SINTEF REPORT

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TITLE

COIN   P1   **Advanced cementing materials**
   SP 1.2 F   **Controlling hydration development**

Retarding admixtures for concrete

State of the art

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CLIENT(S)

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ABSTRACT

There are several retarding admixtures on the market that are used to produce a controlled delay of the setting of concretes. The mechanisms of action of these admixtures in cement-water systems are described by four different types of interaction between the retarder and the cement grains: Adsorption, complexation, precipitation and nucleation. Most retarders act by more than one of these mechanisms.

Liquid set retarding admixtures are mainly found among water soluble organic compounds like lignosulphonates, sugars and hydroxycarboxylic acids and their salts. The most common inorganic compounds with retarding effect on cement hydration are salts of phosphates. Also organic phosphorous compounds like phosphonates are used to some extent. The report gives an overview of these admixtures and their mode of action during cement hydration.

Commercial admixtures with the capability of retarding strength development after setting has occurred ('hardening retarders') do not exist, and recommendations for further research and development of such admixtures are presented in the report.

KEYWORDS	ENGLISH	NORWEGIAN
GROUP 1	Materials technology	Materialteknologi
GROUP 2	Concrete	Betong
SELECTED BY AUTHOR	Retarder	Retarder
	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 cement hydration reactions can be influenced by chemicals added to the cement-water mix. Chemical admixtures affecting these reactions to produce a delay in the process of cement paste stiffening are termed retarding admixtures or simply retarders. Hence, a retarder is added to a concrete mix in order to lengthen setting time and workability time.

Today, only *setting retarders* are commercially available, while *hardening retarders* are not promoted in the market. Some retarders might have other characteristics as well, like water reduction properties at a wide range of dosages and accelerating properties at very high dosages.

The aim of this report is to provide an overview of chemical admixtures reported to retard setting and/or hardening of Ordinary Portland Cement (OPC) pastes and OPC based concrete. After a short description of retarders in general, and an overview of retarder consumption in Norwegian concreting over the last years, specific retarders and their mode of action during cement hydration is treated. Commercial retarders and their ingredients are also discussed. Retarders for high alumina cements, or calcium aluminate cements, are treated only briefly.

2 Background and retarders in general

2.1 Classification of retarders

The European norm EN 934-2:2001 [1] defines a *set retarding admixture* as:

"Admixture which extends the time to commencement of transition of the mix from the plastic to the rigid state"

EN 934-2:2001 does not define a *hardening retarder* as it does for *hardening accelerator*. If a hardening retarder, the analogue to a hardening accelerator, should be defined, it would probably be expressed as the opposite of a hardening accelerator, i.e. the word *increase* replaced by *decrease*:

"Admixture which decreases [instead of *increases*] *the rate of development of early strength in the concrete, with or without affecting the setting time"*

Today, hardening retarders are not commercially available, but some research has been published [2].

Set retarding admixtures are mainly found among organic compounds, but inorganic chemicals may also act as retarders [3]:

Organic chemicals

- *Lignosulphonates*
- *Hydroxycarboxylic acid and their salts*
- *Phosphonates*
- *Sugars (saccharides)*

Inorganic chemicals

- *Phosphates*
- *Borates*
- *Salts of Pb, Zn, Cu, As, Sb*

Lignosulphonates, which are commonly used as water reducers, have secondary retarding effects, while hydroxycarboxylic acids and their salts, common retarders, have secondary water reducing effects.

Among the inorganic retarders listed above, only phosphates are utilized commercially. The other inorganic compounds are seldom used as they are relatively expensive and some show toxicological effects [3]. Probably, the retarding effect of heavy metal salts also depends on the alkalinity of the cement, i.e. the capability of these metal cations to precipitate as hydroxides.

2.2   Benefits provided by retarders

Setting retarder
The main purposes of delaying setting time are [4, 5, 6]:

- To offset the accelerating effect of high ambient temperature (hot weather)

- To keep the concrete workable throughout the entire transport, placing and finishing periods. Particularly important when transporting concrete over large distances, and for the elimination of cold joints and discontinuities in large structural units.

- To prevent setting of the concrete in the truck in case of delay

Hardening retarder
The main purpose of delaying the strength development might be [2]:

- To give an overall decrease in the rate of heat evolution and thereby lowering the maximum temperature to a level where thermal cracks pose less problems.

2.3   General mode of action of retarders

The European Federation of Concrete Admixture Associations (EFCA) gives a general description of the mode of action of retarders [6]:

"Retarding admixtures are used to slow down the speed of the reaction between cement and water by affecting the growth of the hydration products and/or reducing the rate of water penetration to the cement particles"

As a consequence, a delay in setting time is obtained and/or the cement is hydrating at a lower speed. Setting is normally determined by measuring the mechanical stiffness of the cement paste using a penetration needle (e.g. a Vicat apparatus), while the hardening development is determined by compressive strength measurements.

Often setting and hardening are determined indirectly by measuring the heat evolution or temperature increase generated from the chemical reactions between cement and water. The hydration process of cement produces heat due to exothermic reactions. If the hydration is retarded, heat is either produced at a later stage (delay of setting) and/or at a slower rate (delay of hardening). This is illustrated in Figure 1.
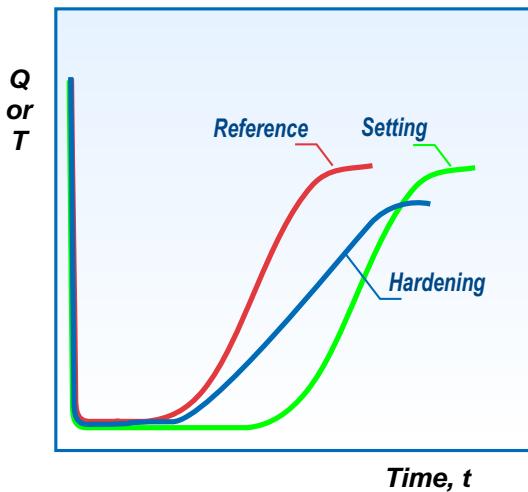

Figure 1   The effects of setting and hardening retarders upon the rate of heat evolution Q (W/kg) or temperature T (^{o}C) during hydration of cement.
Reference: Cement paste without retarder.
Setting: Cement paste with setting retarder.
Hardening: Cement paste with hardening retarder.
The setting retarder produces heat later than the reference, but the slopes of the curves are parallel (equal dQ/dt).
The hardening retarder starts the production of heat at the same time as the reference, but the slope is less steep (lower dQ/dt).

Although a considerable amount of work has been carried out to explain the mechanisms of action of retarders, there are still some divergences. In addition, it seems that retarders function in different ways which make it even more difficult to draw conclusions from the existing studies. The theories are based on various types of interaction between the retarder and the cement particles, and one retarding admixture may act by more than one type of interaction. Table 1 presents a schematic overview of the principles of interactions and reaction mechanisms between retarders and cement.

In addition to type and amount of retarder, the setting time of OPC depends on type of cement, w/c ratio and temperature [7]. Cements with low C_3A and alkali contents are easier to retard compared to cements with large amounts of these constituents [3, 7]. One explanation might be that at lower C_3A contents, smaller amounts of retarder are adsorbed, leaving larger amounts of the admixture to affect and retard the hydration of the C_3S component. The effect of alkalis may involve dissolution and interaction reactions [3].

Table 1

Different mechanisms of action between retarders and cement [3, 8, 9, 10]

Type of interaction	Mechanism of action
Adsorption	Large admixture anions and/or molecules are adsorbed on the surface of the cement particles, which hinders further reactions between cement and water.
Precipitation	The admixture reacts with one or more components of the cement to form a precipitate on the cement particles, imparting a low-permeability coating on the cement particles.
Complexation	The admixture makes complexes with Ca^{2+} that is liberated by hydration and thereby enhancing the early hydration sheath that surrounds the cement grains.
Nucleation	The admixture 'poisons' the $Ca(OH)_2$ and/or the CSH nucleating sites and inhibits bond formation among the hydrated products.

2.4 Consumption of retarders in Norwegian concreting

According to the European Federation of Concrete Admixture Associations (EFCA) [6], set retarding admixtures currently make up about 1.5 % of all concrete admixtures sold in Europe (shotcrete accelerators not included). The consumption in Norway is somewhat higher. In 2006, set retarders stood for 2.1 % of all admixtures (except shotcrete accelerators) sold in Norway [11].

Figure 2 shows the trend in Norwegian consumption of retarders over the last 15 years. There was a minimum in the consumption of retarders from mid 1990s to early 2000s, although the total use of cement in the same period went through a slight maximum (see Figure 3). The reason for this trend is not clear. The trend shown in Figure 2 is also seen in Figure 4, which shows the ratio between the total application of retarders and the total use of cement in Norway. This means that the variation in consumption of retarders overshadows the variation in total consumption of cement. Over the last 5 years the average consumption of retarding admixtures in Norway has been about 0.2 to 0.3 kg/ton cement (see Figure 4).
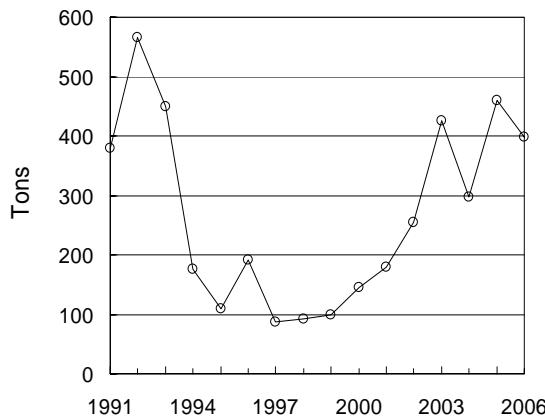
Figure 2   Total Norwegian consumption of set retarding admixtures for concrete
in the period 1991-2006 (Data from NCCA [11]).
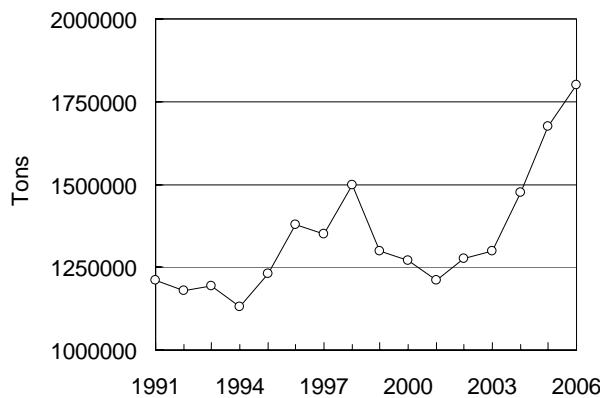
Figure 3   Total use of Portland cement in Norwegian concreting
in the period 1991-2006 (Data from NCCA [11]).
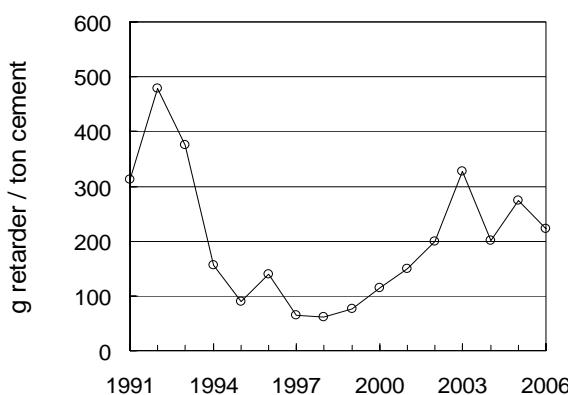
Figure 4   Ratio between the total use of set retarders and the total use of Portland cements in
Norway in the period 1991-2006 (Data from NCCA [11]).

3   Lignosulphonates

Lignosulphonates may vary from unrefined sodium and calcium salts of lignosulphonic acids to refined sugar-free lignosulphonates, or even modified versions blended with small amounts of alkanolamines to compensate for set retardation. The retarding effect of lignosulphonates in OPC is normally attributed to the sugar contents, but the role of sugars is not conclusive [3]. According to Zhor [10], not only the presence of sugars affects the retardation, but salts of hydroxycarboxylic acids like gluconates, often found in unpurified commercial lignosulphonates, will also promote retardation. Unrefined calcium lignosulphonates may contain considerable amounts – up to 40 % – of sugar-like materials which can cause retardation on their own account [9]. Hence, it is often difficult to separate the effect of lignosulphonate from that of other components present in lignosulphonate admixtures. The retarding effects of sugars and hydroxycarboxylic acids and their salts are treated in Chapter 4 and 5 respectively. A typical structural unit of lignosulphonate is shown in Figure 5.
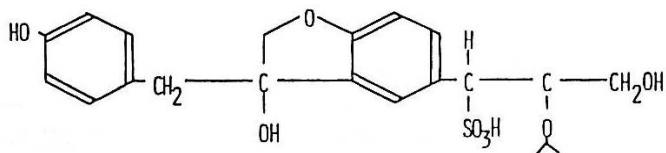

Figure 5   Typical structural unit of a lignosulphonate molecule [3].

The mode of action of lignosulphonates in OPC has been studied extensively for several decades. Zhor [10] reviewed the different mechanisms of retardation described in Table 1, and it seems that several mechanisms contribute – no "favourite" for lignosulphonate is found. Results from different studies are sometimes contradictory [3], but the main characteristics of lignosulphonates presented in recent literature may be summarised like this:

- Lignosulphonates (LSs) retard the hydration of both C_3A and C_3S [3].
- LSs may accelerate the hydration of C_4AF, causing precipitation of gelatinous Fe-compounds on the C_3S hydrate, resulting in the retardation of C_3S hydration [3].
- A small amount of LS (0.1 %) slightly retards or accelerates the C_3S hydration, depending on the chemical composition and molecular weight of the LS [7].
- Addition of LS retards both the C_3A hydration and the conversion of hexagonal hydrates to the cubic phase in the case of low gypsum containing cements [7].
- Ca-LS retards C_3A hydration in the mix of C_3A + gypsum, but a more marked retardation occurs in the conversion of ettringite to monosulphate [7].
- Commercial LSs have a good retarding effect on C_2S hydration at a dosage of about 0.125 % [7].
- The influence of Ca-LS on retardation depends on the SO_3 and C_3A content in the cement [10]. The lower the SO_3 and C_3A content, the more efficient retardation.
- The retardation efficiency of Ca-LS is higher in pure C_3S pastes than in OPC pastes. Alkalis in OPC can offset the retarding effect of Ca-LS. In the presence of Ca-LS alkali sulphates in the clinker accelerate the initial ettringite formation [10]

In his review Young [12] discussed the four basic retarding mechanisms of set retardation caused by organic admixtures (see Table 1). He stated that the retarding effect of LS on OPC happens predominantly through the effect of LS on the kinetics of C_3S hydration, and that the role of C_3A is primarily to remove the LS from solution in order to prevent its strong effect on C_3S hydration. Young suggested a possible combination of the four basic retardation mechanisms by this progression [10, 12]:

(1) *Adsorption*   In the beginning, LS is attached to the surface of C_3A by adsorption.

(2) *Complexation*   Soon after LS complexes with the aluminate ions. This leads to an increase in the concentrations of ions in the solution, and consequently to an increase in the solubility of anhydrous cement compounds.

(3) *Precipitation*   Later, precipitation of insoluble hydrate occurs and the crystal growth is modified which results in a more efficient barrier to further hydration.

(4) *Nucleation*   Finaly, the LS is incorporated into the structure of the hydrated material and removed from the solution. After the period of initial activity, the retardation of silicate hydration predominates, governed primarily by the effect of LS on the $Ca(OH)_2$ nucleation.

4   Sugars

Sugars or saccharides (Greek σάκχαρον meaning "sugar") are carbohydrates, i.e. aldehydes or ketones with many hydroxyl groups added, usually one on each carbon atom that is not part of the aldehyde or ketone functional group. These materials are characterized by functional groups in which oxygen atoms are attached to adjacent carbon atoms, like the α-hydroxycarbonyl group HO−C−C=O [3, 9].

The most common sugar is 'table sugar' or *sucrose*, $C_{12}H_{22}O_{11}$, which is a disaccharide composed of the two monosaccharides *glucose*, $C_6H_{12}O_6$, and *fructose* (fruit sugar), $C_6H_{12}O_6$. Figures 6 and 7 show the chemical structures of common sugars.

Not all sugars retard cement hydration to the same extent. The so-called 'reducing' sugars are moderate retarders, while 'non-reducing' sugars are either very efficient or very inefficient retarders depending on their chemical structures [3, 9, 13].

A reducing sugar is any sugar that, in basic solution, forms some aldehyde or ketone. This allows the sugar to act as a reducing agent. Sugar without this reducing capability are called non-reducing sugars [14].

Examples of reducing and non-reducing sugars:

Reducing sugars	Non-reducing sugars

- *Glucose*
- *Fructose*
- *Lactose (milk sugar)*
- *Maltose (malt sugar)*

- *Sucrose (composed of glucose and fructose)*
- *Trehalose (composed of two glucose units)*
- *Raffinose*

Sucrose (table sugar) is a very efficient retarder, but impractical due to extreme dosage sensitivity. In a typical case, the addition of 0.1 % sucrose on the weight of cement might increase the time of initial setting from 4 hours to 14 hours, while a 0.25 % addition might delay it to 6 days [13]. The retarding effect of different sugars can be divided into three categories [3, 13]:

Very efficient retarders: Non-reducing sugars containing both 5- and 6-membered rings.
Examples: *Sucrose* and *raffinose*

Moderate retarders: Reducing sugars containing only 6-membered rings.
Examples: *Glucose, lactose and maltose*

Inefficient retarders: Non-reducing sugars containg only 6-membered rings.
Example: *Trehalose*

Glucose $C_6H_{12}O_6$
Monosaccharide
Reducing
Moderate retarder

Fructose $C_6H_{12}O_6$
Monosaccharide
Reducing
Moderate retarder

Sucrose $C_{12}H_{22}O_{11}$
Disaccharide
Non-reducing
Very efficient retarder
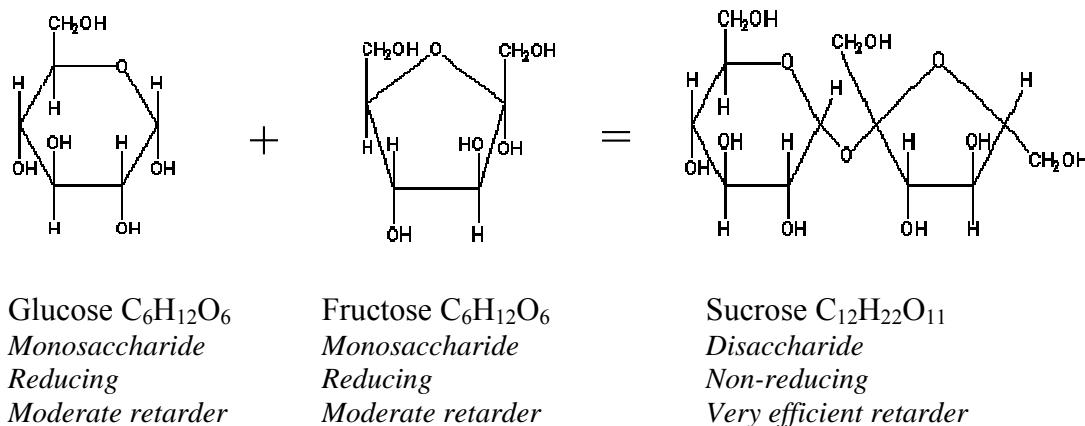
Figure 6   Chemical structures of common monosaccharides and sucrose (table sugar), and their chemical relationship.

Lactose	Maltose	Trehalose
Reducing	*Reducing*	*Non-reducing*
Moderate retarder	*Moderate retarder*	*Inefficient retarder*
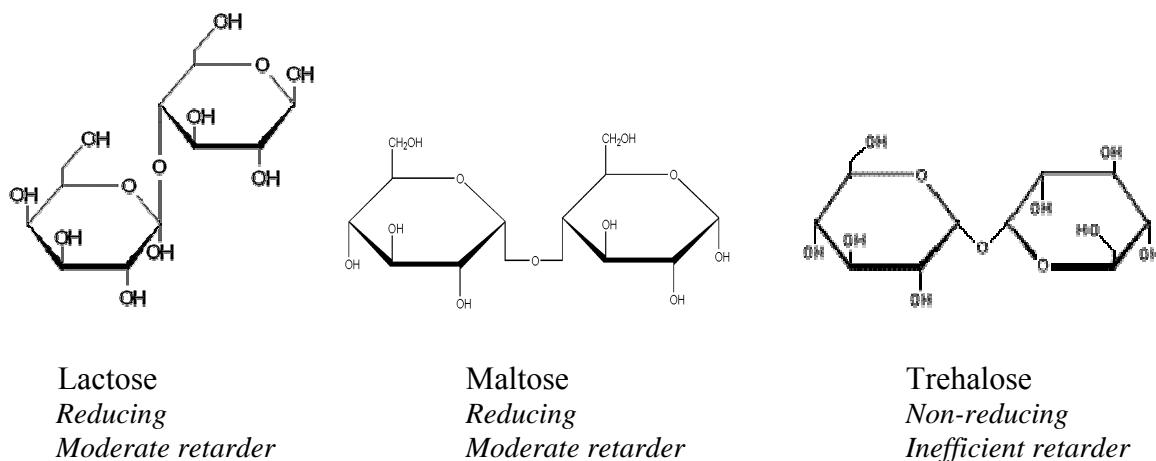
Figure 7   Chemical structures of common disaccharides others than sucrose (table sugar).

A plausible mechanism of retardation by sugars has been summarized by Taylor [13]:

- The retardation arises from the adsorption of sugar molecules on to the surfaces of growing particles of hydrating products.

- The ability to complex calcium seems to decide the retarding effiency. *Sucrose* complexes calcium very well, while the ability of *trehalose* to complex calcium is very weak. The sugar-calcium complex incorporates into the surface of a growing particle of CH or CSH, thereby inhibiting growth.

Also *saccharin*, an artificial sweetener (see Figure 8), is used as retarder for concrete, but studies reporting its mode of action in OPC is not found. A commercial retarder containing saccharin is shown in Table 2 in Chapter 7.
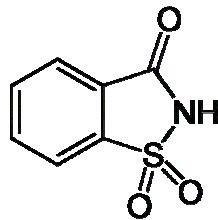
Figure 8   The chemical structure of saccharin (also called benzosulfamide). The hydrogen atom on the nitrogen atom is quite acidic (pKa ~2). The sweetener is usually sold as the sodium salt.

5   Hydroxycarboxylic acids and their salts

Hydroxycarboxylic acids and their salts have chemical properties related to those of sugars, and some of them promote retardation of cement hydration in the same way as sugars do [3]. Hydroxycarboxylic acids are characterized by carboxyl groups (-COOH) and hydroxyl groups (-OH) which interact with the cement [3, 9]. The best hydroxycarboxylic based retarders are found among the α-hydroxycarboxylic acids (with a hydroxyl group adjacent to the carboxyl group).

Salts of hydroxycarboxylic acids were developed as retarders in the 1950s [3]. Figure 9 shows the chemical structure of typical hydroxycarboxylic acids that are efficient set retarders for cement.

Salicylic acid, a phenolic carboxylic acid, has been used as a model compound to study the interaction between cement and hydroxycarboxylic acids [9]. The mechanism of interaction is believed to be of the adsorption type, and the adsorption occurs mainly on the C_3A phase [3, 9]. Only a small amount of the adsorption occurs on the unhydrated phases compared to that on the hydrated products. The hydration products are considered to contain a significant amount of aluminum salicylate complex in the form shown in Figure 10.
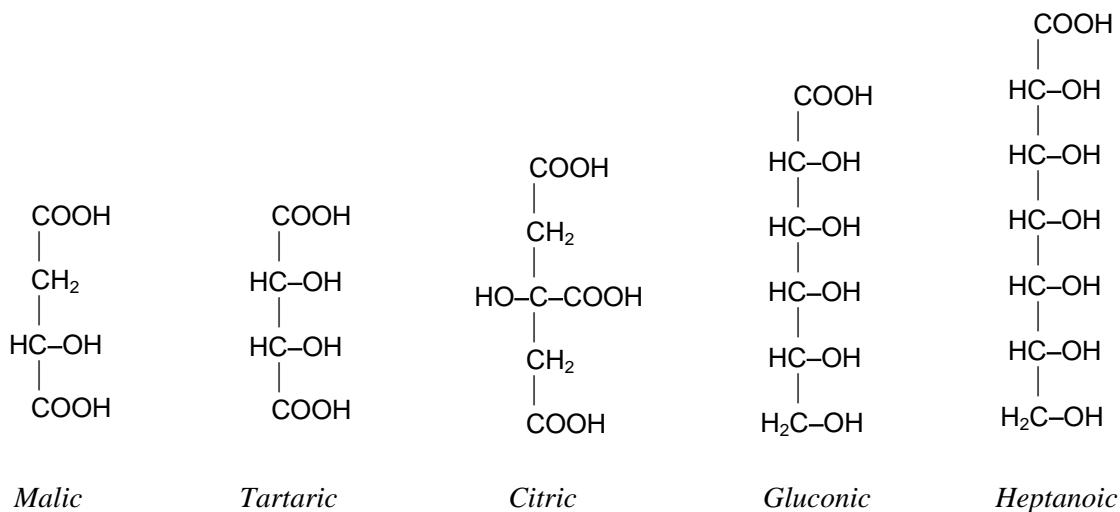

Figure 9 Hydroxycarboxylic acids reported to have a retarding effect on hydration of cement.
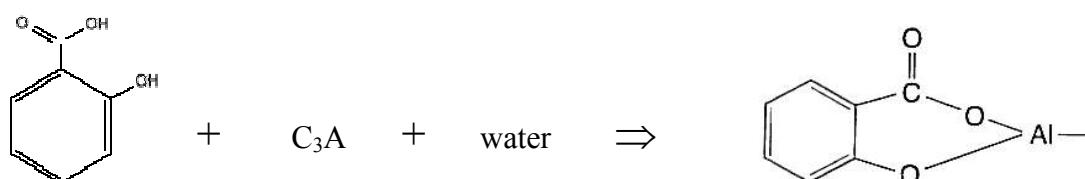
Figure 10 The reaction between salicylic acid and the C_3A phase of cement. (The aluminum salicylate complex from Hewlett [9]).

Lower carboxylic acids and their salts, like formic and oxalic acids, and the lowest hydroxycarboxylic acid, glycolic acid, behave as accelerators rather than as retarders in cements. Their chemical structures are shown in Figure 11. Even higher hydroxycarboxylic acids, known for their retarding effects (see Figure 9), may act as accelerators at very high concentrations. For instance, in one case the potassium salt of citric acid (tripotassium citrate) acted as an accelerator at dosages at about 5 % and higher (see Figure 12). The figure shows that the final setting time obtained by the citrate was approximately 80 hours at 4 % dosage, while it was only 30 minutes at 6 % dosage.

$$HCOOH \qquad \begin{matrix} COOH \\ | \\ COOH \end{matrix} \qquad \begin{matrix} COOH \\ | \\ H_2C{-}OH \end{matrix}$$

Formic   *Oxalic*   *Glycolic (hydroxyacetic)*
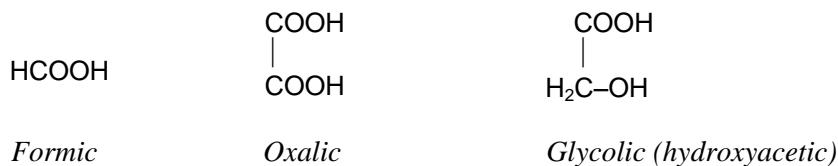
Figure 11 Examples of lower carboxylic acids acting as accelerators in OPC.
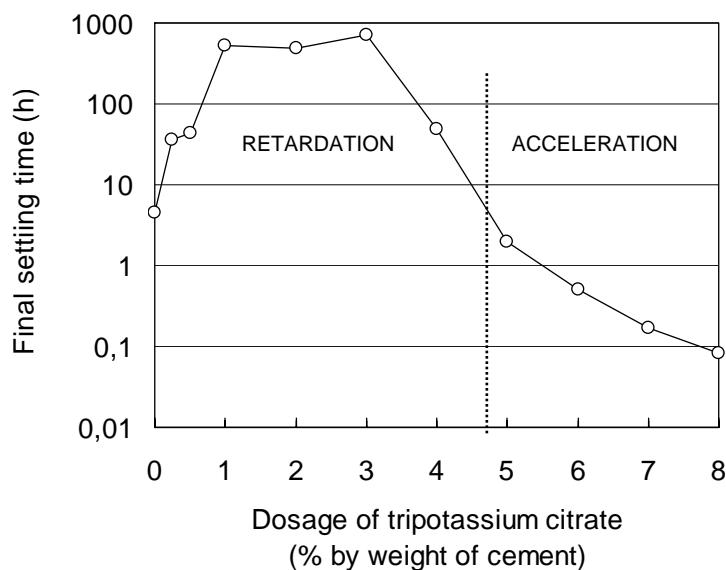
Figure 12   An example of the effect of increasing amount of tripotassium citrate on the final setting of a cementitious system (Data from [15]).

Cody et al [16] investigated the effect of retarders on ettringite nucleation, growth and morphology. They found that most carboxylic acids had no effect on ettringite except for citrate and tartrate (known calcium chelators), which prevented both nucleation and growth.

Rai et al [17] examined the hydration of OPC in the presence of malic acid (not to be mistaken for *maleic* acid), and found that malic acid lowered the setting times at high dosages like potassium citrate in Figure 12. A very high temperature rise was observed during the very first minutes of

hydration in the presence of high dosages of malic acid. This observation, however, was not attributed to heat evolution caused by the hydration of clinker materials, since the non-evaporable water content in the hydrated OPC pastes containing malic acid were much lower than those without, even after 28 days. In contrast to citric and tartaric acid, malic acid does not form any compound with C_3A [17].

Bhatty [18] screened the retarding effect of aromatic compounds containing hydroxyl and carboxyl groups, and concluded that those containing both hydroxyl and carboxyl groups are the most effective retarders, especially 3,4,5-trihydroxybenzoic acid ($C_6H_2(OH)_3COOH$).

Collepardi [19] states that sodium gluconate retards both the production of ettringite and the hydration of silicates, and that the effects are more marked on OPCs without C_3A and rich in C_4AF. Moriconi [20] found that the retarding effect of sodium gluconate increased with the alkali contents of OPCs.

Using the conduction calorimetric technique, Ramachandran [21] screened several potential retarders and found calcium gluconate and sodium heptonate to be the most efficient hydroxycarboxylate based retarders for OPC, while sodium citrate showed only moderate retarding efficiency.

6   Phosphorous compounds

6.1   Phosphates

Most phosphates retard the setting of cement. The adsorption of phosphate ions at the surface of the clinker phase, or on the first hydration product, is thought to result in the precipitation of Ca-phosphates [3]. This is a typical example of the precipitation mechanism described in Table 1. Once insoluble and dense coatings are formed around the cement grains, further hydration slows down considerably. Phosphates are commonly used as an ingredient of commercial set-retarding admixtures [5].

The most useful phosphates for cement retardation are believed to be trisodium ortho-phosphate (Na_3PO_4) and tetra sodium pyrophosphate ($Na_4P_2O_7$) [9]. Since phosphates have no water reducing effect, this type of retarder can be used to adjust setting without unwanted changes in workability.

Ramachandran [21] screened potential retarders for OPC. He found that sodium pyrophosphate was one of the least effective retarders, while sodium hexametaphosphate, ($NaPO_3)_6$, showed a moderate set retarding capacity.

Gong [22] showed that sodium phosphate effectively retards the hydration of alkali-activated red mud-slag cementitious materials.

One supplier reports an almost perfect linear relationship between the dosage of an alkali phosphate based retarder and the setting time (see Figure 13).
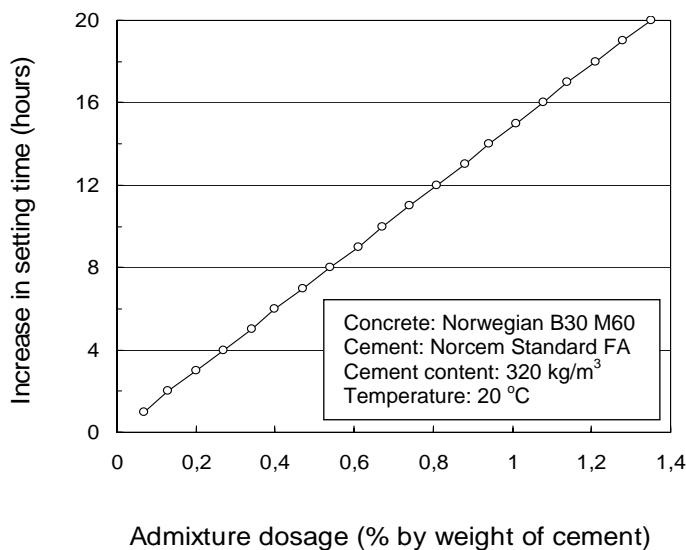
Figure 13   The increase in setting time as a function of dosage of retarder. [23].
Retarder: "Sika Retarder" (25 % solution of alkali phosphate).

6.2   Phosphonates

Figure 14 shows the general structural formula of phosphonic acid. Phosphonic acids and their salts (phosphonates) are known to form complexes with inorganic species, and are very efficient retarders of hydration of cement. According to Collepardi [3] phosponates make chelates or complexes with cations in the cement-water mix, and this effect results in poisoning or stabilizing of the CSH product on the C_3S surface. Such retarders are sometimes denoted "super-retarders" because of their efficiencies [3].

Ramachandran [24] tested different phosphonates and found that *diethylenetriamine-penta(methylenephosphonic acid)*, DTPMP, was the most efficient retarder in OPC pastes. He managed to increase the induction period of an OPC paste from 3 hours (reference mix) to more than 72 hours using only 0.09 % DTPMP by weight of cement. Different phosponates tested in cement are shown in Figure 15.

Using electrical conductivity and AC impedance methods to investigate early hydration and setting behaviour of OPC pastes containing phosphonates, Gu et al [25] confirmed that phosphonates have strong chelating and complexing capability, and that this effect might poison CH and CSH nucleation.
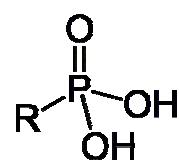
Figure 14   The general structure of an organic phosphonic acid with one alkyl group.
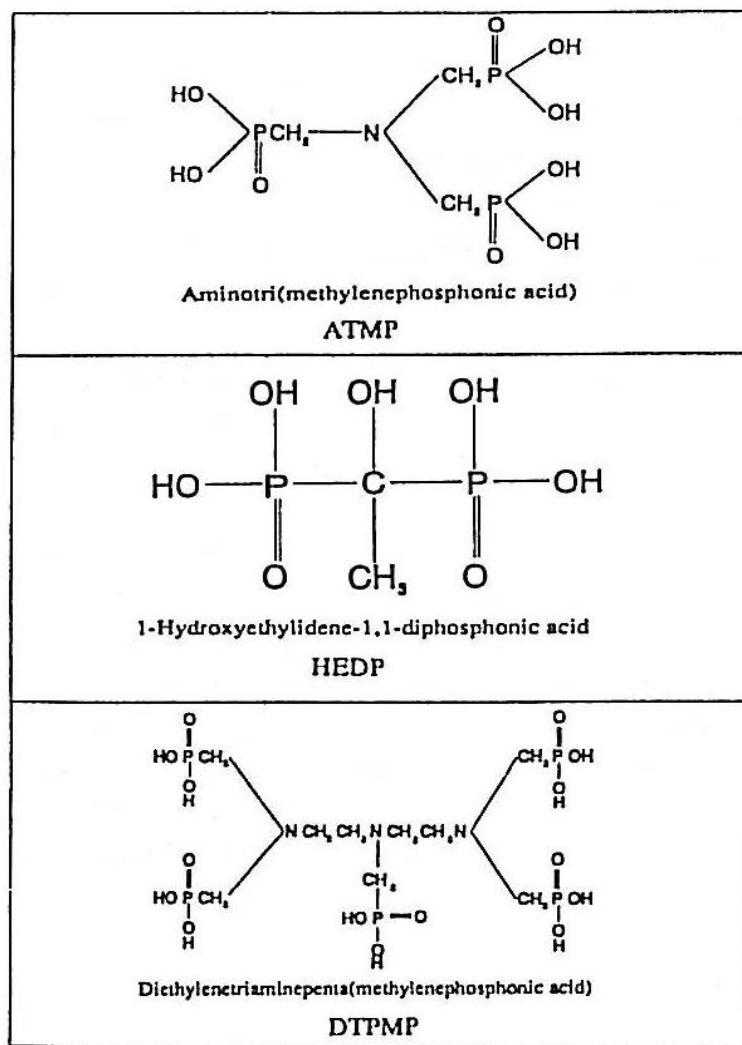
Figure 15   The molecular structures, chemical names and abbreviations of phosphonic acid
            compounds [24].

7 Commercial retarders for concrete

According to Dodson [26] pure retarders (ASTM C 494 Type B – Retarding admixtures) were most popular in the 1930s, and have been replaced by the more sophisticated bifunctional water reducing set retarders (ASTM C 494 Type D – Water-reducing and retarding admixtures). This might be the situation in North America, but in Europe pure retarders are very common.

According to ACI [4] set-controlling admixtures should be batched and dispensed as liquids. From an industrial point of view liquids are normally easier to handle. Accordingly, almost all commercial retarders are delivered as liquids, but powder retarders do exist (one example is given in Table 2).

Although producers of admixtures for concrete seldom disclose the ingredients of their retarders, some information on type of chemical components can sometimes be found in the Technical Data Sheet (TDS) of the products. More information is often found in the Material Safety Data Sheet (MSDS), especially if the admixture contains hazardous components.

Table 2 shows information on ingredients in a selection of 14 well known commercial retarders in Europe and North America. As the information is based on MSDSs only (as of December 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.

From the information given in Table 2 it is seen that:

- Five out of 14 commercial retarders contain hydroxycarboxylates, typically sodium gluconates and sodium glucoheptonates. Only one retarder containing citric acid was found.

- Phosphate was found in four commercial retarders, but only one contained Phosphonate

- Four retarders contain sugar-like compounds, typically together with lignosulphonate

Table 2
A selection of commercial liquid retarders for concrete

| Name of product | Information on ingredients given in the MSDS [1] | | Manufacturer |
	Type of ingredient	% by weight	
Lentan VZ 31 [27]	Tetrapotassiumpyrophosphate	10 – 25	BASF
Lentan VZ 32 [28]	Disodiumfluorophosphate	10 – 25	
Lentan VZ 33 [29]	Saccharose (*sucrose*)	No [2]	
Lasment 10 [30]	Lignosulphonate and saccharide (*sugar*)	29.0 ± 1.4 [3]	
Lasment T29 Pulver [4] [31]	Lignosulphonate	10 – 50	
	Saccharin (*artificial sweetener*)	1 – 10	
Delvo Stabilizer [32]	Amino tris(methylene phosphonic acid)	1.0 – 5.0	
Sika Retarder [23, 33]	Alkali phosphate	25.0 ± 1.0	Sika
SikaTard 930 [34]	Citric acid monohydrate	5 – 10	
Mapetard R [35]	Sodium gluconate	10 – 30	Rescon Mapei
Mapetard D [35]	Potassiumbiphosphate	30 – 60	
Eucon HC [5] [36]	Sodium glucoheptonate	15.0 – 40.0	Euclid Chemical
	Triethanolamine	7.0 – 13.0	
	"Proprietary"	1.0 – 5.0	
Eucon Retarder 75 [5] [37]	Sodium gluconate	30.0 – 60.0	
	4-chloro-3-methylphenol	≤ 1.0	
Eucon Retarder 100 [5] [38]	Sodium glucoheptonate	30.0 – 60.0	
Daratard 17 [5] [39]	Calcium lignosulphonate	No [2]	W. R. Grace
	Corn syrup (*mainly glucose* [40])	No [2]	

[1] MSDS = Material Safety Data Sheet
[2] No = No information given in the MSDS
[3] Information given in the Technical Data Sheet. No information given in the MSDS.
[4] In powder form
[5] Marketed as both set retarder and water reducer

8   Retarders for calcium aluminate cements

As with OPC, hydroxylic organic compounds, such as sugars or citric, tartaric or gluconic acids, are powerful retarders in high alumina cements or calcium alumina cements (CACs) [41]. On the other hand, chloride salts, which are a powerful accelerators in OPC, normally have retarding effects in CAC, somewhat depending on dosage and temperature [42, 43].

Citric acid is reported to produce a very distinct retarding action on CACs, while lithium citrate, in common with other lithium salts, show an accelerating effect [44]. The retardation may be seen as a result of an initial complexation of calcium followed by the precipitation of protective gel coatings around the cement grains [44].

Justnes [45] managed to optimize the setting time of a very fast hardening CAC repair mortar by a combination of lithium carbonate accelerator (~0.02%) and sodium gluconate retarder (~0.05%). Hydroxycarboxylic acids, or their salts, are often used in conjunction with lithium salt accelerators to produce proprietary controlled-set CAC based mortars and concretes [42].

9   Recommendations for future R&D

Today's retarders show acceptable retarding capability regarding setting behavior of OPC pastes. Commercial retarders based on e.g. phosphates or hydroxycarboxylates can be used to prolong the setting time for many hours with acceptable accuracy. Corresponding retarders to decrease the rate of hardening are not commercially available, but some research activities are reported [2].

Future R&D activities within this field should focus on two main challenges:

Hardening retarders
For some concreting operations it is considered important to lower the rate of heat evolution during the hydration of the cement, e.g. in massive concrete structures to minimize the risk of thermal cracks. Urea (or carbamide, $(NH_2)_2CO$) and combinations of hydroxycarboxylic acids and calcium nitrate have the potential to act as hardening retarders of cement hydration [2]. Research activities along this line should continue. The research should also investigate the reported capability of urea to slow down the temperature rise of OPC hydration to produce 'low heat concrete' [46].

Also triethanolamine (TEA), which may show accelerating or retarding effects depending on dosage, should be investigated as a potential part of a hardening retarder. Figure 16 shows an example of heat development in OPC paste with and without TEA [47]. It is seen that a dosage of 0.4 % TEA reduced the maximum heat output (W/kg) by approximately 60 % compared to that of a cement paste without TEA. However, in order to develop a hardening retarder containing TEA (or other alkanolamines) one must formulate an admixture that is able to overcome the unfortunate and well known flash-set behavior of TEA at high dosages.

Alkali-free retarders
There is a growing demand in the market for admixtures that contain low amounts of alkalis, at least if the admixtures are to be used at high dosages. This is to minimize the risk of alkali-aggregate reactions. Retarders are normally added at low to moderate dosages, but the alkali content can be quite high, sometimes higher than 5 % Na_2O-equivalents.

Water soluble alkali-free salts of phosphorous, phosphonic and hydroxycarboxylic acids can be made by neutralizing the acid by alkanolamines. TEA-gluconate and TEA-tartarate have been reported as potential retarders for cement hydration [48]. One should also investigate the possibility of neutralizing the acids by alkali-earth metal hydroxides. However, only very few (if any) of these retarding acids can form water soluble salts with calcium.
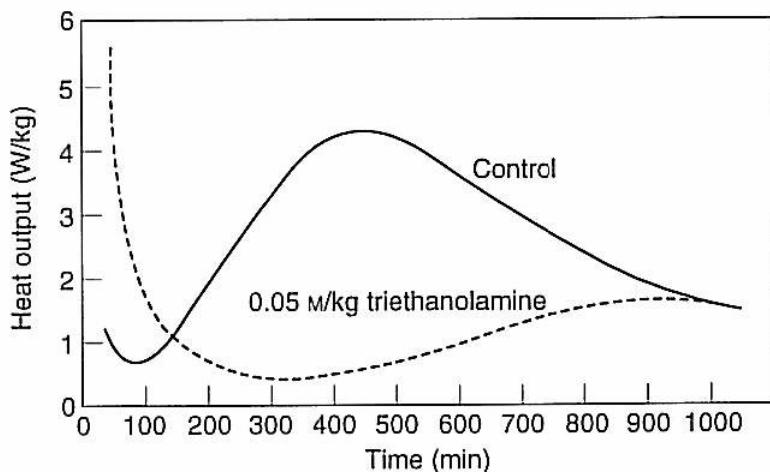
Figure 16 Effect of triethanolamine (TEA) on Portland cement hydration by conduction calorimetry. 0.05 M/kg corresponds to a dosage of about 0.4 % TEA by weight of cement [47].

10 Conclusions

The conclusions from this study are:

- A majority of retarding admixtures for concrete are made of organic compounds. The only practical inorganic retarders are those based on phosphate.

- Four mechanisms of action in cement-water systems are reported:
  Adsorption, Precipitation, Complexation and Nucleation
  Most retarders probably act by several mechanisms.

- It is quite easy to retard setting by admixtures. Several well known set-retarding admixtures are on the market.

- It is difficult to retard hardening of concrete by admixtures. There are no hardening retarders on the market.

- Further research activities should first of all concentrate on developing water soluble hardening retarders, being alkali-free if possible.

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