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Review on chemical (organic) admixtures in the cementitious materials

M. H. R. Khudhair, B. El Hilal, A. Elharfi

Laboratory of Agro resources Polymers and Process engineering (LAPPE), Team of Macromolecular & OrganicChemistry, Faculty of sciences, Ibn Tofail University, BP 133, 14000, Tel: +212 (0) 537 32 94 00, Fax: +212 (0) 537 32 94 33, Kenitra, Morocco.

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- ✓ Plasticizers,
- ✓ Superplasticizers,
- ✓ Setting of an accelerator,
- ✓ Setting of retarders,
- ✓ Air entraining,
- ✓ Durability of concrete,
- ✓ Compressive strength

https://orcid.org/0000-0002-4205-6710
khudhair.mohammed65@gmail.com ;
Phone: +212633431912;

Abstract

In the present review, we have tried to define the different families of chemical admixtures used in the formulations of cementitious materials, namely: plasticizers, superplasticizers, setting accelerators, setting retarders, air entraining, etc…. We have also presented the different families of each type of those polymeric admixtures and their mechanisms of action.These admixtures can be used either to improve the physical properties of the fresh cement paste including the workability, the fluidity, the setting time (depending on the climatic conditions of its installation in winter and/or summer) and the water content, and used either to improve the mechanical performance of mortar and / or concrete in the hardened state, to know the compressive strength, the porosity, the capillary absorption, and the durability. Or the both at the same time, in the fresh and hardened state, reduction of the quantity of mixing water and subsequently improves its mechanical resistance of compression and its durability.

1. Introduction

Concrete is a composite material consisting of a mixture of hydraulic binder (cement), aggregates (gravel and sand), an amount of water required for hydration reactions represents about 25% of the cement mass and another amount of (at least double) water is required in order to obtain satisfactory workability of the fresh concrete during the placing operations, air and, if necessary, admixture [1–4]. Because of its heterogeneity, it is essential to understand the role of each constituent in order to clarify its behavior [5–7]. The water/cement ratio in a Portland cement paste is 0.5 according to the standard EN 196-1. However, the total porosity represents between 25 and 30% of the volume and the pore size varies from nanometer to a few millimeters [8]. This porosity will reduce the mechanical strength and durability of the material.

Concrete is, therefore, a porous composite material [9], whose performance varies according to its capillary porosity and excess water required for the workability of fresh concrete. The installation of concrete requires much more water than the cement requires for its hydration [2,10], in the long-term. Thus, the excess water evaporates, leaving voids in the concrete, which makes the cementitious material brittle in the hardened state [11]. Thinking of adding small quantities of polymeric admixtures to fresh concrete, we can significantly reduce the amount of water needed to achieve the desired workability. Moreover, these organic additives have become widely used in the cement and concrete industry, etc., to prolong the setting times [12,13], reduce water requirements (plasticizers and superplasticizers) [9,14,15] and also for entraining air "air entraining" [16]and to improve the physical properties and mechanical performance of the mortar and/or concrete in the fresh and hardened state. These improvements result from several mechanisms of action among which we find, during hydration, the grains of cement flocculate one on the other. However, in the presence of surfactants "plasticizers", its molecules adsorb into fine grains of cement or additions, subsequently modifying the electrostatic (physical-chemical) forces and creating a dispersant of these grains [17,18]. While the introduction of superplasticizers organic molecules suspended in a cementitious material, many of them are attached to the surface of the cement particles "adsorption", reducing the attractive forces of van der Waals interparticle interactions and also creating an entropic effect [15,19].However, the hydrates that form during the hydration of aluminous cement are metastable and gradually change over time. This process is accelerated under conditions

of heat and humidity. The microstructural changes associated with this phenomenon. The term "conversion membrane" does not imply only a change in the crystalline structure and morphology of the hydrate; these transformations release water with consequent increase of porosity and less cohesion between the grains of cement. This brings significant decreases in strength and durability of the concrete. In whatever way in the presence of plasticizers and superplasticizers, the hydrates released during hydration form a sort of membrane which acts as a brake on the diffusion process which in turn leads to the dormant period [12]. It seems probable that the chloride ion “from the accelerating agent”, due to its small size and its high mobility, makes it possible to penetrate more easily into the pores of the formed membrane, thus allowing a faster unwinding of the process of setting and hardening [20]. Otherwise, when the water is added to the cement, the calcium ions and the hydroxyl ions are released to the surface of the cement particles, the setting retarder reacts with these precipitated ions, crystalizing the hydration products C_2S and C_3S and thereafter the hydration is delayed [21,22]. In the case of an air entraining, a lot of air microbeads are injected to reinforce the granular skeleton of the material, while minimizing its porosity/capillary absorption and increasing its durability [23].
The aim of this review is to present a bibliographic study on the various chemical admixture synthesized especially for use in the formulation of building materials (cement, mortar, and concrete) in order to facilitate their placement according to the conditions and requirements on one hand, and on the other hand, to improve the physical properties and the mechanical performance of these materials in the fresh and hardened state.
However, in this review we will limit ourselves to the cases of organic additives of the plasticizers, superplasticizers, setting accelerators, setting retarders, air entraining.

2. Water reducer plasticizers

The water reducing plasticizers are composed of organic polymers based on lignosulphonates, hydroxylated polymers and hydroxycarboxylic acids which, without modifying the consistency, make it possible to reduce the water content of a given concrete, or which, without modifying the water content, considerably increases the sagging / spreading, or which produces both at the same time.

2.1. Chemical families of water-reducing plasticizers

2.1.1. Lignosulfonates

The lignosulfonate molecule is a substituted phenylpropane unit containing hydroxyl, methoxy and sulfonic acid groups (Figure.1) [17,18,24,25 and 26].

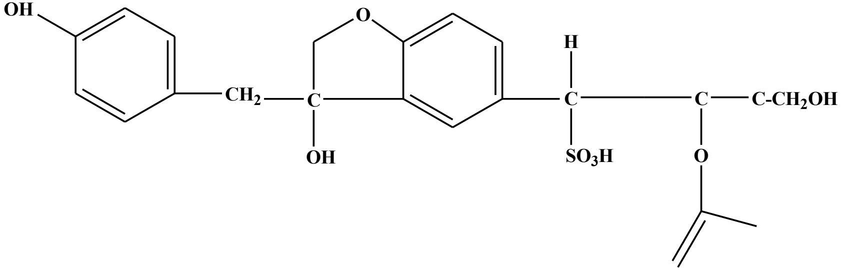


Figure 1: *Repetition of the unit of a lignosulfonate molecule*

The lignosulfonate polymer is in the form of spherical microgels as shown in the Figure (2) [26,27].

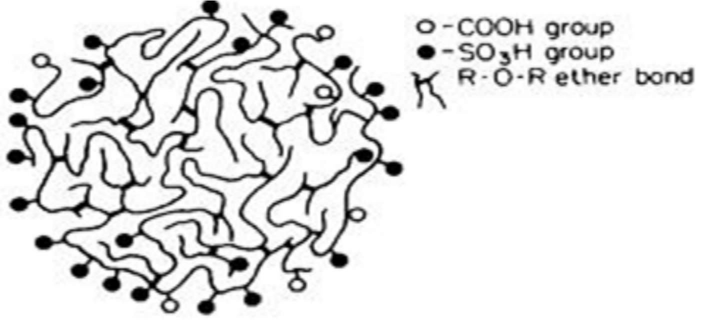


Figure 2:*Schematic representation of a micro-freeze unit of lignosulfonate polyelectrolyte* **[26]**

This material accounts about of 20% of the wood composition “composite material”. While the 80% represents the sulfonation products of lignin, various carbohydrates “sugars” and sulfuric acid or free sulfates. The sugars contained in the lignosulphonates vary according to the type and the concentration. The different types of sugars found are shown in Figure (3), give ventilation of sugars in untreated sulfite lye [18] and two water-reducing commercials [28].

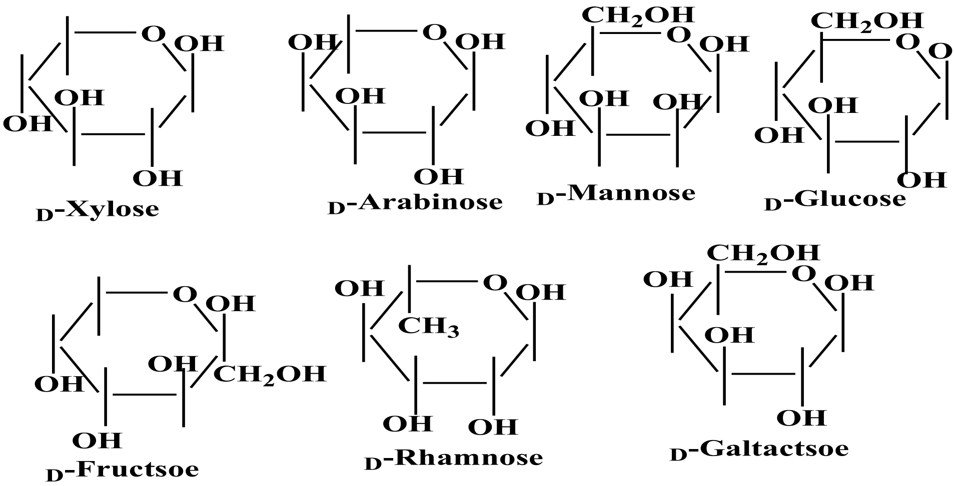


Figure 3:*Formula of sugars found in untreated and purified lignosulfonate materials* [28]

2.1.2. Hydroxycarboxylic acids

As indicated by their names, these are organic chemicals that have hydroxyl and carboxyl groups in their molecules. They are produced from raw materials, which are in the form of ammonia or triethanolamine salts, by chemical or biochemical means, having a constant and high purity. The Tables 1 and 2 show the types and formulas of the materials that have been reported to find application in the formulation of this type of mixture.

Table1: The various types of materials and their formulas which are used in the formulation of hydroxycarboxylic acids

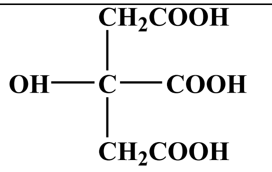
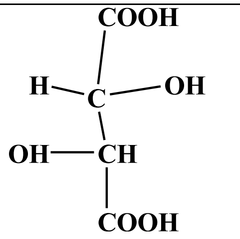
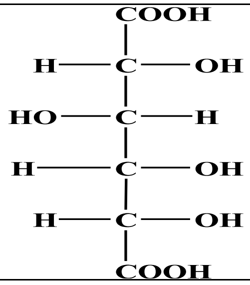
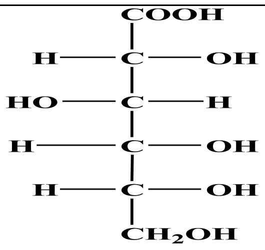
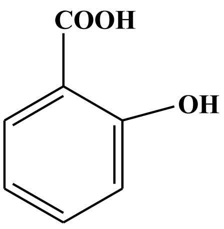
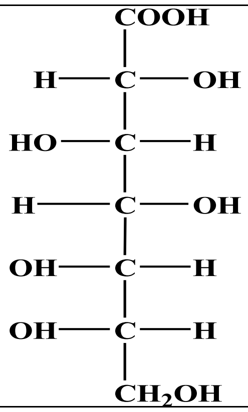
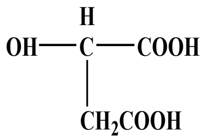
	citric acid [29,30]	**Tartaric acid** [29, 30]	**Mucous acid** [25,30,31]
Group Functionality OH	1	2	4
Group COOH	3	2	2
Molecular weight	192	150	210
Formula			

Table 2: Hydrocarboxylic acids used in admixture

	Gluconic Acid [29,30]	**Salicylic acid** [32]	**Hypotonic Acid**	**Maleic Acid** [30]
Group Functionality OH	5	1	6	1
Group COOH	1	1	1	2
Molecular weight	196	138	230	134
Formula				

2.1.3. The hydroxylated polymers

The hydroxylated polymers are derived from natural polysaccharides, such as corn starch, by partial hydrolysis to form telomer-containing lower molecular polymers consisting of 3 to 25 glycoside units (Figure. 4) [33].

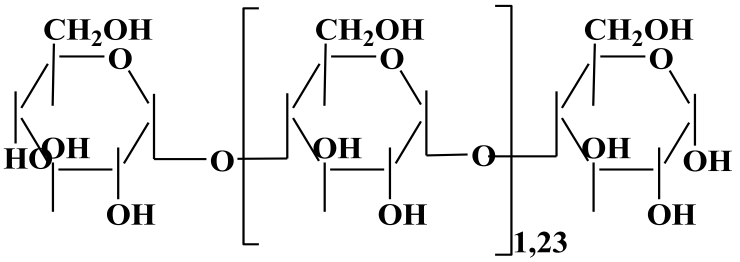


Figure 4: *The hydroxylated polymers of polysaccharide derivatives [33]*

2.2.Mechanisms of action of water reducing plasticizers

The cement in contact with water tends to agglomerate, it is the flocculation. However, in the presence of plasticizers, (which is some sort of surfactants) are substances concentrating at the interface of two immiscible phases thereby modifying the electrostatic "physical-chemical" forces acting on this interface. These substances are adsorbed on fine grains of cement or additions, dispersing the grains of the cement from one another, suspended in water, giving them a negative charge which leads to a repulsion between the grains which are thus deflocculated (Figure. 5).

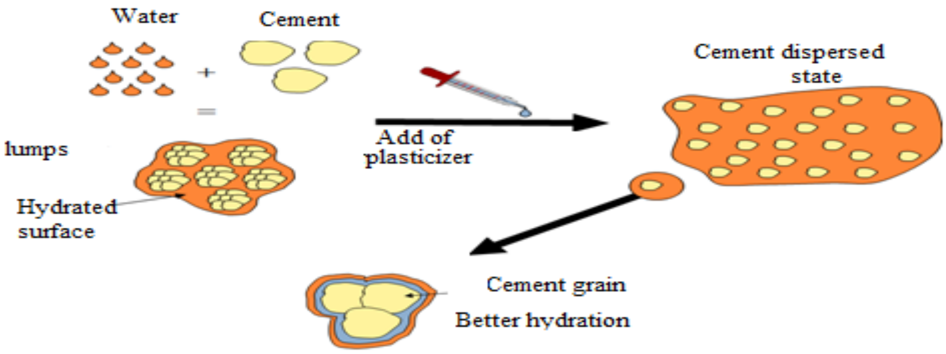


Figure 5: *Mode of dispersion of the grains of the cement by plasticizers)*

1. Superplasticizer with high water reducer

The high water-reducing superplasticizers are synthetic polymers made especially for the concrete industry. They are based on sodium salts or sulfonated naphthalene-formaldehyde (SNF) [34–37], sulfonated melamine-formaldehyde (SMF) [38,39], acrylic ester copolymer (polyacrylates) [40], or high purity lignosulfonate [41,42]. These admixtures allow us without modifying the consistency to greatly reduce the water content of concrete and to improve physical properties and mechanical performance.

1.1.The different families of superplasticizers

1.1.1. Formaldehyde sulfonated naphthalene (FSN)

The FSN was one of the first materials mentioned in the literature as a water-reducing agent [41,42], but only since 1970 has found extensive application in addition formulations. This material is produced from naphthalene treated with the mixture of sulfuric and nitric acid under conditions conducive to the formation of β-sulfonates. The subsequent reaction with formaldehyde leads to the polycondensation of FSN acid by neutralization with sodium hydroxide [27,43,44 and 49]. The process is illustrated in Figure (6).

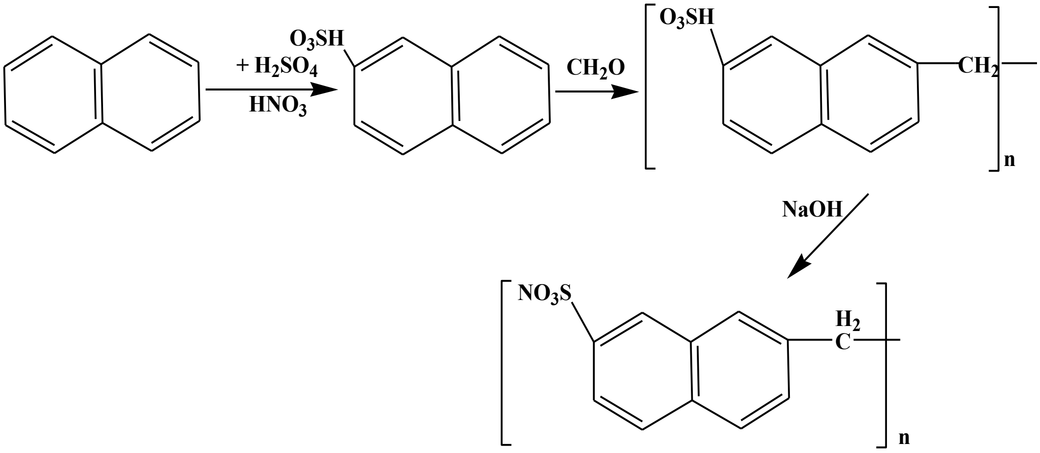


Figure 6: *Formaldehyde sulfonated naphthalene (FSN)*

The value of *n* is generally low which gives telomeric products, but the conditions are chosen to obtain a proportion of high molecular weight product to the polymers because it is more efficient [46]. The amount of sodium sulfate by-product formed by the neutralization of the excess sulfonation reagent varies according to the process used, but may be reduced by a subsequent precipitation process using citricacid[47,48] .

1.1.2. Sulfonated melamine formaldehyde (SMF)

This type of chemical was first developed [49,50] in the 1950s as a dispersant for a wide variety of industries, but it was only ten years later that the possibilities of use in concrete have been recognized. It is manufactured according to standard techniques of resining according to the method [51] shown in Figure (7). The duration of the polymerization time will influence the molecular weight of the product. This material is normally used alone or in combination with FSN. When used alone, it is typified by having minimal effect on air entrainment or setting time.

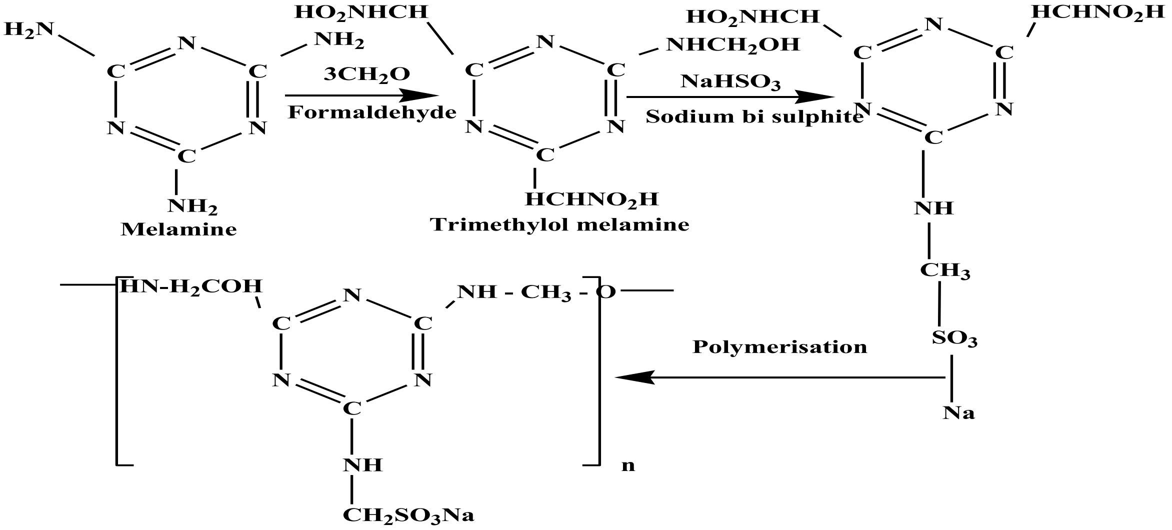


Figure 7: *Sulfonated melamine formaldehyde* [51]

1.1.3. Polyacrylate

The various types of polyacrylate polymers are made from the relevant monomers by a free radical mechanism using peroxide initiators and may be "block" or "random" polymers depending on the degree of pre-polymerization of the monomers used (Figures. 8-10) [11,52].

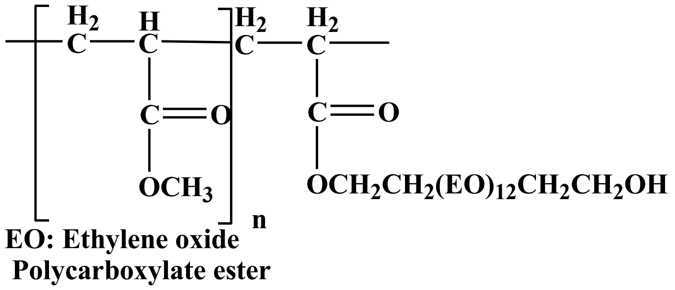


Figure 8: *Polycarboxylate ester* **[52]**

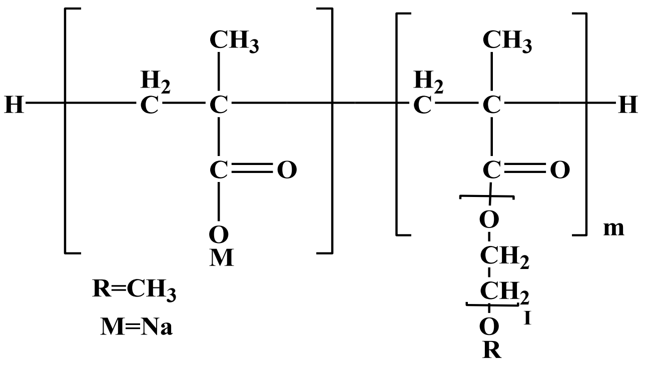


Figure 9: *Copolymer of carboxylic acid with acrylic ester* **[52]**

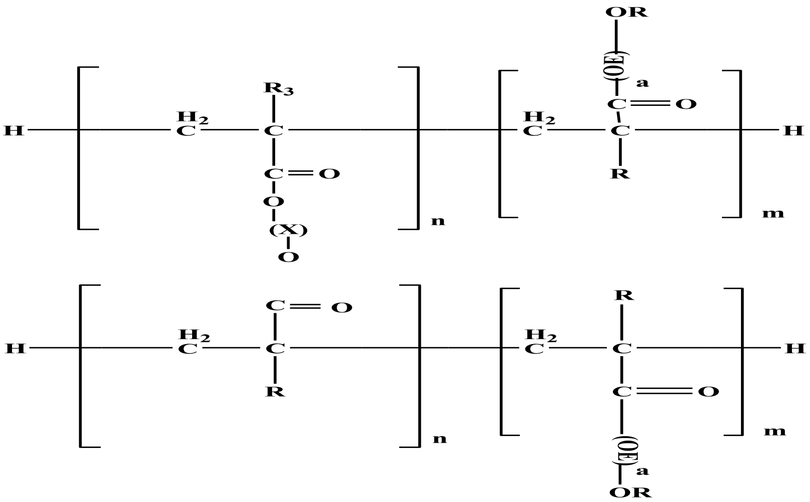


Figure 10:*Crosslinked Acrylic Polymer* **[52]**

1.2.Mechanisms of action of superplasticizers with a high water reducer

When the organic molecules of superplasticizers are introduced into a suspension of a cementitious material, a large part of them is attached to the surface of the cement particles “adsorption”. These latter reduce the attractive forces of interparticle interactions of van der Waals that exist between the atoms of the different particles (Figure .11).

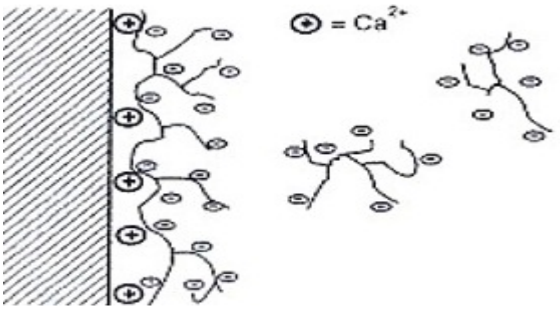


Figure 11:*Schematic representation of the adsorption of a polymer on the surface of a particle according to [57]*

The adsorption of negatively charged polymers takes place via bivalent Ca^{2+} ions. The greater the molecular weight of the polymer and the more Ca^{2+} ions in the interstitial solution, the greater the amount of adsorbed polymers. It, therefore, creates a negative charge on the surface of the repulsive particles (Figure .11). This effect does not depend on the molecular weight of the polymer except in the case of very low molecular weights [53–55].

Another mode of action called an entropic effect requires molecules that one part can be placed or fixed on the surface of the particles and the other part can be deployed in the liquid because of its affinity with the latter. In this case, when two "hairy" particles approach each other so that the chains can interpenetrate, this causes an increase in the energy of the system associated with a repulsive force between the two particles (Figure. 12).

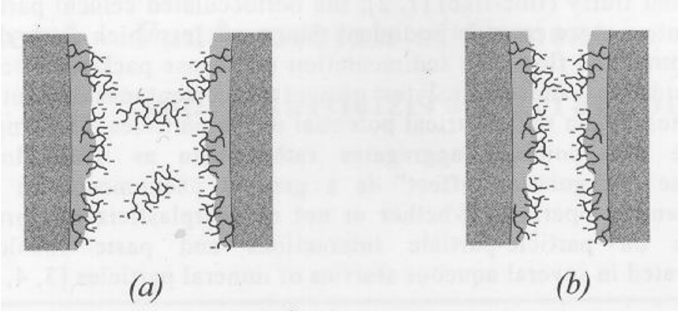


Figure 12:*Schematic representation of the mechanisms of action of superplasticizers: (a) electrostatic repulsion of a charged polymer;b) steric repulsion of an adsorbed polymer according to [59]*

The adsorption of large molecules creates repulsive forces, whether the polymer molecules are charged or not. The polymerized chains cannot penetrate one another, thus preventing any flocculation. This entropy effect is amplified with the molecular weight and degree of branching of the polymer [19,55]. On the other hand, the different molecules of the long chain of superplasticizers act according to the different basic mechanisms developed, by wrapping themselves around the cement grains and giving them a highly negative charge so that they repel each other, leading to a dispersion of the cement grains (Figure .13). The superplasticizers based on sulfonated poly-naphthalene and poly-melamine act mainly on the Van der Waals forces and the double layer interaction force. However, polyacrylate based superplasticizers act mainly because of their entropic effect.

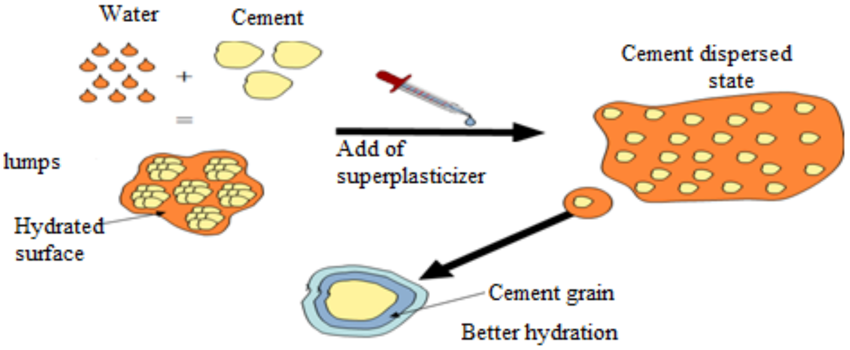


Figure 13: *Mode of dispersion of the grains of the cement by superplasticizers*

2. Setting and hardening accelerators

The setting accelerators are admixtures which are mainly raw materials such as calcium chloride, calcium nitrate, calcium formate [56,57], calcium thiocyanate, and calcium thiosulfate. This increases the rate of cement hardening in the concrete and consequently reduces the setting time so that finishing operations can proceed without undue delay.

2.1.The different families of setting accelerators

2.1.1. Calcium chloride

The calcium chloride ($CaCl_2$) is produced as a by-product of the process for the manufacture of sodium carbonate as shown in Figure (14), [58,59 and 64].

$$\underset{\textbf{Limestone}}{CaCO_3} + 2NaCl \xrightarrow{\textbf{Brine solution}} Na_2CO_3 + CaCl_2$$

Figure 14: *Calcium chloride*

The calcium chloride has been used since 1885 [60]. There has been controversy over the use of this material in concrete containing embedded metal due to the possibility of corrosion, especially when the concrete is porous in nature. However, the calcium chloride remains a highly effective material for use in unreinforced concrete for economical production in winter conditions and its effects on concrete, whether beneficial or undesirable.

2.1.2. Calcium formate

The calcium formate ($Ca(HCOO)_2$) results as a by-product in the manufacture of a polyhydric alcohol, pentaerythritol as shown in the Figure (15) [60 and 61]:

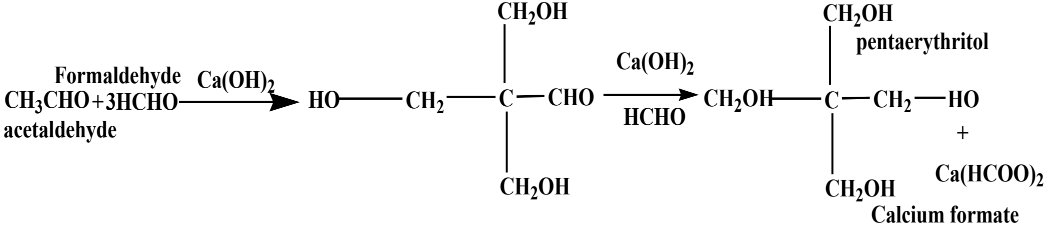


Figure 15:*Calcium formate*

It is obtained in the form of a fine powder and is normally supplied in the form of an accelerating mixture because of its limited solubility in water (about 15% at normal ambient temperature).

2.1.3. Triethanolamine

The triethanolamine (N $(C_2H_4OH)_3$) is an oily liquid soluble in water with a fishy odor. It is produced by the reaction between ammonia and ethylene oxide as illustrated in Figure 16, [12,20 and 22]:

Figure 16:*The Triethanolamine*

It is normally used as a component in other mixing formulations and rarely, if ever, as the sole ingredient.

2.2.Mechanism of action of setting and hardening accelerators

During hydration of cement, the released hydrates form a kind of membrane which acts as a brake on the diffusion process which in turn leads to the dormant period. It seems probable that the chloride ion seen from its small size and its high mobility makes it easier to penetrate the pores of the membrane formed, which allows the diffusion process to unfold more rapidly.

3. Setting retarder

The cement pastes forms as soon as the water is added to the cement which gradually hardens. This hardening is called setting [20]. This setting is a process of transforming an initial state of dispersed concentrated slurry, to a final state of the bonded and reinforced particle system. This transformation is achieved by chemical reactions between cement particles and water “cement hydration” [62,63]. The normal setting of cement is associated with the hydration of Alite (C_3S) and the formation of the calcium silicate hydrate (CSH) phase [64]. However, in hot weather, it causes rapid evaporation of the surface water of the cement and/or concrete paste in the fresh state. Then, retarders are used to shift the acceleration effects of hot weather on setting times or delay the concrete setting when unusual conditions are different [14].

3.1.The different families of setting retarder

The main compounds which are the cause of the manufacture of retarding agents are lignosulphonates or sulfonated lignins which are water-soluble anionic polyelectrolyte polymers: they are by-products from the production of wood pulp using sulfite pulp.

Most de-lignification in the sulfite pulp involves an acid cleavage of ether bonds that connect many lignin constituents. Electrophilic carbocations produced during ether cleavage react with bisulfite (HSO_3^-) ions to give sulfonates.

$$\mathbf{R\text{-}O\text{-}R' + H^+ \rightarrow R^+ + R'OH}$$
$$\mathbf{R^+ + HSO_3^- \rightarrow R\text{-}SO_3H}$$

The main site for ether cleavage is α-carbon “carbon atom attached to the aromatic ring” of the porphyric side chain (linear carbon). The following structures (Figure. 17) do not specify the structure since lignin and its derivatives are complex mixtures. The groups R_1 and R_2 may be a wide variety of groups found in the structure of the lignin. Sulfonation occurs on the side chains, not on the aromatic ring as in p-toluenesulfonic acid.

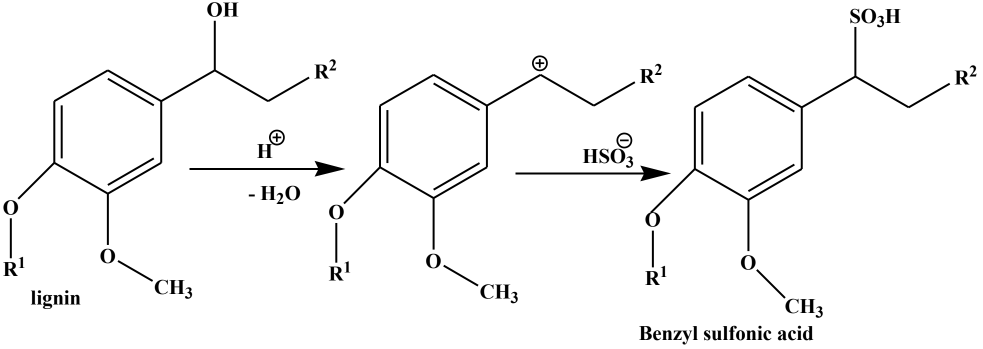


Figure 17: *Lignosulfonates, or sulfonated lignin* [14]

3.2. Mechanism of action of setting retarder

When the setting retarder is incorporated into the mixing water, it is adsorbed by the calcium hydroxide cores, which prevents the growth of the calcium hydroxide nuclei to a certain level of super saturation “Adsorption” (Figure. 18).

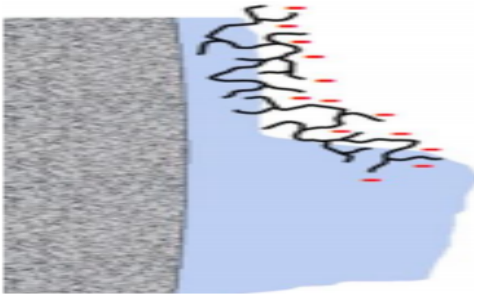


Figure 18: *The adsorption of the retarder mixture on the surface of the cement*

Thus, the period of resemblance was prolonged due to the increase in saturation level of calcium hydroxide before the onset of crystallization [22], [65]. Thereafter, the setting retarder admixture reacts with one or more components of the cement to form a precipitate on the cement particles "precipitation", which confers a low permeability "coating" on the cement particles. Then, the setting retarder adjuvant forms complexes with the Ca^{2+} ions which are released by the hydration → Ca^{2+} reduction available "complexions" (Figure. 19).

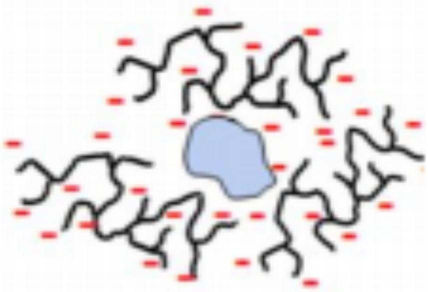


Figure 19: *The formation of complexes with calcium ions*

In other words, it causes a formation of complexes with the calcium ions in solution released by the cement during the first minutes of hydration. This formation increases the solubility of the cement, that is to say, increases the concentration of Ca^{2+}, OH^-, Si, Al, and Fe in the aqueous phase of the cement paste which will occur during hydration in the presence of the retarder [21]. Finally, the setting retarder admixture poisons the nucleation sites of Ca $(OH)_2$ and/or CSH and inhibits the formation of bonds between the hydrated products "nucleation" (Figure 20). In other words, calcium ions and hydroxyl ions accumulate in solution and will not precipitate to form calcium hydroxide [21,66]. In this way, hydration is delayed.

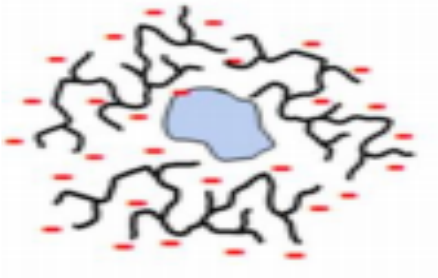


Figure 20: *Nucleation between hydrated products*

4. Air entraining

The air entraining agents are organic materials, usually in the form of a solution which, when added to the mixing water of the concrete, results in a controlled amount of air in the form of uniformly dispersed microscopic bubbles**.**

4.1. The various families of air-entraining admixture

The literature describes numerous chemical surfactants as suitable for the formulation of air entraining agents for concrete. However, in practice, most commercial products based on a relatively limited number of raw materials and are described as following:

4.1.1. Neutralized wood resins

There are several materials that make up this category, including wood-derived tall oïl resins and pine stump extracts sold under the well-known Vinsol ™ brand. They consist of complicated mixtures containing more or less abietic acid (Figure .21) with pimaric acid and phenolic compounds such as phlobaphenes [67].

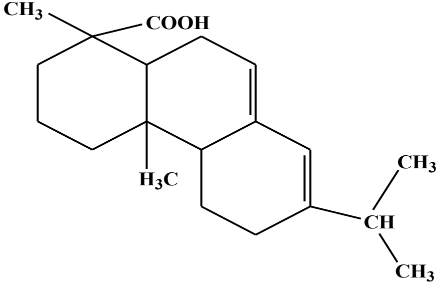


Figure 21: *Abietic acid*[67]

4.1.2. Salts of fatty acids

In order to satisfy the requirements of the user performance and the ability to form stable aqueous solutions of adequate strength, the fatty acids shown in Table 3 are used as air-entraining agents for concrete in the form of alkali metal salts. These acids are present in a chain length distribution in natural fats and oils such as tall oil and coconut oil and are used in the form of such a mixture. These products, in contrast to neutralized wood resins, are compatible in solution with certain lignosulfonates and hydroxycarboxylic acid salts to form mixtures possessing both air entrainment and water reduction capabilities.

Table3: Fatty acids used as air-entraining agents

Fatty acid	Formula	Reference
Oleic acid	$\mathbf{CH_3 — (CH_2)_7 — CH{=}CH — (CH_2)_7COOH}$	[67]
Citric acid	$\mathbf{C_9H_{19}COOH}$	[68]

4.1.3. Alkyl aryl sulfonates

The alkyl aryl sulfonates find application in both the production of lightweight concrete and to improve the freeze-thaw durability of normal concrete. The usual raw material is ortho-dodecyl benzene sulphonate, which is a basic surfactant used in a variety of industrial and domestic detergents. The formula is illustrated in Figure 22.

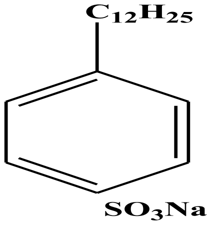


Figure 22: *Orthododecyl benzene sulfonate*

The hydrocarbon base is derived from petroleum and, in fact, contains a chain length distribution with the predominant species C_{12}. In addition, there may be a greater or lesser degree of chain branching. The sulfonation process used may vary from a direct reaction with sulfuric acid to SO_2 / SO_3 mixtures, but always results in an excess of sulfuric acid. Upon neutralization, a proportion of sodium sulfate is produced which is preferably kept to a minimum for the mixing formulations

4.1.4. Alkyl sulfate

The literature describes the use of several materials of this type and these are shown in Table 4. These products are also compatible with many water-reducing agents to produce water-reducing air entrainment agents.

Table 4: Alkyl sulfates used as air entraining agents

Matériel	Formula	Reference
Sodium dodecyl sulfate	$\mathbf{C_{12}H_{25}SO_4Na}$	[16]
Sodium tetradecyl-ate sulfate	$\mathbf{C_{14}H_{29}SO_4Na}$	[69]
Sodium acetyl sulfate	$\mathbf{C_{16}H_{33}SO_4Na}$	[70,71]
Sodium of oleate sulfate	$\mathbf{CH_3(CH_2)_7CH{=}CH—(CH_2)_8SO_4Na}$	

4.1.5. Phenol Ethoxylates

Phenol Ethoxylates (non-ionic materials) are different from the previous four categories. Although not widely used, they are very effective at low levels of addition and solutions of 2-4% by weight of the cement. The most common material is nonylphenol ethoxylate, and limited studies indicated that the largest value of n in Figure 23 is most effective.

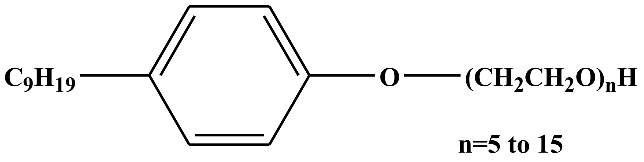


Figure 23: *Nonylphenol ethoxylates*

4.2.Mechanisms of action of air entraining agents

Depending on the chemical nature of the air entraining agents, different mechanisms may occur. Among the main ones, we can mention the reduction of the surface tension of water, the adsorption on the cement particles, and the formation of an insoluble film. The molecules are then found in three different places: a quantity is concentrated at the air/water interfaces, an amount is adsorbed onto the cement particles, and an amount remains in solution. Moreover, as a rule, when an air-entraining agent is absorbed or adsorbed on an interface, this one will orient itself in such a way that each of its two units is in the phase preference (water, air or cement particles). The adsorbed molecules form a film and have their hydrophilic head oriented in the aqueous phase, thereby decreasing the energy required creating air/water contact surfaces (Figure 24). They then facilitate the formation of air bubbles during mixing, stabilize those trapped by the turbulences generated by the blades of the mixer and the particles, prevent their coalescence, and thus make it possible to obtain a homogeneous and dense network of small bubbles, Air [23,72]. Otherwise, if the air-entraining agent is ionic, the bubbles will then acquire a charge, thus causing electrostatic repulsion effects, which results in a separation of the mixture. In the case where the air entraining agent used is nonionic, it will not be able to change the electrical potential of the bubbles. It can then cause the orientation of a layer of water, known as the hydration sheath, around the air bubbles, enabling them to be separated in a much less efficient way, to stabilize and deflocculate the system [73].

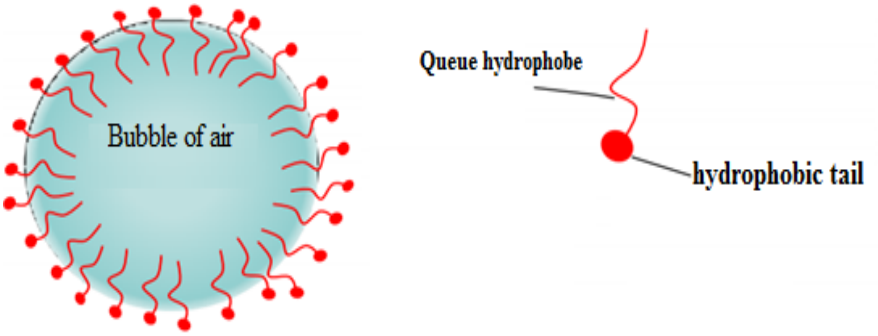


Figure 24: *The air/water surface tension*

The air entraining agents can also adsorb onto the cement particles. Indeed, when the cement is brought into contact with the water, the first hydration reactions take place and the cement particles acquire a positive charge due to the presence of the calcium ions. Thus, due to the electrostatic attraction between positive and negative charges, the anionic surfactants adsorb onto the cement particles. The hydrophobic part of the surfactant is then found in water. The cement particles become hydrophobic and bind to the air bubbles preventing them from rising or fusing with other air bubbles as shown in Figure 25.

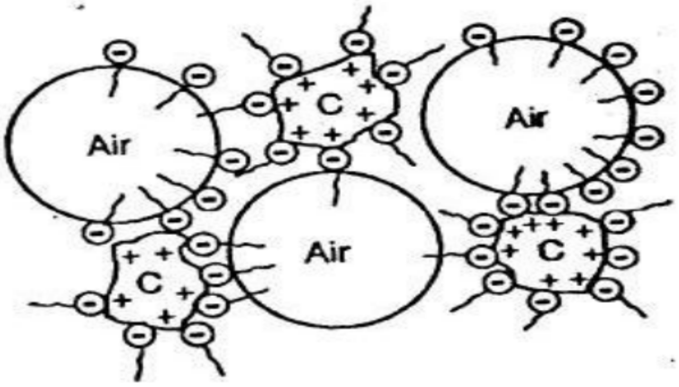


Figure 25: *The adsorption of air entraining agents on the cement particles*

Conclusion

This bibliographical analysis enabled us to appreciate the various efforts carried out in recent years by various researchers in order to try to shed light on all the phenomena that occur in the formulation of cementitious materials based on chemical admixtures (Plasticizer / superplasticizer/ setting accelerator/setting retarder and air entraining). There is currently a very wide variety of these admixtures (polymeric materials) on the market. However, research continues to develop new polymer telomeres and resins that would yield much more interesting performance. Thus, with current global concerns about respect for the environment and sustainable development.

We have found that these admixtures, which can be used in the manufacture of cement and concrete, are used to improve the physical properties of the fresh cement paste, which allowed us to facilitate their installation according to the conditions and the climatic requirements ,or to improve the mechanical performance of the mortar and/or concrete in the hardened state, and / or both at the same time.

The significant increase in compressive strength and durability of the concretes / reduction of the quantity of mixing water; would cause a reduction in the water/cement ratio; / variation in the initial and final time depending on climatic conditions. This would generally reduce the overall porosity of the material while at the same time improving its compressive strength and its durability.

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