USE OF SUPERPLASTICIZERS IN CONCRETE AND THEIR COMPATIBILITY WITH CEMENTS

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ABSTRACT

This investigation formed a prior stage of a research programme which was concerned about performance of various types of concrete under sulphate attack. It was intended to investigate into the use of superplasticizers in concrete, the aspect of compatibility among available cements & superplasticizers and to choose a suitable pair of them for the programme. Three different types of available cements & superplasticizers were considered. Details and results of this investigation are reported in this paper. The investigation clearly showed that compatibility between cement and superplasticizer is an important aspect in concrete making with superplasticizer and its performance under aggressive sulphate attack conditions later on.

Keywords: cement, compatibility, Superplasticizer, workability

1.0 INTRODUCTION

Superplasticizers, also called as High Range Water Reducing (HRWR) Admixtures, are micro-molecular organic or chemically synthesized agents which, according to their chemical contents, have been divided into the following four groups [1,2]: Sulphonate melamine formaldehyde, Sulphonate naphthalene formaldehyde, Modified lignosulphonates and Copolymers containing sulphonamic and carboxyl groups which may contain polycarboxylates and polyacrylates [3]. For normal concrete applications ASTM C494 defines Type F and Type G superplasticizers for normal setting time and retarded setting time conditions respectively. For flowing concrete, supposed to have a slump more than 190 mm, ASTM C 1017 defines them as Type I and Type II respectively [4].

The first generation of superplasticizers, mentioned above, resulted in significant improvements of the properties of fresh concrete and they are still widely used. In these, Lignosulphonates are the by-product of the bisulfitic process of pulp and paper production [5]. These, from a dispersion point of view, are dispersing agents only and are less efficient than synthetic superplasticizers. Increasing demands of high & ultra-high strength and high-performance concrete in the context of improved workability, strength and durability spurred the development of new types of synthetic superplasticizers with higher performance [6,7]. A type of these new generation superplasticizers consists of comb-type copolymers with an anionic backbone on which un-charged polyethylene oxide based chains of variable length are grafted [8]. It commonly has carboxylic and/or sulphonate groups which render a negative charge to the polymer [9,10,11].
Performance of such type of superplasticizer is affected by their structural elements such as side chain length, side chain density and main chain length. Out of these, side chain density controls the capacity of superplasticizer to hold negatively charged group [8]. Though this new class of superplasticizers based on polycarboxylate chemistry is, in general, not as robust or tolerant to different cements or admixtures like polycondensates, much lower water to cement ratios can be achieved with this class, especially in precast concrete because polycarboxylate molecules having specific characteristics provide excellent slump retention of concrete [8]. Macromonomers based on hydroxy terminated poly (ethylene glycol) methacrylate ester chemistry also have been reported to produce superplasticizers of high quality [8]. Some of the important characteristics of superplasticizers are pH, specific gravity, solids content and structural configuration of molecules. Molecular weight of superplasticizer has been reported to affect its performance to a great extent [12,13]. Normally, superplasticizers are combinations of several chemical compounds and it is difficult to determine the exact architecture of a particular superplasticizer. An infrared spectrum may be used to determine the composition and uniformity of a superplasticizer while Gel permeation chromatography, anionic charge density determination and magnetic resonance tests are used for the determination of molecular weight and number of α and β sulphonated sites. As these tests are difficult, time consuming and costly, it is practically prudent to assess the performance of a superplasticizer by its effect on rheology on a reference cement paste or a cement concrete mix [5]. Typical applications of superplasticized concrete are recommended in the making of architectural & high strength concrete, construction of precast / prestressed concrete structures, parking and bridge structures, rapid-cycle high rise projects, industrial slabs, massive concrete structures etc [1].

1.1 Mechanism of Action of Superplasticizers

According to an ACI committee report, superplasticizers are helpful in producing concrete with compressive strengths greater than 41 MPa at 28 days and are essential in achieving strengths that exceed 69 MPa [1]. Superplasticizing admixtures affect the fresh concrete in a positive manner by altering its rheology [14]. They affect the surface chemistry of cement grains due to their charges. Negative charges increase on the surface of cement grains due to the surface adsorption of superplasticizers [7,15,16].

The physical effects of superplasticizer molecules can be considered being of the following three types [5]: Physical adsorption under the effect of Van der Waals & electrostatic forces, Long-range repulsive forces due to a reconfiguration of the superficial charges and Steric repulsive forces among adjacent superplasticizer molecules and adjacent cement particles.

In the electrostatic repulsion, the superplasticizer molecules cover cement particles and due to like charges of superplasticizer, cement particles are subjected to repulsive forces. Polynaphthalene and polymelamine sulphonate types of superplasticizer work under this mode of action. In the steric repulsion mode, superplasticizer molecules are adsorbed on the cement particles [17,18]. Polycarboxylate and polyacrylate superplasticizers are reported to work in this way [19]. While electrostatic repulsion has been described as the main mode of action for naphthalene or melamine based superplasticizers, polycarboxylate type of superplasticizers have dual mechanism of electrostatic and steric repulsion. Steric repulsion is produced due to their side chains of varying lengths, formulated to be a part of the backbone of the molecule. These side chains physically keep the cement particles apart, allowing water to surround more surface area of the cement particles [20]. Because of this fact, polycarboxylate types of superplasticizer are considered to be more effective [2]. The high degree and duration of the fluidity that such admixtures impart to concrete are related to inherent structural factors of them. It is observed that for better fluidity, the main chain of the superplasticizer should be short and lateral chains should be long & more in number [13]. Consequently, the cement grains repel due to electrostatic forces and do not flocculate. This helps in maintaining a homogeneous distribution of cement particles & reducing the internal friction in the fresh concrete and thus improves workability of concrete [21]. It is pointed out that apart from homogenous distribution of cement particles in concrete, the increased wetting effect of pore water
due to its lowered surface tension in the presence of superplasticizers, is also a contributory factor for increase in workability [2].

Superplasticizers can interact with cement particles both physically and chemically. While the physical effect comes due to the above-mentioned effects of electrostatic repulsion and the steric repulsion, chemically they can also react with hydration products of the cement. It is reported that some of them can lower the initial hydration rate by reacting with C₃A preferentially, while others delay the hydration reaction of C₃S component [22]. The incorporation of superplasticizer in cement paste clearly influences rate of the hydration process, manifesting itself in a lower amount of polymerized silicates, which is indicative of lower C–S–H gel formation [7,23,24]. The interaction between cement particles and superplasticizer molecules depends on the physico-chemical characteristics of the cement particles and the architecture of the superplasticizer molecules [5]. The addition of negatively charged dispersants to cement suspensions affects the particle surface charge thus favouring repulsion among particles until the saturation adsorption limit of dispersing agent is attained. This phenomenon is said to occur in correspondence to a critical dispersant concentration [25]. It has been reported that in considering optimization of the molecular architecture, good workability can be achieved by addition of highly charged superplasticizers with long side chains. This has been reported to minimize undesired retardation phenomena, if any [26]. The presence of Lignosulphonates and other such surface-active products results in the entrainment of some air in the form of self-stabilized bubbles. The presence of sugars in these products results in the retardation of setting and hardening of concrete. Though presence of sugars resulting in retardation may be useful in hot weather, it is difficult to use these products in dosages greater than some critical values [5].

1.2 Effects of Superplasticizers and Factors Affecting Their Performance

Superplasticizing admixtures improve concrete properties in the early age. Studies of their effects on cement paste rheology provide much needed knowledge for controlling the chemistry of cement for special applications such as injections of cement suspensions in loose soils as well as to a better understanding of the flow behaviour of mortars and concrete [27]. It has been reported that the effects of the superplasticizers on controlling setting time is not known precisely [28]. Subsequently, after the setting of the cement, the superplasticizer is not expected to affect the properties of the concrete significantly [29]. They have not been found to have adverse effects in the hardened concrete. The influence of superplasticizers on properties of fresh concrete has been found to be directly related to the amount of admixture added to the concrete mix within a range of water cement ratio. They tend to show reducing returns as the water cement ratio of concrete increases [30]. It is also reported that the fluidity of cement matrix depends on the type of superplasticizer and the mixing method [31]. It is reported that in some cases the initial improvement of the rheology of concrete due to superplasticizer is of a short duration. It may be due to a natural affinity of the reactive sites of cement grains for SO₄²⁻ ions, which may be in good supply from calcium and alkali sulphates in cement. Superplasticizer molecules come in competition with these ions for neutralization of such sites, a portion of them reacts with interstitial phase and is no longer available for the dispersion of cement particles [32,33].

Combined effects of temperature and time on the performance of different types of superplasticizers in terms of rheological parameters including yield stress, plastic viscosity, and thixotropy of cement pastes have been investigated. It has been suggested that required dosage of polycarboxylate-based superplasticizers is less than melamine sulfonate- or naphthalene sulfonate-based superplasticizers for ensuring adequate rheological behavior at high temperature and prolonged mixing time [34]. In a study, it was shown that different superplasticizers have widely different effects on changes in yield values and the plastic viscosities of the paste [30]. Up to two additional doses of superplasticizer have been used with success when delays occurred and the required slump had not been maintained [1]. It has been observed that superplasticizers defloculate cement particles much better than water reducers [5]. They have been observed to retard the mixes and the degree of retardation varies with the type and dosage of the admixtures [35]. At the same time, it has been observed that though the presence of polycarboxylate admixture retards the initial cement hydration
reactions, this effect may be offset by possible increased diffusion in later stages [13]. Hydration of cement is said to be delayed by addition of superplasticizers. Generally speaking, the effect of superplasticisers on cement hydration is assumed to involve several factors. The molecules of the superplasticiser hinder water and Ca\(^{2+}\) ion diffusion across the solution–cement interface. The Ca\(^{2+}\) ions form complexes with the superplasticiser molecules, inhibiting the nucleation and growth of Ca-rich species [36]. In concentrated suspensions, individual particles may not be completely separated from each other despite the use of superplasticizers and may form loosely associated clusters.

The morphology of the binder matrix should be related to the complexity of the coagulated structure of the cement particles and the hydration delay of the cement caused by superplasticizers. Effect of architecture of superplasticizers on workability and retardation for differing C\(_3\)A contents in cements have also been investigated. Very few studies have concerned themselves with the influence of superplasticizers on the texture formation of hardening cement [37]. This may explain a conclusion why the effects of the superplasticizers on maintaining the rate of compressive strength are not clearly known [38]. Some studies have been conducted to determine the influence of superplasticizers on hydration of cement compounds up to the age of 28 days [39,40]. The results indicated a significant influence of the superplasticizer on the growth rates of the hydrates and on the state of polymerization of the Silicates [41]. Still, it has been suggested that influence of these chemical admixtures on the microstructure of the hardened concrete and, consequently, on its properties still needs to be extensively evaluated [42]. In various studies, it is reported that the effect of a superplasticizing admixture depends on the composition of cement rather than the amount of cement used [43,44,45]. A higher strength increase for a fixed quantity of superplasticizer takes place for lower cement content. It was also seen in this study that a maximum limit for a superplasticizer can be prescribed which suits to various types of cements and the use of industrial binders and waste products, such as slag and fly ash, may affect the performance of a superplasticizer. Many studies have underlined the significance of cement composition and the nature of other binders in the compatibility and performance of superplasticizers [39,46,47]. In a study, it has been reported that a polycarboxylate-based superplasticizer (PC) showed no plasticizing effect in combination with a retarder while good flowability was observed with another one [2]. It was suggested that admixtures with higher anionic charge density show higher affinity to the binder surface and thus adsorb preferentially [48]. When several admixtures are present, molecules with lower anionic charge density will adsorb only if, sufficient cationic surface charge and adsorption area exists after adsorption of the admixture with higher anionic charge [49]. This may be the reason of additives with high anionic charge density, in particular cases, dramatically reducing or even completely preventing adsorption of additives with low anionic charge density.

However, some studies suggest that non-adsorbed polymers may play an important role, either through depletion interactions or nucleation inhibition [50,51]. This statement is said to hold fully if the additive molecules possess similar chemical structures. For a given cement, the dosage of a superplasticizer to obtain better fluidity increases with the specific area of the cement. Increase in fluidity may, sometimes, be manifested as the effect of either the flocs not being interconnected or of weaker cohesive forces in the matrix of the paste [13]. Though superplasticizers react preferentially with the interstitial phase, some quantity of them may be adsorbed by C\(_3\)A [5]. It has also been shown that fluidity of superplasticized pastes depends also on the type of calcium sulphate utilized. This dependence is said to be less if the C\(_3\)A content is moderate in amount [13]. It has been reported that the use of superplasticizers in concrete has a similar and proportional effect on compressive strength, tensile strength and modulus of elasticity of concrete [52]. Therefore, the same methods and models, which associate all these properties for a normal concrete, may still work well for concretes in which superplasticizer has been used [1]. Superplasticizers restrain the propensity of concrete to bleeding, help in reducing the porosity of the hardened concrete and improve freeze-thaw durability of concrete [1,4,9,53,54]. On the other hand, it has also been suggested that the benefits of use of superplasticizers may not be forthcoming unless sufficient soluble alkali content is present in the pore water of concrete [55,56,57]. Durability aspects, depending on these parameters, are further improved if the water cement ratio is decreased with the use of superplasticizers [1].
Though microstructural modifications in the cement superplasticizer pastes have been reported to reduce the porosity it has also been reported that the mechanical strength of the pastes at either 2 or 28 days of hydration was not affected [58]. Significant reductions in pore size have also been observed in mixes containing superplasticizer. It was also found that the volume of large voids also showed a great reduction with the use of superplasticizer [59]. Interaction of cement and superplasticizer seems to be dependent on fineness of cement as well as on the chemical composition of cement [45,60]. The effect of fineness is found to be more pronounced when the cement is incompatible with the superplasticizer [6]. Though differing views exist regarding quantum of improvement of bond strength of concrete with reinforcement, it is generally accepted that the use of superplasticizer has a positive effect in this regard [52,61,62]. Proper consolidation around reinforcement being more easily achieved with flowing concrete has been cited as a reason for the positive effect [1]. In cement mixes containing fibres, the incorporation of superplasticizers has been found to compensate the adverse effects such as higher viscosity & permeability introduced by fibres [53,59].

Though much work has been done on the interaction of cement and superplasticizer, many questions remain unanswered [63]. Incompatibility between cement and superplasticizer is included among such questions. Use of superplasticizer may result in reduction of the air content of the concrete mixes. Therefore, compatibility of a superplasticizer with an air-entraining agent also should be checked before combining them in a mix. A need of such a checking for different cement types and supplementary cementing materials has also been emphasized [64]. Determination of compatibility and robustness between superplasticizer and cement is important. While compatibility signifies general suitability between them for achieving a particular result, robustness is defined as the influence of a variation of a parameter on a property. A superplasticizer dosage is considered as robust when a variation of 0.1 percent in its dosage does not have any catastrophic effects on the rheology of a cement paste or of a concrete mix [5]. Varying performances of superplasticizers have been observed for different cements depending on various factors in which compound composition of cement is very important. For example, soluble alkali sulphates in cement play a significant role in the robustness of the cement / superplasticizer mixture. In low water cement mixes, alkali sulphates provide SO\(_{4}^{2-}\) ions which are in short supply if the cement contains a high percentage of C\(_{3}\)A and a large portion of superplasticizer is trapped in the C\(_{2}\)AH\(_{6}\) lamellae of the hexagonal hydrates. In such a scenario, superplasticizer molecules would run in short supply and flocculation of cement particles would tend to occur. In such a situation, the cement / superplasticizer combination may not be found to be compatible. Such a situation would not occur in high water cement mixes as SO\(_{4}^{2-}\) ions would be in proper supply and superplasticizer molecules would be used for deflocculation of the cement particles. Following the above context, it may be inferred that though low alkali content in cement is desired due to other reasons, too low an alkali content may not be helpful because superplasticizers, especially polysulphonates, may be found to be incompatible with such a cement, in low water cement ratio mixes where they are meant to be used due to workability considerations. For such cements they would be found to be compatible but for high water cement ratio mixes which do not require superplasticizer for workability and which would not be durable [65]. In such a situation, use of superplasticizer may rather lead to segregation. Thus when the sulphate solubility rate is not well balanced with the C\(_{3}\)A reactivity, it is necessary to use an appropriate superplasticizer in order to control concrete rheology, especially for low water binder applications [66-70].

Superplasticizers can have their own respective ways of action which may affect their compatibility with cements. For example, it has been reported that the more compatible a cement is with a polynaphthalene superplasticizer, the more incompatible it is with a polycarboxylate one and vice-versa [5]. The use of these admixtures is generally based on trial and error because of an incomplete understanding of their mechanism of action [71]. The main reason of compatibility of cement and superplasticizer has not yet been thoroughly understood [56]. The influence of these chemical admixtures on the microstructure of the hardened concrete and, consequently, on its properties still needs to be extensively evaluated [29]. The effect of superplasticizers is obvious when the concrete is in the fresh state. Nevertheless, the influence of superplasticizers on the characteristics
of the hardening and hardened concrete is largely unclear [72]. A better understanding of these aspects is, therefore, essential for further improvement of these admixtures and for analyzing the long-term properties of the concrete [73].

Increased workability of concrete, due to presence of superplasticizer, makes it possible to utilize industrial waste materials such as slag and fly ash [9]. Using these materials would be more efficient, in the presence of superplasticizer due to workability considerations [40,74-76]. Based on laboratory studies, it has been reported that superplasticizers may increase drying shrinkage in concrete at a given water cement ratio and cement content [1]. This aspect may be important especially in mixes, containing waste materials, as the strength of such mixes may be low at early stages. While the effect of superplasticizers has been extensively studied in Portland cement pastes, mortars and concretes, their effect on other binders, such as alkali-activated slag pastes and mortars, has received less attention [77]. A lack of quantitative experimental studies, relating the rheological properties of a mix to the architecture of the superplasticizer polymer has been reported [78]. Data from such studies may corroborate the theoretical predictions based on calculations on inter-particle forces on cementitious systems [79,80]. Systematic studies have been restricted by a limited access to some well-characterised polymers. It has been suggested that further studies of the superplasticizer interaction with pure clinker phases, hydrate phases and the pore solution should be undertaken [26]. In this connection, particle size distribution, surface area and particle packing in a cement paste has to be considered for understanding microstructural evolution in terms of interparticle forces and associated rheological phenomena [81]. It has been suggested that performance standards and specifications should be developed considering physical, chemical and structural mechanisms of working of superplasticizers in concrete. This would lead to improvements in the durability based design methods and life-cycle modeling of concrete structures [80].

1.3 Assessment of Performance

It has been suggested that the most economical way to evaluate the efficiency of a superplasticizer is to undertake rheological tests [65]. Some important parameters found to control the rheology of a cement-superplasticizer mix may be cited as: water-cement ratio, amount of superplasticizer dosage, fineness of cement, compound composition of cement, microstructure & mineralogical phases of clinker, chemical nature & average molecular weight of the superplasticizer, manner of mixing of superplasticizer (single dosage or redosage of superplasticizer), initial temperature of water etc [82-84]. Rheology of pastes in terms of plastic viscosity, yield value and setting time is found to be dependent on elapsed time and temperature. It has been reported that for mixtures made with superplasticizers, the amount of adsorbed and residual polymer in the aqueous phase varies with the temperature of fresh paste [79]. It has been suggested that the type of superplasticizer does not change the pattern of variation of the final setting time with the temperature [85].

Interaction among cement, superplasticizer and calcium sulphate is complex due to various compounds of cement, various forms of calcium sulphate and various types of superplasticizers. For understanding why some superplasticizers are more efficient than others and why some are not compatible with certain cements, different approaches are used [1,5]. Tests on rheology of cement pastes, in which superplasticizers are used, are important also because they limit the time and energy which would otherwise be required to be put in for determining the compatibility of superplasticizers and cements. But it has been found that these tests do not have a full predictive value if their results are applied to concrete [5].

Methods such as flow-table method of ASTM, Mini-slump cone test of Kantro and the Marsh cone test are available to evaluate superplasticizers from the point of view of rheology [86]. An optimum amount is generally suggested for superplasticizer in concrete. Beyond this amount, rather than a proportionate improvement of rheological properties being achieved, it may lead to chances of segregation. These methods are used with superplasticizer content at the “Saturation point”. Saturation point refers to the amount of superplasticizer above which no significant improvement of rheological properties is expected. It has been reported that the influence of superplasticizers on the
Fluidity and slump loss of cement pastes differs considerably [87]. Fluidity of pastes increases with increase in the dosage of superplasticizers. Results of a study have revealed that not only superplasticizers of different base groups behave differently but even the superplasticizers of the same base group behave differently [88]. AC impedance and other methods have been used to study microstructure of pastes containing superplasticizers to determine the mechanism of action of superplasticizers [73,89]. A combination of Marsh cone and resistivity measurements have been made in these studies to evaluate superplasticizers. The method proposes a determination of saturation dosage of superplasticizer and two coefficients named as “inflection time ratio” and “resistivity ratio” which are used to determine the suitability of a superplasticizer for a cement [90].

Techniques of X-ray diffraction and nuclear magnetic resonance have also been used to determine the influence of superplasticizers [8,24]. Use of yield stress and effective viscosity of pastes in determining changes in rheological parameters of concrete due to the use of various superplasticizers has been considered [91]. Workability changes and slump retention in concrete mixes are to be monitored in the case of transportation of concrete & casting of concrete before the initial set. If a curve is plotted between shear stress and shear rate for a cement paste employing a superplasticizer, hysteresis curves are obtained for different cycles. The addition of superplasticizers reduces hysteresis area of the first hysteresis cycle and brings about some modifications in the pattern of the second hysteresis cycle. The down curve of the second hysteresis cycle lies on the lower shear stress side with respect to the upper one, thus indicating the breakdown of the paste structure. It has been suggested that the down curve may be of Newtonian, shear-thinning or shear-thickening type, depending on the nature and amount of additive and the shear rate. While the Shear-thinning characteristics are typical of agglomerated suspensions such as cement pastes at low shear rates, the shear-thickening behaviour is due to weakly adsorbed or unadsorbed content of superplasticizer [25]. Superplasticizers are responsible for shear thickening provided that their dispersing actions create the necessary conditions of occurrence of such a phenomenon. For it, the suspensions must be concentrated and dispersed [58]. The apparent viscosity of the paste is found to decrease with increasing superplasticizer concentration at a fixed shear rate. Due to this, it may be difficult to determine optimum dosage for a superplasticizer considering apparent viscosity only. In such cases, only a range within which paste viscosity is low can be determined for a superplasticizer [92].

It has been suggested that many factors, influencing the fluidity and hydration process of the cement paste, may have synergistic effects. This makes a proposed theory, based on one parameter, irrelevant. Also, it makes it difficult to pinpoint one parameter to be responsible to produce a particular property [93-97]. Flow of cement pastes with superplasticizers has been found to fit in different forms in mathematical models such as Bingham and Herschel-Bulkley [35]. Rate of heat of hydration also gives an indication of the effect of superplasticizer. A fair correlation between the initial set determined by the evolution of heat and that by the change of yield stress of the paste, penetration resistance, rheology, and ultrasonic p-wave method has been observed. The initial setting time determined by the change of yield stress is reported to be more precise information than the penetration depth test of the cement pastes [35]. Adiabatic chemistry can be used to understand the double physico-chemical action of the molecules of superplasticizer. The temperature rise in concrete due to heat of hydration is not significantly affected by the addition of a superplasticizer unless the amount or composition of the paste is changed [1]. It has been observed that a small amount of superplasticizer brings the peak of heat earlier compared to a cement water system without superplasticizer. This may be due to better dispersion of cement particles and a consequent higher rate of hydration. If the superplasticizer dosage is higher, the peak is delayed. This happens because at higher dosage the superplasticizer molecules are adsorbed on the surface of the cement particles, envelopes them and prevent the hydration of cement. At the same time, it is recognized that superplasticizers interfere not only with the hydration of cement phases but also with the dissolution rate of sulphates [5]. Colloidal probe AFM technique has been used determining adsorption of superplasticizer [17]. The use of a compression rheology approach, based on the analysis of centrifugally consolidated suspensions, offers a good tool to study and quantify the effect of the molecular structure of comb-type superplasticizers on the rheological properties [9].
The zeta potential of early hydration products of cement was found to be a key factor for superplasticizer adsorption which may be reflected in its performance and its compatibility with cement [11]. The measured zeta potential represents the composite potential of the particle surface [94]. A highly positive zeta potential results in a strong superplasticizer adsorption whereas a negative zeta potential does not allow adsorption. Cement particles are composed of interstitial phases with a positive potential ranging from 20 to 40 mV which is due to preferential adsorption of Ca$^{2+}$ onto the hydrated calcium sulfoaluminate or ferrite components. The silicate phases, with the less hydrated silicate components, have a lower affinity for calcium [86]. These phases have a negative potential of approximately −10 mV. Superplasticizers have also been reported to modify the rate of formation of ettringite as well as affect its morphology [5]. Ettringite, having a highly positive zeta potential, adsorbs greater amounts of negatively charged superplasticizer compared to what is adsorbed by Monosulfate which has a less positive zeta potential. It has been reported that the incorporation of the superplasticizer clearly enhances the growth rate of ettringite [98]. Syngenite, portlandite and gypsum, with their zeta potential values being around zero or being negative, do not adsorb superplasticizers. This is the reason why changes in the crystal morphology, due to superplasticizers, are predominant in only some of the hydration products of cement. Consequently, a hydrating cement grain has a mosaic structure, with superplasticizer molecules being mainly adsorbed on ettringite, only a little on monosulfate and C–S–H nucleating at surface [82]. Superplasticizers may adsorb also on fly ash, silica fume etc., which are added in a mix. The reason for adsorption in such cases may be the electrostatic interaction between the superplasticizers and the charged surfaces of these powders [99]. The adsorption of a superplasticizer, on the surface of cement grains and hydration products, inverts the nature of the zeta potential from positive to negative. This sign inversion in the zeta potential causes the electrostatically flocculated cement particles to be electrostatically dispersed. This negative zeta potential first increases with the amount of adsorbed superplasticizer and then achieves a constant maximum value. This is the condition when the shear viscosity and the storage modulus attain a minimum value. Any further increase in the amount of superplasticizer, from this stage, leads to increase in the shear viscosity & storage modulus. This fact illustrates the importance of determining the optimal concentration of a superplasticizer to achieve both fluidity and cohesiveness in a cement suspension [94,95,100]. Such determination is considered essential as well as useful in relation to practical and scientific aspects [2]. Achieving an optimized balance between repulsion among cement particles as well as attraction among them for has been emphasized [94]. Repulsion among cement particles is needed for maintaining fluidity of paste while attraction is needed for cohesiveness of concrete [88,101]. It is observed that without superplasticizers, C$_3$S and C$_2$S have negative zeta potentials while C$_3$A and C$_4$AF have positive zeta potentials. Accelerated coagulation of these particles may occur due to their opposite zeta potential. Due to the presence of superplasticizer, the zeta potentials of all of them become negative and fluidity of fresh cement paste is improved due to electrostatic repulsion among particles. A larger amount of any type of superplasticizer is adsorbed on C$_3$A & C$_4$AF than on C$_3$S & C$_2$S. A higher C$_3$S content leads to a lower efficiency of superplasticizer because admixture molecules interact with C$_3$A and no longer contribute to the dispersion of cement particles [41].

A significant influence of the C$_3$A content on the loss of workability has been reported [75,102]. In this reference, it should be appreciated that the adsorption behaviour of superplasticizers is different, in early stage of hydration, for different cements due to diverse composition. A significant influence of C$_3$A on the effectiveness of superplasticizers in the early stage of hydration may be understood better in the context of formation of ettringite from the aluminate content of cement. Ettringite formed from the aluminate phase of the cement and CaSO$_4$·nH$_2$O determines the dosage of superplasticizer to a great extent. Ettringite adsorbs a lot of superplasticizer on its surface and very few of it is left for affecting the rheology of the paste [82]. With other phases of the hydration products, including monosulphate, having little effect on the superplasticizer dosages, the amount of ettringite formed and shape & size of its crystals are important factors for superplasticizer consumption in the early hydration phase. This explains the differences in the requirements of superplasticizers at different stages of hydration after providing water to the mix as its requirement.
would depend on the composition of hydration products at these stages. This may further explain why multiple dosages of superplasticizers may be provided advantageously. A saving of up to 50% of the amount of superplasticizer has been suggested depending on the reduction in zeta potential, specific surface area and amount of ettringite at the time of providing the superplasticizer [82]. In a self-leveling mortar based on the ternary binder system of ordinary Portland cement (OPC), calcium aluminate cement (CAC) and anhydrite, a polycarboxylate-based superplasticizer (PC) showed no plasticizing effect in combination with citrate retarder while good flowability was observed with tartrate. The mechanism behind the incompatibility between PC and citrate was investigated by means of adsorption and zeta potential measurements [2].

Use of superplasticizers along with viscosity modifying admixtures in high-performance concrete has shown that the combination can ensure high deformability and adequate workability leading to better resistance to segregation of such a concrete. Attempt has also been made to correlate rheological properties to consistency of pastes [51,103]. Performance assessment of a superplasticizer on the basis of compressive strength only may sometimes be confusing, especially when some other factors dominate. This may happen when concrete is subjected to aggressive environments and the effects of a variation in quantity of superplasticizer may be difficult to be interpreted from results.

1.4 Sulphate Attack Considerations

Apart from other positive effects of superplasticizers, mentioned above, improvement of resistance of concrete against sulphate attack has been mentioned [53,59]. Superplastized concrete mixes have been reported to be more resistant to aggressive environments due to higher strength [64,104]. At the same time, it has also been reported that the use of superplasticizer did not help much in providing resistance against sulphate attack [48]. Compared to control mixes, changes in flexural strength and compressive strength of specimen containing superplasticizer were not found to be different under the effect of Magnesium sulfate solution [59]. In yet another study, it was observed that compared to control concrete, a superplastized concrete mix gave a better performance in sodium sulphate attack while a non-superplastized concrete mix was better in magnesium sulphate attack [21]. Amount of C3A in cement is considered important for the assessment of likely performance in sulphate attack. It has been reported that high and moderate C3A cements containing limestone filler and superplasticizers were found more susceptible to sodium sulfate attack and less durable than the corresponding plain mortar [105]. It also has been suggested that cement with C3A contents above 12% performs poorly, while cement with contents below 9% usually performs satisfactorily [106]. That other conditions, such as anionic nature of aggressive salt, may affect this general statement is obvious as the same study refers to more pronounced effect of magnesium sulphate solution on cements with lower C3A contents. Cement having C3A content between the two values are reported to show a wide range of performance [106]. As mentioned above, a higher C3A content leads to a lower efficiency of superplasticizer because admixture molecules interact with C3A and no longer contribute to the dispersion of cement particles [41]. A larger amount of any type of superplasticizer is adsorbed on C3A & C4AF than on C2S & C3S. Magnesium sulfate degrades and disintegrates C−S−H gel to M−S−H gel, which is a non-cementitious product and leads to softening of the cement matrix [107]. Superplasticizer molecules are adsorbed only in little quantities on C−S−H [82]. A more pronounced effect of magnesium sulphate on cements with lower C3A, with more superplasticizer available in the cement matrix, may only indicate that chemical role of superplasticizers in augmenting sulphate resistance of cement matrix may be insignificant compared to the physical role, discussed below.

It has been reported that when a superplasticizer is used to reduce the water cement ratio, the sulfate resistance is much higher [1]. Also, It has been suggested that the real factor in providing resistance to sulphate attack is the density of concrete [85]. Use of superplasticizer in concrete is helpful in this regard as it helps in achieving a greater density for a given compaction effort. A greater density is usually expected to lead to greater strength which may point towards a better resistance to sulphate attack, atleast in the physical sulphate attack in which crystallization of sulphates can impose internal stresses in concrete. Use of superplasticizer reduces the pore size and permeable spaces inside
the cement matrix. Consequently, the ingress of water and chemical salts find more resistance on their way into the inside of a cement mortar or concrete. That a more refined paste structure, with a dense interlocking network of C–S–H crystals, will improve resistance to sulfate attack by reducing the ability of the ions to diffuse into the concrete has been emphasized [104]. It has been reported that even cement with high C₃A content can show sulfate resistance if they are impermeable enough [105,106]. Also, superplasticizer content adsorbed on the surface of hydration products may act as a protective cover against the chemical attack, at least for the time being. Thus, improvement of physical properties of cement matrix due to the presence of superplasticizer and the resulting increase in sulphate resistance seems to be the benefit of the use of superplasticizer.

In durability studies, superplasticizers are used to prepare concrete mixes of particular required strengths. Very few studies have derived conclusions focusing on the effect of superplasticizers on the performance of concrete under sulphate attack. This may be because of the presence of many parameters which are instrumental in providing resistance against sulphate attack to concrete. It has been reported that chemical resistance of superplasticized concrete, especially high-performance concrete, has not yet received sufficient attention from the research community [48].

2.0 NEED OF STUDY

A compatible pair of cement and superplasticizer was to be selected, out of various commercial brands, prior to its use in a research programme. The research programme concerned with the long term effect of sulphate acidic environmental conditions on various types of concrete made with the selected cement and superplasticizer compatible to it. This study was undertaken to select the compatible pair.

3.0 EXPERIMENTAL PROGRAMME

In the experimental programme for this study, three different cements (C₁, C₂ & C₃) & three superplasticizers (S₁, S₂ & S₃) were considered. S₁ and S₃ were of the same type but were different commercial products. The experimental programme had the following two phases.

3.1 First Phase

In the first phase of this study, slump tests were conducted on concrete mixes using different combinations of these cements and superplasticizers (such as C₁-S₁, C₁-S₂, etc.). A fixed quantity of superplasticizer, 1% by weight of cement, was used in the first phase. Slump tests were conducted every fifteen minutes to check the retention of slump in each case. The purpose was to first see the effect of superplasticizer on fresh concrete in terms of workability. Because a total of nine combinations of cements and superplasticizers were available, it was expected that more than one pair could be found to be compatible in this phase.

3.2 Second Phase

Out of all the compatible pairs of cement and superplasticizers from the first phase, a pair giving the best performance in concrete, was to be selected from a limited duration study of three months which formed the second phase of this study. Quantities of superplasticizers used in this second phase varied from 1% to 3% of the weight of cement. The purpose of varying the quantity of superplasticizers was to get an idea of the effect of quantity of superplasticizers for different combinations of cement & superplasticizer. This was to simultaneously know the optimum quantity of superplasticizer for the most compatible case which was to be selected in the second phase.

All the concrete mixes were designed for a characteristic compressive strength of 35 N/mm². ‘Good’ quality control was assumed in the design of mixes and a compaction factor of 0.9 was considered. Concrete cubes, of 150 mm size, were tested for compressive strength at 1 day, 3 day, 28 day, 60 day and 90 day. An average value of the results of 3 cube specimen was taken to be the representative value of strength. For each combination of cement & superplasticizer a control mix of the same composition, but without superplasticizer, was made. All the different types of concrete mixes were compared with their respective control mixes and percentage of strength gain in each case due to addition of superplasticizer was determined.

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3.3 Material Properties

Properties of cements and superplasticizers are given in Table 1 and Table 2. Properties of superplasticizers are as reported by the manufacturers. Commercial names of cements and superplasticizers, used in this study, have not been reported in this paper. All the cements were different commercially available ordinary Portland cements. Potable ordinary water was used for the study. Physical properties of fine & coarse aggregates are given in Table 3. The fine aggregate was sand, of grading zone 2, from a nearby river. The coarse aggregate was crushed angular granite stone. Fine aggregate was washed with ordinary water to remove the silt content. Coarse aggregate also was washed with water. All the concrete mixes were prepared in steel trays to obviate the possibility of loss of water & cement due to segregation and bleeding. Following are some properties of the materials used in the study.

<table>
<thead>
<tr>
<th>Property</th>
<th>Cement designation</th>
<th>C1</th>
<th>C2</th>
<th>C3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silicon dioxide (SiO$_2$) (%)</td>
<td></td>
<td>19.87</td>
<td>20.8</td>
<td>19.9</td>
</tr>
<tr>
<td>Aluminum Oxide (Al$_2$O$_3$) (%)</td>
<td></td>
<td>4.42</td>
<td>5.5</td>
<td>4.7</td>
</tr>
<tr>
<td>Iron Oxide (Fe$_2$O$_3$) (%)</td>
<td></td>
<td>3.01</td>
<td>3.2</td>
<td>3.5</td>
</tr>
<tr>
<td>Calcium Oxide (CaO) (%)</td>
<td></td>
<td>62.14</td>
<td>63.7</td>
<td>63.9</td>
</tr>
<tr>
<td>Magnesium Oxide (MgO) (%)</td>
<td></td>
<td>2.91</td>
<td>1.2</td>
<td>2.2</td>
</tr>
<tr>
<td>Sulphur Trioxide (SO$_3$) (%)</td>
<td></td>
<td>3.25</td>
<td>2.4</td>
<td>2.9</td>
</tr>
<tr>
<td>Alkalies (as equivalent Na$_2$O) (%)</td>
<td></td>
<td>0.46</td>
<td>0.48</td>
<td>0.39</td>
</tr>
<tr>
<td>Loss on ignition (%)</td>
<td></td>
<td>2.4</td>
<td>1.5</td>
<td>1.8</td>
</tr>
<tr>
<td>Blaine fineness (Cm$^2$/gm) (%)</td>
<td></td>
<td>2800</td>
<td>3510</td>
<td>3590</td>
</tr>
<tr>
<td>Passing 45 $\mu$m sieve (%)</td>
<td></td>
<td>87</td>
<td>90</td>
<td>92</td>
</tr>
<tr>
<td>Specific gravity</td>
<td></td>
<td>3.15</td>
<td>3.15</td>
<td>3.15</td>
</tr>
<tr>
<td>Compound composition (calculated from Bogue’s equations)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C$_3$S (%)</td>
<td></td>
<td>58.6</td>
<td>52.8</td>
<td>64.0</td>
</tr>
<tr>
<td>C$_2$S (%)</td>
<td></td>
<td>14.7</td>
<td>19.9</td>
<td>8.9</td>
</tr>
<tr>
<td>C$_3$A (%)</td>
<td></td>
<td>7.8</td>
<td>9.2</td>
<td>6.5</td>
</tr>
<tr>
<td>C$_4$AF (%)</td>
<td></td>
<td>11.3</td>
<td>9.7</td>
<td>10.6</td>
</tr>
<tr>
<td>Initial setting time (minute)</td>
<td></td>
<td>60</td>
<td>30</td>
<td>30</td>
</tr>
<tr>
<td>Autoclave expansion (%)</td>
<td></td>
<td>0.10</td>
<td>0.05</td>
<td>0.09</td>
</tr>
<tr>
<td>Compressive strength of 100 mm cubes at different ages (N/mm$^2$)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3 days</td>
<td></td>
<td>24.6</td>
<td>19.3</td>
<td>18.3</td>
</tr>
<tr>
<td>7 days</td>
<td></td>
<td>36.2</td>
<td>24.8</td>
<td>24.5</td>
</tr>
<tr>
<td>28 days</td>
<td></td>
<td>49.10</td>
<td>29.6</td>
<td>29.1</td>
</tr>
</tbody>
</table>

Table 2 - Chemical and Physical Properties of Superplasticizers

<table>
<thead>
<tr>
<th>Property</th>
<th>Superplasticizer designation</th>
<th>S1</th>
<th>S2</th>
<th>S3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Type of superplasticizer</td>
<td>Naphthalene formaldehyde condensate</td>
<td>Sulphonated naphthalene polymer</td>
<td>Naphthalene formaldehyde condensate</td>
<td></td>
</tr>
<tr>
<td>Specific gravity</td>
<td>1.20 at 25$^\circ$ C</td>
<td>1.17 at 25$^\circ$ C</td>
<td>1.22 at 30$^\circ$ C</td>
<td></td>
</tr>
<tr>
<td>Colour and nature</td>
<td>Brown free flowing liquid</td>
<td>Brown free flowing liquid</td>
<td>Brown free flowing liquid</td>
<td></td>
</tr>
<tr>
<td>Air entrainment max. (%)</td>
<td>1.5</td>
<td>--</td>
<td>1.0</td>
<td></td>
</tr>
<tr>
<td>Chloride content</td>
<td>Nil</td>
<td>Nil</td>
<td>Nil</td>
<td></td>
</tr>
<tr>
<td>pH</td>
<td>--</td>
<td>6 to 8</td>
<td>--</td>
<td></td>
</tr>
<tr>
<td>Max. dosage (%)</td>
<td>2.5</td>
<td>3.0</td>
<td>--</td>
<td></td>
</tr>
</tbody>
</table>
Table 3 - Physical Properties of Aggregates

<table>
<thead>
<tr>
<th>Property</th>
<th>Fine</th>
<th>Coarse</th>
</tr>
</thead>
<tbody>
<tr>
<td>Specific gravity</td>
<td>2.61</td>
<td>2.66</td>
</tr>
<tr>
<td>Maximum size (mm)</td>
<td>4.75</td>
<td>20</td>
</tr>
<tr>
<td>Fineness modulus</td>
<td>3.2</td>
<td>6.7</td>
</tr>
<tr>
<td>Moisture absorption (%)</td>
<td>1.62</td>
<td>0.69</td>
</tr>
</tbody>
</table>

4.0 RESULTS & DISCUSSION

The results of first phase of study in terms of slump values & slump retention times for different combinations of cements and superplasticizers are given in Table 4.

Table 4 – Slump values and their retention times

<table>
<thead>
<tr>
<th>Cement</th>
<th>S1</th>
<th>S2</th>
<th>S3</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>initial slump (mm)</td>
<td>Slump retention time (minute)</td>
<td>initial slump (mm)</td>
</tr>
<tr>
<td>C1</td>
<td>120</td>
<td>45</td>
<td>90</td>
</tr>
<tr>
<td>C2</td>
<td>90</td>
<td>30</td>
<td>100</td>
</tr>
<tr>
<td>C3</td>
<td>90</td>
<td>30</td>
<td>90</td>
</tr>
</tbody>
</table>

From Table 4 it may be appreciated that S3 had the best effect on all the cements. S1 also worked well for cement C1 but S3 worked in a better way. Combination C1S3 could have been taken to be the most compatible pair of cement & superplasticizer depending on the slump value and its retention time. But the effect of S3 in cases of C1 and C2 in terms of slump values had only a marginal difference. Consequently, combinations C1S3, C2S3 and C3S3 were considered for the phase 2 of this study. As mentioned above, 150 mm concrete cubes of these combinations with different proportions of superplasticizers (1%, 2% and 3%) were cast to be tested at different ages. Phase 2, with these three combinations, offered a chance of choosing the best combination out of these three and also knowing the optimum quantity of superplasticizer to be used. Strength gain at any age in comparison to control concrete was considered to be the criterion for opting the best combination in this second phase. Percentage gain in compressive strength for concretes containing cements C1, C2 and C3, at different ages for different quantities of superplasticizer S3, is shown in Figure 1 to Figure 3.

![Figure 1](image-url)
It may be appreciated from Figures 1, 2 and 3 that maximum strength gain is obtained if a higher percentage of superplasticizer is used. At the same time, decreasing returns are obtained if the percentage exceeds an optimum amount of superplasticizer. In these cases lesser percentage gain in strength is obtained relatively after 2% quantity of superplasticizer. Strength gains are visible at all ages for all combinations for various proportions of S3. At the same time, larger strength gain is visible for early strengths compared to later strengths. If 2% is considered to be the optimum quantity of S3, cement C3 may not be selected because a significant strength gain is noticeable even after 2% in this case. This applies only for the initial age upto 28 days. Thereafter, this figure also gives the same trend of lesser returns if quantity of S3 exceeds 2%. A larger value of strength gain is noticeable for early strengths because even a small increase in strength in small early strengths would turn out to be a comparatively larger strength gain in percentage terms. Upper two curves in Figure 1 seem to have a more consistent relationship compared to those in Figure 2. Recalling a larger slump obtained in the first phase of the study, cement C1 should be a natural choice to make the most compatible pair with S3.

At this stage, some statistical parameters connected with these curves were considered to gain more insight into how to further develop the procedure for analyzing compatibility of cements and superplasticizers. These parameters were standard deviation, variance, average and the average
deviation (average of deviations from the mean value in a data set) for percentage strength gain values considered above in Figures 1 to 3. Figure 4 shows variations of these parameters.

It may be seen that higher deviations in percentage strength gain values are obtained for the case of 3\% of S3 regardless of the cement. 1\% quantity gives an average percentage gain of 40\% but it may not be selected as further avenues for having more strength gains exist by increasing the quantity of superplasticizer. At the age of 28 day, the percentage strength gain values for 2\% S3 case are 75\%, 80\% and 75\% for C1, C2 and C3 respectively. But cement C1 gives a higher average percentage strength gain of 93.67\% for 2\% of S3 and this value is higher than 86.5\% and 77.2\% obtained for C2 and C3. It is also found that maximum percentage strength gain values are obtained for this combination for the ages of 60 day and 90 day. C1-S3 combination was chosen as the most compatible pair of cement and superplasticizer as it gave the best performance with respect to enhancement of workability and percentage strength gain.

If deviations of percentage strength gain, at different ages for all combinations, from their respective average percentage gains, shown in Figure 4, are taken into consideration & plotted, variation patterns shown in Figure 5 are obtained. The deviations of percentage strength gain at the age of 28 day, in all cases, take the near minimum values in most of the cases. This may be significant as 28 day strength is considered to be the most important yardstick to interpret the quality of concrete.
Considering that all the cements used in this study were ordinary Portland cement and a single type of superplasticizer S3 was used, it was also tried to consider variations obtained for different combinations to find general relationships for percentage strength gain at an age versus the amount of superplasticizer. Trend lines and their equations for C1S3 case are shown in Figure 6. Such trend lines and their equations were found for C2-S3 and C3-S3 cases also with the same respective intercept values as were obtained for 1%, 2% and 3% cases as shown in Figure 5. All these equations are given in Table 5.

![Trend lines for strength gain versus age for C1-S3 combination](image)

**Figure 6**

<table>
<thead>
<tr>
<th>Case</th>
<th>S3%</th>
<th>Equation of trend line</th>
<th>General equation</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1-S3</td>
<td>1%</td>
<td>y = -6.6857x + 67.067</td>
<td>y = -7.44x + 67.067</td>
</tr>
<tr>
<td>C2-S3</td>
<td>1%</td>
<td>y = -7.2902x + 67.067</td>
<td></td>
</tr>
<tr>
<td>C3-S3</td>
<td>1%</td>
<td>y = -8.3451x + 67.067</td>
<td></td>
</tr>
<tr>
<td>C1-S3</td>
<td>2%</td>
<td>y = -19.371x + 161.47</td>
<td>y = -20.67x + 161.47</td>
</tr>
<tr>
<td>C2-S3</td>
<td>2%</td>
<td>y = -20.922x + 161.47</td>
<td></td>
</tr>
<tr>
<td>C3-S3</td>
<td>2%</td>
<td>y = -21.724x + 161.47</td>
<td></td>
</tr>
<tr>
<td>C1-S3</td>
<td>3%</td>
<td>y = -25.924x + 202.67</td>
<td>y = -25.93x + 202.67</td>
</tr>
<tr>
<td>C2-S3</td>
<td>3%</td>
<td>y = -26.297x + 202.67</td>
<td></td>
</tr>
<tr>
<td>C3-S3</td>
<td>3%</td>
<td>y = -25.571x + 202.67</td>
<td></td>
</tr>
</tbody>
</table>

In Table 5, ‘y’ is the percentage strength gain compared to control concrete of ordinary Portland cement. Value of ‘x’ depends on the age step. For 1 day, ‘x’ is equal to 1 as it is the first stage. Similarly, it takes the values of 2,3,4,5 and 6 for 3 day, 7 day, 28 day, 60 day and 90 day respectively. General equations for different cases have been written by taking average values of slopes of trend lines while retaining the same intercept value. General use of these equations is restrained by the type of cement and type & quantity of superplasticizer. Studies involving more parameters may further widen our mathematical reach in this context. Theoretical optimization studies may be taken up in this respect once sufficient data is available.

### 5.0 CONCLUSIONS

Following conclusions may be drawn from the study.

1. Addition of superplasticizer affects the strength at initial stages more than at later stages, in percentage terms.
2. Though all cements were ordinary Portland cements, curves for C3 in Figure 3 show some differences in variations, when compared with curves of C1 and C2 in Figure 1 and Figure 2. This shows that performance of OPC with a superplasticizer depends on many factors. Differences of cement compound composition, fineness of cement etc., may be some of them.
3. There is an optimum amount of superplasticizer for a cement. Quantities of superplasticizers above this optimum amount may give decreasing returns. After the optimum stage, some other method, in addition to use of superplasticizers or in isolation, may have to be used for increasing the strength of concrete economically. Likewise, use of superplasticizers in minute quantities such as less than or near to 1% may not give full returns for the cost of superplasticizers.

4. Theoretical mathematical models may be helpful for gaining further insights into the aspects of compatibility and optimization of quantity of superplasticizers.

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