

RILEM REPORT 10



# Application of Admixtures in Concrete

EDITED BY

**A.M. Paillere**



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# **Application of Admixtures in Concrete**

**State-of-the-Art Report prepared by RILEM Technical Committee  
TC 84-AAC, Application of Admixtures in Concrete**

RILEM – The International Union of Testing and Research  
Laboratories for Materials and Structures

Edited by

**A. M. Paillère**

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## **Preface**

Since it was formed in 1947, RILEM (The International Union of Testing and Research Laboratories for Materials and Structures) has been contributing to continuous transfer and exchange of knowledge and technologies, internationally. Its policy of active cooperation with the scientific and technical community, as well as with the industrial world, through promotion of applied and experimental research, has always been pursued by RILEM to respond to the emerging problems of modern society.

One of RILEM's principal activities is realised through its technical committees: the creation of Technical Committee 84-AAC on Applications of Admixtures for Concrete was approved during the RILEM General Council meeting in Tsukuba, Japan, in September 1984 and its chairman was appointed at that time. The rest of the committee members were chosen following the guidelines of RILEM.

The installation and first meeting of the Committee was held during March 1985 in Monterrey, Mexico. Later, the Committee met on nine occasions: Paris, France in July 1985; Madrid, Spain in April 1986; Treviso, Italy in March 1987; Paris, France in September 1987; Istanbul, Turkey in April 1988; Mexico City and Merida, Mexico in December 1988; Haifa, Israel in March 1989; Barcelona, Spain in May 1990, and Salzburg, Austria in April 1992.

The tasks of Committee 84-AAC were:

1. Definition of admixtures:

Admixtures for concrete, mortar or paste are inorganic (including minerals) or organic materials in solid or liquid state, added to the normal components of the mix, in most cases up to a maximum of 5% by mass of the cement or cementitious materials.

The admixtures interact with the hydrating cementitious system by physical, chemical or physico-chemical action, modifying one or more properties of concrete, mortar or paste, in the fresh, setting, hardening or hardened state.

Materials such as fly ash, slag, pozzolanas, or silica fume which can

be constituents of cement and/or concrete, also products acting as reinforcement, are not classified as admixtures.

2. Preparing a Guide for the use of admixtures

The Guide was published in the RILEM Journal, *Materials and Structures*, Vol. 25, January 1992, pp. 49-56, and is also included as an Appendix to this Report. It includes terminology, definitions of the properties of concrete that can be affected by the use of admixtures and other terms related to admixtures.

3. Preparation of a state-of-the-art of concrete admixtures

This is presented in this volume.

4. Compilation of a bibliography

5. Organization of an international symposium

The symposium 'Admixtures for Concrete: Improvement of Properties' was held in Barcelona, Spain in May 1990 and the proceedings volume was published by Chapman & Hall.

Following the introductory chapter on the interaction of admixtures in the cement-water system, this volume is divided into two parts, the first part covering the most commonly used admixtures and the second part those not so commonly used.

The tasks of the Committee were accomplished by all its members even though an individual member was designated to prepare a specific paper; all the subjects were discussed and approved paragraph by paragraph by the Committee.

I must express on behalf of RILEM and myself my appreciation and special thanks to all members of this Committee for the effort and hard work to accomplish the tasks of RILEM TC 84-AAC.

The most sincere gratitude is also offered to all the organizations which allowed a member of their staff to be part of this Committee and provided them with all the facilities and support with which all the works assigned to the Committee were accomplished.

*Prof. Dr. Ing. R. Rivera-Villarreal*  
*Chairman of TC 84-AAC*



## **RILEM Technical Committee TC 89-AAC**

This state of the art was drafted within the framework of RILEM Technical Committee 89-AAC *Application of Admixtures for Concrete*, which was comprised as follows:

### *Chairman*

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# 1

## **Interaction of admixtures in the cement–water system**

*V. S. Ramachandran*

### 1.1 ABSTRACT

Physical adsorption, chemisorption and chemical interactions occur between admixtures (such as accelerators, retarders, water reducers and superplasticizers) and hydrating cement. The mechanism of action of admixtures, changes in water demand, microstructure, strength and durability of fresh and hardened cement can be explained by the interaction effects.

### 1.2 INTRODUCTION

Admixtures confer certain beneficial effects to concrete, including reduced water requirement, increased workability, controlled setting and hardening, improved strength and better durability.

Many approaches have been adopted to investigate the role of admixtures. One approach is to determine the state of the admixture in concrete at different times of curing. The admixture may remain in a free state as a solid or in solution, or interact at the surface or chemically combine with the constituents of cement or cement paste. The type and extent of the interaction may influence the physico-chemical and mechanical properties of cement. In this chapter an attempt is made to discuss the possible interactions of different types of admixtures in the cement–water system, with particular reference to the changes in physico-mechanical properties.

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### 1.3 DISCUSSION

#### 1.3.1 Accelerators

Many inorganic compounds such as chlorides, fluorides, carbonates, silicates, aluminates, borates, nitrites, thiosulphates, triethanolamine, diethanolamine, and formates have been advocated for use as accelerators.

Calcium chloride is perhaps the most efficient and economical accelerator. In the hydration of  $C_3S$  ( $C = CaO$ ,  $S = SiO_2$ ,  $H = H_2O$ ) there is evidence that calcium chloride exists in different states in the  $C_3S$  paste. Based on thermal analysis and leaching studies, Ramachandran [1] has concluded that, depending on the time of hydration, the chloride may exist in a free form (extractable by ethyl alcohol), incorporated strongly into the C-S-H phase (unleachable with water), chemisorbed or in interlayer positions (leachable with water). At 168 h about 20% of the added chloride is incorporated strongly into the C-S-H phase. The rest is in a chemisorbed state in the interlayers (easily leachable with water). These results may have implications in explaining the mechanism of the accelerating action, microstructural development, differences in the C/S ratio of C-S-H products, corrosion potential of chlorides and intrinsic properties of Portland cement. Calcium chloride accelerates the reaction between  $C_3A$  and gypsum, and monochloroaluminate is formed after all gypsum is consumed [2]. Using leaching and pressure techniques it has been found that more chloride is immobilized by the  $C_3A +$  gypsum mixture than by  $C_3S$  or Portland cement [3].

##### (a) Triethanolamine

Triethanolamine is termed an accelerator. It acts, however, as a retarder of  $C_3S$  hydration [4]. An examination of the thermal behaviour of  $C_3S$  hydrated to different periods in the presence of triethanolamine reveals the development of exothermal peaks that could be attributed to the decomposition of a complex of the amine with the hydrated products of  $C_3S$ . This complex may be responsible for early retardation and possibly for the higher C/S ratio of the C-S-H product. Triethanolamine accelerates the reaction between  $C_3A$  and gypsum [5]. The cation-active amine may react with aluminium and calcium ions on the surface of  $C_3A$ . In cements, at a

dosage of 0.1 or 0.5% triethanolamine, setting occurs rapidly within about 2–6 min; this is attributed to the accelerated formation of ettringite and  $C_3A$ -hydration products [5].

(b) Formates

Calcium formate is used as a non-chloride accelerator. In cements more ettringite is formed with formate than with calcium chloride [6]. The increased formation of ettringite in the presence of calcium formate is attributed to the formation of the complex  $C_3A \cdot 3Ca(HCO_2)_2 \cdot 30H_2O$  at ordinary temperatures, analogous to ettringite. Enhanced formation of ettringite in the presence of calcium acetate and calcium propionate is also explained by their ability to form hexagonal prism-type phases with  $C_3A$  [7]. Calcium formate accelerates the hydration of the  $C_3S$  surface [8].

(c) Other accelerators

Sodium carbonate decreases the setting time of cement by 2–4 h but after 10–12 h the hydration is retarded due to the precipitation of  $CaCO_3$  by the reaction of  $Na_2CO_3$  with lime. The precipitation occurring within the pores of the product decreases permeability [9]. Oxalic acid may also act as an accelerator by decreasing the setting time of cement by 43% and increasing strengths by 12% [10]. Strength development is explained by the formation of calcium oxalate, although the amount formed may be small.

Although calcium chloride is a comparatively simple molecule compared to other accelerators, its accelerating mechanism is not resolved. At least 12 theories have been proposed for its action [11]. It can therefore be appreciated that the role of more complex compounds involving organic compounds is not easily resolved.

### 1.3.2 Retarders

Organic compounds such as unrefined Na, Ca or  $NH_4$  salts of lignosulphonic acids, hydroxy-carboxylic acids, carbohydrates and inorganic compounds (oxides of Pb and Zn phosphates, Mg salts, fluorates and borates) act as retarders.

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##### (a) Sugars

Theories of retarding effect are based on adsorption, precipitation, complexation or nucleation. In all these processes, interactions are involved. According to Milestone, sugar and sugar acids adsorb on to  $\text{Ca}^{2+}$  ions on the hydrating  $\text{C}_3\text{S}$  surface and poison the C-S-H nucleating sites [12]. Adsorption of glucose, for example, results in the zeta potential becoming negative from the positive values. Poisoning of CH nuclei by adsorption of sugars is also envisaged [13].

According to the precipitation theory, addition of mono or polysaccharides increases the concentration of Ca, Al and Fe. Sugars may combine with them to form insoluble metal organic complexes on the cement grains and retard hydration [14]. All sugars do not retard cement to the same extent. Non-reducing sugars, for example containing five-membered rings (sucrose, raffinose), are the best retarders. Although no sucrose-silicate or calcium complex has been detected with these sugars, it is suggested that a half salt formed by attachment of Ca and OH groups to the five membered ring may poison CH and C-S-H nuclei [15]. Retardation of  $\text{C}_3\text{A}$  to the cubic  $\text{C}_3\text{AH}_6$  is explained by the formation of interlayer complex of the hexagonal aluminate hydrate with the organic compounds [16, 17].

It appears that no single theory can be applied to explain the behaviour of all sugars on all cement components under all conditions of hydration. Adsorption need not occur only on unhydrated or hydrated surfaces. Some sugars accelerate the initial formation of ettringite in the  $\text{C}_3\text{A}$ -gypsum- $\text{H}_2\text{O}$  system and others retard it. Sucrose is an accelerator, whereas raffinose and trehalose are retarders. When sucrose is used, it is assumed that adsorption occurs on the anhydrous surface, preventing the formation of an impermeable layer of ettringite [18]. Why this does not occur with other sugars needs to be examined.

The precipitation theory cannot be applied for all cases. For example, the stability constants of calcium complexes of various compounds do not bear correlation with their potency as retarders. A study of many complexes has shown that some are retarders and others are not. The theory based on poisoning of  $\text{Ca}(\text{OH})_2$  nuclei by itself may not always cause retardation. Although  $\text{Ca}(\text{OH})_2$  growth can be modified by incorporation of dyes it does not show any retarding characteristics [18]. Nucleation effect of C-S-H should also be considered. A combination of two mechanisms may occur and it is not

easy to separate the occurrence of two mechanisms. For example, EDTA retards the hydration of  $C_3S$ . The retarding action may be explained by the precipitated gel coating of C-S-H on the hydrating  $C_3S$ , consequent on the formation of a complex between EDTA and  $Ca(OH)_2$  in the solution phase [19]. The idea that retarding agents should contain the  $\alpha$ -hydroxy carbonyl group could be questioned. According to Daugherty and Kowalewski [20], organic compounds with two or more (OH) groups are necessary for the retardation of  $C_3A$  hydration.

(b) Hydroxycarboxylic acids

Adsorption studies have been carried out on hydroxycarboxylic acids such as salicylic acid on cement and cement components [21–23]. Only a small amount of adsorption occurs on the unhydrated phases compared to that on hydrated products of cement minerals. A complex of salicylic acids with aluminium may be responsible for the retardation of hydration of  $C_3A$  contents. At lower  $C_3A$  contents, smaller amounts of retarder are adsorbed leaving larger amounts of the admixture to affect the  $C_3S$  component. Alkalies may affect dissolution and interaction reactions.

Early hydration of  $C_3A$  + gypsum + CH may be accelerated and later reaction involving the conversion of ettringite to monosulphoaluminate may be retarded by citric acid [24]. Acceleration in the initial states may be due to preferential adsorption of citric acid which promotes hydrolysis of  $C_3A$  to hexagonal phases. The later retardation may be due to the formation of a complex between citric acid and monosulphate. Calcium citrate formed by reaction of lime and  $CaCO_3$  (impurities) with citric acid may hinder the development of nuclei in the hydration of plaster of paris.

Correlation between solubility and retarding behaviour is not always possible. Solubility of oxalic acid is  $5 \times 10^{-6}$  M and that of gluconic acid is  $8 \times 10^{-5}$  M. Oxalic acid is not a retarder for  $C_3A$  hydration although less soluble, but gluconic acid is more soluble and is a good retarder [25].

(c) Lignosulphonates

The relative retarding effects of sugars and lignosulphonate are not easy to resolve. The hydrating  $C_3A$  adsorbs irreversibly substantial amounts of lignosulphonate and hence it is possible that pure

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lignosulphonate contributes to the retarding effect.

Thermograms show that both commercial and sugar-free lignosulphonates are equally effective in retarding the hydration of cement [26]. Both the commercial and pure lignosulphonates retard setting times. According to other investigations either the sugar-free lignosulphonate is a poor retarder or inert in its action on cement. The disagreement may be due to the difficulty of preparing pure lignosulphonate and the differences in its molecular weights.

### (d) Inorganic retarders

Many inorganic salts retard the hydration of cement. These salts form insoluble hydroxides in alkaline solution and may form a coating on the cement particles. There is evidence that inorganic compounds form complexes with the hydrating cement hydration. Zinc oxide retards the hydration of the  $C_3S$  and does not influence the hydration of  $C_3A$  + gypsum mixture. The formation of calcium hydroxyzincate  $Ca(Zn(OH)_3H_2O)_2$  by the reaction of the  $Ca(OH)_2$  with  $ZnO$  has been confirmed [27]. At an addition of 10% Zn equivalent of hydroxyzincate, 3.3% Zn may be incorporated into the C-S-H phase. The retardation effect of  $Pb(NO_3)_2$  is attributed to the very rapid precipitation of a protective  $Pb(OH)_2$  on the cement grains [28]. Most phosphates retard setting. 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 calcium phosphates.

### 1.3.3 Water reducers

Water reducers consist of Ca, Na or  $NH_4$  salts of lignosulphonic acid, Na,  $NH_4$  or triethanolamine salts of hydroxycarboxylic acid and carbohydrates. Lignosulphonates containing (OH), (COOH) and  $SO_3H$  groups are more widely used than others. Hydroxycarboxylic acids, such as citric acid, tartaric acid, salicylic acid, heptonic acid, saccharic acid and gluconic acid, contain (OH) and (COOH) groups. Gluconic acid-based admixtures are used extensively. Carbohydrates include glucose, sucrose or hydroxylated polymers obtained by partial hydrolysis of saccharides. The role of water reducers (normal, accelerating or retarding) in terms of their effect on hydration of cement is similar to that of retarders, accelerators and superplasticizers.

The effect of some accelerating and retarding admixtures has already been discussed. In this section the interaction of lignosulphonates with cement will be emphasized.

The plasticizing action of water reducers is related to their adsorption and dispersing effects in the cement–water system. In other words, some sort of interaction seems to be involved.

(a) Tricalcium aluminate

The hydration of tricalcium aluminate is retarded by lignosulphonate. The interaction between lignosulphonate and hydrating  $C_3A$  can be studied by adsorption experiments. Adsorption isotherms cannot be obtained in the  $C_3A$ –lignosulphonate– $H_2O$  system because hydration of  $C_3A$  occurs during the measurements, especially at low admixture concentrations. It is possible to determine the adsorption–desorption isotherm in the system hexagonal aluminate–lignosulphonate– $H_2O$ . Scanning loops in the isotherms show complete irreversibility, indicating a complex formation. Increase in the c-axis spacing of the hexagonal phase containing lignosulphonate is caused by the formation of an interlayer complex. The interlayer complex would impede the conversion of the hexagonal phase to the cubic phase. In a non-aqueous phase,  $C_3A$  does not adsorb any lignosulphonate. The retarding effect seems to be due to the reaction of hydrating  $C_3A$  and lignosulphonate. Jawed *et al.* [29] observed more fluidity in the cement paste containing a mixture of lignosulphonate and  $Na_2CO_3$  than when each of them was used separately. They proposed that an ionic complex occurred between lignosulphonate and  $CO_3$  and it was more anionic than lignosulphonate and, hence, acted as a better dispersant.

The conversion of ettringite to monosulphoaluminate is retarded by adding a water reducer to  $C_3A$  + gypsum. One of the suggested mechanisms of the plasticizing action may be related to a lower water demand caused by the retardation of ettringite formation and decrease in the interlocking of the ettringite particles. This observation has to be confirmed by a more extensive investigation.

(b) Tricalcium silicate

The hydration of tricalcium silicate is retarded by lignosulphonate. Apparent adsorption–desorption isotherms of the system  $C_3S$ –lignosulphonate– $H_2O$  can be explained by dispersion and hydration effects [30]. There is only partial reversibility during



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desorption, indicating the existence of a strongly bound surface complex involving  $C_3S$ , lignosulphonate and  $H_2O$ . Such a complex may cause retardation of hydration of  $C_3S$ . That the hydrated  $C_3S$  paste adsorbs irreversibly substantial amounts of lignosulphonate may be concluded from adsorption isotherms on the completely hydrated  $C_3S$ . Even in the non-aqueous medium the hydrated  $C_3S$  adsorbs calcium lignosulphonate, unlike the anhydrous  $C_3S$  phase. These results suggest that the retarding effect involves a reaction of lignosulphonate with the hydrating  $C_3S$  surface.

### (c) Tricalcium aluminate - tricalcium silicate

The  $C_3A$  phase adsorbs larger amounts of lignosulphonate than  $C_3S$  when exposed to aqueous solutions of lignosulphonate. Therefore, in cements hydrating  $C_3A$  may act as a sink for lignosulphonate. It is known that when lignosulphonate is added a few minutes after water has come into contact with cement, the hydration of  $C_3S$  is retarded more strongly. This would mean that the hydrated  $C_3A$  phase adsorbs less lignosulphonate and leaves larger amounts of the admixture in the solution phase for retardation of  $C_3S$  hydration.

The effect of lignosulphonate on cement depends not only on the amounts of  $C_3A$  and  $C_3S$  but also on the alkalis,  $SO_3$ , particle size of cement, etc. Depending on these factors and others early set may be retarded or accelerated but the final set is generally retarded.

The early acceleration of set is prompted in cements with higher aluminate/ $SO_3$  ratios. At early times, due to the adsorption of lignosulphonate on  $C_3S$ ,  $Ca(OH)_2$  is not released and the rate of formation of ettringite is increased. This implies that  $C_3A$  + gypsum reaction to form ettringite is faster than that containing  $Ca(OH)_2$ .

It is apparent that the role of the cationic lignosulphonate molecule as a water reducer is related to its adsorption on the cement components. The amount of adsorption, the rate and how strongly it is adsorbed may play a role in the setting, dispersibility, microstructure, shrinkage, durability and other properties of cement. The effect of cations and the material weight of lignosulphonate on cement properties has not been explored fully.

#### **1.3.4 Superplasticizers**

Most superplasticizers are based on sulphonated melamine formaldehyde (SMF), sulphonated naphthalene formaldehyde (SNF) and modified lignosulphonates. The action of water reducers involves adsorption and dispersion in the cement–water system. Similarly, effective surface interaction and dispersion of cement occur when superplasticizers are used. A study of the rate and amount of adsorption of superplasticizers on cement and cement compounds has provided some information on the rheological, setting and hydration characteristics. The general results of interaction and adsorption characteristics of SMF are similar to those of SNF.

##### **(a) Tricalcium aluminate**

The hydration of  $C_3A$  in the presence of SMF indicates that hydration is retarded. Adsorption of SMF on  $C_3A$  occurs as soon as the solution comes into contact with it [31]. The amount and rate of adsorption on the  $C_3A$  phase far exceed those on  $C_3S$  or Portland cement. In a non-aqueous medium adsorption is nil on  $C_3A$  but small amounts of SMF are adsorbed by the hexagonal phase. Adsorption is irreversible, indicating that a chemical interaction occurs between the hydrating  $C_3A$  and SMF. Thus the retardation of  $C_3A$  may be explained by strong adsorption of SMF on the hydrating  $C_3A$  surface.

The reported results on the rate of hydration of  $C_3A$  + gypsum mixture containing superplasticizers are contradictory. Adsorption of SMF has been studied on the  $C_3A$  + gypsum system prehydrated for various periods. Desorption experiments show that SMF is irreversibly adsorbed. A surface chemical or chemical interaction seems to occur between the hydrating  $C_3A$  or  $C_3A$ -gypsum mixture with SMF. The enhanced dispersion effect of superplasticizer when it is added a few minutes after mixing water is added to concrete can be explained as outlined in section 1.3.3.

##### **(b) Tricalcium silicate**

Hydration of  $C_3S$  is retarded by SMF. Irreversible adsorption is indicated in the system containing  $C_3S$ -SMF- $H_2O$ . This may involve interaction between hydrating  $C_3S$  and superplasticizer. The interaction of superplasticizers with hydrating  $C_3S$ ,  $C_3A$  and  $C_3A$  + gypsum components cannot be directly applied to the cement

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behaviour. The interaction within the cement system is much more complex because, in addition to interfering effects of the silicates and aluminates, the alkalis and  $\text{SO}_3$  also play an important role.

### (c) Cement

The amount of adsorption of SMF on cement varies with length of exposure to the solution. Within a few seconds there is a steep increase in adsorption due to the  $\text{C}_3\text{A}$ - $\text{C}_4\text{AF}$  components in the cement. Further adsorption does not occur up to about four to five h, after which it increases continuously. Adsorption beyond about five h is mainly due to the hydrating  $\text{C}_3\text{S}$  component. These results suggest that adsorption and interaction of SMF with the cement components are involved in the dispersion of cement and retardation of cement hydration.

The amount of adsorption of superplasticizer on cement can be related to workability. With the SNF superplasticizer the mini slump values increase as the amount of adsorption increases [32]. The adsorption values of SNF on three types of cement decrease as follows:

Type III > Type I > Type II [33].

The  $\text{C}_3\text{A}/\text{SO}_3$  ratios in the cements follow the same trend. That adsorption is dependent on  $\text{C}_3\text{A}$  content becomes clear: for the same workability, a higher dosage of superplasticizer is required for Type I than for Type V cement. According to the ASTM designation, Types I, II, III, IV and V are described as, general purpose, moderate sulphate resistant-moderate heat of hydration, high early strength, low heat and sulphate resisting cements.

Zeta potential development in suspensions of cement, alite,  $\text{C}_3\text{A}$  and  $\text{Ca}(\text{OH})_2$  containing superplasticizers has been studied. It is generally found that both adsorption and zeta potential values increased as the concentration of superplasticizer added to cement is increased [34].

The mechanism of retardation of hydration and even dispersion may not be entirely due to the adsorption effect of the anions. In SNF superplasticizer containing  $\text{NH}_4$ , Co, Mn, Li and Ni cations, the time for the development of maximum heat is 12.7 h with  $\text{NH}_4$ , and only 9.25 h with Ni [35]. The relative roles of cations in the superplasticizers are not well understood.

Higher-than-normal workability of concrete containing a superplasticizer is maintained for about 30–60 min after which the slump value decreases. In the period during which slump loss is occurring the  $C_3A$  phase reacts with gypsum. It is possible that the extent of reaction of  $C_3A$  and gypsum and the crystalline form of the product would have an important effect on the workability of concrete. Addition of superplasticizer enhances the initial reaction between  $C_3A$  and gypsum. Alkalies enhance this reaction. According to Hattori [36] coagulation of the particles plays a more important role than the chemical bonding in slump losses. Experiments on  $C_3S$ –SMF– $H_2O$  system have shown that rapid loss of slump occurs in this system [37]. Thus the contribution of the  $C_3S$  phase should also be taken into account. All these mechanisms involve some sort of interaction with the superplasticizer.

One of the methods of maintaining the slump in superplasticized concrete is to add retarders such as calcium gluconate to cement [38]. It is possible that the retarder, although not interfering with dispersion caused by the superplasticizer, adsorbs on the cement components, affecting the chemical or physical processes that cause agglomeration or interlocking of the cement particles.

#### 1.4 CONCLUSIONS

Admixtures in aqueous solutions or in the solid form may interact with the hydrating cement compounds in the cement–water–admixture system. Physical, chemical and mechanical properties of the cement paste are affected to different extents by these interactions. In many instances, conclusion on interaction processes are speculative because they are based on indirect evidence. A study of interaction occurring in systems containing more than one admixture becomes even more complex. Even the so-called single component commercial admixture may contain a small amount of a chemical that could interfere with the interaction of the main component. Disagreement in reported results on interactions in cement systems may be traced to the variability in the characteristics of the starting materials, methods of curing, testing methods and interpretation.

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## **PART ONE**

### **ADMIXTURES FOR CONCRETE IN MOST FREQUENT USE**





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## 2

# Air entraining admixtures

*R. Rivera*

### 2.1 DEFINITION

Air entraining admixtures cause the formation of fine uniformly distributed micro-bubbles for air in the concrete or mortar, and remain after hardening. Air entraining makes hardened mortars and concretes freeze-thaw resistant.

### 2.2 INTRODUCTION

Some air entraining agents used in cement paste or mortar are not considered as admixtures according to the RILEM admixtures definition, but as air entraining admixtures when they are incorporated in amounts higher than 5% of cementitious constituents.

These admixtures act by physical action. The air cells are usually added to the mixer as a stable preformed foam and thoroughly blended into the mix. The air cell may also be made mechanically by entrapping air during high speed mixing of the cement paste or mortar materials, when a surface active agent is added.

The air bubbles produced by air entraining admixtures are dispersed throughout the cement paste due to surface active properties of these admixtures. The bubbles are separate from the capillary pore system in the cement paste and they never become filled with the products of hydration of cement as gel can form only in water [p. 291 of 1].

The improved resistance of air entrained concrete to frost attack

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was discovered accidentally in the late 1930s when it was observed that concrete pavements in New York State made with cement that has been manufactured with grinding aids, that included beef fat, calcium stearate and fish oil, were more durable than others and had acted apparently as air entraining agents [2].

Air entraining improves the workability and consistency of fresh concrete and reduces its segregation and bleeding. Therefore, it is possible to take advantage in proportioning, using less water and sand. The strength of the hardened concrete is decreased as the amount of air is increased, but the effects are compensated by the appropriate proportioning changes.

### 2.3 COMPOSITION

Air entraining agents belong to a class of chemicals called surfactants, which is a short for surface active substances, whose molecules are absorbed strongly at air-water or solid-water interfaces. This behaviour is due to a specific molecular property that is called amphipathic [3].

The essential requirements of an air-entraining agent are that it rapidly produces a system consisting of a large number of stable finely divided small voids uniformly distributed through the cement paste, that the individual bubbles must resist coalescence, and that the foam must have no harmful chemical effect on the cement.

Numerous proprietary brands of air entraining agents are available commercially [3, 4, 5]. They have been categorized in different ways [1]. One of them is [6] as follows:

1. Salts and wood resins (vinsol);
2. Synthetic detergents;
3. Salts of petroleum acids;
4. Salts of proteinaceous materials;
5. Fatty and resinous acids and their salts;
6. Organic salts of sulphonated hydrocarbons.

A list of some suppliers is given in Table 5.2 on p. 273 of [7] showing brand names and some of the properties of the admixtures. The performance of the unknown ones should be checked by trial mixes.

Most of the commercial air-entraining admixtures are available in liquid state, although a few are powder, flakes or semi-solids.

## 2.4 MECHANISM OF ACTION

For each concrete mix there is a minimum volume of voids required for protection from frost. It was found [8] that this volume corresponds to 9% of the volume of mortar and it is essential that the air bubbles are distributed throughout the cement paste. The adequacy of air entrainment can be estimated by the spacing factor. This factor is the maximum distance of any point in the cement paste from the periphery of a nearby air void [9]. A maximum spacing factor of 0.20 mm is required for full protection from frost damage [10]. The smaller the spacing factor, the better the durability of concrete [11]. The voids are not all of the same size, and range usually up to 300  $\mu\text{m}$ . If bubbles are bigger than 300  $\mu\text{m}$  the air entrained is not effective [p. 292 of 7].

## 2.5 MAIN FACTORS INFLUENCING THE MECHANISM OF ACTION

### 2.5.1 Amount of air

Generally the larger the quantity of the admixture, the more air is entrained, but there is a dosage limit beyond which there is no further increase in the volume of voids [pp. 293, 295 of 1].

There are some other aspects influencing the amount of air actually entrained in concrete when a given amount of air entraining admixture is added, due to variations in its ingredients, such as cement type, supplementary cementing materials, other admixtures, and mixing, handling and temperature:

1. Smaller amounts of air entraining admixtures are generally required as the fineness of the cementitious products increase.
2. Alkali content in cement increases the amount of entrained air [pp. 293, 295 of 1].
3. An increase in carbon content of fly ash (PFA) and silica fume or bentonite decreases the amount of entrained air [12]. Recent

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research suggests that adding polar compounds which absorb into the carbon improves the performance of certain air entraining agents in the presence of pulverized fuel ash [13].

4. The use of water reducing admixtures leads to an increase in the amount of entrained air even if the water reducing admixture has no air-entraining properties per se [pp. 293, 295 of 1, pp. 279, 281 of 7].
5. The more the proportion of fines in aggregate the greater the air content in the concrete [14]. But the material in the 300–600  $\mu\text{m}$  range increases it [pp. 293, 295 of 1].
6. As the maximum size of the coarse aggregate increases, the air requirement of the concrete decreases [pp. 279, 281 of 7]. This effect is indirect, because the larger the maximum size, the smaller the mortar fraction.
7. The amount of air entrained admixture required to obtain a given air content will vary widely depending on the particle shape and grading of the aggregate used [12].
8. More workable mixes holds more air than drier mixes.
9. The higher the slump of the concrete, the higher will be the air content.
10. An increase in water/cement ratio results in an increase in air content and in large air voids [12].
11. Mixing time and speed should be optimized because lower values cause a non-uniform dispersion of the bubbles, while over-mixing gradually expels some air [15, 16].
12. Prolonged transportation and vibration reduce the amount of entrained air (hence, the air content of concrete should be determined just before placement) [pp. 293, 295 of 1].
13. A higher temperature of fresh concrete results in a lower air content, and vice versa. The effect is more significant at higher slumps [pp. 279, 281 of 7].
14. Atmospheric pressure steam curing of concrete may cause expansion of air bubbles and may lead to incipient cracking.
15. Blends of ordinary Portland cement and silica fume in mortars exhibit a higher range of water reducer and air entraining admixture demand [17].

### **2.5.2 Air void spacing factor and stability**

Critical to the durability of concrete undergoing freezing and thawing mechanical actions is the air void spacing factor. The spacing factor and the spacing factor stability can not be determined from the measurement of the air content. The air void spacing factor is measured when concrete is hardened. For mix conditions and materials, the production and the stability of the air void system is related to the air entraining agent dosage.

The real value of laboratory tests to predict field performance of the air-void system of a given mix is questionable and should be reserved for comparative tests. Still more problems arise as a result of the introduction of new materials into the concrete. Some findings are given next.

1. It is possible not only to produce field silica fume concrete with a satisfactory air void spacing factor, but to do so without affecting the stability of the air void system [18].
2. Superplasticizer can sometimes destabilize the air void system significantly. Low dosages of superplasticizers appear to be less harmful than higher ones [19, 20].
3. Retempering concrete with enough water to increase the slump by approximately 50 mm to about 100 mm has no significant influence on the air void spacing factor value although it often causes a small increase in air content [21].
4. Retempering concrete with an air entraining agent diluted in a small amount of water after 45 min, permits the improvement of the spacing factor value if the quantity of admixtures added is high (30 to 50% of the normal dosage) to cause a marked increase of the air content [21].
5. A significant increase in the soluble alkali content of the cement can improve significantly the stability of the air void system, particularly in concrete mixtures to which a superplasticizer is added 15 min after initial mixing [22].

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### 2.6 EFFECT IN MORTAR OR CONCRETE

#### 2.6.1 Fresh stage

##### (a) Unit mass

Air entrainment affects the unit weight of concrete of mortar.

##### (b) Workability

The increase in workability brought about by air entrainment is usually ascribed to some sort of ball bearing action of the air bubbles, kept spherical by surface tension [23, 24].

The air bubbles act as fine aggregate of very low surface friction and considerable elasticity, and actually make the mix like an over-sanded mix. For this reason, the addition of entrained air should be accompanied by a reduction in the sand content.

Workability is desirable in all concretes, but those that are inherently harsh and unworkable, such as lean lightweight aggregate concretes, specially benefit from the use of air entrainment.

*Consistency* An air entrained concrete increases the flowability, at the same water content.

*Plasticity* The mix can be said to be more plastic for the same workability. The mix containing entrained air is easier to place than and air free mix.

*Cohesion* The mix is more cohesive due to the surface tension of the bubbles acting with the cement paste interface, at equal cement content or water/cement ratio [25].

*Pumpability* High pressure pumping of concretes with a high content of air entrainment causes the bubbles to be compressed, and workability decreases. This is due to the ball bearing effect being diminished when friction increases because of the applied pressure. If the pipe is too long the reduction in air volume due to pressure can absorb all the movement of the piston pump and concrete will not flow through the end. For these reason air entrained concrete is pumped for distances commonly up 45 m [p. 133 of 1].

**Compactability** Air entrainment increases the compactability because of its ball bearing effect.

**Finishability** There are thousands of air bubbles per cubic centimetre of cement paste; they allow for easier deformation when the concrete is worked, resulting in an increase of finishability. However, proper magnesium or aluminum alloy floats must be used and a suitable delay may be observed before starting the finishing operations [26, 27]. Indeed, because of the lack of problems caused by bleed water, proper finishing of the air entrained concrete is easy, and a durable surface is ensured.

(c) Segregation

Air entrained concrete is less prone to segregation during handling and transportation but it can not be expected to cure excessive ills that are responsible for segregation, such as excessively lean and wet mixes, poor grading of the aggregate, an improper handling of the concrete [p. 284 of 7].

Segregation is also improved, providing the fresh concrete is not over-vibrated [p. 298 of 1]. Over-vibration expelled air bubbles.

(d) Freeze-thaw resistance

Air entrainment increases the resistance of concrete to change of volume due to freezing and thawing.

## **2.6.2 Setting stage**

(a) Plastic shrinkage

For the same water/cement ratio and consistency, reduced or unchanged amounts of cement are needed compared to reference mixtures.

(b) Bleeding

The entrained air is beneficial to reduce bleeding. The air bubbles appear to keep the solid particles in suspension so that sedimentation is reduced and water is not expelled [33].



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### 2.6.3 **Hardening stage**

*Strength development* Air entraining admixtures have no appreciable effect on the rate of hydration of cement.

### 2.6.4 **Hardened stage**

#### (a) Unit mass

Air entrainment affects the unit weight of concrete or mortar, inversely to the air content.

(b) Compressive, tensile and flexural strength, modulus of elasticity Each of these properties is reduced at the same w/c ratio. Some relationships have been found. The usual approximate rule for predicting the result is that each percent of air will reduce the strength by about 5% [28, 29].

#### (c) Durability

*Capillary absorption* The capillary absorption is lower for properly air entrained mortar or concrete [p. 297 of 7], because of the decrease in water content and because the bubbles reduce the capillary rise.

*Permeability to liquids and gases* Air entrainment results in decreasing mixing water for the same workability and results in a decrease in the water/cement ratio; it greatly decreases the permeability of paste [30].

*Freeze-thaw resistance* Specimens of cement paste, if kept continually wet, will usually be damaged when frozen, even if they are air-entrained. Depending on the degree of drying, the specimen will be subjected to varied degrees of frost attack, ranging from destruction to apparent immunity. This will depend largely on the properties of the concrete, regardless of the mechanism of frost action.

Early attempts to explain the damage to concrete caused by freezing were based on the fact that water expands when freezing. Later, however, Collins introduce a concept which was based on frost heaving in soil [31]. This was related to water migrating from unfrozen areas to form ice in large pores, establishing ice lenses and causing

considerable pressure. Powers proposed that the destructive stress is produced by the flow of water away from the region of freezing, and the concrete structure resisting such a flow [32]. Accordingly, if the water content is above the critical saturation point, there will be a critical length of flow path or critical thickness beyond which the hydraulic pressure exceeds the strength of the material, because the resistance to flow is proportional to the length of the flow path. This critical thickness was stated to be of the order of 0.25 mm and accounted for the necessity of entrained air in concrete. The air bubbles were considered to be reservoirs where excess water produced by freezing would migrate without causing pressure.

This hypothesis was modified by Power and Helmuth [33], who concluded that most of the effects of freezing in cement pastes were caused by the movement of water to the freezing sites; the magnitude of pressure generated at a freezing site depended on whether the cavity was filled with solution or ice. In the presence of salt solution, it was considered that pressure may also be generated by osmotic forces due to differences in the concentration of salts in the paste created by freezing of water in large pores.

According to Litvan, some damage may be caused by the ice formation but the actual process of migration of water is the main source of damage [34]. As this migration is not unlike drying and is initiated only when an ice crystal forms in a large pore (creating a lower vapour pressure), it can be concluded that the latter part of this mechanism does not play a major role. Nevertheless, the importance of water migration should be recognized.

MacInnis and Beaudoin studied the effect of maturity, porosity and degree of saturation on the degree of frost damage in cement paste [35]. They concluded that the major mechanism responsible for frost damage, especially at low levels of maturity, was the hydraulic pressure created in the liquid by the formation of ice. It was suggested that other mechanisms may operate in more mature pastes.

Despite these slightly divergent views, it should be recognized that damage is enhanced by migration of water and that high degrees of saturation and rapid cooling are both detrimental. Air entrainment can be effective in providing reservoirs to prevent the accumulation of ice.

In concrete, the role of aggregates should also be considered. The pores in the aggregates may be such that the pore can be really frozen. Large pores, equivalent to air entrained bubbles (of diameter

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600 Å) may not exist in the aggregates. Thus, the volume increase due to freezing of water will either be taken up by the elastic expansion of aggregate or the water flowing out from the aggregate under pressure. According to Powers a maximum of only 0.3% volume of pores can be tolerated in an average aggregate [36]. For saturated aggregates, there must be a critical size [37, 38, 39] below which no frost action occurs, but there is no assurance that the excess water can be accommodated by the air-entrained bubbles in the surrounding paste.

Durability of air entrained slag-cement concretes, with regard to water freezing and thawing, is essentially equivalent to that of concrete containing solely Portland cement. Air entrained slag-cement concretes are somewhat less resistant to laboratory deicer scaling tests than air entrained concrete containing solely Portland cement, despite the fact that both concretes had adequate air-void systems [40].

In general, the addition of silica fume improves both the spacing factor and the specific surface of concrete, whereas tests with high content of silica fume resulted in less favourable values than those shown for the control concrete [41]. The air entrained concrete incorporating 20 and 30% silica fume showed very poor freezing and thawing resistance [42]. It is difficult to entrain more than 5% of air in such concretes and this amount of air may not provide satisfactory void spacing factor values in hardened concrete [43].

The anti-washout concrete cast under water shows poor resistance to freezing-and-thawing compared with the control concrete. The osmotic pressure may be the main reason why the concrete with anti-washout admixtures shows poor durability [44].

It is not easy to predict the probable behaviour of concrete exposed to freezing and thawing. It is generally suggested that potential frost resistance of concrete can only be judged by tests which take into account the environmental conditions to which concrete may be subjected.

*Attack by aggressive solutions resistance* Air entrainment improves the resistance of concrete to deterioration by sulphate attack [45, 46, 47]. The effect seems to be directly related to the decrease in water/cement ratio for the same workability that is obtained decreasing permeability and to ingress of attacking solutions. Thus, the influence is indirect.

*Efflorescence resistance* Efflorescence is lower for properly air entrained mortar or concrete. This reduction occurs because the changes in the capillary structure decrease the migration of salt solution to the surface.

*Combined attacks* Malhotra and coworkers [48] in a large scale project related to 9 years field performance in a marine environment and freezing and thawing of normal and lightweight concretes incorporating supplementary cementing materials, reported that the amount of deterioration was bigger with increasing replacement of cement with slag and fly ash.

## **2.7 Use**

To achieve the greatest uniformity in a concrete mixture and in successive batches, it is recommended that air entraining admixtures are added to the mixture in the form of solutions dissolved in the mixing water rather than solids. If other admixtures are also used, the air entraining admixtures should be added separately rather than mixed with the other admixtures, because sometimes there are reactions between materials that result in a decrease in effectiveness of the air entraining agent [p. 274 of 7]. Usually, only small quantities of air entraining admixtures are required to entrain the desired amount of air. These are about 0.005% of active ingredient by mass of cement [p. 292 of 1]. If the admixture is in the form of powder flakes of semisolid, a proper solution must be prepared prior to use, following the recommendation of the manufacturer. If the manufacturers recommended amounts of air entraining admixture do not result in the desired air content, it is necessary to adjust the amount of admixture added.

The alternative way of using air-entraining agents in some countries is to intergrind them with the cement when it is manufactured, obtaining a so-called 'air entraining cement'. The advantage in using air entraining cements is that uncertainties and difficulties that sometimes occur when an admixture is used, can be avoided. The disadvantage is that the air content of concrete is influenced by variables other than the amount of admixture; in that case, one may get a concrete with either less or more air than desired, if an air

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entraining cement with a fixed amount of admixture is used. Under such circumstances, additional air entraining admixture may be needed.

Attention should be given to proper storage of air entraining admixtures, most of which have a shelf life of at least a year, and are not usually harmed by freezing. The manufacturer's storage recommendations should be followed. Air entraining admixtures are not dangerous, but manufacturer's caution should be followed.

For determining the air content, see RILEM TC 85-TAC Test for Concrete Admixtures.

The mix proportioning of air entrained concrete is not much different to that of non-air entrained concrete, but it must be considered that the air bubbles increase the consistency and workability of concrete and, at the same time, decrease its strength. Because of the change in consistency and workability, less water and fine aggregate are needed for air entrained mixtures, if the consistency is maintained constant. The increase in air volume in the mixture is offset by the decrease in water volume and by the fine aggregate, as when it is designed by the absolute volume method.

### **2.8 Applications**

Because of its greatly improved resistance to frost action, air entrained concrete should be used wherever concrete is exposed to freezing and thawing. The air entrainment increases generally the resistance of concrete to the destructive action of de-icing agents.

Air entraining improves the workability of concrete. It is effective in lean mixtures, which otherwise may be harsh and difficult to work with. It is beneficial in reducing segregation during handling and transporting, and bleeding.

As a result of its effects in fresh concrete, its use increases the amount of water tightness and, consequently, the durability of concrete.

### **2.9 Substitute for air entraining agents**

Air entraining admixtures are generally used to minimize freezing and thawing attack. Many problems arose trying to adjust the required

amount of air with the right amount of bubble size and spacing factor due to the variability of concrete normal ingredients, mixing, retempering, placing methods, supplementary cementing materials, other admixtures and high strength concretes.

Many of the problems involved with the use of air entraining agents were minimized by adding preformed bubbles reservoirs in the form of porous particles.

A method was developed to produce hollow plastic micro-spheres with diameters between 10 and 60  $\mu\text{m}$ . Adding 1% by weight of cement of these microspheres to concrete corresponds to 0.7% by volume of concrete. The spacing factor using these spheres is 0.07 mm which is below the permissible maximum. Adequate frost resistance was attained using 1.0% of the micro-spheres, and in order to be as effective as 5% entrained air, the 28 day strength was higher than the resistance with 5% entrained air [49, 50].

It was demonstrated that porous particles made with fired clay bricks, diatomaceous earth, vermiculite, pumice and perlite can be added to concrete in order to increase its frost resistance. These results show that concretes containing particles are generally more durable than plain concrete [51].

At lower particle concentration the reduction of compressive strength for vermiculite, pumice and perlite has to be lower if compression is made in relation to the air-entrained concrete [52].

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## 3

# Hardening accelerators

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### 3.1 DEFINITION

Hardening accelerators increase the rate of strength gain of concrete at early ages and generally reduce the setting time.

### 3.2 INTRODUCTION

Hardening accelerators are primarily used in cold weather concreting operations although they may be used in other situations where reduced setting times and early gain of strength are required. Accelerators do not depress the freezing point of water significantly and should not be referred to as 'antifreeze' admixtures.

Hardening accelerators improve early strength, usually because they increase the rate of hydration of  $C_3S$  and  $C_3A$ , but do not improve long-term strength unless they incorporate water reducers. Most accelerating water reducing admixtures are mixtures of accelerating components blended with water reducing admixtures such as salts of lignosulphonic acids, salts of hydroxycarboxylic acids or low molecular weight polysaccharides [1].

### 3.3 COMPOSITION

Substances used as accelerators for concrete include alkali hydroxides, silicates, fluorosilicates, calcium nitrite, calcium nitrate, calcium or

sodium thiosulphate, calcium or sodium thiocyanate, aluminium chloride, potassium, sodium or lithium carbonate, sodium chloride, calcium chloride and organic compounds such as triethanolamine, formaldehyde and calcium formate [2].

Until recently calcium chloride or admixtures in which calcium chloride is the main active component, have been almost the only accelerators used [3, 18, 20, 21]. Calcium chloride offers many advantages that make it popular as a concrete hardening accelerator. It is very effective in providing a substantial increase in early strength gain and reduces setting time.

In recent years problems have occurred as a result of the corrosion of steel reinforcement promoted by the presence of chloride ions in the concrete. For this reason, several non-chloride accelerators [7] based on calcium formate, calcium nitrite, calcium nitrate, sodium or calcium thiocyanate [3], or triethanolamine have been developed but some of them do promote corrosion. On the other hand, there is one which is a water soluble organic material belonging to the carboxylic acid group [4].

The accelerators are divided into two groups:

- chloride-based accelerators,
- non-chloride accelerators.

### 3.4 MECHANISM OF ACTION

#### 3.4.1 Chloride-based accelerators

The most common accelerator is calcium chloride. The earliest reference to the use of calcium chloride in concrete is 1885 [6]. Since then it has been extensively used either by itself, or as the main ingredient in many accelerating admixtures.

The accelerating effect of calcium chloride on cement is related mainly to its action on the  $C_3S$  phase. Calcium chloride not only alters the rate of hydration of cement minerals but may also combine with them. It also influences such properties as strength, chemical composition, surface area, morphology and pore characteristics of hydration products. Calcium chloride decreases the dormant period in the hydration of  $C_3S$ . The increase in strengths at earlier periods with

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calcium chloride addition may be explained by the increased amount of hydration products formed.

Calcium chloride accelerates the hydration of  $C_2S$ . At early periods the accelerating action in  $C_2S$  is only marginal compared to that observed in the hydration of  $C_3S$ .

Calcium chloride accelerates the reaction between  $C_3A$  and gypsum. Calcium chloride reacts with  $C_3A$  to form chloroaluminate after gypsum is consumed in the reaction with  $C_3A$ .

The effect of calcium chloride on the hydration of  $C_4AF$  does not seem to be different from that on  $C_3A$ .

A number of investigators [13, 22, 23, 24, 32] have examined its effects on the hydration and hardening behaviour of  $C_3S$ . The effects of calcium chloride on the kinetics of the hydration of  $C_3S$ , on the morphological features, pore volume and surface area changes, as well as on strength development in the  $C_3S$  phase, were studied separately, but no consensus was achieved which would provide a satisfactory explanation for the overall effects of calcium chloride in concrete.

#### 3.4.2 Non-chloride accelerators

The most common accelerators in this class are calcium formate and triethanolamine which are often used to offset the retarding effects of water-reducing admixtures, or to provide non-corrosive accelerators.

Calcium formate accelerates hydration of the  $C_3S$  phase of cement. It is, however, not as effective as calcium chloride.

Triethanolamine is known to accelerate the hydration of the  $C_3A$  phase of cement and retard the hydration of the  $C_3S$  and  $C_2S$  phases. It is used as a constituent in admixtures where precise control of the set extension is required. It is also used to offset the retardation effects of other admixtures.

One belonging to the carboxylic acid group is considered to be a catalyst on hydration of the silicates in the cement [4].

### 3.5 MAIN FACTORS THAT INFLUENCE THE MECHANISM OF ACTION

#### 3.5.1 Type, composition and dosage of admixture

The effect of hardening accelerators depends on the chemical composition and its dosage.

(a) Calcium chloride

Calcium chloride is very effective in providing a substantial increase in early strength and in the rate of setting and reduces both the initial and final setting times of concrete. The optimum dosage of calcium chloride in unreinforced concrete is between 1 and 4%. However, it is generally recommended that the dosage should not exceed 2% by weight of cement, if flaky commercial calcium chloride is used, and 1.5% by weight of cement, if anhydrous calcium chloride is used.

(b) Calcium formate

Calcium formate accelerates setting time and increases the early strength. However, it is not as effective as calcium chloride and a higher dosage is required to impart the same level of acceleration. Calcium formate is sometimes blended with other compounds, for instance sodium nitrite, to obtain enhanced early strength development.

(c) Triethanolamine

Triethanolamine is more effective than calcium chloride in accelerating setting times, consequently only one tenth is required to achieve the same rate of set acceleration as calcium chloride [12]. With up to 0.05%, the initial setting time is retarded slightly but at 0.1% and 0.5%, rapid setting occurs (2, 5, 15).

Triethanolamine reduces strength as the amount is increased [14].

(d) Calcium nitrate

Calcium nitrate accelerates setting times but moderately accelerates hardening.

(e) Calcium nitrite

Calcium nitrite is an effective accelerator for set and hardening.

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(f) Sodium thiocyanate

Sodium thiocyanate is a strength accelerator but is not very effective in setting acceleration.

(g) Calcium thiosulphate

Calcium thiosulphate was found to be a better accelerator than the corresponding sodium salt in terms of strength development.

(h) Sodium and potassium carbonate

Sodium and potassium carbonate at dosages greater than 0.1% accelerates setting time [19].

(i) Lithium carbonate

Lithium carbonate accelerates setting time at all concentration.

(j) Carboxylic acid

The carboxylic acid group accelerates setting time and increases the strength.

#### 3.5.2 Type of cement

The accelerating effect depends on the chemical composition of the cement as well as the gypsum content [17]. Calcium chloride accelerates slow setting Portland cements more efficiently than faster setting cement. Calcium chloride has an accelerating effect on the hydration of pozzolanic cements. In blast furnace cements, calcium chloride can act as an accelerator at higher temperatures. Under steam curing conditions, it is possible to increase early strength by 15–20% [2].

Concretes containing calcium formate showed accelerated compressive strength when Portland cement containing a low gypsum content was used. Calcium formate is an effective accelerating admixture when the ratio of  $C_3A$  to  $SO_3$  is greater than 4 [17].

#### 3.5.3 Temperature

The accelerating effect of calcium chloride is reported to be higher at

0°C and 5°C than at 20°C, and is more pronounced with rich mixtures than with lean ones [9].

### 3.6 EFFECTS

#### 3.6.1 Fresh stage

(a) Workability

Accelerators have no significant effect on workability. It is however observed that addition of calcium chloride increases slightly the workability and reduces the water required to produce a given slump of concrete (2, 6, 8, 10, 21].

(b) Stiffening

Accelerators shorten the setting times of concrete. Consequently, the consistency loss becomes slightly greater than the reference concrete.

#### 3.6.2 Setting stage

(a) Setting

Accelerators shorten the setting times of concrete. Calcium chloride significantly reduces both the initial and final setting times of concrete.

(b) Heat of hydration

Accelerators increase the rate of hydration of cement and the rate of heat liberated.

(c) Bleeding

Accelerators reduce the rate and amount of the bleeding of the concrete because the hydration reactions during the setting stage are speeded up.

#### 3.6.3 Hardening stage

(a) Heat of hydration

Some reported effects [29] are an increase in the rate of heat evolution



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at early stages, but on the calcium chloride total heat of hydration is almost the same in comparison to control concrete [25].

##### (b) Strength development

The major beneficial effect of the use of accelerator is in the development of high early strength. The maximum rate of increase in strength is reported to be within the first three days of curing [8]. The effect depends on many factors including amount of accelerator added, mixing sequence, temperature, curing conditions, water/cement ratio and cement type.

#### 3.6.4 Hardened stage

##### (a) Strength

Calcium chloride increases early strength of concrete, but lowers the long term strength. Calcium formate, unlike calcium chloride, increases 28 day compressive strength of concrete [5].

Calcium nitrite increases 1, 3 and 28 day compressive strength.

Sodium thiosulphate accelerates the setting time, but the compressive strengths are slightly reduced with respect to the reference concrete at dosages of 0.5 and 1.0% [5].

Formaldehyde at a rate of 0.07% causes a significant setting time reduction but decreases 28 day compressive strength [5].

##### (b) Modulus of elasticity

Modulus of elasticity is related to the compressive strength of concrete. Therefore modulus of elasticity is increased at early ages with calcium chloride but at 90 days the values are almost the same for concrete containing 0% or 1–4% calcium chloride of cement.

It has been reported that the modulus of elasticity has not changed after 10 years [26].

##### (c) Durability

*Freeze-thaw resistance* Resistance to freezing and thawing at early ages is increased [25], but at later ages is decreased [2, 8]. To overcome it use of air entraining admixture is recommended.

*Attack by aggressive solutions* If more than 2% calcium chloride is added, sulphate attack resistance can be lowered [27].

*Alkali-aggregate reaction* Alkali-aggregate reactivity can be increased by some accelerators [28]. Accelerators containing relatively large amounts of alkali may promote alkali-silica reaction.

*Efflorescence* Sodium chloride causes efflorescence [28].

*Corrosion of reinforcement* There has been a great deal of controversy with regard to the use of calcium chloride in reinforced concrete. The presence of chlorides in concrete can promote corrosion activity in the reinforcement. Chloride ions can cause a breakdown in the passive layer that protects the reinforcement against corrosion. In an alkaline medium such as that existing in concrete, corrosion does not occur because the pH value is higher than 10 [2, 7]. But if there are significant amounts of chlorides present, corrosion can occur even when the Ph is in excess of 12.5. The greater the concentration of chloride, the higher the pH value required to protect the reinforcement against corrosion. The actual amount of chloride required to cause depassivation of the reinforcement is not known with certainty.

It is reported that of the other chloride additives stannous chloride is the best. This compound produces the same accelerating effect as calcium chloride and causes less corrosion of reinforcement. It has not been adopted in field practice because of its higher cost [14].

Triethanolamine and calcium formate as non-chloride accelerators are used to provide non-corrosive accelerators.

Calcium nitrite and amino alcohol type accelerators have been shown to improve the corrosion resistance of reinforced concrete [30].

#### **(d) Volume change and creep**

*Creep* The addition of calcium chloride to concrete causes an increase in creep under all conditions [2, 7, 10].

Creep was increased by addition of triethanolamine in concrete specimens loaded after 7 days of curing whereas on difference occurred for specimens loaded at 28 days [16].

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**Shrinkage** There is some disagreement on the effect of calcium chloride on drying shrinkage. It was found that large amounts of chloride increased the drying shrinkage of concrete. The value decreased as the degree of curing was increased [11].

### 3.7 USE

#### 3.7.1 Chloride limit

The accelerators containing relatively large amounts of total chloride may accelerate corrosion of steel bar. An addition rate of 2% by weight (77% flake form calcium chloride, by weight of cement) is the most widely used limitation level. But it is not allowed where sulphate resisting cement is used nor in prestressed concrete (CSA, BS, AS).

In West Germany, the content of chloride ion (including other halogen) ions) of admixtures for ordinary concrete and prestressed concrete is limited to be less than 0.2 and 0.1% respectively [31].

Tables 1 and 2 show chloride limits in concrete.

Table 1. Limits for chloride; ACI Committee 212 IR-81, Chemical Admixtures

Category of concrete	Max. Cl <sup>-</sup> ion content by % of cement
Prestressed concrete	0.06
Conventionally reinforced concrete in a moist environment and exposed to chloride.	0.10
Conventionally reinforced concrete in a moist environment but not exposed to chloride.	0.15
Above ground building construction where the concrete will stay dry (does not include locations such as kitchens, parking garages, and waterfront structures, where the concrete will be occasionally wetted).	No limit for construction

Table 2. Limits for chloride; JIS A 5308 Ready Mixed Concrete

	Max. $\text{Cl}^-$ ion content by kg of 1 m <sup>3</sup> concrete
Normal concrete	0.30
When permitted by purchaser	0.60

One of the alternative methods of acceleration when chloride limits must be kept low is the use of chloride-free accelerators.

### 3.7.2 Proportioning of concrete

Accelerators have no significant effect on the workability or air content, therefore the proportioning of concrete with accelerators is similar to that of the reference concrete.

### 3.7.3 Dosage

The abnormal setting behaviour by an overdose should be avoided.

The optimum dosage of calcium chloride suggested by various investigators [2, 5, 6, 8] at which the strength is a maximum varies between 1 and 4%. However, it is generally recommended that the dosage should not exceed 2% by weight of cement, if anhydrous calcium chloride is used.

The optimum amount of calcium formate to accelerate the compressive strength appears to be 2 to 3% by weight of cement.

### 3.7.4 Addition

Accelerators are supplied in solid or liquid form. Calcium chloride is preferred for use in solution form. Calcium chloride should not come directly into contact with cement as it may cause flash set. It is usually added to the mixing water and introduced into the mixer at the same

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time as other materials.

Where different types of admixture are used, they should be added to the batch separately unless it is known that they can be mixed together satisfactorily. The supplier of the admixtures should recommend proper procedures.

##### **3.7.5 Storage**

Different accelerators should be stored in different containers individually. They should be protected against dust or other impurities.

Accelerators in liquid form should be protected against exposure to heat during storage to prevent decomposition and also be protected against freezing. There are admixtures which contain a suspension of solids and the solids may settle with time. These admixtures should be agitated before use.

Accelerators in solid form absorb moisture readily. They should be protected against exposure to moisture to prevent caking or deliquescence.

Accelerators which are stored for a long term and have unusual viscosities, colours or smells, should be retested before use.

##### **3.7.6 Others**

In hot weather, some accelerators can produce detrimental effects such as more rapid heat evolution due to hydration, rapid setting and shrinkage cracks. This should be used with care.

The use of calcium chloride for reinforced concrete subjected to steam curing should be avoided because of the corrosion.

#### **3.8 APPLICATION**

The benefits of hardening accelerators may include:

- earlier form removal,
- shorter period of protection necessary to avoid damage to concrete by freezing or other factors,

- earlier completion of a structure or repair,
- partial or complete compensation for the effects of low temperatures on rate of strength development.

The benefits of a reduced time of setting may include:

- earlier initiation of surface finishing,
- reduction in pressure on forms or reduction of length of time during which forms are subjected to hydraulic pressures,
- more effective plugging of leaks against hydraulic pressure.

### 3.9 SPECIFICATIONS

Accelerators are recognized by American, European, Australian and other countries. The following are some standards.

<i>Standards</i>	<i>Type of admixture</i>
ASTM C-494 (USA)	Type C; accelerating
BS 5075 (UK)	accelerating
AS 1478 (Australia)	Type AC; set-accelerating
AFNOR P18-103 (France)	accelerating
JIS A 6204 (Japan)	

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## 4

### **High-range water reducers (superplasticizers)**

*S. Biagini*

#### 4.1 DEFINITION

High-range water reducing agents (superplasticizers) are admixtures which procure a considerable increase in the workability of mortars and concretes at constant water/cement ratio. The duration of the effect is generally temporary and variable. Mortars and concretes of constant workability can be made with smaller amounts of water, saving more than 12% without undue retardation, excessive entrainment of air or detrimental bleeding.

#### 4.2 INTRODUCTION

‘High-range water reducers (superplasticizers)’ are subjected in different countries to a control of their ability to reduce mixing water or increase the workability of cement mixes. The limit of the improvement has been quantified in order to distinguish these admixtures from those defined as ‘water reducers’.

#### 4.3 COMPOSITION

The high-range water reducers presently used in the market can be classified [1] according to their chemical nature in the following main groups:

- beta-naphthalene sulphonate formaldehyde condensates;
- melamine sulphonate formaldehyde condensates;
- modified lignosulphonates;
- esters of sulphonic acids;
- salts of carboxylic/hydroxycarboxylic acids.

There is also a large number of patents [2, 3] claiming the fluidity ability of a series of different chemical compounds, but the commercial importance of these admixtures is today negligible.

#### 4.4 MECHANISM OF ACTION

The mechanism of action of high-range water reducers is mainly based on their ability to be adsorbed on the surface of cement particles and modify the rheological behaviour of the cement matrix [4, 5]. The rate of adsorption of high-range water reducers depends on the chemical and mineralogical composition of the cement, its fineness and in particular on the  $C_3A$  ( $C_3A = 3CaO \cdot Al_2O_3$ ) content. It has been found that calcium aluminate [6–9] adsorbs very rapidly the high-range water reducer molecules, while calcium silicate in the first hours of hydration adsorbs only a lower amount of the high-range water reducers.

The increase of workability that can be obtained in a concrete by the use of superplasticizers can be correlated with the following properties.

1. The value of zeta potential of the electric double layer that is formed on the surface of the cement particles by the polar groups of adsorbed superplasticizer chains [10–14].
2. The molecular weight of the superplasticizer [15, 16].

The rate of workability loss is correlated to the retardation produced on the hydration of cement.

#### 4.5 EFFECTS

The different properties of concrete are examined and the alternative names high-range water reducers or superplasticizer will indicate the

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specific way of using the admixture, that produces the modification described. It is intended that if one of the two names of the admixture is not indicated, the corresponding way of using the admixture does not exert a particular action on the specific property cited.

### 4.5.1 **Fresh state**

#### (a) Unit mass

Unit mass of concrete is usually increased when high-range water reducers are used.

#### (b) Workability

*Consistency* Superplasticizers dramatically increase the ability of concrete to flow.

*Cohesion* Cohesion is largely improved by the use of high-range water reducers as a consequence of the reduction of water in concretes.

*Air content* Air content may be slightly increased, especially in the case of use of high dosages of the admixtures as superplasticizer.

*Slump loss* At the same initial workability, slump loss may be higher in concretes with high-range water reducers than in concrete without admixture. At the same water/cement ratio, slump loss of concrete with superplasticizer may be higher or lower than the control concrete without admixture as a function of the type of superplasticizer used.

*Pumpability* Pumpability of concrete is improved by the use of superplasticizer, as a consequence of the increase in workability, and due to cohesion in case of use as high-range water reducers.

#### (c) Segregation

Segregation decreases when the admixture is either used as a high-range water reducer or as a superplasticizer, provided that an adequate mix design of the concrete is done.

#### 4.5.2 Setting state

(a) Setting

Generally the admixture used as a superplasticizer mildly retards the setting of concrete [23], while use as a high-range water reducer at normal dosage does not give significant retardation.

(b) Plastic shrinkage

Plastic shrinkage cracking can be increased by the use of high-range water reducers if the ambient conditions are such that evaporative demands are greater than the reduced bleeding capacity of the high-range water reduced concrete.

(c) Bleeding

Bleeding is reduced by the use of high-range water reducers. If the aggregate size distribution is not properly designed, bleeding can be increased when superplasticizer is used [1].

#### 4.5.3 Hardened state

(a) Strength

The strength of concretes is considerably increased by the use of high-range water reducers as a consequence of the reduction of the water/cement ratio [24], while strength is not substantially modified in case of use as a superplasticizer.

(b) Porosity

*Capillary absorption* Capillary absorption of concrete is strongly reduced when the admixture is used as a high-range water reducer.

*Permeability* The permeability of concrete is directly linked to its capillary porosity which is influenced by the water/cement ratio, that can be largely reduced by the use of the admixture as a high-range water reducer.

*Freeze-thaw attack* High-range water reducers-superplasticizers normally induce some air entrainment in the concrete mixes, but some

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of the air bubbles introduced are larger than those of air entraining agents, and therefore are not useful to increase the freeze-thaw durability of concretes [26].

*Attack by aggressive solutions* The resistance of concretes to attack by aggressive solutions is increased by high-range water reducers because of the reduction of concrete capillarity porosity. The use of the admixture as superplasticizer does not change the resistance of the concrete [26, 27, 28].

### (c) Volume change

*Creep* The use of high-range water reducers reduces creep due to the reduction of the water/cement ratio of the concrete.

*Drying shrinkage* The shrinkage of concrete is reduced by high-range water reducers mainly because of the reduction of the water content of the concrete. When a concrete is manufactured with the admixture used as a superplasticizer, its shrinkage, for the same percentage of moisture loss, has been found [27] to be higher than in a concrete produced with the same quantity of water but without the use of the superplasticizer. On the other hand it has been also shown [19] that with the same curing conditions, the shrinkage of a superplasticized concrete is similar to that of a corresponding plain concrete.

The conclusion can be drawn that the better dispersion of cement particles in a superplasticized concrete produces a finer capillary structure, which reduces the rate of moisture loss of the concrete under normal ambient conditions, so that the shrinkage of superplasticized concrete is practically similar to that of a normal concrete manufactured with the same amount of water.

## 4.6 USE

The admixtures classified 'high-range water reducers/superplasticizers' are normally aqueous solutions, with a dry active material content between 30 and 40% by weight. They are commonly added to the cement mix together with the mixing water. However, addition after the mixing water has been found to be beneficial for obtaining better

performance.

There are some examples of superplasticizer used in powder form, and in this case they are added to the aggregates and the cement before the mixing water is added.

The optimum dosage of high-range water reducers can vary from one product to other, and must be used according to the producer recommendation.

#### 4.7 APPLICATIONS

The success of high-range water reducers in the market is due to a series of advantages that can be summarized as follows:

(a) Use as high-range water reducers

Reduction of the water/cement ratio with a consequent improvement of all characteristics of the concrete (increase of compressive and flexural strength, decrease of permeability, creep, shrinkage).

(b) Use as superplasticizer

Production of high quality concretes with high workability [17–20]. Easy placing of concretes also in case of presence of high density of steel reinforcement.

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# 5

## Water reducing/retarding admixtures

*M. Ben-Bassat*

### 5.1 DEFINITION

#### (a) Water reducer

A water reducing admixture can be defined as an admixture that reduces the amount of the mixing water of mortar and concrete for a given workability. They can sometimes have a secondary effect of retardation or acceleration on the setting time of the concrete.

#### (b) Retarder

A retarding admixture can be defined as an admixture which retards the set and the initial hardening of the concrete.

### 5.2 INTRODUCTION

This chapter summarizes present knowledge of the use of the water reducing/retarding chemical admixtures in concrete.

In general, water reducers/retarders reduce the water requirement of the mix and, at the same time, can modify the properties of the fresh and hardened concrete. The admixtures are classified according to type of constituting materials, or the characteristic effect of their use. Commercial admixtures may contain materials that separately would belong in two or more groups.

Water reducing/retarding admixtures may be used to modify the properties of the fresh and hardened concrete in such a way as to

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make it more suitable for work in modern concrete technology, and gain desired concrete properties.

The successful use of admixtures depends upon proper selection and dosage.

### 5.3 WATER REDUCERS

#### 5.3.1 Composition

The main materials used in water reducers are:

1. lignosulphonic acids and their salts;
2. modifications and derivatives of lignosulphonic acids and their salts;
3. hydroxylated carboxylic acids and their salts;
4. modifications and derivatives of hydroxylated carboxylic acid and their salts;
5. other materials which include: zinc salts, phosphates, chlorides, carbohydrates, polysaccharides, and sugar acids. Certain polymeric compounds, melamine derivatives, naphthalene derivatives, and others.

#### 5.3.2 Mechanism of action

Water reducing admixtures can be divided into three groups:

- normal water reducers
- retarding water reducers
- accelerating water reducers.

Water–cement systems usually exhibit flocculations of solid particles which tend to agglomerate into clusters. In the presence of a water reducing admixture a reduction of the attraction forces between particles occurs and, as a result, the clusters break down and the particles become more mobile. Some mechanisms explain the reduction of these attraction forces when water reducers are added to a given concrete mix by:

- reduction of interfacial tension [1]
- multilayer absorption of organic molecules [2, 32]
- increase in electrokinetic potential [16, 23]
- protective adherent sheet of water molecules [1]
- release of water trapped in cement clumps [4]
- change in the morphology of the hydrated cement compounds [15, 18].

### **5.3.3 Factors influencing mechanisms of action**

#### **(a) Composition, brand and dosage of admixture**

The effect of different brands or types of commercial water reducers on water reduction depends on the chemical composition and its concentration [23, 30]. The higher the dosage of the admixture the higher the water reduction. Generally increasing content, for example more than 0.1% (solid content of admixture by weight of cement), does not yield much additional effect in reducing the water content.

#### **(b) Type, brand and content of cement**

Cement composition, especially  $C_3A/C_3S$  ratio and  $C_3A$  content, as well as a sulphate form, may affect the efficiency of the admixture [11, 23, 24].

#### **(c) Type of aggregate**

In some cases aggregates from a general source may have a different effect on water reduction compared to those from another source which differ in grading, shape, physical properties, mineralogical composition, etc [30].

#### **(d) Types and amount of additive such as slags and fly ash**

A higher dosage of admixture is usually required in concretes containing slag or fly ash in order to obtain the same water reduction as that of mixes without slags or fly ash. This could be due to higher absorption of water reducers by the additive. In the case of silica fume, high-range water reducers are required.

#### **(e) Temperature**

Except for setting time temperature does not affect dosage.

#### **5.3.4 Effects on fresh concrete**

(a) Unit mass

For a given workability the concrete unit mass can be increased by adding water reducing admixtures [30].

(b) Workability

Workability of concrete is improved when water reducers are incorporated into the mix at a given water content. For a given consistency, the admixture-treated concrete with reduced water generally is more workable [7, 10]. Improving concrete workability by admixture treatment means better appearance [6, 10], uniformity [10, 29], pumpability [31] and finishing characteristics [6, 31].

It has been found [6, 23] that the admixture efficiency and capability to reduce water content is higher for high slump concrete.

Concretes containing admixtures are more sensitive to retempering. The additional amount of water needed to reach a required variation in slump would be smaller for concrete with admixture than the amount of water needed for concrete without admixture [7, 10].

(c) Bleeding

For a given slump water reducers can modify the rate or capacity for bleeding or both.

(d) Heat of hydration and temperature rise

When water reducers are used, then heat of hydration and temperature rise of concretes may be higher at early ages. When the water reducer is used to reduce the mixing water of concrete for a given workability, without modifying the mix proportions.

(e) Plastic shrinkage

Generally, plastic shrinkage occurs by loss of moisture during the first 2 to 5 h from placing and compacting of the concrete. If plastic shrinkage causes cracking, water reducing admixtures can aggravate the cracking problem.

### **5.3.5 Effects on hardened concrete**

The effect of water reducing admixtures on the properties of hardened concrete depends mainly on the mode of use of these admixtures.

(a) When the admixture is used to improve workability without modifying the mix proportions, there is an insignificant influence on the properties of the hardened concrete.

(b) Reduction of both cement and water by incorporating admixtures to maintain workability level and the designed strength also have an insignificant influence on the properties of the hardened concrete.

(c) Reducing the mixing water of the concrete mix by water reducer, in order to maintain the workability level without modifying the cement content, will have a substantial influence on the properties of the hardened concrete. The physical properties (specific gravity, porosity, surface properties, permeability, drying shrinkage, creep, etc), mechanical properties (compressive strength, flexural strength, etc) and chemical properties (durability, sulphate resistance, etc) are affected by the water reducers, particularly when the admixtures are used to reduce water, to reduce the water/cement ratio and to perform a better concrete class. There will be no further discussion on this issue in this chapter.

### **5.3.6 Use**

Water reducers/retarders should be used according to the dosage recommended by the supplier. Typical recommended dosages of the admixture are in the range of 0.2–0.4% of the cement content, by mass.

Admixtures of all classes are available in either powder or liquid form. Since relatively small quantities are used, it is important that suitable and accurate dispensing equipment should be used. For water reducers/retarders it is preferable to use the admixture in liquid batching system.

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### (a) Admixture addition procedure [23]

Admixtures should be incorporated in the concrete mix in such a way that the most rapid and uniform dispersion of the admixture is obtained. Maximum benefit is obtained by adding the admixture just at the end of the mixing period of the aggregates, cement and water. However, with this procedure there are some practical difficulties in obtaining the desired workability and the uniform dispersion of the admixture, particularly when large concrete mix batches have to be prepared, like in a ready-mixed concrete operation.

A reasonable compromise between good technical performance and practical use of water reducers can be achieved by the following procedure. After an initial mixing period of 15–30 seconds of aggregates, cement, and approximately 50% of the mixing water, the admixture dissolved in part (up to 30%) of the gauging water is introduced into the mix, and finally the remainder of the water is added, until the required workability is obtained. The addition sequence can also affect the setting time and the compressive strength. Influence of the addition procedure of the admixture can also be assessed in terms of different dosage used to achieve approximately the same concrete performance.

### (b) Testing

A test should be made to evaluate the effect of the admixture on the properties of concrete made with job materials under the anticipated ambient conditions and construction procedures to be used. Tests of water reducing admixtures and set controlling admixtures should indicate their effect on the following properties of the concretes:

- water requirement
- air content
- consistency
- bleeding of water and possible loss of air from the fresh concrete
- time of setting
- compressive (flexural) strength
- resistance to freezing and thawing
- drying shrinkage.

All the properties should be tested according to the test procedures as specified in the relevant standards or codes of practice.

Accidental overdosage of 2–3 times the supplier's recommended dosage, can cause a significant retardation in setting time and a decrease in early compressive strength (24–48 hours), increase of air entrained and changes of other properties. It has been found [31] that in these cases, extended curing does not damage compressive strength at later ages.

Before use, admixtures should be tested for one or more of the following reasons:

1. to determine the compliance with a purchase specification;
2. to evaluate the effect of the admixtures on the properties of the concrete;
3. to determine within batch uniformity of the product.

During the use of the admixture, tests should be done periodically to provide data showing that any batch is the same as that previously supplied.

### **5.3.7 Application**

There are three major modes of use of these admixtures:

1. to reduce the content of mixing water of concrete for a given workability;
2. to reduce both water and cement content so that workability and strength water/cement ratio of the concrete are similar to those of the control concrete mix;
3. to improve workability without modifying the mix proportions.

The decision to use the admixture in one of the modes described above depends on the comparative gain in cement saving, strength increase, or improved workability, to attain the designed performance properties of the concrete mix.

Some of the more important engineering purposes for which admixtures are used are listed here:

- to increase workability without increasing water content or to decrease the water content at the same workability;



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- to reduce or prevent settlement;
- to modify the rate or capacity for bleeding, or both;
- to reduce segregation;
- to improve pumpability;
- to accelerate the rate of strength development;
- to increase durability;
- to decrease permeability;
- to increase bond of concrete to steel reinforcement.

#### **5.3.8 Standards and codes of practice**

Different types of water reducers, water reducers/retarders and retarders are recognized by the Standards in Europe, Japan, Canada, America and other countries. In Tables 1–3 [23] a comparison is given of standard requirements in different countries.

ACI committee report 212 [1] gives a wide review and a guide for use of admixtures in concrete.

### **5.4 RETARDERS**

#### **5.4.1 Composition**

The ingredients used as retarders are very much the same as the ingredients used for water reducers (see Section 5.3.1). The degree of effect depends upon the relative amounts of each ingredient used in the formulation, type, brand and content of cement [4, 5, 15, 19].

#### **5.4.2 Mechanism of action**

Retarding admixtures can be divided into two groups:

- normal retarder,
- retarder/water reducer.

When a retarder is added to the cement–water system, physical adsorption and chemical reactions occur generally with the cement

Table 1: Comparison of Standard Requirements for Water-Reducing Admixtures (23)

Standard	Type of admixture	Initial setting time (with respect to control mix)	Water reduction, min. (with respect to control mix)	Compressive strength, min. (% of control mix)	Shrinkage max. (% of the control mix)
ASTM C – 494 – 81	Type A: water reducing	Min: 1 h earlier Max: 1 1/2 h later	5%	110 (3, 7, 28 days)	135 *
BS 5075: 1982 <sup>x</sup>	Normal water reducing	Min: 1 h earlier ** Max: 1 h later **	8%	110 (7, 28 days)	–
CAN 3 – A266 2 – M78	Type WN: normal setting	Min: 1h 20 min earlier Max: 1h 20 min later	5%	115 (3, 7, 28 days )	135 *
AFNOR NF P 18 – 103	Water reducing *	Min: 1 1/2 h earlier Max: 3 h later	6.5 ***	110 (3, 7, 28, 90 days )	105
JIS A 6204	Type A: water reducing	Min: 1 h earlier Max: 1 1/2 h later	4%	115 (3 days) 110 (7 and 28 days)	120
UNI 7102 – 72	Water reducer (plasticizer)	After 1 h on cement paste	5%	105 (1, 3 days) 110 (7 days) 115 (28, 90 days)	0.01 <sup>+</sup>

\* % of control limit applies when shrinkage of control is not less than 0.030%; when shrinkage of control is less than 0.030%, the increase over control limit should be less than 0.010%.

\*\* Penetration resistance 0.5 N/mm<sup>2</sup>.

\*\*\* A minimum value of 8.6% is required for low – C<sub>s</sub>A cements ( $\leq 4\%$ ).

<sup>+</sup> Maximum increase over control (mortar).

<sup>x</sup> Compacting factor relative to control mix: not more than 0.02 below.

• At the same workability of the control mix.

Table 2: Comparison of Standard Requirements for Water-Reducing and Retarding Admixtures (23)

Standard	Type of admixture	Initial setting time (with respect to control mix)	Water reduction, min. (with respect to control mix)	Compressive strength, min. (% of control mix)	Shrinkage max. (% of the control mix)
ASTM C – 494 – 77	Type D: water reducing and retarding	Min: 1 h later Max: 1 1/2 h later	5%	110 (3, 7, 28 days)	135*
CAN 3 A266.2 – M78	Type WR: water reducer – set retarder	Min: 1 h later Max: 3 h later **	5%	115 (3, 7, 28 days)	135*
BS 5075 – 82 <sup>x</sup> 2 – M78	Retarding – water reducing	Min: 1 h later **	8%	110 (7, 28 days)	135*
JIS A 6204	Type D: water reducing and retarding	Min: 1 h later Max: 3 h later	5%	105 (3 days) 110 (7, 28 days)	120
UNI 7107 – 72	Retarding water reducer	Min: 3/4 h later	5%	110 (3 days) 110 (7 days) 115 (28 days)	0.01 <sup>+</sup>

\* % of control limit applies when shrinkage of control is not less than 0.030%; when shrinkage of control is less than 0.030%, the increase over control limit should be less than 0.010%.

\*\* Penetration resistance of 0.5 N/mm<sup>2</sup>.

<sup>+</sup> Maximum increase over control (mortar).

<sup>x</sup> Compacting factor relative to control mix: not more than 0.02 below.

Table 3: Comparison of Standard Requirements for Retarding Admixtures (23)

Standard	Type of admixture	Initial setting time (with respect to control mix)	Water reduction, min. (with respect to control mix)	Compressive strength, min. (% of control mix)	Shrinkage max. (% of the control mix)
ASTM C – 494 – 81	Type B: regarding admixture	Min: 1 h earlier Max: 3 1/2 h later	5%	90 (3, 7, 28 days)	135*
BS 5075 – 82 <sup>+</sup>	Retarding	Min: 1 h later **	5%	90 (7 days) 95 (28 days)	135*
CAN 3 – A266.2 – M78	Type R: moderate set retarder	Min: 1 h later Max: 3 h later	3%	110 (3, 7, 28 days )	135*
CAN 3 – A266.2 – 78	Type R <sub>x</sub> : extended set regarder	Min: 5 h later	3%	100 (3 days) 110 (7, 28 days)	135*
AFNOR NF P 18 – 103	Retarding * admixture	Min: 3/4 h later to 24 h Range initial and final setting time ≤ 8 h		80 (7 days) 90 (28 days) 100 (90 days)	125 (7 days) 110 (28, 90 days)
UNI 7104 – 72	Retarding admixture	Min: 3/4 h later		100 (28 days)	0.01 <sup>+</sup>

\* % of control limit applies when shrinkage of control is not less than 0.030%; when shrinkage of control is less than 0.030%, the increase over control limit should be less than 0.010%.

\*\* Penetration resistance 0.5 N/mm<sup>2</sup>.

<sup>+</sup> Maximum increase over control (mortar).

<sup>x</sup> Compacting factor relative to control mix: not more than 0.02 below that of the control mix.

\* At the same workability of the control mix.

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components, and especially with the  $C_3A$  and the  $C_3S$ . The retardation of the setting times of the concrete is very sensitive to the generic group of the retarder and the cement composition.

### **5.4.3 Factors influencing mechanisms of action**

See Section 5.3.3.

### **5.4.4 Effects on fresh concrete**

(a) Unit mass

No effect.

(b) Workability

The retarder admixture keeps workability for a longer period.

(c) Slump loss

Most retarders are also water reducers. They increase initial and final setting times of the cement paste, and they increase the time required to reach the vibration limit. Therefore, it has been assumed that they also reduce slump loss. Laboratory and field experience demonstrate that water reducers/retarders do not substantially affect the absolute slump loss [26, 27, 31]. Distinction must be made between admixture addition at given water/cement ratio and at a given slump. Ramachandran [25] examined the effect of some water reducers/retarders on the slump loss of concrete at a given water/cement ratio. The initial slump of the concrete increased with the addition of the admixture. The rate of slump loss of the admixture-treated concrete was higher than that of the reference mix. Perenchio [17] found that, at a given initial slump, water reducers increased the rate of slump loss. The slump of the admixture-treated concrete was lower than that of the reference mix.

All these phenomena are affected by the cement composition and content, type, brand and dosage of admixture, ambient temperature, adding procedure of the admixture into the concrete, etc. It is possible to overcome the problem on the job site by planning ahead and design of the concrete mix based on all the data available concerning the

specific job [3, 8, 9, 17, 20, 21].

(d) Bleeding

Retarders affect the rate and capacity of fresh concrete to bleed and settle under the influence of gravity. Different admixtures influence bleeding and settlement of concrete differently. For a given water/cement ratio [24] gluconate increases bleeding, glucose decreases it, and lignosulphonate has no effect on it. A higher reduction of bleeding is observed in the presence of air entraining agent [30]. The increase of partial mobility in presence of admixtures caused channelled bleeding and hence a great rate of settlement.

(e) Setting

Use of a retarding admixture in concrete generally causes a delay in initial and final setting times [23]. The specific retardation with a particular cement and different admixtures should be determined only by trial mixes [23]. All the commercial retarding admixtures should comply with the standards. A practical and simple test to determine the initial and final setting time of concrete is the Proctor penetration test, which is shown to be more efficient than the Pin-pull test [23].

By changing the dosage of the admixture, the vibration limit can be delayed for the desired length of time for an easy pouring of each layer of concrete to avoid cold joints. For any initial ambient temperature and concrete temperature, the dosage can be adjusted to maintain the desired time for the vibration of the concrete.

The retardation in initial and final setting times caused by a given amount of admixture, will probably be different at different temperatures. If the retarding effect is expressed in time, there will be a very small difference in the rate of setting between admixture-treated concrete and the reference mix.

(f) Heat of hydration and temperature

Heat of hydration and temperature rise of concretes containing retarders are less at early ages, and they equal at about 3–7 days. Sometimes they can be slightly higher than the reference mix at later ages. At a designed strength and slump, incorporation of water reducers decreases the heat of hydration and the temperature rise because of the reduction in the cement content [15].

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### (g) Plastic shrinkage

This generally occurs by loss of moisture in the first few hours (2–5 h) from placing and compacting of the concrete. If cracks are caused by plastic shrinkage, the retarding admixtures can aggravate the cracking problem.

### **5.4.5 Effects on hardened concrete**

The effect of retarding admixtures on the properties of hardened concrete is very small. No further discussion on this issue will be done in this chapter.

### **5.4.6 Use**

See Section 5.3.5.

### **5.4.7 Application**

Retarders are often treated under the same category as "water reducers and retarders". This is because the main components used for retarders are also present in water reducing and retarding admixtures. As a result, many retarders reduce the water requirement and many water reducers retard the setting of the concrete.

Also, standard requirements for the initial and final setting times are approximately the same; though there are some differences in water reduction requirements and compressive strength.

Some of the more important engineering purposes for which retarders are used are:

- to retard time of initial and final setting;
- to reduce rate of slump loss;
- to retard or reduce heat evolution during early hardening;
- to increase vibration time.

#### 5.4.8 Standards and code of practice

See Section 5.3.7.

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## **PART TWO**

### **OTHER ADMIXTURES**



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## 6

# **Antiwashout admixtures for underwater concrete**

*S. Nagataki*

### 6.1 DEFINITION

Antiwashout admixtures for underwater concreting reduce segregation of the concrete due to increasing cohesiveness.

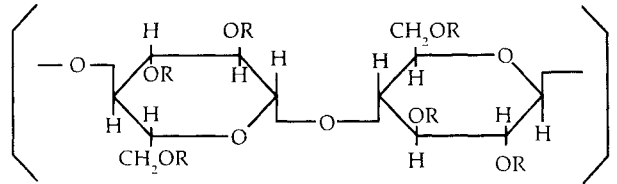
### 6.2 INTRODUCTION

When concrete is being placed underwater, the cement may be washed out from the concrete, with consequent reduction of the strength of the concrete and pollution of the surrounding water. In order to resolve these problems, antiwashout admixtures composed mainly of water-soluble polymer are used. Concrete containing antiwashout admixture is a new type of underwater concrete which does not easily segregate even when placed directly under water [1].

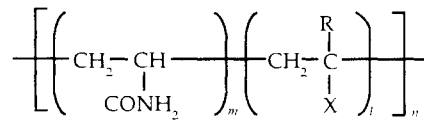
### 6.3 COMPOSITION

Antiwashout admixtures for underwater concrete can be divided into two types [2]. One has water-soluble cellulose ether [2, 3] as its main component, the other has water-soluble acryl-type polymer [4] as its main component.

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Chemical formula of water-soluble cellulose ether



Chemical formula of water-soluble acryl-type polymer

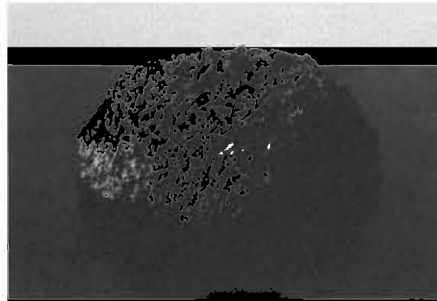
### 6.4 MECHANISM OF ACTION

These admixtures increase the cohesiveness of the concrete by increasing the viscosity of water [3] in the concrete and thereby improving the resistance to segregation. The resistance to segregation depends mainly on the dosage and molecular weight of the admixture.

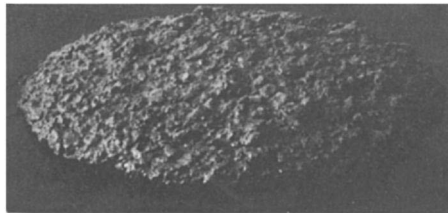
### 6.5 EFFECTS ON CONCRETE IN THE FRESH STAGE

#### 6.5.1 Workability

Concrete containing antiwashout admixture has high cohesiveness compared with ordinary concrete. The concrete containing the admixture has excellent self-levelling properties [2, 3, 5]. This property appears in the slump test. Slump increases gradually for about 10 minutes and the final slump value for a range of practical values is 23–26 cm as shown in Fig. 1 [5].



Immediately after pulling up slump cone



Three minutes after pulling up slump cone

Fig. 1. Slump test

#### **6.5.2 Segregation**

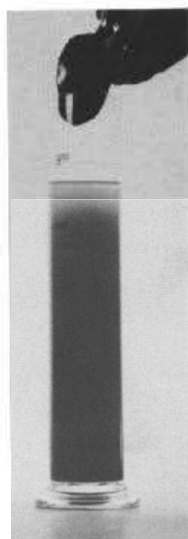
When a concrete containing antiwashout admixture is poured under water by free fall, it is hardly segregated, as shown in Fig. 2 [5]. But ordinary concrete without the admixture is completely segregated.

The results of falling through water test to evaluate resistance to segregation are shown in Figs 3 and 4. pH value and turbidity of the water decreased with the increase in dosage of the admixture [2, 4, 5].

Underwater concrete containing high fineness slag has excellent resistance and strength developing properties [9].

The method of the falling-through-water test is as follows: 3 litres of concrete are allowed to fall through water in a container of 30 cm diameter and 50 cm height. The Ph value and turbidity of the water near the surface are measured 60 seconds later.





Ordinary concrete



Concrete containing  
antiwashout admixture

Fig. 2. Underwater segregation resistance test

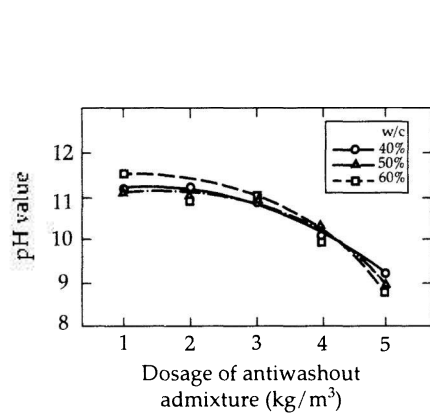


Fig. 3. pH value

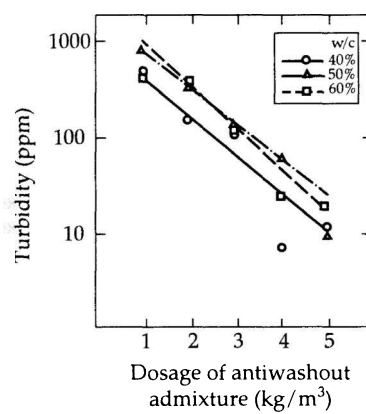


Fig. 4. Turbidity

## 6.6 EFFECTS ON CONCRETE IN THE SETTING STAGE

### 6.6.1 Setting

Concrete containing cellulose ether tends to delay setting time [2, 3, 5, 6]. Concrete containing acryl-type polymer hardly affects setting time [8], but when using with water reducer and/or superplasticizer, it tends to have a delayed setting time.

### 6.6.2 Bleeding

Concrete containing an antiwashout admixture has a high water retentivity due to viscosity increase and causes no bleeding at all even when a small dosage of the admixture is added [2].

## 6.7 Effects on concrete in the hardened stage

Strength [2–10]: As shown in Fig. 5, the strength ratio  $f^l_w/f^l_a$  ( $f^l_w$  and  $f^l_a$  are compressive strength at the age of 28 days of specimens cast in water and in air respectively) increased with the increase in dosage of antiwashout admixture due to high resistance to segregation in water [5].

## 6.8 USE

Most antiwashout admixtures are dosed in the range 1–1.5% by weight of water (unit weight 2–3 kg/m<sup>3</sup>) and are frequently used in combination with superplasticizers [3].

Antiwashout admixture are usually discharged into the mixer at the same time as other materials (cement, aggregate and water).

## 6.9 APPLICATIONS

Concrete containing antiwashout admixture for underwater concrete is very effective for the following uses:

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- foundations of bridge piers in water and slabs;
- revetments, piled piers and breakwaters of ports;
- prevention of scouring near underwater structures and protection of river beds;
- concrete for reinforcing rubblestone of breakwaters;
- reinforced concrete for slabs of caissons.

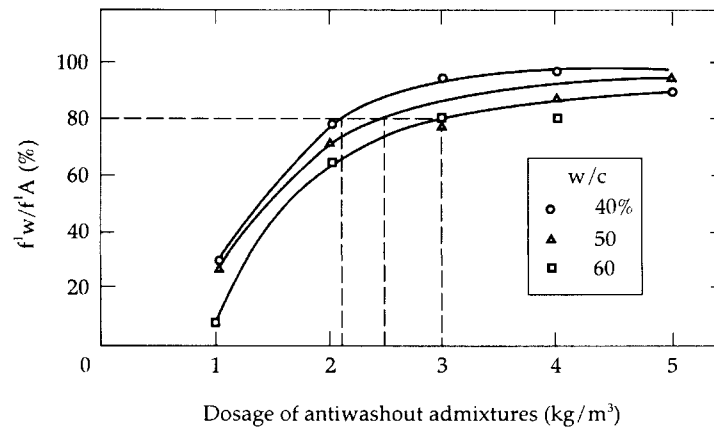


Fig. 5 Relationship between dosage of antiwashout admixture and  $f_w/f_A$

### 6.10 SPECIFICATIONS

Specifications of concrete containing antiwashout admixture for underwater concrete in Japan are shown in Table 1.

Table 1. Specifications of concrete containing antiwashout admixture for underwater concrete [11].

Item		Standard type	Retarded type
Bleeding (%)		< 0.01	< 0.01
Air (%)		< 4.5	< 4.5
Slump flow loss (cm)		< 3.0 After (30 min)	< 3.0 After (2 h)
Initial setting time (h)		> 5	> 18
Final setting time (h)		< 24	< 48
Compressive strength of specimen cast in water (kg/cm <sup>3</sup> )	7 days	> 150	> 150
	28 days	> 250	> 250
<u>Strength of specimens cast in water</u> Strength of specimens cast in air (%)	7 days	> 80	> 80
	28 days	> 80	> 80
Falling through water test	SS (mg/l)	< 50	< 50
	pH	< 12.0	< 12.0

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# 7

## Corrosion inhibitors

*E. Vazquez*

### 7.1 DEFINITION

A corrosion inhibitor is a chemical compound added to reinforced concrete, to delay corrosion of the steel.

### 7.2 INTRODUCTION

The corrosion resistance of reinforcement is affected adversely by chloride ions and by the decrease in the pH of the concrete pore solution. The main factor influencing this decrease is the carbonation of the concrete cover by atmospheric carbon dioxide. Low permeability of concrete is the best protection for the reinforcement. But in some cases when supplementary protection of the reinforcement is needed, it is advisable to treat the steel or the concrete. The addition of corrosion inhibitors to concrete can increase the protection of the steel.

### 7.3 COMPOSITION

Corrosion inhibitors can be divided in three classes

1. anodic
2. cathodic
3. mixed.

These interfere with corrosion reactions at anodic or cathodic sites, or both.

For anodic inhibitors the most commonly used materials are calcium and sodium nitrite. In some countries calcium nitrite is the only corrosion inhibitor available. Sodium benzoate and sodium chromate can also be used.

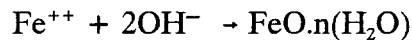
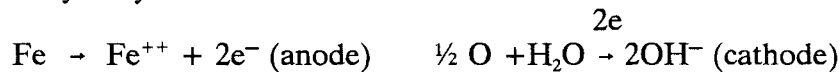
Most cathodic inhibitors are investigated only on a laboratory scale. The principal work has centred on aniline and its chloro alkyl- and nitro- substituted forms.

Mixed inhibitors contain one or two types of molecules with proton and electron acceptor groups. Both groups can be in the same molecule (aminobenzenethiol) or salt can be formed by the different orienting groups of two separate molecules.

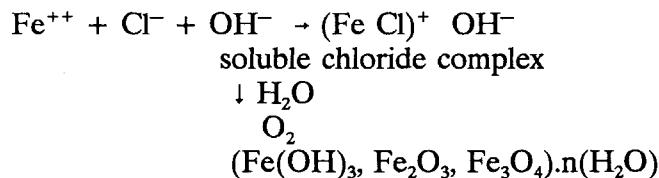
#### 7.4 MECHANISM OF ACTION

Chlorides may be present in concrete derived from the aggregates, cement or water or they can penetrate from the outside.

In the presence of chloride the protective passivating layer of the steel is breached. The passivating layer formed in the surface is destroyed by these reactions:



This takes place because  $\text{Fe}^{++}$  in the form of chloride complex migrate away, exposing the steel to corrosion. The chloride complex is further oxidized to different  $\text{Fe}^{+++}$  compounds:

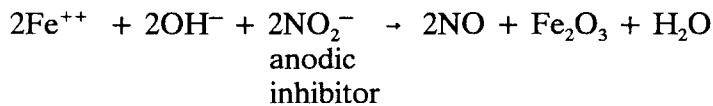


The corrosion products have a larger volume than that of the original steel, and pressures build up that exceed the tensile strength

## 90 *Application of admixtures in concrete*

of the concrete, causing cracking.

With the addition of nitrite ( $\text{Na}^+$  or  $\text{Ca}^+$ ) to the concrete a competing oxidation reaction is initiated at the surface of the steel which regenerates the passivating layer with  $\text{Fe}_2\text{O}_3$ :



The carbonation of concrete by atmospheric  $\text{CO}_2$



dramatically decreases the pH values, and corrosion potentially reaches active values. When  $\text{NO}_2^-$  is added the change in pH values is the same, but the corrosion potential remains in passive values. So, the  $\text{NO}_2^-$  avoids corrosion as much in alkaline as in neutral media. Nitrite ions rapidly oxidize ferrous ion to ferric, blocking further passage of ferrous ion from steel into the electrolyte.

Some authors have reported that  $\text{NO}_2^-$  oxidizes in concrete to  $\text{NO}_3^-$  reducing the time of action of the corrosion inhibitor. Other authors have reported that  $\text{NO}_2^-$  acts on steel only as an oxidant and it reduces.

Nitrites, like other substances such as chlorides, combine with  $\text{C}_3\text{A}$  and  $\text{C}_4\text{AF}$ , and their effective amount in concrete is less than that added, because the only effective amount is that which can reach the steel surface. Their effectiveness also depends on their proportion in relation to the amount of chloride and the ambient humidity.

More calcium nitrite will protect against more chloride. If the ratio of inhibitor : chloride ratio is small the protective film repair by the nitrite ion and chloride attack occur simultaneously, corrosion will dominate and become localized.

Cements containing higher levels of  $\text{C}_3\text{A}$  offer better corrosion resistance.

### (a) Cathodic inhibitors

These act by slowing the cathodic reaction or selectively precipitating on cathodic sites to increase the circuit resistance and restrict the diffusion of reducible species to the cathode.

(b) Mixed inhibitors

These contain molecules in which electron density distribution causes the inhibitor to be attracted to both anodic and cathodic sites.

## 7.5 EFFECTS ON CONCRETE

### 7.5.1 Fresh state

*Workability* Workability is slightly increased by the inorganic salts used as corrosion inhibitors. Organic inhibitors seem not to affect workability.

### 7.5.2 Setting stage

*Setting* Inorganic admixtures, as nitrites, accelerate initial and final set times. With some corrosion inhibitors, if the acceleration is not desired, a retarder can be added.

In general terms, the effect of this admixture on properties of concrete in the setting stage are the same as accelerators.

### 7.5.3 Hardening stage

(a) Strength

Calcium nitrite slightly increases compressive strength. Sodium nitrite has no effect on compressive strength at early ages and decreases 28 day strength slightly. The same tendency is observed for chromates.

Sodium benzoate significantly reduces concrete strength at all ages.

Similar effects are observed for flexural strength.

(b) Bond

In some cases the inhibiting layer formed by the inhibitor on the steel surface decreases the bond strength between steel and concrete.

#### **7.5.4 Hardened state**

(a) Alkali-aggregate reaction

Inhibitors based on sodium salts such as sodium nitrite and sodium benzoate may increase the effects of alkali-aggregate expansion if reactive aggregates are present.

(b) Efflorescence

Inhibitors based on sodium salts such as sodium nitrite and sodium benzoate can increase efflorescence.

### **7.6 USE**

#### **7.6.1 Calcium nitrite**

Calcium nitrite is the most used corrosion inhibitor. It is also an accelerator. The admixture solution contains about 30% calcium nitrite solid by weight. It is normally added to concrete during the batching process and is dispersed throughout the concrete. As a general rule, a minimum amount of 3% by weight of cement is recommended. In Japan it is used at rates from 0.9 to 1.2 kg (solid weight) per unit volume ( $\text{m}^3$ ) of concrete.

The protection given by the inhibitor depends on the quality of the concrete. The length of time of protection may be short in poor quality concrete. Calcium nitrite improves the resistance of concrete to chloride attack at water/cement ratios under 0.5. Some authors report that when water reducing agents were used, the time of corrosion protection could be extended. So calcium nitrite is frequently used in combination with superplasticizers.

In air entrained concrete the addition of calcium nitrite requires higher dosages of air entraining agent to keep the air content at a given level. Curing at elevated temperature or alternate wetting and drying promotes corrosion and reduces the effectiveness of calcium nitrite.

Most authors report that calcium nitrite does not completely avoid corrosion but it always reduces it significantly allowing a lengthening of the service life.

#### **7.6.2 Sodium nitrite**

In the absence of chlorides sodium nitrite is used effectively at dosages of 1–2% by weight of cement. In the presence of chlorides the dosage should be higher. Sodium nitrite is less used because of the disadvantages associated with the presence of  $\text{Na}^+$ .

#### **7.6.3 Sodium and potassium chromates**

They are used at 2–4% by solid weight of cement. The effects are similar to those of the nitrites. Potassium chromate produces a light green colour of concrete.

#### **7.6.4 Sodium benzoate**

It is seldom used but some authors found its effect to be more persistent than other admixtures mentioned.

#### **7.6.5 Stannous chloride and hydrazine hydrate**

These have only been investigated and found by some authors to be efficient.

#### **7.6.6 Cathodic and mixed inhibitors**

These are less used. Dosage is generally at the level 1–2% by cement weight.

### **7.7 APPLICATIONS**

Calcium nitrite has been used in reinforced concrete and prestressed concrete structures exposed to chloride attack.

Sodium benzoate has been used in some cases in the UK, and sodium nitrite in different applications in Europe.

## 7.8 SPECIFICATIONS

The only nationally recognized standard is the Japan Industrial Standard A-6205 'Corrosion inhibitor for reinforcing steel in concrete'.

As electrochemical measurements including potential and polarization measurements of steel in concretes are the best methods of determining corrosion, they can be used in the evaluation of corrosion inhibitors. The use of open-circuit potential measurements is considered in the Special Technical Publication 713 of ASTM (1980).

The main reference for test methods are:

*Rapid Method of Studying Corrosion Inhibition of Steel in Concrete.*  
Portland Cement Association Research and Development Bulletin 187,  
PCA, Skokie, Illinois.

Among other interesting publications the following may be mentioned:

Berke N.S (1986) The use of anodic polarization to determine the effectiveness of calcium nitrite as an anodic inhibitor, ASTM STP 906, Philadelphia.

## 8

# Gas forming admixtures

*D. Dimic*

### 8.1 DEFINITION

Gas forming admixtures generate or liberate bubbles of gas in the fresh mixture during the hydration process before the initial set of the cement paste matrix takes place [1, 2, 3].

### 8.2 INTRODUCTION

Gas forming admixtures are used for a number of different purposes:

- to control settlement and bleeding [4–7],
- to improve the intrusion of grouts and mortars in preplaced-aggregate concrete, by producing an expansion of 5–10% [8], or even up to 14% [9],
- for the production of aerated concrete and mortars [10].

### 8.3 COMPOSITION

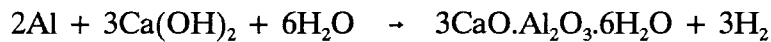
The components used as gas forming admixtures are metallic aluminium, zinc or magnesium, hydrogen peroxide, nitrogen and ammonium compounds, and certain forms of activated carbon or fluidized coke [1, 2, 10]. The nitrogen compounds used are azo or hydrazin compounds with at least one N–N bond in the molecule.



#### 8.4 MECHANISM OF ACTION

When a gas forming admixture is added to a grout, mortar or concrete, a reaction between the gas forming admixture and the components present in the fresh hydraulic cement mix takes place. When a known quantity of the gas forming admixture is added, meaning the liberation of a known volume of gas, a predetermined rate of expansion can be expected. For a given application the rate of expansion and its duration are important factors for the properties of the mortar or concrete. The homogeneity of the distribution and size of the bubbles generated by the reaction are important factors, too.

Hydrogen, oxygen, nitrogen or air are released by the chemical reactions. Hydrogen gas is produced by the reaction of calcium hydroxide, liberated by cement hydration, with aluminium powder. The gas formation which occurs in this case may be illustrated by the following simplified equation [10]:



If hydrogen peroxide and calcium hypochloride (bleaching powder) are used, a reaction in which oxygen is evolved instead of hydrogen takes place.

The calcium chloride released by this reaction acts as an accelerator for the cement hydration process; however, the reader is cautioned to evaluate the corrosion potential of the calcium hypochloride and calcium chloride.

Nitrogen gas is produced by the decomposition of the N-N bond of the compound, influenced by the action of activators. Activators like aluminates or copper salts are used.

Certain forms of activated carbon or fluidized coke, with a moisture content of about 3%, liberate adsorbed air [2].

#### 8.5 MAIN FACTORS INFLUENCING GAS EVOLUTION

The following factors affect the rate and duration of the gas evolution.

#### **8.5.1 Mix proportions**

The amount of water and the consistency of the fresh mix influence the rate and continuity of the hydrogen liberation. There is an optimal amount of water and an optimal consistency of the grout, mortar or concrete at which maximum expansion is obtained. At highly plastic or flowable consistencies a significant amount of gas may escape from the mix before setting [11, 12, 13]. Use of a thickener will increase expansion efficiency by preventing the gas from escaping [14].

#### **8.5.2 Characteristics of the cement**

The fineness and alkali content of the cement are important for the gas evolution. Gas evolution accelerates as cement fineness and alkali content increase. The activity and relative content of the minerals, particularly tricalcium silicate, influence the speed of hydrogen release and the duration of the expansion [2, 9]. The type of cement also affects gas generation rates and the expansion starting time [15].

The reactions when nitrogen or oxygen are liberated are independent of the cement characteristics, as they are initiated and controlled by activators.

#### **8.5.3 Characteristics of the admixture**

Aluminium powder may be used in unpolished or polished form, depending on the desired speed of the gas evolution. Unpolished aluminium powder is generally preferred. It reacts faster, whereas polished powder is used when a slower reaction is desired. Aluminium powder with a specially treated surface is also used for reaction control [15, 16].

The fineness and particle shape of the aluminium powder also influence the rate and the duration of gas evolution and have an influence on the size and shape of the air pores in the hardened mix [1, 10].

When using fluidized coke, the fineness and moisture content are important factors for the gas evolution process [2].

#### **8.5.4 Temperature**

The ambient temperature and the temperature of the mix influence hydrogen generation considerably. Nitrogen, oxygen or air producing systems are not directly influenced by temperature [2].

The reaction of aluminium powder with calcium hydroxide is faster at higher temperatures, so higher dosages of admixture are used at lower temperatures to ensure the same rate of expansion as is reached at normal ambient or mix temperatures.

It is possible to speed up the rate of gas generation in cold weather by the addition of accelerators such as sodium hydroxide, hydrated lime or trisodium phosphate [2, 10]. This may ensure sufficient gas generation before setting.

### **8.6 EFFECTS**

#### **8.6.1 Fresh stage**

##### **(a) Unit weight**

The unit weight of the grout, mortar or concrete is reduced, depending on the degree of expansion, the degree of restraint, and the stability of the bubbles.

##### **(b) Workability**

Gas forming admixtures have no significant influence on workability or workability loss.

##### **(c) Volume changes**

When properly predetermined, the admixture produces expansion which compensates for the volume change caused by settlement and plastic shrinkage, and causes a slight expansion of the freshly mixed grout, mortar or concrete.

#### **8.6.2 Setting stage**

Gas forming admixtures do not alter the initial and final setting times of the mixes. Retarders are often used for grouting long ducts or rock

anchors and for oil well grouting, where high temperatures and pressures may be encountered and the distances are relatively great [1, 2, 15, 16].

### **8.6.3 Hardened stage**

#### **(a) Strength**

Strengths are reduced to some extent [11]. The reduction in strength depends on the degree to which the expansion of the mixture is restrained; little reduction in strength may be achieved if suitably restrained. If the placed mix is not fully restrained, the gas bubbles tend to be displaced upwards and are therefore not uniformly dispersed throughout the hardened mix. In this case the reduction of strength may be very significant. It is therefore important that the forms be tight and well sealed.

Water reducers or high-range water reducers present in the multicomponent admixtures may be able to compensate or modify loss of strength.

#### **(b) Volume changes**

Gas forming admixtures do not overcome the shrinkage caused by drying or carbonation. Usually the drying shrinkage of grouts, mortars or concretes containing gas forming admixtures is increased [12].

#### **(c) Durability**

Gas forming admixtures are not used specifically to improve durability [12, 17, 18].

## **8.7 APPLICATION**

Aluminium powder as extensively used is normally added at rates between 0.006% and 0.02% by weight of the cement, although larger quantities may be used to produce lightweight concrete. Higher amounts are required when the temperature is lower. Commercially available products are generally premixed with fine powder materials (sand, cement, pozzolana) because of the very small quantities of the aluminium powder generally used.

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As gas forming admixtures are commonly used for specific purposes like structural grouting and the cementing of oil wells, they are usually produced as a combination of a gas forming agent and a plasticizing agent, retarder, accelerator or other materials in order to impart the special properties desired.

Preblended mixtures of cement, sand or filler, gas forming and other admixtures are available on the market as ready-to-use grouts with specific properties.

Gas forming admixtures as single or multicomponent admixtures are used to produce the following products.

### (a) Grouts, mortars or concretes with controlled expansion

The controlled expansion avoids excess pressure build up, but sufficient expansion is developed to provide good bond of the fresh mix to the contact surface, with the reduction of voids [4, 6, 8, 9, 19, 20, 21]. They can be used for:

- the grouting of cable ducts in post-tensioned concrete,
- the setting up of heavy machinery,
- the fixing, jointing and anchoring of precast concrete elements,
- repair work,
- the grouting of joints between inversely placed concrete elements.

### (b) Intrusion grouts or mortars for preplaced aggregate concrete

The admixtures used for this special type of grout or mortar, also called intrusion aids, shall comply different requirements; up to 14% in US [9]; in Japan the expansion should be in the range from 5 to 10% [8]. This concrete is produced preferably as mass concrete, for underwater concreting and for placing heavyweight concretes.

### (c) Cellular concrete

Of the various methods in which air cells may be formed in the concrete, the one of chief practical importance today is the aluminium powder process [10].

## 8.8 SPECIFICATIONS

At present, the use, sampling and testing of gas forming admixtures is

covered by various standards, guides or recommendations. The table overleaf gives some of them.

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Australia	AS-2073-79	Methods for testing of expanding admixtures for concrete, mortar and grout
	AS-2072-79	Methods for sampling of expanding admixtures for concrete, mortar and grout
USA	CRD C 621-83	Corps of Engineers Specification for nonshrink grouts
	CRD C 619	Corps of Engineers Specification for grout fluidifier
	ASTM C 937-80	Standard specification for grout fluidifier for preplaced-aggregate concrete
	ASTM C 938-80	Standard specification for proportioning grout mixtures for preplaced-aggregate concrete
	ASTM C 1090-88	Standard test method for measuring, changes in height of cylindrical specimen from hydraulic cement grout
	ASTM C 1107-89	Standard specification for packaged dry, hydraulic-cement grout (nonshrinkable)
Great Britain	BS 5400: 1978	Steel, concrete and composite bridges. Grouting of prestressing tendons. Clause 3.12, Part 7 and Part 8
Switzerland	SIA-Norm 162	Norm für die Berechnung, Konstruktion und Ausführung von Bauwerken am Beton, Stahlbeton und Spannbeton
Austria	ÖNORM B 4250	Spannbetontragwerke, Berechnung und Ausführung, 1974
France		Directive provisoire sur les injections des graines des ouvrages en beton precontraint
Germany	DIN 4227 Teil 5	Spannbeton. Einpressen von Zementmörtel in Spannkannäle
Yugoslavia	JUS U.E3.015.86	Grouts for use in bonded posttensioned prestressed concrete

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## 9

# Pumping aids

*E. Vazquez*

### 9.1 DEFINITION

Pumping aids are admixtures that enhance the pumpability of concrete.

### 9.2 INTRODUCTION

Fresh concrete for pumping must be sufficiently mobile, cohesive enough not to segregate and capable of flowing with reduced friction along pipe walls. Air entraining admixtures and water reducers improve flow at normal cement dosages. Superplasticizers are more effective in richer concretes. These admixtures are excluded in this chapter from the category of pumping aids. Pumping aids considered in this state-of-the-art report are admixtures used to pump marginally pumpable concrete. They improve the plastic properties of concrete in special situations.

### 9.3 COMPOSITION

Pumping aids usually consist of the following materials:

- synthetic and natural organic polymers, soluble in water. In this class are cellulose ethers, polyethylene oxides, carboxyl vinyl polymers, polyvinyl alcohol and others,
- dispersions of natural gums, styrene copolymers with carboxyl groups and synthetic polyelectrolytes,

- acrylic emulsions.

According to the definition of admixtures, products such as condensed silica fume, fly ash, kaolin, rock dust and pozzolanic materials are not included in this report.

#### 9.4 MECHANISM OF ACTION

These products act by physical means on concrete properties.

The admixture should lubricate the fresh concrete to give an increase in cohesiveness, and reduce bleeding, especially in low cement content mixes.

So-called thickeners increase the viscosity of the mixing water.

Dispersions of natural gums, styrene copolymers with carboxyl groups and synthetic polyelectrolytes are products that increase viscosity by promoting interparticle attraction. They are flocculants which are adsorbed on the cement particles.

Acrylic emulsions are products that increase viscosity by interparticle attraction and also by supplying superfine particles in the cement paste.

#### 9.5 EFFECTS

##### 9.5.1 Fresh state

*Workability* The effect of a pumping aid admixture on the workability of concrete depends upon the cement type and the dosage, and the aggregate grading. High dosages of admixture may cause excessive water demand as well as poor workability. Classical tests of workability can not be applied in this case.

##### 9.5.2 Setting stage

###### (a) Setting

Most synthetic and natural organic polymers soluble in water are retarders.

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### (b) Air entrainment

Overdosage can cause air entrainment.

### (c) Bleeding

Pumping aid admixtures generally reduce bleeding.

## 9.5.3 Hardening stage

*Strength* At early ages a reduction of strength can be expected. This reduction depends on the dosage of the admixture and the retardation effect, or excessive air entrainment.

## 9.6 USE

The so-called thickeners are dosed in the range 0.02–0.5% solid by weight of cement and added in the mixer. They should be dissolved in water prior to addition to ensure uniform distribution in the concrete.

Dispersions of natural gums, styrene copolymers with carboxyl groups and synthetic polyelectrolytes are dosed in the range 0.01–0.10% solid by weight of cement and added at the mixer.

Acrylic emulsions are dosed in the range 0.10–1.50% solid by weight of cement and added at the mixer.

The presence of water reducing admixtures generally requires lower dosages of the pumping aid admixture.

## 9.7 APPLICATIONS

These admixtures can be used with any concretes.

## 9.8 SPECIFICATIONS

There are no test methods for measuring pumpability, and only indirect indications of effectiveness of the admixture can be determined, as bleeding or water retentivity.

There are no standards or specifications to regulate the use of pumping aids. Only a few documents with information on use, effects and properties are available.

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# 10

## Shotcrete admixtures

*D. Dimic*

### 10.1 DEFINITION

Shotcrete admixtures, also called quick accelerators or stiffening admixtures, accelerate the stiffening process in fresh concrete.

### 10.2 INTRODUCTION

Shotcrete admixtures make possible the spraying of concrete on vertical and overhead surfaces by quick stiffening in order to build up thick layers and to reduce rebound. They may also be used for special applications requiring rapid setting and early strength development, like sealing leaks in below-grade structures, for patchwork and emergency repairs.

In the definition of admixtures according to RILEM TC 84-AAC, provision is made that the dosage shall not exceed 5% by weight of cement. Shotcrete admixtures generally exceed this dosage, but are nevertheless included here.

### 10.3 COMPOSITION

The most common substances used as shotcrete admixtures are sodium and potassium aluminates, hydroxides and carbonates [1–9], triethanolamine [10], ferric sulphate [11], fluorosilicates [4], sodium fluoride and alkali silicates [4]. Commercial shotcrete admixtures are

generally mixtures of various proportions of different ingredients.

Often the admixtures are combined with one or more other materials in order to obtain specially desired modifications. They may include wetting agents, stabilising agents for liquids, corrosion inhibitors and others. Recently some new formulations based on inorganic neutral salts and some others based on neutral organic compounds have been developed [3]. A new shotcrete admixture based on calcium aluminate minerals was developed recently [12, 13, 14].

#### 10.4 MECHANISM OF ACTION

Shotcrete admixtures promote the stiffening of the cement matrix mostly through the acceleration of the reaction between  $C_3A$  and gypsum [2, 3, 10]. Most of them probably act by precipitating as insoluble hydroxides or other salts. By forming larger quantities of ettringite at early age, some of them also modify the hydration of  $C_3S$  [3]. The rapid reaction of  $C_3A$  disturbs the harmonious reaction between the calcium silicates and water [15].

#### 10.5 MAIN FACTORS AFFECTING THE MECHANISMS OF ACTION

There are many factors that affect the action of shotcrete admixtures, e.g.

##### *Mix design*

- cement (type, brand, composition, content etc),
- the presence of other admixtures - air entraining agents, finely divided mineral additions (inert, hydraulic or pozzolanic reactive solids),
- the water/cement ratio.

##### *Conditions prevailing during the shotcreting*

- admixture dosage,
- mix temperature,
- ambient temperature,

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- prehydration of the cement,
- proper addition of the admixture.

Differences between cements, types and brands can vary enough to cause changes in the reaction with the shotcrete admixture. Cements with a higher content of  $C_3A$ , as well as more finely ground cements, react faster. Usually the shotcrete admixture is formulated for a Portland cement of average mineralogical composition. However, the formulation of the shotcrete admixture can be varied to suit the chosen cement [8]. Very-low- $C_3A$  sulphate-resistant Portland cement requires a specially formulated shotcrete admixture [16, 17].

Before the application of any shotcrete admixture, a compatibility test must be carried out, and the optimum proportions must be determined at the site with the materials, mix and temperature prevailing. One compatibility test for a shotcrete admixture and Portland cement combination has been proposed by ASTM Sub Committee C 09.03.08.07, Admixtures for Shotcrete [18]. This test will determine the compatibility of the admixture–cement combination, but will not necessarily indicate the time of set this combination will produce in actual shotcreting, or give the optimum proportion of the admixture.

## 10.6 EFFECTS

### 10.6.1 Fresh stage

Shotcrete admixtures should contribute to good cohesion and produce a dry gritty mix, so that thicker layers of shotcrete can be built up on overhead or vertical surfaces during a single shift.

### 10.6.2 Setting stage

Shotcrete admixtures provide rapid stiffening or setting. At optimum dosages the initial setting time may be reduced to 3–4 minutes, while the final setting time can vary between 10 and 15 minutes. More rapid ‘flashset’ setting times can be achieved by careful selection of a suitable combination of cement and admixture. Fig. 1 gives an example of the

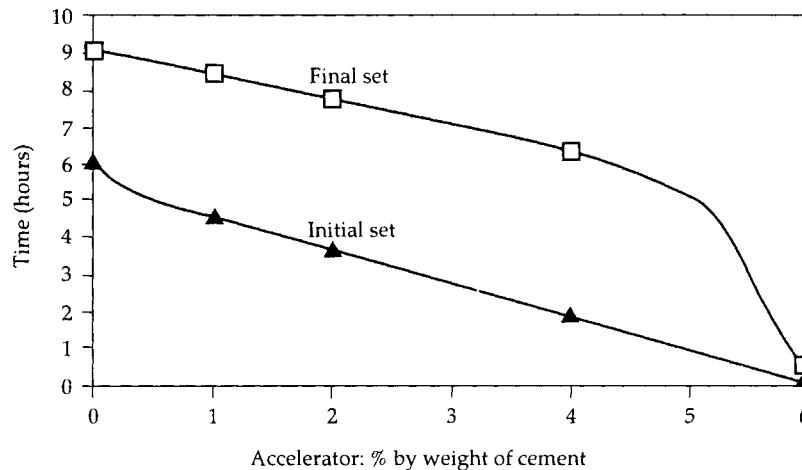


Fig. 10.1 Influence of dosage of a caustic shotcrete admixture on setting time of a shotcrete mix [19] (ASTM C 403 Test Method)

influence of an increasing admixture dosage on the setting time of a plain shotcrete for a particular, highly caustic shotcrete admixture [19].

### 10.6.3 Hardening stage

Beside the rapid stiffening and setting of the concrete mix, another beneficial effect of the use of a shotcrete admixture may be more rapid early strength development. The maximum rate of strength increase is reported to be within the first few hours [19, 20].

### 10.6.4 Hardened stage

The development of the physical and mechanical properties of shotcrete, such as strength, shrinkage, permeability and durability, is different from that of ordinary concrete.

#### (a) Strength

Some decrease in the mechanical strength of the concrete at later ages can be observed when shotcrete admixtures are used. The 28 day strength is usually lower by 20 to 25% at optimum dosages compared



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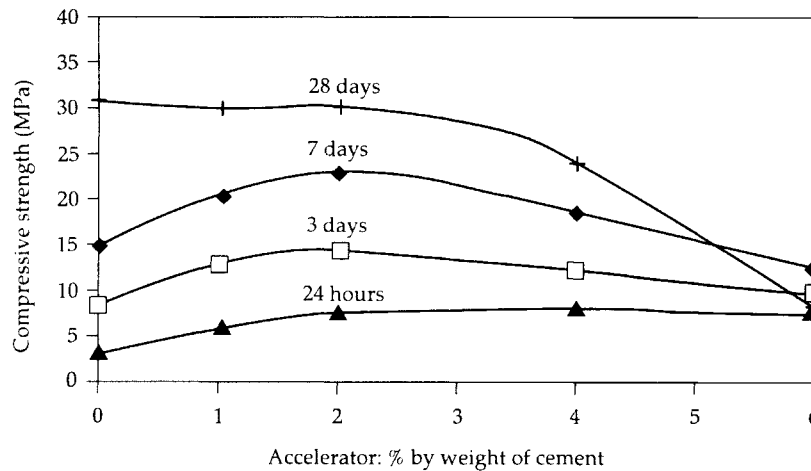


Fig. 10.2 Influence of dosage of a caustic shotcrete admixture on compressive strength development of a plain shotcrete mix [19]

to the reference concrete mix. At higher dosages some shotcrete admixtures cause a strength reduction of up to 50% [19, 20, 21]. Some factors that may cause low strength are: formation of C-S-H with a higher C/S ratio; disturbed  $C_3S$  hydration; very rapid setting followed by greater heat development; and a more porous structure [1]. Fig. 2 gives an example of the influence of increasing admixture dosage on the compressive strength development of a plain shotcrete for a particular, highly caustic shotcrete admixture [19]. Some new formulated admixtures are reported to have a less detrimental effect on long-term strength development. In some cases, even no reduction is reported [13].

### (b) Shrinkage

It has been found that the drying shrinkage of shotcrete increases when a shotcrete admixture is used.

### (c) Durability

There are indications that shotcrete admixtures can adversely influence the durability of shotcrete. Resistance to freezing and thawing is decreased [22]. In the case of alkali-aggregate reactivity, admixtures based on alkali substances can increase the reaction.

(d) Modulus of elasticity

In general, the relationship between compressive strength and modulus of elasticity is similar to that of plain concrete. If adequate curing is provided, values of modulus increase with age [1].

## 10.7 USE

Shotcrete admixtures are available either in dry or liquid form. Both liquid and powder admixtures can be used with dry-mix and wet-mix process shotcrete equipment [13].

Powder admixtures are generally used at addition rates of 2 to 10% by weight of the cement. Dispensing powder admixture is difficult, so suitable apparatus for dosage of the admixture to the concrete is required. In order to reduce dust-raising and the generation of static electricity caused by the dry mixture passing through the hose, it is desirable to use aggregate with a moisture content of 3 to 5%. However, if the cement remains for a certain time in contact with damp aggregate, partial hydration will take place. This will cause delaying of the setting time of the cement and a reduction in the acceleration effect of the admixture [18].

Liquid admixtures are usually batched by volume ratios, with the admixture : water ratios ranging from 1 : 1 to 1 : 20 [1]. Liquids can be accurately dispensed by positive flow pumps into the gauge water. This provides a good overall distribution.

Most commercially available shotcrete admixtures contain chemicals that are caustic and require caution in handling. They can cause reactions on the exposed skin, causing mild to severe burns. With liquid admixtures, burns can occur immediately. The material must be kept from getting in the eyes and mouths of workers. Personal protection equipment is required for all those in the vicinity of the shotcrete machine and nozzle.

A new method has been developed, to solve technological and environmental problems, which no longer relies on chemical agents, but allows the wet-mix shotcrete to harden immediately after placement as a result of a physical process [23].

## 10.8 SPECIFICATIONS

There are no standards in existence for shotcrete admixtures. There are different recommendations for shotcrete admixtures [2, 24, 25, 26]. In general the following recommendations are fairly typical for shotcrete with an admixture:

1. The initial and the final set should occur within 3 and 12 minutes respectively.
2. The rate of strength development should be such that values of the order of 4.0 MPa are attained at 8 hours, and 10 Mpa at 24 hours,
3. The decrease in 28 day strength should be less than 30% compared to the concrete without an admixture.

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## **APPENDIX**

### **Guide for use of admixtures in concrete**



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84-AAC: APPLICATION OF ADMIXTURES FOR CONCRETE

Guide for use of admixtures in concrete

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1. DEFINITION

Admixtures of concrete mortar or paste are inorganic (including minerals) or organic materials in solid or liquid state, added to the normal components of the mix, in most cases up to a maximum of 5% by weight of the cement or cementitious materials.

The admixtures interact with the hydrating cementitious system by physical, chemical or physico-chemical action, modifying one or more properties of concrete, mortar or paste in the fresh, setting, hardening or hardened state.

Materials such as fly ash, slag, pozzolanas or silica fume which can be constituents of cement and/or concrete, also products acting as reinforcement, are not classified as admixtures.

2. EFFECTS OF ADMIXTURES FOR  
CONCRETE IN MOST FREQUENT USE

2.1 Main effect exerted in the fresh state

*Water reducing agents* either increase the slump of freshly mixed mortar or concrete without increasing the water content or maintain workability with a reduced amount of water.

*High-range water reducing agents (super-plasticizers)* are admixtures which procure a considerable increase in the workability of mortars and concretes at constant water to cement ratio. The duration of the effect is generally temporary and variable. Mortars and concretes of constant workability can be made with smaller amounts of water, saving more than 12%, without undue retardation, excessive entrainment of air or detrimental bleeding.

2.2 Main effect exerted at the setting stage

*Set-retarders* are products which regard the initial rate of reactions between cement and water. They increase the time taken by mortars and concretes to pass from the plastic to the solid state.

*Set-accelerators* are products which accelerate the initial rate of reactions between cement and water. They reduce the time taken by mortars and concrete to pass from the plastic to the solid state.

2.3 Main effect exerted in the hardening stage

*Hardening accelerators* are admixtures which accelerate the development of early strength in the concrete, or mortar or grout, whether or not they affect the setting time.

2.4 Main effect exerted in the hardened stage

*Air-entrainers* are products which cause the formation of minute, uniformly distributed micro-bubbles of air in the concrete or mortar. They remain after hardening. Air-entraining gives hardened mortars and concretes freeze-thaw resistance.

3. ADMIXTURE INTERACTION IN THE  
WATER-CEMENT SYSTEM

There are often several different types of interaction between cements and admixtures. They vary according to the nature of the admixture. Chemical reactions which may develop at the beginning of contact between cement and water are complex. Not all the mechanisms of admixture action are completely



understood. These mechanisms can involve phenomena of physical or chemical adsorption and chemical reactions with certain cement constituents.

**Accelerators** (organic or inorganic) generally act by accelerating either the hydration of the aluminates (in combination with gypsum) or the hydration of silicates contained in the cement.

**Retarders** such as sugar, hydroxycarboxylic acids or lignosulphonates promote reaction by absorption or by formation and fixing of compounds at the surface of aluminates or silicates. It is often accepted that retardation is also due to the formation of a protective layer on the surface of cement grains which slows down initial hydration reactions.

**Admixtures which modify the rheological properties of cement** (superplasticizers or water-reducing agents) generally act by fixing on the surface of cement grains, modifying the surface state. This produces 'dispersion' or deflocculation of cement grains in the fresh concrete. This type of surface interaction can explain certain secondary effects, as in the case of certain lignosulphonates, which are not only water-reducing agents and plasticizers but also retarders.

The control of *setting* depends particularly on an equilibrium, which is quite difficult to ensure, between the reactivities and the respective contents of the different sulphates and binder. This equilibrium may be modified in certain cases by interaction with the admixture. This has been observed sometimes with certain combinations of cement–lignosulphonate or gluconate cements. For this reason it is appropriate to undertake preliminary tests with the cement and the admixture chosen for a specific structure, preferably by using an extra amount of admixture, to make sure there

is no excessive modification of the cement setting characteristics.

**Air-entraining agents** promote adsorption reactions at the water–air interface (giving rise to entrapped microscopic air bubbles) and sometimes on certain solid surfaces of concrete containing fly ash with a high calcium content. Air-entrainers are adsorbed on them, thus higher than normal amounts of the admixture would be needed.

#### 4. EFFECTIVENESS OF ADMIXTURES

The effectiveness of each admixture may vary depending on its concentration in the concrete and various constituents of the concrete, particularly the cement.

Each class of admixture is defined by its main function. It may have one or more secondary functions and its use may result in side-effects. The *main function* is characterized by the effect(s) it has on the required properties of the concrete. The *secondary function(s)* concern(s) effects that are in most cases independent of the main function. An example is as follows:

Main function – water reducing  
Secondary function(s) set-retarding, air-entraining

The use of an admixture may result in effects on the properties or behaviour of the concrete that, even though unsought, are inevitable. These effects are known as side-effects (examples include a loss of mechanical strength, set-retarding, increased shrinkage, etc.). These side-effects must be detected or confirmed, often by means of preliminary investigations specific to each case. Table 1 indicates the

Table 1 Main and secondary effects possible for every type of admixture in frequent use. These effects are not a general rule but depend on the admixture formulation. Some formulations containing chloride may be deleterious to reinforcement

Effect <sup>a</sup>	Type of admixture					
	Water-reducers and high-range water-reducers	Super-plasticizers	Setting accelerators	Setting retarders	Hardening accelerators	Air-entrainers
Water reduction (see Tables 2 and 3)	x x	x				x
Workability increased (see Tables 2 and 3)	x	x x				x
Setting (see Tables 2 and 4)	x	x	x x	x x	x	
Hardening (see Tables 2, 4 and 5)	x		x	x	x x	
Air entrainment (see Tables 2 and 6)	x					x x
Strength (see Tables 2 and 5)	x x	x			x x (early age)	x
Durability (see Tables 2 and 6)	x					x x

<sup>a</sup> x x = main effect, x = secondary effect.



main functions and possible secondary effects of non-chloride admixtures.

## 5. THE USE OF ADMIXTURES

Depending of the materials available (cements, aggregate), limitations in mixing or placing, ambient conditions and placement problems associated with the project requirements, it is impossible to produce satisfactory concrete without the use of an admixture. Consequently, admixtures can be considered as constituents of the concrete, just as are cement, aggregates and water. They are often used to optimize the cost-effectiveness of a concrete mix.

It should be emphasized that admixtures provide

additional means of controlling the quality of the concrete by modifying some of its properties, but they cannot, whatever the conditions, correct poor quality of materials, unsatisfactory proportioning of the concrete and inappropriate placement procedures.

## 6. CONCRETE PROPERTIES AFFECTED BY ADMIXTURES

### 6.1 The fresh stage

This is the period of time during which concrete already made can be handled, transported, poured and finished before initial setting takes place.

*Unit mass* is the mass of fresh concrete per unit

Table 2. Effect of types of admixture in frequent use on concrete properties which can be modified

	Type of admixture					
	Water-reducers	High-range water-reducers	Super-plasticizers	Accelerators	Retarders	Air-entrainers
Dosage by weight of cement (%)	< 0.5	0.5 to 3.0	0.5 to 3.0	< 0.5	< 0.5	0.02 to 0.10
Method of introduction into mix	Into mixing water	Into mixing water	Before placing	Into mixing water	Into mixing water	Into mixing water
Air content	(0) or (+)	(0) or (+)	(0) or (+)	(0)	(0) or (+)	(+)
<i>Fresh stage</i>						
Unit mass ( $\text{kg m}^{-3}$ )	(+)	(+)	(+)	(0)	(0) or (+)	(-)
Workability	Can modify setting times					
Water demand	(-)** (0)*	(-)**	(0)*	(0)	(0) or (-)	(-)** (0)*
Consistency	(0)** (+)*	(0)**	(+)*	(0) or (-)	(0) or (+)	(0)** (+)*
Consistency loss	(0)** (+)*	(+)**	(+)*	(0) or (+)	(0)	(0)
Pumpability	(+)** (+)*	(+)**	(+)*	(0)	Can modify water demand	Improvement
Segregation	(-)** (0)*	(-)**	(+)* or (0)	(0)	(0) or (+)	(0) or (-)
<i>Setting and hardening stage</i>						
Setting time						
Initial	(0) or (+)	(0) or (+)	(0) or (+)	(-)	(+)	(0) or (+)
Final	(0) or (-)	(0) or (+)	(0) or (+)	(-)	(+) or (0)	(0) or (+)
Strength development	(+)** (0)*	(+)**	(0)*	(+)	(-)	(0)
Bleeding	(-)** (+)*	(-)**	(0) or (-)	(-)	(0) or (+)	(-)
Plastic shrinkage	(0) or (-)	(+)	(+)	(-)	(+)	(0) or (-)
<i>Hardened stage</i>						
Strength						
Flexural < 3 days	(0) or (+)** (0)* or (-)*	(+)**	(-)* or (0)*	(+)	(0) or (-)	(-)*
> 28 days	(+)** (0)*	(+)**	(-)* or (0)*	(0) or (-)	(0)	(-)*
91 days	(+)** (0)*	(+)**	(+)**	(0) or (-)	(0) or (+)	(-)
Compressive < 3 days	(0) or (+)** (0)* or (-)*	(+)**	(-)* or (0)*	(+)	(0) or (-)	(-)*
> 28 days	(+)** (0)*	(+)**	(-)* or (0)*	(0) or (-)	(0)	(-)*
91 days	(+)** (0)*	(+)**	(+)**	(0) or (-)	(0) or (+)	(-)*
Modulus of elasticity	(0) or (+)	(0) or (+)	(0) or (+)	(0)	(0)	(-)
<i>Durability</i>						
Capillary absorption/permeability	(-)** (0)*	(-)**	(0)*	(0)	(0) or (-)	(+)
Freeze-thaw resistance	(+)** (0)*	(+)** (0)**	(0)*	(0)	(0) or (+)	(+)
Thermal expansion	(0)	(0)	(0)	(0)	(0)	(-)
Creep	(0) or (+)	(0) or (-)**	(0)*	(0)	(+)	(+)
Shrinkage	(0) or (+)	(0) or (+)	(0)*	(0)	(0) or (+)	(0) or (+)
Corrosion of steel	(-)** (0)*	(-)**	(0)*	(0)	(0) or (+)	(-)** (-)*

(0) No effect, (+) increase, (-) decrease, \*constant W/C as reference, \*\*constant slump as reference.

volume. This volume is absolute or apparent. The absolute volume is free of air. The apparent volume includes the air content.

*Workability* is the combination of properties of freshly mixed concrete which enables it to be placed, compacted and finished easily without loss of homogeneity. It includes the following:

1. *Consistency*: the relative ability of freshly mixed concrete to flow.
2. *Plasticity*: the property of freshly mixed concrete which determines its resistance to deformation or ease of moulding.
3. *Cohesion*: the property of a freshly mixed concrete to preserve its homogeneity.
4. *Consistency loss*: the reduction in consistency that occurs with time in relation to an initial measurement taken from the same batch.

5. *Pumpability*: the ability to convey the fresh concrete by pressure through either a rigid pipe or a flexible conduit.

6. *Compactability*: the ability of freshly placed mortar or concrete to reduce its initial volume to the minimum practical space by vibration, centrifugation, tamping or some combination of these, to mould within forms or moulds and around embedded parts and reinforcement, and to eliminate voids other than entrained air.

7. *Finishability*: the ability of freshly placed concrete to be levelled, smoothed or to have its surface worked to provide the desired appearance and serviceability.

*Segregation* is the non-uniform distribution of solid constituents of a fresh concrete.

*Frost resistance*. Deterioration occurs if the freezing takes place during setting and/or in the green concrete.

Table 3 Non-chloride frequently used admixtures modifying the workability of concretes and mortars

	Type of admixture			
	Water-reducers	High-range water-reducers	Superplasticizers	Air-entrainers
Main chemical family	Lignosulphonates, hydroxycarboxylic acids, carbohydrates	Melamine formaldehyde condensate, sulphonated naphthalene formaldehyde condensate, modified lignosulphonates, acrylic (graft) copolymer, amino aromatic sulphonic acid, phenol formaldehyde condensate		See Table 6
<i>Main effects</i>				
Effect on workability	At constant workability water reduction >6.5% <sup>a</sup>	At constant workability water reduction >12% <sup>b</sup>	At constant water to cement ratio, highly fluidizing effect, slump >8 cm	Slightly water reducing at constant workability
Effect on strength (1, 3, 7, 28 and 91 days)	Higher than the reference: increase due to water reduction (10% minimum)	Higher than the reference: increase due to water reduction (15% minimum)	Compared to reference at the same water to cement ratio, small strength decrease is possible	Less than the reference depending on the amount of air entrained (maximum 20%)
<i>Secondary effects</i>				
Favourable	(i) Increase of compactness, decrease of permeability (ii) Possible improvement of resistance to chemical aggressive environments for the same cement contents	Very high strength concretes can be achieved by adopting very low water to cement ratios		(i) Improvement of surface aspect (ii) Improvement of freezing resistance
Unfavourable	(i) Setting retardation with certain formulations (ii) Possible increase of shrinkage (iii) Stiffening by possible admixture-cement interaction	(i) Slump loss except for special formulas and depending on the temperature (ii) Possible shrinkage increase	(i) Segregation when excess of water or admixture or bad grading (ii) Efficiency very sensitive to fines content of cement and sand (iii) Slump loss except for special formulas and depending on temperature (iv) Possible shrinkage increase	Efficiency varying as a function of fine elements, mixing and method of placing concrete

<sup>a</sup>10% in Japan.

<sup>b</sup>16% in Japan.



Table 4 Non-chloride frequently used admixtures modifying the setting time and hardening of cement

	Type of admixture		
	Setting accelerators	Setting retarders	Hardening accelerators
Main chemical family	Calcium nitrites, nitrates, thiosulphates-formates, triethanolamine, etc.	Gluconate-salicylic acid-Ca lignosulphonates, sodium boroheptonate, etc.	Calcium nitrites, nitrates, thiosulphates, formates, triethanolamine, etc.
<i>Main effects</i>			
Effect on setting time	Acceleration very variable as a function of admixture content, type of cement and temperature	Retardation very dependent on admixture content, type of cement and temperature	Acceleration very variable as a function of admixture content, type of cement and temperature
Effect on strength			
Before 3 days	Increased at 1 or 2 days	Decreased at 1 or 2 days	Increased (until 7 days)
After 28 days	Slightly decreased (the greater the reduction in strength, the greater the setting acceleration)	Slightly increased	Unmodified or slightly decreased
<i>Secondary effects</i>			
Favourable	In cold weather increase of heat of hydration during first few hours	Water reduction	In cold weather increase of heat of hydration during first few hours
Unfavourable	(i) In hot weather (ii) Increase of heat of hydration during first few days (iii) Slight increase of shrinkage (iv) Possible stiffening (v) Alkali-aggregate reactions possible if admixture contains alkalis	Shrinkage unmodified or slightly increased	(i) In hot weather (ii) Increase of heat of hydration during first few days (iii) Slight increase of shrinkage (iv) Possible stiffening (v) Alkali-aggregate reactions possible if admixture contains alkalis

Table 5 Non-chloride frequently used admixtures modifying the strength

	Type of admixture				
	Water-reducers	High-rate water-reducers	Hardening accelerators	Setting retarders	Air-entrainers
Main chemical family	See Table 6	See Table 3	See Table 4	See Table 4	See Table 6
<i>Main effects</i>					
Effect on strength					
Before 3 days	Higher than reference at all ages, increase due to water reduction for same workability	At constant workability much higher than the reference, at all ages	Hardening possible between 2 and 10 °C	Lower than reference	See Table 6
After 28 days		Utilization in high-strength concretes	Possible reduction of final strength, depending on nature of admixture	Possible increase of final strength	
<i>Secondary effects</i>					
Favourable	(i) Increase of compactness (ii) Improvement of resistance to chemical aggressive agents (iii) Improvement of surface aspect	(i) Increase of compactness (ii) Improvement of resistance to chemical aggressive agents (iii) Improvement of surface aspect	Setting acceleration for certain formulas		See Table 6
Unfavourable	(i) Setting retardation with certain formulations (ii) Possible increase of shrinkage (iii) Stiffening by possible cement-admixture interaction	(i) Possible increase of shrinkage (ii) Possible incompatibility with certain air-entrainers	Possible increase of shrinkage	Possible increase of shrinkage	

**6.2 The setting stage**

This is the period of time during which fresh concrete in place starts setting, up to before hardening initiates.

*Setting* is a condition defined as occurring at the instant when concrete becomes unsuitable for placement.

*Heat of hydration* is heat evolved by chemical reactions associated with cement hydration during its setting and hardening.

*Plastic shrinkage* is the reduction in volume during setting and/or hardening of concrete due to excessive and rapid evaporation of bleeding water, setting up hydrostatic tension in capillary pores within the mass.

*Bleeding* is the displacement of water from freshly placed concrete caused by settlement or flocculation of solid materials within the mass. It is also called 'water gain'.

**6.3 The hardening stage**

This is a physico-chemical phenomenon causing the particles of hydraulic binders to combine and form the solid skeleton as a result of progressive hydration of the anhydrous components, resulting in a progressive strength gain after setting. *Heat of hydration* is evolved and *strength development* takes place.

*Shrinkage* is the reduction in volume occurring at the hardening and hardened stage of the concrete, caused by physical changes and/or chemical reactions. It is a

function of time but not of external causes like temperature and load.

**6.4 The hardened stage**

This is the period of service life of concrete after a specified attained strength. It is characterized by *unit mass* and by *strength*, measured as follows:

1. *Compressive strength*: the maximum resistance of a concrete to axial loading.
2. *Flexural strength*: the calculated ultimate stress in the outer fibre of a concrete beam specimen subjected to bending.
- 2a. *Direct tensile strength*: the maximum unit stress which a concrete is capable of resisting under axial tensile loading.
3. *Bond*: the adhesion and grip of concrete to reinforcement.

*Modulus of elasticity* is the ratio of the normal stress, below the limit of proportionality of concrete, to the measured instantaneous unit deformation.

*Durability* is the ability of concrete to resist weathering action, chemical attack, abrasion and other conditions of service. It comprises the following factors:

1. *Porosity*: the ratio, usually expressed as a percentage, of the volume of voids in a material to its total

Table 6 Non-chloride frequently used admixtures modifying the resistance against aggressive media (durability)

	Type of admixture	
	Water-reducers and/or high-range water-reducers	Air-entrainers
Main chemical family	See Table 3	Salts of wood resins, fatty and resinous acids and their salts, organic salts of sulphonated hydrocarbons, etc.
<i>Main effects</i>		
Freeze thaw resistance	Improvement due to increased compactness and mechanical strength by using less water but maintaining workability	Highly increased
Resistance to aggressive atmospheric agents (CO <sub>2</sub> , sea weathering)	Improvement due to increased compactness and mechanical strength by using less water but maintaining workability	?
Resistance to chemical aggressive agents (sulphates, sea water, etc.)	Improvement due to increased compactness and mechanical strength by using less water but maintaining workability	Possible improvement due to lowering of capillary absorption
Water penetration	Decrease due to increase of compactness by water reduction	Possible decrease due to lowering of capillary absorption
<i>Secondary effects</i>		
Favourable	Increase of mechanical strength due to water reduction for same workability	Improvement of surface aspect
Unfavourable		Possible decrease of mechanical strength (maximum 20%)



volume, including the voids. It affects

(a) *capillary absorption*: the suction of water into the capillary pores of solidified concrete when one face has been placed in contact with water for a given period, and

(b) *permeability*: the capacity of a hardened concrete to allow flow of a fluid through it under a hydraulic gradient.

2. *Freeze-thaw resistance*: resistance of the hardened concrete to freezing and thawing cycles.

3. *Attack by aggressive solutions*: physico-chemical reaction between cement paste and soluble sulphates in surrounding media, primarily with tricalcium aluminate hydrates.

4. *Carbonation*: reaction between carbonic acid and the lime in the hydrated cement paste to produce calcium carbonate.

5. *Alkali-aggregate reaction*: a reaction between the alkali oxides (sodium and potassium) in some Portland cements and a reactive silica component in certain aggregates, causing abnormal expansion and cracking of concrete in service.

6. *Efflorescence*: a deposit of salts, usually white,

crystallized on the surfaces of building materials and caused by capillary rise or the leaching associated with water penetration.

*Corrosion of reinforcement* is oxidation and deterioration of the reinforcement in concrete by an electro-chemical process. It involves *ionic diffusion*, the migration of ions through materials due to environmental changes.

*Volume change* is either an increase or decrease in volume:

1. *Thermal expansion* is expansion caused by increase in temperature.

2. *Creep* is time-dependent deformation due to sustained load, obtained by subtracting from the total deformation the instantaneous deformation at the instant of loading and the drying shrinkage during this period.

3. *Shrinkage*.

*Miscellaneous effects* include biological attack due to micro-organisms.

The properties that may be modified by the main types of admixtures are summarized in Table 2. Tables 3-7

Table 7 Information sources

Characteristics to be known	Verification or information provided by			
	Verification procedure of conformity with standards	Laboratory testing	Suitability tests	Others
Acceptance		x	x	
Quality control	x			
Efficiency main function	x		x	Technical assistance of manufacturer and/or supplier
Secondary functions	x	x Adapted to importance of work	x Adapted to importance of work	
Secondary effects within the limits of the standard requirements	x	x Depending on specific character of work		
Secondary effects possibility affecting durability	x Standard requirements	x Depending on specific character of work		
Critical characteristics of product	x		x	
Admixture proportioning appropriate to the job site		x Depending on type of work	x	
Interaction with cement used at job site		x	x	Technical assistance of laboratory of cement manufacturer

indicate the contributions of the main types of admixture according to the modification required.

#### **7. PRECAUTIONS IN THE USE OF ADMIXTURES**

It is essential when using admixtures to verify the following:

1. The expected effect by means of *testing*. The effect obtained should not be too sensitive to small variations in the amount of the admixture used, or in the amounts of the other concrete constituents.
2. The extent of *side-effects*. The important points that should be checked are summarized in Table 7.
3. That the effectiveness of admixtures is not affected by the *heat curing regime* to which the concrete may be exposed. In this case it is advisable to follow the manufacturer's recommendations and to verify the effect by laboratory and field tests.

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