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1. Introduction

The beneficial effects of some organic polymers on the properties of concrete were discovered quite by chance just before the Second World War.

It came to light that polynaphthalene sulfonate and lignosulfonates could reduce the amount of mixing water by about 5% when producing a concrete of a given workability. These chemicals started to be sold as water reducers. It was also discovered that introducing a small amount of some tensioactive agents when mixing concrete entrained millions of tiny air bubbles that significantly improved the workability of the fresh concrete and the freeze-thaw resistance of hardened concrete

Other molecules that could accelerate or retard Portland cement hydration were also discovered more or less by serendipity, giving rise to the admixture industry. At that time, admixtures were basically extracted from cheap by-products to keep them competitive and profitable given the very low cost of Portland cement.

The late 1960s and early 1970s witnessed efforts to further increase concrete workability without additional mixing water, leading to the development of synthetic polynaphthalene and polymelamine sulfonates in Japan and Germany, respectively. This new generation of water reducers - called superplasticizers - made it possible to reduce the water requirement from 5% to 15%. Superplasticizers started to be used to increase the workability of concretes of given water - cement ratios (w/c), to decrease the w/c for a given workability, or to both increase workability and decrease the w/c.

The performance of these new polymers was crucial to the development of high - performance concrete, making it possible to produce workable high - slump concretes with w/c between 0.30 and 0.40 and, in some cases, as low as between 0.25 and 0.30. Practice revealed, however, that not all Portland cements - supposedly equivalent through standardization-reacted the same way with the same superplasticizer. This gave rise to the notion of cement- superplasticizer compatibility and robustness to account for the fact that some cements worked well with polysulfonates, while others did not. In the latter case, workability could be increased for a very short period of time, but was lost very rapidly, even within 10 to 30 minutes in the worst cases.

Since the market for high-performance concrete was rapidly developing, a significant amount of research went into better understanding the behavior of Portland cement in the presence of polysulfonates. This research effort, carried out during the 1990s, resulted in the creation of the science of admixtures. It can now be said that admixtures are developed more scientifically rather than by trial and error.

Their mode of action is better understood, while compatibility and robustness problems can be explained and corrected in some cases. More recently two new types of admixtures have appeared on the market to improve some aspects of concrete performance: viscosity modifying agents and shrinkage reducing admixtures.

The benefits of polysulfonate and polycarboxylic superplasticizers, viscosity modifying agents, and shrinkage reducing admixtures will be reviewed briefly in this paper.

2. Portland cement flocculation

Portland cement particles flocculate more or less rapidly when they come into contact with water. This phenomenon can be readily observed by dispersing 50g of any Portland cement in a 1-L graduated container of water. After 10 to 30 minutes, cement particles will have settled to the bottom of the container and occupy 2 to 3 times the volume of the 50g of dry cement. After adding 5 ml of superplasticizer to the solution and shaking the container, it can be observed that the Portland cement suspension remains stable and that the cement particles settle according to their grain size. This sedimentation can be used to determine cement particle size.

This strong tendency of Portland cement particles to flocculate when in contact with water is related to the numerous electric charges that appear on their surface during final grinding. Cement flocs entrap some water, so that additional mixing water is needed to improve concrete workability (Figure 1)

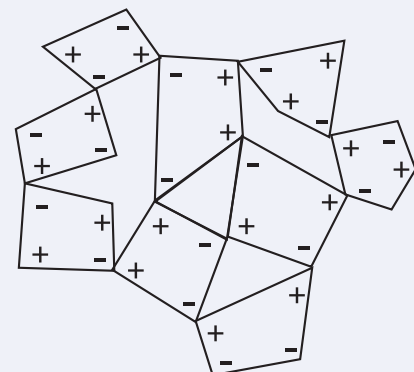
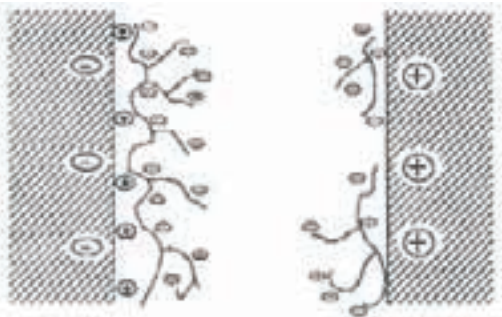


Fig. 1. Flocculation of cement particles

The addition of this water that will not combine with Portland cement particles is catastrophic from the standpoint of durability and strength because it weakens the concrete. The basic rule is the greater the water added, the weaker and less durable the concrete.

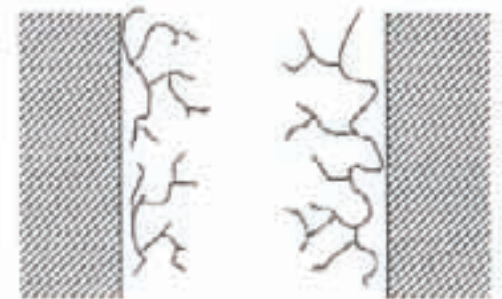
Water reducers and superplasticizers, which are, in fact, relatively efficient dispersants, counteract the tendency of cement particles to flocculate. The neutralization of the electric charges can be essentially electrostatic in nature, in the case of sulfonates (lignosulfonates, polynaphthalene, and polymelamine), or results from steric repulsion, in the case of polycarboxylates (Figure 2).

Electrostatic repulsion



Cement particle

Steric repulsion



Cement particle

Fig.2. Modes of action of superplasticizers

As stated above, experience shows that the particles of some cement can be readily dispersed, while flocculation is only somewhat delayed in other cases. What accounts for this difference? Why do some superplasticized concretes retain their slump or only lose a few centimeters during the 90 minutes after mixing, while, in other cases, retention doesn't last more than 10 minutes? The answer is that polysulfonates and polyacrylate polymers have secondary effects other than

simply neutralizing surface electric charges on Portland cement particles. In particular, they react more or less rapidly with some active sites on the surface of the cement particles, essentially C_3A sites, as shown in Figure 3.

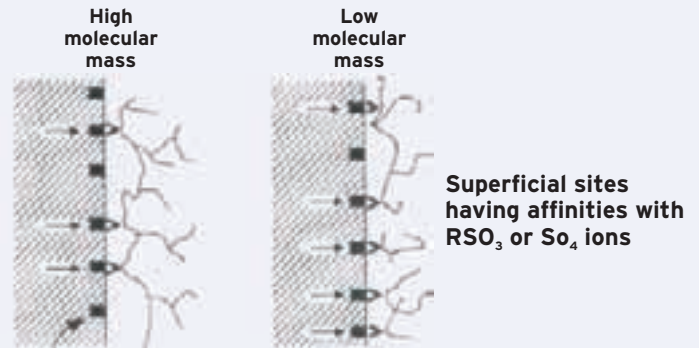


Fig.3. Neutralization of active sites by a polysulfonate

2.1. Polysulfonates

Depending on the reactivity of the C_3A and the initial availability of SO_4^{2-} ions during cement hydration, polysulfonate molecules are consumed to varying degrees, reducing concrete slump. In fact, polysulfonate molecules compete with gypsum molecules in neutralizing C_3A during and after mixing. The cement - superplasticizer combination is said to be incompatible when slump occurs rapidly. For example, it is common knowledge that most white cements are not compatible with polynaphthalene and polymelamine sulfonates because they usually have very high C_3A and very low alkali - sulfate contents.

This loss of polysulfonate molecules also explains why polysulfonates should be introduced at the end of mixing rather than at the beginning. This procedure ensures that a maximum of C_3A sites are neutralized by the calcium sulfate added during final grinding before the superplasticizer is introduced. This mode of action also accounts for why some concrete technologists recommend using a sacrificial lignosulfonate at the start of mixing, followed by the introduction of a polynaphthalene or polymelamine sulfonate at the end of mixing, or a double introduction technique in which a certain amount of superplasticizer is introduced at the beginning of mixing (about) -

knowing that it will be lost - and the rest at the end of mixing.

Since the efficiency of polysulfonates is linked to the electrical charges and active sites on the surface of cement particles, the proportion of clinker phases and their distribution on the surface of cement particles are very important. For example, let us consider the action of a polysulfonate on the five theoretical cement particles shown in Figure 4.

For polysulfonate molecules, particle G_1 is composed exclusively of silicates, particle G_2 is composed exclusively of interstitial phase, and particle G_3 , is a mixture of both. More polysulfonate molecules will react with particle G_2 than with particle G_3 ; none will react with particle G_1 . Particles G_4 and G_5 have the same interstitial phase, although the C_3A and C_4AF contents are reversed. A polynaphthalene molecule will react more with particle G_4 than with particle G_5 because C_4AF is less reactive than C_3 .

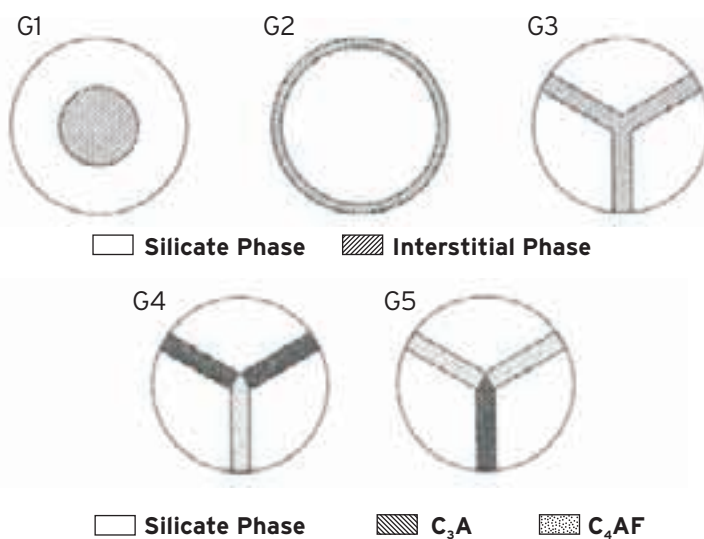


Fig.4. Theoretical cement particles

Moreover, the solubility of the alkali sulfates that are formed in the clinker during its firing and by the calcium sulfate added during final grinding greatly influence polysulfonate performance because the SO_4^{2-} liberated by these sulfates complete with the So^{3-} termination of the polysulfonate when reacting with the C_3A .

Finally, it is well - known that there are significant

differences in the initial solubility of gypsum, hemihydrate, dehydrated gypsum (also improperly referred to as soluble anhydrite), and natural anhydrite. It is further common knowledge that the different forms of C_3A (cubic or orthorhombic) influence its reactivity: cubic C_3A is the more reactive form. In clinker, C_3A is cubic when clinker alkali content is low and orthorhombic when clinker alkali content is high. In fact, both forms of C_3A occur in the same clinker.

Given this great diversity of situations, it should be obvious that polysulfonate action on particular cement can vary extensively.

2.2 Polycarboxylates

Synthetic organic polymers bearing a carboxylic group (COOH) - referred to as either polyacrylates or polycarboxylates - are efficient Portland cement dispersants. Indeed, the carboxylic group becomes ionized in alkaline solutions such as a Portland cement suspension. Polycarboxylates have a secondary effect in that they are very effective complexants for di- and trivalent ions and they can sometimes entrain air bubbles. Formulations of polycarboxylates first appeared in the early 1980s.

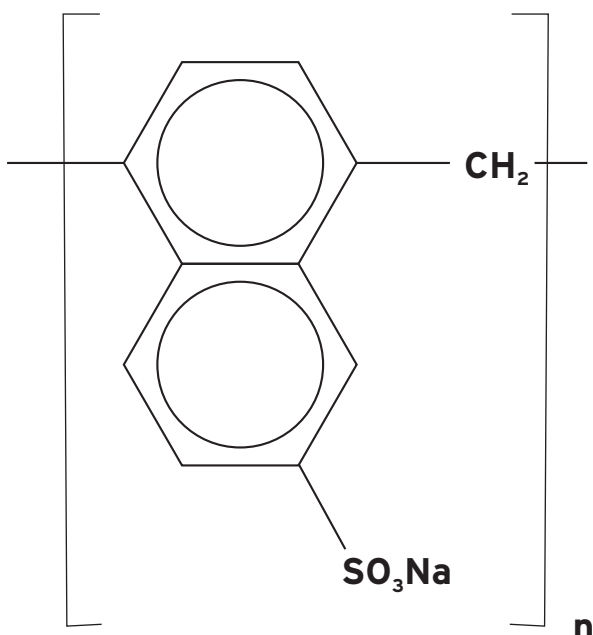
Chemically, most polycarboxylate polymers share a common polyacrylate or polymethacrylate main chain (backbone). Various side chains are grafted on to the main chain as pendant groups: polyethylene oxides (PEO), polypropylene oxides (PPO), or mixed PEO - PPO. When all the side chains are aligned parallel or perpendicularly to the main chain, the polymers look like a comb, so they are referred to as comb like polymers.

Variations in backbone length, side-chain density, and side chain length, can generate a great variety of polymers with a quite broad range of physicochemical and functional properties. Moreover, since various other functional groups (such as phosphates, sulfates, hydroxyls, ethers, amides, and amines) can be grafted into the acrylate-derived polymer, it is possible to generate a nearly infinite variety of polymers with mixed functionality. Hopefully, a few new formulations will provide the basis for an in-depth evaluation of these superplasticizers with various types of cementitious systems, as was done in the 1990s with polynaphthalene and polymelamine sulfonates.

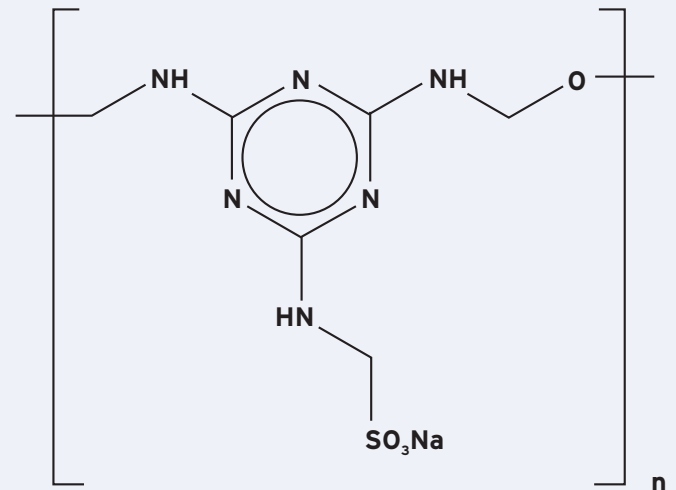
The perfect, universal polycarboxylate - if it exists, which I personally doubt - has not been discovered yet, despite the claims in some enthusiastic and optimistic marketing literature. The current issue with polycarboxylate superplasticizers is that they are still in their infancy technologically. New formulations are appearing almost every year and the chemical formulation of some commercial polycarboxylate superplasticizers changes 2 or 3 times in a year and yet are marketed under the same name.

In principle, the multifunctional approach offers great potential for optimizing the dispersion and fluidification properties of the different cementitious systems used. As things now stand, however the lack of understanding of how the different functional groups interact with the numerous phases in cementitious systems means that polycarboxylate formulations are developed by trial and error. The compatibility and robustness of polysulfonate - cement combinations were not easy to study with such "simple" polymers as poly sulfonates, so it is reasonable to expect that the phenomena involved in using polycarboxylates will be even more complex.

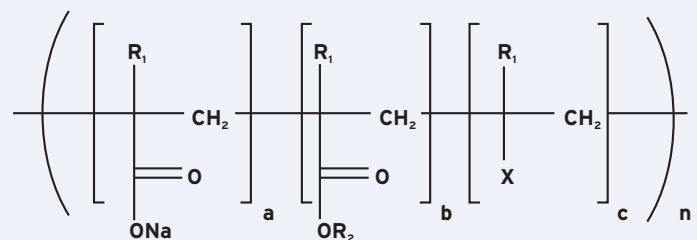
The generic molecular structure of three major superplasticizers is shown in Figure 5



Sodium poly-β-naphthalene sulfonate



Sodium polymelamine sulfonate



$R_1 = \text{H or } \text{CH}_3$
 $R_2 = \text{CH}_3, \text{EO, PO or EO-PO}$
 $X = \text{CN}, \text{SO}_3, \text{etc}$

Polyacrylate copolymer

Fig. 5. Generic molecular structure of some superplasticizers
3. Viscosity modifying admixtures

Compatible, robust cement - superplasticizer combinations can yield concretes with an initial slump of about 200 mm without any risk of segregation, when the w/c ranges from 0.30 to 0.40. Such mixes retain their slump of about 150 mm for 90 minutes after mixing, allowing placement with a minimum of vibration.

Increasing the initial slump over 200 mm becomes problematic due to the dramatically higher risk of segregation; the cement paste is too fluid to maintain the sand particles in suspension and /or the mortar is too fluid to hold the coarse aggregate in suspension. Obtaining an almost fluid concrete termed "self compacting" that flows freely requires making the cement paste more viscous. This can be achieved in a number of ways. One is to increase the fines content in the mix and of course, the amount of superplasticizer. This is the method recommended by cement

producers. Another way is to add a viscosity modifying admixture (VMA) to the mix without increasing the amount of fines to increase paste viscosity. Most commercial VMAs are composed of methylcellulose, or different gums, and the like. This is the approach advocated by admixture companies. The third alternative consists in slightly increasing the amount of fines by using small amount of VMA and adjusting the amount of superplasticizer. Usually, I prefer this approach, since it offers more flexibility, although it requires an optimization process. I recognize that the other two ways have been used successfully in the field.

4. Shrinkage reducing admixtures

One of the main causes of plastic, autogenous, and drying shrinkage is the surface tension and angle of contact of the menisci developed in the capillary pore system of the cement paste. Shrinkage occurs in pores 2.5 to 5 μ m in diameter. Menisci cannot form in smaller pores and tensile stresses generated in larger ones are too small. Consequently, one approach to reducing shrinkage is to add an admixture to the mix that will reduce the surface tension of the interstitial liquid in the fresh and hardened concrete. This is precisely what commercial shrinkage reducing admixtures (glycol, either blend) do. Shrinkage reducing admixtures do not eliminate autogenous or drying shrinkage; they reduce it to a level that practically eliminates the risk of cracking. They can also be used effectively as a complement to fogging or water curing or to the use of saturated lightweight aggregates. The advantage of shrinkage reducing admixtures is that they act on the mass of the concrete.

My personal recommendation for fighting plastic shrinkage is to use fogging, followed by 7 days of water curing to counter autogenous and drying shrinkage. I further recommend the use of a shrinkage reducing admixture as a complement in critical cases in which the two preceding methods cannot be easily implemented.

As far as drying shrinkage is concerned, concrete elements that have been water cured for 7 days can withstand drying shrinkage with a minimum of cracking.

5. Conclusion

Admixtures are definitely key components of modern concrete, used in small quantities, they can drastically improve the properties of fresh and hardened concrete, its long-term durability, and its economical competitiveness. Admixtures are no longer extracted from cheap byproducts; most are now specially made for concrete according to a relatively complicated synthesis process. These are not any miracle products because the new science of admixtures is developing. We now have a clearer understanding of how admixtures work and this spurs the development of new products. Four admixtures were presented in this paper to focus on progress in this new science.

The perfect universal admixture appears forever beyond our grasp because Portland cement clinker is made from unprocessed (not beneficiated), very cheap and have a highly variable composition at the level of their minor components. While these minor components occur in very small proportions in the clinker, their effects on admixture action can be significant and not always positive.

Admixture use in the future will be affected by the cement industry's recent trend towards using all kinds of waste in preparing the raw meal and waste-based fuels (the so-called alternative fuels) for firing the kilns. This will increase the variability of the Portland cement clinker and complicate somewhat the use of concrete admixtures that are increasingly synthetic products specially prepared for the cement and concrete industries. This represents an interesting challenge for researchers. In the not-so-distant future, cement will be marketed with a list of recommended compatible admixtures.