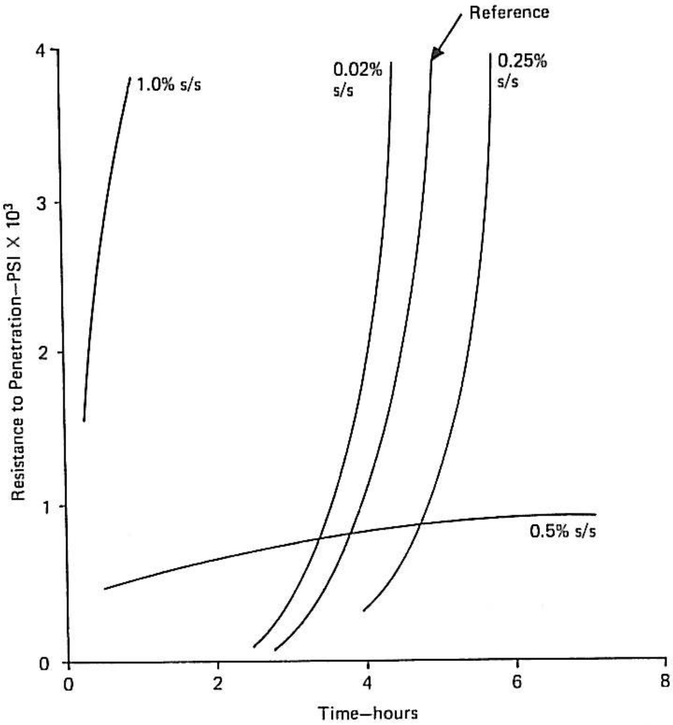


Figure 9.1 The effect of dosage of TEA on setting and hardening of OPC concretes [8]. The curves show the resistance to penetration as a function of time for four different dosages of TEA and a reference without TEA.

The data in Figure 9.1 indicate that at a dosage of 0.02 %, TEA acts as an accelerator, at 0.25 % as a retarder, at 0.5 % as a severe retarder and at 1.0 % as a flash-set accelerator. Similar behaviour was found by Ramachandran [31] when measuring the initial and final setting characteristics of OPC mortar treated with 0 – 0.5 % TEA (see Figure 9.2).

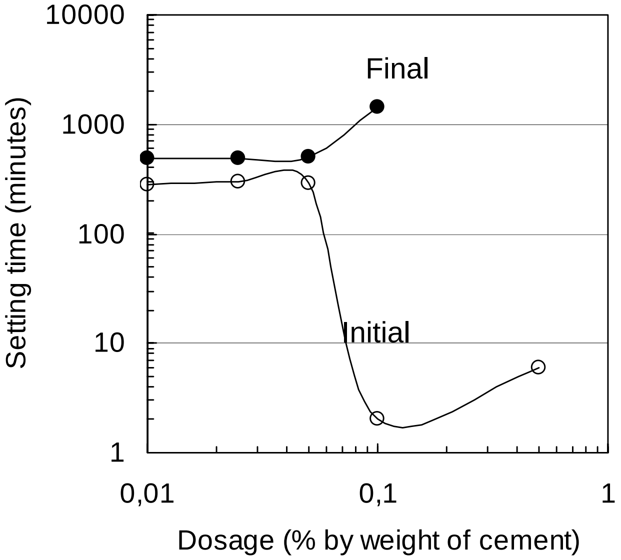


Figure 9.2 Effect of dosage of TEA on initial and final setting of OPC mortar (Data from [31]).

Although it has been shown that TEA decreases the strength of OPC, it acts differently with blast furnace cements. It has been found that TEA (in a mortar containing 30 % OPC and 70 % slag) accelerated the hydration kinetics by increasing the rate of reaction of gypsum with slag in the presence of lime [31].

Heren [47] was the first to publish data (in 1995) on the effect of monoethanolamine (MEA), $NH_2(CH_2CH_2OH)$, and diethanolamine (DEA), $NH(CH_2CH_2OH)_2$, on cement hydration. He compared MEA, DEA and TEA at dosages 0.1 to 1.0 % in white Portland cement and found no significant effect on the initial setting times at low dosages, but significant retardation at higher dosages for all three types. Besides, both MEA and TEA lowered the compressive strength after 3 days, while cement pastes containing DEA were close to that of the control sample [47]. Unfortunately, Heren did not publish results on lower dosages (potential dosages for accelerating effects). However, his results indicate that DEA, at proper dosages, could be an interesting potential accelerator, and even better than TEA. In that respect it is interesting to note that several alkali-free shotcrete accelerators contain DEA (see Chapters 11 and 13). Another related amine, methyldiethanolamine (MDEA), $N(CH_3)(CH_2CH_2OH)_2$, is used in commercial accelerators for normal concrete (see Chapter 12).

Triisopropanolamine (TIPA)

In 1991 TIPA was suggested as a strength enhancer for OPC [27]. Later, in 1997, Ichikawa [48] studied the effect of 0.01 % TIPA (by weight of cement) in cements with different compositions of clinker minerals, and he found that the strength enhancement of cement mortar by TIPA depends on the quantity of ferrite phase (C_4AF). No effect was obtained on the cement prepared from the clinker with only 1 % C_4AF. Sandberg [49] carried out similar tests on 10 different OPCs – all containing “normal” distributions of clinker minerals – and found approximately 10 % increase in 28 days strength for all samples containing 0.02 % TIPA (by weight of cement).

Aggoun [50] tested the effect of the admixture combinations TIPA / TEA / calcium nitrate on setting time and early strength in OPC, and found that the combination amine / calcium nitrate produced significant and promising results with respect to both setting and hardening acceleration. Moreover, regardless of the cement type used, Aggoun [50] found that the performance of TIPA as a hardening accelerator is greater than that of TEA.

TIPA has also been evaluated as a possible grinding aid component for cement production (a common role of TEA today) [51].

10 Antifreeze admixtures

Winter concreting practice has remained almost unchanged since the 1930s [52]. The concrete ingredients must be heated, the substrate must be thawed, and the concrete itself has to be thermally protected until it has cured. An alternative approach to cold weather concreting is to use antifreeze admixtures. This is not yet fully recognized by standard practice, except in Russia where the use of antifreeze admixtures (often containing chloride salts) has been acceptable practice for nearly five decades [53, 54]. In the last two decades antifreeze admixtures (without chlorides) have been tested in North America, Scandinavia, Finland, China and Japan [7, 17, 54].

Antifreeze admixtures are sometimes considered a special class belonging to the general category of accelerating admixtures. One of their mode of actions is to affect the physical condition of the mixing water, i.e. being capable of depressing the freezing point of water in the fresh concrete, but the main action is to accelerate the hydration of cement like conventional accelerators [55]. The principal objective of using such admixtures is twofold [8]:

(1) To give the OPC in the concrete an opportunity to hydrate to a point that if the remaining water in the pores freezes, it has sufficient volume of empty pores into which it can expand.

(2) To give the concrete sufficient strength to resist damage by the expansion of the freezing water.

It should be noticed that, in order to obtain a significant lowering of the freezing point, one has to dissolve a considerable quantity of solute in the solvent. Dodson [8] calculated that an addition of 2 % anhydrous $CaCl_2$ (by the weight of cement) to a typical concrete mix design would lower the freezing point of the remaining water – assuming that 30 % of the originally added water was consumed during the early hydration – by less than 1^oC. Consequently, larger dosages must be used compared to conventional admixtures in order to obtain significant freezing point depression. For example, 8 % $NaNO_2$ (by weight of cement) has been used to keep water in the liquid state in concrete at a temperature of -15^oC [7].

Korhonen [56] screened a series of inorganic and organic chemicals in OPC mortars in the temperature range 0^oC to -20^oC, and found the following relation between the freezing point (FP) of the water and the molality (M) of the chemical solved in the water:

$$FP(^{o}C) = -1.76M - 1.28 \qquad (10.1)$$

This relation is independent of type of chemical used, provided the chemical remains soluble at low temperatures. (Molality is defined as number of moles of particles (ions, molecules) dissolved into 1 kg of water). Equation 10.1 is a good first estimate of expected freezing point whenever the chemical composition of the admixture is known.

Generally, antifreeze admixtures utilize both freezing point depressants and accelerators [8, 54, 55, 56, 57]:

Freezing point depressant (may act as weak accelerator or even retarder)

- Sodium nitrite, $NaNO_2$
- Sodium chloride, NaCl
- Weak electrolytes
- Non-electrolytic organic compounds, such as high molecular weight alcohols, and urea (carbamide, $(NH_2)_2CO$)

Accelerator (acts also as freezing point depressant)

- Binary and ternary admixture systems that contain potash, K_2CO_3
- Additives based on calcium chloride ($CaCl_2$) combined with sodium chloride (NaCl), sodium nitrite ($NaNO_2$), calcium nitrate ($Ca(NO_3)_2$) and urea (carbamide, $(NH_2)_2CO$)

Generally, for concrete cured at low temperatures higher strengths are obtained by binary admixtures at lower dosages than when the individual components are used singly [7]. Good results have been obtained with the combination of K_2CO_3 and a retarder [7]. Korhonen [57] evaluated a number of potential chemical compounds and their ability to promote concrete strength at $-5^{o}C$, and concluded that the best antifreeze admixture formulation was 3 parts of $NaNO_3$ and 1 part of Na_2SO_4, and that the recommended dosages varied from 6 to 8 % by weight of cement. However, a major disadvantage of this admixture is that it adds a lot of alkalis to the concrete mix.

Korhonen [57] also reported results from an evaluation of the commercial accelerator PolarSet®, intended for concreting under very cold conditions. This admixture is a blend of calcium bromide, calcium nitrate, calcium nitrite, diethylene glycol and methyl-diethanolamine (see Table 12.1). The technical data sheet of PolarSet® states [58]:

"*PolarSet is specially formulated to reduce concrete setting times and increase early strengths for concrete in very cold conditions, and may be used to reduce the time that concrete must be protected against freezing in ambient temperatures as low as –7°C (20°F).*"

The results of Korhonen [57] showed that PolarSet® did perform well at temperatures above $0^{o}C$, but its strength performance at sub-zero temperatures did not meet the preset acceptance criteria (even at 8 % dosage): An admixture that would promote concrete strength at $-5^{o}C$ to meet or exceed the strength of admixture-free concrete at $+5^{o}C$.

11 Shotcrete accelerators

In modern shotcreting a liquid accelerator is added as a separate component at the nozzle during spraying, providing rapid stiffening of the concrete, final setting within few minutes, and high early strength [59, 60, 61]. Accelerator dosages are higher than those for normal concrete, typically in the range of 6 to 8 % admixture by weight of cement, or even higher. The active dry matter contents of commercial liquid shotcrete accelerators are typically in the range of 40 to 50 % (see Table 13.1). Shotcrete accelerators can be divided into two main groups:

- Alkaline accelerators (conventional – high pH)
- Alkali-free accelerators (modern – low pH)

A conventional shotcrete accelerator is normally a one-component material, i.e. an alkaline compound dissolved in water as the sole active ingredient, while modern alkali-free accelerators are blends of several ingredients dissolved in water.

Conventional alkaline shotcrete accelerators (alkali salts dissolved in water) [60]

- Sodium silicate (water glass, $nNa_2O{\cdot}SiO_2$, $n \approx 3.3$)
- Alkali aluminates ($NaAl(OH)_4$, $KAl(OH)_4$)
- Alkali carbonates and hydroxides (Na_2CO_3, K_2CO_3 and $NaOH$, KOH)

Alkali carbonates and hydroxides mainly accelerate C_3S hydration, while sodium aluminates react with gypsum in the cement, thus preventing ettringite formation around the cement grains, allowing almost instantaneous reaction of the C_3A [60]. Water soluble sodium silicate (water glass) provides rapid setting by reaction with calcium in the cement to form insoluble calcium silicates [60, 61].

Among the conventional accelerators, only water glass is used in today's Norwegian shotcreting. In modern shotcrete technology, particularly in Northern parts of Europe, alkali aluminates, carbonates and hydroxides are considered problematic due to:

- Highly caustic materials that require caution in handling
- Addition of a lot of alkalis and the risk of promotion of alkali-aggregate reaction
- Decrease in final strength

Water glass, the classical shotcrete accelerator used for decades and still having a significant market share, is characterized by [60]:

- Compatible with all types of cement
- Less caustic than aluminates (pH lower than that of fresh concrete)
- Low early strengths
- Decrease in the E-modulus with time
- Reduced final strength at high dosages
- Decrease in the water proofing characteristics due to the extraction of lime when the concrete is subjected to a continuous exposure to moisture
- High viscosity at low temperature which requires heating of the material during shotcrete operations

For these reasons the use of water glass as shotcrete accelerator has been restricted in Germany and Austria [60].

Alkali-free shotcrete accelerators (weakly acidic solutions of aluminum salts) [61, 62]

Alkali-free accelerators were originally developed to solve some of the problems caused by the alkaline accelerators. However, it seems that the large market share of alkali-free accelerators in Scandinavia today is mainly caused by the capability of these accelerators to give very high early strengths, rather than their lack of "alkali problems".

The chemical compositions of alkali-free accelerators are closely guarded trade secrets and therefore little published information is available. Normally, the main ingredient is aluminum sulphate [61, 62]. Admixtures containing large amounts of aluminum salts and complexes are weakly acidic (pH=2-3) due to the hydrolysis caused by aluminum ions, Al^{3+}, given by the equilibrium [61]:

$$Al^{3+} + H_2O = Al(OH)^{2+} + H^+ \tag{11.1}$$

Aluminum sulphate, $Al_2(SO_3)_3 \cdot nH_2O$ ($n \approx 15$-18), is a low cost bulk chemical with high solubility. At high dosages aluminum sulphate causes flash setting of OPC [35]. Bürge [62] investigated the mechanism of action of aluminum sulphate in cement and found that aluminum sulphate reacts with lime and produces ettringite and aluminum hydroxide according to:

$$Al_2(SO_3)_3 + 6\,Ca(OH)_2 + 32\,H_2O = 3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 32H_2O + Al(OH)_3 \tag{11.2}$$

Ettringite is responsible for the rapid setting [62, 63]. As a by-product of the reaction, $Al(OH)_3$ is formed which is also known to be an accelerator [62].

Maltese [64, 65] investigated to what extent type of calcium sulphate setting regulator in OPC (gypsum, α-hemihydrate, β-hemihydrate or anhydrite) affected the setting behavior of shotcrete accelerated by an inorganic acid based alkali-free accelerator containing aluminum sulphate. He found that the lower the instantaneous dissolution rate of the calcium sulphate, the more efficient the accelerator (see Table 11.1).

Table 11.1
Alkali-free accelerator and type of setting regulator in OPC (data from [64])

Type of setting regulator in OPC	Dissolution rate of setting regulator (Ca^{2+} ions, g/l min)	Final setting time of OPC paste	
		Without accelerator	With accelerator
β-hemihydrate	92	5 h 30 min	8 h 30 min
α-hemihydrate	60	5 h	6 min 30 s
Gypsum	48	5 h 30 min	3 min 5 s
Anhydrite	7	5 h 30 min	1 min 18 s

Ferric sulphate, TEA and sodium fluoride are also reported as ingredients in shotcrete accelerators [35]. According to patent literature alkali-free shotcrete accelerators may contain ingredients like:

- Amine and glycolic acid [66]
- Hydrofluoric acid, diethanolamine, methyldiethanolamine and ethylenediamine tetraacetic acid (complex binder) [67]
- Magnesium sulphate, phosphorous acid, oxalic acid, maleic anhydride and diethanolamine [68]
- Citric and malic acids and their alkali metal salts [69]. (Malic acid should not be confused with *maleic* or *malonic* acid, both of which are different types of dicarboxylic acids.)
- $Al(OH)_xR_y$, where $x+y=3$, R=organic acid (formic, acetic, 4-toluenesulphonic, lactic or oxalic) or nitric acid [70]

Some information on ingredients in commercial shotcrete accelerators is disclosed in their Safety Materials Data Sheets provided by the producers (see Chapter 13).

In order to gain very high early strengths in shotcrete Myrdal [71] tried to combine a nozzle added alkali-free accelerator with a “dormant accelerator” that was added in the concrete during mixing. The idea was that the “dormant” should not react with the cement until activated or “ignited” by the alkali-free accelerator. A doubling of early compressive strengths was obtained using a proprietary “dormant blend” of water soluble carbonate, alkanolamine, hydroxycarboxylate and phosphonate [71].

It is generally believed that the high content of aluminum sulphate in alkali-free accelerators may promote an internal form of sulphate attack in the concrete, but so far no conclusive results have been found concerning the durability of field shotcrete [72, 73].

12 Commercial accelerators for normal concrete

Suppliers of accelerators seldom disclose the ingredients of their accelerators, neither in their open technical documents nor in their responses to direct inquiries. Occasionally, the Technical Data Sheet (TDS) of the product gives some information on the main chemical ingredient.

Due to stricter safety regulations over the last years more information is often found in the Material Safety Data Sheet (MSDS) of the product. One should notice that information given in a MSDS can vary from country to country for the very same product. This might be a result of specific national regulations or national safety practices. For instance, more detailed information on chemical ingredients can sometimes be found in Swedish MSDSs compared to MSDSs from continental Europe for the same chemical admixture. This unfortunate practice should be stopped by proper authorities so that users of admixtures can receive identical information regardless of national belonging.

Table 12.1 shows information on ingredients in a selection of well known commercial accelerators in Europe and North America. As the information is based on MSDSs only (as of November 2007), one should bear in mind that additional ingredients may be present in the products, e.g. ingredients not disclosed either due to lack of demand in regulations for that particular chemical, or other reasons. Obviously, an accelerator of which the MSDS states content of ingredients in the range of 10 % must contain additional ingredients.

The information given in Table 12.1 shows that:

- Most commercial accelerators for normal concrete consist of calcium nitrate and/or sodium thiocyanate, either as sole component or in combination
- Nitrite is not a common ingredient, and used mainly in North America
- It is common to add small amounts of amine (typically alkanolamine)
- The only carboxylic acid found was lactic acid
- No information on calcium formate in MSDSs for liquid accelerators has been found (Calcium formate is sold in powder form on the American market [74])

13 Commercial shotcrete accelerators

As for accelerators for normal concrete, information on ingredients of shotcrete accelerators can be found in MSDSs. Table 13.1 on next page gives an overview of well known commercial alkali-free shotcrete accelerators on the market in Europe and North America. Some characteristics can be found:

- All contain aluminum salts
- Almost all (probably all) contain aluminum sulphate
- Many contain diethanolamine
- Some contain fluorides
- Few contain organic acids (oxalic, formic) and/or inorganic acid (phosphorus)

Table 12.1
A selection of commercial liquid non-chloride accelerators for concrete

Name of product	Information on ingredients given in the MSDS[*)]		Manufacturer
	Type of ingredient	% by weight	
Pozzolith NC 534 [75]	Calcium nitrate	30 – 60	BASF
	Sodium thiocyanate	1 – 5	
Pozzutec 20+ [76]	Ammonium calcium nitrate	30 – 60	
	Sodium thiocyanate	1.0 – 5.0	
SikaRapid-1 [77]	Sodium nitrate	10 – 20	Sika
	Sodium thiocyanate	10 – 20	
	Methyldiethanolamine	5 – 10	
	Lactic acid	5 – 10	
SikaRapid-2 [78]	Sodium thiocyanate	2.5 – 3	
	2,2'-(methylimino)diethanol	1 – 5	
SikaRapid-3 [79]	Calcium nitrate	No [**)]	
Mapequick SA [80]	Calcium nitrate	50	Rescon Mapei
Antifreeze N [80]	Sodium nitrate	30 – 60	
Antifreeze AK [80]	Sodium thiocyanate	30 – 60	
Eucon ACN [81]	Calcium nitrate	> 60	Euclid Chemical
Accelguard NCA [82]	Calcium nitrate	> 60	
	Sodium thiocyanate	1.0 – 5.0	
Daraset 400 [58]	Calcium nitrate	25 – 50	W. R. Grace
	Calcium nitrite	1 – 10	
	Sodium thiocyanate	1 – 10	
Polarset [58]	Calcium nitrate	10 – 25	
	Calcium nitrite	10 – 25	
	Calcium bromide	1 – 10	
	Methyldiethanolamine	1 – 10	
	Diethylene glycol	1 – 10	
Catexol 1000 RHE [83]	Calcium nitrate tetra hydrate	65 – 75	Axim
Catexol 2000 RHE [84]	Calcium nitrate	40 – 60	
	Sodium Isothiocyanate	10 – 20	
	Amine derivative	1 – 5	

[*)] MSDS = Material Safety Data Sheet
[**)] No = No information given in the MSDS

Table 13.1
A selection of commercial liquid alkali-free accelerators for shotcrete

Name of product	Information on ingredients given in MSDS[*)]		Manufacturer
	Type of ingredient	% by weight	
Meyco SA 160 [85]	Aluminum sulphate	30 – 45	BASF
	Diethanolamine	1 – 4	
Meyco SA 163 [86]	Aluminum sulphates/fluorides	15 – 30	
	Diethanolamine	1 – 5	
	Oxalic acid di-hydrate	1 – 6	
Meyco SA 164 [87]	Aluminum sulphates/fluorides	20 – 40	
Meyco SA 170 [88]	Aluminum sulphate, hexadecahydrate	25 – 50	
Meyco SA 172 [89]	Aluminum sulphate	30 – 50	
	Formic acid	0.5 – 2.5	
	Meyco SA 170	30 – 50	
Meyco SA 175 [90]	Aluminum sulphate	20 – 30	
	Maleic anhydride	1 – 4.5	
	Oxalic acid di-hydrate	1 – 4.5	
	Phosphorous acid	1 – 4.5	
Meyco SA 180 [91]	Aluminum sulphate	20 – 30	
	Diethanolamine	1 – 4.5	
	Phosphorous acid	1 – 5	
Sigunit–L 50 AF [92]	Aluminum sulphate	No[**)]	Sika
Sigunit–L 53 AF S [92]	Aluminum salts	No	
Sigunit–L 5450 AF (N) [93]	Aluminum salts	No	
Sigunite–L 72 AF VP [92]	Aluminum sulphate	35 – 50	
	Formic acid	2 – 10	
	2,2"-iminodiethanol (diethanolamine)	1 – 3	
	Glycerin (propane-1,2,3-triol)	1 – 5	
Mapequick AF 2000 [94]	Aluminum sulphate	20 – 25	Mapei
	Aluminum fluoride	5 – 9.99	
Mapequick AF D 02 [94]	Aluminum sulphate	25 – 34.99	
	Manganese sulphate	0.5 – 0.99	
Mapequick AF 400 [94]	Aluminum sulphate	12.5 – 19.99	
	Inorganic fluoride	2.5 – 2.99	
	Manganese sulphate	1 – 2.49	
Sure-Shot AF [95]	Aluminum sulphate (anhydrous)	> 60.0	Euclid Chemical
	Diethanolamine	3.0 – 7.0	

[*)] MSDS = Material Safety Data Sheet
[**)] No = No information given in the MSDS

14 Accelerators for calcium aluminate cements

Many inorganic salts affect the setting of calcium aluminate cements (CACs), and are effective in concentrations of 0.1 to 0.5 % by weight of cement [96, 97]. The effect on setting times differ greatly both in direction and in relative magnitudes from those observed with Portland cements. The setting times of CAC caused by various admixed ions are reported to increase in the following order [96]:

Cations: $Li^+ \ll Na^+ <$ control (without accel.) $< K^+ \leq Ca^{2+} < Mg^{2+} < Sr^{2+} < NH_4^+$

Anions: $OH^- \ll$ control (without accel.) $< Cl^- < NO_3^- < Br^- < CH_3COO^-$ (acetate)

This means that LiOH is an effective accelerator, while $Ca(NO_3)_2$ tend to retard setting of CAC. Generally, lithium salts like Li_2CO_3, LiOH, LiCl and $LiNO_3$ are most efficient and widely used accelerators for CAC [96, 98, 99].

The accelerating effect of lithium salts has been explained by the precipitation of lithium aluminate hydrate which acts as a heterogeneous nucleation substrate [96].

Alkali-earth metal salts of chloride, nitrate and formate may act as weak accelerators or retarders depending on concentration and temperature [96, 100].

It seems that the chemical mechanisms of action of these admixtures are not well understood.

15 Recommendations for future R&D

Future R&D should aim at developing more efficient non-chloride accelerators for concrete, and it is considered important to focus the efforts on:

- Chemicals that speed up early hardening of OPC blended with pozzolanic materials
- Technical grade bulk chemicals
- Safety (chemicals friendly to humans and natural environment)
- Low alkali content
- Synergistic effects of chemical blends

Acceleration of early hardening
There is a well pronounced problem that today's non-chloride hardening accelerators do not perform well enough, especially in "slow hardening" blended cements. There is a lack of accelerators that efficiently speed up the strength development during the first 24 hours. It seems that research on setting accelerators is not that important. Today's most common setting accelerator based on technical grade $Ca(NO_3)_2$ fulfils the requirements in the market.

Technical grade bulk chemicals
From a commercial point of view it is important that the main chemical in a formulated admixture is easily available at acceptable low cost. The use of more expensive and specific chemicals, as minor parts of admixture formulations, is possible as long as the total material cost of the chemical formulation is kept low. Total material cost higher than roughly ½ EUR/kg seems unrealistic.

Safety

The development of future admixtures must take both human and environmental safety into consideration. This means that caustic, as well as highly acidic, admixtures are out, e.g. shotcrete accelerators based on alkali aluminates and acidic alkali-free accelerators with very low pH should be avoided. For normal concrete, both nitrite and thiocyanate based accelerators on the market today are (or should be) labelled *Xn, Harmful*. The "worst labelling" of a potential admixture for the future would probably be *Xi, Irritant*. Other labels describing risk to humans and nature should be avoided:

Xi	Xn	T	C	N
				
Irritant	Harmful	Toxic	Corrosive	Dangerous for environment

Acceptable –| –– *Unacceptable* ––––––––––––––––––––––––––––

Low alkali content

The term "alkali-free" is already well established for shotcrete accelerators. It would be extremely difficult to enter the European market today with a new non-aluminate, non-silicate or non-carbonate shotcrete accelerator containing alkali metals above 1 % Na_2O-equivalents. Attempts at developing alkali-free hardening accelerators for normal concrete should also be aimed at, especially if the accelerator is to be used at high dosages, as for antifreeze admixtures.

Synergistic effects

A lot of potential chemicals have already been tested as accelerators for concrete. Future R&D efforts should focus on, in a systematic way, synergistic effects occurring when several chemicals are mixed. For instance, a synergistic effect is reported with a mixture of TEA and calcium formate [27].

Potential accelerating chemicals and their combinations

Although a harmful material labelled *Xn*, thiocyanate should not be abandoned completely. Thiocyanate is a well established accelerator in Europe, and should be investigated further, but as minor component in formulations together with nitrate, alkanolamines and/or hydroxycarboxylic acids and their salts. Alkali metal thiocyanate, like today's sodium thiocyanate, should be avoided. Instead, soluble alkali-free thiocyanates can be made by neutralizing thiocyanic acid with a non-alkaline base, for instance $Ca(OH)_2$ or alkanolamine:

$$\underset{\textit{Diethanolamine}}{NH(CH_2CH_2OH)_2} \quad + \quad \underset{\textit{Thiocyanic acid}}{HSCN} \quad = \quad [NH_2(CH_2CH_2OH)_2]^+SCN^- \qquad (15.1)$$

In this way an alkali-free accelerator can be formulated using ingredients that separately show accelerating effects as well. Possible synergistic effects of such combinations have not been published earlier.

Similar approach can be utilized for developing soluble non-alkali salts of carboxylic acids, e.g. formic and oxalic acids. The effect of non-calcium formate on the hydration of OPC with different C_3A/SO_3 ratios should be compared to the C_3A/SO_3 sensitivity reported for calcium formate (see Chapter 8).

A parallel R&D activity should be a screening of alkanolamines. From literature it seems that DEA and TIPA are the most promising, while other amines can be found in MSDSs of commercial accelerators (see Table 12.1).

A systematic investigation of the effects of carboxylic acids (and their salts) on OPC hydration is highly appreciated, especially the properties of α-hydroxycarboxylic acids and their salts.

Further development of antifreeze admixtures should focus on combinations of chemicals already tested and reported. An ideal antifreeze admixture would consist of a *temperature depressant* (major part) and a *non-chloride accelerator* (minor part). It is important to find temperature depressants with low alkali metal content. Technical grade calcium nitrate is a promising temperature depressant. At high dosages, however, short setting times may require the addition of a retarder in the admixture. The hardening accelerator part can be found among the normal non-chloride accelerators. However, an accelerator to be combined with a temperature depressant based on a calcium salt cannot form sparingly soluble salts with Ca^{2+}. This solubility requirement excludes many carboxylic acids, e.g. oxalic acid and to a certain degree formic acid.

If better alkali-free shotcrete accelerators are to be developed, one should investigate the effects of phosphorous and carboxylic acids in commercial shotcrete accelerators (see Table 13.1). As for accelerators for normal concrete synergistic effects may occur and should be investigated.

Due to a possible risk of internal sulphate attack caused by the latge amounts of aluminum sulphate in most alkali-free accelerators for shotcrete, an ideal shotcrete accelerator would be both alkali-free and low-sulphate. Possible alternatives to aluminum sulphate could be aluminum salts of inorganic acids (e.g. nitric and phosphorous) and carboxylic acids (e.g. formic).

A major challenge linked to the development of a low-sulphate aluminum salt based accelerator for shotcrete would be to dissolve technical grade aluminum hydroxides in acids by cost-effective means.

The effect of water soluble silicon complexes on hydration of OPC is another intriguing possibility that might be considered.

As part of the research and documentation of any new accelerator, possible leaching of the chemical compound(s) from hardened concrete should be investigated.

16 Conclusions

The best all-round accelerator to date has been calcium chloride. Due to restrictive regulations prohibiting the use of chlorides in steel reinforced concrete, there has been a continuous search for an alternative, one without its limitations.

In Europe calcium nitrate has replaced calcium chloride as a setting accelerator, while sodium thiocyanate has replaced calcium chloride as hardening accelerator. In North America calcium chloride is partly replaced by calcium and sodium nitrite and calcium formate (in powder form). Alkali shotcrete accelerators have partly replaced the conventional alkali silicates and aluminates, particularly in Northern part of Europe.

The mechanisms of action of the new non-chloride accelerators are not fully understood. The synergistic effect of combinations of chemicals on hydration rates is a relatively new research field, and few results have been published in open reports. There is a trend that different carboxylic acids and their salts are used in commercial accelerators. Near future research will probably focus on synergistic effects of chemicals already tested as sole admixtures.

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