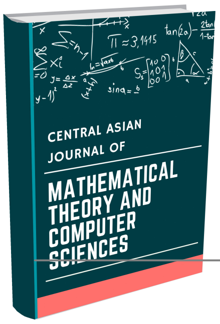


CENTRAL ASIAN JOURNAL OF MATHEMATICAL THEORY AND COMPUTER SCIENCES

https://cajmtcs.centralasianstudies.org

Volume: 04 Issue: 6 | Jun 2023 **ISSN: 2660-5309**

SUPERPLASTICIZERS FOR MORTARS AND CONCRETES. REVIEW ARTICLE

Kh. Kh. Kamilov, D. R. Abdazov
Tashkent University of Architecture and Construction
dilshod_abdazov@taqu.edu.uz
https://orcid.org/0000-0002-2905-3021

Abstract

Superplasticizers are chemical additives that improve the flow and workability of concrete and mortar, making them indispensable components of modern construction. This scientific article reviews the latest advances in the development of superplasticizers for mortars and concretes. First, an overview of the chemistry and properties of superplasticizers is presented, including their mechanisms of action and classification based on their chemical composition. It then highlights recent research on the synthesis and effectiveness of new superplasticizers, including those based on polycarboxylate esters, lignosulfonates, and other organic and inorganic compounds. The issues associated with the use of superplasticizers are also discussed, such as their potential impact on concrete durability and environmental sustainability. Our article is a comprehensive resource for researchers and practitioners interested in using superplasticizers to improve the performance of mortars and concretes.

ARTICLEINFO

Article history:
Received 13 Apr 2023
Revised form 14 May 2023
Accepted 15 Jun 2023

Keywords: *Superplasticizers, chemical additives, polycarboxylate, naphthalene sulfonate, naphthalene formaldehyde, lignosulphonate.*

***

Introduction

Chemical additives continue to play a crucial role in modern concrete. Until recently, the most important technological improvements in concrete technology came from the introduction of innovative additives, while cement production itself has matured somewhat and focused more on waste management to contribute to a closed-loop economy [1-2].

Superplasticizers are chemical additives used in the construction industry to improve the workability of concrete. They have been in use for decades, and their history dates back to the early 20th century.

The use of lignosulfonate as a superplasticizer was developed in the 1930s. Lignosulfonate is a byproduct of the pulp and paper industry and is derived from lignin, a natural polymer found in wood and other plant materials. Lignosulfonate superplasticizers are very effective in reducing the viscosity of concrete, making it easier to pour and shape.

In the middle of the 20th century, research into the development of superplasticizers continued. In the 1960s, the use of naphthalene-based superplasticizers was developed. These additives were found to be very effective in reducing the water-cement ratio in concrete, increasing its strength and durability.

In the 1980s, a new type of superplasticizer based on polycarboxylate chemistry was developed. Polycarboxylate superplasticizers effectively reduce the water-cement ratio in concrete, providing higher strength and durability while reducing the amount of cement needed.

Since the 1980s, the use of superplasticizers has continued to grow and they have become an important tool in the construction industry. Today, superplasticizers are used in a wide range of applications, from large-scale infrastructure projects to residential construction.

Overall, the development of superplasticizers has significantly improved the workability and durability of concrete, enabling the construction of larger and more complex structures. Continuous research and development of new superplasticizers will continue to stimulate innovation in the construction industry, leading to even better and more efficient construction technologies in the future.

There is no doubt that superplasticizers are at the heart of chemical additive technology [3-5]. First, because of their ability to improve the workability of building materials (which usually results in enormous cost savings), and second, because of their enormous volume. For polycarboxylate superplasticizers alone, global production is now well over 10 million tons per year. [6], and constantly new manufacturers are entering the market with products based on existing know-how or new advanced molecular designs adapted to local needs.

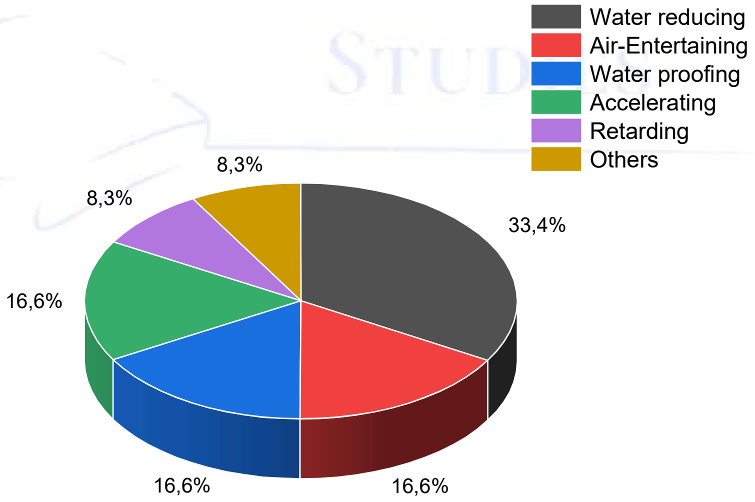


Figure 1. Percentage of the use of different superplasticizers in building materials worldwide.

The American Standard C494/C494M-17 contains classifications for chemical additives for concrete. Chemical additives are added to concrete to control its properties or behavior during placement and curing. The standard recognizes the following types of chemical admixtures [8]:

Type A - water-reducing additives: these additives reduce the amount of mixing water needed to produce concrete of a certain consistency, resulting in increased strength and durability.

Type B - Setting retarding additives: These additives slow down the setting time of concrete, which gives more time for paving and finishing. They are especially useful in hot weather or for large pours.

Type C - Accelerating Additives: These additives accelerate the setting time of concrete, reducing the time needed for curing and allowing for shorter construction times.

Type D - water-reducing and setting retarding additives: these additives combine the properties of additives type A and B, reducing the amount of mixing water required and increasing the setting time.

Type E - water-reducing and accelerating additives: these additives combine the properties of additives type A and type C, reducing the amount of mixing water required and accelerating the setting time.

Type F – High-Performance Water-Reducing Additives: These additives reduce the amount of mixing water required to produce high-strength concrete and improve workability and finishing properties.

Type G - Highly effective water-reducing and setting retarding additives: These additives combine the properties of type F and type B, reducing the amount of water required for mixing as well as increasing the setting time.

Type S - Special Performance Additives: These additives are used to achieve specific performance characteristics of concrete, such as improved frost resistance, reduced permeability, or improved workability. They are classified based on the intended performance characteristics and can be used in combination with other additives.

It is important to note that these additives should be used by the manufacturer's recommendations and industry standards to ensure proper performance and durability of the concrete:

- Enhance the workability of a given mixture composition to improve the characteristics of concrete placement;
- Decrease the mixing water at a given cement content and workability to reduce the water-cement ratio (W/C) and thereby increase the strength and improve the workability;
- Decrease the amount of water and cement for a given workability and strength to save cement and reduce creep, shrinkage, and thermal deformations caused by the heat of cement hydration.

Today superplasticizers are used in all important projects around the world in high-rise buildings, prestressed concrete, thin elements with overloaded and densely packed reinforcement, precast elements of beams and slabs, and long thin columns [9].

Superplasticizers are oligomeric compositions with different molecular weights and, according to the classification adopted in Great Britain, can be divided into three main categories [10]:

1) sulfated melamine-formaldehyde resins and complex additives based on them;
2) condensation products of naphthalene sulfonic acid and formaldehyde and complex additives based on them;
3) modified (purified and practically sugar-free) lignosulfonates and complex additives based on them.

Later, the condensation products of oxycarboxylic acids were assigned to a fourth, less common group

Lignosulfonates

Lignosulfonates are the most widely used raw materials for the production of water-reducing agents and were first used in the 1930s. The average molecular weight of lignosulfonates is in the range of 20,000-30000 with a molecular weight distribution of several hundred to 100,000 [12,13].

Technical lignosulfonate, denoted by the abbreviation (LST), was first available in the Russian industry in 1937. It was the result of processing in the processes of pulp and paper production. It is a waste product, characterized by the presence of calcium, sodium, and ammonium salts (lignosulfonate acids) in the composition [14].

The structure and composition of lignosulfonates are too complex (Fig. 1), they can be represented as a phenylpropane-substituted polymer with hydroxyl (-ON), methoxyl ($-OSH_3$) groups, phenyl rings ($-C_6$ H.) and subgroups ($-S0_3$ H) [15].

Lignosulfonate superplasticizers are chemical additives used in the construction industry to improve the workability of concrete. They are derived from lignin, a natural polymer found in wood and other plant materials. Lignosulfonate superplasticizers are commonly used because they are inexpensive and can greatly improve the flowability of concrete, making it easier to pour and shape.

However, the effectiveness of lignosulfonate superplasticizers may be limited by certain factors, such as the pH and temperature of the concrete mixture. To overcome these limitations, modifications of lignosulfonate superplasticizers have been developed. These modifications can improve the performance of the superplasticizer, making it more effective over a wider range of conditions.

One type of modification is the sulfation of lignosulfonate. This involves treating lignin with sulfuric acid to create sulfonic acid groups that increase the solubility of lignosulfonate in water. Sulfated lignosulfonate superplasticizers are more effective at lower pH levels and lower temperatures, making them more versatile than unmodified lignosulfonate superplasticizers.

Another modification of lignosulfonate superplasticizers is the addition of other polymers such as polyethylene glycol (PEG). PEG-modified lignosulfonate superplasticizers are very effective in reducing the water-cement ratio in concrete mixtures, which can increase the strength and durability of the final product.

In addition, changing the molecular weight of lignosulfonate can also improve its performance as a superplasticizer. Higher molecular weight lignosulfonates are more effective in reducing the viscosity of concrete, which can make it easier to pump and handle.

In general, modifications to lignosulfonate superplasticizers can increase their effectiveness and versatility, allowing them to be used in a wider range of conditions and applications. These modifications can improve the quality and durability of concrete structures, making them valuable tool for the construction industry.

Mechanism of LSP action

The mechanism of action of LSPs is that they reduce the surface tension of water, which allows the concrete to better distribute inside the formwork and fill it better. This results in increased density and strength of the concrete.

In addition, LSPs have a dispersing effect, which means that they help break up wisps of cement into tiny particles, which improves its bonding properties with water and other mixture components.

LSPs may also be present as positively charged ion-exchange groups that can interact with negatively charged surfaces of cement particles, resulting in improved cement dispersion and water bonding properties.

So, the mechanism of action of LSP is associated with a decrease in the surface tension of water, dispersion of cement, and improving the bonding properties of cement with water and other components of the mixture. This increases the fluidity of concrete, reduces its water absorption, and increases its strength.

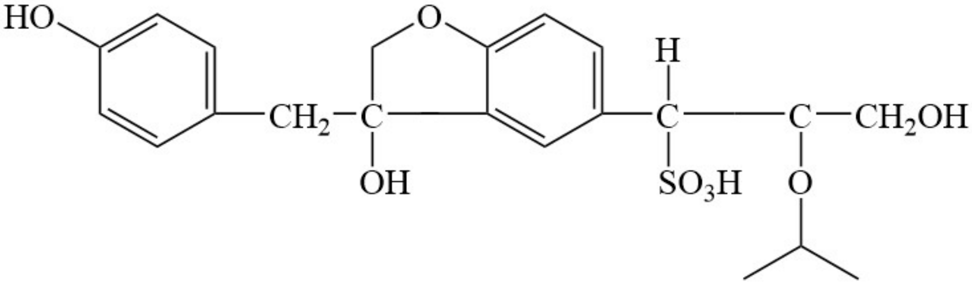


Figure 2. Chemical structure of lignosulfonate molecules [16]

Modified lignosulfonates LTM:

Modified lignosulfonates (MTM) are a type of superplasticizer used to improve the flowability of concrete mortars and increase the strength of structures. MTM are lignin derivatives obtained by treating wood with alkali and sulfites.

There are several types of modified lignosulfonates, such as CHDSC-1 modified with mechanochemical treatment with alkali [17], CHDSC-3 modified with the introduction of polyethylene glycol, MTS-1 introduced higher fatty alcohols or wastes of their production, NIL-20 treated with cement suspension [18], NIL-21 introduced with propynol defoamer [19], MLS condensation with formaldehyde, OKZIL (calcium chromium-lignosulfonates) treated with bichromates in an acid medium, CPM fractionated lignosulfonates with calcium hydroxide followed by treatment with soda, LST-MSH-1 by adding waste monosulfite liquor and KOD-S by adding soapstock which differ in the method of production and introduction of additional components.

Foreign manufacturers also produce power-plasticizing additives based on modified lignosulfonates, such as Betokem LP, Plastiment BV40, FN Liquidate VS and WRDA (WRDA) additives based on modified and sugar-free lignosulfonates [20,21], and Addiment BV 3 (Addiment BV-3) Product in the form of brown liquid with a density of 1.12 kg / l; gives waterproofing properties to concrete and mortars. Does not contain substances that cause corrosion of reinforcement [22].

These additives can significantly reduce the water excess in concrete and improve its fluidity, which increases the efficiency of construction works. In addition, they do not contain substances that cause corrosion of reinforcement, which ensures durability of structures.

Thus, the use of modified lignosulfonates and power-plasticizing additives based on them is an effective way to improve the properties of concrete mortars and improve the quality of construction works.

Sulfomelamine and sulfonaphthalene formaldehyde

The history of these superplasticizers is considered to have begun in Japan and Germany in the 1960s. Dr. Alois Eignesberger was the pioneer who recognized the importance of melamine-based polycondensate superplasticizers for concrete technology. On the Japanese side, simultaneously and independently of his German colleague, Dr. Kenichi Hattori developed polycondensates based on β-naphthalenesulfonic acid and formaldehyde. For this outstanding achievement both scientists were awarded the Hans-Kuhl Medal of the GDCH Construction Chemistry Section in 2003. [23].

The second superplasticizer, Melment, contained sulfonated melamine-formaldehyde condensate and was introduced in Germany the same year. A decade later, the use of superplasticizers was achieved in the Americas in 1970. Water-soluble resins developed by the German scientist Alois Eignesberger obtained by condensation of aminostriazines of the formula where R represents H, NH_2 , OH or $C\ H_{n2n+1}$, where n is an integer from 1 to 9, with lower alkanals or alkanones in the presence of sulfites to produce anionic resins have only a minor effect on the surface tension of water. Nevertheless, they interact synergistically with all conventional anionic organic surfactants, dramatically reducing the surface tension of water below that achieved by surfactants alone. Some resins stabilize the initial solutions of perfluorinated anionic surfactants [24].

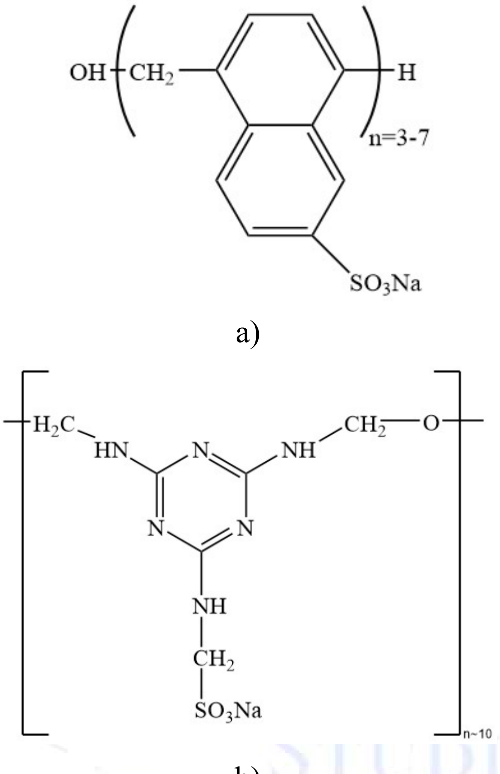
Mechanism of action

The mechanism of action of these superplasticizers is related to their ability to reduce the surface tension of water and improve the dispersion of cement particles, which allows more efficient use of water in the mixing process of concrete and increases the plasticity and flowability of the mixture.

Sulfomelamine superplasticizers usually contain sulfonated melamines that form complexes with cement, increasing its solubility and accelerating the hydration process. This improves the strength of the concrete and reduces the curing time.

Sulfonaphthalene-formaldehyde superplasticizers contain sulfonated naphthalene-formaldehyde resins, which also help to reduce the surface tension of water and increase the fluidity of the concrete mixture. They can also accelerate cement hydration and increase cement strength.

In general, sulfomelamine and sulfonaphthalene-formaldehyde superplasticizers are highly effective additives for concrete that improve its properties and quality.



a)

b)

Figure 3. a) ß-naphthalene sulfonic acid-formaldehyde developed by Dr. Kenichi Hattori [21]; b) Melamine formaldehyde sulfite condensate developed by Dr. Alois Eignesberger [21]

The use [25] of this additive allows to obtain concretes with high, technical and economic characteristics. In this case the surface finish of concrete is significantly improved. Cast-in-place concrete with superplasticizer does not separate water. The usual dosage is 1-2% of the weight of the cement. Despite the higher cost, cast-in-place concrete is economical, because its use reduces labor costs by 30-90%: the increased mobility of the mixture provides unloading truck mixer for 5 minutes (instead of 20 minutes) and allows you to lay concrete to replace five or six workers one. Additional savings are due to the accelerated turnover of the molds and increased productivity of the equipment. Maximum strength growth of concrete during the first three days of hardening is provided up to 170-190%, the concrete adhesion with the armature during 28 days increases by 160%. When introducing 2-3% of the additive "Melment L-10" into concrete mixture, concrete quickly achieves the necessary operational properties, such as water resistance, high resistance to chemical attack, frost resistance, resistance to "defrosting" salt, and abrasion resistance.

In 1974, for the first time the Research Institute of Reinforced Concrete was brought from Germany (University of Heidelberg) "Melment" called "super-plasticizer", based on naphthalene-sulfated polymers. The composition obtained as a result of mass spectrometry made it possible to make "C-3" - an analogue of "Melment" with the addition of SDB [26].

The first information about the effect of superplasticizers in technology of concrete works in the former USSR appeared in 1976. Since the beginning of 1977 in VNIIZhelezobetone, Mendeleev Moscow Chemical Institute, NIIZhB and other institutes superplasticizers, which are sulfated products of melamine condensation were developed: with formaldehyde - "10-03", APS, NIL-10. It was found experimentally that their effects are almost identical. Another series of additives based on condensation of naphthalene sulfonic acids with formaldehyde has been developed by VNIIZhelezobeton ("30-03") and NIIZhB together with NIIOPiK (C-3). These additives on their main effects are not inferior to the best foreign superplasticizers. Since 1978 their industrial production was started. The use of SP allowed several times to reduce the labor intensity of molding, in some cases to eliminate vibration or replace it with a short-term shaking, to reduce the energy consumption by one-third and to 25% - the consumption of cement [27].

Superplasticizers are used in conjunction with other additives to give the concrete mixture and concrete special properties. For example, several researchers recommend using sulfated melamine-formaldehyde resin mixed with polyvinyl acetate emulsion, polyvinyl alcohol, and sodium sulfate to obtain an easily pumpable mixture for seamless floors. Sulfated melamine-formaldehyde resin can be used in combination with metal chlorides and bichromates, lignosulfonates, and water-soluble starch to produce high-strength concrete. To intensify the process of hardening concrete, various gas pedals of hardening are introduced into its composition together with superplasticizers. Additional additives of calcium gluconate, sucrose, polyphosphates and hexametaphosphates, tartaric acid or its salts, and cane sugar have been proposed to increase the vitality of concrete mixtures with superplasticizers [28, 26].

Modifications of sulfomelamine and sulfonaphthalene formaldehyde

Sulfomelamine and sulfonaphthalene are organic compounds that can be modified to produce formaldehyde superplasticizers.

The modification occurs by joining formaldehyde to sulfomelamine or sulfonaphthalene molecules. This process makes it possible to increase the effectiveness of these compounds as superplasticizers.

There are several options for modifying sulfomelamine and sulfonaphthalene-formaldehyde superplasticizers such as thinner C-3 additives based on sodium salts of the condensation products of naphthalene sulfonic acid and formaldehyde. A dark-brown liquid or non-tracking powder, well soluble in water [29], CMF Thinner (a modification of Thinner C-3) is a mixture of polymeric compounds of different molecular weights, obtained by condensation of naphthalene and P-phenolsulfonic acids with formaldehyde, neutralized with caustic soda. Brown aqueous solution [19], Dophen DF is a product of polycondensation of naphthalene sulfonic acids, its derivatives and analogs with formaldehyde using wash acids - wastes of purified naphthalene production [30], superplasticizer 10-03 oligomeric product of polycondensation of sulfated trimethylene melamine [31], superplasticizer NKNS 40-03 additive is a mixture of sodium salts of polycondensation products with formaldehyde of sulfated aromatic hydrocarbons produced during catalytic cracking and pyrolysis of oil products [32], melamine-formaldehyde anionic resin grade MF-AR. The product of polycondensation of melamine, formaldehyde, and sodium sulfonylate.

There are also superplasticizers from foreign manufacturers such as Agiplast, a product based on sulfated naphthalene-formaldehyde compounds [33], Izola FM-86, Conplast ML, Melment L10 (Melment F) an additive based on sulfated melamine-formaldehyde resins [34,35,38], Cormix, Chriso fluid and Lomar D an additive based on sulfated naphthalene formaldehyde compounds [20,36,37], Peramin F a transparent aqueous solution of melamine sulfonate, Peramin FP a white powder of melamine sulfonate and Peramin FS aqueous solution of modified melamine sulfonate [39], Reobuild 2000 a liquid chlorine-free hyperplasticizer, designed for high-quality concrete with a cement consumption of at least 400 kg/m^3. Water-soluble additive based on sulfonate polymers with different molecular weights [38], Fluimax. Additive based on sulfated naphthalene formaldehyde compounds [41], PSP Additive based on sulfated naphthalene formaldehyde compounds [33], Sikament-FF Additive based on sulfated melamine formaldehyde resins [41].

Polycarboxylates

In 1980, Nippon Shokubai Co., Ltd. in Osaka began a new product development project, and in less than a year a revolutionary polycarboxylate ester superplasticizer technology was created. Back in the 1980s, sodium polyacrylate, Nippon Shokubai's main product at the time, was widely used as a dispersant for pigments, detergents, and scale inhibitors. These applications benefited from its exceptional dispersing and chelating properties in particulate suspensions. Therefore, Nippon Shokubai first investigated the dispersion efficiency of sodium polyacrylate in cement [42].

Dr. Hirata invented polycarboxylate superplasticizers in the laboratories of Nippon Shokubai, Osaka, Japan, in 1981 [43]. The discovery of this new group of superplasticizers ushered in an entirely new era and moved concrete technology into a new era in which self-compacting concrete and extra high-strength concretes was suddenly possible.

Generally, when cement is mixed with water, agglomeration occurs due to dispersion forces (or Van der Waals forces) [44]. Consequently, these agglomerates cause high viscosity and poor workability. Thus, water-reducing additives are used to improve the workability of the cement mixture. Although initially it was thought that these early superplasticizers based on melamine or naphthalene polycondensates act due to electrostatic repulsion between cement particles [45]. It is now accepted that the effect of steric hindrance represents the actual cause of their dispersing ability [46 - 49]. The reason is that the high ionic force present in the cement pore solution results in a very short Debye length, which far exceeds the range of Van der Waals attraction forces [55,56]. Polymers are adsorbed at the solid-liquid interface between particles and the aqueous phase through their sulfonate groups, -SO^{-} - 3. Thus, steric forces are generated between the cement particles, and trapped water or air is released, which provides dispersion. Consequently, to understand the behavior of sodium polyacrylate as a cement dispersant, the Nippon Shokubai research team investigated its adsorption behavior on cement particles.

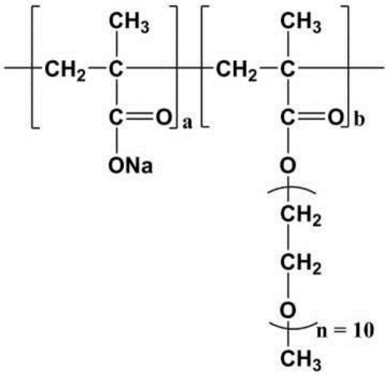


Figure 4. Chemical structure of the first polycarboxylate superplasticizer MPEG synthesized in 1981. [57].

In concrete testing, it was quickly discovered that the new superplasticizer was not only much more efficient in dosage than naphthalene sulfonate but also worked well at very low water/cement ratios (<0.40), when polycondensates such as naphthalene sulfonate normally do not work. Thus, it becomes apparent that polycarboxylate mixtures allow the production of high-tech products in the form of self-compacting concrete in a much more reliable and durable manner [58].

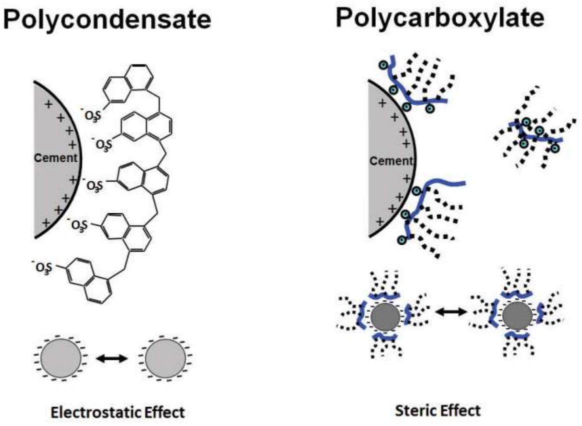


Figure 5. Illustration of the two dispersion mechanisms known for concrete superplasticizers [48].

After the discovery of polycarboxylate superplasticizers, the construction chemistry industry began to develop rapidly. One by one, scientists began to use various macromonomers to synthesize polycarboxylates. The basis of this discovery was the MPEG monomer by Dr. Hirata.

Modifications of polycarboxylates

Polycarboxylates based on MPEG PCE macromonomers

PCEs based on methacrylate esters, first commercialized in 1987 by Nippon Shokubai Co., Ltd. in Japan, still dominate the European superplasticizer market by volume. MPEG PCEs can be synthesized in two different ways: methoxypoly(ethylene)glycol is grafted onto a poly(methacrylic acid) base in an acid-catalyzed grafting reaction conducted at high temperature (~150-175 ◦C) and in a vacuum [57]. This method results in a relatively regular (statistical) copolymer exhibiting a fairly uniform distribution of side chains along the main chain; alternatively, free-radical copolymerization of methacrylic acid with ω-methoxy poly(ethylene glycol) methacrylate ester macromonomer at ~75˚ C can be chosen for PCE preparation [58]. This process (which was used by Nippon Shokubai in the first PCE synthesis) yields a gradient polymer, which is characterized by a change in side chain distribution along the main polymer chain due to the different reactivity of the macromonomer and the acid-bearing monomer [56]. In the production of MPEG PCE by free-radical copolymerization, there is a problem with macromonomer availability, which is sometimes limited. To solve this problem, some PCE manufacturers produce the macromonomer themselves by esterifying methacrylic acid anhydride with ω-methoxypoly(ethylene glycol) in a vacuum. MPEG PCEs are currently believed to be inferior in dispersion efficiency to more modern generations of PCEs, such as HPEG or IPEG polymers. However, it has been reported that MPEG PCEs are less prone to bleed and segregate in concrete. This behavior can be explained by the lower HLB value, which makes the concrete more cohesive ("sticky") [57].

Polycarboxylates based on APEG PCE macromonomers

This type of polycarboxylate, first patented by Nippon Oil & Fats in 1987, can be obtained from maleic anhydride and the macromonomer rn-methoxy-allyl poly(ethylene glycol) either in aqueous solution or (for nEO < 34) even in bulk. [58].

APEG-PCE represents the second generation of PCE. They are produced by free-radical copolymerization of the macromonomer α-allyl-ω-methoxypoly(ethylene glycol) (APEG) and maleic acid anhydride. In some cases, small additives of styrene are used instead of a maleic acid anhydride. By using these monomers, the disadvantage of monomer homopolymerization could be eliminated. Since thermodynamically favorable interactions between two monomers can only occur in alternating order in the main chain, APEG-PCEs always exhibit a very homogeneous side-chain distribution [59]. This strictly alternating arrangement leaves less freedom in the adaptation of these PCEs concerning anionic activity, and only the side chain length can be varied. The advantage of these PCEs is that the polyethylene glycol is connected to the main polymer chain by a strong ether bond, which makes the side chains completely resistant to hydrolysis in an alkaline environment [60].

Polycarboxylates based on VPEG PCE macromonomers

Vinyl ester PCEs were first invented in Germany in the 1990s, but they have since evolved into a larger family of copolymers. "Classic" VPEG PCE, patented in 1995 [61], consists of a terpolymer consisting of maleic anhydride, vinyl ester macromonomer (C_2), and acrylic acid (hence also known as "MVA" PCE). Its synthesis must be carried out at room temperature (preferably <25˚ C) to avoid the formation of undesirable toxic decomposition products such as acetaldehyde from the vinyl ester of 4-hydroxybutylpoly(ethylene glycol). The more pronounced reactivity of vinyl ether compared to allyl ether allows a wider range of molecular compositions to be achieved in low-temperature synthesis and to obtain PCE with both water-reducing and anti-swell properties.

Polycarboxylates based on HPEG PCE monomers

HPEG-type PCEs: they use α-methyl-ω-methoxy- or ω-hydroxypoly(ethylene glycol) ester as a macromonomer [62]. Compared to the APEG macromonomer, the GPEG macromonomer has much greater reactivity, since resonance stabilization is not possible here. For this reason, the synthesis of PCE using HPEG macromonomers is a better and simpler approach. At present, HPEG-type PCEs are the dominant products in China. When HPEG macromonomer reacts with acrylic acid, a lot of reaction heat is released during the polymerization process. Consequently, a process has been developed and widely used in China in which copolymerization is performed at room temperature using redox initiators [63].

Polycarboxylates based on IPEG PCE monomers

(sometimes also called TPEG-type PCE) are made from isoprenyloxy poly(ethylene glycol) macromonomers by copolymerization with acrylic acid [64]. Recently, this type of PCE has become very popular due to the ease of production from versatile raw materials and high efficiency in concrete.

Polycarboxylates based on PAAM PCE monomers

these zwitterionic PCEs have mixed side chains consisting of polyamidoamine (PAAM) and PEO segments; this structural feature fundamentally distinguishes them from all other PCEs, which contain exclusively polyethylene oxide and polyphenylene oxide side chains. PCE of the PAAM type is said to liquefy cement at a water/cement ratio of only 0.12 [65]. Its disadvantage is the high cost of the PAAM side chain.

Zwitterionic (amphoteric) polycarboxylates

Amphoteric or zwitterionic superplasticizers include cationic and anionic charges. Superplasticizers can be distinguished by the position of the ionic charges in the molecules. For example, the charges may be placed in the main chain or the side chains of the superplasticizer. The reason for combining the differently charged anchor groups in the same polymer was to provide higher adsorption of the superplasticizer on the surface of cement particles and hydration products. In addition, it was intended to integrate the desired properties of the cationic polymers into the anionic superplasticizer. For example, cationic polymers are highly resistant to clay because they can occupy bentonite clay interlayers [66] and prevent clay swelling [67, 68].

Mechanism of action

Polycarboxylate superplasticizers are chemical additives commonly used in the construction industry to improve the workability and strength of concrete. The mechanism of action of polycarboxylate superplasticizers is their ability to disperse cement particles more effectively and reduce the water-cement ratio.

Polycarboxylate superplasticizers contain a long polymer chain with several carboxylate groups. These groups have a strong affinity to cement particles and can adsorb on their surface. This adsorption creates a repulsive force between the cement particles, allowing them to disperse more easily in the concrete mixture. As a result, the concrete becomes more workable and easier to handle.

In addition to their dispersing action, polycarboxylate superplasticizers can also reduce the water-cement ratio in the concrete mixture. This is achieved by the steric hindrance effect of the polymer chain, which can prevent water molecules from interacting with the cement particles. As a result, less water is required for the same level of workability, which can lead to higher strength and durability of the final product.

Another important mechanism of action of polycarboxylate superplasticizers is their ability to slow down the setting time of concrete. This is achieved by the adsorption of the polymer chain on the surface of the cement particles, which can slow down the hydration reaction between cement and water. This allows for longer working times and better control of the concrete setting.

In general, the mechanism of action of polycarboxylate superplasticizers is their ability to disperse cement particles, reduce the water-cement ratio and delay the setting time of concrete. The result is a more workable and durable end product.

Conclusion.

In conclusion, superplasticizers play a crucial role in improving the quality and durability of mortars and concrete. The use of superplasticizers also makes it possible to produce high-performance concrete with a lower water-cement ratio, which reduces the environmental impact and improves durability. Although there are several types of superplasticizers, their effectiveness in improving the quality and performance of concrete is widely recognized in the construction industry. As the demand for sustainable and durable construction continues to grow, the use of superplasticizers will likely become even more common in the future.

It should be noted that the use of superplasticizers is an effective way to improve the quality of building materials and reduce production costs. At the same time, it is necessary to take into account the environmental aspects of superplasticizers and improve their properties to achieve optimal results. Further research and development in this area may lead to the creation of even more effective and environmentally safe superplasticizers.

Nowadays there is a real construction boom in the world and the construction materials industry, including construction chemistry, is developing rapidly. Today there are many chemical additives for concrete synthesized in the world.

Scientists from all over the world, particularly from China, Japan, Germany, and the United States, are working to improve superplasticizers.

List of references

1. P.-C. Aïtcin, M. Baalbaki, Concrete admixtures key components of modern concrete, in A. Aguado, R. Gettu, S.P. Shah (Eds.), Concrete Technology: New Trends, Industrial Applications, E&FN Spon, London, 1994, pp. 33-47.
2. P.K. Mehta, Advances in concrete technology, Concr. Int. 21 (1999) 69-76.
3. R.J. Flatt, Towards a prediction of superplasticized concrete rheology, Mater. Struct. 37 (2004) 289-300.
4. Y. Ma, J. Bai, C. Shi, S. Sha, B. Zhou, Effect of PCEs with different structures on hydration and properties of cementitious materials with low water-to-binder ratio, Cem. Concr. Res. 142 (2021), 106343.
5. R.J. Flatt, Y.F. Houst, A. simplified view on chemical effects perturbing the action of superplasticizers, Cem. Concr. Res. 31 (2001) 1169-1176.
6. http://chinaconcretes.com, Retrieved on August 31, 2021.
7. US Standard Specification for Chemical Admixtures for Concrete. Designation: C494/C494M-17
8. Shah, S. R., Aslam, M., Shah, S. A., & Oad, R. (2014, july). Behaviour of Normal Concrete Using Superplasticizer under Different Curing Regimes. Pak. J. Engg. & Appl. Sci. Vol. 15, pp. 87-94.
9. Tamrakar, R., & Mishra, S. Experimental Studies on Property of Concrete due to Different Ingredient based Superplasticizer. International Journal of Science, Engineering and Technology Research,Volume 2, Issue, pp. 1036-1040.
10. E.V. Tkach. Modifiers in construction technology: Textbook. Karaganda State University. - Karaganda: Publishing house KarGTU, 2006.- 14 p.
11. Z. A. Kamalova, R. Z. Rakhimov, E. Y. Ermilova, O. V. Stoyanov. Superplasticizers in the production technology of composite concrete. Bulletin of Kazan Technological University. 2013
12. Ensberger F.M. and France W.G. Some physical and chemical properties of weight-fractionated lignosulphonic acid, including the dissociation of lignosulphonates. Journal of Physic and Colloid Chemistry 52:267-76, 1948

13. Rixom M.R.. Chemical Admixtures for Concrete, London E&F.N. Spon LTD. 1978
14. https://promplace.ru/himicheskie-soedineniya-staty/lignosulfonat-2298.htm#menu-1
15. https://bstudy.net/854620/tehnika/superplastifikatory
16. Ramachandran V.S. Additives in concrete. Reference Guide. Stroy publishing. 1988. 91-c.
17. Yakimovich E.T., Levina T.A., Ryzhovsky N.D., Kuten I.I., Rushkevich A.A., Podluzskaya G.I. Complex additive for concrete mixture. Patent RU 2039718 C1. 1995
18. https://vunivere.ru/work45184/page2
19. Karpis V.Z. High-performance concretes with additives LST modified with foam suppressants /NIL-21/, for precast concrete: Dissertation ... Candidate of Technical Sciences. / M., 1989. 22c
20. Concretes. Materials. Technologies. Equipment. M.: Stroyinform, Rostov n / d: Phoenix, 2006. -424 f.: ill.
21. Plasticizing additives for concrete. Specialized industrial and practical guidebook. Edited by V. Lozhkin. P. 2013.
22. Kastornykh L.I. Additives in concrete and mortars. Educational and reference manual. 2 ed. 2007-y. 12-page.
23. PLANK, J., Verleihung der Hans-Kühl-Medaille 2003, GDCh-Monographie 27, Hrsg
24. Alois Aignesberger, SURFACTANT COMPOSITION. United States Patent Office, 1972
25. [https://pandia.ru/text/80/371/51558-3.php
26. Trinker A.B. Lignosulfonates and electrolytes in concrete. History of creation and application. Surfactants and ersavers. https://ardexpert.ru/article/12864
27. Tkach E.V., Imanov M.O., Rakhimov M.A. Application of hydrophobic modifiers for obtaining hydrophobic cements of low water consumption // Bulletin of the Kazakh Academy of Transport and Communications. - Almaty.- 2005. -№3 (34). - C. 7-12.
28. Kh. Kamilov , A. Zaitov, A. Tulaganov. On a formula finding fractal dimension. Archives of Materials Science and Engineering. Volume 104, Issue 1, p.19-22, 2020. DOI:10.5604/01.3001.0014.3865
29. Recommendations for physical and chemical control of composition and quality of superplasticizer C-3. NIIZHB GOSSTROY OF THE USSR. Moscow 1984
30. M.N. Dolgacheva, M.G. Osmolovskaya. Study of application and dosage of plasticizing additives in concrete mixtures taking into account mineralogical and material composition of cement. "Bulletin of the Belarusian State University of Transport: Science and Transport". 2013. № 2 (27)
31. V.S. Izotov, Yu.A. Sokolova. Chemical additives for concrete modification. Moscow: Kazan State University of Architecture and Civil Engineering: Publishing house "Paleotype", 2006. - 244 c.
32. https://studref.com/546733/stroitelstvo/kratkaya_harakteristika_dobavok
33. A.P. Shvedov, S.F. Yakubovsky. Production of chemical additives in concrete based on sulfurization of inorganic products. INDUSTRY. APPLIED SCIENCES. Chemical Technology. №11 2011 г.
34. https://bstudy.net/815827/tehnika/plastifitsiruyusche_vodoredutsiruyuschie_dobavki
35. http://stroy-server.ru/notes/vidy-plastifitsiruyushchikh-dobavok
36. https://www.cormix.com/product-hilight/
37. Lomar® D Powder Product Bulliten. Website: www.geosc.com

38. Modern superplasticizers and thinners for concrete. Edited by Lozhkin V.P. Specialized industrial and practical handbook. Kaliningrad, 2013.
39. P.S. Krasovsky. Physico-chemical bases of cement structure formation Concretes: textbook / P.S. Krasovsky. - Khabarovsk: Publishing house Far Eastern State University of Railway Transport, 2013 - 204 p.
40. Yargin I.N., Yavorsky A.A. Modern chemical additives in the technology of monolithic concrete. INTERUNIVERSITY COLLECTION OF ARTICLES. Nizhny Novgorod State University of Architecture and Civil Engineering. 2009 г. 272-page.
41. Sikament FF - Technical Data Sheet.
42. T. Hirata, Working Mechanism and Material Design of Polycarboxylate-ether (PCE) Superplasticizers for Concrete, Hokkaido University, 2010. Ph.D. thesis.
43. T. Hirata, Cement dispersants, JP patent, 842022 (S59-018338), 1981.
44. R.J. Flatt, Dispersion forces in cement suspensions, Cem. Concr. Res. 34 (2004) 399-408
45. K. Hattori, Development of superplasticizers, Concr. J. 40 (2002) 27-35.
46. K. Yoshioka, E. Sakai, M. Daimon, A. Kitahara, Role of steric hindrance in the performance of superplasticizers for concrete, J. Am. Ceram. Soc. 80 (1997) 2667-2671.
47. J.A. Lewis, H. Matsuyama, G. Kirby, S. Morissette, J.F. Young, Polyelectrolyte effects on the rheological properties of concentrated cement suspensions, J. Am. Ceram. Soc. 83 (2000) 1905-1913.
48. P.F.G. Banfill, A discussion of the papers "rheological properties of cement mixes" by M. Daimon and D. M. Roy, Cem. Concr. Res. 9 (1979) 795-796.
49. G. Gelardi, R.J. Flatt, Working mechanisms of water reducers and superplasticizers, in: P.-C. Aïtcin, R.J. Flatt (Eds.), Science and Technology of Concrete Admixtures, Elsevier, 2016, pp. 257-278.
50. R.J. Flatt, P. Bowen, Electrostatic repulsion between particles in cement suspensions: Domain of validity of linearized Poisson-Boltzmann equation for nonideal electrolytes, Cem. Concr. Res. 33 (2003) 781-791
51. Lei Lei, Tsuyoshi Hirata, Johann Plank. 40 years of PCE superplasticizers - History, current state-of-the-art and an outlook. Cement and Concrete Research. 2022
52. Z. A. Kamalova, R. Z. Rakhimov, E. Y. Ermilova, O. V. Stoyanov. Superplasticizers in the production technology of composite concrete. Bulletin of Kazan Technological University. 2013
53. Lei Lei. A Comprehensive Study of Interactions Occurring Between Superplasticizers and Clays, and Superplasticizers and Cement. Dissertation. Lehrstuhl für Bauchemie, Technische Universität München, München 2016
54. J. Guicquero, P. Maitrasse, M. Mosquet, A. Sers, A water soluble or water dispersible dispersing agent, FR patent, 2776285, 1999.
55. J. Plank, K. Pöllmann, N. Zouaoui, P. R. Andres, C. Schaefer, Synthesis and performance of methacrylic ester based polycarboxylate superplasticizers possessing hydroxy terminated poly (ethylene glycol) side chains, Cem. Concr. Res. 38 (2008) 1210-1216.
56. S.A. Weckwerth, W. Radke, R.J. Flatt, A method for characterizing the chemical heterogeneity of comb-copolymers and its dependence on synthesis routes, Polymers. 13 (2021) 1921.
57. A. Lange, T. Hirata, J. Plank, Influence of the HLB value of polycarboxylate superplasticizers on the flow behavior of mortar and concrete, Cem. Concr. Res. 60 (2014) 45-50.
58. S.-I. Akimoto, S. Honda, T. Yasukohchi, Additives for Cement, EP 0291073, 1987.

59. Lange, A., Studien zur Zementkompatibilität von Polycarboxylat-Fließmitteln sowie zum Einfluss ihres HLB-Wertes auf das rheologische Verhalten von Mörtel. Dissertation, Lehrstuhl für Bauchemie, Technische Universität München, München 2015
60. Markus Philipp Schönlein. Investigations on the very first nucleation and growth of early cement hydrate phases. Dissertation Lehrstuhl für Bauchemie.
61. G. Albrecht, J. Weichmann, J. Penkner, A. Kern, Copolymers based on oxyalkyleneglycol alkenyl ethers and derivatives of unsaturated dicarboxylic acids, EP 0736553 B1, 1996
62. D. Hamada, F. Yamato, T. Mizunuma, and H. Ichikawa. Additive mixture for cement-based concrete or mortar contains a copolymer of polyalkoxylated unsaturated acid and a mixture of alkoxylated carboxylic acid with a corresponding ester and/or an alkoxylated alcohol. DE 10048139, 2001.
63. Z. Wang, Y. Xu, H. Wu, X. Liu, F. Zheng, H. Li, S. Cui, M. Lan, and Y. Wang. A room temperature synthesis method for polycarboxylate superplasticizer, CN 103897119, 2013
64. M. Yamamoto, T. Uno, Y. Onda, H. Tanaka, A. Yamashita, T. Hirata, and N. Hirano. Copolymer for cement admixtures and its production process and use, US Patent, 6,727,315, 2004.
65. T. Amaya, A. Ikeda, J. Imamura, A. Kobayashi, K. Saito, W. Danzinger, and T. Tomoyose. Cement dispersant and concrete composition containing the dispersant, US 7393886, 2000
66. S. Ng, J. Plank, Interaction mechanisms between Na montmorillonite clay and MPEG-based polycarboxylate superplasticizers, Cem. Concr. Res., 42, 2012, 847-854.
67. M. Nehdi, Clay in cement-based materials: critical overview of state-of-the-art, Constr. Build. Mater., 51, 2014, 372-382
68. L. Bailey, M. Keall, A. Audibert, J. Lecourtier, Effect of clay/polymer interactions on shale stabilization during drilling, Langmuir, 10, 1994, 1544-1549.