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Mechanism of Action of Superplasticizers and the Contribution of Superplasticizers to Early Strength and Economy

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ABSTRACT: The greatest contribution to the field of concrete technology has been that of admixtures, both chemical and mineral admixtures. Of all the admixtures known, superplasticizers (SPs) have emerged as the most advantageous admixtures which can affect the flowability of concrete and its performance on a larger scale. The superplasticizers are long chain polymers which get adsorbed on the surface of cement and modify its fresh and hardened behaviour. The working of superplasticizers is a complex phenomenon which has become the centre of attention of various authors and many theories have come up. In this paper, one such mechanism of action has been discussed. The working of superplasticizers is based on a dispersion mechanism which has been explained in this paper. The study focuses on the mechanism of action of SPs and their contribution to early hydration and economical viewpoints.

KEYWORDS: Dispersion, Adsorption, Repulsion, Workability, Agglomeration, Potential.

I. INTRODUCTION

Superplasticizers are chemical admixtures made of long chain polymers added to ready mix concrete to modify its plastic and hardened properties. These are high range water reducers which permit a reduction in water content by about 30% or more. Superplasticizers have good impact on concrete rheology. They are known as superfluidizers, superfluidifiers and super water reducers. The various superplasticizers are classified into four main groups which are Sulhonated melamine formaldehyde condensates (SMF), Sulphonated Napthalene formaldehyde condensates (SNF), Modified lignosulphates (MLS), and other sulfonic acid esters and carbohydrate esters. Lignosulphate based air entraining water reducer was the first superplasticizer used followed by beta nephtalene sulphonate base. The superplasticizers increase the workability or the ease with which concrete can be mixed, transported, placed without much loss of homogeneity in the fresh state and strength and durability of concrete in the hardened state. The strength of concrete is inversely proportional to the water content. Since the superplasticizers decrease the water content required for normal concrete, these increase its strength and durability in the hardened state. The superplasticizers permit decrease in water content of fresh concrete for same workability or fluidity. These can also increase the workablity of fresh concrete for the same water content. Superplasticizers can also decrease the cement content of concrete for the same strength as these decrease the water content required and to maintain a particular water cement ratio and thus the strength, the cement content has to be decreased thus making it more economical. The superplasticizers by their dispersion action make water that is initially entrapped between the cement agglomerates, available for increasing the workability of the mix.

The Paper is organized in five sections. Section II gives a brief literature review about the work done in this field of concrete technology, Section III presents the discussion in which the mechanism of action of superplasticizers has been explained followed by Section IV in which the study results are stated. Section V presents the conclusion and the necessity of superplasticizers.

II. LITERATURE REVIEW

Muhsen Salem, Salahaldein Alsadey and Megat Azmi Megat Johari in their paper, "Effect of superplasticizer dosage on workability and strength characteristics", conducted the experimental tests for fresh and hardened properties of concrete for three mixes of 30 MPa grade and the results were compared with normal concrete. The tests considered

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for study were slump test, slump loss, flow table and compressive strength test. The results showed that, for the constant water cement ratio, increase of superplasticizer dose in properties of concrete leads to gain of good workability. Moreover, there is also increase in compressive strength than that of normal concrete mix.

Ming Liu, Jiaheng Lei, Bo Huang in their paper, "Synthesis, properties and dispersion mechanism of sulphonated acetone-formaldehyde superplasticizer in cementitious system", studied about the Sulfonated acetone formaldehyde superplasticizer (SAF) and stated that the cement paste mixed with SAF shows good fluidity. SAF exerts little retarding effect on cement paste and it behaves like a typical polycondensate superplasticizer. The main dispersion mechanism of SAF is attributed to electrostatic repulsion.

Collepardi, L. Coppola, R. Troli, and M. Collepardi in their paper, "Mechanisms of Actions of Different **Superplasticizers For High Performance Concrete**", studied about that the composition of superplasticizers, mechanism of action (electrostatic repulsion and steric hindrance), influence of the cement composition (C3A, alkali, SO3), mode of addition of superplasticizer, slump loss, blending of superplasticizers and stated that the superplasticizers can be used for three different purpose, to increase workability without changing the mixture composition, to reduce the amount of mixing water in order to reduce the water-cement ratio and then to increase strength and/or improve durability, and to reduce both water and cement in order to reduce cost in addition to reducing creep, shrinkage and thermal strains caused by heat of cement hydration

Mengting Li1, Yi Wang1, Haidong Jiang1, Chunyang Zheng1 and Zhaolai Guo1 in their paper, "Synthesis, characterization and mechanism of polycarboxylate superplasticizer with slump retention capability", stated that the polycarboxylate superplaticizer with hydroxyethyl group prepared in their study had good dispersing performance and high slump retention capability for concrete.

III.DISCUSSION

Out of the amount of water used in concrete in the mixing stage, only about thirty to forty percent of water is used in the process of hydration, that is the reaction of water with cement and the formation of a variety of complex compounds which impart the strength and hardness characteristics to the concrete like the calcium-silicate-hydrates (C-S-H) gel. The remaining water, almost sixty to seventy percent, is used in the lubrication of aggregates both coarse and fine and its entrapping in the agglomerates of cement. If this water is used effectively in the mix, the workability or fluidity of the mix can be increased. When cement is mixed with water, the cement particles have an irresistible tendency to attract or flocculate in the mix as the Van Der Waals forces of attraction is greater than the positive charge on the cement particles because of the presence of Tricalcium Aluminate (C3A). The addition of water to cement therefore causes agglomeration or the formation of flocs of cement. These agglomerates so formed entrap a certain amount of water which could be used to make the concrete more workable and to increase its fluidity, if free. The water reducing admixtures especially the superplasticizers release this entrapped water from the cement agglomerates and increase its workablity at the same water content. This is done by a process called dispersion.

A cement dispersant is molecule that has a tendency to separate the cement particles physically. Superplasticizers function as cement dispersants by their negative charge characteristics due to which they neutralize the forces of attraction between the cement particles temoprarily and thus break the agglomerates and release the entrapped water giving concrete a much more fluid like consistency and making it easier to work upon. The process of dispersion is carried out by the superplasticizers in two steps, adsorption and electrostatic repulsion.

IV.RESULTS

ADSORPTION

The surface of cement particles carries a positive charge due to the presence of calcium ions from calcium aluminates (C_3A) and calcium silicates (C_2S,C_3S) . The superplasticizers which are large chain polymers carry a negative charge due to which the SPs get attracted towards the positive surface of the cement particles and therefore get adsorbed irreversibly over them. Adsorption of SPs over the cement is influenced primarily by the type of cement used. The type III cement (which is a cement with high early strength as it is ground finer so that the hydration and the resultant strength attainment is earlier) was found to have the highest adsorption degree followed by Type I and then Type II cement. Also, different superplasticizers show different degree of adsorption on the same type of cement. For Sulphonated Melamine Formaldehyde (SMF) superplasticizers, the adsorption on tricalcium aluminate C_3A occurs within a few seconds. The hexagonal aluminates adsorb a large amount of superplasticizer and do not convert to the

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cubic form in the system C_3A -H₂O-SMF immediately because of the formation of complexes between SMF and C_3A . However, for the adsorption of SMF superplasticizer on Tricalcium Silicate (C_3S), a little adsorption occurs for the first hour. The adsorption is negligible till 4 to 5 hours but then the adsoption increases continuously. SMF superplasticizer is mostly adsorbed by C_3A and gypsum in cement. This adsorption occurs within a few minutes. To lower the rate and the amount of adsorption, the superplasticizers can be added 5 to 30 minutes after the hydration begins. By delaying the addition of admixtures to the concrete, enough admixtures will be left in the solution to produce effective dispersion of the silicate phase which will inturn improve the workability of the mix. The adsorption beyond the first 5 hours is mainly due to the calcium silicate hydrates in cement. Adsorption is also influenced by the concentration of the superplasticizer in the mix. Higher concentration of superplasticizers increase the adsorption rate and amount as well.

ELECTROSTATIC REPULSION AND DEFLOCCULATION

After the adsorption of the long chain negatively charged superplasticizers on the positive surface of the cement particles, the cement particles attain an overall negative charge as there is a residual negative charge left on the cement particles after the charge neutralization takes place. Because of this negative charge, the flocculated cement particles repel each other and the intensity of repulsion is known as the Zeta potential. This repulsion makes the cement particles move away from one another thus causing the agglomerates of cement particles to crack.

The water that is entrapped between the agglomerates is released and is free to increase the fluidity of the mix without any additional supply of water.

CONTRIBUTION TO EARLY STRENGTH AND ECONOMY

After the addition of superplasticizers to conventional concrete, there is an early attainment of strength of concrete. This is explained as follows. As explained in the mechanism of action section of this paper, the agglomerates of cement particles break as the result of electrostatic repulsion between the cement particles. As the aglomerates break, the surface area of cement particles increases and more area is made available for hydration. Hydration involves the reaction of the cement with water to form complex hydrates which provide strength and hardening to the concrete. Due to the early hydration of cement attributed to the increase in surface area, there is an early attainment of strength in superplasticizer admixtured concrete. Due to this reason, the superplasticizers become mandatory when mineral admixtures such as fly ash and ground granulated blast furnace slag are used. Because the mineral admixtures are very fine and thus have a large surface area, they require a huge quantity of water for hydration and lubrication, this high demand of water is fulfilled by introducing superplasticizers to the mineral admixtured concrete.

The use of superplasticizers in concrete allows the reduction in cement content for the same strength, durability and workability. This is because strength of concrete is a function of its water cement ratio. By using superplasticizers, the water content is reduced by about 30%. To maintain the same water cement ratio, the quantity of cement is also reduced per square metre of concrete and the strength is maintained as constant since the water cement ratio is constant. Since the cement is the most expensive ingredient of concrete, the reduction in its quantity allows the better utilisation of the economy of construction.

A test was conducted to examine the early attainment of strength using SMF superplasticizers. The results are shown under.

	7 Day strength of M30 Concrete	7 Day strength of M40 Concrete
Without SP	23.45MPa	33.87MPa
With SP	28.27MPa	38.32MPa

V. CONCLUSIONS

The paper presents the working of superplasticizers by one of the probable mechanisms. It is thus reviewed that the superplasticizers work to release the entrapped water in the agglomerates of cement by the action of dispersion in which the superplasticizers get adsorbed on the surface of cement particles and then break the agglomerates by virtue of electrostatic repulsion with zeta potential. Experiments were conducted to observe the effect of superplasticizers on the early strength of concrete and it was found that by incorporating superplasticizers in normal concrete, the early strength

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increases. It was also found that the use of superplasticizers in concrete can reduce the amount of cement required for the same strength parameters thus making the construction economical. Therefore the use of superplasticizers in modern construction is highly recommended.

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