

The Role of Superplasticizers in The Development of Environmentally-Friendly Concrete

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THE ROLE OF SUPERPLASTICIZERS IN THE DEVELOPMENT OF ENVIRONMENTALLY-FRIENDLY CONCRETE

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ABSTRACT

Since their introduction in the early 60's, superplasticizers have become an essential component of concrete. By reducing substantially the amount of water in concrete, superplasticizers have contributed to a significant reduction in its porosity and to a concomitant increase in its compressive strength and durability. These chemical admixtures have also been at the forefront of the use of mineral admixtures such as silica fume, fly ash and blast-furnace slags in high-performance concrete. By making possible the use of these industrial by-products as a partial replacement of cement, superplasticizers are also contributing to reduce the emission of CO₂ in the atmosphere, a key-issue in several industrialized countries.

This paper will review some important aspects related to the use of superplasticizers in concrete. Important properties related to the chemistry and to the mode of action of these chemical admixtures will first be briefly recalled. The impact that superplasticizers have exerted and still continue to exert on concrete technology will then be examined through two important aspects of sustainable development, namely reduction of CO₂ emissions and durability.

INTRODUCTION

According to the United Nations, there will be at least 20 megacities of more than 10 millions habitants in the year 2025. These cities will require large amounts of construction material for buildings and municipal infrastructures as well as for facilities necessary to handle food, drinking water and sewage. With an annual production of approximately 7 billion tons, portland cement concrete is the most commonly used construction material throughout the world and it is expected that its use will continue to expand significantly in the next few years. Mostly due to its relative low cost, easy availability and versatility, portland cement concrete has found many useful applications, from massive dams to high-rise buildings.

With regards to concrete technology and sustainable development, two important aspects need to be considered. First, it is important to examine the short-term impact that the production of portland cement has on the environment. For instance, it has been estimated that the production of one ton of portland cement is associated to the release in the environment of an equivalent amount of CO₂. Any means that would reduce the use of cement while maintaining the overall performance of concrete could thus certainly be considered as beneficial to the environment. The long-term behavior of concrete or durability is the second aspect that is important to evaluate, since it does not make any sense to reduce the short-term impact on the environment if, by doing-so, we exert a higher detrimental long-term influence on the environment.

The objective of this paper is to evaluate the impact that superplasticizers have exerted on the concrete industry through the development of high performance concrete (HPC). More precisely, we will concentrate on how these polymers contribute to sustainable development by favoring the use of mineral admixtures in concrete and by increasing the durability of concrete structures.

CHEMISTRY OF SUPERPLASTICIZERS

Until the early 1930's, the composition of portland cement concrete consisted primarily of cement, water and aggregates. The accidental discovery of the benefits of air entrainment in concrete by chemical admixtures in the 1940's was the first major breakthrough in concrete technology. This finding rapidly led to the development of several chemical products and admixtures that enhanced various properties of concrete such as workability, setting time and early strength. In the early 1960's, high-range water reducers or superplasticizers were developed and introduced into the concrete technology market.

Superplasticizers are chemical admixtures that can be considered to pertain to the category of polymeric dispersants. In terms of chemical structure, superplasticizers can be broadly classified into two general categories. The first category, the sulfonate-based superplasticizers, are the most important group of superplasticizers currently in use in the concrete industry. The first and most-widely accepted compounds of this group are the poly-*n*-naphthalene sulfonates (PNS), the molecular structure of which is illustrated in Fig. 1. The synthesis of PNS superplasticizers involves several steps. It begins with the sulfonation of molten naphthalene with concentrated sulfuric acid at high temperature and pressure for several hours, followed by condensation of the *n*-naphthalene sulfonate with formaldehyde, neutralization with a suitable alkali and filtration to

eliminate calcium sulfate. The resulting product is clear dark-colored liquid containing between 30 and 40% solids.

Polymelamine sulfonates (PMS) are a second family of sulfonated superplasticizers that are also widely used in the concrete industry. Typical molecular structure of PMS is illustrated in Fig. 2 and, as for the PNS described above, the synthesis of this superplasticizer involves several steps. First, formaldehyde reacts with the amino groups of melamine in alkaline conditions, yielding an addition product containing one or more methylol groups (CH_2OH), depending on the formaldehyde/melamine ratio. Sulfonation of one of the methylol groups is then performed using sodium bisulfite under the same alkaline conditions. Polymerization of the sulfonated monomeric units is then initiated by mild heating under slightly acidic conditions. Finally, when the desired degree of polymerization has been obtained, the reaction is stopped by increasing the pH to slightly basic pH values and the final product is filtered to eliminate any non-desirable by-products.

Organic polymers bearing carboxylic acid groups constitute the second category of superplasticizers. Several polycarboxylate polymers and in particular polyacrylates have been proposed as concrete superplasticizers since the early 1980's. Polyacrylate polymers (typical molecular structure shown in Fig. 3) are prepared by a free radical addition polymerization of acrylic monomers. The polymerization reaction between the monomeric units, typically acrylic acid ($\text{CH}_2=\text{CH}-\text{COOH}$) or methacrylic acid ($\text{CH}=\text{C}(\text{CH}_3)-\text{COOH}$) and ester derivatives of these monomers, is initiated by a free radical initiator species, typically a peroxide. The acrylic free radical reacts with an acrylic monomer to form a dimer free radical which, in turn, reacts with a third monomer and so on. This chain reaction propagates until the free radical species are quenched by free radical scavengers to form inactive terminal products. The average molecular weight of the final product depends on the concentration of the free radical initiator, higher concentration resulting in more polymers of lower average molecular weight.

HYDRATION OF PORTLAND CEMENT

Even though the details of the chemical reactions that take place during the hydration of portland cement are quite complex, it is generally agreed that the processes that transform portland cement paste into a hard solid mass are now relatively well understood, at least from a macroscopic point-of-view. As illustrated in Fig. 4, the initial hydration of portland cement can be schematically decomposed into five steps (1,2). The first step, the mixing period, is characterized by a rapid dissolution of the different ions provided by the various phases. This step is exothermic and the surface of the cement particles becomes partially covered with hydrated calcium silicate (C-S-H) and with ettringite (a hydrated trisulfo-aluminate salt of calcium). The heat released is due to a combination of phenomena such as wetting, dissolution of electrolytes (i.e. CaSO_4), surface hydration reactions, and absorption of solution species. The presence of a superplasticizer tends to decrease the heat evolved. This is generally attributed to the adsorption of superplasticizer's molecules on the cement particles that slows down the hydration rate.

During the second step or dormant period, the pH and Ca^{+2} ion content that had rapidly increased during the mixing period slows down the dissolution of the clinker phase. Heat evolution is much lower but still measurable. During this period, the aqueous phase becomes saturated in Ca^{+2} , but

lime ($\text{Ca}(\text{OH})_2$) does not precipitate, most probably because of its slow germination rate in comparison with that of the competing C-S-H. Some flocculation of the cement grains might also occur during this period. The addition of superplasticizer tends to lengthen the dormant period, a very helpful property when it comes to the transport and placement of concrete.

The following step or initial setting period is characterized by a sudden activation of the hydration reaction triggered by the precipitation of lime when there is almost no more silicate in the aqueous phase. The dissolution of all the portland cement components is accelerated by the sudden consumption of Ca^{+2} and OH^- ions. The heat evolution starts to increase, slowly at first (because of endothermic C-H precipitation) but more rapidly at a later stage. During this phase, the hydrated silicate and aluminate phases start to create some interparticle bonding, resulting in a progressive stiffening of the paste. The addition of superplasticizer slightly retards the setting and the hydration processes and higher dosages will generally induce a longer retardation.

Since in most portland cement, there is less calcium sulfate than the amount necessary to react with the aluminate phase, the SO_4^{-2} ions are generally totally consumed during the formation of ettringite. During the fourth step or hardening period, between 9 and 15 hours after initial mixing, ettringite becomes the source of sulfate to form monosulfo-aluminate with the remaining aluminate phase. This reaction generates heat and accelerates the hydration of silicate phases.

Finally, during the fifth step, the cement grains are covered by a layer of hydrates that becomes thicker and thicker so that it becomes progressively harder for water molecules to reach the still unhydrated cement particles. Hydration slows down, as does the heat evolution, mainly because it is now governed by the rate of diffusion of water molecules through the hydrate layers. Portland cement hydration stops either when there is no more anhydrous phase (well cured high water/cement ratio concrete), or when water can no longer reach the unhydrated phases (very dense and highly deflocculated systems) or when there is no water available, if that happens (very low water/cement ratio). Addition of superplasticizer have also a retarding effect on these last two phases and generally the overall heat is lower in the presence of superplasticizer.

MODE OF ACTION OF SUPERPLASTICIZERS

It has long been known that the strength of any given concrete is inversely related to the water/cement ratio, i.e. the lower the water content of the concrete, the stronger it is. Water is an essential ingredient of concrete where it plays two basic roles: 1) it gives concrete the required rheological properties and 2) it participates in the reactions of hydration. The ideal concrete should thus only contain the minimal quantity of water necessary to develop the maximum possible strength of cement while providing sufficient workability for placement. However, since cement particles have a strong tendency to flocculate when they are brought in contact with water, it is necessary to add more water than is necessary in order to obtain a certain level of workability. Since this additional water will never be used in the hydration reactions, it will generate porosity within the hydrated cement paste, resulting in a weakening of the mechanical properties of concrete and in a decrease of its durability.

Superplasticizers are powerful dispersing agents. As with most dispersing agents in aqueous solutions, they first act by being adsorbed onto the surface of cement particles. As illustrated in

Fig. 5, a significant proportion of the added superplasticizer is adsorbed onto cement particles at concentration commonly used in concrete. A schematic description of the adsorption mechanism is shown in Fig. 6. Adsorption of negatively charged PNS on the surface of cement particles that are also negatively charged is made possible by the presence of calcium ions that have been solubilized from the cement.

Following adsorption of the superplasticizer, several physico-chemical effects might take place in the cement paste. For instance, the adsorbed superplasticizer molecules might contribute to minimize interactions between the particles through electrostatic repulsive forces or to the induction of short-range repulsive forces due to steric hindrance between polymer layers. Superplasticizer molecules might also adsorb preferentially onto the aluminate phases of cements (particularly C_3A) and compete with SO_4^{2-} ions in the reactions that control the early hydration of C_3A .

SUPERPLASTICIZERS AND MINERAL ADMIXTURES

As stated before, the portland cement industry is one of the most important contributor of anthropogenic CO_2 released in the atmosphere. Portland cement is also the most energy intensive component of a concrete mixture and therefore its partial replacement by silica fume, fly ash or other cementitious by-products from thermal power production and metallurgical operations might result in a significant energy savings and in an important reduction of global CO_2 emissions. In recent years, several investigations have been performed that were aimed at the development of concrete in which a significant proportion of cement (typically between 20 and 60%) was replaced by these industrial by-products. In the following section, we will review some of the data that were obtained in those studies and we will outline the contribution that superplasticizers have made to this field.

Silica fume

Silica fume is a by-product resulting from the reduction of high purity quartz with coal in electric arc furnaces in the manufacture of silicon, ferro-silicon and other alloys of silicon. Silica fume, which is highly pozzolanic, has a high content of amorphous silicon dioxide in the form of very fine spherical particles, averaging a diameter of about 0,1 μm . Its use in concrete was first reported in the early 50's, but it is only since the 1970's in Scandinavia and 1980's in North America that silica fume really started to be used as a supplementary cementitious material in concrete. Because of its extreme fineness, the water demand of mortars and concretes incorporating silica fume has been shown to increase with increasing amounts of silica fume and, if the workability is maintained by increasing the water content rather than by using a superplasticizer, the increase in strength of silica fume concrete over control concrete is largely offset by the higher water demand. For example, Carette and Malhotra (3) have shown that substituting 30% of cement by silica fume resulted in an almost 30% increase of the water demand when compared to a control concrete, the water/cement ratio increasing from 0.64 to 0.84 (Fig. 7). The use of a superplasticizer is thus an absolute prerequisite in order to achieve proper dispersion of the silica fume and to utilize its contribution to the strength to the largest possible extent. For instance, a recent study (4) showed that the compressive strength of a

superplasticized silica fume concrete in which 10% of cement was replaced by silica fume was somewhat higher than that of the superplasticized control concrete.

Fly ash

Coal is the combustible material used in most thermal power plants. Depending on its grade, substantial amounts of non-combustible impurities, from 10 to 40%, are usually present in the form of clay, shale, quartz, feldspar and limestone. Following the combustion of the volatile matter and carbon in the high-temperature zone of the furnace, most of the mineral impurities are fused and remain suspended in the flue gas. Upon leaving the combustion zone, the molten ash particles are cooled rapidly and they solidify as spherical, glassy particles. Some of the fused matter agglomerates to form bottom ash, but most of it flies out with the flue gas stream and is therefore called fly ash.

Superplasticizers have been also used in concrete incorporating large amounts of fly ash. For example, Mukherjee *et al* (5) report that a significant increase in compressive strength was observed with superplasticized concrete containing 37% fly ash when compared with un-superplasticized control concrete (Fig. 8), a result mostly due to a 20% reduction in water content that was brought by decreasing the water/(cement + fly ash) ratio from a value of 0.35 to 0.28.

Blast-furnace slags

Metallurgical slags are mostly generated by the iron and steel industries. Blast-furnace slags are produced during the production of pig iron from iron ore and steel slags are produced during the conversion of pig iron to steel. Both slags are rich in calcium (35-40% CaO) and a cementitious granulated product is obtained when they are rapidly cooled from the molten state. The compressive strength of superplasticized concrete incorporating 50 to 70% granulated blast-furnace slag as replacement for portland cement was shown to be similar to that of the control concrete that contained only portland cement and superplasticizer (6). These results, shown in Fig. 9, suggest that the interactions between the superplasticizer molecules and these cementitious by-products are similar to those between superplasticizer and portland cement.

DURABILITY

Compressive strength of normal concrete varies typically from 20 to 40 MPa, a range that is adequate for most structural applications. However, the tensile and flexural strength of this material is relatively low and it tends to crack easily under tensile stress, with the consequence that concrete structures can become rapidly exposed to detrimental environmental conditions. As a result, structures with much shorter service life than expected have been observed in several parts of the world, especially in countries with high humidity or where aggressive chemicals are used (i.e. deicing salts). For example, the United States National Materials Advisory Board estimated in 1987 that about 250 000 bridge decks were very deteriorated and that about 35 000 were being added to the list every year. Durability of concrete has thus become a matter of concern in several countries and numerous studies have been devoted to this aspect.

Aggressive agents that attack concrete might be schematically classified into two general categories: external or internal. External agents such as chloride ions, carbon dioxide, sulfate,

freeze-thaw cycles, bacteria and abrasives attack concrete by being brought into contact with it while internal agents such as chloride ions, incorporated when certain accelerators are used, and cement alkalis, when potentially reactive aggregates are used, attack concrete by reacting chemically with various concrete components. However, despite the fact that internal attacks on concrete might sometimes be quite important, most of the problems associated with concrete durability are due to external factors.

Impact of chloride ion on the durability of concrete

Chloride ion penetration is one of the most important factor responsible for the degradation of reinforced structures made of ordinary concrete. Following penetration into the interstitial solution, these ions can react with unhydrated C_3A to form monochloroaluminates ($3CaO \cdot Al_2O_3 \cdot CaCl_2 \cdot 10H_2O$), a mineral compound that can have a favorable impact on the microstructure of concrete. However, chloride ions are most susceptible to reach the reinforcing steel rebars and corrode them rapidly, with potentially devastating results. This corrosion usually starts with the development of a network of microcracks that facilitates the penetration of additional chloride ions, ending up in chipping and flaking of the coverconcrete owing to the expansive forces resulting from the formation of rust. A new surface of concrete gets exposed to the damaging action of the chloride ions and this cycle is repeated until the structure is completely destroyed.

Lowering the porosity and the permeability of concrete is the only way that can reduce the intensity of an aggressive attack on a concrete structure (2). By doing so, the penetration of the aggressive agents will be slowed down and the life-span of the attacked structure will be increased. In order to offer the best possible resistance to external attacks, it is necessary that the concrete be made as compact and as impervious as possible. As indicated in Table 1, a lower water/cement ratio decreases the permeability of the concrete but it does so at the expense of workability. However, the addition of a superplasticizer to the concrete mix restores this property to a satisfactory level and, if desired, it even allows to use a lower water/cement ratio concrete with lower permeability and higher compressive strength.

Impact of freezing and thawing cycles on the durability of concrete

In northern countries, freezing and thawing resistance of concrete is an important property that must be met satisfactorily when this material is used for outdoor constructions. Several investigations in North America and Japan have indicated that the incorporation of a closely spaced and uniformly distributed network of air bubbles through the use of an air-entraining agent provides good protection for freezing and thawing of ordinary concrete. In North America, the resistance of concrete to freezing and thawing is generally established using Procedure A of the ASTM C 666 testing procedure. This procedure consists in cycling the temperature of the concrete specimens between -17.8 and 4.4 C in not less than 2 or more than 5 hours and with not less than 25% of the time being used for thawing. This test is performed for 300 cycles and the specimen is said to be resistant to freezing and thawing if, at the end of the cycling period, the relative dynamic modulus of elasticity still reaches 60% of the initial modulus. For ordinary concrete with a water/cement ratio between 0.4 and 0.45, it is generally agreed that the spacing factor (approximately the average half-distance between two adjacent air bubbles) should not exceed 200 μm .

For high performance concretes that incorporate superplasticizers, and especially naphthalene- and melamine-based superplasticizers, it has been found that this value is generally exceeded. However, in spite of this increased bubble spacing, the resistance to freezing and thawing cycles of concretes that incorporate superplasticizers is not impaired to a significant extent (7), whether the concrete is tested according to ASTM Standard C 666, Procedure A (freezing and thawing in water) or Procedure B (freezing in air and thawing in water) (Table 2).

CONCLUSION

The use of superplasticizers in concrete has expanded considerably since their introduction in the late 60's. From their first applications as high-range water reducers in ordinary concrete, these chemical admixtures have greatly broadened their range of application in cementitious systems and they are rapidly becoming an essential component of concrete. For instance, the use of silica fume as well as a high proportion of granulated blast furnace slags as a partial replacement of portland cement would not be possible without the addition of superplasticizers. With the growing concern that is currently expressed towards CO₂ emissions, partial replacement of portland cement by various industrial products means that less CO₂ will be emitted in the atmosphere, less energy will be used and that our natural resources will be better utilized.

By decreasing the water/cement ratio, superplasticizers have also been shown to play an important role in increasing the durability of concrete structures by making concrete more compact and impervious. Moreover, the reduction of the water content of high performance concrete might result in the presence of cement grains that are not all well hydrated. These unhydrated cement particles may play an important role in the durability of the concrete structure by providing a 'reserve' of cement that will hydrate, if for any reason, the environmental conditions are harsher than anticipated and water penetrates the concrete. We believe that the rising costs of repair and maintenance will make the use of high performance concrete mandatory for most of the urban and industrial infrastructures in the few years to come. We also believe that the use of superplasticizers will continue to expand as more and more is known about the chemistry and the behavior of these admixtures in cementitious systems.

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Table 1. Impact of the addition of a superplasticizer on water permeability and workability of concrete

W/C RATIO	Compressive strength (MPa)		Water permeability (m/s x 10 ⁻¹⁴)		Slump (mm)	
		+SP		+SP		+SP
0.6	20	-	35	-	118	-
0.55	31	30	25	22	58	200
0.5	41	40	15	12	30	125
0.45	50	50	5	5	18	80
0.4	-	60	-	3	-	70

Table 2. Freezing and thawing resistance of a superplasticized concrete. (7)

W/C RATIO	ASTM C 666, Procedure A					ASTM C 666, Procedure B		
	Air content (%)	Spacing factor (mm)	Freezing and thawing cycles	Relative dynamic modulus Pc (%)	Durability factor	Freezing and thawing cycles	Relative dynamic modulus (%)	Durability factor
0.7 ^a	2.4	0.62	0	43	1	16	1	1
0.7 ^b	6.2	0.23	300	91	91	300	98	98
0.7 ^c	6.7	0.26	300	91	91	300	98	98
0.5 ^a	2.2	0.59	15	39	2	48	20	3
0.5 ^b	6.8	0.13	300	96	96	300	100	100
0.5 ^c	6.5	0.18	300	95	95	300	98	98
0.35 ^a	2.0	0.73	12	78	3	300	90	90
0.35 ^b	5.7	0.14	300	94	94	300	100	100
0.35 ^c	5.0	0.23	300	95	95	300	98	98

a: plain; b: air entrained; c: air entrained and superplasticized with a naphthalene-based superplasticizer at a 0.75% by weight of cement dosage rate.

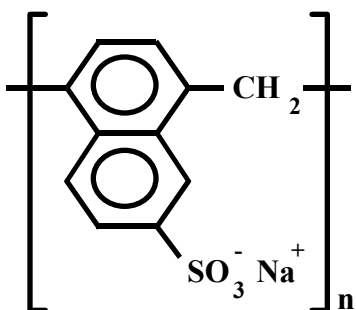


Fig. 1. Simplified chemical structure of a poly-naphthalene sulfonate (PNS) polymer.

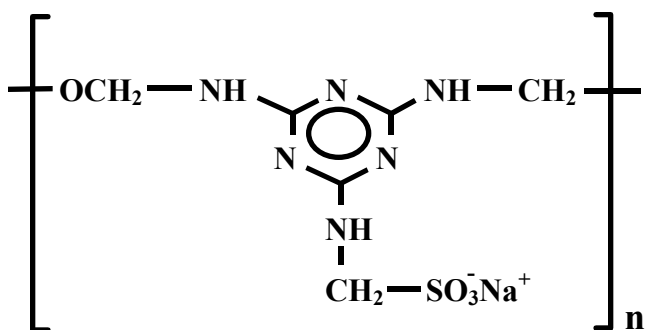


Fig. 2. Simplified chemical structure of a polymelamine sulfonate (PMS) polymer.

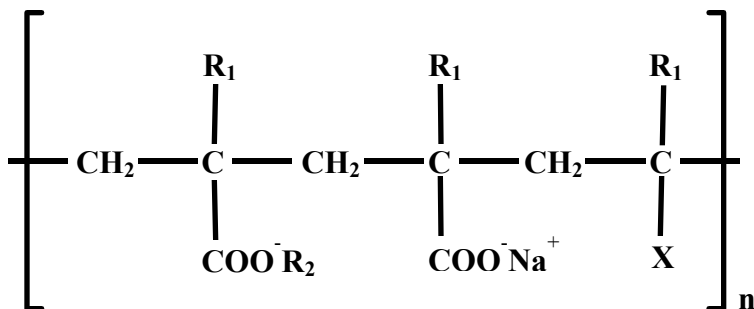


Fig. 3. Simplified chemical structure of a polyacrylate copolymer, where R_1 is H or CH_3 , R_2 is a poly-ether chain (i.e. polyethylene oxide) and X, a polar or ionic group.

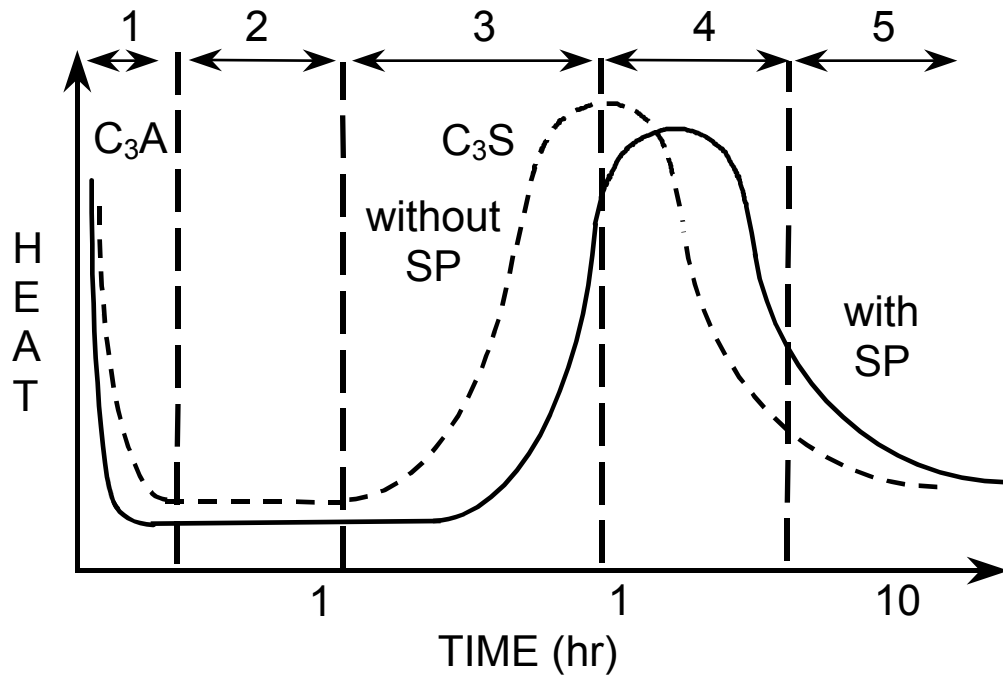


Fig. 4. Kinetics of hydration of Portland cement.

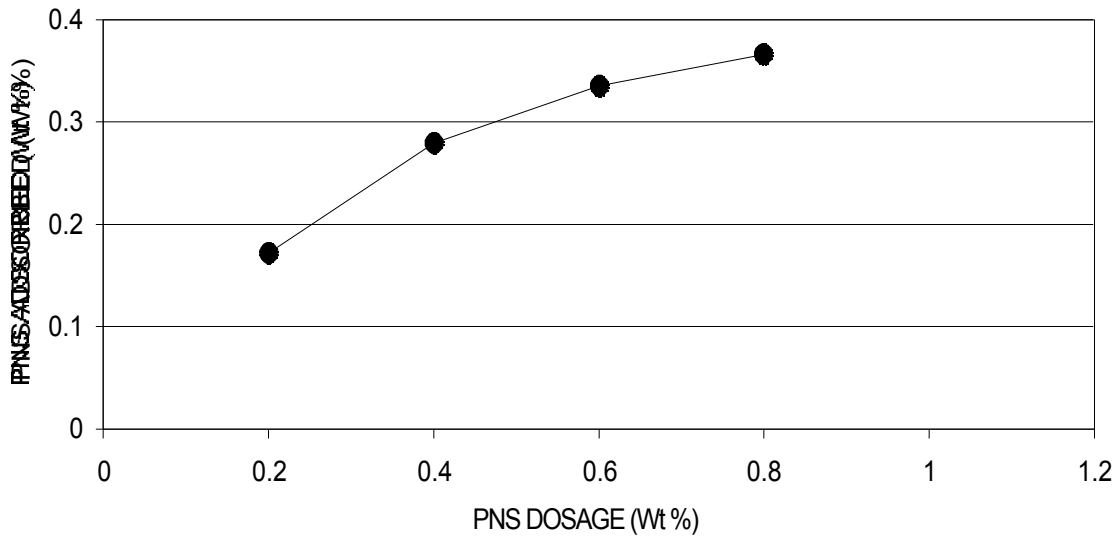


Fig. 5. Adsorption of superplasticizer on portland Type 10 cement particles.

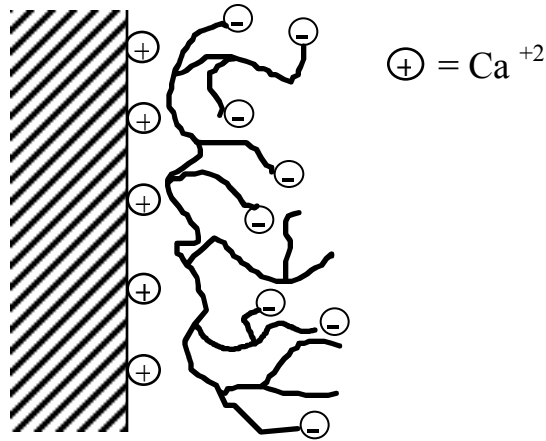


Fig. 6. Schematic description of the adsorption of a superplasticizer molecule onto the surface of a cement particle.

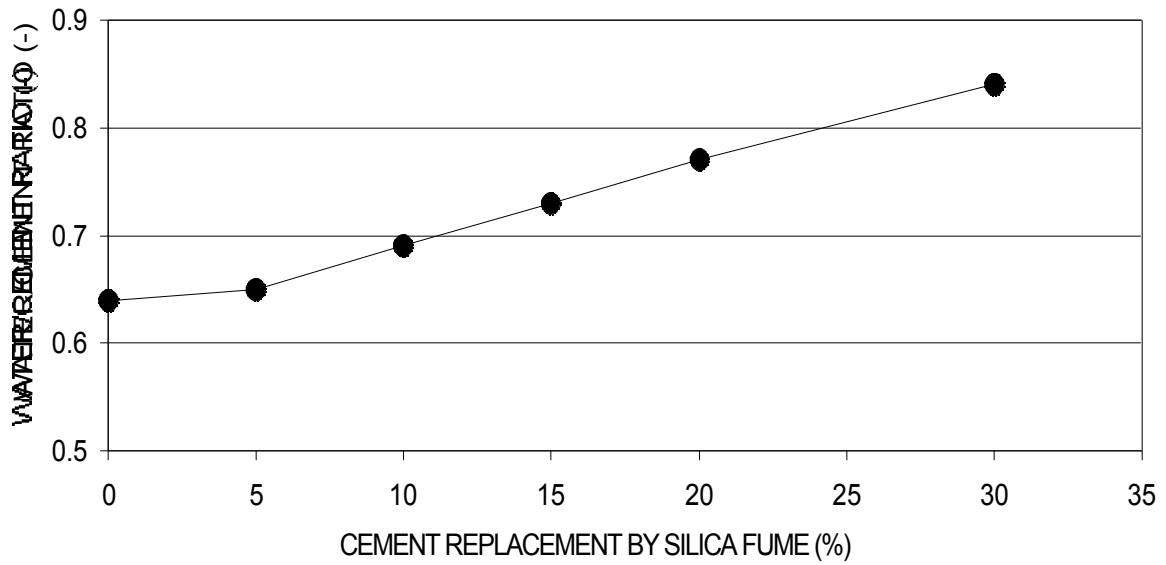


Fig. 7. Water/cement ratio necessary to maintain concrete compressive strength when silica fume is substituted for cement (3).

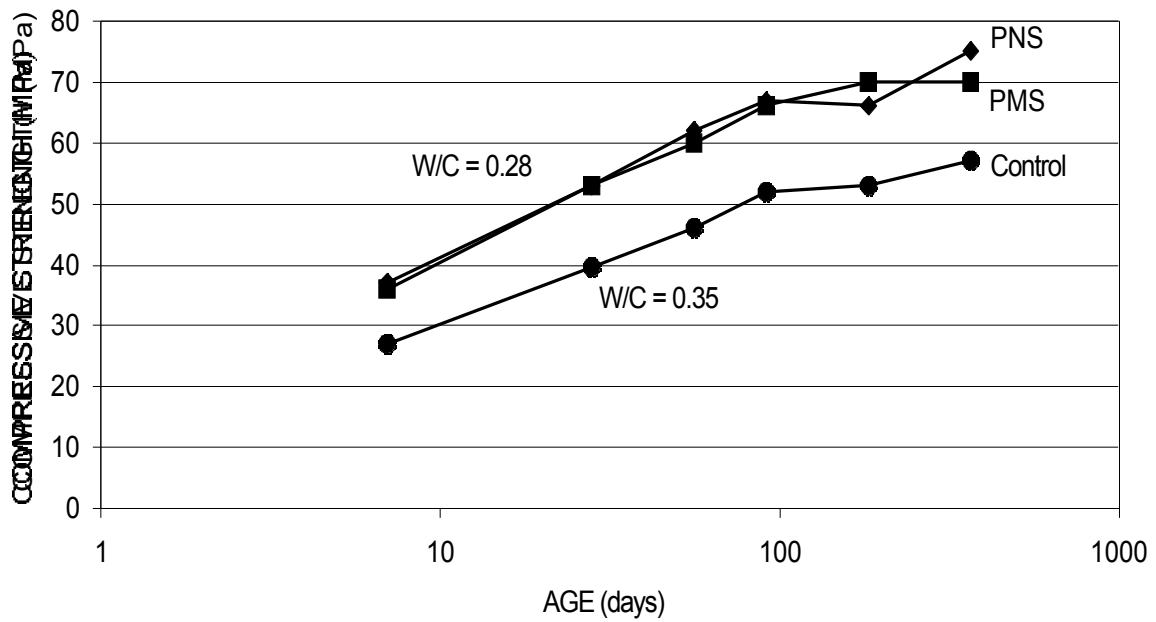


Fig. 8. Compressive strength of superplasticized concretes containing fly ash. (5)

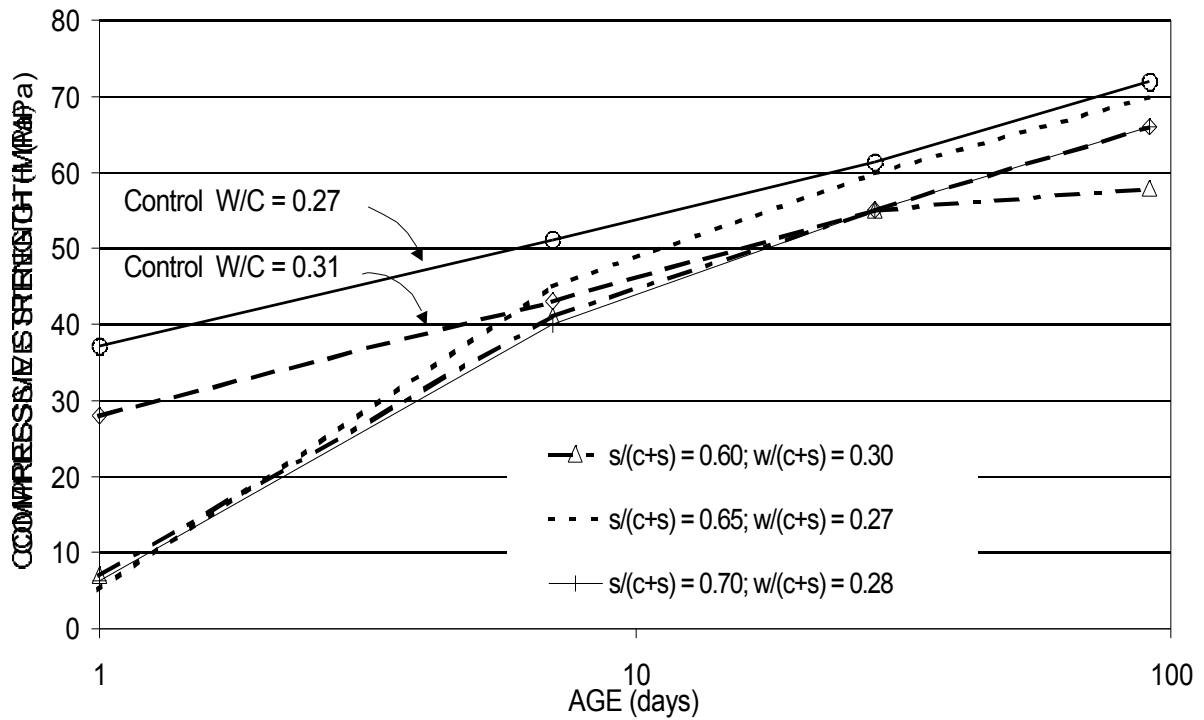


Fig. 9. Compressive strength of superplasticized high-volume slag concrete. (6)